

UNIVERSIDADE DE LISBOA INSTITUTO SUPERIOR TÉCNICO

Controlling the microscopic and macroscopic aspects of high harmonic generation in solids

Mukhtar Hussain

Supervisor: Doctor Marta Leitão Mota Fajardo Co-Supervisors: Doctor Gareth Oisin Williams Doctor Hamed Merdji

Thesis approved in public session to obtain the PhD Degree in

Technological Physics Engineering

Jury final classification: Pass with Distinction



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Resumo

A geração de harmónicas de ordem elevada (HHG) ocorre quando um pulso de laser intenso força um electrão a oscilar na presença de uma carga positiva (ião) e, consequentemente, os fotões direcionados pelo laser são convertidos em fotões de energias mais elevadas. Este processo resulta num pulso com comprimentos de onda entre o ultravioleta profundo (DUV) e raios-X suaves que podem ser utilizados para imagens attossegundo de orbitais moleculares, observação em tempo real de tunelamento de electrões e fornece uma nova ferramenta para física ultravioleta, como o electrão ou dinâmica molecular em semicondutores de óxidos metálicos e materiais bidimensionais. O processo HHG pode ser perturbativo ou não perturbativo, dependendo da intensidade do campo de direção e das propriedades do material. O aumento do interesse por HHG não perturbativo em sólidos foi impulsionado pelo aparecimento de fontes ultravioleta extremas de estado sólido compactas (XUV) e a perspectiva de separar as propriedades do material por meio da interação entre campos fortes e sólidos.

Tradicionalmente supõe-se que as harmónicas mais brilhantes e de ordem inferior são puramente perturbativas por natureza. No entanto, a fronteira entre os regimes perturbativos e não perturbativos muitas vezes permanece obscura. Aqui, a geração de segundas harmónicas (SHG) e a geração de terceiras harmónicas (THG) em cristais de MgO (Cr: MgO) dopados com crómio e MgO (Cr) prístinos foram explorados com uma fonte de comprimento de onda próxima do infravermelho (NIR) operando a 800 nm, 40 fs e com taxa de repetição de 1 kHz. Ao girar o cristal em relação à polarização do campo de direção, o comportamento perturbativo isotrópico e caótico da eficiência de SHG em MgO puro e Cr: MgO é observado. Além disso, mostrámos que com a introdução de impurezas, o comportamento não perturbativo do THG é perdido devido ao bloqueio das oscilações intrabanda e ao aumento das vias de absorção linear introduzidas pelos níveis de energia dopante em Cr: MgO.

O modelo semi-clássico de trajetórias de electrões (modelo não perturbativo) e o modelo perturbativo são adotados para explicar o comportamento não perturbativo e perturbativo de THG em MgO e Cr: MgO. O efeito da concentração de dopagem no rendimento dos sinais SHG e THG foi investigado. Em particular, o aumento da reabsorção da segunda harmónica (SH) e da terceira harmónica (TH) aumenta com a concentração de Cr dopante e, portanto, limita a eficiência geral alcançável. Além disso, harmónicas abaixo da lacuna de banda, como a terceira (H3) e quinta (H5) de 3 μ m, 40 fs, operando a 100 kHz foram geradas em MgO, Cr: MgO (1300 ppm e 9500 ppm) e a simetria dos cristais foi mapeada medindo a dependência da orientação de H3 e H5. Este trabalho mostrou que, ao introduzir dopantes em cristais simples, a estrutura electrónica pode ser modelada para adequar a resposta óptica não linear em termos de eficiência e dependência angular. Este estudo abre caminho para a fusão de engenharia de bandgap e geração de harmónicas de estado sólido para personalizar processos de conversão de frequência. Talvez de igual importância, é a perspectiva de testar experimentalmente teorias do mecanismo HHG de estado sólido com estruturas electrónicas adequadas, com o fim de fazer um mapeamento totalmente óptico da estrutura de bandas dos sólidos.

Além disso, SH e TH foram geradas em dielétricos de largura de banda larga, como em safira (Sa), cristais de SiO₂ e sílica fundida (FS) devido a sua maior lacuna de banda e maior limite de dano em

comprimento de onda de condução de 800 nm. Mapeámos a resposta do cristal medindo a polarização e a resposta de elipticidade dessas harmónicas. Macroscopicamente, a propagação não linear do intenso campo de direção de NIR em materiais de banda larga representa um desafio para controlar as propriedades espectrais de HHG em sólidos. Portanto, investigámos os efeitos de propagação não linear do campo de condução NIR ultrarrápido intenso nos dielétricos de bandgap amplo, como MgO, Cr: MgO, Sa, SiO₂ cristais e FS. Para evitar os efeitos de propagação não linear, SH e TH foram geradas na geometria de reflexão e comparados com as harmónicas da geometria de transmissão em cristais Sa, SiO₂ e FS.

Também separámos as contribuições das harmónicas (SH e TH) dos filmes finos de nitrato de alumínio (AlN), nitrato de alumínio e gálio (AlGaN) depositados no substrato Sa na geometria de transmissão e reflexão. A geração e a separação dessas harmónicas de baixa ordem destacaram a possibilidade de gerar fontes XUV a partir de filmes finos. Além disso, SHG e THG foram geradas em (100) orientada óxido de gálio único, policristalino, e (010) orientada policristalino (Ga₂O₃) a 800 nm e mapearam a resposta de simetria do cristal medindo a dependência da orientação das harmónicas. Curiosamente, observámos um forte sinal de SH e TH na polarização elíptica e circular dos pulsos de laser de condução do policristal (010) Ga₂O₃. As harmónicas de largura de banda mais baixas H3, H4, H5, H6, H7, H8 e H9 de comprimento de onda de 3 μ m em Ga₂O₃) (100) e (010) policristalino foram geradas no Laboratório de Intenso Lasers (L2I), IST, Lisboa. Além disso, mapeámos a simetria dos cristais medindo a dependência de orientação dessas harmónicas, destacando o potencial de mapear a estrutura de banda electrónica por meio da dependência de orientação das harmónicas. Isso pode abrir um novo horizonte para os pulsos XUV e, possivelmente, pulsos de attosegundos isolados, através da polarização completa dos materiais electrónicos de potência.

Harmónicas de ordem elevada revelaram uma riqueza de perspectivas, como mapeamento totalmente óptico da estrutura de banda electrónica, informações quânticas ultra rápidas e a criação de novas fontes attossegundo de estado sólido. Esforços significativos foram feitos para compreender os aspectos microscópicos do HHG em cristais, enquanto os efeitos macroscópicos, como os efeitos de propagação não linear do pulso de condução dentro do meio sólido denso e seu impacto no processo de HHG, são frequentemente negligenciados. Portanto, o HHG e os efeitos de propagação dos pulsos de condução em HHG em cristais de silício (Si) e óxido de zinco (ZnO) foram gerados no laboratoire d'Optique Appliquee (LOA), Paris, França, usando o laser NOVAE. Neste estudo, os efeitos macroscópicos foram explorados comparando dois materiais com propriedades ópticas distintas, Si e ZnO. Ao scanear a posição focal de 85 fs, pulsos de comprimento de onda de 2.123 μ m dentro dos cristais (varredura Z), revelámos mudanças espectrais nas harmónicas geradas. Nós interpretamos o blueshift geral do espectro harmónico emitido como uma impressão da modulação espectral do campo de direção que ocorre durante a propagação dentro do cristal. Esta interpretação foi suportada por simulações numéricas. Este estudo demonstra que através da manipulação do campo de direção fundamental por meio de efeitos de propagação não linear, o controle preciso do espectro de HHG emitido em sólidos pode ser realizado. Este método pode oferecer uma forma robusta de adaptar os espectros de HHG para uma variedade de aplicações espectroscópicas.

A flexibilidade de geração de comprimento de onda por meio do processo HHG em sólidos abriu um novo horizonte para manipular a forma dos feixes e permitiu a geração de imagens de estruturas de difração na nanoescala. A técnica de imagem de difração coerente sem lente (CDI) de pticografia permitiu a obtenção de imagens de amostras estendidas no campo distante usando fontes de iluminação de raios-X ou XUV. Neste trabalho, gerámos as harmónicas em semicondutores (ZnO e Si) e visualizámos a superfície do cristal gravado a partir da emissão harmónica de um semicondutor. A formação do feixe espacial de harmónicas foi controlada por placas de zona espiral (SZP) gravadas na superfície de ZnO e nanocircuitos em cristais de Si pela técnica de feixe de iões focado (FIB). A reconstrução de imagens de padrões de difração simulados e medidos experimentalmente no campo distante foi validada com a pticografia na biblioteca PyNX.Ptycho. As harmónicas difratadas das SZP's geram feixes de momento angular orbital (OAM) que têm muitas aplicações que vão desde microscopia até informações quânticas. Este estudo pode abrir caminho para abrir um novo horizonte para o uso de HHG de estado sólido para aplicações plasmónicas e imagens de domínios magnéticos a partir da auto-emissão de harmónicas em materiais magnéticos.

Exploramos as aplicações que usam as harmónicas de fase gasosa, muito mais brilhantes para obter dados de sonda de bombearde disparo único de um sólido, à medida que ele se transforma em plasma. Essa rota pode oferecer uma perspetiva única sobre a compreensão da dinâmica dependente do tempo do próprio processo HHG de estado sólido, pois uma sonda de feixe pode medir as transições eletrónicas que ocorrem durante o tempo ultrarrápido.

Palavras-chave: Geração de alta harmónica, Aspectos microscópicos e macroscópicos, Harmónicos perturbativos e não perturbativos, Efeitos de propagação não-linear, Imagem ultrarrápida espectroscopia

Abstract

High harmonic generation (HHG) occurs when an intense laser pulse forces an electron to oscillate in the presence of a positive charge (ion), and consequently, driving laser photons are converted to higher energies photons. This process results in an ultrashort pulse of deep ultraviolet (DUV) to soft Xrays employed for attosecond imaging of molecular orbitals, real-time observation of electrons tunneling. It provides a new tool for ultrafast physics, such as electron or molecular dynamics in metal oxide semiconductors and two-dimension materials. HHG can be perturbative and non-perturbative depending on the driving field strength and the material properties. The surge in interest towards non-perturbative HHG in solids has been driven by the appeal of compact solid-state extreme ultraviolet (XUV) sources and the prospect of untangling the material properties through the intimate interplay of strong fields and solids.

The traditional assumption is that the brighter, lower-order harmonics are purely perturbative. However, the border between the perturbative and non-perturbative regimes often remains unclear. Here, second-harmonic generation (SHG) and third-harmonic generation (THG) in pristine MgO and chromium (Cr) doped MgO (Cr: MgO) crystals have been explored with a near-infrared (NIR) driving wavelength operating at 800 nm, 40 fs, 1 kHz repetition rate. On rotating the crystal relative to the driving field polarization, the isotropic and chaotic perturbative behavior of SHG efficiency in pure MgO and Cr: MgO is observed. Furthermore, we show that with the introduction of impurities, the non-perturbative behavior of THG is lost due to the blocking of intraband oscillations and the increased linear absorption pathways introduced by the dopant energy levels in Cr: MgO.

The semi-classical electron trajectories model (non-perturbative model) and perturbative model are adopted to explain the non-perturbative and perturbative behavior of THG in MgO and Cr: MgO crystals. The effect of doping concentration on the yield of SHG and THG signals has been investigated. In particular, increased re-absorption of the second-harmonic (SH) and third-harmonic (TH) increases with Cr dopant concentration, limiting the overall achievable efficiency. Furthermore, below bandgap harmonics such as third (H3) and fifth (H5) of 3 μ m, 40 fs, operating at 100 kHz has been generated in MgO, Cr: MgO (1300 ppm and 9500 ppm) and mapped the symmetry of the crystals by measuring the orientation dependence of H3 and H5. This work has shown that the electronic structure can be shaped to tailor the non-linear optical response in terms of efficiency and angular dependence by introducing dopants into simple crystals. This study paves the way for merging bandgap engineering and solid-state harmonic generation to tailor frequency up-conversion processes. Perhaps of equal importance is the prospect of experimentally testing theories of the solid-state HHG mechanism with tailored electronic structures, with a final view towards all-optical mapping of the band structure of solids.

Furthermore, SH and TH have been generated in wide bandgap dielectrics such as Sapphire (Sa), silicon oxide (SiO_2) crystals, and fused silica (FS) due to their wider bandgap and higher damage threshold at 800 nm driving wavelength. We have mapped the crystal response by measuring the polarization and ellipticity response of these harmonics. Macroscopically, the non-linear propagation of the intense near-infrared (NIR) driving field in wide bandgap materials poses a challenge to control the spectral properties

of harmonics in solids. Therefore, we have investigated the non-linear propagation effects of the ultrafast intense NIR driving field in the wide bandgap dielectrics such as MgO, Cr: MgO, Sa, SiO₂ crystals, and FS. To avoid the non-linear propagation effects, SH and TH have been generated in reflection geometry and compared with the transmission geometry harmonics in Sa, SiO₂ crystals, and FS.

We have also disentangled the contributions of harmonics (SH and TH) from aluminum nitrate (AlN), aluminum gallium nitrate (AlGaN) thin films deposited on the Sa substrate in transmission and reflection geometry. The generation and disentangling of these low-order harmonics have highlighted the possibility of generating XUV from thin films. Furthermore, SHG and THG have been generated in a (100) oriented single, and polycrystal, and (010) oriented polycrystal Gallium Oxide (Ga₂O₃) at 800 nm. We have mapped the crystal symmetry response by measuring the orientation dependence of harmonics. Interestingly, we have observed a strong signal of SH and TH at elliptical and circular polarization of the driving laser pulses from (010) oriented polycrystal Ga₂O₃. The below bandgap harmonics H3, H4, H5, H6, H7, H8, and H9 of 3 μ m wavelength in (100) and (010) oriented polycrystal Ga₂O₃ have been generated at The Laboratory for Intense Lasers (L2I), IST, Lisbon. In addition, we have mapped the symmetry of the crystals by measuring the orientation dependence of harmonics. This can open up a new horizon for the XUV pulses and possibly isolated attosecond pulses through polarization gating from the power electronic materials.

High harmonics have revealed a wealth of perspectives such as all-optical mapping of the electronic band structure, ultrafast quantum information, and the creation of novel all-solid-state attosecond sources. Significant efforts have been made to understand the microscopic aspects of HHG in crystals. In contrast, the macroscopic effects, such as non-linear propagation effects of the driving pulse inside the dense solid media and its impact on the HHG process, are often overlooked. Therefore, non-linear propagation effects of the driving pulses on low and high harmonics in silicon (Si) and zinc oxide (ZnO) crystals have been generated at the laboratoire d'Optique Appliquee (LOA), Paris, France, by using the NOVAE laser. This study explores macroscopic effects by comparing two materials with distinct optical properties, Si and ZnO. By scanning the focal position of 85 fs, 2.123 μ m wavelength pulses inside the crystals (Z-scan), we reveal spectral shifts in the generated harmonics. We interpret the overall blueshift of the emitted harmonic spectrum as an imprint of the driving field spectral modulation occurring during the propagation inside the crystal. This is supported with numerical simulations. This study demonstrates that manipulating the fundamental driving field through non-linear propagation effects can realize the precise control of the emitted low and high harmonics spectrum in solids. This method could offer a robust way to tailor HHG spectra for a range of spectroscopic applications.

The flexibility of generating new wavelengths through the harmonics process in solids has opened up a new horizon to manipulate the shape of beams. It enables the imaging of nanoscale structure in diffraction. Ptychographic lensless coherent diffraction imaging (CDI) technique had enabled the imaging of extended samples in the far-field by using XUV or X-rays illumination sources. Here, we have generated the harmonics in semiconductors (ZnO and Si) and imaged the etched crystal surface from the harmonic emission. The spatial beam shaping of harmonics is controlled by etched spiral zone plates (SZP) on the surface of ZnO and nanocircuits on Si crystals by the focused ion beam (FIB) technique. The reconstruction of diffraction imaging of simulated and experimental measured diffraction patterns in the far-field validated with the ptychography in PyNX. Ptycho library. The harmonics diffracted from the SZP's generate the orbital angular momentum (OAM) beams with many applications ranging from microscopy to quantum information. This study could pave the way to open a new horizon to use solidstate harmonics for plasmonic applications and imaging of magnetic domains from the self-emission of harmonics in magnetic materials.

We explore applications using the much brighter gas-phase harmonics to achieve single-shot pumpprobe data of a solid as it transforms to a plasma. This route could offer a unique insight into understanding the time-dependent dynamics of the solid-state HHG process itself, as a probe beam can measure the electronic transitions occurring during the ultrafast time.

Keywords: High harmonic generation, Microscopic and macroscopic aspects, Perturbative and non-perturbative harmonics, Non-linear propagation effects, Ultrafast imaging spectroscopy.

Publications

List of publications included in this thesis

- Mukhtar Hussain, S. Kaassamani, T. Auguste, W. Boutu, D. Gauthier, M. Kholodtsova, J-T. Gomes, L. Lavoute, D. Gaponov, N. Ducros, S. Fevrier, R. Nicolas, T. Imran, P. Zeitoun, G. O. Williams, M. Fajardo and H. Merdji, "Spectral control of high order harmonics through non-linear propagation effects" Appl. Phys. Lett. **119**, 071101 (2021); https://doi.org/10.1063/5.0053152.
- Patricia Estrela, Gareth O. Williams, Mukhtar Hussain, and Marta Fajardo, "Lithium fluoride detectors for high spatial resolution imaging of tabletop XUV from high harmonic generation in gases", JOSA B,(2021). https://doi.org/10.1364/JOSAB.422767
- Mukhtar Hussain, Hugo Pires, Willem Boutu, Dominik Franz, Rana Nicolas, Tayyab Imran, Hamed Merdji, Marta Fajardo and Gareth O. Williams, "Controlling the non-linear optical properties of MgO by tailoring the electronic structure", Appl. Phys. B 126, 46 (2020).
- 4. Thomas Wodzinski, Swen Künzel, Jayanath C. Koliyadu, Mukhtar Hussain, Barbara Keitel, Gareth O. Williams, Philippe Zeitoun, Elke Plönjes, and Marta Fajardo, "High-harmonic generation wave front dependence on a driving infrared wave front", Applied optics, 59(5),1363-1370, (2020).
- 5. Mukhtar Hussain, Fernando Lima, Willem Boutu, Hamed Merdji, Marta Fajardo and Gareth O. Williams, " Demonstration of non-perturbative and perturbative third-harmonic generation in MgO by altering the electronic structure", Ready to submit in Optics Express.
- Mukhtar Hussain, Gareth O Williams, Tayyab Imran and Marta Fajardo,"Non-linear propagation effects of intense femtosecond pulses on low order harmonics in solids" In review in Laser Physics Letters, (https://arxiv.org/abs/2104.10629).
- Gareth O. Williams, Mukhtar Hussain, Patricia Estrela, Jayanath Koliyadu, Thomas Wodzinski, Swen Kunzel, Marta Fajardo, "Imaging the solid to plasma transition in laser heated titanium", In preparation.
- 8. Mukhtar Hussain, Gareth O. Williams, Marta Fajardo *et al.*,"Solid-state harmonic generation based ptychography of nanostructures and nanocircuits" In preparations.
- Mukhtar Hussain, Gareth O. Williams, Joana Alves, Hugo Pires, Marco Peres, Katharina Lorenz, Goncalo Figueira, and Marta Fajardo, "Anisotropic harmonic generation in gallium oxide", In preparation.
- 10. Mukhtar Hussain, Gareth O. Williams, Marta Fajardo *et al.*, "Disentangling the low order harmonic generation from thin films and bulk", In preparation.

List of publications not included in this thesis

- M. Naeem, Noor-ul ain Fatima, Mukhtar Hussain, T. Imran, A. S. Bhatti, "Design Simulation of Czerny-Turner Configuration-based Raman Spectrometer using physical optics propagation algorithm". under review in optics. (http://arxiv.org/abs/2108.00292)
- M. Naeem, R. Munawar, Mukhtar Hussain, T. Imran, A. S. Bhatti, "Simulation and analytical analysis of the Blumlein discharge circuit for the generation of coherent UV pulses in air", Majlesi Journal of Electrical Engineering 15(2), 65-71 (2021). https://doi.org/10.52547/mjee.15.2.65
- Mukhtar Hussain, Tayyab Imran, Adam Borzsonyi, "Thermal lensing measurements of Ti: sapphire crystal by an optical wavefront sensor." Microwave and Optical Technology Letters 61.12, 2901-2909 (2019). https://doi.org/10.1002/mop.31962.
- Qaid, S. M., Mukhtar Hussain, Hezam, M., Khan, M. M., Albrithen, H.Ghaithan, H. M., and Aldwayyan, A. S. Structural and optical investigation of brookite TiO2 thin films grown by atomic layer deposition on Si (111) substrates. Materials Chemistry and Physics, 225, 55-59 (2019). https://doi.org/10.1016/j.matchemphys.2018.12.067
- T Imran, Mukhtar Hussain and C P João "Pulse compression of white-light continuum generated at 1053 nm in bulk sapphire: an experimental study." Laser Phys. Lett. 15 116101 (2018). https://doi.org/10.1088/1612-202X/aadf60.
- Mukhtar Hussain, T. Imran "Design and characterization simulation of Ti: Sapphire-based femtosecond laser system using Lab2 tools in the NI LabVIEW," Microw Opt Technol Lett. 60:1732– 1737 (2018). https://doi.org/10.1002/mop.31232.
- T. Imran, Mukhtar Hussain, "An overview of LabVIEW-based f-to-2f spectral interferometer for monitoring, data acquiring and stabilizing the slow variations in carrier-envelope phase of amplified femtosecond laser pulses", Optik-International Journal for Light and Electron Optics 157 (C), 1177-1185 (2018). https://doi.org/10.1016/j.ijleo.2017.11.175.
- T. Imran, Mukhtar Hussain, "Development of thermal lensing compensated 30 fs pulse duration chirped pulse amplification laser system and single-shot intensity-phase measurement", Acta Physica Polonica A, 133(1), 28-31, (2018). http://dx.doi.org/10.12693/APhysPolA.133.28
- T. Imran, Mukhtar Hussain, and G. Figueira. "Computer-controlled multi-shot frequencyresolved optical gating diagnostic system for femtosecond optical pulse measurement." Microwave and Optical Technology Letters 59(12), 3155-3160, (2017). https://doi.org/10.1002/mop.30894.

Oral Presentations at Conferences, Meetings and Workshops

 G. O. Williams, M. Hussain, P. Estrela and M. Fajardo, "Imaging the solid to plasma transition" 47th EPS Conference on Plasma Physics, 21th -25th June 2021.(Online) http://ocs.ciemat.es/EPS2021ABS/html/contrib.html

- M. Hussain, T. Imran, G. O. Williams, M. Fajardo and H. Merdji, "Non-linear propagation effects of intense femtosecond pulses on low order harmonics in solids" ISMTP-2021 Govt. College University Faisalabad, Pakistan, 17th -18th March 2021. (Online).
- M. Hussain, S. Kaassamani, M. Kholodtsova, D. Gauthier, W. Boutu, T. Imran, G. O. Williams, M. Fajardo and H. Merdji, "Intensity dependent spectral blueshifts in harmonics generated in semiconductors", PhD Open Days Instituto Superior Tecnico, University of Lisbon, Portugal, 26th -28th October 2020. (Online).
- Gareth O. Williams, M. Hussain, Jayanath Koliyadu, Thomas Wodzinski, Swen Künzel, Marta Fajardo, "Imaging the solid to plasma transition", 3rd European Conference on Plasma Diagnostics, Lisbon, Portugal, 6-9 May 2019.

Poster Presentations at Conferences, Meetings and Workshops

- G. O. Williams, M. Hussain, P. Estrela, J. Koliyadu, T. Wodzinski and M. Fajardo, "Ultrafast XUV imaging of titanium undergoing the solid-to-plasma transition induced by femtosecond laser heating",47th EPS Conference on Plasma Physics, 21th -25th June 2021. http://ocs.ciemat.es/EPS2021ABS/html/contrib.html
- M. Hussain, Gareth O. Williams, Willem Boutu, Dominik Franz, Hamed Merdji and Marta Fajardo, "Harmonic generation in solids using a near IR driving field", 7th International Conference on Attosecond Science and Technology, Szeged, Hungary, 1-5 July 2019.
- M. Hussain, Gareth O. Williams, Willem Boutu, Dominik Franz, Hamed Merdji and Marta Fajardo, "Solid-state harmonics generation near IR driving field" IV International Conference on Applications of Optics and Photonics, Lisbon, Portugal, 31 May - 4 June 2019.
- M. Hussain, Gareth O Williams, Hamed Merdji and Marta Fajardo, "Ultrafast imaging the solid to plasma transition", PhD Open Days, Instituto Superior Tecnico, University of Lisbon, Portugal, 9-10 April 2019.
- P. Estrela, M. Fajardo, D.C. Leitao, S. Kunzel, J. Kollyadu, T. Wodzinski, M. Hussain, G.O. Williams, "Nanofabrication and characterization of Fresnel Zone Plates for 3D XUV Imaging". IUVSTA Nano-Optics international School, INL, Braga, Portugal, 18th -22nd February 2019.
- M. Hussain, Gareth O Williams, Hamed Merdji and Marta Fajardo "Applications of high harmonic generation: understanding ultrafast dynamics in solids and plasma", PhD Open Days Instituto Superior Tecnico, University of Lisbon, Portugal, 21-22 March 2018.

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Nomenclature

- ϵ_0 Electric Permittivity of Vacuum.
- γ Keldysh Parameter.
- \hbar Reduced Planck's Constant.
- ω Laser Frequency.
- ω_0 Laser Central Frequency.
- au Lifetime of the Excited State.
- c Speed of Light.
- I Light Intensity.
- *P* Pressure.
- Q Atom Effective Electric Charge.
- T Temperature.
- E_0 Electric Field Amplitude.
- BZ Brillouin Zone.
- CCD Charge-Coupled Devices.
- DFT Density Functional Theory.
- HED High Energy Density.
- HEDS High Energy Density States.
- HH High Harmonic.
- HHG High Harmonic Generation.
- LDA Local Density Approximation.
- MPI Multi-Photon Ionization.
- OAM Orbital Angular Momentum.

- SH Second Harmonic.
- SHG Second Harmonic Generation.
- SSHG Surface Second Harmonic Generation.
- SZP Spiral Zone Plate.
- TDDF Time Dependent Density Functional Theory.
- TH Third Harmonic.
- THG Third Harmonic Generation.
- TI Tunnel Ionization.
- WF Wavefront.
- XUV Extreme Ultra Violet.

Chapter 1

Introduction

Laser pulses of nano to femtosecond duration can be obtained through Q-switching or mode-locking techniques. However, these techniques are costly, bulky, and required to deposit a considerable amount of energy to the medium. The ability to achieve high field without depositing a large amount of energy is a pivotal question to address. Thanks to the medium's non-linear effects, which offered a way to achieve shorter pulses on the interaction of laser pulses in a high field regime without depositing too much energy onto the medium. A tunable wavelength and shorter pulses have been achieved through a process known as harmonic generation. High harmonic generation (HHG) has enabled to explore the ultrafast phenomena with a high spatial and temporal resolution that has never been achieved before [1]. The process of HHG in gases was first reported in 1987 by McPherson et al. [2]. HHG in gases has been explained through a three-step model (tunnel ionization, acceleration, and recombination) [3]. The strong non-linear interaction of driving laser pulses with the gases produces a train of light bursts in the extreme ultra-violet (XUV) spectral region with attosecond duration [4, 5]. HHG is a robust method to up-convert near-infrared or visible light into XUV or even soft X-rays in gases [6, 7], providing a new tool for ultrafast physics. This has offered the opportunities for attosecond studies in spectroscopy [8, 9], photo-emission timescales from solids [10], ultrafast current switching in solids [11]. The imaging of molecular orbitals [12] and fundamental timescales of ionizations [13] have been enabled through HHG in gases. HHG has been exploited for attosecond science [14], and attosecond imaging of molecular orbitals [12, 15]. The last 20 years have seen most of the effort in HHG focused on gasses [16], molecules [17], and plasma in the high-intensity regime [18].

In solids, the up-conversion of driving photon energies at moderate laser intensities, due to the nonlinear polarizability of the medium is known as perturbative harmonic generation [19]. In this regime, the harmonic generation efficiency falls off rapidly with the increasing order [20]. One of the nonlinear perturbative response of material on the interaction of intense laser pulses results in the frequency doubling or second-harmonic generation (SHG) [21, 22, 23, 24, 25, 26]. Similarly, the frequency tripling in solids has been observed through the mixing of frequencies, i.e., the sum of SHG frequency and fundamental frequency [27, 28, 29]. These frequency doubling and tripling have been attributed to the perturbative response of solids in which the intensity of harmonics scales linearly with the driving intensity of the laser. Recently, third-harmonic generation (THG) has been shown to display some characteristics of non-perturbative high harmonic generation (NP-HHG) at high field strengths with 800 nm [30] and 1.3 μ m [31] driving wavelengths. In the non-perturbative regime, the up-conversion of frequencies is demonstrated through the motion of electrons under the influence of a strong driving electric field where the intensity of generated harmonics scales non-linearly. However, at longer driving wavelengths, the perturbative response persists even at high field strengths [31], making the two regimes difficult to untangle through THG. The perturbative and non-perturbative response of harmonics can be disentangled through the Keldysh parameter ' γ ' under the given experimental conditions [32]. For example, in the perturbative response of harmonics $\gamma > 1$ and in non-perturbative regime, $\gamma < 1$.

In 2010, a robust method of high-order NP-HHG in solids was demonstrated for the first time by Ghimire et al. [33] that has opened the door to myriad of discoveries in the solid-state that have already been demonstrated in the gas phase. Experiments and theories following this discovery have shown that the process is extremely sensitive to the electronic structure and crystal orientation relative to the laser field polarization. The first report of solid-state NP-HHG in wide bandgap semiconductors by employing few-cycle mid-infrared pulses has exhibited the linear scales of cutoff energy with the driving laser field. Interestingly, the solid-state HHG efficiency strongly depends on the parameters of the driving field of lasers, such as laser intensity and polarization, along with the optical and structural properties of solids.

In the last decade, solid-state HHG has been studied in a wide variety of crystals, amorphous solids and tailored structures [31, 33, 34, 35, 36, 37, 38, 39, 40, 41, 42, 43, 44, 45, 46]. The physical picture of solid-state HHG is in its infancy and is the subject of ongoing discussion [47, 48, 49, 50, 51, 52]. A better understanding of the physical process of solid-state HHG will not only lead to improve the secondary sources but could offer an ability to map the nonlinear properties and possibly allow all-optical mapping of the electronic structure of solids [38, 53, 54, 55, 56, 57]. Usually, in solids above bandgap harmonics are termed as high harmonics generation (HHG) [44]. More recently, HHG has been realized in the strong field regime, where electron tunneling, inter-band transitions and intra-band electron motion lead to non-perturbative harmonic generation [31, 33, 56, 58]. These processes are typically associated with higher-order harmonics in the flat plateau region of the harmonic spectrum. Such harmonics have shown an intriguing dependence on the driving field orientation [31, 59, 60], band-structure [58] and intra-band electron motion [31, 58].

HHG in solids can be realized in materials transparent or less opaque to the driving laser pulse wavelength. As femtosecond duration pulses are generally generated in the near to mid-infrared region, insulating and semi-conducting solids are the materials of choice for HHG. HHG process in solids shares some similarities with HHG in gases, at least conceptually [57, 61]. The first step is an inter-band transition that promotes a charge carrier to the conduction band. Once there, this electron is driven by the fundamental field and can emit harmonics due to oscillations within a band (intra-band) or excitation and relaxation between bands (inter-band) [34, 38]. For example, HHG in ZnO [33, 39, 40] has been shown to reveal both the inter and intra-band mechanisms.

A full quantum mechanical approach has been adopted which demonstrated the interplay between the intra-band and inter-band transitions in solids (semiconductors and dielectrics) which entails that only the inter-band transitions contribute to HHG process [61]. Several numerical methods have been adopted by others to explain the process of HHG in solids such as time-dependent Schrodinger equations (TDSE) [35, 49, 50, 59, 62, 63, 64], semiconductor Bloch equations (SBE) [34, 54, 55, 57, 61, 65, 66, 67, 68, 69, 70, 71] and time-dependent density functional theory (TDDFT) [51, 52, 58, 72, 73, 74]. It has been computed that the driving laser field ellipticity acts differently and strongly influence the mechanisms of inter-band and intra-band [58]. The inter-atomic bonding contributions to the HHG in solids could open the possibility to retrieve the inter-atomic potential of using own electrons of material and consequently, the valence electron density [31].

Apart from the microscopic physics of carrier generation and motion, the properties of the HHG emission can be influenced by the propagation of the electric fields inside the crystal. This macroscopic propagation is highly non-linear for the driving field and linear for the harmonics, owing to their much lower intensity. This makes the HHG spectrum an intricate fingerprint of the complex interplay of microscopic and macroscopic processes. The macroscopic aspects of HHG particularly propagation of the intense driving field has been previously linked with redshifts in the HHG spectrum in plasmas and gases [75, 76, 77]. This effect is attributed to the delayed emission of HHG from excited states or resonant states [78] or dislocation of molecules [79]. In solids, numerically computed HHG spectra have shown redshifts in the higher plateaus due to higher band transitions [36]. In sapphire, intensity-dependent redshifts and blueshifts were observed in the spectrum of harmonics and attributed to the long and short electron/hole trajectories, respectively [80]. These studies showed the electronic effects on the HHG process, while the macroscopic or propagation effects of the driving field on the spectral profile of harmonics haven't been fully explored. We have demonstrated that the strong photoionization process is the only process that contributes to the non-linear propagation effects on harmonics in solid-state-HHG [81]. Other studies demonstrated the propagation effects on harmonics [14, 82, 83, 84] while Vampa et al. offered a way to avoid the propagation effects [41]. In addition, an ab initio computational study reported the impact of the thickness of thin films on the efficiency of harmonic generation and revealed efficient harmonics generated from only the few-tens of nanometer [85]. The computational study of ultrafast light propagation effects in thin films of different thicknesses showed the saturable absorption is the key factor for non-linear effects [86].

Recently, HHG in the XUV spectral region has been generated in titanium nitride (TiN) thin films deposited on Magnesium oxide (MgO) substrate, which illustrated that the intensity scaling of harmonics and angular anisotropy attributes to the anisotropic nature of the conduction band of TiN, indicating the source of harmonics in metals corresponds to intra-band transitions [87]. This generation of XUV in the conductive metallic film can open up new opportunities towards the efficient and compact frequency combs where the electric field can be enhanced around and inside the TiN antenna, [88, 89]. This can be employed to replace the large cavity systems [90]. The enhanced high-order harmonic generation has been reported from the metal surface by tuning the electronic band structure [91], highlighting the possibility to generate XUV pulses in the range of 10-100 eV and in the "water window" spectral range (282-533 eV). The solid-state HHG has opened up the prospect of new XUV light sources [92] and generation of isolated attosecond pulses [93]. The shorter driving wavelengths for the generation of HHG provide an

excellent source of narrow-band XUV frequencies, which have many applications such as photoelectron spectroscopy of atoms and molecules [94]. The prospect of measuring and controlling dielectrics with ultrafast optical pulses for signal processing and optoelectronic devices has already been highlighted [11, 95] but research in this field is just emerging.

1.1 Thesis outline

The goal of this thesis is to investigate the ultrafast response of a matter under extreme conditions, mainly to generate below bangap (low-order) and above bandgap (high-order) harmonics in solids. The process of low-order harmonics is presented by controlling the microscopic and macroscopic effects such as tailoring the electronic structure by doping and through the non-linear propagation of intense driving fields in thin solids. We have generated low-order harmonics in solids at 800 nm and investigated the transitions from non-perturbative to perturbative harmonics by tailoring the electronic structure in solids. The spectral control of high harmonics is demonstrated through the non-linear propagation effects of the driving pulses. In addition, we have displayed harmonic emission as a source for the self-imaging of different spiral zone plates, single slit, different nanostructures. We have reconstructed the isolated nano-structures images in simulation and experimental data by adopting ptychography. We have generated and imaged the intensity distribution of the orbital angular momentum harmonics beams from the etched surface of semiconductors. Furthermore, the perspective of the ultrafast high energy density states in Titanium (Ti) using femtosecond laser pulses in pump-probe setup demonstrated. We have shown the changes in the XUV optical properties and electronic structure using ultrafast HHG spectroscopy.

The present thesis work consists of the following parts:

An overview of harmonics in gases and solids:

In chapter 2, we have described the basics and presented an overview of harmonics in gases and solids. A comparison of perturbative and non-perturbative harmonics has been introduced. We have discussed the harmonics dependence on the driving wavelength, conversion efficiency, polarization or orientation, and ellipticity dependence in gases and solids. We have presented the results for the optimization of HHG in gases that have been carried out at the VOXEL laboratory for imaging and probing solid-density plasma.

Low-order harmonic generation in dielectrics and thin films:

• In chapter 3, initially, SHG and THG in wide-bandgap dielectrics such as MgO and Chromium (Cr) doped MgO (Cr: MgO) at 800 nm driving wavelength of the pulse duration of 40 fs, operating at 1 kHz is investigated at VOXEL laboratory, Instituto Superior Tecnico (IST) (see, table 1.1). We have investigated the impact of Cr doping concentration on the SHG (400 nm) [26] and THG (267 nm). The non-linear response has been mapped through the polarization and ellipticity dependence of these below bandgap harmonics. We have shown perturbative SHG, and non-perturbative THG can be controlled in the tailored cubic crystals (Cr: MgO). The semi-classical electron trajectories model (non-perturbative model) and perturbative model are adopted to explain the non-perturbative and perturbative behavior

of THG in MgO and Cr: MgO. Furthermore, below bandgap harmonics such as third (H3) and fifth (H5) of 3 μ m, 40 fs, operating at 100 kHz have been generated in MgO, Cr: MgO (1300 ppm and 9500 ppm) in The Laboratory for Intense Lasers (L2I), IST, Lisbon (see, table 1.1). In addition, the crystal symmetry is mapped by measuring the orientation dependence of H3 and H5 at a fixed laser polarization.

• The non-linear propagation of the intense near-infrared (NIR) driving field in amorphous and crystalline materials poses a challenge. It can offer an opportunity to control the spectral properties of harmonics in solids. To address this challenge, we have investigated the non-linear propagation effects of the intense ultrafast NIR in the crystalline and amorphous materials such as MgO, SiO₂, sapphire (Sa), and fused silica (FS). The impact of non-linear propagation of NIR on the SHG and THG have been investigated in transmission and compared with the SHG and THG in reflection geometry [96].

• The isotropic and anisotropic polarization response of SHG and THG have been observed in single and polycrystal oriented along (100) and (010) Gallium Oxide (Ga₂O₃) at 800 nm driving wavelength. Interestingly, a strong signal of SHG and THG has been observed at the elliptical and circular polarization of the driving field in (010) oriented polycrystal Ga₂O₃, highlighting the possibility to use elliptical/circular harmonics for probing magnetic materials or chirality of molecules. In addition, below bandgap harmonics such as third (H3), fourth (H4), fifth (H5), sixth (H6), seventh (H7), eighth (H8), and ninth (H9) in (100) and (010) oriented polycrystal Ga₂O₃ have been generated at 3 μ m wavelength in L2I, IST, Lisbon (see, table 1.1). We have mapped the symmetry of the crystal by measuring the orientation dependence of harmonics which can open us the horizon to map the electronic bandstructure of solids through non-perturbative harmonics.

• In addition, SHG and THG have been investigated in thin films such as Aluminium Nitrate (AlN), Aluminium Gallium Nitrate (AlGaN) deposited on the Sa substrate at 800 nm (see, table 1.1). We have disentangled the contribution of harmonics from the substrate and thin films by adopting transmission and reflection geometry.

| Material | Driving wavelength | Thickness (μm) | bandgap (eV) | Harmonics order |
|---------------|------------------------------|---------------------|----------------|-----------------|
| Si | $2.1 \ \mu \mathrm{m}$ | 2 and 300 | 1.11 | H3-H9 |
| STO | $2.1~\mu{ m m}$ | 300 | 3.25 | H3-H7 |
| ZnO | 800 nm and 2.1 $\mu {\rm m}$ | 200 | 3.3 | H2 and $H3-H7$ |
| AlGaN | 800 nm | 0.5 | 4.7 | H2, H3 |
| Ga_2O_3 | 800 nm and 3 $\mu {\rm m}$ | 300 | 5.02 | H2,H3-H9 |
| Cr: MgO | 800 nm and 3 $\mu {\rm m}$ | 200 | 5.36 | H2, H3, H5 |
| AlN | 800 nm | 3 | 6.2 | H2, H3 |
| MgO | 800 nm and 3 $\mu {\rm m}$ | 200 | 7.8 | H2, H3, H5 |
| SiO_2 | 800 nm | 200 | 9 | H2, H3 |
| \mathbf{FS} | 800 nm | 300 | 9 | H2, H3 |
| Sapphire | 800 nm | 200 | 10 | H2, H3 |

Table 1.1: Harmonic generation in various solids of different bandgaps ranging from 1-10 eV has been studied in this thesis at different driving wavelengths. We have measured harmonics' spectral, spatial, polarization, ellipticity response, and the impact of non-linear propagation on harmonics. H2: second-harmonics, H3: third-harmonics,....., H9: ninth-harmonics.

High harmonics in semiconductors and imaging of nano-patterns through solid-state ptychography:

• In chapter 4, initially, we have generated the below and above bandgap harmonics (high harmonics) (up to 9^{th} -order) in thick and thin Silicon (Si), Zinc Oxide (ZnO), and Strontium Titanate SrTiO3 (STO) (see, table 1.1). We have investigated the polarization response of harmonics to map the crystals symmetry at 2.123 μ m. By scanning the focal position of 85 fs, 2.123 μ m wavelength pulses inside the crystals (Z-scan), we have revealed spectral shifts in the generated harmonics with the translation of the laser peak intensity in crystals, thus revealing the control of spectral properties of the generated harmonic spectrum within the bulk, with wider bandgap materials (such as ZnO used in this study) allowing for less re-absorption and greater control of the harmonic spectrum as compared to silicon. We have supported our experimental findings with the calculations of the non-linear propagation of the driving field inside the bulk material.

• In the second part of chapter 4, we have implemented the solid-state harmonics based ptychography to image the nano-structures from the self emission of harmonics from the etched surfaces. We have etched nanostructures on the Si surface by focused ion beam (FIB) and recorded diffraction patterns with self-emission of harmonics from Si. The reconstruction of diffraction imaging of simulated and experimental measured diffraction patterns in the far-field validated with the ptychography in PyNX.Ptycho library. This study could pave the way to open a new horizon to use solid-state harmonics for plasmonic applications and imaging of magnetic domains from the self-emission of harmonics in magnetic materials. Finally, the spatial beam shaping of harmonics is controlled by etched spiral zone plates (SZP) on the surface of zinc oxide (ZnO). The harmonics diffracted from the SZP's has generated an orbital angular momentum (OAM) beams. The intensity distribution of vortex beams of fifth harmonics is imaged to show that harmonics photons carrying an OAM. We show that the shaping of the material surface can modulate the intensity distribution of harmonics which can produce focused optical vortices up to nanometers scale.

Conclusions and perspectives:

The chapter 5 consists of conclusions, perspectives and achievements that have been attained during this thesis work. The perspectives included the investigation of electronic and molecular dynamics of ultrafast charge carriers in semiconductors by solid-state harmonics as a probe beam in conjunction with the photo-emission spectroscopy. A brief description of femtosecond time-resolved imaging system based on the single-shot transmission of XUV light from HHG in Xenon (Xe) in a femtosecond laser-heated titanium foil is highlighted as a perspective with the idea to use a solid-state HHG sources to probe the solid to plasma transition in future.

Chapter 2

Basics and overview of high harmonic generation in gases and solids

In this chapter we have explained the basics of high harmonic generation (HHG) in gases and solids. The phenomena of low-order perturbative harmonic generation is demonstrated in section 2.2. The nonperturbative HHG in gases and its related aspects are explained in section 2.3. The optimization of HHG in gases which is carried out at VOXEL laboratory has been described in section 2.3.5. The process of non-perturbative HHG in solids and related aspects of solid-state HHG has been demonstrated in section 2.4. Finally, the propagation effects of the driving field on harmonics are discussed in section 2.5.

2.1 Introduction

High harmonic generation (HHG) is a non-linear mechanism in which the intense driving field (nearinfrared (NIR), Mid-IR, or IR wavelengths) interacts with the non-linear medium and generates the integer frequencies of the driving field frequency. The intense driving field dictates the coherent motion of electrons which results in HHG emission. Typically HHG is divided into two types; 1) perturbative harmonics, which scale (perturbatively) linearly with the driving field intensity. The perturbative harmonics can be generated through the multiphoton ionization (MPI) process or wave-mixing. 2) Non-perturbative harmonics originated through the electron's tunnel ionizations (TI), and the intensity of such harmonics scales non-perturbatively with the driving field intensity. Perturbative and non-perturbative harmonics can be generated simultaneously under the influence of an intense driving laser field in the medium. By calculating the Keldysh parameter ' γ ', one can have an idea which process is dominated, either perturbative or non-perturbative under the given experimental conditions [32]. The Keldysh parameter is calculated as

$$\gamma = \omega \frac{\sqrt{2mV}}{eE} \tag{2.1}$$

Where V is the ionization potential of the given non-linear medium, m and e are the mass and charge of an electron, ω and E are the driving field's frequency and electric field strength, respectively. For the MPI, $\gamma > 1$ and for TI process, $\gamma < 1$, respectively [97, 98]. So by calculating the γ under the given experimental conditions, we can predict whether the observed harmonic generation process is perturbative or non-perturbative in addition to the intensity scaling of the harmonics on the driving field intensity.

2.2 Perturbative harmonic generation

The perturbative harmonic can be generated through the wave-mixing or multiphoton ionization process. An electron from the valence band absorbs "n" photons of the intense driving laser pulse having frequency ω , jumps to higher energy levels (conduction bands in case of solids), and emit photons of "n ω " frequency. The second harmonic generation (SHG) is the perturbative harmonic in nature. It is the first non-linear response of solids when intense laser pulses interact with the solids. The two photons of the driving laser pulses are absorbed by the solids and emit another photon with the twice frequency of the driving photon as shown in figure 2.1(a). The energy level diagram for the process of SHG is shown in figure 2.1(b). The driving photon absorbs by an electron and jumps from the ground state to a first virtual state which further jumps to the next virtual state by absorbing another photon of the same frequency ω . The excited electron decay to the ground state by releasing a photon having the frequency of 2 ω . This phenomenon is termed as SHG. The intense driving laser field induces the non-linear polarization in the medium, which is given as

$$P = \epsilon_0 \chi^{(1)} E^1 + \epsilon_0 \chi^{(2)} E^2 + \epsilon_0 \chi^{(3)} E^3 + \dots + \epsilon_0 \chi^{(n)} E^n$$
(2.2)

Where, $\chi^{(n)}$ are the nth order non-linear susceptibilities, ϵ_0 is the vacuum permittivity, $\chi^{(1)}$ is responsible for the linear polarization. The SHG is induced by the second-order non-linear susceptibility $\chi^{(2)}$ of the medium. Similarly, $\chi^{(3)}$ induces the third harmonic generation (THG) and so on...

The SHG was first reported experimentally by Peter Franken et. *al.* in 1961 [19] by focusing the 694 nm on the quartz crystal and measured the spectrum of 347 nm on the photographic paper. The theoretical explanation of SHG was demonstrated in 1962 [99] and demonstrated various rules about the interaction of light with the non-linear medium, which results in SHG. The SHG is forbidden in the centrosymmetric materials or having the inversion symmetry [100] as the higher-order even harmonics. However, even for these materials, SHG can be generated at the interfaces or the surfaces where the symmetry is broken [26] which is termed as surface second harmonic generation (SSHG). SSHG had been used to probe the molecular monolayers adsorbed to surfaces [101]. The most common way to generate the SHG is to use the birefringent medium. Another way of generating an efficient SHG is to vary the refractive index of the medium periodically and meet the quasi-phase-matching conditions.

One of the third-order non-linear response of solids can be observed when an intense laser driving field interacts. As a result the optical THG is observed which is attributed to the third-order non-linear susceptibility $\chi^{(3)}$ as shown in figure 2.2(a). The three photons of the driving laser pulses are absorbed



Figure 2.1: (a) The geometry of SHG in solids, ω and $\chi^{(2)}$ are the frequency of light and second-order non-linear susceptibility of the solid. (b) Energy level diagram for SHG in solids. An electron absorbs two photons of driving laser, jumps to a higher virtual state in between the bandgap, and emits a photon of frequency ($\omega_{SHG}=2\omega$) when de-excited to the valence band. Red and cyan line arrows indicate the fundamental and second harmonic photons.



Figure 2.2: (a) The geometry of THG in solids, ω and $\chi^{(3)}$ are the frequency of light and third-order non-linear susceptibility of the solid. (b) Energy level diagram for perturbative THG in solids. An electron absorbs three photons, jumps to a higher virtual state in between the bandgap, and emits a photon of frequency ($\omega_{\text{THG}}=3\omega$) when de-excited to the valence band. Red and blue line arrows indicate the fundamental and third harmonic photons.

by the solids through multiphoton absorption process and emit a photon which has three times frequency to the fundamental photon. The energy level diagram for the process of THG is shown in figure 2.2(b). The driving photon absorbs by the electron and jumps from the ground state to a first virtual state and further jumps to the next virtual state by absorbing second photon of the same frequency ω . Finally reaches to a third virtual state by absorbing third photon of the same frequency ω . The excited electron de-excited to the ground state and released a photon having the frequency of 3ω . This process is known as perturbative optical THG.

The THG is one of the non-linear optical process [102, 103] which is more efficient generally at the few end layers of surfaces or interfaces [81, 104, 105, 106]. The conversion efficiency of perturbative harmonics in solids depends upon the careful alignment of the crystal to obtain the phase-matching condition. Under the phase matching condition, the fundamental and harmonics beam travel with the same phase velocity in the crystal, and as a result the generated harmonics beam buildup at the medium's exit. The intensity of the nth harmonics $I^{(n)}$ varies perturbatively with the intensity I(t) of the driving laser field as follows.

$$I^{(n)} = \chi^{(n)} I(t)^n \tag{2.3}$$

Where n is the order of the perturbative harmonics and $\chi^{(n)}$ is the nth order non-linear susceptibility. With the increase of the order of harmonics, the probability of converting the driving laser photons into harmonics decreases in the medium through multiphoton process. As a result, the efficiency of harmonics falls rapidly. The generated harmonics scale perturbatively at the relatively lower driving intensity. The perturbative harmonics generated throughout the non-linear crystals added up coherently through phase matching. The conversion efficiency of the perturbative harmonics is mainly limited by the imperfect phase matching and dispersion of crystals. The matching of pump spectrum and non-linear crystal spectral acceptance monitored the efficiency of the SHG process [107]. Suppose the group velocity mismatch (GVM) in a non-linear crystal is smaller than the driving pulse duration. In this case, the efficiency of SHG and THG can be enhanced. The efficiency of the SHG and THG processes mainly depends on the non-linear crystal properties and driving laser intensity.

There have been an intense exploration for such non-linear materials [108]. Bismuth borate, BiB_3O_6 (BiBO), Beta-Barium Borate (BBO), Lithium Triborate (LBO), and Potassium Titanyl Phosphate (KTP) are the well known non-linear crystals that are often used to generate efficient SHG, and THG [108, 109, 110, 111, 112]. BBO is given preference over other crystals and is widely used for SHG and THG due to its good phase-matching and thus higher conversion efficiency. For the efficient SHG and THG in non-linear crystals, the compensation of phase and group velocity mismatch along with the lower-order group velocity dispersion (GVD) must be taken into account [109]. The phase matching can be obtained by using different thickness, rotating and tilting of crystals. The spatial walk-off angle can be observed during the propagation of pulses in birefringent crystals. The intensity distribution drifted away from the wave vector direction. Whereas in a temporal walk-off, the temporal overlap of pulses is lost due to the group velocity mismatch. The walk-off effects such as spatial and temporal walk-off can be compensated using various thicknesses of non-linear crystals. In summary, the odd perturbative harmonics can be generated in the medium which lacks the inversion symmetry. In contrast, the even-order harmonics vanished in the medium having inversion symmetry such as in gases. The first even-order perturbative harmonics can be generated at the surfaces of cubic crystals [26] or at the interfaces. Usually, the higher-order harmonic generations observed through the TI process, which falls under the umbrella of a non-perturbative regime.

2.3 Non-perturbative HHG in gases

2.3.1 Basic HHG process

HHG in gases has been intensively studied for three decades which was first reported at the University of Illinois [2] and later at CEA Saclay [113]. The emission of HHG was observed in the noble gases when subjected to intense laser frequency. The microscopic process of HHG in gases described by Paul Corkum in 1993 [3] which is known as a three-step model as shown in figure 2.3. The first step (1) of this model, an electron is released from the parent atom through tunnel ionization. In the second step (2), an electron is accelerated by the applied laser field in the continuum and gains kinetic energy. In the third step (3), the accelerated electron recombines to the parent ion with a certain probability of reversing applied field direction and emits photons whose energy is equal to the sum of kinetic energy gained by the electron during motion plus the ionization potential of the atom. This process is repeated after every half cycle of the driving laser field. The spectrum of HHG can be obtained by taking the Fourier transform of the attosecond train of generated pulses. The real and momentum space picture for the atomic (gas-based) HHG is shown in the figure 2.11c and 2.11d, respectively.



Figure 2.3: Schematic illustration of the three-step model for HHG in gases. (taken from [38])

The yield of HHG in gases can be tuned by optimizing the intensity in the range of $(10^{14}-10^{15})$ Wcm⁻² of the laser field, beam waist at focus position, aperture diameter, size of the gas cell and by tuning the pressure in the gas cell. A balance condition between phase matching, generation, and re-absorption should be achieved to maximize the generation efficiency of harmonics. As gas is an isotropic medium

and lacks inversion symmetry, therefore only odd-order harmonics can be observed. The even and oddorder harmonics can be generated in the gas by tweaking the symmetry considerations. The symmetry conditions can be perturbed by using a two-color driving field which can result in even as well as odd harmonics in gases. The efficiency of HHG in gases depends on the driving wavelength, phase matching conditions, and linear polarization of the driving field.

2.3.2 Wavelength dependence of HHG in gases

The frequency of the high harmonic cutoff which is the highest frequency generated in the harmonic spectrum can be calculated as follows [114]

$$\hbar\omega = I_p + 3.2U_p = I_p + \frac{e^2 E^2 \lambda^2}{16\pi^2 mc^2}$$
(2.4)

Where \hbar is the reduced Planck constant, I_p is the ionization potential, U_p is the pondermotive energy, mand e are the mass and charge of the electron, respectively. The cutoff energy of the harmonic spectrum increases with square of the electric field and square of the driving wavelength. The Ti: sapphire-based laser driving wavelength centered around 800 nm has been used as an ideal source to generate high harmonics in gases in the past. Recently, the Mid-IR driving wavelength was also adopted to generate high harmonics in gases. The Mid-IR driving wavelengths extend the cutoff to quadratic wavelength scaling of the pondermotive energy [115]. However, with the increase of the driving wavelength, the efficiency of the HHG in gases dramatically decreases as predicted theoretically on the scale of $\lambda^{(-5-6)}$ [116] and measured experimentally on the scale of $\lambda^{(-6-7)}$ [117]. This decrease in intensity of HHG with the increase of driving wavelength is attributed to the spreading of the dipole and non-dipole effects [118, 119].

2.3.3 Conversion efficiency

The conversion efficiency of HHG from driving photons to harmonic photons depends upon the driving wavelength, driving intensity, the polarization of the driving field, gas medium, and pressure in the gas cell. The conversion efficiency is high, about one order in magnitude at 800 nm as compared to 1550 nm driving wavelength [120]. The conversion efficiency in various noble gases varied due to their different ionization potential. At 800 nm driving wavelength, the conversion efficiency of Xenon gas is 10^{-4} , Argon has 10^{-5} while Neon gas has the conversion efficiency of 10^{-7} [120, 121, 122, 123]. Similarly, the calculated HHG efficiencies in helium at different driving pulse energies and pressures showed that the efficiency could be increased by few orders of magnitude with higher energetic driving pulses. HHG in gases are efficient when the driving wavelength is highly linearly polarized or weakly elliptical. With the increase of ellipticity, the efficiency of the HHG in gases rapidly falls. This is because when the driving field has elliptical polarization, the chances of accelerated electrons to recombine with the parent ions are minimal. As a result, emission of harmonics decreases and eventually drops to zero at circular polarization of the driving field in gases [124].

2.3.4 Phase matching condition

To achieve the highest conversion efficiency from driving photons to harmonic photons, the phase velocity of the generated harmonics and the driving wavelength should be same in the medium (gas) while traveling. This builds up the coherent flux of the harmonic signals, which is known as phase matching [103]. The phase mismatch Δk for HHG in gases introduced by the medium dispersion, neutral gaseous dispersion, free-electron plasma dispersion, the dispersion induced by the focus of the laser field, and the atomic phase dispersion can be written as [125]

$$\Delta k = \Delta k_N + \Delta k_P + \Delta k_{Gouy} + \Delta k_{at} \tag{2.5}$$

Where Δk_N is phase mismatch subjected to the neutral gaseous medium, Δk_P is the plasma introduced phase mismatch. Δk_{Gouy} is the Gouy phase mismatch induced due to the driving laser focus position in the gas cell, and Δk_{at} is the atomic phase mismatch. The optimized phase match conditions can be obtained by optimizing the various parameters such as intensity of the driving field, adjusting the pressure of the gas in the gas cell, and focus position of the driving wavelength [126, 127]. For the optimized HHG in gases, following conditions must be satisfied [121].

$$L_{med} > 3L_{abs}; and L_{coh} > 5L_{abs}$$

$$(2.6)$$

Where, L_{med} is the HHG length, L_{abs} is the absorption length of harmonics signal, and L_{coh} is the coherence length which is the propagation distance over which the harmonics signal add constructively.

2.3.5 Optimization of high harmonic generation in gases at VOXEL

HHG in gases are routinely generated, optimized [128], controlled [129], used for imaging [130] and dense plasma diagnostics in the VOXEL laboratory at IPFN, IST, Lisbon, Portugal. The typical schematic illustration of the experimental setup to generate HHG in gases is shown in figure 2.4. The output of the Astrella laser of 7.5 mJ pulses is directed to a 50 : 50 beam splitter and used only the reflected part of laser energy. The reflected energy is further controlled by using two irises and focused in the rear edge of a gas cell having a dimension of 10 mm in diameter and 15 mm long by 750 mm focal length lens. The Al filter of 464.5 nm thickness of 28.5% calibrated XUV transmission is inserted, which blocks the near-IR pulses and transmits the high harmonics (HH) signal directed to the XUV-CCD camera by a flat mirror. The measured footprints of the HH are shown in the inset of figure 2.4 which are optimized for different aperture size, focus position and gas pressure in the gas cell. After optimizing the footprints of HH by XUV-CCD, we have set up the grating-based spectrometer for spectral measurements of HHs.

The HHG pulses in a gas cell are filtered by 464.5 nm and 150 nm Al filter one by one and together as well. The HH signal after the Al filters are incident at a grazing angle of 9° on a spherical mirror with a radius of curvature of 3 m. The focused HH pulses are directed to a gold transmission grating having 1000 lines/mm by a gold-coated flat mirror, which resolves the signal into its spectral components. The



Figure 2.4: Schematic illustration of the experimental setup for HHG in gases. Laser parameters: 800 nm, 40 fs, 1 kHz and used estimated peak intensity $\approx 10^{14}$ Wcm⁻². Inset (left) shows footprints of HHG and inset on right shows one of the spectral profile of HHG in gases. The footprints and spectral components of HHG were measured alternatively by translating the grating out and in the HHG beam path.

distance between the grating and the XUV-CCD (Princeton Instruments PIXIS-XO 1024B) is kept at 36 cm. The resolved spectral components of HH pulses are imaged on the XUV-CCD, as shown in the inset of figure 2.4.

The best optimized conditions were obtained from recording the footprints of HHG in Ar at (400 & 800) nm, Xe, and Ne gases at a gain of 3 of XUV-CCD, which corresponds to one electron per count. The energy of HHs in Ar at (400 & 800) nm, Xe, and Ne is calculated from the spectrometer calibration counts. The energy of HHG in Ar, Xe, and Ne under the optimized conditions is listed in table 2.1 which is measured by using the transmission grating-based XUV spectrometer.

| Gas | P(mbar) | Aperture size(mm) | HH Photon No. | HH Energy (nJ) |
|-----------------|---------|-------------------|---------------|----------------|
| Ar | 13.5 | 8 | 6.94E + 07 | 2.34 |
| Ar^* | 7.5 | 11 | 4.54E + 07 | 1.53 |
| Xe | 3.5 | 8 | 6.27E + 07 | 2.12 |
| Ne | 15 | 8 | 5.97E + 05 | 0.02 |

Table 2.1: The optimized conditions for high harmonic generation (HHG) in gases to obtain maximum energy. * corresponds to two colour driving wavelength (400 nm & 800 nm).

Spectral measurements of HHG in gases

The integrated and normalized spectrum of HHG in Ar is shown in figures 2.5(a) and 2.5(b). The HH21, HH23, HH25, and HH27 have a higher brilliance. At the same time, HH25 is the dominant one at near-IR (800 nm) driving wavelength, as shown in figure 2.5. Furthermore, HHG in Ar are generated by collinearly focusing the fundamental pulses (800 nm) and second harmonic (400 nm), generated in 100 μ m thick BBO crystal. Odd and even order harmonics are attributed to the two-color driving fields (800 nm and 400 nm). The integrated spectrum and normalized spectrum of even and odd order harmonics in Ar gas at two-color driving wavelengths is shown in figure 2.6. In contrast, HH17, HH19, HH21, and HH23 have higher photon numbers at two-color driving wavelengths (800 nm and 400 nm). In the two-color driving wavelength, the HH21 is dominant in the HH spectrum, as shown in figure 2.6(b).



Figure 2.5: Spectral measurements of HHG at 800 nm in Ar. (a) Integrated spectrum, (b) Normalized spectrum.



Figure 2.6: HHG spectrum in Ar at 800 & 400 nm driving wavelength. (a) Integrated spectrum, (b) Normalized spectrum.

The shifting of peaks and generation of relatively lower order harmonics in Ar when pumped by fundamental and its second harmonic pulses ascribed to the lower energy of the focused incident pulses into the gas cell, attributable to the lower conversion efficiency BBO crystal. Furthermore, the contribution from the long trajectories results in a small HH signal because they lead to a short coherence length L_c compared to the short trajectories.



Figure 2.7: Spectral measurements of HHG at 800 nm in Xe. (a) Integrated spectrum, (b) Normalized spectrum.

The high harmonic spectrum in Xe and Ne under the optimized conditions are shown in figures 2.7 and 2.8, respectively. The HH19 is dominant in Xe, and HH37 is the brightest one in Ne generated high harmonics. The energy of the harmonics calculated from the spectrometer is 5.44 times smaller than that of the CCD measurements. The throughput of our spectrometer is 18.4%.



Figure 2.8: Spectral measurements of HHG at 800 nm in Ne. (a) Integrated spectrum, (b) Normalized spectrum.

Pressure and stability scan of HHG in Ar and Xe

The high harmonic intensity in Ar for each HH order is recorded using the spectrometer setup for different pressure of the gas cell. We have the fixed the other experimental conditions such as pulse energy, beam diameter, lens position, and focusing position of the laser pulses in the gas cell. The behavior of the normalized integrated photon number variation for each HH order with different gas cell pressure in Ar is shown in figure 2.9(a). At higher pressure, in the gas cell, the intensity of the HH is low, which is attributed to the low phase-matching conditions. The other factor of lower intensity is due to the inefficiency of the vacuum system to extract leaked Ar gases from the gas cell, which can absorb the generated HH signals. The HH beam stability is important for the spatial measurements or spatial applications and intensity from shot to shot to confirm repeat-ability. The intensity stability of high harmonic generation in Ar under optimized pressure (13.5 mbar) is recorded for the integration time of 50 ms. The shot-to-shot stability of each HH order is shown in figure 2.9(b).



Figure 2.9: (a) Pressure scan of the integrated signal per HH order in Ar, (b) Shot to shot stability of each HH in Ar at 13.5 mbar.

The dependence of integrated count number and shot to shot stability of higher-order HH in Xe gas



Figure 2.10: (a) Pressure scan of the integrated signal per HH order in Xe, (b) Shot to shot stability of HHG in Xe at 3.8 mbar.

is shown in figure 2.10. The maximum number of counts for each HH in Xe gas is observed on the XUV-CCD at 3.8 mbar (see figure 2.10(a)). Furthermore, the variations in integrated count number for each HH from shot to shot at the optimized pressure have the same approximate pattern as shown in figures 2.9 and 2.10 for Ar and Xe gases, respectively. The sharp decrease in the yield of HHs attributed to the phase mismatch introduced by the dispersion of the gases. This shows that to obtain the stable and efficient XUV source from the gases, the optimum pressure, focus position, and suitable intensity of the driving laser pulses in the gas cell should be considered.

2.4 Non-perturbative harmonics in solids

2.4.1 Introduction

HHG in gases are routinely generated in research laboratories and formed the basis of attosecond science. However, gas-based HHG phenomena involve a complex and expensive setup consisting of chirped pulse amplification (CPA) femtosecond laser systems, vacuum chambers, vacuum pumps, and gas sources that should be confined to a short interaction volume required the sophisticated optics and expensive detection system. Interestingly, solid-state medium offer an alternative way to generate high harmonics without using such a complex system as far gas based harmonics. A decade ago, HHG in solids was observed by focusing the 3.25 μ m driving field to 500 μ m thick ZnO crystal [33] and observed the harmonics up to 25th order at 5 TWcm^{-2} . These observations have opened up a new dimension of strong-field interaction with solids and attosecond science. Interestingly, the cutoff high energy scales linearly with the strength of laser field in solids as compared to the quadratic dependence as anticipated by the three-step re-collision model [3, 114]. Ghimire et al. observed the strong deviation of harmonics yield from the power-law as anticipated from the perturbative non-linear optics. This poses a question about the explanation of HHG in solids. The observed results cannot be explained by the traditional perturbative non-linear optics or strong field re-scattering kinematics. To address this, HHG have been generated in wide variety of solids ranging from graphene [131], amorphous solids [37] to wide bandgap dielectrics [31, 60, 132], tailored structures [44, 46, 133] and in metals [87]. Several studies reported that

the solid-state HHG could be employed to map the electronic properties of solids [57, 59, 134]. Yet, the solid-state HHG is in its fancy and is the subject of ongoing discussion related to its explanation [33, 31, 34, 46, 58, 68, 87, 135, 136].



Figure 2.11: The microscopic process of HHG in solids and atomic level. (a) Real-space illustration of HHG in solids, the driven electron can scatter from the periodic potential, recombine to the associated hole (ion), and re-collide with the nearest hole (ion) due to the closely packed arrays of atoms. (b) The momentum-space picture of HHG in solids illustrates the intra-band Bloch oscillations in the conduction band and the inter-band polarization through tunneling between valence and conduction band. Both transitions result in the emission of high-frequency photons in the forward direction. (c) Real-space picture of three-step model for HHG in atomic level (gases). (d) Momentum space representation of HHG in gases where the electron tunnels from the bound state to the continuum state where the field accelerates it in the parabolic continuum and then recombine with the parent ion to emit high-frequency photons. (taken from [38])

Microscopically its imperative to contemplate the difference between solid-state HHG and the threestep re-collision model qualitatively. Due to the higher number density of solids compared to gases, there is a significant overlap of atomic orbitals from the adjacent atoms of the solids. This creates the delocalization of the valence and conduction band states in solids. The energy band occupied by the valence electrons is called the valence band. The band above the valence band separated by some energy bandgap is termed as conduction band in which electrons can move freely. The schematic illustration of solid-state HHG and atomic case in real and momentum space is shown in figure 2.11. In solids, HHG can be observed through Bloch oscillations (intra-band transitions) or inter-band polarization or through both process (see, figure 2.11 (a-b). Whereas in gases only inter-band polarizations results the HHG (see, figure 2.11(c-d). Although it is more appropriate to work in the reciprocal space by considering the Bloch wave functions and use the Houston picture [137] in the presence of driving laser electric field $(E(\tau))$.

In the Houston space picture, single-particle states evolved and are given as

$$k \to k(t) = k_0 + \frac{e}{\hbar} \int E(\tau) d\tau$$
 (2.7)

where k_0 and k(t) are the time independent and dependent lattice wave vectors, e is the charge of an electron and \hbar is reduced Planck, s constant.

Within a band, the single-particle state moves periodically in the absence of scattering. At the strong driving field, this single-particle state diffracts from the Brillouin Zone (BZ) boundaries within half the cycle of the driving field and is known as Bloch oscillations (see, figure 2.11(a)). These Bloch oscillations are also termed intra-band transitions. The rate at which the single-particle state travels through BZ at the laser peak field E and a lattice constant d is given as $\omega_B = \frac{eE}{d\hbar}$ which is know as Bloch frequency. The momentum space schematic illustration of harmonics (figure 2.11(b)) indicates the dynamics of electrons and holes in the lowest conduction band and highest valence band, respectively. An electron is excited from the valence band to the conduction band of the crystal by the driving laser field. Both the electron and hole will move in the opposite direction in the conduction and valence band, respectively dictated by the vector potential of laser light. On the reversal of electric field direction, the electron and hole can recombine beyond the Γ -point and emit harmonics [61]. This kind of transition is known as interband HHG. In solid-state HHG, the intra-band (within the band) and inter-band (in between the bands) transitions occurred. Whereas in gas-based HHG, only the inter-band transitions lead to the HHG signal.

A full quantum mechanical approach is required to explain the interplay between the intra-band and inter-band transitions, contributing to the emission of harmonics in solids (semiconductors and dielectrics). For this, one can adopt the density matrix approach or time-dependent many-body Schrodinger equations. The solution of these approaches provided by the semiconductor Bloch equations (SBE) [65]. Below are few essential steps that shows how to get a spectrum of harmonics from SBE. The total emission of harmonic intensity $I_{tot}(\omega)$ from the solids can be expressed as

$$I_{tot}(\omega) \propto |\mathcal{F}(\frac{\partial P(t)}{\partial t} + J(t))| \propto |\omega P(\omega) + iJ(\omega)|^2$$
(2.8)

Where, $\frac{\partial P(t)}{\partial t}$ is the inter-band polarization current, J(t) is the intra-band current. $P(\omega)$ is the Fourier transform of time dependent polarization P(t) which observed due to electron-hole motion. $J(\omega)$ is the Fourier transform of J(t) and is given as

$$P(t) = \sum_{k} d_k p_k(t) + c.c.$$
 (2.9)

$$J(t) = \sum_{k,\lambda \in \{e,h\}} j_k^{\lambda} f_k^{\lambda}(t)$$
(2.10)

Where, d_k is the dipole matrix element, p_k is the microscopic polarization, $j_k^{\lambda} = \frac{e}{\hbar} \Delta_k \epsilon_k^{\lambda}$ are the matrix elements of current, $f_k^{\lambda}(t)$ corresponds to occupations of electron and hole in band. The p_k and f_k are the solutions of the SBE and is given elsewhere [65].

However, the underlying microscopic mechanism of HHG in solids is controversial and under intense debate. Several approaches have been adopted to explain the underlying microscopic mechanism of HHG in solids. HHG generated in MgO found that only the inter-band transitions are contributing to the emission of harmonics [138]. At the same time, it could be varied for other crystals. Such as HHG in the thin film of poly-crystalline SiO₂ showed that only intra-band transitions contribute to the emission of harmonics rather than inter-band transitions [56]. An important factor that affects the microscopic phenomena of HHG in solids is the driving wavelength. As reported [68, 139] that intra-band transitions are dominated when the driver wavelength is longer. While at shorter wavelengths such as 1.0 to 5.0 μ m, the inter-band transitions are dominant for the generation of harmonics in solids. Therefore, microscopically the HHG in solids is a complex interplay between intra-band and inter-band transitions. Both mechanisms can be tuned by the experimental conditions and non-linear properties of a material under investigation.

There are several aspects of solid-state HHG that will be discussed here:



2.4.2 Wavelength dependence of solid-state harmonics

Figure 2.12: Recent progress of HHG in solids depending on the photon energy of the highest harmonic with the driving photon energy. Harmonic generation in most of the solids crystal in red boxes will be discussed in this thesis. For this, the driving wavelength of 800 nm, 40 fs operated at 1 kHz has been employed. Crystals enclosed with the green box are derived at 3 μ m to generate low and high-order harmonics. The low bandgap semiconductor, such as encircled by blue are driven at 2.1 μ m to explore the process of HHG until 5.3 eV. We have generated harmonics up to 4.7 eV at 800 nm driving wavelength, shown in black squares. (taken from [38]).

The driving wavelength immensely influenced the process of HHG in solids. For low bandgap materials, longer driving wavelength and low energy driving photons are essential to avoid the optical damage threshold of materials. For wide bandgap materials such as MgO, fused silica, Quartz, Sapphire, etc., harmonics can be generated at 800 nm. Such femtosecond lasers wavelengths are commercially available in most of the research laboratories. Due to the smaller bandgap in metals and semiconductors, the process of HHG can be explored efficiently if the driving source has a wavelength in the range of mid-infrared. The dielectrics having a wide-bandgap can be pumped by the near-infrared wavelength to generate the XUV photon energy through the HHG process. Apart from this, at the longer wavelength, the contributions of the inter-band drop exponentially as $\lambda^{-11.4\pm 2.9}$ [140] and the intra-band contribution to the emission of high harmonics will be dominant. More driving photons are required to make a transition from the valence band to the conduction band and drive inter-band transitions at the longer wavelength. Therefore its contribution decreases. The recent progress of HHG in solids for various driving wavelengths is shown in the figure 2.12, black squares are the energy of the harmonic which have been generated during this thesis for different driving wavelengths such as 800 nm, 2.1 μ m and 3 μ m.

2.4.3 Polarization or orientation dependence of solid-state harmonics

The prominent feature of strong polarization dependence of harmonics in solid distinguished it from the gas-based HHG. As the gas medium is isotropic, the efficiency of harmonics is independent of the applied linear polarization direction to the gaseous medium. Whereas in solids, the anisotropic nature of crystal structure and non-parabolic nature of the electronic bandstructure contributes to the harmonics. In the intra-band regime, the motion of electrons in the conduction band is controlled by the linear polarization of the driving field, and the laser polarization dictates its direction of propagation. Therefore, the motion of the electron wave packet is influenced by the dispersion of the band structure. The different harmonics correspond to the oscillation of electrons to a different region of the energy band. Hence the band dispersion energy can control the group velocity of electrons. Thus the harmonic efficiency can be tuned by either rotating the crystal and keep the laser polarization or vice versa. The orientation/polarization dependence can predict the crystal symmetry and most probably electronic bandstructure [58]. Solid-state HHG is anisotropic and depends on the symmetry of crystal structure. The understanding of the real space picture of HHG can lead to exploring the strong sensitivity of the HHG to the atomic-scale structure [33, 31, 51, 60, 105].

Ghimire et al. [33] in 2010, first time observed the strong anisotropic response of HHG by rotation of ZnO crystal with the laser driving field as shown in figure 2.13(c). Similarly, You et al. [31] had reported that maximum emission of high harmonics strongly depends on the laser driving field polarization angle to the orientation of crystal (figures 2.13(a) and 2.13(b)). The efficient harmonics have been observed when the driving field is aligned to the major axis of MgO, i.e., along Mg-O or O-O bonding direction and have minimum efficiency in between (figures 2.13(a) and 2.13(b)). The microscopic origin of this strong anisotropy attributed by electron trajectory model and found that intensity of harmonics increases (decreases) when the electron trajectories connected (missed) the first and second nearest-neighbor sites. We have calculated the electron trajectories under linear and elliptical polarization to explain the THG



Figure 2.13: (a) Polarization dependence of THG at 1.3 μ m for different driving field strength (b) Polarization dependence of HHG in MgO (taken from [31]). (c) Polarization dependence of high order of harmonics in ZnO (taken from [33]). (d) Polarization dependence of high order of harmonics in Si with the rotation of the crystal. (taken from [141]).

process in MgO and as explained in section 3.2.10. It has been observed that the low-order harmonics are less sensitive than the higher-order harmonics to the laser polarization. The high-order harmonics originate from the intra-band regime and are more sensitive to the band structure and incoming laser polarization.

Vampa et *al.* [141] observed the strong anisotropic response of HHG in Si by rotating the Si crystal with respect to the laser driving field as shown in figure 2.13(d). Strong anisotropy of HHG was observed recently in thin-film metals of TiN, and this anisotropy is attributed to the anisotropic nature of TiN conduction band [87]. The polarization dependence of HHG can be explained with electron trajectory models [31, 60, 132] and can provide the opportunity to determine the crystal structure and band structure. Thus the anisotropy of polarization dependence of harmonics is mainly dependent on the crystal symmetry and conduction band structure. This anisotropy technique can be employed to generate the isolated attosecond pulses in solids through polarization gating.

2.4.4 Ellipticity dependence of solid-state harmonics

The ellipticity of the driving field is another crucial parameter for the solid-state HHG. You et *al.* [31] measured the ellipticity dependence of HHG in MgO and observed the secondary maxima at the circular polarization, highlighting the possibility of generating circularly polarized harmonics from solids as shown in figure 2.14. The shifting of ellipticity of harmonics had been observed by rotation of crystal concerning the laser driving field polarization. When the MgO crystal rotated by 45° and laser polarization aligned to O-O. Alternatively, Mg-Mg bonding direction, the ellipticity peaks shifted to ± 0.65 . The ellipticity dependence of HHG has been explained with the electron trajectories model, which highlights the emission peak corresponds to the electron collision to the nearest neighbor as shown in figure 2.14 (c and d).

The yield of harmonics is dependent on the band curvatures at various k-values. The yield of harmonics can be more potent at elliptical or circular polarization of the driving field. As simulation results showed that the inter-band and intra-band harmonics behave differently to the ellipticity [51]. Therefore, the ellipticity dependence of each harmonic behaves independently attributed to the delocalization of electrons for different regions of the Brillouin zone [51]. As predicted [58] that circularly polarized harmonics can be generated in solid crystals. Experimentally, circularly polarized harmonics in solids have been observed by a single color driving pulses [142, 143, 144]. Compared to gas-based HHG, which can only be efficiently generated at linear polarization. Because at the circular polarization of driving field, electron misses the collision to parent ion in gases. However, HHG in solids has the advantage that they can be generated even when the driving laser field has a high degree of ellipticity due to the intra-band transitions in the non-parabolic bandstructure. This can open up a new horizon for the mapping of the magnetic domain in materials through circular polarized solid-state XUV pulses.



Figure 2.14: Ellipticity dependence of 19^{th} order harmonics in MgO (a) Measured 19^{th} harmonics when laser polarization was aligned to Mg-O bonding direction laser, (b) Measured 19^{th} harmonics when laser polarization has been aligned to O-O bonding direction laser (c) Semi-classical electron trajectories when the major axis has kept along Mg-O bonding direction,(d) Semi-classical electron trajectories when the major axis has kept along O-O bonding direction. (taken from [31]).



Figure 2.15: Conversion efficiency and average power of visible and UV harmonics versus order of the harmonics in ZnO at 3.8 μ m driving wavelength. (taken from [39]).

2.4.5 Conversion efficiency of solid-state harmonics

The number density of solids is higher as compared to the gases which can give an advantage over gases due to the higher number of emitters during the HHG process. At the same time, the re-absorption of the generated harmonics in solids can limit the efficiency of harmonics. As the order of harmonics increases, the more they get attenuated during propagation in the solids [145]. As a result, the harmonics generated at the front surface or deep inside the crystal can't be detected due to the crystal dispersion. Therefore, to achieve the highest signal of harmonics, the laser focus should be translated to the rear side of the solid target. The conversion efficiency and average power of visible and UV harmonics vs order of the harmonics in ZnO at 3.8 μ m driving wavelength has been reported [39] as shown in figure 2.15. The conversion efficiency varies from 10⁻⁶ to 10⁻⁷ for the 11th to 17th order harmonics. A similar conversion efficiency of harmonics has been achieved in noble gases at 800 nm driving wavelength [121]. It shows that solid-state HHG can be used as a source of XUV pulses for spectroscopy applications.

2.4.6 Intensity scaling for non-perturbative solid-state harmonics

Typically, harmonics having photon energy smaller than the bandgap of the solids scale perturbatively. In comparison, the above bandgap harmonics scales non-perturbatively with the intensity of the driving field [33, 39]. However, the border between the perturbative and non-perturbative, particularly for low-order harmonics is vague and required to untangle. We have disentangled the perturbative and non-perturbative response of low order harmonics (THG) in the chapter 3. We showed that the perturbative and non-perturbative behavior of THG is material-dependent at a fixed intensity of the driving laser pulses.



Figure 2.16: Dependence of the individual high harmonics intensity on the driving field intensity. (taken from [33])

The non-perturbative scaling equation for the harmonic intensity is given as

$$I^n = I(t)^q, q \neq n \tag{2.11}$$

Where *n* is the order of harmonics and *q* is the scaling factor of the driving intensity. The intensity scaling of non-perturbative high order harmonics in 500 μ m thick ZnO had illustrated [33] as shown in figure 2.16. It shows that the intensity scaling of harmonics varied from the perturbative (dotted black line for fifth harmonics scaling). The process of HHG in sapphire crystal explored at the 800 nm driving wavelength to draw a relation between the order of harmonics *n* and scaling factor *q* [105] and reported *q* = 3.8,6.0,8.3 and 5.0 for H7, H9, H11, and H13 harmonics. The intensity of the driving field is an order of magnitude smaller than the gas-based HHG for solid-state HHG. Usually, to generate the efficient HHG process in solids, the intensity of the driving field is in the range of $(10^{11} - 10^{13})$ Wcm⁻² depending upon the bandgap of solids [33, 31, 38].

2.5 Propagation effects of driving field in solids

Apart from the microscopic aspects, the macroscopic factors can modulate the overall process of harmonics. Non-linear propagation effects of the driving field are one of the macroscopic effects which can tune the generation process of harmonics in solids. For example, at the normal incidence of the laser beam to solids, the transmitted power of the laser beam can be obtained through the Fresnel transmission coefficient. The Fresnel transmission (T_f) in solids having linear refractive index n can be written as

$$T_f = \frac{4n}{(1+n)^2} \tag{2.12}$$

The linear refractive index is different for different driving wavelengths and solids. For example, at 2.1 μ m driving wavelength, ZnO and Si have the linear refractive index of $n_{ZnO}=1.92$ [146] and $n_{Si}=3.4492$ [147], respectively. Similarly, the linear refractive index of magnesium oxide (MgO) at 800 nm driving wavelength is 1.73 [148]. The linear absorption of the driving laser beam in solids is pronounced depending upon the optical properties of the solids. For a uniform absorption in medium, the output intensity of the driving laser beam can be given as $I_z = I_0 e^{-\alpha z}$, where I_0 is the input intensity of the driving laser beam, α is the absorption coefficient. Z is the propagation distance in the medium. The non-linear optical properties of the medium can contribute to their role at high field, depending on the medium and laser driving intensity. The Kerr effect can induce self-phase modulation and self-focusing in the space and time domain, respectively. The interaction of an intense laser field with the solids has of great importance for its many applications ranging from biomedical technologies [149], micro-machining of optical materials [150, 151, 152], optical data storage [153], white light continuum generation [154, 155] and at below damage threshold of solids can generate the HHG [33, 31, 38, 132].

The theoretical aspect of non-linear propagation effects of the driving field in solids and the observed impact of the non-linear propagation effects on harmonics will be discussed in section 4.2.

2.6 Conclusion

In this chapter, we have explained the underlying physics of the harmonic generation and various factors which can tune the generation process in gases and solids. The process of harmonics generation in gases can be demonstrated through the three-step model (inter-band transitions). Whereas in solids, the harmonics phenomena can be explained through inter-band and intra-band transitions. Solid-state harmonics have the advantage over gas-based due to the anisotropic nature of materials, can predict the crystal symmetry, and map electronic bandstructure through orientation/polarization response of harmonics. However, the process of harmonics can be controlled in solids either by tuning the electronic band structure through doping or by the non-linear propagation effects of the driving field. The yield of harmonics can be more substantial at elliptical or circular polarization of the driving field due to the different **k**-values of band curvatures. In comparison, harmonics in gases can only be observed at linear polarization of the driving laser. This gives an advantage of solid-state harmonics to generate an elliptical or circular polarized light, which can be used to study chirality or explore ferromagnetic materials. As, the number density is higher in solids than in gases, which could offer a way to have brighter deep ultraviolet (DUV) sources for spectroscopy applications.

Chapter 3

Low-order harmonic generation in dielectrics and thin films

In this chapter, we discuss the non-linear response of wide-bandgap dielectrics such as MgO, Chromium (Cr) doped MgO (Cr: MgO), Sapphire (Sa), SiO₂, and fused silica (FS), in single and polycrystal gallium oxide (Ga₂O₃) in terms of second-harmonic (SH) and third-harmonic (TH) on the interaction of 800 nm, 40 fs operating at 1 kHz driving laser beam. We have investigated the impact of the driving field intensity, polarization/orientation and ellipticity on the emission of SH and TH. The doping effects on the low-order harmonic sby tailoring the electronic structure have been explored in MgO. We have disentangled the harmonic emission (SH and TH) from thin films (AlN and AlGaN) and Sa substrate. The TH and fifth-order harmonics in MgO, Cr: MgO, and harmonics up to ninth-order have been generated in single and polycrystal Ga₂O₃ at mid-infrared (MIR) 3 μ m driving wavelength. In this chapter, we have also highlighted the non-linear propagation effects of the driving field on the SH and TH.

3.1 Effects of chromium dopants on second-harmonic generation in MgO

3.1.1 Introduction

Second-harmonic generation (SHG) is one of the first perturbative non-linear response of solids at high driving fields. Efficient SHG is not possible in centrosymmetric solids due to symmetry conditions that forbid phase-matching. Near surfaces and interfaces, this symmetry is broken, and the phenomenon of SHG can occur. This process is termed surface second-harmonic generation (SSHG). In centrosymmetric crystals such as MgO used in this study, SHG phase matching conditions are not met in the bulk. For example, perturbative and non-perturbative high harmonics have been generated from the surface states of solids. It has been shown the suppression of higher harmonics in bulk material due to lack of phase matching [30]. For an in-depth theoretical and experimental treatment of SHG, we refer the reader to the following works [21, 22, 23, 24, 25, 156]. Practical uses of SSHG are widespread, including SHG

spectroscopy for imaging to investigate the bio-molecular interactions at interfaces [157], optical imaging [158, 159], characterization of the interface of semiconductors [160], and near-field and far-field optical microscopy of microelectronics structures [161].

Here, we introduce Chromium (Cr) into pure single crystal magnetium oxide (MgO) to experimentally investigate the role of doping in the SHG process. Cr is a transition metal with higher energy occupied electron orbitals than MgO. Doping MgO with Cr will have the effect of adding electrons at normally unoccupied energy levels in the MgO energy states. Chromium atoms have been shown to replace Mg sites during the doping process [162, 163]. Simulations showed the homogeneous distribution of Cr at the oxygen sites at low doping concentration [163]. It has been shown to generate less local stress compared to other transition metals when introduced into MgO, making it a good candidate for doping [164]. Cr-doped MgO possesses long-range order and several active optical sites, making it a good candidate for optical measurements. The change in the optical properties of MgO by introducing Cr dopants has been attributed to the new optical transitions made available from the Cr to the MgO orbitals [162]. The Cr dopants introduce electronic states in the MgO bandgap, which give rise to new optical transitions [165]. MgO doped with Cr, Cr: MgO shows practical promise in several areas. The impact of doping concentration and crystal polarization on SHG is a relevant scientific and practical question. By introducing dopants, we can alter the electronic structure and change the non-linear optical properties of the crystal. This could be used to tailor certain materials for strong field optoelectronics applications, for example, allowing a new degree of control in solid-state high harmonics [166].

In this section, we will report the generation of the second-harmonic in pure MgO and Cr: MgO crystals. The impact of crystal polarization and doping concentration on the yield of the SHG signal will be demonstrated. Experimental results have been explained by calculating the electronic structure using density functional theory (DFT) of pure MgO and Cr doped MgO crystals.

3.1.2 Experimental setup for SHG

We used near-infrared (NIR) laser pulses of 40 fs at 800 nm operating at a repetition rate of 1 kHz, which is focused on the solid crystals to generate the second-harmonic (SH). The schematic illustration of the experimental setup is shown in figure 3.1. The pulse duration of the driving field was measured by an autocorrelator, as shown in figure 3.2(a), and the spectral profile of the fundamental field measured by a UV-VIS spectrometer which is shown in figure 3.2(b). Femtosecond laser pulses of $\approx 20 \ \mu$ J energy were focused on the 200 μ m thick pure MgO and Cr-doped MgO bulk crystals to $\approx 100 \ \mu$ m diameter by a convex lens of 750 mm focal length. The estimated peak intensity of $\approx 1.0 \times 10^{13} \ Wcm^{-2}$ is below the damage threshold of MgO and Cr: MgO crystals. The incident beam was kept normal to the surface plane of the crystal to avoid birefringence. The crystal was mounted on a three-dimension translation stage as well as on a motorized rotational stage to keep the focal spot fixed at a point in the crystal during the rotation of the target. We can rotate the polarization of the driving field through a half-wave plate rather than rotating crystal about its axis but due to the unavailability of a half-wave plate, it was not possible.

The MgO crystal is cubic with 001-cut and (100) edge polarization. The pure MgO crystals were



Figure 3.1: Schematic illustration of the experimental setup for second-harmonic generation in MgO. The driving laser parameters: 40 fs, central wavelength 800 nm operating at 1 kHz.

fabricated by a three-phase electric arc furnace as a single bulk crystal. The Cr powder is introduced directly into the MgO during the growth process and hence is uniformly distributed throughout the MgO. The fundamental and second-harmonic pulses are separated using the chromatic dispersion of the side edge of a convex lens of a 100 mm focal length. The fundamental pulses are blocked by an iris and a short pass filter. The SH pulses are further focused by a 50 mm focal length into the optical fiber, which is connected to a UV-VIS spectrometer. The laser polarization has been kept fixed while the target rotated about its axis to observe the polarization/orientation response of SHG in the pure and doped Cr: MgO crystals. The SHG spectrum is measured by a UV-VIS spectrometer. The SHG is first optimized by tuning the laser focus to maximize the SHG yield in pure MgO. These focusing parameters are then kept fixed for all the doped samples to compare the SHG response.



Figure 3.2: (a) The temporal profile of the driving pulses which are measured from the autocorrelator, (b) Spectrum of the driving pulses measured by the UV-VIS spectrometer.

3.1.3 Doping impact on the yield of SHG

In this section, we have investigated the impact of Cr dopant concentration in pure MgO on the SHG efficiency. To validate the wavelength of the SH, we present the spectral measurements of the SH at a fixed polarization of the driving laser pulse, as shown in figure 3.3(a). The spectral shape is identical for all dopant concentrations, yet the intensity varies significantly. This is consistent with the different overall intensities presented in figure 3.4(a). About a two-fold higher intensity of SHG is observed for a doping concentration of 740 parts per million (ppm) compared to the pure MgO crystal. Interestingly, as the concentration of Cr is increased further, the SHG intensity monotonically decreases, as shown in figure 3.3(b). To observe the global dependence of Cr concentration we present total SHG yield accumulated over all angles for several dopant concentrations. The impact of doping on the yield of SHG is shown in figure 3.3(b). The yield is measured as the average over one complete rotation of the crystal. This shows that at the lowest concentration of doping, which is 740 ppm here, the yield is highest. The yield of SHG decreases as the dopant concentration increases further.



Figure 3.3: (a) SHG spectrum at a given angle ' θ ' of rotation of pure MgO and MgO with different dopant concentrations of Cr. Pure MgO crystals (red diamonds), 740 ppm of Cr dopant in MgO crystal (blue dots), 1300 ppm of Cr dopant in MgO crystal (green squares), and 9500 ppm dopant concentrations of Cr in MgO (yellow circles),(b) Angle averaged SHG intensity as a function of Cr dopant concentration.

To understand the dependence of efficiency on the Cr doping concentration, we now discuss the effect of Cr doping on the electronic, structural and optical properties of MgO, with reference to previous studies. At low dopant concentrations, most of the chromium ions take the position of the Mg ions [167]. Higher dopant concentrations of Cr have been shown to introduce different crystal phases, which may affect the SHG process [165]. Furthermore, it has been reported that by increasing the concentration of Cr doping, the number of atom-sized holes at the surface increases, which could also affect the efficiency of SHG [162]. The atom-sized hole may increase the symmetry breaking and thus enhance the SHG. At increasing levels of dopant concentration, structural changes occur, yet the influence of these new crystal phases on the optical properties is expected to be small. SSHG may not be strongly affected by the overall crystal structure as it is confined to the surface, yet small imperfections at the crystal surface may play a role.

Doping common oxide crystals to alter their optical properties is a widely known and well-developed industrial technique [168, 169]. Here, we look at other works that have independently measured the effect of Cr doping in MgO on the optical properties. We are primarily concerned with our wavelengths of interest (800 nm and 400 nm). Cr: MgO has shown that transmission of optical light decreases overall with increasing doping concentration [170], relevant for both our wavelengths of interest. The optical properties are a direct consequence of the electronic structure of the material. To clarify how the electronic structure changes in MgO when Cr atoms are introduced, we have conducted DFT simulations of pure and Cr doped MgO. The results of these calculations, along with a discussion of how to explain the experimental results are presented in Section 3.1.5.

MgO (pure) — Cr: MgO (740 ppm) Cr: MgO (1300 ppm) --Cr: MgO (9500 ppm) Orientation dependence of SHG in different MgO samples 90 4 90 -2-- 3 1. 150000 200000-45 135 135 45 150000 00000 00000 000 0000 180 0 180 0 225 315 225 315 270 270 (a) (b)

3.1.4 Orientation dependence of SHG

Figure 3.4: (a) Orientation response of SHG in pure and Cr-doped MgO crystal at fixed driving laser polarization and crystal rotation about its center. Pure MgO crystal (red), 740 ppm of dopant (blue), 1300 ppm of dopant (green), and 9500 ppm of dopant (yellow). (b) Sample dependent orientation dependence of SHG in different MgO identical crystals.

At a fixed polarization of driving laser pulses, the crystals were rotated to observe the crystal orientation response of SHG with respect to the electric field. An anisotropic and a continuous response of SHG on the crystal orientation is observed in pure MgO as shown in figure 3.4(a). This polar graph has the linear axis in arbitrary units. The behavior shown here underlines the complex dynamics of SHG in pure MgO and is attributed to the sensitivity of surface structural effects [171, 172, 173]. The exact shape of the orientation response of SHG may vary depending on crystal surface features or quality, as SH is generated due to the roughness of the crystal surface. Conversely, isotropic emission is observed for all crystals containing Cr dopant, as shown in figure 3.4(a). Furthermore, the Cr-doped MgO samples show a higher SH efficiency for all dopant concentrations. The angular anisotropy of the second-harmonic emission relative to the crystal orientation present in pure MgO is lost when dopants are introduced. We have found that the exact angular dependence pattern of pure MgO to be sample dependent as shown in figure 3.4(b). Crystals 1 and 2 are new ones, while 3, 4 are exposed many times under intense laser intensity. However, all crystals have a similar thickness, cut, and edge orientation. Nevertheless, we found the orientation dependence similar to each other. Moreover, SHG was not observed from MgO samples with two polished surfaces, which shows that the disordered surface morphology is the source of SHG in this study. However, the overall efficiency of SHG is dependent on the doping concentration as shown in section 3.1.3.

3.1.5 Electronic Structure Calculations from Density Functional Theory

The SHG process has an inherent dependence on the allowed energy states and their related occupation in the crystal. To better understand the role of the Cr doping, theoreticians in our group Dr. Gareth Williams and Fernando Lima have performed density functional theory (DFT) calculations of the pure and doped crystals (shown in figure 3.5(a) and 3.5(b), respectively). The DFT calculations were performed using the VASP package [174, 175, 176]. Projected augmented wave (PAW) pseudo-potentials [177] and the generalized gradient approximation (GGA) for the exchange-correlation functional was used in combination with 300 bands and a $12 \times 12 \times 12$ automatically generated k-point mesh. The recently measured valence band structure of MgO agrees with our DFT calculations [178]. The single difference in the calculations of the pure MgO and doped Cr: MgO cases here was the inclusion of a Cr atom at the central site normally occupied by Mg. The cell size was 64 atoms in total, therefore introducing a Cr atom at the center of this cell would correspond to a ≈ 1.6 percent dopant concentration. This is higher than our maximum dopant concentration of ≈ 1 percent in the experiment. However, the increase in cell size necessary for calculations with lower dopant concentrations becomes computationally prohibitive. Nonetheless, the physical effect of the dopant on the electronic structure remains qualitatively valid. A further increase in dopant concentration would increase the occupation of higher energy states and ultimately converge to the electronic structure of metallic Cr.

We present calculations of the band dispersion in the Γ -X direction of pure and Cr doped MgO in figure 3.5(a) and figure 3.5(b), respectively. In pure MgO (figure 3.5(a)), we note an optical bandgap of bulk MgO of around 4.7 eV. This lies in clear contrast to the accepted band-gap of around 7.8 eV [179]. The discrepancy between the accepted band-gap and the value reported here is due to the choice of xc functional used. Here we use the GGA to the xc functional, which is known to underestimate the band-gap. In fact, calculations similar to those presented here have yielded similar bulk band-gaps from 4.6 to 5 eV for bulk MgO [179, 180]. It should be noted that surface bandgaps of MgO have been shown elsewhere [179, 180] to be in the 5 eV range. Coincidentally, the bulk DFT band-gaps reported here are closer to the measured surface MgO band-gaps, where the SHG process reported here largely occurs.

It has been shown elsewhere that band-gaps of MgO can be well reproduced with other, more computationally expensive methods [179]. Calculations of the band-structure of MgO have been shown to match experimental values when more complex approaches (using hybrid Hartree-Fock methods) to the


Figure 3.5: (a) The band dispersion plots using DFT, calculated in the Γ -X direction for MgO (pure). The lattice constant used was a=4.2 Å. The red arrows indicate the driving laser photon energy, and the blue arrows show the photon energy of the second-harmonic. The occupation of the various bands is indicated in the respective legends,(b) The band dispersion plots using DFT, calculated in the Γ -X direction for chromium doped, MgO. The lattice constant used was a=4.2 Å. The red arrows indicate the driving laser photon energy, and the blue arrows show the photon energy of the second-harmonic. The occupation of the various bands is indicated in the respective legends.

xc functional have been employed [180]. However, these approaches have the downside of often been computationally more intensive. Since our cell size is already at the limit of our computational resources, we restrict our calculations to the more efficient, but less accurate GGA approach. Despite the expected underestimation of the optical band-gap in bulk, MgO reported here, we maintain that this difference does not affect our conclusions: the reduced band-gap by introducing Cr dopants increases the photon absorption process, thereby increasing the SHG efficiency.

In figure 3.6 the highest occupied energy level (Fermi energy) is indicated by the vertical dash-dot line around 3 eV. There are no available energy levels for blue (SHG) photon transitions around the Fermi energy for pure MgO. Therefore, a multi-photon absorption process must occur to drive electrons to the higher energy states (red arrows in figure 3.6 (a)). Conversely, the Cr: MgO has higher-lying occupied (defect) states due to the Cr doping (sharp peak around 8 eV). This higher-lying occupied (defect) state allows for direct driving and recombination of electrons without the need for prior multi-photon absorption processes to occur. This increases efficiency by allowing a more probable two-photon process to excite the electrons. The dependence of SHG efficiency on the direction of the driving field is minimal, as the highest occupied state (dashed line in figure 3.6(b) is a narrow, atomic-like line that varies little in energy to crystal polarization. This lack of angular dependence on the initial and final state in the electronic structure translates to a lack of observed angular dependence with Cr: MgO, as shown in figure 3.4(a). Hence, we can tailor the efficiency and polarization response of non-linear processes in crystals



Figure 3.6: The density of states (DOS) is calculated with density functional theory (DFT). The red arrows indicate the energy of a photon of the fundamental near-infrared (NIR) driving laser field. The blue arrows indicate the energy of a second-harmonic photon and the red arrows indicate the driving fundamental photon. (a) MgO, (b) Cr: MgO.

by manipulating the electronic structure. The efficiency, however, can be limited by the changing optical properties as the dopant concentration is increased. This shows that a delicate balance of the element and concentration of the dopant is essential for improving solid-state SHG in terms of yield.

This shows that the electronic structure can be shaped to tailor the non-linear optical response in terms of SSHG efficiency and angular dependence by introducing dopants into simple crystals. We show that Cr can increase the SSHG efficiency and mitigate angular polarization dependence when introduced to MgO and that efficiency favors dopant concentration on the order of 740 ppm. This study paves the way for merging bandgap engineering and solid-state harmonic generation to tailor frequency upconversion processes from surface states. Perhaps of equal importance is the prospect of experimentally testing theories of the solid-state high harmonic generation (HHG) mechanism with tailored electronic structures, with a final view towards all-optical mapping the band structure of solids.

3.2 Effects of dopants: transition from non-perturbative to perturbative third-harmonic generation in MgO

The surge of interest in non-perturbative high harmonic generation (NP-HHG) in solids has been driven by the appeal of compact solid-state XUV sources and the prospect of untangling the material properties through its response to strong fields. The traditional assumption is that the brighter, lower-order harmonics are purely perturbative. However, the border between the perturbative and nonperturbative regimes often remains unclear. Here, we show that third-harmonic generation (THG) using 800 nm, 40 fs pulses displays a non-perturbative response in a wide band-gap insulator in MgO. Furthermore, we show that with the introduction of dopants, this non-perturbative behavior of THG reverts to the more common perturbative behavior. We attribute this to the blocking of the non-perturbative pathways and the increased linear absorption pathways caused by the dopant energy levels.

3.2.1 Introduction

As explained in chapter 2, in solids, the up-conversion of driving photon energies at moderate laser intensities due to the non-linear polarizability of the medium is known as perturbative harmonic generation [19] (normally second or third). In this regime, harmonics efficiency falls off rapidly with the increasing harmonic order [20]. More recently, HHG has been realized in the strong field regime, where electron tunneling, inter-band transitions, and intra-band electron motion lead to non-perturbative harmonic generation [33, 31, 56, 58]. These processes are typically associated with higher-order harmonics in the harmonic spectrum's flat 'plateau' region. Such harmonics have shown an intriguing dependence on the driving field orientation [31, 59, 60], band-structure [58] and intra-band electron motion [31, 58].

Most of the naturally occurring crystals are centrosymmetric and support odd high-harmonic generation due to inversion symmetry. In NP-HHG studies, the lower-order harmonics are generally assumed to be perturbative and are largely ignored. However, third-harmonic generation (THG) has been shown to display some characteristics of NP-HHG at high field strengths with 800 nm [30] and 1.3 μ m [31] driving wavelengths. At longer driving wavelengths, the perturbative response persisted even at the high field strengths [31], making the two regimes difficult to untangle through THG. The THG of standard laser wavelengths (800 nm) is nearly always the brightest harmonic in centrosymmetric crystals. It is still easy to manipulate (it can propagate in the air). Therefore, it could be an attractive candidate for NP-HHG studies in solids. For example, the role of the material properties on NP-HHG and their impact on the generation mechanism remains an open question. In particular, how changes in the electronic structure influence the harmonic generation mechanism is not yet fully understood. This understanding is crucial for knowing what information can be gleaned from solid-state harmonics in the perturbative and non-perturbative regimes. This has been highlighted by a recent study of chromium (Cr) doped MgO, showing increased in high-order HHG emission [181] and in the lower-order harmonics [26] with altered electronic structures.

In this section, we show THG in MgO with 800 nm wavelength displays a largely non-perturbative behavior. We alter the electronic structure in MgO with increasing concentrations of Cr dopant. We find that at the highest Cr concentration, the non-perturbative response reverts largely to the perturbative regime. We attribute this behavior to the changing electronic structure of the material with increasing dopant concentrations. This work shows that THG generation carries all the hallmarks of a non-perturbative process involving electron motion beyond the parent atom in the suitable material.

3.2.2 Experimental setup for THG generation in MgO and Cr: MgO crystals

NIR laser pulses at a wavelength of 800 nm and 40 fs in duration are focused on the crystals to generate the third-harmonic (TH). An illustration of the experimental setup is shown in figure 3.7a. Driving field pulses of energy $\approx 20 \ \mu$ J are focused to a 100 μ m diameter spot with a 75 cm lens into 200 μ m thick pure MgO and Cr doped MgO (Cr: MgO) crystals. The peak intensity is estimated to be $\approx 1.0 \times 10^{13}$ W cm⁻². The crystals are oriented along the (100) edge with a 001 cut (Crystal GmbH). The same crystals (Cr: MgO) used in the SHG [26] were adopted with different Cr doping concentrations (740, 1300, 5000,



Figure 3.7: (a)Schematic illustration of experimental setup for THG in pure and Cr: MgO crystals showing the half-wave plate (HWP), quarter-wave plate (QWP), convex lenses (L1 and L2), crystals (C) and harmonic filter (HF), iris is used to block the scattered NIR. (b) Band diagram illustration of non-perturbative THG showing field-ionization (FI) between the valence band (VB) and conduction band (CB), the intraband electron motion in the CB of pristine MgO results the emission of TH signal. Inset shows the single unit cell of MgO (c) Band diagram illustration of perturbative THG in Cr: MgO, showing THG can occur either between the virtual states (VS) and the vacancy defect band (VDB) or between CB and impurity defect band (IDB). A single photon linear absorption occurring between the VS and the CB, and the splitting of the CB by higher Cr levels (Cr). Inset shows the single unit cell of Cr: MgO, V_{mg} represents the vacancy of Mg.

and 9500 parts-per-million (ppm)) for THG. After the crystal, the THG pulses are filtered by a harmonic filter (HF) and focused by a convex lens (L2) of 10 cm focal length into a UV-VIS spectrometer.

The sketch of the underlying electronic excitation in pure MgO and Cr: MgO is shown in figures 3.7(b) and 3.7(c), respectively. On the interactions of the intense laser field, an electron wave packet is excited from the valence band (VB) to the first conduction band (CB) through field ionization (FI) at the Γ point. In the CB, the excited electron experienced intra-band accelerations and emits THG signal (see, figure 3.7(b)). Whereas in Cr: MgO crystals, the impurity defect band (IDB) appears near to CB and the vacancy defect band close to the VB (see, figure 3.7(c)). We have observed the splitting of CB by Cr energy levels in DFT calculation, see the reference [26]. These additional energy levels can increase the one-photon absorption process, block the intra-band transitions. The Fermi energy level lies in between the VDB and first CB [182], therefore the VDB initially has the electrons. This can lead to a multiphoton transition from VDB to virtual states (VS) and results the emission of TH photons either between the VS and the vacancy defect band (VDB) or between CB and impurity defect band (IDB) as illustrated in figure 3.7(c) but the most probable transition would be between VS and VDB or VB. The THG from this transitions agreed well with our experimental data.

3.2.3 Spectral and linear transmission of TH in MgO and Cr: MgO crystals

The spectral profile of THG in MgO and Cr: MgO crystals measured with the spectrometer is shown in figure 3.8(a). The peak of THG in MgO is centered at 266.5 nm with an FWHM of 4.25 nm. We have observed the spectral broadening of the TH signal in lower doped (740 ppm) and higher doped (9500 ppm) crystals. The FWHM of TH from Cr: MgO (740 ppm) and Cr: MgO (9500 ppm) is broadened to 6.54 nm and 8.1 nm, respectively. The peak of TH in Cr: MgO (9500 ppm) is broaden and red-shifted and centered at 268.5 nm. Whereas the FWHM of TH signal generated in Cr: MgO (1300 ppm) and Cr: MgO (5000 ppm) reduces to 4 nm and 4.15 nm, respectively (see figure 3.8(a)). The spectra of THG signal from MgO in transmission (T, red dots) and reflection (R, blue dots) were measured with another UV-VIS spectrometer (Sarspec). NIR/3 (black dotted in air and black line in MgO) to match the peak of TH theoretically is shown in figure 3.8(b). The THG signal generated in transmission showed multiple pronounced peaks structure due to non-linear propagation effects than the TH signal observed from reflection geometry.

For the linear transmission of THG (267 nm) in MgO and Cr: MgO crystals, we have generated a strong 267 nm signal in the SiO₂ crystal at an intensity of $\approx 1.0 \times 10^{13}$ Wcm⁻². The transmitted spectral measurements of 267 nm through the MgO (pure) and different doped Cr: MgO crystals are shown in figure 3.8(c). Minimal linear absorption of 267 nm by the MgO (pure) crystal is observed. In comparison, the transmission of 267 nm through Cr: MgO crystals decreases with doping concentration. There is a strong linear absorption of 267 nm by the Cr: MgO crystals. This shows that the THG from the front surface of the doped crystal will be absorbed, and the observed TH signal can be obtained from the back surfaces in the doped crystal (Cr: MgO). To understand the broadening effect, a careful study of NIR propagation through MgO and Cr: MgO is reported in section 3.2.11. It explains that the non-linear effects such as strong photoionization, and self-phase modulation are inducing the change in the medium's

refractive index, which induces the phase shift in the driving pulses and spectrum modulations. This effect has been imprinted on the TH spectrum. Therefore, spectra of TH in low and higher doped crystal are broaden.



Figure 3.8: (a) Spectral measurements of THG in MgO (pure) and Cr: MgO with different doping concentrations at normal incidence of the driving field to crystals. At low and higher doping concentrations, the TH spectrum exhibits broadening and a redshift, (b) Spectral measurements of THG in transmission (blue dots) and reflection (red dots) in MgO. Where R: reflection and T corresponds to transmission. NIR/3 (black dotted in air and black line in MgO) to theoretically match TH's peak. (c) Transmission of THG signal through MgO and Cr: MgO crystals.

3.2.4 Intensity dependence and doping impact on the yield of THG

The intensity variation of THG in pure MgO and Cr doped MgO versus the estimated driving field intensity is illustrated in figure 3.9(a). A perturbative TH process typically scales I^3 with the intensity dependence as observed in Cr: MgO (9500, pink squares), whereas we have observed a $I^{1.45}$ and $I^{1.30}$ dependence in MgO and Cr: MgO (1300 ppm) as shown in figure 3.9(a), which is more characteristic of a non-perturbative mechanism. Intensity scaling for MgO and low doped MgO exhibits a non-perturbative response, whereas higher doped MgO (9500 ppm) shows a perturbative response ($I^{2.97\pm0.2}$).

The yield of the generated TH versus the doping concentration of Cr in MgO is shown in figure 3.9(b) (blue diamonds). There is a sharp decrease (≈ 3.5 -times) in THG intensity in Cr: MgO crystals for 740 ppm and further reduction (≈ 5.5 -times) for 1300 ppm. The efficiency decreases even more for more significant dopant concentrations. To untangle the contributions of linear and non-linear optical properties to the decrease of TH intensity as dopants are introduced, we have measured the linear optical properties at the TH wavelength through the pure and Cr: MgO crystals. The linear transmission of TH (blue dots) in MgO and Cr: MgO crystals is shown in figure 3.9(b) and follows the TH intensity closely. The linear transmission of the NIR transmission (square black dots) in MgO and Cr: MgO crystals as shown in figure 3.9(b). The decrease in the intensity of THG in Cr: MgO with the doping concentration is attributed to the increased absorption of the NIR photons and the TH photons generated in the bulk of the doped crystals. This increased absorption is rooted in the altered electronic structure of the Cr: MgO crystals, that allows photon absorption between VS and the CB transition (see figure 3.7c). As the additional electronic states such as vacancy defect band (VDB) and the IDB emerged or vacancies



Figure 3.9: (a) The dependence of the yield of TH in MgO (red diamond points), Cr: MgO (1300 ppm, blue dots), and Cr: MgO (9500 ppm, pink squares) crystals versus the estimated driving intensity (I). Power law fitting gives an exponent value of (1.45 ± 0.04) (red dotted line) for MgO, (1.30 ± 0.04) , blue dotted line) for Cr: MgO (1300 ppm) and (2.97 ± 0.2) , pink dotted line) for Cr: MgO (9500 ppm). (b) The doping concentration impact on the NIR transmission (square black dots) generated THG intensity (red diamonds) and linear transmission of TH wavelength (blue dots) through the crystal (red circles) in MgO and Cr: MgO crystals. All vertical axes are normalized to one.

emerged into the MgO electronic bandstructure by the Cr dopants [167, 165, 162] which give rise to new optical transitions.

3.2.5 Perturbative model for polarization and ellipticity response of THG

The anisotropic THG linear polarization response is compared with the perturbative model [102, 183]. The third-order polarization for cubic crystal is given as [184]

$$P_i(3\omega) = 3\chi_{xxyy}E_i(EE) + (\chi_{xxxx} - 3\chi_{xxyy})E_iE_iE_i$$
(3.1)

where, *i* refers to the three cubic axes. χ_{xxxx} is tensor component of third-order susceptibility along the [100] crystallographic axis of cubic crystal.

The intensity of THG for s-polarized driving field is given as [102]

$$I_{ss}(3\omega)\alpha[(\chi_{xxxx} - 3\chi_{xxyy})\cos(4\phi) + 3(\chi_{xxxx} + \chi_{xxyy})]^2 |E_s(\omega)|^6$$
(3.2)

In equation 3.2, the $|3(\chi_{xxxx} + \chi_{xxyy})|^2$ and $|(\chi_{xxxx} - 3\chi_{xxyy})|^2$ are the isotropic and anisotropic contributions to the non-linear response, respectively.

The ellipticity dependence of THG in MgO has been compared to the perturbative model [185]. According to the perturbative model, the intensity of harmonic 'q' is given as

$$I_q = I_{q0} + \gamma \left(\frac{1-\epsilon^2}{1+\epsilon^2}\right)^{q-1}$$
(3.3)

where I_{q0} corresponds to base-line harmonic intensity, γ , q and ϵ are the proportional factor, harmonic order and laser field ellipticity, respectively.

3.2.6 Semi-classical analysis of electron and hole trajectories (Non-perturbative model)

The semi-classical analysis of electron trajectories inside the crystal of MgO for linear and elliptical polarization has been reported [31, 132, 60]. These semi-classical electron trajectories cannot predict the quantitative nature of harmonic yield, but for the angular distribution of harmonics, this analytical analysis is quite helpful. According to the semi-classical model, the motion of electron in the energy band under the influence of driving laser field $E(t) = E_0 cos(\omega)t$ is given as

$$\frac{d\vec{k}}{dt} = -\vec{E}(t) \tag{3.4}$$

Where, k is the crystal momentum. The evolution of the position of electron wave-packet in the conduction band can be written as \rightarrow

$$\frac{d\vec{r}}{dt} = \frac{\partial\varepsilon(\vec{k})}{\partial(\vec{k})} \tag{3.5}$$

Where, $\varepsilon(\vec{k})$ is the conduction band energy dispersion. For the face centered crystal (FCC), the energy dispersion of crystal in the plane of (001) is approximated by the tight-binding model and is expressed as

$$\varepsilon(k_x, k_y; k_z = 0) = 3(A+B) - A(\cos\frac{k_x a}{2} + \cos\frac{k_y a}{2} + \cos\frac{k_x a}{2}\cos\frac{k_y a}{2}) - B(1 + \cos(k_x a) + \cos(k_y a)) \quad (3.6)$$

Here, A and B are the constants that are given some values to fit the structure of crystals, as A=1.25 and B=0.6 given by Tan et al. [186] to fit with the structures of MgO.

Vampa et *al.* reported in their semi-classical analysis that on the interaction of laser field with the solids, holes also translate in the valence beyond the Γ -point [34]. Therefore, we have also calculated the hole dynamics under the influence of the NIR driving field of $\approx 0.9 \text{ V/Å}$ strength. The corresponding electron and hole dynamics will be presented in the subsection 3.2.9

To demonstrate the angular distribution of THG in MgO in non-perturbative model, We follow the same assumptions for our calculation in pure MgO as reported in [31] that the yield of THG is essentially dependent on the closeness of the trajectories of electrons regarding ionic cores in the crystal and considered Gaussian symmetrical charge distribution in MgO (pure) around the ionic cores. The yield of high harmonics have been expressed as

$$I_{HHG} \propto C_{mg} e^{-\frac{(r-r_{mg})^2}{a_{mg}^2}} + C_o e^{-\frac{(r-r_o)^2}{a_o^2}}$$
(3.7)

Where C_{mg} and C_o are the strength of harmonics corresponding to the collisions with the magnesium and oxygen atom, a_o and a_{mg} are the size of the ionic core while r_o and r_{mg} are the location of ionic core of oxygen and magnesium, respectively. r is the closest distance of electron from the center of ionic core. By using this semi-classical model, You et al. [31] has chosen $C_0 = 0.15$ and $C_{mg} = 1$ to match the relative maxima along O-O and Mg-O directions for 21^{st} harmonics while $a_o = 0.35a$ and $a_{mg} = 0.1a$ taken from the reference [187], where a=4.2 Å is the lattice constant of MgO. We have chosen $C_0 = 1$ and $C_{mg}=0.05$, $a_o = 0.35a$ and $a_{mg} = 0.1a$ to match the relative maxima along O-O and Mg-O directions for 3^{rd} harmonics in MgO conduction band under the electric field strength of $\approx 0.90 \text{ V/Å}$. The measured angular distribution of THG agreed with the semi-classical analysis as shown in figure 3.10(a).

3.2.7 Polarization response of THG in MgO and Cr: MgO

Further to the overall intensity dependence of the harmonic yield, the variation in the yield as a function of the driving field polarization orientation has been shown to reveal critical signatures of the generation mechanism [31]. To further untangle the THG mechanism, we have carried out the linear and elliptical polarization dependence. We have compared the results to perturbative (see subsection 3.2.5) and non-perturbative theories (see subsection 3.2.6). To measure the linear polarization response, we have kept the crystals at a fixed orientation and vary the linear polarization of the driving field using a half-wave plate (HWP). We have observed a clear anisotropic four-fold polarization response of THG in MgO and low doped Cr: MgO (1300 ppm). Whereas a more isotropic response is observed for higher doped crystals (Cr: MgO (9500 ppm)) (shown in figure 3.10(a)). In pure MgO, You et *al.* [31] measured a more isotropic response and four-fold symmetry for THG at moderate field strength, and an additional 4-fold symmetry along the cubic bonding direction (Mg-O) at higher field strength (making 8-fold symmetry in total). We have only observed a 4-fold symmetry of THG along the O-O bonding direction at a driving wavelength of 0.8 μ m. Other studies have observed 4-fold symmetry along the Mg-O direction at a driving wavelength of 1.55 μ m for the higher-order harmonics [181]. Comparing these studies shows a complex interplay between the driving field, harmonic order, and crystal orientation.

We have compared the measured polarization response of THG with the perturbative [102, 183] and non-perturbative models [31, 60], as shown in figure 3.10(a). Perturbation theory predicts smooth TH peaks along the O-O bonding direction in MgO, coupled with the isotropic emission. This theory matches well with our observed polarization dependence of Cr: MgO (9500 ppm). For lower doped and pure MgO, sharper, more well-defined peaks along the O-O direction emerge. This shows our data diverging from perturbative theory, and we must look to non-perturbative approaches for further insight. NP-HHG begins with the promotion of an electron from the valence band to the conduction band (figure 3.7b). The electron then undergoes intra-band oscillations or inter-band transitions due to the driving field. These transitions can support the emission of higher photon energies in the process. The crystal band structure dictates both intra-band electron motion and inter-band transitions, making the NP-HHG sensitive to the orientation of the crystal relative to the polarization direction. We follow a semi-classical approach used elsewhere [31] that captures the electron motion within the conduction band of the crystal. As direct inter-band transitions are unlikely to contribute to the TH generation, we consider only intra-band motion.

We have followed similar assumptions for electron trajectories in pure MgO as reported in [31], i.e.,



Figure 3.10: (a) Polarization response of THG in MgO (red diamond), analytical perturbative (green line), non-perturbative model (black dotted line), Cr: MgO for 1300 ppm (blue circles), and 9500 ppm (pink squares). Lines connecting the markers are used to guide the eye. (b) The semi-classical electron trajectories for linearly polarized laser pulses for different polarization angles relative to the crystal axis of MgO.

that the yield of THG is dependent on the distance of closest approach to the neighboring ionic cores in the crystal. For the description of NP-HHG model see section 3.2.6 and for the perturbative model see section 3.2.5. The electron trajectories are calculated for a range of linear polarization of the driving field. We have considered that the electron tunneling originates from the O atom. The nearest neighbors to these atoms are considered for collisions. Along the cubic bonding direction $(0^{\circ} \text{ and } 90^{\circ})$, the electron crosses several distinct atomic sites (see figure 3.10(b)) and results the emission of THG signal. As we shift the linear polarization away from the cubic bonding direction, the intensity of TH increases and reaches a maximum when linear polarization is aligned to the O-O bonding direction. As the linear polarization of the driving field begins to align towards the Mg-O bonding direction, the intensity of THG decreases and reaches to minimum signal again. Both the perturbative and non-perturbative approaches show qualitatively similar patterns. However, the measured angular polarization distribution of THG in low doped (1300 ppm) agrees with the non-perturbative model (sharper, more well-defined peaks). While at the highest dopant concentration (9500 ppm), the polarization response reverts to a shape better described by the perturbative model (broader and less defined peaks). The observed experimental differences in the polarization response could be due to different THG mechanisms. Nevertheless, the patterns could, in principle, be fit to either model with the right choice of parameters. The stringent test that can discern between these two descriptions is needed: the dependence of THG on the ellipticity of the driving field polarization.

3.2.8 Ellipticity dependence of THG in MgO and Cr: MgO

It has been shown elsewhere that the intensity of HHG driven by elliptically polarized driving fields is a key signature of a non-perturbative mechanism [31, 58]. In the semi-classical one-electron picture, elliptical driving fields result in more curved electron trajectories in the crystal than linear polarization. These curved trajectories make the harmonic emission dependant on the crystal orientation and the driving field ellipticity, which can differ greatly from the perturbative behavior. We have measured the ellipticity response of THG in pure and doped MgO at four angles (0°, 15°, 30° and 45°) between the linear polarization position of the driving field, and the O-O the axis of the crystals. The linear polarization of the driving field along the O-O direction with an HWP to generate the maximum THG signal. A quarter-wave plate (QWP) is placed behind the HWP (as shown in figure 3.7a) and rotated to measure the THG intensity at a range of ellipticities. The yield of THG in pure MgO is maximum (red diamond) at linear polarization (ε =0, along the O-O axis) and minimum at circular polarization (ε =±1) (figure 3.11a). It is expected that the HHG signal decreases with increasing ellipticity [58, 188] as we have observed with all crystals (figure 3.11a). The peak to valley ratio is, however, much less for the pure and low doped crystals.

The same measurement is repeated, with linear polarization of the driving field shifted by 15° , 30° and 45° from the O-O bonding direction. For 15°, the THG peak in MgO (red diamonds) shifts from $\varepsilon = 0$ to $\varepsilon = -0.5$ in figure 3.11b, and for 30° the peak THG signal shifts to $\varepsilon = -0.3$ (figure 3.11c). For 45°, the emission peak of THG shifts from linear to elliptical ($\varepsilon = \pm 0.65$), showing a unique twopeak structure, as shown in figure 3.11d. The shape of the Cr: MgO (9500 ppm) ellipticity dependence remains approximately centered at linear polarization for all the orientations as shown in figure 3.13. In comparison, the low doped MgO (1300 ppm) depart significantly from this trend, especially at 45° (see figure 3.12. The ellipticity dependence of THG in MgO has been compared to the perturbative model [185], and the non-perturbative model [31]. The ellipticity dependence of THG from Cr: MgO (9500 ppm, cyan squares) follows the perturbative model closely, which predicts diminishing intensity as ellipticity increases for all orientations (as shown in figure 3.13). However, the yields of THG in MgO (red diamonds) and 1300 ppm doped Cr: MgO (blue dots) closely follow the non-perturbative response as shown in figures 3.11 and 3.12. To explain the observed non-perturbative patterns, we graph the electron trajectories in the pure MgO crystal for 0° and 45° orientations using (Figs. 3.14(a) and figure 3.14(d), respectively). We have also graphed the electron trajectories under linear, elliptical, and circular polarization for the field strength 0.9 V/Å when linear polarization of driving field-aligned 15⁰ away from O-O bonding direction (see figure 3.14(b)) and when linear polarization of driving field-aligned 30^0 away from O-O bonding direction (see figure 3.14(c)).

In figure 3.14(a), the electron hits O atomic site and results in the maximum emission of THG for $\varepsilon=0$ (figure 3.11a). Similarly, at an elliptical polarization ($\varepsilon=\pm0.5$) of the driving fields, the electron trajectory is close to the first neighbor Mg atom and the second nearest atomic site leading to a lower TH signal. Finally, for circular polarization ($\varepsilon=\pm1$), the electron trajectory connects only to Mg atom sites while misses the closest O atomic sites. Therefore the contribution to the emission of TH is maximum at linear and minimum at circular polarization (figure 3.11a). Along the Mg-O bonding direction (45°), the electron trajectory crosses only Mg atomic sites at linear polarization ($\varepsilon=\pm0.5$) they miss Mg atomic sites, and at circular polarization ($\varepsilon=\pm1$) electron trajectories are connected to the O atomic sites. Therefore, the emission of TH is minimum at linear and maximum at linear and maximum at linear and maximum sites.



Figure 3.11: Ellipticity dependence of THG in MgO. Linear polarization (vertical black long dasheddotted, ε =0), elliptical polarization (vertical gray dotted, ε =±0.5) and circular polarization (ε =±1). The measured response of THG in MgO (red diamonds), perturbative model (green curve), and nonperturbative model (black dotted curve). Lines connecting the markers are used to guide the eye. Linear polarization of driving field-aligned (a) to O-O bonding direction, (b) 15° away from O-O bonding direction, (c) 30° away from the O-O bonding direction (d) to Mg-O bonding direction.



Figure 3.12: Ellipticity dependence of THG in Cr: MgO (1300 ppm). Linear polarization (vertical black long dashed-dotted, ε =0), elliptical polarization (vertical gray dotted, ε =±0.5) and circular polarization (ε =±1). The measured response of THG in Cr: MgO 1300 ppm (blue circles), perturbative model (green curve), and non-perturbative model (black dotted curve). Lines connecting the markers are used to guide the eye. Linear polarization of driving field-aligned (a) to O-O bonding direction, (b) 15° away from O-O bonding direction, (c) 30° away from the O-O bonding direction (d) to Mg-O bonding direction.



Figure 3.13: Ellipticity dependence of THG in Cr: MgO (9500 ppm). Linear polarization (vertical black long dashed-dotted, $\varepsilon=0$), elliptical polarization (vertical gray dotted, $\varepsilon=\pm0.5$) and circular polarization ($\varepsilon=\pm1$). The measured response of THG in Cr: MgO 9500 ppm (cyan squares), perturbative model (green curve), and non-perturbative model (black dotted curve). Lines connecting the markers are used to guide the eye. Linear polarization of driving field-aligned (a) to O-O bonding direction, (b) 15° away from O-O bonding direction, (c) 30° away from the O-O bonding direction (d) to Mg-O bonding direction.



Figure 3.14: The non-perturbative electron trajectories in MgO under linear (0), elliptical (± 0.5) and circular (± 1) polarization. (a) Linear polarization of driving field considered along O-O bonding direction. (b) Linear polarization of driving field-aligned 15^o away from O-O bonding direction. (c) Linear polarization of driving field-aligned 30^o away from O-O bonding direction. (d) Linear polarization of driving field-aligned 30^o away from O-O bonding direction.

circular polarization (figure 3.11d). The peaks at circular polarization predicted by the non-perturbative model are not observed in the experimental data in figure 3.11d. Furthermore, the peak emission is not achieved at circular polarization for all orientations, as shown in figure 3.11. The non-perturbative model considers the trajectory of a single electron and does not include macroscopic aspects, such as phase matching, that will be minimized for circular polarization in all cases. The ellipticity response of the Cr: MgO (9500 ppm) crystal is congruent with the expected perturbative response, see figure 3.13. However, the marked deviation of the driving field ellipticity response in pure and low doped MgO cannot be explained with perturbative theory. In contrast, a good match with the NP-HHG model is found.

This behavior can be explained in terms of the electron structure of pure and doped MgO. The Cr dopants change the electronic structure of pure MgO, and change the possible direct electron transitions (inter-band) and electron trajectories (intra-band). In pure MgO, an electron is first field ionized from the valence band (VB) to conduction band (CB), where the electron is driven by the field and its oscillations cause non-perturbative THG (NP-THG) (figure 3.7b). In Cr: MgO, however, new Cr energy levels appear between the VB and CB, and within the CB itself [26, 181]. Although we have approximated the Cr: MgO band-structure here, it is in broad agreement with other works [26, 181]. Moreover, the observed increased absorption of the NIR and TH frequencies in figure 3.9(b), are consistent with the approximation. These new levels allow single photon transitions from the VS or IDB to CB, and split the CB by Cr levels (figure 3.7c), effectively blocking long range intra-band oscillations in lieu of single photon intra-band transitions. Therefore, at high Cr doping concentrations, the NP-THG mechanisms are greatly limited by the introduction of new energy levels causing linear absorption of the driving photons, and blocking long range pathways of the free electrons. The remaining available THG mechanism in these crystals is perturbative, that occurs either between the VS and the vacancy defect band (VDB) or between CB and impurity defect band (IDB). The most probable transition would be between VS and VDB or VB as the THG from this transitions agreed well with our experimental data. In the Cr: MgO (9500 ppm) crystal, the ellipticity dependence follows the purely perturbative predictions, whereas in pure and low doped MgO, the electron motion within the conduction band causes NP-THG, which can be explained in terms of intra-band electron motion.

Although THG is generally assumed to be perturbative, we have shown that NP-THG can be generated in a wide bandgap insulator such as MgO using 800 nm light. We have confirmed this behavior by comparing the pure MgO results to crystals with increasing dopants that alter the electronic structure. As dopant concentration increases, the pathways for NP-THG to occur decrease, and we observe a purely perturbative response. This study shows that even the lowest order odd harmonics can be non-perturbative, and the emission intensity is sensitive to the band structure and crystal properties. Moreover, the non-perturbative process allows for significantly more emission of circularly polarized light than the traditional perturbative process, which could be an attractive probe for magnetic materials.

3.2.9 Electron and hole dynamics in one-dimension in MgO

We have calculated the electron dynamics for different driving fields such as at low driving field 0.1 V/Å, moderate 0.5 V/Å, relatively high field 0.9 V/Å and at higher field 1.5 V/Å. To observe the effect

of the driving wavelength on the dynamics of electrons, we have chosen 800 nm, 1300 nm, and 2100 nm wavelengths, as such wavelengths are primarily available at the research laboratories. The position of the electrons at various field strengths for different wavelengths are calculated in the conduction band by considering the non-parabolic (np) nature of the band along the $\Gamma - X$ direction as shown in figure 3.15. The evolution of E-field E(t) for various electric field strength E_0 is shown in the black curve in each graph of figure 3.15. At the low electric field strength of $E_0=0.1 \text{ V/Å}$, the electron trajectories for the propagation time 0 to $2\pi/\omega$, where ω is the driving frequency at 800 nm, 1300 nm, and 2100 nm driving wavelength follows the parabolic profile and behave similarly. Except for the longer driving wavelength, the excursion distance transverse by the electron is longer, as shown in figure 3.15(a). For the moderate field $E_0=0.5 \text{ V/Å}$, the electron trajectories in real space begin to differ, particularly for longer driving wavelength especially at 2100 nm as shown in figure 3.15(b). The electron trajectories under the influence of 800 nm driving wavelength still follow the parabolic path even at the field strength of $E_0=0.9 \text{ V/Å}$ (figure 3.15(c)).

Similarly, a 1-dimension analysis of the velocity of an electron in the conduction band under the influence of various driving field strengths are shown in figure 3.16 for different driving wavelengths such as 800 nm (pink), 1300 nm (dark yellow), and 2100 nm (dark blue). At the low electric field strength (figure 3.16(a), the velocity trajectories of an electron for all driving wavelengths are parabolic. Whereas for moderate (0.5 V/Å) and higher field strength (1 to 1.5 V/Å), the velocity trajectories of an electron are highly non-parabolic, see figures 3.16(b), 3.16(c) and 3.16(d). Although at 800 nm driving wavelength, the velocity trajectory of an electron shows parabolic behavior at a field strength of (0.5 V/Å). These trajectories show that the driving wavelength and the electric field strength play a vital role in the dynamics of an electron in the conduction band. At low driving wavelength and electric field strength, they exhibit non-parabolic behavior.

The momentum gained by the electron in the conduction band in 1-dimension real space under the influence of various field strength is shown in figure 3.17 for different driving wavelengths such as 800 nm (pink), 1300 nm (dark yellow), and 2100 nm (dark blue). The evolution of E-field E(t) for various electric field strength E_0 is shown in a black dotted curve in each graph of figure 3.17. At low field strength such as 0.1 V/Å, the momentum of the electron follows the parabolic response as shown in figure 3.17(a). With the longer driving wavelength, higher momentum is gained by the electron in the conduction band of MgO. Even at the moderate field and higher field strength, the momentum gained by the electron for all driving wavelengths shows the parabolic nature.

The hole dynamics in valence band in 1-dimension real space at an electric field strength of $E_0 = 0.9 \text{ V/Å}$ is calculated by considering the energy dispersion equation 3.6. For this, the energy dispersion equation 3.6 for holes in the valence band holds with A=-0.25 and B=0. The hole dynamics such as propagation distance, velocity, and momentum gained by the hole in 1-dimension are shown in figure 3.18. The evolution of E-field E(t) (black dotted curve), hole propagation distance (violet curve) is in the units of lattice constant a. The velocity gained by the hole (red curve) and momentum gained by the hole (blue curve) is shown in atomic units (a.u.). The propagation distance, velocity, and momentum



Figure 3.15: The dynamics of an electron in conduction band for different driving wavelength (800, 1300, and 2100 nm) in 1-dimensional real space, the evolution of E-field E(t) (black dotted curve) The distance of electron is expressed in the units of "a" which is the lattice constant of MgO (a=4.2Å), np represent the non-parabolic band. (a) 0.1 V/Å, (b) 0.5 V/Å, (c) 0.9 V/Å and (d) 1.5 V/Å.



Figure 3.16: Electron velocity trajectories in the conduction band for different driving wavelengths (800, 1300, and 2100 nm) in 1-dimensional real space at different electric field strengths. The black dotted curve shows the evolution of E-field E(t) for various electric field strength E_0 . The electron velocity is expressed in the atomic units (a.u.) and normalized to 1 for clarity. (a) 0.1 V/Å, (b) 0.5 V/Å, (c) 0.9 V/Å and (d) 1.5 V/Å.



Figure 3.17: The trajectories of the momentum gained by the electron in the conduction band under different field strengths for different driving wavelengths such as 800 nm (pink), 1300 nm (dark yellow), and 2100 nm (dark blue) in a 1-dimension real-space picture. The evolution of E-field E(t) for various electric field strength E_0 is shown in the black dotted curve in each graph. The electron's momentum is expressed in the atomic units (a.u.) and normalized to 1 for clarity. (a) 0.1 V/Å, (b) 0.5 V/Å, (c) 0.9 V/Å and (d) 1.5 V/Å.



Figure 3.18: The hole dynamics in the valence band in real space in one-dimension at an electric field strength of $E_0 = 0.9 \text{ V/Å}$. The evolution of E-field E(t) (black dotted curve), hole propagation distance (violet curve) is in the units of lattice constant a, velocity gained by the hole (red curve), and momentum gained by the hole (blue curve) are shown in atomic units (a.u.).

gained by the hole in 1-dimension are calculated for initial phase 0 to final phase $2\pi/\omega$, where ω is the angular frequency of the driving field at 800 nm. The hole-trajectories show that the hole dynamics are limited to the ionic core and do not propagate much in a lattice. How particularly the hole dynamics contribute to the emission of HHG in solids is still an open question?

3.2.10 Electron trajectories in MgO for linear and elliptical polarization

In this section, we have calculated the electron and hole dynamics in 2-dimension for different electric field strengths. Initially, we have calculated the electron trajectories in 2-dimension momentum space of MgO under the influence of the linear polarization driving field of 800 nm. The electron trajectories in the conduction band of MgO under linear polarization for different linear polarization angles of the driving field with the major axis of the crystal, i.e., along the Mg-O bonding direction in 2-dimensional momentum space are shown in figure 3.19. The electron trajectories under the field strength of $E_0=0.1$ V/Å at 800 nm wavelength is shown in figure 3.19(a) for different linear polarization angles aligned to the major axis of MgO (Mg-O). The electron trajectories in MgO for 0°, 15°, 30°, 45°, 60°, 75° and 90° at low field strength ($E_0=0.1$ V/Å) are similar and don't cross the first unit cell as shown figure 3.19(a). The propagation of the electron trajectories are considered with the initial phase of $0.1\pi/\omega$ to $0.8\pi/\omega$, where ω is the angular frequency of the driving field at 800 nm. At the field strength of 0.5 V/Å, the electron trajectories are shown in figure 3.19(b), which shows that the electron can surpass multiple unit



Figure 3.19: The electron trajectories under linear polarization for different angles relative to the crystal axis in the conduction band under different field strengths for 800 nm driving wavelength. (a) 0.1 V/Å, (b) 0.5 V/Å, (c) 1 V/Å, (d)1.5 V/Å.

cells. The electron trajectories are symmetrical along with the major (Mg-O) and minor-axis (along O-O) of the MgO. The electron trajectories for the field strength of 1 V/Å and 1.5 V/Å are shown in figure (3.19(c) and 3.19(d)) at 800 nm driving wavelength. The electron can pass the four-unit cell of MgO, and the electron trajectories are symmetrical along the Major and minor axis of MgO. At the same time, they begin to deviate and showed curve behavior for other polarization angles $(15^{\circ}, 30^{\circ}, 60^{\circ} \text{ and } 75^{\circ})$. The electron trajectories are highly curved for the field strength of 1.5 V/Å (see figure 3.19(d)) due to the multiple interactions with the atomic sites which caused the collision and scattering with the atomic core.

The electron trajectories (solid lines) in the conduction band and hole trajectories (dashed lines) in valence band in MgO under linear polarization aligned along crystal axis for different field strengths at 800 nm driving wavelength. Figures 3.20(a) and 3.20(b) shows the electron and hole trajectories at an electric field strength of 0.5 V/Å and 0.9 V/Å for the linear polarization of the driving field. Both electrons and holes are traveling in opposite directions. The holes are limited to the oxygen ionic core while the electrons cross multiple atomic sites depending on the driving field strength.

We have also calculated the electron and hole trajectories for elliptical and circular polarization of the driving field to see the influence of the driving field polarization on trajectories. The electron trajectories (solid lines) in the conduction band and hole trajectories (dashed lines) in valence band in MgO under linear polarization (0°, 90°), elliptical (15°, 30°, 60°, 75°) and circular (45°) polarization with respect to crystal axis for different field strength for 800 nm driving wavelength at 0.5 V/Å (see figure 3.20(c)) and at 0.9 V/Å (see figure 3.20(d)). At the elliptical and circular polarized driving fields, the electron and holes trajectories are highly curved, minimizing the chances of recombination of electrons and holes, thus controlling the inter-band transitions. This can reduce the efficiency of higher-order harmonics under elliptical fields as highlighted earlier [34]. We have observed such effects in the case of THG in MgO that the intensity of THG is low at elliptical and circular polarization of the driving field. This shows that the emission of harmonics involves multiple atomic sites in MgO.



Figure 3.20: The electron trajectories (solid lines) in the conduction band and hole trajectories (dashed lines) in valence band in MgO under linear polarization aligned along crystal axis for different field strength at 800 nm driving wavelength. (a) 0.5 V/Å, (b) 0.9 V/Å. The electron trajectories (solid lines) in the conduction band and hole trajectories (dashed lines) in valence band in MgO for linear polarization $(0^{\circ}, 90^{\circ})$, elliptical $(15^{\circ}, 30^{\circ}, 60^{\circ}, 75^{\circ})$ and circular (45°) polarization to crystal axis at a different field strength of 800 nm driving wavelength. (c) 0.5 V/Å, (d) 0.9 V/Å.

3.2.11 Propagation effects of the NIR driving field in MgO and Cr: MgO crystals

The propagation of an intense driving field can induce the permanent change in the refractive index of the medium with and without the occurrence of structural changes [189]. These changes are attributed to the photoionization of an electron from the valence band to the conduction band, free-carrier absorption, free-carrier interaction, and some self-induced effects that greatly perturb the propagation of the driving field in solids. However, during the harmonic process, the intensity of the driving field is always kept lower than the damage threshold to avoid any permanent change in solids. Nevertheless, the driving intensity is sufficient to generate efficient harmonics, which can induce non-linear effects during the propagation of laser pulses in a solid medium. Such non-linear effects have been observed in MgO and Cr: MgO.

The spectrum of driving field NIR centered at 800 nm and propagated through the MgO (pure) and Cr: MgO crystals at an intensity of $\approx 1.0 \times 10^{13}$ Wcm⁻² is shown in figure 3.21. The Gaussian fit FWHM of NIR in the absence of crystals is 23.8 nm while FWHM of NIR through MgO is 40.96 nm as shown in figure 3.21(a). We have observed the broadening and blue-shifting in the transmitted spectra as seen in the Gaussian fit (red dotted curve of NIR and the blue dotted curve represents the transmission of NIR through MgO). With the increase of the doping concentration of Cr in MgO, the transmitted spectra of NIR broaden as shown in figures 3.21(b-e). The FWHM of NIR transmitted through Cr: MgO (5000 ppm and 9500 ppm) increased to 35.3 nm and 38.5 nm, respectively. We have observed the broadening and blue-shifting in the transmitted spectra, attributed to the strong photoionization and self-phase modulation effect (SPM).

The amount of blue-shifted spectral broadening in MgO (figure 3.21(a)) is limited due to the multiphoton absorption process, counterbalance of free-carrier density, and the components of blue-shifted frequency experience Kerr non-linearity at the leading edge, and attenuation at the trailing edge of the optical pulse [190]. The refractive index of the medium modulated due to the Kerr effect and free-carrier density due to the self-focusing effect and multiphoton absorption process. The Kerr non-linearity induces the blue shift in the spectrum of a pulse at the trailing edge and the redshift at the leading edge. In contrast, the increase in free-carrier density induces a blue shift at both edges of the pulse [190]. Thus, we observe a net blue-shifted spectrum in MgO. The self-focusing effect is observed in Cr: MgO crystals [191] which induces the SPM effect. SPM is a non-linear effect that induces the varying refractive index with the interaction of light with the medium. The variation in the refractive index of the medium produces the phase shift, and as a result, the pulse spectrum changed. We have observed broaden transmitted driving spectra through Cr: MgO (figure 3.21(b-e)). Furthermore, the transmission of the driving field decreases with the increase of doping concentration, particularly for 9500 ppm dopant concentration which induces more non-linear effects. This has been observed on the propagated spectrum in Cr: MgO (9500 ppm), see figure 3.21(e).



Figure 3.21: Propagation of focused NIR (800 nm) in 200 μ m solids crystals. (a) The spectrum of NIR (red) when there is no sample has the FWHM=23.8 nm and the transmission of NIR (blue) through MgO has the FWHM=40.9 nm. (b) Transmission in Cr: MgO(740 ppm), (c) Transmission in Cr: MgO(1300 ppm), (d) Transmission in Cr: MgO(5000 ppm), (e) Transmission in Cr: MgO(9500 ppm).

3.2.12 Below bandgap harmonic generation in MgO and Cr: MgO at 3 μ m driving wavelength

High-order harmonics in dielectrics at longer driving wavelengths are favorable as dielectrics can withstand at the higher critical fields than the shorter wavelength. This can generate more efficient below and above bandgap harmonics. Therefore, we have explored the below bandgap harmonics at the longer driving wavelength Mid-infrared (MIR) 3 μ m driving wavelength in MgO and Cr: MgO crystals. This driving wavelength has advantageous over IR (800 nm) due to its smaller photon energy. MIR offers an opportunity to deposit more energy on the crystal and avoid damage of crystals such as MgO and Cr: MgO. At a longer driving wavelength, in the non-perturbative regime, electrons excursion distance in the conduction band is longer compared to shorter driving wavelength highlighting the possibility to map the bandstructure of solids beyond the Γ -point.



Figure 3.22: (a) Illustration of an experimental setup to generate harmonics in MgO and Cr: MgO in transmission. The driving laser parameters: 40 fs, central wavelength 3 μ m operating at 100 kHz to an estimated peak intensity $\approx 1.5 \times 10^{13}$ Wcm⁻², (b) Spatial profile of driving beam recorded with the CCD shows elliptical spatial profile. (c) The spectral profile of laser. Where W: wedge, L1: 10 cm focal length, L2: 5 cm focal length, C: crystal, M: mirror.

We have used a Mid-infrared (MIR) laser of driving wavelength of 3 μ m, 40 fs operating at 100 kHz. The schematic of the experimental setup to generate harmonics (third: H3 and fifth: H5) at MIR driving wavelength in MgO and Cr: MgO crystals is shown in figure 3.22(a). The spatial and spectral profile of the driving pulses is shown in figures 3.22(b and c). The MIR laser pulses have the energy of 60 μ J, which were reduced to between 4.5 to 5.5 μ J by using a calcium fluoride wedge (W) and focused on the crystals (C) as shown in figure 3.22(a). The driving beam of 1 cm diameter is focused to a beam waist of $\approx 20 \ \mu$ m by 10 cm focal length lens (L1) on the crystals to an estimated intensity of $\approx 1.5 \times 10^{13}$ Wcm⁻² by considering the refractive index (n=1.691 at 3 μ m) of MgO. The fundamental and harmonics beams are separated by using ultrafast prism dispersion. The fundamental beam is directed to the MIR beam dumper to avoid any damage surrounding the experiment space. The harmonics are focused on the UV-VIS spectrometer (Sarspec) by 5 cm focal length lens (L2) as shown in figure 3.22(a).

3.2.13 Spectral and Z-scan measurements of below bandgap harmonics in MgO and Cr:MgO at 3 μ m



Figure 3.23: Spectral measurements of below bandgap harmonics in 200 μ m thick MgO and Cr: MgO crystals in transmission at a 3 μ m driving wavelength at an estimated peak intensity $\approx 1.5 \times 10^{13}$ Wcm⁻². (a) H3, (b) H5.

The spectral measurements of below bandgap harmonics (H3 and H5) in MgO (red), Cr: MgO (1300 ppm) in green and Cr: MgO (9500 ppm) in blue are shown in figures 3.23(a) and 3.23(b), respectively. We have observed that the central wavelengths of the harmonics in Cr doped crystal are blue-shifted due to the strong photoionization of the valence band. The absorption of the driving photon increases in doped crystals at the given intensity compared to pure MgO due to the low bandgap. This induced the modulation in the refractive index of the medium. As a result, the propagated driving spectrum blue-shifted as we have observed in other crystals [81]. Consequently, this blue-shifting is imprinted on the spectral profile of the generated harmonics.

To explore the generation depth of harmonics (H3 and H5) in MgO and Cr: MgO crystals, we have carried out the Z-scan measurements by translating the focus position of the MIR pulses in crystals. The beam waist at the focus position is 20 μ m. The calculated Rayleigh length (646 μ m) under our experi-



Figure 3.24: Z-scan of below bandgap harmonics in 200 μ m thick MgO (red dots) and Cr: MgO (for 1300 ppm, green squares and for 9500 ppm blue diamonds) crystals at a 3 μ m driving wavelength. (a) H3, (b) H5.

mental conditions is larger than the thickness of the crystals. We have observed almost a flat intensity profile of 200 μ m width of H3 in all crystals as shown in figure 3.24(a), equal to the thickness of crystals. Although, the intensity of H3 is a bit lower from the front surface as compared to the back surface (figure 3.24(a)) due to the linear absorption. Similarly, we have carried out the Z-scan for H5. As the focus position of the MIR is translated into crystals, we have observed the shifting H5 peak more towards the back surface, particularly for the doped crystals as shown in figure 3.25(b). We have attributed this to the more absorption of H5 photons generated from the front surface of the crystals. The intense H5 is observed when the focus position of MIR is near the back surface which can avoid the re-absorption of generated photons.

The below bandgap harmonics can be modulated in the medium during their propagation due to the coherence length (L_c) [82]. We have calculated the L_c of H3 and H5 at 3 μ driving wavelength generated in MgO. For H3, L_c is 31.8 μ m and 13.4 μ m for H5, respectively. The L_c for H3 in MgO at 800 nm driving wavelength is 4 μ m. This shows that the coherence length of below bandgap harmonics is larger for the longer driving wavelength, which has attracted the attention of a long driving wavelength source for the HHG process in solids.

3.2.14 Orientation dependence of below bandgap harmonics in MgO and Cr: MgO at 3 μ m

The orientation dependence of below bandgap harmonics (H3 and H5) was measured to map the crystal symmetry by rotating the crystals. The orientation dependence of H3 (shown in figure 3.25(a)) and H5 (shown in figure 3.25(b)). We have observed the four-fold anisotropic response of H3 in MgO



Figure 3.25: Orientation dependence of below bandgap harmonics in 200 μ m thick MgO (red dots) and Cr: MgO (for 1300 ppm, green squares and for 9500 ppm blue diamonds) crystals at a 3 μ m driving wavelength. Inset shows the MgO unit cell. The violet and cyan color ball represents Mg and O atom, respectively. (a) H3, (b) H5.

and Cr: MgO crystals. The nature of H3 is isotropic, yet the peaks of H3 are observed along the O-O bonding direction (as shown in the inset of the crystal unit cell). Similarly, we have also measured the orientations dependence of H5 in these crystals as shown in figure 3.25(b). The orientation dependence of H5 in MgO and Cr: MgO (1300 ppm) is highly anisotropic as compared to Cr: MgO (9500 ppm) crystal and aligned to the O-O bonding direction. The response of low-order harmonics along the Mg-O bonding direction is minimal and differs from what has been reported earlier for higher-order harmonics [31, 46]. This shows the intricate orientation dependence of the order of harmonics on the driving wavelength.

Conclusion

We have generated SH and TH in wide bandgap pure MgO and Cr: MgO crystals with different doping concentrations at a driving wavelength of 800 nm. The intensity response of THG in pristine MgO shows characteristics of a non-perturbative response. We have observed a decrease in THG intensity in Cr: MgO as the doping concentration increases, which we attribute to inter-band processes. A four-fold anisotropic linear polarization response of THG is observed in pristine MgO and low doped Cr: MgO characteristic of the non-perturbative harmonic process. However, we observe the regression to a typical perturbation response at higher dopant concentrations, which matches well with models and experimental results of perturbative responses shown elsewhere. The ellipticity response of THG in Cr: MgO for low doping follows the non-perturbative response. In contrast, at higher doping, it reverts to perturbative and shows a more atomic-like response. This is attributed to the splitting of the deep Mg conduction band by Cr energy levels. Our work demonstrates that a non-perturbative THG can be achieved in a wide bandgap insulator and is highly sensitive to the underlying crystal properties. The change of behavior at large dopant concentrations is attributed to the Cr impurities allowing linear inter-band absorption and blocks long-range intra-band transitions within the conduction band, contributing to perturbative THG. This study highlights the potential to use the anisotropic response of even low-order harmonics for polarization spectroscopy. The signal is orders of magnitude larger to probe spatial symmetry and band structure in the strong-field regime with commonly available Ti: Sa laser wavelengths of 800 nm.

We have also calculated electron and hole position trajectories, velocity trajectories, and momentum trajectories in the conduction and valence band, respectively, for linear and elliptical polarized field at different field strength and driving wavelengths. The trajectories showed the non-parabolic and curved pathway of electrons and holes at the high electric field strength and longer driving wavelength. In addition, the non-linear propagation effects have been observed in MgO and Cr: MgO crystals. The strong photoionization and self-phase modulation induce the blue-shifted and broadening of the driving pulses, which has imprinted on the harmonics in MgO and Cr: MgO.

Furthermore, below bandgap harmonics (H3 and H5) have been generated in MgO and Cr: MgO crystals at MIR laser pulses of the driving wavelength of 3 μ m, 40 fs operating at 100 kHz. We have observed the blue-shifted spectrum of harmonics in Cr: MgO crystals as compared to harmonics spectra generated in the pristine MgO. This is attributed to the strong photoionization of the valence band of Cr: MgO crystals which blueshifted the driving wavelength that imprints on the generated harmonics. Z-scan showed the flat H3 signal from MgO and Cr: MgO crystals, whereas the intensity of H5 is maximum when the driving pulse of MIR is focused near the back surface of crystals. We have observed strong four-fold anisotropy of orientation dependence of H5 compared to H3 in MgO and Cr: MgO crystals indicating the intricate orientation dependence of the order of harmonics on the driving wavelength. Propagation of the below bandgap harmonics is limited by the coherence length of harmonics and re-absorption of the crystals. We showed that with the increase of harmonics order, the efficient generation region is shifted to the back surface of the crystal due to the decrease in coherence length with harmonic order. The coherence length of the generated harmonics is directly dependent on the driving wavelength frequency. This has attracted the longer driving wavelength source as a potential candidate for the HHG process in solids.

3.3 Low-order harmonic generation in amorphous and crystalline substrates

In this section, we have explored the low-order harmonics such as SHG and THG in amorphous and crystalline substrates such as fused silica (FS), quartz (SiO₂), and Sapphire (Sa) at the driving pulses of 800 nm, 40 fs, operating at 1 kHz [96]. The bandgap of these dielectrics is higher than MgO. Therefore, these dielectrics can withstand at a higher driving intensity without any optical damage than MgO and Cr: MgO. Furthermore, these crystalline substrates lack inversion symmetry, which gives us a leverage to generate SHG and map its polarization/orientation symmetry response. We have explored the polarization response of these harmonics and driving wavelength ellipticity's impact on low-order harmonics. In addition, the non-linear propagation effects on SHG and THG were discerned and avoided in reflection geometry.

3.3.1 Spectral measurements of SHG in fused silica (FS)

The 30 μ J pulse energy of 40 fs at 800 nm is focused on the 300 μ m thick fused silica (FS) to generate the second-harmonic (SH) beam. The driving pulses are focused by 70 cm focal length to FS (9 eV bandgap) to $\approx 100 \ \mu$ m with an estimated peak intensity of $\approx 5.0 \times 10^{13} \ Wcm^{-2}$ which is below the damage threshold ($\approx 10^{14} \ Wcm^{-2}$) of FS [192]. The SH and fundamental pulses are blocked by the iris and harmonic filter (HF) as shown in figure 3.26. The filtered SH pulses are focused on the optical fiber by a short focal length lens of 10 cm. The optical fiber is connected to the spectrometer to collect the second-harmonic signal. The spectral profile of SHG in FS in transmission (red data points) and reflection (blue data points) is shown in figure 3.27(a). We have observed fringes in the SHG spectrum both in reflection and transmission, which are separated by 3.15 nm. These fringes are imprinted from the driving pulses, as shown in figure 3.27(a).



Figure 3.26: The schematic illustration of the experimental setup for SHG and THG in amorphous and crystalline substrates in transmission and reflection geometry (dotted rectangle). For reflection geometry, solids are aligned to 45° to the incoming driving laser pulses and reflected the signals filtered by HF and focused to UV-VIS spectrometer by L2. The driving laser parameters: 40 fs, central wavelength 800 nm operating at 1 kHz at a field strength of $\approx 1 \text{ V/Å}$ corresponding to the estimated peak intensity $\approx 5.0 \times 10^{13} \text{ Wcm}^{-2}$, Where HWP: half-wave plate, QWP: quarter-wave plate, W: wedge, L1: 75 cm focal length, L2: 10 cm focal length, C: crystal, HF: harmonic filter, M: mirror.

3.3.2 Polarization response of SHG in FS

The FS were mounted on the translation stage to translate at the focus point of the driving field to measure the strong signal of SH. The polarization of the driving field is rotated by the HWP to observe the polarization response of SH in both reflection and transmission geometry. The polarization response of SHG showed a perturbative response in FS. We have observed the more isotropic response of SHG in FS in transmission geometry (red data points) as shown in figure 3.27(b) having small bumps of peaks along with the horizontal polarization. SHG shows the anisotropic response in reflection geometry and has strong two-fold symmetry along the vertical linear polarization direction (see, figure 3.27(b)). This anisotropic response of SHG in reflection geometry of FS is similar to SiO₂ response as shown in the black curve of figure 3.27(b).



Figure 3.27: The driving laser parameters: 40 fs, central wavelength 800 nm operating at 1 kHz at a field strength of $\approx 1 \text{ V/Å}$ corresponding to the estimated peak intensity $\approx 5.0 \times 10^{13} \text{ Wcm}^{-2}$ (a) Spectral measurements of SHG in 300 μ m thick fused silica (FS) in transmission (red data points) and reflection (blue data points) geometry. NIR/2 (black dotted in air and black line in FS) to theoretically match SH's peak. (b) Polarization response of SHG in FS in transmission (red data points) and reflection (blue data points) geometry. The polar graph has the linear axis in arbitrary units.

3.3.3 Propagation effects and spectral measurements of THG in FS

The schematic illustration of an experimental setup to generate THG in FS is shown in figure 3.26. The central wavelength of 800 nm and temporal duration of 40 fs, operating at 1 kHz of the driving laser field [26] is used to generate the THG in FS. We have used the Astrella femtosecond laser and insert a wedge (W) to reflect few mW laser pulses to drive the FS. The 30 mW laser pulses focused to 300 μ m thick FS by a 75 cm focal length convex lens. The fundamental NIR filtered by using the corresponding harmonic filter (HF) and further focused to UV-VIS spectrometer (Sarspec) by 10 cm focal length convex lens as shown in figure 3.26. The spectral measurements of the THG in FS are shown in figure 3.28(b). The spectrum of the THG has multiple peaks, which are imprinted due to the fundamental driving NIR

source (figure 3.28(a)). The FWHM of the NIR driving field in transmission (28.5 nm) and reflection (27.7 nm) is increased as compared to the fundamental FWHM (25.97 nm). Due to non-linear effects, the transmitted spectra (red) scales up at the trailing edge compared to fundamental driving field spectra (black curves). This broadening has been imprinted on the TH spectrum as well as compared to the reflected TH. The FWHM of TH generated in the transmission is 5.44 nm, and in reflection geometry, it has an FWHM of 4.66 nm (figure 3.28(b)).



Figure 3.28: The driving laser parameters: 40 fs, central wavelength 800 nm operating at 1 kHz at a field strength of $\approx 1 \text{ V/Å}$ corresponding to the estimated peak intensity $\approx 5.0 \times 10^{13} \text{ Wcm}^{-2}$. (a) The NIR (black) after transmission through FS (red) and reflection (blue) from FS. The FWHM of transmitted NIR is 28.5 nm, and reflected NIR is 27.7 nm, respectively. At the same time, the FWHM of fundamental NIR is 25.97 nm. (b) Spectral measurements of THG in FS in reflection (blue data points) having FWHM of 4.66 nm and transmission(red data points) having FWHM of 5.44 nm. NIR/3 (black dotted in air and black line in FS) to theoretically match TH's peak.

Due to non-linear propagation effects, the transmitted spectra (red) showed multiple enhanced peak structures at the trailing edge compared to the fundamental driving field (black curves). We have observed that the enhanced NIR spectra at the trailing edge in transmitted and quite small enhancement at the trailing edge in reflected NIR from the FS, which attributes to the strong photoionization effect. Furthermore, we have observed fringes in the SHG spectrum both in reflection and transmission, separated by 3.15 nm. These fringes are imprinted from the driving pulses as shown in black dotted (NIR/2) in figure 3.27(a). Noted that the central peak of the SHG spectrum is blue-shifted when compared with the theoretically driving SH spectrum (NIR/2 black dotted spectrum). The broadening effect has been observed in the TH in transmission compared to the reflected TH signal in FS. We have observed that the spectral profile of TH in reflection is blue-shifted than in transmission. Similarly, we have observed multiple peaks on THG in transmission (red dots), which are imprinted due to the fundamental driving NIR pulses (figure 3.28(a)). The transmitted driving pulses NIR/3 (black dotted line) in FS are blueshifted than NIR/3 (dotted black) in the air due to non-linear propagation effects. Therefore, the THG generated in the transmission is blue-shifted, with multiple pronounced peaks are the leading part of the pules.

The fringes are equally spaced before and after the central peak with the separations of 1.6 nm. This modulation appears in the spectrum of THG due to the driving spectrum modulation as shown in figure 3.28(a). There is a possibility of appearing of fringes on the harmonic spectrum while spectral modulation is absent on the driving field [193]. This could be due to the interference of harmonic signals generated from the interface and the bulk solid crystals. Such modulation in the spectrum of SHG [194], and in THG and fifth-order harmonics in transparent solid medium, [195] has been reported. The fringes spacing is inversely proportional to the temporal separation between the harmonic signal generated from the bulk and thickness of the solid medium. Similarly, there could be other reasons for fringe spacing due to the non-linear effects of high intensity inside the solids medium, [196]. The pulse splitting of the fundamental beam occurs when it interacts with the solids medium, which eventually leads to the spectral modulation of harmonics and the fundamental driving beam.



3.3.4 Polarization and ellipticity measurements of THG in FS

Figure 3.29: (a) Polarization response of THG in FS in reflection (violet dots) and transmission (red dots) geometry at 800 nm driving wavelength, (b) Ellipticity response of THG in transmission geometry in FS at 800 nm driving wavelength.

The polarization response of THG in FS is measured by employing the HWP to rotate the horizontal polarization of the driving field. Although, FS is amorphous (non-crystalline) in nature and does not exhibit any symmetry. However, the THG shows two fold-symmetry as illustrated in figure 3.29(a) (red data points). The intensity of the THG is maximum for the linear polarization and has minimum generation efficiency along with the vertical linear polarization. We have also measured the polarization response of THG in reflection geometry (violet data points) as shown in figure 3.29(a). The polarization response of THG in reflection demonstrates highly anisotropic four-fold symmetry similar to the response of crystalline SiO₂ (see, figure 3.31). Although the amorphous quartz (FS) lacks the long-range periodicity

but still can exhibit strong polarization dependence of below bandgap harmonics in reflection (four-fold)) and transmission (two-fold). We attributed this to the localization of electron excursion distance in FS as reported earlier [37].

In the next step, we have aligned the horizontal polarization of the driving field to obtain the peak of THG in FS and have inserted the QWP before the HWP as shown in figure 3.26 to measure the ellipticity dependence of THG by rotating the ellipticity of the driving field. The ellipticity response of the THG in FS is illustrated in figure 3.29(b). The maximum of the THG can only be generated when the driving laser field is linearly polarized (ellipticity=0). At the same time, the intensity of THG in FS falls to a minimum, almost negligible at circular polarization (ellipticity= ± 1). Nevertheless, there is quite strong THG in FS at elliptical driving polarization (ellipticity= ± 0.5) as shown in figure 3.29(b). This shows that even from the amorphous solids, elliptical harmonics can be generated, which is advantageous over the atomic phase harmonics.



3.3.5 Spectral measurements of SHG and THG in SiO₂

Figure 3.30: (a) Spectral measurements of SHG and THG in SiO_2 at 800 nm driving wavelength, (b) Incident average power (mW) scan for THG in SiO_2 .

We have generated the low-order harmonics (SHG and THG) in the crystalline SiO₂ oriented along (0001) having dimension $10 \times 10 \times 0.2 \text{ mm}^3$. Due to the non-centrosymmetric nature of SiO₂, the evenorder harmonics can be generated at the given driving field. The schematic illustration of the experimental setup to generate harmonics at 800 nm is shown in figure 3.26. The spectral measurements of SHG and THG in SiO₂ measured with the UV-VIS spectrometer are shown in figure 3.30(a). The acquisition time for SHG was adjusted to 10 ms and for THG to 1s, respectively. There was no spectral modulation observed in the spectrum of THG as we have observed in the spectral modulation of THG in FS (figure 3.28(b)). The SHG spectra exhibits the modulation with the double peak structure. The peaks are separated by 13.5 nm. These double peaks appeared due to the spectral interference of SHG signals generated from the front surface and bulk of SiO₂ crystal. We have observed the appearance of multiple
peak spikes in the THG spectrum with the increase of the driving laser peak power as shown in figure 3.30(b). The increase of the driving field peak power, which consequently increased the peak intensity of the driving field, results in the broadening of the THG spectrum.



3.3.6 Polarization and ellipticity measurements of SHG and THG in SiO₂

Figure 3.31: Polarization response of SHG and THG in SiO_2 at 800 nm driving wavelength. (a) Transmission geometry,(b) Reflection geometry (c) Ellipticity response of SHG (blue dots) and THG (cyan dots) in transmission in SiO_2 .

To map the crystal symmetry, we measured SHG and THG's polarization response in SiO₂ by rotating the HWP. The polarization and ellipticity response of SHG and THG in SiO₂ is shown in figures (3.31(a) and 3.31(c)), respectively. The polarization response of SHG is asymmetric four-fold while THG has the 2-fold symmetric response in transmission as shown in figure 3.31(a). This asymmetric anisotropic polarization response of SHG is attributed to the perturbative nature of SHG in SiO₂. While the twofold anisotropic polarization response of THG inclined towards non-perturbative (Cyan data points) as shown in figure 3.31(a). Figure 3.31(b) shows the polarization response of SHG and THG in SiO₂ in reflection geometry. The polarization response of SHG is two-fold, while THG showed four-fold anisotropic response. The polarization response of SHG and THG in reflection geometry is highly anisotropic, with sharp peaks as the propagation effects are absent. The ellipticity measurements of the SHG and THG is demonstrated in figure 3.31(c) which shows that the harmonics have maximum intensity at the linear polarization (ellipticity=0). The SHG has adequate strength at the circular driving field, while the THG has the minimum intensity at circular polarization as shown in figure 3.31(c).

3.3.7 Spectral measurements of SHG and THG in Sapphire (Sa) crystal

Sapphire (Sa) is one of the most commonly used non-linear optical elements, owing to its large bandgap (10 eV) and high damage critical power of 1.7 MW [197]. Therefore, we have explored the process of SHG in 200 μ m thick Sa (Al₂O₃) at 800 nm driving wavelength. The experimental setup to generate SHG is shown in figure 3.1. The driving pulses are focused by 70 cm focal length to Sa to $\approx 100 \ \mu$ m. The focused pulses have the peak intensity of $\approx 5.0 \times 10^{13} \text{ W cm}^{-2}$ which is well below the damage threshold of Sa. The spectral measurements of SHG in the Sa crystal are shown in figure 3.32(a), showing the pre-peak before the main peak.



Figure 3.32: Spectral measurements of SHG and THG in Sa crystals at 800 nm driving wavelength. (a) SHG, (b) THG.

We have also generated THG in Sa. The experimental setup is the same for the Sa crystal as described in FS (see section 3.3.3). The acquisition time for THG has been chosen 1s and signal acquired with an average of over five acquisitions by a UV-VIS spectrometer. The spectrum of THG generated in 200 μ m thick Sa crystal is shown in figure 3.32(b). We have observed only a single peak at 264.5 nm without any spectral modulations or fringes. Furthermore, we have increased the power of the driving field to see the intensity-dependent effect on the spectra of THG as illustrated in figure 3.33(a). The intensity of



Figure 3.33: Average driving power (mW) scan for the spectral measurements of THG in Sa at 800 nm driving wavelength.

the THG increases with the increase of the power of the driving field, and corresponding THG spectra broaden.

3.3.8 Polarization and ellipticity measurements of SHG and THG in Sa

The Sa crystal was mounted on the motorized rotation stage and rotated about its axis for a complete rotation to observe the polarization response of SHG. The polarization response of SHG and THG in Sa is measured at the driving intensity of $\approx 5.0 \times 10^{13}$ Wcm⁻². The SHG generated in the Sa is perturbative. We have observed the isotropic response of SHG in Sa as shown in figure 3.34(a). The polarization response of SHG in Sa is more atomic-like in nature. The anticipation of the structure of Sa could not be mapped from the SHG, but it could be mapped from the higher-order harmonics [105, 198].

The polarization response of THG has been measured by rotating the HWP. We have observed the two-fold response of THG in Sa as shown in figure 3.34(b). The polarization angle of the driving field is a relative one to the crystal axis. Similarly, we have measured the ellipticity response of THG in Sa which is oriented along (0001) direction. For this, the peak of THG is initially obtained by rotating the HWP and then inserted the QWP before the HWP to observe the ellipticity response. The ellipticity response of THG in Sa is shown in figure 3.34(c) which shows a more efficient THG signal at the linear polarization (ellipticity=0) and falls rapidly by switching the driving polarization from linear to elliptical and falls to a minimum at circular polarization (ellipticity=±1). These measurements depict that we can still generate elliptical THG in the Sa.



Figure 3.34: The polarization response of SHG and THG in Sa measured at 800 nm driving wavelength at an estimated intensity of $\approx 5.0 \times 10^{13}$ Wcm⁻². (a) Polarization response of SHG in Sa, the angle is arbitrary relative, (b) Polarization response of THG in Sa crystal, (c) Ellipticity response of THG in Sa.



3.3.9 Non-linear propagation effects on the spectra of harmonics in Sa

Figure 3.35: (a) Propagation of NIR (800 nm) in 200 μ m Sa crystal. NIR (black) FWHM=25.97 nm, transmission (red) and reflected from the front surface of Sa (Blue) having FWHM=22.63 nm and FWHM=26.67 nm, respectively. (b) Spectral measurements of SHG in transmission (red data points) and reflection (blue data points) geometry. NIR/2 (black dotted in air and black line in Sa) to theoretically match SH's peak. (c) Spectral measurements of THG in reflection (blue data points) and transmission(red data points). NIR/3 (black dotted in air and black line in Sa) to theoretically match TH's peak. Where R: reflection and T corresponds to transmission.

We have explored the propagation effects on the spectral profile of the driving spectrum and the impact on the spectral profile of SHG and THG in Sa. The experimental setup to observe non-linear propagation effects of driving pulses and generation of below bandgap harmonics is described in figure 3.26. The transmitted spectra of the driving field through Sa are compressed and have more enhancement towards the leading edge of spectra, and the trailing edge of spectra falls as compared to the driving NIR spectrum. As a result, the FWHM of NIR transmitted through Sa is 22.63 nm while the FWHM of NIR is 25.97 nm and the reflected FWHM of NIR from Sa is 26.77 nm which is more blue-shifted and has pronounced peaks at the trailing edge, as shown in figure 3.35(a).

We have generated SHG and THG in Sa, oriented along (0001) having dimension $10 \times 10 \times 0.2 \text{ mm}^3$ at $\approx 5.0 \times 10^{13} \text{ Wcm}^{-2}$. The acquisition time for SHG 100 ms and THG was chosen to 1s with an average over five acquisitions to measure the spectrum of THG by UV-VIS spectrometer. The spectral measurements of SHG in Sa in transmission and reflection geometry are shown in figure 3.35(b). The SH spectrum has the FWHM of 6.42 nm transmission, whereas reflection geometry has an FWHM of 6.27 nm. The spectral measurements of THG in transmission and reflection geometry are shown in figure 3.35(c). FWHM of TH signal in the transmission is 5.43 nm, while in reflection geometry has the FWHM of 5.35 nm. The THG signal generated in the transmission is broader as compared to reflection in Sa (figure 3.35(c)). We have quantified the non-linear propagation effects in Sa. The fundamental propagated NIR driving spectrum in Sa does not show any significant changes as compared to the reflected one (see, figure 3.35(a)). However, the THG measured in the transmission is red-shifted. In reflection, it is blue-shifted, highlighting the non-linear propagation effects such as strong photoionization.

3.4 Comparison of low-order harmonic generation in single and polycrystal solids

Gallium oxide (Ga_2O_3) has attracted a huge interest owing to its wide bandgap (5.02 eV), high thermal stability, and high breakdown field of 8 MV/cm, and high laser induced damage threshold \approx 0.36 Jcm^{-2} [199]. This make it an attractive candidate for solar-blind ultraviolet (UV), high power electronic devices [200] and a promising laser crystal element due to its low phonon energy and good thermal properties [201]. The Ga₂O₃ crystal lies under the umbrella of a mono-clinic $C_{2/m}$ space group having a three-dimensional structure with two nonequivalent Ga^{+3} sites. The first Ga^{+3} site bonded with the six O^{-2} atoms to form octahedral of GaO^{-6} and the second Ga^{+3} site bonded with the four O^{-2} atoms to form GaO^{-4} tetrahedral to form two types of polyhedral structural representation. Such structure is a pure octahedra layer, and mixed of octal and tetrahedral [202]. The dispersion of the refractive index of β - Ga₂O₃ thin films investigated by RF-sputtering which range between 1.75 to 1.9 [203] which is quite close to MgO crystals. Similarly, the α -Ga₂O₃ crystal has the same structure as α -Sa. Thus lacking the inversion symmetry. This lack of inversion symmetry in the Ga_2O_3 crystal can enable to generate the even-order harmonics. Therefore, we have generated SHG and THG in Ga_2O_3 at 800 nm driving wavelength and explored the linear and elliptical polarization dependence of SHG and THG. In addition, the non-linear propagation effects on the driving wavelength spectrum and its impact on the spectral profile of SHG and THG have been investigated.

3.4.1 SHG and THG in single versus ploycrystal Ga₂O₃ at 800 nm

The non-linear response of Ga_2O_3 crystals is explored by focusing on the 800 nm driving wavelength of a pulse duration of 40 fs operating at 1 kHz. The laser beam is propagated to (100) surface plane of the single crystal, polycrystal (see figure 3.36(a), and (010) polycrystal Ga_2O_3 (see figure 3.36(b)). The Ga_2O_3 polycrystal oriented along (100) and (010) is 500 μ m and 650 μ m thick. The schematic of the experimental setup to observe propagation effects and to generate harmonics are shown in figure 3.26. For the sake of clarity, (100) surface plane and (010) surface plane polycrystal are expressed as (100) and (010) polycrystal. The propagated spectrum of focused driving wavelength (NIR) in the air (red color), through (100) single crystal Ga_2O_3 (blue dots), (100) polycrystal (camel color), and (010) polycrystal (green color) Ga_2O_3 is shown in figure 3.37(a). There was no significant change observed in the propagated NIR in polycrystal except in (100) single crystal Ga_2O_3 . We have observed the nonlinear propagation effects of the driving wavelength in (100) single crystal Ga_2O_3 . The propagation of the driving field induces the blueshifts in the driving field due to non-linear effects. The non-linear effects induce the change in the refractive index of the medium on the interactions of intense femtosecond pulses with the Ga_2O_3 .

The low-order harmonics (SHG and THG) of 800 nm wavelength are generated by focusing with the 75 cm focal length to $\approx 75 \ \mu m$ beam waist. SHG and THG have been generated at an estimated peak intensity of $\approx 0.5 \ \text{TWcm}^{-2}$ in Ga₂O₃. SHG and THG have been measured with the corresponding harmonics filter with the UV-VIS spectrometer (Sarspec) as shown in figures (3.37(b) and 3.37(c)). The



Figure 3.36: (a) Schematic illustration of the lattice of single and polycrystal Ga_2O_3 when the laser beam is propagating through a (100) polycrystal. Inset shows the sample holder with the crystal lattice with the view direction of lattice in $\langle 201 \rangle$, (b) Laser beam is propagated to the (010) surface plane of polycrystal Ga_2O_3 . Courtesy of Dr. Marco Peres from CTN, IST.



Figure 3.37: (a) NIR transmitted spectrum in air (red color), through a (100) single crystal Ga_2O_3 (blue dots), (100) polycrystal (camel color) and (010) polycrystal (green square) Ga_2O_3 . (b) Spectral measurements of SHG in (100) single crystal (blue dots), (100) polycrystal (camel color), and (010) polycrystal (green square). In the absence of HWP, the spectral measurements of SHG in (100) polycrystal (cyan diamond). NIR/2 (black dotted in air and black solid line in (100) single crystal Ga_2O_3) to match the peak of SH theoretically. (c) Spectral measurements of THG in Ga_2O_3 , (100) single crystal (blue dots), (100) polycrystal (camel color), and (010) polycrystal (green square). NIR/3 (black dotted in air and black solid line in (100) single crystal Ga_2O_3) to theoretically match the peak of TH.

fringes observed on the driving laser spectrum are imprinted on the spectrum of second-harmonic (SH). This imprinting of the spectral fringes corresponds to the intensity-dependent non-linear effect of the driving field in the (100) single crystal Ga_2O_3 . Such non-linear effects of high intensity inside the solids medium have been reported [196]. Interestingly, the spectral fringes on the SHG spectrum disappeared when we remove the HWP from the beam path (cyan diamond, figure 3.37(b)). We have observed the blue-shifted SH spectrum in (100) polycrystal Ga_2O_3 in camel color as shown in figure 3.37(b). This indicates that the fine-tuning of the THG central wavelength can be witnessed through the non-linear propagation effect. This highlights that the non-linear propagation can induce blueshifts and redshifts depending on the nature of solid materials, corresponding non-linear refractive index, and driving field intensity. In the next step, we have measured the polarization and ellipticity response of SHG and THG for different orientations of the crystal axis to the linear laser polarization.

3.4.2 Polarization and ellipticity measurements of SHG and THG in Ga₂O₃ crystal

The polarization response of the SHG and THG in a (100) single crystal Ga_2O_3 at $\approx 0.5 \times 10^{13}$ Wcm⁻² is measured by rotating the linear polarization of the driving field by HWP. The polarization response of SHG (blue dots) is shown in figure 3.38(a) and THG (blue dots) in figure 3.38(b). The SHG polarization response is more perturbative, relatively isotropic, and has the maximum efficiency and linear horizontal polarization. A dip in the polarization response observed along the vertical linear polarization direction could be due to the detection system (spectrometer) or less conversion efficiency. We have observed identical polarization response at low and higher driving peak power. The THG exhibits the anisotropic symmetrical polarization response. Along with the horizontal linear polarization, the prominent two-fold peak of THG was observed. In contrast, a two-fold minor peak of THG was observed along the vertical polarization of the driving field.



Figure 3.38: Polarization response of harmonics in (100) single crystal (blue dots), (100) polycrystal (camel color) and (010) polycrystal (green square) Ga_2O_3 at 800 nm driving wavelength. (a) SHG (b) THG.



Figure 3.39: Ellipticity response of the harmonics in (100) single crystal (blue dots), (100) polycrystal (camel color), and (010) polycrystal (green square) Ga_2O_3 , the vertical black dotted line represents the linear polarization (ellipticity =0) of 800 nm driving wavelength. (a) Ellipticity response of SHG (b) Ellipticity response of THG.

Surprisingly, the polarization response of SHG and THG from the polycrystal Ga_2O_3 in both surface plane (100) and (010) polycrystal showed different behavior as shown in figures (3.38(a) and 3.38(b)). The polarization response of SHG in (100) and (010) polycrystal Ga_2O_3 exhibits the four-fold structure and broad four-fold peaks having more isotropic contributions, respectively. Similarly, polarization response of THG in (100) and (010) polycrystal Ga_2O_3 showed multi-peak structure, see figure 3.38. The polarization dependence of SHG and THG in surface plane (100) single crystal Ga_2O_3 is shown in blue data points for comparison in figure 3.38. This noticeable different harmonics response is attributed to the different periodic arrangements of atoms in lattice and possibly exploration of electron dynamics in the different regions of the non-parabolic band of Ga_2O_3 .

The generation process of below bandgap harmonics in solids is greatly affected by the ellipticity of the driving beam [58]. Therefore, we have explored the ellipticity response of SHG and THG in a single crystal Ga_2O_3 oriented along (100) surface plane at the NIR driving wavelength of 800 nm. A QWP has been used before the HWP and rotated it to observe the driving field ellipticity effect on the emission of the SHG and THG processes.

The ellipticity response of SHG in the (100) single and polycrystal Ga_2O_3 behaves similarly, maximum at linear polarization (ellipticity=0) and minimum at the circular polarization (ellipticity=±1) as shown in figure 3.39(a). The yield of SHG decreases monotonically with the increasing ellipticity of the driving laser. The distribution of SHG yield is symmetric around ellipticity=0 and behaves atomic-like. Whereas, the ellipticity response of SHG in (010) polycrystal shows non-atomic-like behavior, shows the secondary peak (bump like) at ellipticity=±0.65 as shown in figure 3.39(a). The ellipticity response of THG in (100) single crystal of Ga_2O_3 shows maximum yield at linear and secondary maximum at circular polarization (ellipticity=±1) as shown in figure 3.39(b). Whereas THG in the (100) and (010) oriented polycrystal Ga_2O_3 exhibit pronounced deviation from the Gaussian profile distribution. This non-atomic

non-monotonic response of THG was observed at a fixed crystal axis. The yield of THG is asymmetric around ellipticity =0, indeed increases with the increase of ellipticity of the driving field and reaches to maximum at driving field ellipticity= ± 1 .

This different behavior of ellipticity response is attributed to the different crystal structures and the non-perturbative response of THG. The non-perturbative response of THG resulted from the intra-band transitions of electrons driven by the strong NIR field. It has been reported earlier that the circular harmonics are governed by the symmetry group of crystals at the circular polarized driving field [204]. However, Klemke et *al.* demonstrated that polarization states of harmonics are not only controlled by the symmetries of crystal but also depend on the inter-band and intra-band electron dynamics [188]. Our results show that the strong signal of THG can be generated at elliptical and circular driving polarization from the polycrystal Ga_2O_3 . The non-atomic response of SH and TH in polycrystals indicates that the electrons explore the non-parabolic region of electronic band structures.

3.4.3 Spectral measurements of below bandgap harmonics in polycrystal Ga_2O_3 at 3 μ m driving wavelength



Figure 3.40: Spectrum of harmonics in Gallium oxide at 3 μ m driving wavelength of an estimated peak intensity of $\approx 1 \times 10^{13}$ Wcm⁻². (a) (100) polycrystal Ga₂O₃, the photoluminescence signal indicated in dotted ellipse, (b) (010) polycrystal Ga₂O₃.

To investigate the below bandgap harmonics generation in polycrystal Ga₂O₃, we have derived these crystals with the mid-infrared (MIR) laser pulses. The detailed description of the experimental setup to generate below bandgap harmonics in (100) polycrystal and (010) polycrystal Ga₂O₃ is shown in figure 3.22. The MIR pulses of 3 μ m, 40 fs operating at 100 kHz are focused by 7.5 cm focal length lens (Calcium fluoride, CaF₂) to a beam waist 18 μ m to Ga₂O₃ crystal. The estimated peak intensity of $\approx 1 \times 10^{13}$ Wcm⁻² is used by considering the linear refractive index 1.95 of Ga₂O₃ [205] to generate harmonics up to 9th order containing both odd and even order harmonics. The even-order harmonics have been observed due to the lack of inversion symmetry in Ga₂O₃ crystals. The generated harmonics are separated by the ultrafast prism and focused to UV-VIS spectrometer by 5 cm focal length lens. The spectral measurements of below band harmonics in (100) polycrystal Ga₂O₃ and (010) polycrystal Ga_2O_3 are shown in figure 3.40(a) and 3.40(b), respectively. The photoluminescence peak is observed in between H5 and H6 harmonics in (100) polycrystal Ga_2O_3 as shown in figure 3.40(a). Multiple peaks



Figure 3.41: The spectral fringes measurements of H5 in Ga_2O_3 polycrystal oriented (100) and (010) at 3 μ m driving wavelength field.

have been observed in the H5 spectrum in both (100) polycrystal and (010) polycrystal Ga₂O₃ due to the interference of H5 generated from the front surface and bulk crystal. For more clarity, the spectral response of H5 in (100) polycrystal and (010) polycrystal Ga₂O₃ is shown in figure 3.41 which shows a structured (multiple peaks) fringe spectra. Such structured spectra of THG and H5 reported earlier [195]. H5 from (100) polycrystal is a broader and red-shifted wing with the fringe spacing of ≈ 8 nm, whereas the fringe spacing in the H5 spectrum of (010) polycrystal Ga₂O₃ crystal is ≈ 6 nm. The calculated fringe space for 500 μ m thick (100) polycrystal is ≈ 7.5 nm, and for 650 μ m thick (010) polycrystal is \approx 5.75 nm as enlisted in table 3.1.

| Thickness μm | Measured fringe spacing (nm) | Calculated fringe spacing (nm) |
|-------------------|------------------------------|--------------------------------|
| 500 | 8 | 7.5 |
| 650 | 6 | 5.75 |

Table 3.1: The measured and calculated spectral fringe spacing of H5 in polycrystal Ga₂O₃ at 3 μm driving wavelength.

The fringe spacing are calculated as

$$\Delta \lambda = \frac{\lambda^2}{c\Delta t} = \frac{\lambda^2}{c.d.(\frac{1}{v_{q,\omega}} - \frac{1}{v_{q,5\omega}})}$$
(3.8)

Where c is the speed of light, Δt is the temporal separation between the harmonic pulses generated at the surface and throughout the crystal, $v_{g,\omega}$ and $v_{g,5\omega}$ are the group velocities of fundamental and fifth-order harmonics pulses, respectively. The group velocity is calculated as $v_g = \frac{c}{n}(1 + \frac{\lambda}{d}dn/d\lambda)$. The fringe spacing $\Delta\lambda$ is inversely proportional to the temporal separation of the two pulses. This shows that the fringe spacing will be smaller for the thick crystal as observed in 650 μ m thick, which is 5.75 nm as compared to 8 nm fringe spacing in 500 μ m thick polycrystal. This kind of structured harmonics spectra depends on the driving energy, order of harmonics, propagation distance, the thickness of crystals, and group velocity phase mismatch of generated beams. For a thick crystal, the temporal separation ' Δt ' can be large, resulting in smaller fringe spacing that could be beyond the spectrometer's resolution. On the other hand, the Δt could be small for relatively thin crystals, resulting in large fringe spacing. The fringe spacing could be larger than the bandwidth of the harmonic pulses, therefore unable to detect.

3.4.4 Orientation dependence of below bandgap harmonics in Ga_2O_3 at 3 μm driving wavelength



Figure 3.42: Orientation dependence of below bandgap at 3 μ m driving wavelength of an estimated peak intensity of $\approx 1 \times 10^{13} \text{ Wcm}^{-2}$ in polycrystal Ga₂O₃ with different surface plane to the driving laser field. (a) Odd-order harmonics in (100) Ga₂O₃. (b) Even-order harmonics in (100) Ga₂O₃. (c) Odd-order harmonics in (010) Ga₂O₃. (d) Even-order harmonics in (010) Ga₂O₃.

We initially generated below bandgap harmonics using MIR at 3 μ m, 40 fs, 100 kHz pulses in (100) polycrystal and (010) polycrystal Ga₂O₃. Then to map the crystal symmetry response through harmonics, orientation dependence of harmonics are measured by rotating the crystal about its axis. A four-fold anisotropic polarization response of odd-order harmonics (H3, H5, H7, and H9) and in even-order harmonics (H4, H6, and H8) have been observed in (100) polycrystal Ga₂O₃ along Γ -X as shown in figures 3.42(a) and 3.42(b), respectively. Similarly, in (010) polycrystal Ga₂O₃, the orientation response of harmonics has the strong four-fold anisotropy along Γ -N bonding direction as shown in figures 3.42(d), respectively. This shows that the orientation response of harmonics in (100) and (010) polycrystal depends on the electronic structure of crystal largely or the way crystals are cut and oriented with respect to the driving field.

3.4.5 Low-order harmonics wavelength dependence on the bandgap of solids



Figure 3.43: Central wavelength dependence of harmonics versus bandgap of solids at 3 μ m driving wavelength.

We have observed the central wavelength of low-order harmonics are shifting for different bandgap crystals at the 3 μ m driving wavelength. Particularly, we have compared the central wavelength of H3 and H5 generated in MgO, Cr: MgO (5000 and 9500 ppm), (100) polycrystal, and (010) polycrystal Ga₂O₃ as shown in figure 3.43. With the increase of the crystal's bandgap, the central wavelength of harmonics are red-shifted or vice versa at the 3 μ m driving wavelength of 40 fs, operating at 100 kHz. We anticipated that harmonics in wide bandgap crystals are generated from the leading part of driving laser pulse. Whereas in low bandgap crystals, harmonics are generated from the trailing part of the driving pulses. As the refractive indices of both crystals (MgO and Ga₂O₃) are similar(n_{MgO}=1.7 and n_{Ga₂O₃=1.75) [148, 203]. Therefore, the effective parameter for the wavelength shifting of harmonics is} the bandgap and the laser driving intensity.

Our theoretical simulation showed that the non-linear effects could influence the driving spectrum during the propagation of intense driving pulse. The non-linear propagation effects induced the instantaneous varying refractive index due to strong photoionization. As a result, the driving spectrum gets blue-shifted. This blueshifting imprints on the generated harmonics. As the bandgap decreases, the impact of non-linear propagation effects increases. This can induce the more blue-shifted driving spectrum, and consequently, the harmonics would be blue-shifted. We anticipate that tuneable wavelengths can be generated in solids by using different crystals of various bandgap at fixed laser driving wavelengths. The tuneable wavelengths can map atomic transitions and through molecular spectroscopy to deduce the molecular or atomic dynamics.

3.5 Low-order harmonic generation in thin films

HHG in gases, thick and thin solids have been routinely explored and attracted tremendous attention due to their flux of XUV and generation of isolated attosecond pulses. Whereas solid-state HHG has offered an alternate route than gas-based HHG to realize the XUV light sources. However, the damage threshold and absorption of harmonics in solids are limiting the flux of harmonics. Therefore, interest has been developed to explore the harmonics process in thin films as the efficient harmonics is generated from few end layers of solids [85]. In addition, the non-linear propagation effects could be minimum in thin films. Here, we have explored the process of low-order harmonics (SHG and THG) in thin films such as Aluminum Gallium Nitrate (AlGaN), and Aluminum Nitrate (AlN) deposited on the Sapphire substrate at a driving wavelength of 800 nm, 40 fs operating at 1 kHz. We are thankful to Dr Marco Peres and Dr Katharina Lorenz from the CTN capmus of IST for providing us these thin films.

3.5.1 Transmission and reflection of NIR from thin films

In this section, we have initially measured the driving field's spectrum in transmission and reflection from thin films. The propagation effect of intense NIR driving wavelength in transmission through solids induces non-linear effects in photoionization or self-phase modulation, which can induce the blueshift/redshift and spectral broadening of the driving pulses. In thin films, the distance of propagation of intense driving pulse is small, and the spectral modulation can be limited or controlled precisely by the thickness of thin films. To control the driving beam spectrum, we have used a 3 μ m thick AlN and 500 nm thick AlGaN thin films deposited on the Sa substrate. Initially, we have measured the driving field's transmission effect and disentangled by comparing it with the reflection of driving pulses from these thin films and substrates. The ultrafast laser irradiated and unirradiated thin films morphology was measured with the Atomic Force Microscopy (AFM) to observe the change on the thin film surface. Later on, we have generated SHG and THG in transmission and reflection geometry (see figure 3.44) to avoid the propagation effects and disentangle the thin films and substrate contributions to SHG and THG.

These thin films have hexagonal structures with a C-plane cut. AlN belongs to the III-V group of

semiconductors with a bandgap of 6.2 eV and has a high damage threshold [206] for femtosecond pulses, thus enabling the interaction of the intense driving field with the thin films. All thin film grown on Sa have used to realize the compact frequency comb high harmonic source in the spectral range of vacuum ultraviolet (VUV) [207] and observed the more efficient THG in transmission geometry facing the thin films at the rear-surface of the substrate. It has been observed that TH generated from the AlN thin films is 3-times intense, and fifth harmonics is 1000-times intense from alone Sa substrate [207]. High harmonic have been generated in AlN which showed a clear signature of the origin of the harmonic generation in solids from surface effects [208].

AlGaN is an alloy of GaN and AlN of an energy bandgap of 4.7 eV. AlGaN has been employed to generate the deep ultraviolet [209] and ultra-deep ultraviolet (UDUV) light-emitting diodes (LEDs) [210] which make it an exciting candidate for the harmonic generations. SHG has been generated in the AlGaN, and GaN [211] thin films deposited on Sa substrate having a different thickness at 1040 nm Nd: YAG Q-switched laser. However, free-standing thin films of nanometers, like AlN or AlGaN, are impossible to use practically, and disentangling it from the bulk contribution is essential, as it must be deposited on a substrate.



Figure 3.44: Schematic illustration of the experimental setup to generate low-order harmonics AlN and Al-GaN thin films deposited on Sa. (a) Transmission geometry (b) Reflection geometry. NIR: near-infrared, HWP:half-wave plate, QWP:quarter-wave plate, L1 and L2:lens, HF: harmonic filter, Sa: sapphire.

The schematic illustration of the experimental setup to generate low-order harmonics in thin films such as AlN and AlGaN at 800 nm, 40 fs in transmission and reflection geometry is shown in figure 3.44. In transmission geometry, thin films are faced on the rear-surface to generate harmonics from the thin films (figure 3.44(a)) while in reflection geometry, thin films are on the front surface to reflect the fundamental and harmonics as shown in figure 3.44(b).

The transmission spectra of intense driving field NIR (black curve) through the Sa substrate (blue curve), AlN thin films (red curve), and AlGaN thin film (pink curve) are shown in figure 3.45(a) while the spectra of NIR in reflection geometry is shown in figure 3.45(b). The FWHM of the NIR driving field transmitted through AlN and AlGaN is ≈ 26 nm and 26.4 nm, which is close to the actual FWHM of the driving field (25.97 nm). In contrast, the transmitted spectra of the driving field through Sa are compressed and have more enhancement towards the leading edge of spectra, and the trailing edge of spectra falls as compared to the driving IR spectrum. As a result, the FWHM of NIR transmitted through Sa is 22.63 nm. We have observed the propagation effects of the driving field in AlN and AlGaN thin films sample, which exhibits the blue shifts in the driving field (see figure 3.45(a)), whereas in Sa, we have observed the compression of the driving field at the trailing edge. We have observed minor broadening of the driving field in reflection geometry having FWHM of 27 nm, 26.5 nm, and 25.5 nm in Sa, AlN, and AlGaN, respectively (see figure 3.45(b)). In reflection geometry, the NIR driving field is more inclined towards redshifts in AlN.



Figure 3.45: The spectral measurements of the driving field propagated through thin films deposited on Sa substrate (blue curve), AlN (red curve), and AlGaN in the pink curve. The FWHM of NIR in each sample is given on the graph. (a) Transmission, (b) Reflection.

3.5.2 Morphology measurements of unirradiated and irradiated thin films

In the raw Sa sample, there is a tiny ripple-like morphology (by zoom out the image, one can see parallel lines) with deposits (bright) on some places as shown in figure 3.46(a) taken by AFM. Figure 3.46(b), the laser radiated Sa shows some spots the ripple-like morphology (left bottom), but in some places (top), we can see a sort of granular structures due to the laser interactions.

The AFM images of AlGaN thin films deposited on Sa substrate measured for two different zones are shown in figure 3.47. The un-irradiated zones of AlGaN thin films exhibit the granular structures with



Figure 3.46: Atomic Force Microscopy images of the surface of a Sa crystal. (a) Un-irradiated, (b) Irradiated with 40 fs, 800 nm laser pulses.



Figure 3.47: Atomic Force Microscopy images of the surface of a 0.5 μ m AlGaN thin film deposited on Sa crystal. (a) Un-irradiated zone1 (roughness 3.6 nm), (b) Un-irradiated zone 2 (roughness 4.7 nm).



Figure 3.48: Atomic Force Microscopy images of the surface of a 0.5 μ m AlGaN thin film deposited on Sa crystal. (a) zone1 radiated with 40 fs, 800 nm laser pulses (roughness close to 19 nm), (b) Zoom in to nm scale, (c) Zoom in for single spot, (d) The line-out profile of dashed line drawn in (c).



Figure 3.49: Atomic Force Microscopy images of the surface of a AlN thin film deposited on Sa crystal. (a) Un-irradiated zone1 (roughness 2.5-6.5 nm) (b) Un-irradiated zone 2 (roughness 2.5-6.5 nm), (c) Zone 1 irradiated with 40 fs, 800 nm laser pulses, (d) Zone 2 irradiated with 40 fs, 800 nm laser pulses.

the roughness of thin-film ranging from 3.6 to 4.7 nm. Whereas AFM images of the surface of a 0.5 μ m AlGaN thin film deposited on Sa crystal for zone 1 radiated with 40 fs, 800 nm laser pulses shown in figure 3.48(a). The irradiated zone does show marked differences as a hole structure (with hole depths of 40-50 nm) than un-irradiated thin films (figures 3.47). Consequently, the roughness increases by one order of magnitude, up to almost 20 nm. The zoom-in of figure 3.48(a) up to nm scale shown in figure 3.48(b) which shows more granular surface due to femtosecond laser irradiation. The line out of a single spot (figure 3.48(c)) of an irradiated surface is shown in figure 3.48(d), which shows the depth of the hole of almost 40-50 nm indicating surface morphology modification of AlGaN thin films.

The AFM images of unirradiated thin films of AlN deposited on Sa substrate are shown in figures (3.49 (a) and (b)) which exhibits the triangular structures. The roughness of AlN thin films was measured in the range of 2.5-6.5 nm. The AFM images of irradiated zones of AlN thin films show a sort of triangular structures as well with some tiny structures on the irradiated one (bottom left and top right) as shown in figures (3.49 (c) and (d)) with the roughness of irradiated thin films of 7 nm.

3.5.3 Spectral measurements of SHG and THG in AlN and AlGaN thin films



Figure 3.50: The spectral measurements of SHG from thin films deposited on the Sa substrate (blue dots), AlN (red dots), and AlGaN (pink dots). NIR/2 (black dotted in air and black line in Sa, green and cyan lines through AlGaN and AlN thin films) to theoretically match SH's peak. (a) In transmission, (b) In reflection.

The spectral measurements of SHG in Sa, AlN, and AlGaN in transmission and reflection geometry are shown in figures 3.50(a) and 3.50(b). The SH spectra have the FWHM of 6.42 nm, 6.4 nm, and 6.87 nm in Sa, AlN, and AlGaN, respectively in transmission. Whereas, in reflection geometry, FWHM of 6.27 nm (Sa), 6.4 nm (AlN), and 6.2 nm (AlGaN) is observed. The SHG spectrum in AlN is red shifted in reflection and has the enhanced fringe peaks. Whereas, in Sa and AlGaN, fringes peaks are less intense than the main peaks (see figure 3.50(b). In the transmission geometry, the secondary peaks of SHG in all

samples match each other. In reflection geometry, we are catching the harmonics signal from the front surfaces where thin films are deposited. In this way we can avoid the non-linear propagation effects of the driving field. The propagation effect is observed in Sa and AlGaN as the FWHM of SH is increased by 6.7 % and 7.3 % in transmission as compared to reflection, respectively.



Figure 3.51: The spectral measurements of THG from thin films deposited on Sa substrate (blue data points), AlN (red data points), and AlGaN in pink data points. NIR/3 (black dotted in air and black line in Sa, green and cyan lines through AlGaN and AlN thin films) to theoretically match the peak of TH. (a) In transmission, (b) In reflection.

Similarly, the spectral measurements of THG in Sa, AlN, and AlGaN in transmission and reflection geometry are shown in figure 3.51. FWHM of TH signal in Sa, AlN, and AlGaN in transmission geometry is 5.43 nm, 4.99 nm, and 6.87 nm, respectively. The TH generated in AlGaN thin films sample is more blue-shifted while the TH spectrum AlN thin film has lessened at the trailing part of the pulse and enhanced at the leading edge as shown in figure 3.51(a). The TH spectrum measured in reflection geometry from Sa, AlN, and AlGaN has the FWHM of 5.35 nm, 4.35 nm, and 5.66 nm, respectively (figure 3.50(b)). The THG generated in the transmission is broader than in reflection which is attributed to the non-linear propagation effects such as self-phase modulation effects, strong-photoionization in AlGaN. These none-linear effects can broad and blue-shifted the driving field. This broadening and blue-shifting can imprint on the harmonics as we have observed in transmission geometry in thin films.

3.5.4 Polarization dependence of SHG and THG in thin films

To map the non-linear response of thin films, we have employed the HWP to rotate the driving field polarization to measure the polarization response of harmonics. The measured polarization response of SHG and THG in transmission and reflection are shown in figure 3.52 and figure 3.53, respectively. The polarization response of SHG in transmission in Sa (substrate) (blue data points), AlN (red data points), and AlGaN (pink data points) are all identical and demonstrated the two-fold symmetry with a highly



Figure 3.52: Polarization measurements of SHG from thin films deposited on Sa substrate (in blue data points), from AlN (in red data points), and AlGaN (in pink data points) at 800 nm driving wavelength. (a) In transmission, (b) In reflection.



Figure 3.53: Polarization measurements of THG from thin films deposited on Sa substrate (in blue data points), from AIN (in red data points), and AlGaN (in pink data points) at 800 nm driving wavelength. (a) In transmission, (b) In reflection.

isotropic response as shown in figure 3.52(a). In the next step, we have measured the polarization response of SHG in reflection geometry (figure 3.52(b)). The polarization response of SHG is more anisotropic in Sa and AlGaN, while AlN shows the isotropic response. This is due to the fact of avoiding non-linear propagation effects of the driving pulses. The polarization response of THG in AlN, AlGaN thin films, and Sa substrate in the transmission is shown in figure 3.53(a). Thin films exhibit a two-fold response of THG in transmission, whereas polarization response THG in Sa behaves differently.



Figure 3.54: Ellipticity measurements of THG in Sa substrate (blue data points) and AlGaN (pink data points) at 800 nm driving wavelength.

The polarization response of THG in thin films and Sa in reflection geometry are shown in figure 3.53(b). Clearly, THG from Sa and AlN shows four-fold symmetry while the AlGaN shows anisotropic two-fold symmetry. The polarization response of THG from the thin films are more anisotropic as compared to the substrate due to the anisotropic nature of electronic band structure. The polarization response of thin films behaves differently than Sa, both in transmission and reflection. The THG has more isotropic contribution than anisotropic contributions in Sa, while a strong anisotropic polarization response observed from the samples on which thin films are deposited. Finally, we have employed the combination of HWP and QWP to measure the ellipticity response of THG in Sa and AlGaN. We have observed the intense emission of THG at linear polarization (ellipticity=0), which falls as we shifted from linear to elliptical (ellipticity= ± 0.5). We have observed minimum intensity at circular polarization (ellipticity= ± 1) as shown in figure 3.54. The ellipticity response of AlGaN (pink dots) has the maximum intensity at linear polarization (ellipticity= ± 1) as shown in figure 3.54. This study shows that the efficient low-order harmonics in thin films can be generated and disentangled from the substrate in reflection. Strong anisotropy of low-order harmonics has been observed in thin films along with the behavior of ellipticity which deviates

from the perturbative response. This study highlights the mapping of the anisotropic nature of electronic band structure through low order harmonics in thin films at most commonly available laser sources.

3.6 Conclusion

In this chapter, we have demonstrated the generation of low-order harmonics in wide bandgap dielectrics and thin films at 800 nm and 3 μ m driving wavelength. We have controlled the non-linear response of MgO by tuning the electronic structures through doping. We show that Cr doping can increase the SSHG efficiency and mitigate angular polarization dependence when introduced to MgO. The non-perturbative response of THG reverts to perturbative on the introduction of impurity. We show that even the lowest odd harmonic order can originate from a non-perturbative process and that the emission intensity is sensitive to the band structure and crystal properties. The observed results are validated with the support of DFT calculations and semi-classical analysis of the electron trajectories model.

Furthermore, SHG and THG have been generated in amorphous and crystalline solids at 800 nm which shows the strong polarization dependence of below bandgap harmonics in FS and SiO₂. We attributed this to the localization of electron excursion distance in FS and SiO₂. In addition, we have generated SHG and THG in a single and polycrystal Ga₂O₃ at 800 nm, and symmetry of these crystals mapped by polarization measurements of harmonics. SHG shows more isotropic polarization response whereas THG exhibits a strong anisotropic polarization response in single and polycrystals. Four-fold anisotropic orientation dependence of harmonics observed in (100) polycrystal along Γ -X bonding direction and whereas in (010) polycrystal Ga₂O₃ along Γ -N at 3 μ m driving wavelength. The strong signal of THG has been generated at elliptical and circular polarization from the polycrystal Ga₂O₃. We attributed the strong anisotropic response of harmonics to the complex interplay of crystal surface plane to the laser beam, inter and intra-band transitions. We have also successfully disentangled the contributions of SHG and THG from thin films (AlN and AlGaN) and Sa at 800 nm driving wavelength.

Furthermore, we have investigated the non-linear propagation effects of the ultrafast intense nearinfrared driving field at 800 nm, 40 fs duration in the wide bandgap dielectrics. We attributed the broadening of driving pulses in transmission due to the self-phase modulation. The observed propagation effects are imprinted on the below bandgap harmonics. This work shows the sensitivity to control the spectral profile of harmonics by manipulating the driving field, showing the possibility of new tailored solid-state harmonics sources for optical diagnostics. We attributed the complex interplay of the crystal surface plane to the laser beam, inter and intra-band transitions to the non-perturbative low-order harmonics. This study highlight the potential to use wide-bandgap dielectrics as deep ultraviolet and possibly XUV sources through the solid-state harmonics process in a vacuum for spectroscopy applications.

Chapter 4

High harmonics in semiconductors and imaging of nano-patterns through solid-state ptychography

In this chapter, initially, low and high harmonics have been generated in silicon (Si) and zinc oxide (ZnO), and Strontium Titanate (SrTiO₃ or STO) at 2.123 μ m laser wavelength and mapped the crystal symmetry through polarization response of harmonics, which are described in section 4.1. We have measured the spatial and spectral profile of harmonics with the UV-enhanced CCD camera and UV-VIS spectrometer. The spectral profile and orientation dependence of SHG have been demonstrated in ZnO at 800 nm in subsection 4.1.5 and 4.1.6, respectively. The spectral control of high order harmonics through non-linear propagation effects in Si and ZnO has been presented in section 4.2. The experimental and simulated reconstruction of images of nano-patterns and nano-structures by ptychography has been demonstrated in subsection 4.3. Finally, we have described the generation of OAM's beams in solids and imaging the intensity distribution of vortex beams at fifth-order harmonics in section 4.4.

4.1 High harmonic generation in Si, ZnO and STO

4.1.1 Introduction

In this chapter, initially, low and high harmonic (above bandgap) generation in semiconductors and the non-linear propagation effect of the driving pulses on harmonics [81] will be presented. We have generated low (H3) and above bandgap harmonics which are termed as high order harmonics (H5, H7 and H9) in ZnO and Si crystals at 2.1 μ m driving wavelength. The spectral and spatial profiles of these high-order harmonics are measured. To reveal the generation region of harmonics in the ZnO and Si crystals, we have carried out the z-scan measurements by translating the crystals along with the focus point in the optical axis of driving pulses. We have observed that H3 generated from the bulk ZnO is less intense, about half intense as the signal generated from near the surfaces with splitting the spectrum into two peaks. The z-scan demonstrated that the crystals structure is absorbing the H5 and H7 generated from the front surfaces. The observed harmonics (H5 and H7) are attributed from the rear surfaces of the crystals. The propagation-dependent blueshifts in the spectrum of the generated harmonics have been observed with the translation of focus position of the driving field in crystals. Furthermore, the simulation of the propagation of the focused driving field is carried out to map the non-linear response of ZnO and Si crystals at ≈ 0.29 TWcm⁻² of laser intensity.

Additionally, the mapping of the crystal structure have be unfolded by the polarization measurements of harmonics, provided that the driving field has sufficient strength to drive the electrons away from the parent ions. Therefore, we have measured the polarization dependence of low and high harmonic in Si, ZnO, and STO. An anisotropic four-fold symmetric polarization response is observed in Si crystals, revealing the exploration of electron-hole dynamics in the Γ -K-M direction in reciprocal space. The isotropic response of polarization dependence of harmonics has been observed in ZnO owing to low driving field strength that can be advantageous when using etched spiral zone plates (SZP) to manipulate the beam to generate OAM beams. This study highlights the potential to control the spectral properties of harmonics in semiconductors and enables mapping the crystal symmetry and electronic band structure at nJ pulses.

4.1.2 Experimental setup to generate high harmonics in Si and ZnO

A schematic representation of the experimental setup for high harmonics generation in the semiconductor is shown in figure 4.1(a). The photograph of the actual setup is shown in figure 4.1(b). We have employed a fiber laser (NOVAE Company) operating at 2.123 μ m with a pulse energy of ≈ 8 nJ and a repetition rate of 19 MHz. To enable a tighter focus and thus achieve higher intensities, the size of the laser beam is magnified by a factor of 3.75 times using a telescope (T). The 85 fs duration pulses are focused on the crystals by a convex lens of 3 cm focal length up to a maximum peak intensity of a ≈ 0.29 TWcm⁻² well below the damage threshold of crystals. The generated diverging harmonics are further focused on a convex lens of 15 cm focal length either on a UV-enhanced CCD camera or a UV-VIS spectrometer for spatial and spectral beam characterization. Band-pass filters centered at each harmonic wavelength are used to separate and characterize the HHG properties. Z-scans are performed to localize the longitudinal medium response by using the optimized coupled spectrometer, as illustrated in the inset of figure 4.1(a).

4.1.3 Spectral and spatial measurements of harmonics in Si

We have generated efficient harmonics up till ninth order (H9) in 2 μ m thick, (100) oriented silicon samples. The spectral and spatial profiles of H3, H5, and H7 harmonics have been measured in both crystals. The spatial profile of H3 in Si 2 μ m thick has many aberrations owing to the imaging setup limitations. Therefore the spatial profile of H3 is excluded (figure 4.2). We could only observe the H9 in Si crystal through the UV-enhanced PCO-CCD camera. Therefore its spectrum is absent in figure 4.2).





Figure 4.1: (a) Schematic representation of the experimental setup to generate high order harmonics (H3, H5, and H7) in the 300 μ m thick silicon (Si) and 200 μ m thick-(100) oriented ZnO crystal at 2.123 μ m driving wavelength. The convention for the Z-scan notation is explained in the inset. Note that, P: polarizer, L: lens, T: telescope, S: sample, HF: harmonic filters, FM: flip mirror, CCD: charged coupled device, (b) Photograph of the actual experimental setup.



Figure 4.2: The spectral and spatial measurements of low and high harmonics at 2.123 μ m driving wavelength in 2 μ m thick Si crystal. Each harmonic's spectral and spatial profile was measured separately with the corresponding harmonics filters for different acquisition times by UV-VIS spectrometer and UV-enhanced PCO-CCD camera, respectively.

4.1.4 Polarization measurements of harmonics in Si

The mapping of the non-linear response of Si crystals are measured by rotating the vertical polarization of the driving field to the [100] crystal direction. The polarization dependence of harmonics (H3, H5, H7 and H9) in the 300 μ m and 2 μ m thick Si is shown in figure (4.3(a) and 4.3(b)), respectively. The polarization measurements of harmonics (H3, H5, H7, and H9) in Si revealed a four-fold anisotropy. The anisotropic response of the harmonic efficiency is consistent with the crystal structure of (100) Si [141]. The crystallographic structure of (100) Si exhibits the four-fold symmetry in the atomic arrangement and demonstrates the four-fold symmetry of Raman signals [212].

We have measured the polarization response of harmonics in the Si crystal at 2.123 μ m at 0.29 TWcm⁻². In the 300 μ m thick Si crystal, as the harmonic order increases, the angular contrast becomes higher. The polarization dependence of H7 and H9 are the most contrasted ones which correspond to the non-perturbative response of harmonics as shown in figure (4.3(a)). In the Si (2 μ m) thick), H3 exhibits a perturbative response while H5, H7, and H9 are non-perturbative, as shown in figure (4.3(b)). The harmonic signal maximizes when the driving field has been rotated to the direction of (110). The electron-hole pairs created by the intense driving field along this orientation are accelerated along with the projection of Si-Si bonds onto the (001) plane. This corresponds to the Γ -K-M direction in the reciprocal space of Si. The harmonic efficiency is minimal when the polarization of the driving field is aligned along the (100) direction, which corresponds to the Γ -X in the reciprocal space. The observed strong polarization dependence of the harmonics can only be demonstrated by considering the microscopic generation mechanism, as the Si possesses isotropic linear properties. Therefore, the phase matching or absorption process does not explain the strong polarization dependence of the harmonics in Si.



Figure 4.3: Polarization response of high order harmonics in Si crystals of different thicknesses at 2.123 μ m driving wavelength. (a) 300 μ m, (b) 2 μ m.

4.1.5 Spectral measurements of SHG in ZnO at 800 nm

SHG has been generated in bulk ZnO crystals, ZnO nanofibers, and ZnO thin films as well [213, 214, 215]. The reflective SHG in the ZnO thin films is demonstrated the three-fold symmetry [216]. The ZnO has a wide range of applications and has a great potential for optoelectronic devices [217, 218]. The transmissive SHG in ZnO crystals and its polarization response need to investigate. It is expedient to understand the clear picture of underlying non-linear processes in thin ZnO.

The ZnO crystal is a wurtzite hexagonal structure having crystallographic orientation (0001), with the edge < 11 - 20 >. ZnO is a non-centrosymmetric uni-axial crystal. To generate the SHG in ZnO, 40 fs pulses of $\approx 4 \ \mu$ J energy focus on the 500 μ m thick ZnO crystal. The focused pulses have the peak intensity of $\approx 4 \times 10^{11}$ Wcm⁻² which is below the damage threshold of ZnO. The dimension of ZnO crystal is $5 \times 5 \times 0.5$ mm. The second-harmonic and fundamental pulses are separated by the chromatic dispersion of a convex lens and blocked by the iris and a short pass filter, as shown in figure 3.1. The filtered second-harmonic pulses are focused on the optical fiber by a short focal length of 5 cm. The optical fiber is connected to the spectrometer to collect the second-harmonic signal. To observe the polarization response of SHG, thin solid crystals were mounted on the motorized rotational stage to rotate the crystal about its axis. The computer controls the steps of the motorized rotational stage. Furthermore, the rotational stage is mounted on the linear translational stage to translate the crystal towards or away from the focus point of driving pulses.

The spectral measurements of SHG in the low bandgap ZnO crystal are shown in figure 4.4(a). The spectrum of SHG in pure MgO (blue curve) and Cr: MgO (red curve) is measured under the same conditions (same energy and focal spot). The second-harmonic signal generated in ZnO is recorded at lower driving pulse energy. The energy was reduced to avoid optical damage, as the ZnO has a lower bandgap (3.37 eV) than the MgO bandgap (7.8 eV). The signal of SHG in ZnO is relatively lower. The

bandgap is smaller than MgO, and only a few NIR photons are involved in the phenomena of SHG.



Figure 4.4: (a) The spectral measurements of SHG in ZnO crystal generated at 800 nm driving wavelength, (b) Polarization response of SHG in ZnO at 800 nm driving wavelength. The polar graph has the linear axis in arbitrary units. The optical axis is kept perpendicular to the surface of the ZnO crystal during polarization response measurements.

4.1.6 Polarization response of SHG in ZnO at 800 nm

The ZnO crystal was mounted in the rotation stage and rotated about its axis for a complete rotation. The driving pulses are linearly horizontal polarized at fixed driving polarization to observe the Polarization response of SHG. The SHG generated in the ZnO is perturbative and is generated through the below bandgap. An anisotropic and more symmetrical response is observed in ZnO crystal, showing the sensitivity of SHG on the crystal structure. This anisotropic emission of SHG in ZnO is due to the thick periodic solid. The polarization response of SHG exhibits the six-fold symmetry as shown in figure 4.4(b). This six-fold symmetry polarization response of SHG is consistent with the breaking of inversion symmetry along the 'c' axis of the crystal. The observed anisotropic response of polarization dependence of SHG in ZnO is inconsistent with the higher-order even harmonics symmetry [33].

4.1.7 Polarization measurements of low and high harmonics in ZnO at 2.123 μ m

The polarization dependence of the generated harmonics in ZnO is measured by rotating the vertical polarization of the driving field with the half-wave plate (HWP) while keeping the focus point in the crystal fixed. The corresponding polarization dependence of harmonics is measured with the UV-enhanced PCO-CCD camera. We have observed the isotropic dependence of the harmonic signal on the laser polarization for below bandgap harmonics (H3 and H5). At the same time, there is some chaotic response of polarization dependence for H7 as depicted in figure 4.5. The observed isotropic polarization response

for low-order harmonics is different from the reported anisotropic polarization response for higher-order harmonics [33, 39, 219].



Figure 4.5: Polarization measurements of harmonics (H3, H5, and H7) generated in ZnO at 2.123 μ m driving wavelength at an intensity of 0.29 TWcm⁻².

This non-identical behavior of polarization dependence of harmonics than the reported one [33] is attributed to the low driving field strength. The crystal symmetry or electronic bandstructure can be mapped if the strength of the laser pulses is strong enough to make the substantial electrons' trajectories. In our case, the intensity of the driving field is 0.29 TWcm⁻². Therefore the motion of electrons around the parent ion is not much affected by the potential of neighboring atomic sites. As a consequence, the atomic-like response of polarization dependence of harmonics is observed in ZnO at an intensity of ≈ 0.29 TWcm⁻².

4.1.8 Harmonic generation in strontium titanate (SrTiO₃ or STO) at 2.123 μ m driving wavelength

Strontium titanate (SrTiO₃) single crystal has its lattice parameters which match with the most materials and has a Perovskite crystal structure of bandgap of 3.2 eV [220]. Therefore, STO has been widely used as a crystal substrate for epitaxial growth of oxide thin films and superconducting thin films. It has been widely used for optical windows and high-quality sputtering targets. STO has been used as a substrate for the thin films of BiFeO₃ (BFO) by pulsed laser deposition technique with a 5 nm conducting buffer layer of SrRuO₃ [159]. Because of its transparency to 2.123 μ m wavelength, STO is a potential candidate to explore the process of harmonics. We have generated harmonics up to the 7th order in STO. The experimental setup to generate the 3rd (H3), fifth (H5), and seventh (H7) in STO at 2.123 μ m wavelength is illustrated in figure 4.1(a).

4.1.9 Spatial measurements of harmonics in STO

The spatial profiles of H3, H5, and H7 measured by UV enhanced PCO-CCD camera for different acquisition times in STO with the corresponding harmonic filters are shown in figure 4.6. We have observed the decrease in the spot size of the harmonic with the increase of harmonic order.



Figure 4.6: Spatial measurement of harmonics in STO recorded by UV-enhanced PCO-CCD camera at 2.123 μ m driving wavelength at an intensity of ≈ 0.29 TWcm⁻². (a) H3, (b) H5, (c) H7.

4.1.10 Polarization and ellipticity measurements of harmonics in STO

The polarization and ellipticity dependence of H3 (red dots) and H5 (blue dots) in SrTiO₃, oriented along (001) measured with the UV-enhanced PCO-CCD camera as shown in figures (4.7(a), 4.7(b)), respectively. The signal of H7 generated in STO was weak, therefore excluded for the polarization and ellipticity measurements. The polarization and ellipticity response of harmonics are observed with the rotation of HWP and QWP, respectively. Figure 4.7(a) shows the four-fold symmetry of polarization response of H3 (red dots) and H5 (blue dots). The peaks of H3 and H5 are shifted by 45^{0} , showing different polarization. This shows that even below band harmonics exhibit different polarization behavior depending on how transitions are generated. Figure 4.7(b) shows the ellipticity response of harmonics, strong emission of H3 (red dots) and H5 (cyan dots) observed at the linear polarization of the driving field (ellipticity=0). H3 has the minimal intensity at the circular polarization (ellipticity= ± 1), whereas H5 still has sufficient signal even at the circular polarization(ellipticity= ± 1), see figure 4.7(b). This response of ellipticity dependence of harmonics validated with the earlier prediction that different harmonics behave differently to ellipticity due to the different origin of harmonics [58].



Figure 4.7: (a) Polarization response of H3 (red dots) and H5 (blue dots) in STO crystal at 2.123 μ m driving wavelength. (b) Ellipticity response of H3 (red dots) and H5 (blue dots) in STO crystal at 2.123 μ m driving wavelength.

4.1.11 Conclusion

We have generated a second-harmonic in the low bandgap ZnO crystal at 800 nm driving wavelength, 40 fs pulse duration at an estimated peak intensity of $\approx 1.5 \times 10^{11}$ Wcm⁻². SHG has been investigated relative to the polarization angle between the crystal and laser polarisation. An anisotropic and mirrorsymmetrical response is observed in ZnO crystal, showing the sensitivity of SHG on crystal electronic structure. In comparison, harmonics (H3, H5, and H7) have been generated at 2.123 μ m driving wavelength at an intensity of ≈ 0.29 TWcm⁻². At the longer driving wavelength with the low driving field strength, the isotropic polarization response of harmonics has been observed in ZnO, highlighting the atomic-like response of polarization dependence of harmonics in ZnO. We have also generated efficient harmonics up till H9 in 300 μ m and 2 μ m thick Si crystals and mapped the crystal symmetry by measuring the polarization response of harmonics. The polarization measurements of harmonics in Si revealed a strong four-fold anisotropy. H3 demonstrated perturbatively, whereas H5, H7, and H9 showed a nonperturbative response. In addition, we have observed four-fold symmetry of H3 and H5 in STO with maximum emission of H3 and H5 at ellipticity =0. Whereas, H5 exhibits the relative higher signal than H3 at the circular polarization (ellipticity =±1). These results pave the way towards generate circular polarized pulses chirality measurements and to explore the magnetic domains of ferromagnetic materials.

4.2 Spectral control of high order harmonics through non-linear propagation effects

High harmonics in crystals has revealed a wealth of perspectives such as all-optical mapping of the electronic band structure, ultrafast quantum information, and the creation of all-solid-state attosecond sources. Significant efforts have been made to understand the microscopic aspects of HHG in crystals. In contrast, the macroscopic effects, such as non-linear propagation of the driving pulse and its impact on the HHG process, are often overlooked. This work studies macroscopic effects by comparing two materials with distinct optical properties, silicon (Si) and zinc oxide (ZnO). By scanning the focal position of 85 fs duration, 2.123 μ m wavelength pulses inside the crystals (Z-scan), we reveal spectral shifts in the generated harmonics. We interpret the overall blueshift of the emitted harmonic spectrum as an imprint of the spectral modulation of the driving field on the high harmonics. This process is supported with numerical simulations. This study demonstrates that through manipulation of the fundamental driving field through non-linear propagation effects, precise control of the emitted HHG spectrum in solids can be realized. This method could offer a robust way to tailor HHG spectra for a range of applications.

4.2.1 Introduction

In the last decade, solid-state HHG has been studied in a wide variety of crystals, and amorphous solids [33, 31, 37]. The physical picture of solid-state HHG is in its infancy and is the subject of ongoing discussion [47, 48, 49, 50, 51, 52]. A better understanding of the physical process of solid-state HHG will not only lead to improved secondary sources but to an ability to map the nonlinear properties and possibly allow all-optical mapping of the electronic structure of solids [53, 54, 55, 56, 57, 38]. HHG in solids can be realized in materials transparent to the driving laser pulse wavelength. As femtosecond duration pulses are generally generated in the near to mid-infrared region, insulating and semi-conducting solids are the materials of choice for HHG. The HHG process in solids shares some similarities with HHG in gases, at least conceptually [57, 61]. The first step is an inter-band transition that promotes a charge carrier to the conduction band. Once there, this electron is driven by the fundamental field and can emit harmonics due to oscillations within a band (intra-band) or excitation and relaxation between bands (inter-band) [34, 38].

The initial inter-band excitation requires a tunneling or a multi-photon absorption process, and the rate of free carrier generation is therefore inversely proportional to the bandgap. Apart from the microscopic physics of carrier generation and motion, the properties of the HHG emission can be influenced by the propagation of the electric fields inside the crystal. This macroscopic propagation is highly nonlinear for the driving field and linear for the harmonics, owing to their much lower intensity. This makes the HHG spectrum an intricate fingerprint of the complex interplay of microscopic and macroscopic processes. For example, HHG in ZnO [33, 39, 40] has been shown to reveal both the inter and intra-band mechanisms. Similarly, harmonics have been generated in the most widely used material in electronics, silicon (Si), at 2.1 μ m driving wavelength [88] and used to disentangle the surface and bulk contributions in Si [136], and topological insulators [221]. It has also been shown that HHG in Si and ZnO can be

controlled and monitored by manipulating the crystal surfaces [133, 44]. For example, spatial shaping of the crystal surface has been used to create HHG beams that carry an orbital angular momentum (OAM) [222] without the need of costly devices for spatial phase control. These generated OAM beams have many applications varying from the manipulation of nanoparticles to quantum cryptography [223].

Microscopic processes have previously been attributed to spectral shifts during HHG. The propagation of the intense driving field has been linked with redshifts in the HHG spectrum in plasmas and gases [75, 76, 77]. This effect is attributed to the delayed emission of HHG from excited states or resonant states [78] or dislocation of molecules [79]. In solids, numerically computed HHG spectra have shown redshifts in the "higher plateaus" due to higher band transitions [36]. In sapphire, intensity-dependent redshifts and blue-shifts were observed in the spectrum of harmonics and attributed to the long and short electron/hole trajectories, respectively [80].

Other works have also quantified the macroscopic propagation effects in the HHG process [14, 83, 84]. Ghimire *et* al. showed theoretically that the efficiency of below band-gap harmonics is modulated mainly by phase-matching conditions, and the above band-gap harmonics are limited by re-absorption in the material itself [82]. Similarly, numerical simulations of the propagation effects in semiconductors have shown that the dephasing of harmonics reduced the HHG signal [224]. Vampa *et* al. experimentally demonstrated HHG in a reflection geometry with the aim to avoid propagation effects [41]. Propagation effects have been shown to impact the HHG process in solids. Nevertheless, some studies report that efficient harmonics are generated from only a few tens of nanometers, [85, 86], whereas the driving field usually propagates within the solid for hundreds of microns. These studies highlight the importance of non-linear driving field propagation and its impact on the HHG process in solids.

Here, we have generated third (H3), fifth (H5), and seventh (H7) order-harmonics in Si and ZnO crystals with a central driving wavelength of 2.123 μ m in the sub-TWcm⁻² intensity regime. We have investigated the impact of the non-linear macroscopic beam propagation on the HHG process in Si and ZnO, particularly to anticipate the role of the non-linear propagation of the driving pulse and the effect on the spectrum of the harmonics. Although the tuning of the driving laser wavelength can allow tuning of the HHG, commercial laser systems traditionally operate with a fixed central laser wavelength, making tuning impossible. Alternatively, the non-linear propagation of intense driving pulses in solids offers a route to control the spectral profile of harmonics. By tailoring the generation scheme in terms of the generating medium, crystal thickness, and laser focusing geometry, we show that it can offer flexible and precise control over the HHG frequency comb while using a fixed driving laser frequency.

This section is structured as follows; the experimental setup to generate HHG and to observe the propagation effects of the driving field is described in section 4.1.2. HHG in Si and ZnO, and their spectral shift are reported in sections 4.2.2 and 4.2.3, respectively. Section 4.2.4 presents a discussion of the experimental results linked with numerical propagation of a focused driving laser field in Si.

4.2.2 Spectral shifting of harmonics in Si

We have generated harmonics in a 300 μ m thick, (100) oriented Si crystal. The spectral and spatial profiles of H3, H5, and H7 harmonics are shown in figure 4.8(a). The z-scans for H3 and H5 are recorded

with steps of 10 μ m as shown in figure 4.8(b). The signal of H7 is feeble and is therefore excluded from the Z-scan study. The yield of H3 and H5 reaches their maximum when the focus position of the driving field is on the back surface of the Si crystal. This is attributed to the absorption of the harmonics generated at the front surface and inside the bulk of the Si crystal. Compared to H3, the efficient generation region of H5 is translated $\simeq 5 \ \mu$ m towards the back surface (see figure 4.8(b)) due to its stronger absorption in the crystal. In parallel, we have measured the spectral of the harmonics generated in the Si crystal as a function of the focus position of the driving laser.



Figure 4.8: Spectral and spatial measurement of high order harmonics in a 300 μ m thick Si crystal. Each harmonic's spectral and spatial profile was measured separately for different acquisition times with corresponding harmonic filters. (a) H5 multiplied by 100 and H7 by 1000 to make them visible in the combined graph. (b) Z-scan measurements of H3 (red dots) and H5 (blue dots) in the Si crystal.

The driving intensity (I_z) at the surface of the crystal is estimated as $I_z=2P/\pi w_z^2$, where w_z is the beam waist at z calculated using hyperbolic function [225] by considering the non-linear refractive indices of crystals with a confocal parameter b=46 μ m and P is the peak power which is 0.05 MW (as shown in figure 4.9(a)). A spectral shift of about 3.4 nm for H3 and 3.9 nm for H5 is observed in Si (see. figure 4.9(a)) as the laser focus is scanned from outside the crystal (at the position -60 μ m) to inside the bulk (at the position of +60 μ m) a spectral blue shift in H3 and H5 is observed. Indeed, when the laser focus is outside the crystal, the spectrum of H3 is centered at 704 nm. In comparison, H5 is centered at 425 nm, corresponding to harmonics of the central driving wavelength in a vacuum. In this configuration, we expect that non-linear propagation effects are minimal. However, when the laser is focused inside the crystal (+60 μ m), the spectrum of H3 shifts to 701 nm, while that of H5 is shifting to 421 nm (see figure 4.9(a)).

We have observed the variation in full-width half maximum (FWHM) of H3 (red dots) and H5 (blue dots) as shown in figure 4.9(b). The behavior of FWHM in H3 decreases as the focus position moves towards the crystal's back surface, reaches a minimum when focus reaches the back surface and further


Figure 4.9: (a) Spectral shifting of the harmonic signal generated in the 300 μ m thick Si crystal with the focus position. The driving intensity evolution (I_z) at the rear face of the crystal with the focus position z (green squares). The spectral shift in H3 (red squares) and spectral shift in H5 (blue squares). (b) Variation of FWHM of harmonics with the propagation distance.

increases as the focus are translated inside the Si crystal. At the same time, the FWHM of H5 increases as the focus position of the driving pulses moves towards the back surface and inside the Si crystal. This variation in FWHM of harmonics is attributed to the non-linear propagation effects of the driving pulses, such as variation in the non-linear refractive index of the medium through strong photoionization of the valence band to the conduction band.

4.2.3 Spectral shifting of harmonics in ZnO

The combined harmonic spectrum (H3, H5, and H7) generated in ZnO and the corresponding spatial profiles are shown in figure 4.10(a). The measured harmonic signal (H3, H5, and H7) as a function of the focus position of the driving beam in the ZnO crystal is shown in figure 4.10(b). The Z-scan of H3 exhibits a double peak structure corresponding to the front and back of the crystal. The signal of H3 is reduced when the focus position is in the center of the crystal. H3 generated before and after the focus point in the bulk contributes destructively due to the phase mismatch of H3 pulses at the exit of the crystal. As a result, the signal of H3 drops when the laser focus position is at the center of the crystal, while the signal of H3 is maximum when the laser is focused near the surfaces. Such behavior has been reported elsewhere [195, 106, 30].

We observe a single peak for H5 and H7, which shows the detected harmonics originate from the rear surface of the crystal. As the harmonic order increases, the region of efficient harmonic generation moves closer to the back surface of the crystal. This is likely due to longer phase-matching conditions for the lower-order harmonics.

Figure 4.11(a) shows the spectral response of H3 for different focus positions. A spectral modulation and splitting of the H3 peak are observed, showing two peaks separated by up to 12 nm when the focus



Figure 4.10: (a) Spectrum of the harmonic emission in ZnO at Z=0 for different acquisition times, with the harmonic beam profiles in insets, (b) Z-scan measurements of H3 (red dots), H5 (blue diamonds) and H7 (violet hexagons) order harmonics.

of the driving field is in the middle of the ZnO crystal. The first peak of H3 begins to decrease, while the second peak of H3 builds up with the translation of the driving focus towards the front surface. The reduction of the intensity of the harmonics when the driving field is focused inside the bulk crystal has been reported elsewhere and attributed to phase mismatch between two harmonic sources, from the front surface and bulk [195, 30], and in sapphire crystals due to phase mismatch in bulk due to geometrical focusing effects [106]. The effective Rayleigh length here is long enough to generate H3 from the surface of the crystal, even when the focal point is near the center of the ZnO crystal (see figure 4.10(b)). This creates a pulse of H3 from the surface that propagates at its group velocity in the crystal. The main driving envelope propagates at a different group velocity and drives H3 generation throughout the bulk of the crystal. The different group velocities of these two H3 pulses can cause overall destructive interference of the H3 signal, as seen in (figure 4.10(b)). Our spectral measurements of H3 highlight this interference effect as a function of the focus position in figure 4.10(b). Such spectral modulations have been attributed to such interference effects elsewhere [80, 226].

The intensity of H3 increases with the spectral blueshift as we move the focus from outside the crystal towards the crystal (from $z = -60 \ \mu \text{m}$ to z = 0, triangle data points of figure 4.11(b)) and reached a maximum at z = 0 which corresponds to the rear surface of the ZnO crystal. When further translating the laser focus inside the crystal ($z = +40 \ \mu \text{m}$), the intensity of H3 decreases. However, the width of the spectral shift increases even more. H3 generated from the front surface (red rectangles) and a back surface (black triangles) of the crystal undergoes blueshifts (8 nm and 12 nm respectively) as shown in figure 4.11(b).

We have also observed the spectral blueshifts in the spectrum of H5 and H7 in ZnO as shown in figure 4.11(b). There were no spectral modulations and splitting as observed for H3. The signals of H5 and H7



Figure 4.11: (a) Spectral shifting and splitting of H3 in ZnO. (b) The evolution of the driving intensity (I_z) at the rear surface of crystal for different focus positions z (green dots). H3 is generated from the front surface (red data points) and at the ZnO crystal's back surface (triangle data points). H3 exhibits a blueshift as the focus of the driving field translates towards the back and front surfaces. The z = 0 corresponds to the front surface for the red data points and the back surface of the crystal for the triangle data points—the spectral shift in H5 (blue diamonds) and spectral shift in H7 (violet diamonds).

have increased when translating the laser focus position towards the rear surface. By further translating the focus of the driving field inside the crystal, the signal of H5 and H7 decreases. The total spectral blueshifts across our measurement range are about 3.9 nm for H5 and H7, as shown in figure 4.11(b).

We have observed the variation in full-width half maximum (FWHM) of H3 (red dots) from the front surface and (black dots) corresponds to back surface as shown in figure 4.12(a). The behavior of FWHM in H3 increases as the focus position moves towards the crystal's front surface, reaches a maximum when focus reaches the front surface, and further decreases as the focus is translated inside the ZnO crystal. Similarly, the FWHM of H3 generated from the back surface increases as the driving pulses' focus position is translated towards the back surface and has a maximum FWHM of 18 nm at the back surface, which rapidly decreases when the focus position is translated out of crystal. Surprisingly, the FWHM of H3 in the center of the crystal is smaller than front and back surfaces, which could be due to the filamentation inside ZnO and defocusing of the driving pulses, which eventually destroy the phase-matching conditions. As a result, the emission of H3 is low and therefore corresponding FWHM of the H3 signal. Whereas the FWHM of H5 (blue diamonds) increases and H7 (violet dots) decreases as the focus position of the driving pulses moves towards the back surface and inside the ZnO crystal as shown in figure 4.12(b). This variation in FWHM of harmonics is attributed to the non-linear propagation effects of the driving pulses, such as variation in the non-linear refractive index of the medium through strong photoionization of the valence band to the conduction band.



Figure 4.12: Variation in FWHM of the spectral profile of harmonics in ZnO with propagation distance (a) H3. (b) H5 and H7.

4.2.4 Modelling and Discussions

To understand the physical processes that give rise to the harmonic spectral shift, we have modeled the propagation of the driving field inside the Si and ZnO crystals. Dr. Auguste Thierry carried out the modeling for the propagation of femtosecond pulses which help us to understand the shifting of spectral profile of harmonics in Si and ZnO. We restrict the calculation to $z >> z_R$, where z is the focus position inside the crystal and z_R is the Rayleigh length. We have used the model described in Ref. [189], with the exception that only the instantaneous Kerr effect is taken into account in our model. The group velocity dispersion and higher-order dispersion are calculated using a Taylor expansion in $\omega - \omega_0$ up to the fifth order of the frequency-dependent wavevector, $k(\omega)=n(\omega)\omega_0/c$. Where ω_0 is the central driving frequency, ω is the shifted frequency, $n(\omega)$ is the index of refraction, and c is the speed of light. We then solve the paraxial wave equation in a cylindrical geometry coupled to the equation describing the electron density evolution. The detailed theoretical description of driving pulse evolution in the solid medium is described as; The laser propagation in semiconductors is modeled by considering the paraxial wave equation in cylindrical geometry.

In the pulse frame, it writes [189, 227]:

$$\frac{\partial \epsilon}{\partial z} = \frac{i}{2k} U^{-1} \left(\frac{\partial}{\partial r^2} + \frac{1}{r} \frac{\partial}{\partial r} \right) \epsilon + i \sum_{m=1}^{\infty} \frac{1}{m!} \left(\frac{\partial^m k}{\partial \omega^m} \right)_{\omega = \omega_0} \left(i \frac{\partial}{\partial \tau} \right)^m \epsilon - \frac{\sigma}{2} (1 + i\omega_0 \tau_c) U^{-1} [\rho \epsilon] + i k_0 n_2 U^{-1} T^2 [|\epsilon|^2 \epsilon] - \frac{E_g}{2} U^{-1} T \frac{W_{PI} \epsilon}{|\epsilon|^2}$$

$$(4.1)$$

where $\epsilon = \epsilon(r, z, \tau)$ is the amplitude of the electric field in the moving frame with the group velocity of wave, $v_g = (\frac{\partial \omega}{\partial k})_{\omega = \omega_0}$, where ω_0 is the central carrier frequency. τ is the retarded time, given as $\tau = t - z/v_g$ and is measured in the moving frame. The first and second terms in the right side of 4.1 are linear in ϵ and responsible for the beam diffraction in the radial direction and the pulse dispersion in the medium. The summation term corresponds to the frequency-dependent wave vector $k(\omega) = \frac{n(\omega)\omega}{c}$ in $\omega - \omega_0$ and obtained from the Taylor expansion up to m=5. The index of refraction $n(\omega)$ is given by the Sellmeier equation of the crystal and $k(\omega_0) \equiv k$. The ρ and σ parts of equation 4.1 related to the plasma refraction and absorption terms while the second last term of equation 4.1 related to the instantaneous Kerr-induced self-focusing effect. Whereas, W_{PI} corresponds to the photoionization-induced absorption of the driving beam, E_g is the bandgap of the medium, U^{-1} is the space-time focusing operator and is given as $U=1+\frac{i}{kv_g}\frac{\partial}{\partial\tau}$ and operator T^2 is the responsible for self-steepening of the pulse in the medium and is related as $T=1+\frac{i}{\omega_0}\frac{\partial}{\partial\tau}$

The cross-section for the inverse bremsstrahlung absorption (σ) is obtained from the Drude model and is given as [228]

$$\sigma = \frac{e^2}{n_0\omega_0\epsilon_0c} \frac{\omega_0\tau_c}{1+\omega_0^2\tau_c^2} \tag{4.2}$$

where τ_c is the electron-hole re-collision time. The photoionization rate is obtained from the Keldysh's formula [32].

If the driving field intensity is higher than the damage threshold of the solid, then irreversible damage occurred in the crystals, and the yield of the harmonics falls abruptly. This damage threshold of the crystal depends on the intensity, repetition rate of the driving field, and bandgap of the medium. At a shorter driving wavelength, this damage often occurred as few photons were required to bridge the gap of the valence band to the conduction band. For longer wavelength, even at higher intensities, the damage does not appear due to more photon absorption required for the electron to jump from the valence band to the conduction band electrons absorption via sub-conduction band transition plays a vital role in the damage of dielectrics on the interaction of femtosecond pulses ranging from near-ultraviolet to visible [229]. The wavelength-dependent laser-induced damage threshold for different bandgap solids has highlighted the dependence of damage threshold on material properties and irradiation parameters [229, 230, 231, 232]. The thermal change can be subsided if the operating frequency is low such as an order of Hz, and heat can be dissipated before the subsequent pulses. In contrast, this heat dissipation is difficult at the MHz driving system.

However, the propagation of the intense driving field can induce the permanent change in the refractive index of the medium with and without the occurrence of structural changes [189]. These changes are attributed to the photoionization, free-carrier absorption, free-carrier interaction, and some self-induced effects that greatly perturb the propagation of the driving field in solids. The evolution of the electron density in the solids under the influence of the driving field can be written as

$$\frac{\partial \rho}{\partial t} = W_{PI}(|\varepsilon|) + \frac{\sigma}{U_i}\rho|\varepsilon|^2 - \frac{\rho}{\tau_r}$$
(4.3)

In equation 4.3, first term corresponds to the photoionization which contributes to the generation of free-electrons from valence to conduction band [233]. $\frac{\sigma}{U_i}\rho|\varepsilon|^2$ describes the avalanche ionization and $\frac{\rho}{\tau_r}$ represents the electron recombination process. Where, ρ density of electron, W_{PI} is ionization rate, σ is the cross section of plasma absorption and τ_r represents the characteristics mean time of recombination of electron.

For the high harmonics process, the intensity of the driving field is always less than the damage threshold. Therefore the process of avalanche ionization can be ignored. Since the recombination time of electrons with the corresponding parent is of the order of a few hundred femtoseconds [234], and harmonics phenomena are generated within the half cycle of the driving field. Therefore, the second and third terms of 4.3 will be ignored when considering the propagation effect of the driving field on the harmonics process. Therefore, the photoionization process is the only process that contributes to the non-linear propagation effects along with the crystal's non-linear properties [189] such as dispersion, diffraction, etc. on harmonics as we have observed in ZnO and Si [81]. Other studies demonstrated the propagation effects on harmonics [14, 82, 83, 84] and offer a way to avoid the propagation effects [41]. In addition, an ab initio computational study reported the impact of the thickness of thin films on the efficiency of harmonic generation which highlighted that efficient harmonics have been generated from the few tens of nanometer [85]. The computational study of ultrafast light propagation effects in graphite thin films of different thicknesses showed that saturable absorption is the key factor for non-linear effects, which enables the deeper penetration of the light pulse in the medium at driving intensity I $\geq 2 \times 10^{11}$ Wcm⁻² [86].

The equation 4.1 is solved in the frequency domain and is given as

$$\frac{\partial \hat{\epsilon}}{\partial z} = \frac{i}{2k(1 + \frac{n_g\omega}{n_0\omega_0})} \left(\frac{\partial}{\partial r^2} + \frac{1}{r}\frac{\partial}{\partial r}\right) \hat{\epsilon} + i\sum_{m=1}^{\infty} \frac{1}{m!} \left(\frac{\partial^m k}{\partial \omega^m}\right)_{\omega=\omega_0} \omega^m \hat{\epsilon}
- \frac{\sigma}{2} \frac{1 + i\omega_0 \tau_c}{1 + \frac{n_g\omega}{n_0\omega_0}} \widehat{\left[\rho\epsilon\right]} + ik_0 n_2 \frac{(1 + \frac{\omega}{\omega_0})^2}{1 + \frac{n_g\omega}{n_0\omega_0}} \widehat{\left[\left|\epsilon\right|^2 \epsilon\right]} - \frac{E_g}{2} \frac{1 + \frac{\omega}{\omega_0}}{1 + \frac{n_g\omega}{n_0\omega_0}} \left[\widehat{\frac{W_{PI}\epsilon}{|\epsilon|^2}}\right]$$
(4.4)

where $\hat{U} = 1 + \frac{\omega}{kv_g} = 1 + \frac{n_g\omega}{n_0\omega_0}$, and $\hat{T} = 1 + \frac{\omega}{\omega_0}$. The symbol $\hat{.}$ represents the time Fourier transform and $n_g = n_0 - \lambda_0 (\frac{dn}{d\lambda})_{\lambda=\lambda_0}$ represents the group index of refraction.

For further details of the wave equation in different forms, see the reference [235]. We have considered crystals as a continuous medium in this modeling and characterize it by its macroscopic properties such as atomic density ρ_{at} , etc. Therefore, the geometry of crystals is excluded from these calculations.

We have propagated the electric field in z-direction by solving the coupled set of equations 4.4 and 4.3 on a grid of $N_r \times N_z$ points with a step size of $\Delta r = \Delta z = 0.1 \mu m$ and the envelope of the pulse is discretized on N_t =1024 points. The linear and non-linear components of ϵ of equation 4.4 are solved separately with the standard split-step method [236] with O(Δz^2) error. The linear of ϵ is solved using the Cranck-Nicholson scheme, and the Laplace operator is discretized by a finite difference method based on a three points centered scheme. The nonlinear part is propagated in z using a fifth-order Runge-Kutta scheme, with Cash-Karp coefficients [237]. This method is also used for solving the equation on the time evolution of the free-electron density equation 4.3.

We have chosen Neumann boundary conditions $\left(\left(\frac{\partial \epsilon}{\partial r}\right)_{r=0} = \left(\frac{\partial \epsilon}{\partial r}\right)_{r=r_m} = 0\right)$, along with the spatial filter to prevent spurious reflection of propagated wave on the external edge of the grid. The spatial filter is defined as:

$$\begin{cases} 1 \quad if \quad r \le r_p \\ 1 - \left(\frac{r - r_p}{r_m - r_p}\right)^4 \quad if \quad r > r_p \end{cases}$$

$$\tag{4.5}$$

The solution of 4.4 is filtered periodically in frequency to dump the higher frequencies, which may

induce if there is a pulse self-steepening effect. Although under our experimental conditions, the self-steepening effect cannot be reached yet, the filter is applied after 50 steps in z as follows:

$$\begin{cases} 1 - \left(\frac{i_t}{N_t/2}\right)^2 & i_t \in [1, N_t/2] \\ 1 - \left(\frac{i_t - 1 - N_t/2}{N_t/2}\right)^2 & i_t \in [N_t/2, N_t] \end{cases}$$
(4.6)

Along with these conditions, the laser pulse is assumed to be a Gaussian, both in time and space. One can also use an experimental pulse envelope for the calculation.

The laser parameters used were an 85 fs pulse duration, $\simeq 7$ mm Gaussian beam diameter focused onto the 300 μ m Si and 200 μ m ZnO crystals to beam waist of 0.83 μ m and 1.45 μ m respectively, by a 3 cm focal length lens. Initially, we have assumed that the conduction band is empty. Crystal properties of Si are taken from [238, 239, 240, 241], as shown in table 4.1 and ZnO [242, 243, 244], as shown in table 4.2. The simulation parameters and laser focusing parameters for Si and ZnO crystals are enlisted in tables 4.1 and 4.2, respectively.

| Si crystal parameters | | | Laser and focusing parameters |
|-----------------------|--|--------------|-------------------------------|
| thickness | $300~\mu{ m m}$ | λ | $2.123 \ \mu \mathrm{m}$ |
| n_0 | 3.449 | au | 85 fs |
| E_{g} | 1.11 eV | Ε | 5 nJ |
| m^* | 0.26 | \mathbf{R} | $7 \mathrm{mm}$ |
| $	au_c$ | $0.33 \mathrm{~fs}$ | f | $3~{ m cm}$ |
| $	au_r$ | 2.5 ns | ω_0 | $0.831 \ \mu m^{(*)}$ |
| $ ho_{at}$ | $4.99 \times 10^{22} \text{ cm}^{-3}$ | z_R | $3.56 \; \mu m^{(*)}$ |
| n_2 | $1.65 \times 10^{-13} \text{ cm}^2/\text{W}$ | z_0 | -60 to +60 μm |

Table 4.1: Si crystal parameters, the laser and focusing parameters for Si crystal. ^(*) inside the crystal by considering the refractive index of Si.

| ZnO crystal parameters | | | Laser and focusing parameters |
|------------------------|--|--------------|-------------------------------|
| thickness | $200~\mu{ m m}$ | λ | $2.123~\mu\mathrm{m}$ |
| n_0 | 1.919 | au | 85 fs |
| E_{q} | $3.3 \ \mathrm{eV}$ | Ε | 5 nJ |
| m^{*} | 0.245 | \mathbf{R} | $7 \mathrm{mm}$ |
| $	au_{c}$ | 4.31 fs | f | $3~{ m cm}$ |
| $	au_r$ | $150 \mathrm{\ ps}$ | ω_0 | $1.493 \ \mu m^{(*)}$ |
| $ ho_{at}$ | $4.148 \times 10^{22} \text{ cm}^{-3}$ | z_R | $6.4 \ \mu m^{(*)}$ |
| n_2 | $5~\times 10^{-15}~{\rm cm^2/W}$ | z_0 | -60 to +60 μm |

Table 4.2: ZnO crystal parameters, the laser and focusing parameters for ZnO crystal. ^(*) inside the crystal by considering the refractive index of ZnO.

Where E_g is the bandgap of materials, τ_c and τ_r are the electron and hole collision and recombination time, m^* is the effective mass of electron, ρ_{at} is the atomic density, n_0 and n_2 are the linear and nonlinear refractive indices of materials, respectively. λ , τ , E are the driving wavelength, pulse duration and energy of the laser pulses, respectively. f, ω_0 and z_R are focal length of lens, beam waist in the medium at focus position and Rayleigh length by considering the refractive indices of the medium, respectively and z_0 is the scanning range. In figure 4.13(a) and 4.13(b), we have reported the spatially integrated output spectrum as a function of focus position for Si and ZnO crystals, respectively. The focus was moved by 60 μ m from each side of the rear surface. The spectral blue shift and absorption are larger in Si than ZnO, the bandgap is small, and the peak intensity inside the crystal is higher for Si. When focusing behind the crystal, the shift rapidly drops to zero in both cases.



Figure 4.13: Evolution of the spatially integrated output spectrum with the focus position of laser pulses. (a) Si. (b) ZnO.

Figures 4.14(a) and 4.14(b) depict the spectral profile for respectively Si and ZnO crystals, and for $z_0 = -60$, 0 and $+60 \ \mu\text{m}$. In Si, the spectrum narrows as the focus is moved inward the crystal, and a red wing appears. The width, measured at half-maximum, is 51.2 nm for $z_0 = -60 \ \mu\text{m}$, 56.5 nm for $z_0 = 0$, and 72.9 nm for $z_0 = +60 \ \mu\text{m}$. The latter value is close to 76.4 nm achieved for a Fourier transform-limited pulse of 85 fs duration. For ZnO, the spectrum full-width at half-maximum remains close to the value for the Fourier transform-limited pulse, and the profile is not modified.



Figure 4.14: Spectral shape of the propagated driving spectrum for the different focus position $z_0=-60$ μ m (blue, when focus position is in air), 0 (red, when focus position is at the front surface), and +60 μ m (black, when focus position is inside the crystals). (a) Si. (b) ZnO.

Figure 4.15(a) quantifies the (absolute) shift of the central driving wavelength for both crystals. The maximum shift, reached inside the crystal, is 54.0 nm for Si and 17.4 nm for ZnO. The spectral blue

shift, as well as the absorption, are larger in Si than for ZnO due to the smaller bandgap that facilitates free carrier generation. When focusing behind the crystal, the shift rapidly drops to zero in both cases as seen in figure 4.15(a).

The macroscopic non-linear propagation of the laser pulses in the crystal induces a spectral blueshift in the driving field. This shifts the central wavelength of any high-order harmonics generated at the rear side of the crystal. Figure 4.15(b) compares the measured spectral shift at z =0 for the different harmonic orders with the expected HHG wavelengths from the numerical propagation of the fundamental pulses. Qualitatively, the model predicts the direction of the spectral shift (blue) for all high harmonics. However, the measured shift for harmonics in Si and ZnO is less shifted as predicted by the modeling values (see figure 4.15(b)). The model considers only the driving pulse and does not include the complex dynamics in the HHG process. Therefore, we do not expect an exact agreement between the HHG central wavelength and the propagated driving wavelength.



Figure 4.15: (a) The spectral shift of the driving wavelength with the focus position in Si (black squares) and ZnO (red dots) for the focus position $z = -60 \ \mu m$ (moving from vacuum towards the back surface) to $+60 \ \mu m$ (inside crystals), respectively. (b) The spectral shift in HHG when the focus of the laser is at z = 0 (backside of crystals), non-shifted (blue diamonds), Si (empty black squares), ZnO (empty black circles), and as per modeling in Si (black squares) and ZnO (empty red circles).

We attribute the HHG spectral shifts to the non-linear propagation of the intense driving field inside the crystal. Photo-ionization drives the generation of free-electrons in the optical transition from the valence band to the conduction band. The increased free carrier density induces a change in time and space-dependent refractive index that up-shifts the driving laser frequency. This is a well-documented effect observed in short-pulse laser ionization in gasses [245, 246, 247]. In turn, this up-shift in driving frequency results in an up-shift of the harmonic frequencies, which we observe as an overall blue-shift in HH wavelengths. Through modeling of the non-linear propagation, we find that increased free-carrier density through photo-ionization is the principal physical mechanism causing these shifts (figure 4.15(a)). This is consistent with our general experimental observations, in that the blue-shift increases when the distance of the driving pulses propagation inside the crystal is greater, resulting in the generation of more free carriers (Figs. 4.9(a) and 4.11(b)). The band-gap of the material is also shown to play a crucial role. Above band-gap harmonics are limited to the last few microns of the material, where spectral control is possible but limited due to re-absorption. Below band-gap harmonics (such as H3 in ZnO) can be created from the surfaces and bulk of the material, allowing not only blue-shifted but strongly modulated spectra (figure 4.11(a)).

4.3 Imaging of the nano-patterns by solid-state harmonics ptychography

The flexibility of the generating wavelength through the HHG process in solids has opened up a new horizon to manipulate the shape of beams. It enables the imaging of nanoscale structure in diffraction. Ptychography lensless coherent diffraction imaging (CDI) technique had enabled the imaging of extended samples in the far-field by using XUV or X-rays illumination sources [248]. Here, we have generated the harmonics in semiconductors (ZnO and Si) and imaged the etched crystal surface from the harmonic emission by adopting ptychography. The spatial beam shaping of harmonics is controlled by etched spiral zone plates (SZP) on the surface of zinc oxide (ZnO) and nano-patterns on silicon (Si) crystals by the focused ion beam (FIB) technique. The reconstruction of diffraction imaging of simulated and experimental measured diffraction patterns in the far-field has been validated with the ptychography in PyNX.Ptycho library. Furthermore, we show that the harmonics diffracted from the SZP can generate the orbital angular momentum (OAM) beams which have many applications ranging from microscopy to quantum information. This study could pave the way to open a new horizon to use solid-state harmonics for plasmonic applications and imaging of magnetic domains from the self-emission of harmonics in magnetic materials.

4.3.1 Introduction

The observation of HHG in solids [33] has opened up a new horizon towards its applications [249] particularly spatial beam shaping and imaging of surfaces [222]. The monitoring and controlling of solidstate HHG can be done by manipulating the surface of solids [44, 133, 222] which gives it an advantage over the gas-based HHG. The spatial profile of the generated harmonics in ZnO manipulated by etching different SZP on the surface of ZnO crystal to generate and image OAM beams in the focal plane [222]. Conventionally, lensless X-ray microscopy or coherent diffraction imaging (CDI) is adopted to acquire the atomic level resolution of an object in diffraction. Recently, CDI has employed for femtosecond single-shot nanoscale imaging [250, 251, 252] and for broadband imaging [253] purpose.

For wide-field imaging, the conventional CDI is unable to scan the non-isolated samples or objects. For this, an extension of CDI, named ptychography, has been adopted. In the ptychography multiple diffraction patterns recorded [254, 255] through raster/spiral scanning of sample with the probe beam. The recorded diffraction patterns should be well overlapped (about 70 to 75%). The ptychography enables imaging of extended objects and opens a new horizon for applications of diffractive imaging [256, 257]. Several iterative phase retrieval algorithm introduced to reconstruction object modulus and phase [258, 259, 260] along with the ptpy [261], SHARP [262] and PyNX.Ptycho [263, 264, 265] which are several ptychograpical solvers. Ptychography often used to characterize the x-ray phase vortices [266], far-field diffraction imaging of objects ranging from periodic nanopatterns [267] to biological samples [248, 268]. So far, ptychography has been adopted to reconstruct the image either by X-ray or XUV probe beam generated through gas-based HHG. Here, the first time we have employed the concept of single solid-state HHG as a probe and object to make the realization of robust and compact setup for the reconstruction of nano-structures and nano-patterns.

We have generated the efficient fifth-order harmonic (H5) in ZnO and Si crystals at 2.123 μ m driving wavelength at 0.29 TWcm⁻². The spatial profile of H5 is measured with the UV-enhanced PCO-CCD. We have etched the different nano-patterns such as single-mode spiral zone plate (SMSZP), double-mode spiral zone plate (DMSZP), triple-mode spiral zone plate (TMSZP), off-axis spiral zone plate (OASZP), and single slit on the surface of ZnO crystal by FIB. These nano-structures contribute to the spatial beam shaping of the harmonics. We have recorded the diffraction patterns of these nano-structures by the H5 (≈ 422 nm) with an objective microscope (numerical aperture= 0.65) coupled with the corresponding harmonic filters (HF) and the UV-enhanced PCO-CCD camera. The images of the intensity distribution of OAM beams generated by the SMSZP is measured by the H5 harmonic. The reconstruction of the diffraction imaging by the lensless diffraction imaging technique called ptychography of these OAM beams are underway at the moment. Although, we have shown the reconstructed simulated images by using ptychography.

In the second experiment, nano-patterns were etched on the surface of 5 μ m thick Si crystal by FIB and generated the efficient H5 at the etched nano-patterns surface. These nano-structures and nano-patterns are fabricated by Dr. Willem Boutu, CEA-Saclay, France. The diffraction pattern of the corresponding nano-patterns is recorded at each point of the spiral scan. Finally, we have reconstructed the diffraction imaging of etched nano-patterns from simulation and experimental diffraction patterns by employing ptychography in PyNX.Ptycho library.

4.3.2 Focused ion beam etching of crystals

The nano-patterns and nano-structures are engraved on the ZnO and Si crystal by FIB. The different nano-structures and nano-patterns on the surface of Si crystal are etched by a focus ion beam (FIB) by Dr. Willem Boutu from CEA-Saclay, France. We uploaded the design of the structure as a image on the FIB program. The value of each pixel defines the ion (Ga) dose received by the sample at this spot, with 255 being the dose defined by the parameters and lower values lead to a part of that (i.e., a pixel with a value of 124 would receive a dose of Defined dose $\times 124/255$). To set the dose, we defined: the ion beam current (50 pA for the 1st test), the time spent on one given spot (5ms once + 50 \times 0.1ms), and the step size (because there is an overlap between successive spots) (here 30nm). The matter removes by the ion beam does not fully go in the chamber, but part of it goes back on the surface behind the beam (the deeper you pattern, the larger this part), standing long on each spot will not lead to a good structure. Therefore, it is better to use a short dwell time and pattern the full object several times. We have etched



Figure 4.16: Geometry of FIB

the SZP's sample on ZnO surface in dimension of $10 \times 10 \ \mu$ m while nano-patterns are etched on the Si surface having dimension of $13 \times 18 \ \mu$ m (length × width). For the experiment we have successfully reconstructed the Ptychography images of the nano-patterns etched on 5 μ m thick Si with a depth of 50 nm as shown in figure 4.22(a).

4.3.3 Reconstruction of simulation data using PyNX library

Several parameters are needed to simulate in the far-field diffraction patterns of objects and reconstruct the phase from simulated or experimental diffraction figures, such as the size of the simulated sample in pixels, the adequate pixel size of the detector, the wavelength of the harmonic beam, the distance of detector from a sample, the size of a pixel in the object plane, and the increment step of the scan and pixels as well as the diameter of the probe. All these requirements have been defined in the Python code. Second, information related to the object, probe, scan type (raster or spiral) and the type of beam, the noise, the pixel size of the beam, and the number of photons is mandatory. This information is then used in the simulation class, which will then simulate the various diffraction patterns. For the initiation of reconstruction, the set of far-field diffraction images is of the same matrix size as the simulated data, and we considered the probe size in pixels. The diffraction patterns are simulated from the probe and initial object, which eventually generate the Ptychography data. Then various mathematical algorithms are employed for the reconstruction from the ptychography data.

Finally, in our simulation, we have employed various mathematical algorithms such as difference map (DM) [255, 269], alternating projection (AP) [270], and maximum likelihood refinement (MLR) [271] are executed for the reconstruction of diffraction images in the ePIE [260] in the PyNX.Ptycho [265, 264] ptychograpical solvers library. In the ePIE algorithm, initial guesses for the object and probe are mandatory. Therefore, the object is initially considered a free-space and probe waveform, respectively, updated at each scan point. The movement of the probe performed by the Python script during the simulation in raster scanning with a step size of 500 nm. Each point corresponds to a different diffraction pattern. The random sequence of diffraction pattern taken into account, by starting with the initial diffraction pattern and the product of the current object guess with the shifted probe guess yields the exit-wave guess. In the next step, the modulus of the Fourier transform of the exit-wave replaced the square root of the random sequence diffraction pattern. Consequently, the updated exit wave was obtained through an inverse Fourier transform. The updated probe and object guesses were obtained from the two updated functions as reported [260]. This update process of probe and object guesses recommence for the diffraction pattern of each scan point to complete an ePIE iteration. Thus ePIE enables the reconstruction of both the wavefront of the object and probe simultaneously.

Initially, we have used SMSZP and generates the simulated diffraction pattern at 50 μ m (figure 4.17(a)) distance to execute the reconstruction of the phase and amplitude of an object. A raster/spiral scan with a step of 730 nm is considered to generate the scan points with an overlap of more than 75% with a total of 900 scans points. The simulated diffraction patterns at some distinct scan points at a wavelength of 422 nm are shown in figure 4.17(b). We have introduced an offset of 10 % of the step size to circumvent the periodic artifacts. We have introduced the Poisson noise distribution, and with this arrangement, far-field diffraction patterns of SMSZP simulated with a total photon count of 1 × e⁸. The Fresnel number (N) can be calculated as $N = a^2/L\lambda$, a is the radius of focused beam, λ is the harmonics wavelength and L is the distance of imaging setup from the focus position. The N at 50 μ m distance from focus position is found to be 0.097 which shows that we are in far-field regime. The reconstructed modulus of object and phase is obtained after 15 iterations with the numerical error calculated between two successive iterations LLKn(p) is 2.340 at 50 μ m far-field distance.

In the next step, we have introduced a nano-patterns having dimension of $15 \times 10 \ \mu$ m (length × width) as shown in figure 4.22(a) to reconstruct the object modulus and phase, and probe modulus and phase in simulation. The reconstructed object modulus and phase, and probe modulus and phase is shown in figures 4.18(a) after 10 iterations with the numerical error calculated between two successive iterations LLKn(p) is 0.40 for 4.18(a). Figure 4.18(b) shows the simulated diffraction pattern for some distinct scan points of nano-patterns. In addition to this, we have used another nanocircuit of different etching structure to confirm the ptychography simulation library. The reconstructed object and probe, modulus and phase is shown in figure 4.19(a). Figure 4.19(b), shows the far-field diffraction pattern at several distinct scan points. The calculated Fresnel number N is found to be less than 1 (≈ 0.097) for the given conditions for all these nano-patterns and nanocircuits.

In the next step, we have introduced a nano-patterns having dimension of $15 \times 10 \ \mu m$ (length \times width) as shown in figure 4.22(a) to reconstruct the object modulus and phase, and probe modulus and phase in simulation. The reconstructed object modulus and phase, and probe modulus and phase is shown in figure 4.20(a) after 10 iterations with the numerical error calculated between two successive iterations (LLKn(p)) is 12.5 for 4.20(a). Figure 4.20(b), shows the simulated diffraction pattern for some distinct scan points of nano-patterns.

Apart from the simulation reconstruction, we have obtained the diffraction patterns of all the nanopatterns and OAM beams by probing the self-emission of H5 harmonics from the etched surfaces. We have successfully implemented the reconstruction of the SZP images and nanostructure images etched on the Si and ZnO by using the PyNX library by using the combination of alternating projection and



Figure 4.17: (a) The simulated ptychography reconstruction of SMSZP at a far-field. The calculated Fresnel number N is found to be less than 1 (≈ 0.097) for the given conditions. The image has reconstructed object amplitude, phase, and probe amplitude and phase. (b) Far-field diffraction pattern at some distinct scan points.



Figure 4.18: (a) The simulated ptychography reconstruction of nano-patterns diffracted images at farfield. The image has reconstructed object amplitude, phase, and probe amplitude and phase. (b) Far-field diffraction pattern at six distinct scan points.

DM/o # 2, LLKn(p)= 0.354



Figure 4.19: (a) The simulated ptychography reconstruction of nano-patterns diffracted images at farfield. The image has reconstructed object amplitude, phase, and probe amplitude and phase. (b) Far-field diffraction pattern at several distinct scan points.



Figure 4.20: (a) The simulated ptychography reconstruction of nano-patterns diffracted images at farfield. The image has reconstructed object amplitude, phase, and probe amplitude and phase. (b) Far-field diffraction pattern at various distinct scan points.

difference map algorithms. For further detail of the experimentally data reconstruction see the subsection 4.3.4.

4.3.4 Experimental setup for solid-state harmonics ptychography

A schematic representation of the experimental setup for the solid-state harmonics based ptychography is shown in figure 4.21. The 85 fs pulses of central wavelength 2.123 μ m, operating at 19.6 MHz, are focused near the exit etched surfaced of crystals by 3 cm focal length convex lens to a size of $\approx 2.5 \ \mu$ m with the peak intensity of $\approx 0.29 \ \text{TWcm}^{-2}$. At this driving intensity, harmonics up to ninth order are observed in the air. The corresponding band-pass filter selects H5. Therefore, H5 (422 nm) is employed as a probe pulse for the diffraction imaging of nano-structures and nano-patterns due to its sufficient photon flux and sample fabrication characteristics.



Figure 4.21: (a) The schematic of the experimental setup for solid-state harmonic generation-based ptychography. The H5 generated in the 5 μ m thick Si crystal at 0.29 TWcm⁻² of 85 fs, 19 MHz of central wavelength 2.123 μ m employed as a probe beam to image the etched surfaces of crystals. The spiral scan points result in a series of sufficient overlapped scan images, which eventually enables the reconstruction of the object. HWP: half-wave plate, L: lens, T: telescope, HF: harmonic filter, OL: Objective lens (N.A.= 0.65), CCD: charge-coupled device.

One of the images of nano-patterns etched on the surface of Si crystals is shown in figure 4.22(a). Image of nano-patterns etched on the surface of 5 μ m thick Si crystal patterned with FIB with a depth of around 50 nm. The sample size is 13x18 μ m². The etched sample is mounted on the motorized XYZ translation stage to translate the sample in the spiral scan pattern to generate the diffraction patterns at each scan point. The electronic motorized controlled Labview program carries out the spiral scan of nano-structures and nano-patterns with sufficient overlap of (70-75)%. Dr. Maria Kholodtsova wrote the Labview program from CEA-Saclay, France. The zero-order diffraction of nano-patterns and nano-patterns through H5 (\approx 422 nm) is measured by employing an objective lens (numerical aperture= 0.65) which coupled with the harmonic filter (HF) and UV-enhanced PCO-CCD camera.

4.3.5 Reconstruction of the experimental data



Figure 4.22: Experimentally ptychography reconstruction of the nano-patterns by solid-state harmonics (422 nm). (a) Image of nano-patterns etched on the surface of 5 μ m thick Si crystal patterned with FIB with a depth of ≈ 50 nm. The sample size is 13 \times 18 μ m². (b) Using Alternative Projection (AP) and Difference Map (DM) algorithms for n=185 iterations in six cycles. One cycle of 30 iterations of the AP algorithm followed by one iteration of DM and artificially increasing the camera pixel size and sample to detector distance by a factor of 15 at a fixed probe diameter of 1.7 μ m. (c) Using AP and DM algorithms for n=185 iterations in six cycles of the AP algorithm followed by one iteration of DM and artificially increasing the camera pixel size and sample to detector distance by a factor of 15 at a fixed probe diameter of 1.7 μ m. (c) Using AP and DM algorithms for n=185 iterations in six cycles. One cycle of 30 iterations of the AP algorithm followed by one iteration of DM, no change in camera pixel, and fixed probe diameter of 2.5 μ m. (d) Using only AP algorithms for n=200 iterations.



Figure 4.23: Experimentally ptychography reconstruction of the nano-patterns by solid-state harmonics (422 nm) using AP and DM algorithms for six cycles. One cycle consists of 30 iterations of the AP algorithm followed by one iteration of DM without an update in probe plus 20 iterations with the AP algorithm by updating the probe. (a) Modulus of the reconstructed object. (b) The phase of the reconstructed object.

Once the diffraction figures have been processed. It is desired to reconstruct the phase and modulus of of the samples. To reconstruct the modulus and phase of the objects, we have used the PyNX library [263, 264]. We have used Alternative Projection (AP) and Difference Map (DM) algorithms to for the reconstruction of images in the PyNX library. The best reconstruction of ptychography of nano-patterns is obtained when the combination of AP and DM algorithms is used in a cycle. Total six cycles of 30 iterations of the AP algorithm followed by one iteration of the DM algorithm have been executed to fix the probe. The fixed probe diameter of 1.7 μ m is used, and artificially increasing the camera pixel size and sample to detector distance by a factor of 15. The reconstructed image is shown in figure 4.22(b). At a probe diameter of 2.5 μ m without the artificially change in camera pixels, the reconstruction of the image is shown in figure 4.22(c) by using AP and DM algorithms for n=185 iterations. We have reconstructed the image by only using the AP algorithm at 200 iterations as shown in figure 4.22(d) at a fixed probe diameter of 2.5 μ m without manipulating the camera pixels and sample to camera distance. The sharpness of the reconstructed image is a bit blurred.

We have also reconstructed the image of nano-patterns through ptychography by using AP and DM algorithms for six cycles. One cycle consists of 30 iterations of the AP algorithm followed by one iteration of DM without an update in probe plus 20 iterations with the AP algorithm by updating the probe. The Modulus of the reconstructed object is shown in figure 4.23(a) and the phase of the reconstructed object is shown in figure 4.23(b).

Finally, we have reconstructed the ptychography imaging of spiral zone plates (SZP) which were etched on the ZnO surface. The diameter of SZP is 10 μ m and etched depth ≈ 205 nm. The amplitude of the reconstructed images for loop4 and loop6 is shown in figure 4.24(a-b) and the reconstructed phase of the SZP is shown in figure 4.24(c-d), respectively. Each loop consists of 30 iterations of the AP algorithm and 2 iterations of DM algorithms. The phase and amplitude of the etched SZP on ZnO are successfully reconstructed through the self-emission of harmonics (H5). This has enabled a robust method of imaging of non-isolated nano-objects in far-field diffraction by solid-state ptychography.



Figure 4.24: Experimentally ptychography reconstruction of the spiral zone plate (SZP) by solid-state harmonics (422 nm) using AP and DM algorithms for six cycles. One loop consists of 30 iterations of the AP algorithm followed by two iteration of DM by updating the probe. Amplitude of the reconstructed images for loop4 and loop6 (a-b). The phase of the reconstructed images for loop 4 and loop6 (c-d). The color bar of the images are twilight.

Indeed, we notice that the signal-to-noise ratio in the simulations is higher than the signal-to-noise ratio of the experimental data. In addition, the number of iterations and the choice of the reconstruction algorithm (AP, ML, DM) have a significant impact on the reconstruction when the corrective factor M is integrated into the script of Python. It is assumed that the AP would allow the sample phase to be reconstructed because the reconstruction error converges to a minimum value. We have tested different reconstruction algorithms, such as the AP, DM reconstruction algorithm for different iterations and enables us to reconstruct the object through high resolution up to few nm. Our results has open up a new horizon for the imaging of the nano-patterns or nano-structures through a table-top setup by using solid-state HHG which can enable the real time observations of ultrafast phenomena in the electric circuits.

4.4 Orbital angular momentum harmonics beam generation from semiconductor

The interaction of orbital angular momentum beams (OAM) with the matter is intensively studied for a wide range of applications [223]. There have been extensive efforts theoretically as well as experimentally to generate such vortex beams from the latest light sources [272, 273, 274]. Recently, it has been confirmed the transfer of OAM beams from laser to the harmonic generations [275, 276]. There are generally two approaches to generate OAM harmonics beams in solids [222]: 1) the driving laser beam carrying the OAM beams and focused on the solids, 2) A spiral zone plate (SZP) etched on the surface of the solids which can act as diffractive optics. We have adopted the second approach to generate an OAM harmonics beam. We have etched the binary SZP on the surface of 200 μ m thick ZnO crystal by focused ion beam (FIB). The dimension of the SZP is 10 × 10 μ m with an etch depth of \approx 200 nm. The etched SZP is shown in the inset of figure 4.25.



Figure 4.25: Schematic illustration of the experimental setup to generate orbital angular momentum (OAM) harmonics beam in ZnO. Inset shows the etched binary SZP (diameter= 10 μ m) on the surface of the ZnO crystal. P: polarizer, L: lens, T: telescope, HF: harmonic filters OL: Objective lens (N.A.= 0.65), CCD: charge-coupled device, SZP: Spiral zone plate.

The schematic illustration of the experimental setup to generate OAM harmonics beams is shown in figure 4.25. The 85 fs, 19 MHz of central wavelength 2.123 μ m is used to derive the SZP etched ZnO surface. Laser pulses are focused on the rear side of ZnO crystals to an estimated intensity of ≈ 0.29 TWcm⁻² by 3 cm focal length. The generated OAM harmonics beam of H5 (422 nm) is filtered with a harmonic filter (HF) and imaged by using an objective lens of numerical aperture =0.65 which is coupled with the PCO-CCD camera.

The intensity distribution of OAM harmonics beams generated by the binary single-mode spiral zone plate (SMSZP) with the emission of H5 (422 nm) at different distances (60 μ m, 80 μ m, 100 μ m, 200



Figure 4.26: The intensity distribution of the orbital angular momentum (OAM) harmonic beam generated by the single-mode spiral zone plate (SMSZP) at various distances from the focus plane. (a) 60 μ m, (b) 80 μ m, (c) 100 μ m, (d) 200 μ m.



Figure 4.27: (a) The FIB engraved structures on the ZnO surface (i) Double-mode spiral zone plate (DMSZP), (ii) Triple-mode spiral zone plate (TMSZP), (iii) Off-axis spiral zone plate (OASZP), (iv) Single slit. (b) The intensity distributions of OAM harmonics beams generated from the etched surface of ZnO at the focal plane (i) DMSZP, (ii) TMSZP, (iii) OASZP, (iv) H5 diffraction pattern from the single slit.

 μ m) from the focus plane is shown in figure 4.26. The intensity distribution of the H5 diffraction pattern disperse, and the size of the diffraction image increases with the translation of imaging setup away from the focus plane of single-mode SZP (figure 4.26). We have observed the OAM of topological charge (l = 1) to the H3 and H7 harmonics, but the annular shape of the OAM has aberrations and deformations. The imperfections of the annular shapes of OAM imprinted into the H3 and H7 harmonics could be attributed to the fabrication faults and aberrations in the driving pulses.

We have also etched different nano-objects on the ZnO such as double-mode spiral zone plate (DM-SZP), triple-mode spiral zone plate (TMSZP), off-axis spiral zone plate (OASZP), and single slit as shown in figure 4.27(a). The intensity distribution of OAM harmonics beams from these SZP's near the focus plane is imaged by using imaging setup as shown in figures 4.27(b) (i-iii) to validate the OAM of topological charge l = 2 from DMSZP (see figure 4.27(b)(i)) and l = 3 from TMSZP as shown in figure 4.27(b)(ii). The intensity distribution near the focal plane of DMSZP and TMSZP is not super sharp and contrasted one . The imperfections and distortion of diffraction imaging by H5 owe to be the illumination of limited zones of SZP's and fabrication faults. The other reasons for imperfect imaging of higher mode SZP are the defaults of fabrication (etching width and depth, etc.), residual aberrations, and misalignment of the driving pulses. The generated H5 harmonics has a limited size $\approx 2.5 \ \mu$ m, which only illuminates the central regions of the SZP's. To measure the complete image of the diffraction pattern of these SZP's, one can adopt the lens-less coherent diffraction imaging technique ptychography [259, 260, 277], as we have adopted for the nano-patterns (see section 4.3).

The intensity distribution of H5 for the binary OASZP at the focal plane is imaged as shown in figure 4.27(b)(iii). The contrast of mode quality for the OASZP is much better than the mode quality of DMSZP and TMSZP. This improved contrast of mode quality for the OASZP is attributed to more illumination of density zones at the focal plane by the H5 beams than the zones illumination of DMSZP and TMSZP. The first-order diffraction of binary and non-binary OASZP at the blazed grating shows more diffraction of photons in the first-order for the non-binary OASZP [222]. The diffraction patterns generated by the OASZP have been employed to measure the topological charge [222] with the interferometric measurements.

Finally, we have imaged the intensity distribution of H5 from 1 μ m thick single slit and managed to record the diffraction order up to the fourth-order as shown in figure 4.27(b)(iv). The diffraction of light through silt has many applications, such as excitation of the surface plasmon-polaritons in graphene [278] and imaging of surface plasmon polariton fields [279]. Due to the bugs in code and intensity distribution issues in the recorded diffraction figures, the reconstruction of these patterns are underway with the improvement in data and code. The present study suggests that further work needs to be done for the reconstruction of SZP's in terms of fluency, size and depth of etched crystals, and calibration of imaging setup to materialize the ptychography for nano-patterns and nano-structures from self-emission of harmonics.

4.5 Conclusion

In this chapter, initially, we have generated below and above bandgap harmonics (high harmonics) in semiconductors such as ZnO, Si and STO at 2.123 μ m wavelength at an estimated intensity ≈ 0.29 TWcm⁻². We have measured the spatial, spectral profile of harmonics in these crystal and demonstrated the polarization dependence of harmonics. The polarization response of harmonics in Si and STO revealed strong four-fold anisotropy. Interestingly, relative higher signal of H5 is observed in STO than H3 at the circular polarization (ellipticity =±1). We have observed front and back surface emission due to phase matching of the H3 in ZnO, while back surface emission due to re-absorption of over bandgap harmonics in Si and ZnO. In ZnO, the generation of the H3 is efficient from the crystal's front and rear surfaces, and a modulated spectrum is observed when focusing at the center of the crystal. We attribute this spectral modulation to the group-velocity mismatch of surface and driven part of H3 pulses during propagation, indicating the interference pattern of the temporal separated H3 pulses. The isotropic polarization response of harmonics in ZnO, highlighted the atomic-like response due to the low driving intensity. This could pave the way towards circular polarized harmonics for chirality measurements and to explore the magnetic domains of ferromagnetic material.

Furthermore, we have explored the non-linear propagation effects of the driving pulses on the harmonics in Si and ZnO. We have demonstrated the changes in the emitted harmonic spectrum to drive laser focal position in the crystals. We observed that all the harmonic peaks are blueshifted as the focus position is translated into the crystals. Due to the dependence on the focal position and hence the propagation length in the crystal, we attribute the observed blueshifts to non-linear propagation effects of the driving laser. This is supported by calculations of the non-linear propagation of the driving field in Si and ZnO, which exhibits a blueshift of the central frequency attributed to the photoionization of valence band electrons. Even in samples that strongly absorb the HHG spectrum, we show that since the emitted harmonics come from a small region at the end of the crystal, modulation of the driving pulse before the point of generation can be used to control the HHG spectrum. For materials with bandgaps higher than the harmonic photon energy, further spectrum control can be obtained from front and back surface emission, as we have demonstrated with the third-harmonic in ZnO. This study reveals the fine control of the harmonic emission spectrum through macroscopic non-linear effects in the bulk crystal alone. This technique could be used for tailoring frequencies for ultrafast spectroscopic techniques or spectral shaping for ultrashort pulse generation.

Furthermore, we have imaged the non-isolated nano-patterns etched on the Si crystal surface and SZP on ZnO surface from the self-emission of harmonics by adopting the lensless imaging technique ptychography. We have successfully reconstructed the modulus and phase of the nano-patterns from the self-emission of harmonics by using the PyNX library. In addition, we have also implemented the simulation reconstruction of various nanostructures and nano-patterns by ptychography. So far, ptychography has been adopted to reconstruct the image either by X-ray or XUV probe beam generated through gas-based HHG. For the first time to our knowledge, we have employed the concept of a single solid-state harmonics as a probe and object to realize a robust and compact setup for the reconstruction of nano-structures and nano-patterns. Our results could pave the way towards a new horizon for diffractive imaging applications through solid-state ptychography and imaging of magnetic domains of ferromagnetic materials by self-generated harmonics emission.

Finally, the spatial beam shaping of harmonics has been controlled by etching the SZP's on the surface of ZnO. The intensity distribution of vortex beams of H5 at 2.1 μ m driving wavelength has been imaged to show that harmonics photons are carrying an OAM of topological charges l = 1, 2 and 3. Our investigation shows that the spatial beam shaping in terms of OAM can be materialized in solid-state harmonics. We show that the shaping of the material surface can modulate the intensity distribution of harmonics which can produce focused optical vortices up to nanometers scale.

Chapter 5

Conclusions and Perspectives

5.1 Conclusions

In the framework of this thesis, we have generated low and high-order harmonics in the semiconductors, thin films, and wide bandgap dielectrics of bandgap ranging from 1.11 eV to 10 eV under different driving wavelengths. The generation process of harmonics has been explored with laser properties such as the different driving wavelengths (800 nm, 2.123 μ m and 3 μ m), intensity, polarization, and ellipticity of the driving fields. We have also measured the macroscopic propagation effects and found that they can influence the spectral content of the high harmonics.

In chapter 3, SHG and THG are demonstrated in pristine MgO and Cr: MgO crystals with a NIR driving field operating at 800 nm, 40 fs, operating at a 1 kHz repetition rate. On rotating the crystal relative to the driving field polarization, an anisotropic and chaotic behavior of SHG efficiency has been observed. The SHG signal was isotropic and symmetrical, attributed to the complex interplay between surface and non-linear effects for SHG in MgO. The isotropic emission of SHG is attributed to the minimal angular dependence of the Cr valence band, which we identify as the most probable initial energy state of the multi-photon NIR absorption process through our DFT calculations. A four-fold anisotropic response of THG is observed in pure MgO and low doped Cr: MgO. We showed that THG in MgO displays a non-perturbative response which is supported by the intensity dependence and driving field ellipticity studies. Furthermore, we showed that with the introduction of new energy levels through doping, this non-perturbative behavior of THG reverts to the more common perturbative behavior. We attributed this to the blocking the non-perturbative pathways and the increase in linear absorption caused by the dopant energy levels. This work has shown that the electronic structure can be shaped to tailor the non-linear optical response in terms of efficiency and angular dependence by introducing dopants into simple crystals. Furthermore, we have generated H3 and H5 in MgO and Cr: MgO crystals at 3 μ m MIR driving wavelength. The non-linear response of crystals is mapped through the orientation measurements of harmonics, which showed the similar pattern of H3 and H5 as observed at 800 nm.

We have investigated the non-linear propagation effects of the ultrafast intense NIR driving field in wide bandgap amorphous and crystalline solids. We have explored spectral, polarization and ellipticity dependence of SHG and THG in these amorphous and crystalline solids. Compared with the transmission geometry, the low-order harmonics have been generated in reflection geometry to avoid the non-linear propagation effects in FS, SiO₂, and Sapphire crystals. We attributed that the strong photoionization, free-carrier density, and self-phase modulation induce the spectral shifts and broadening of the driving field spectrum. This work shows the sensitivity to control the spectral profile of harmonics by manipulating the driving field, highlighting the possibility of new tailor solid-state harmonics sources for optical diagnostics.

Furthermore, the process of low-order harmonics in single versus polycrystal Gallium Oxide (Ga₂O₃) at 800 nm and 3 μ m driving wavelength have been explored. The crystal symmetry has been mapped through the orientation dependence of harmonics. A strong signal of SH and TH have been observed at the elliptical and circular polarization of the driving laser pulses (at 800 nm) in (010) polycrystal Ga₂O₃. The observation of harmonics at the elliptical or circular polarization in (010) polycrystal Ga₂O₃ is fascinating. It offers the possibility of the generation of elliptical or circular light sources, which can apply to measure a molecule's chirality or magnetic domains of magnetic materials.

Finally, SHG and THG in thin films have been explored at 800 nm driving wavelength. We have disentangled the harmonics, particularly THG, from the thin films and substrate in reflection. The THG has more isotropic contributions in Sapphire substrate, while in the thin films response of THG is highly anisotropic. This is attributed to the different symmetry responses of thin films. Harmonic generation from thin films could open a new horizon and offered a route to beat the non-linear propagation effects and absorption limit of above bandgap harmonics due to the controlled growing thickness. However, the free-standing thin films of nanometers, like AlN and AlGaN, are impossible to use practically, and disentangling them from the bulk contribution is essential. This study highlights the potential to generate higher-order harmonics from thin films deposited on the substrate and possibly new DUV secondary sources.

In chapter 4, Below and above bandgap harmonics in silicon (Si), zinc oxide (ZnO), and STO crystals have been explored at 2.123 μ m driving wavelength. We have studied macroscopic effects (non-linear propagation effects) on low and high harmonics by comparing two materials with distinct optical properties, silicon (Si) and zinc oxide (ZnO). By scanning the focal position of 85 fs, 2.123 μ m wavelength pulses inside the crystals (Z-scan), we reveal spectral shifts in the generated harmonics. We interpret the overall blueshift of the emitted harmonic spectrum as an imprint of the driving field spectral modulation occurring during the propagation inside the crystal. This is supported with numerical simulations. This study demonstrates that through manipulation of the fundamental driving field through non-linear propagation effects, precise control of the emitted harmonics spectrum in solids can be realized. This method could offer a robust way to tailor HHG spectra for a range of spectroscopic applications.

In the second of chapter 4, we have imaged the isolated nano-patterns etched on the Si crystal surface from the self-emission of harmonics by adopting lensless imaging technique ptychography. We have successfully reconstructed the modulus and phase of the nano-patterns from the self-emission of harmonics by using the PyNX library. We have also implemented the simulation reconstruction of various nano-structures and nano-patterns by ptychography. This study could pave the way to open a new horizon to use solid-state harmonics for plasmonic applications and imaging of magnetic domains

from the self-emission of harmonics in magnetic materials. Finally, the spatial beam shaping of harmonics have been controlled by etching the SZP's on the surface of ZnO. Our investigation shows that the spatial beam shaping in terms of OAM can be materialized in solid-state harmonics. We show that the shaping of the material surface can modulate the intensity distribution of harmonics which can produce focused optical vortices.

In addition, I have also participated in other experiments during my Ph.D particularly in the aligning, executing experiments and helping other graduate students to get the experimental data. In the first experiment, we have presented a systematic study of the dependence of the aberrations of the high harmonics (HHS) on the aberrations of the driving infrared (IR) laser. We showed that we could control the astigmatism of the HHS by changing the astigmatism of the driving IR laser while keeping the high harmonic (HH) photon number controlled. We show that we can control the astigmatism of the HHS by changing the astigmatism of the driving IR laser without compromising the HH generation efficiency with a WF quality from $\lambda/8$ to $\lambda/13.3$. This allows us to shape the XUV beam without changing any XUV optical element. [129].

In the second experiment, we have studied Lithium Fluoride (LiF) crystals, traditionally used for X-ray, as a detector for a tabletop XUV source from HHG in gases. We have successfully recorded a scan of the focal plane of a Fresnel Zone Plate with a high dynamic range. With this study, we showed that lithium fluoride (LiF) could be used as a detector for HHG XUV, with a high potential to do near field imaging of complex objects such as the focus of structured light [130].

Finally, we have presented the the results of experiments about the femtosecond time-resolved imaging system based on the transmission of extreme ultra-violet (XUV) light from high harmonic generation in Xenon (Xe). We used the much brighter gas-phase harmonics to achieve single-shot pump-probe data of a solid as it transforms to a plasma. This route could offer a unique insight into understanding the time-dependent dynamics of the solid-state HHG process itself, as a probe beam can measure the electronic transitions occurring during the ultrafast time.

5.2 Achievements

The main achievements of this thesis are presented hereunder;

• Surface-second-harmonic generation (SSHG) observed in MgO and Cr: MgO at 800 nm driving wavelength. The impact of doping concentration on the yield and orientation dependence of SHG has been demonstrated. The process of SSHG has been aided with the DFT calculation at VOXEL laboratory, IST, Lisbon [26].

• Demonstration of perturbative and non-perturbative THG in MgO and Cr: MgO at 800 nm driving wavelength highlights the inferring of the information through THG that have shown high-order harmonics. This has been achieved at VOXEL laboratory, IST, Lisbon (Ready to submit in Optics Express).

• We have successfully demonstrated the process of SHG and THG in amorphous and crystalline solids such as FS, SiO_2 , and Sa at 800 nm driving wavelength. In addition, polarization and ellipticity response of harmonics have been successfully demonstrated at VOXEL laboratory, IST. The non-linear propagation effects of the intense femtosecond pulses on low-order harmonics in the amorphous and crystalline solids have been successfully demonstrated at the VOXEL laboratory IST [96].

• An efficient signal of SHG (400 nm) and THG (265 nm) has been generated in single and polycrystal Ga_2O_3 at the elliptical and circular polarization of the NIR pules at VOXEL laboratory, IST. Such elliptical and circular polarized ultraviolet pulses can be employed to study the chirality and probing magnetic materials. In addition, harmonics up to the ninth order of 3 μ m driving wavelength have been generated in (100) and (010) oriented polycrystal Ga_2O_3 . We have observed anisotropic orientation dependence of harmonics which showed a complex interdependence of the crystal cut and orientation relative to the laser driving polarization (manuscript in preparation).

• We have successfully disentangled the response of SHG and THG from thin films and bulk at 800 nm driving wavelength in VOXEL laboratory, IST (manuscript in preparation).

• Below and above bandgap harmonics in Si, ZnO and STO have been generated at the laboratoire d'Optique Appliquee (LOA), with the collaboration of CEA-Saclay, Paris, France. The macroscopic control of spectral profile of high-order harmonics in semiconductors is successfully demonstrated by the non-linear propagation effects of the driving laser pulses (2.123 μ m) [81].

• The reconstruction of the images of nano-structures etched on semiconductors by ptychography using solid-state harmonics has been implemented at Laboratoire d'Optique Appliquee (LOA), with the collaboration of CEA-Saclay, Paris, France.

• We have successfully generated the orbital angular momentum harmonics beams of different topological charges in semiconductor and imaged the voxtex beams in near and far-filed.

• I have also participated in other experiments to control the wave-fronts of XUV pulses generated in gases [129] and high spatial resolution imaging through lithium fluoride detectors for a tabletop XUV source [130].

• Finally, we have successfully imaged the solid to plasma transition in titanium (Ti) foil through femtosecond pulses of soft x-rays created through HHG in gases at VOXEL laboratory, IST, Lisbon.

5.3 Perspectives

In this section of the thesis, the results achieved during this work in terms of possible applications are presented.

• Realization of a compact and table-top XUV ultrafast light source based on the solid-state HHG at the VOXEL and L2I, IPFN, IST.

• Implementation of the solid-state HHG spectroscopy for all-optical probing of the electronic band structure of solids. This solid-state HHG spectroscopy can be implemented in the L2I laboratory, IST,

owing to the presence of MIR (3 μ m laser wavelength).

• The solid-state HHG based ptychography can be used for the plasmonic applications and imaging of magnetic domains from the self-emission of harmonics in magnetic materials.

• The measurements of charge transport and kinetics of recombination in metal oxide semiconductors (MOS) can be foreseen by using the XUV pulses generated through the solid-state HHG process by a time-resolved transient XUV spectroscopy. This time-resolved transient XUV spectroscopy can be implemented at VOXEL and L2I laboratories to study the charge transport in MOS.

• Measurements of the ultrafast charge carrier dynamics in two-dimension (2D) photocatalytic materials with the deep UV ultrashort pulses generated by high harmonics in solids (MgO, fused silica) in conjunction with the pump-probe photoemission spectroscopy. The understanding of the charge carrier dynamics at the surface of photocatalytic materials can lead to efficient photocatalytic materials by tuning 2D material. This will be implemented during my postdoctoral at the Vaida Lab., Department of Physics, University of Central Florida, Orlando, USA.

5.3.1 Imaging of ultrafast transition from solids to plasma

One of the most challenging states of matter in the intermediate realm between solid and plasma is referred to as warm dense matter (WDM), where quantum, Coulomb, and plasma considerations are necessary to consider [280]. Critical physical properties, such as dielectric function, electrical conductivity, and equation of state, can be fully described by the configuration of two systems: the electrons and ions yet untangling the role of each are impossible in equilibrium [281, 282]. Femtosecond lasers have facilitated large amounts of energy to be deposited in the electron system of solids, leaving the heavier ions to respond one thousand times slower [283, 284]. This heating method opens a unique temporal window through the ultrafast electron dynamics, electron-ion coupling, and eventual equilibrium conditions in extreme conditions can be viewed, independently [285, 286].

A laboratory platform has been used to create and measure ultrafast high energy density states using femtosecond laser pulses and imaged the XUV optical properties and electronic structure changes using ultrafast HHG spectroscopy in VOXEL laboratory, IST, Lisbon. Femtosecond pulses of soft x-rays created through HHG in gases have been used to probe in space and time to study these exotic states. The laserinduced solid-to-plasma transition presents a dynamic transformation from the well-described solid state to the strongly coupled plasma state. The transition involves a range of comparable parameters, such as Coulomb, quantum, and structural effects, that must be accounted for in models. This constitutes a grand challenge to describe accurately within current theoretical frameworks, making experimental measurements essential. Exploring the effects of electronic excitation and structural changes can elucidate the impact of these two systems, providing practical constraints to models. The degree to which these plasmas absorb light of a specific frequency, the opacity, can be used to explore the electronic and structural changes and directly compared to models. These laser-induced changes can only be resolved with femtosecond time resolution diagnostics, as the equilibration of the electronic and ion systems is on the scale of picoseconds.

Here, we have presented a femtosecond time-resolved imaging system based on the transmission of XUV light from HHG in Xenon (Xe). We image in transmission a femtosecond laser-heated titanium foil with extreme ultraviolet light to measure the changing optical properties as a function of time. We use a grazing incidence focusing and imaging system that images in transmission a laser-heated titanium foil of 100 nm in a single shot. We find a drop in transmission that occurs on a picosecond timescale, indicating structural effects rather than electronic. We attribute the decrease in transmission to increased optical absorption through increased inter-band pathways as the ion structure disintegrates.

Experimental setup to generate and image the HED states

A schematic illustration of the experimental setup to create an image of HED states is shown in figure 5.1(a). We use a femtosecond laser system producing near-infra-red (NIR) pulses at a wavelength of 800 nm and a duration of 50 fs at full width half maximum (FWHM). The initial pulse is split using a polarising beam splitter. The pump pulse used as an optical heater is 1 mJ in energy and focused on a titanium foil of 100 nm thickness with a 5 nm carbon passivization layer on the front and back. The other portion of the split pulse is focused into a gas cell filled with Xenon at a pressure of 3.5 mBar to create an XUV spectrum of discrete photon energies to probe the laser-heated titanium in transmission. An aluminum filter of 100 nm thickness was placed before the chamber entrance and directly in front of the CCD to filter the NIR light from the probe arm and block optical light from the CCD. We use two Kirkpatrick-Baez (KB) configuration optics to focus the XUV pulse onto the target (KB1 in figure 5.1(a) and to image the transmitted XUV light at the back of the target (KB2 in figure 5.1(a)). Each Kirkpatrick-Baez optic consists of two silicon dioxide mirrors of a 3-inch diameter positioned at an angle of 10° . Each mirror is positioned at an angle of 45° relative to the plane of the laboratory floor, and each mirror in the KB optic is positioned at 90° . In this way, the beam exiting the KB pair does not continue to elevate as it propagates. In other words, it propagates in parallel to the laboratory floor, making further angle correcting mirrors unnecessary and increasing the overall beam-line transmission. The picture of the vacuum chamber with the illustration of NIR, XUV beams, and KB, s and focusing lens is shown in figure 5.1(d).

The spectrum of the HHG pulse was measured at the exit of the KB2 optic using a slit and grating combination. The extracted HHG spectrum is shown in figure 5.1(b). The entire spectrum was used to form the image of the HHG light transmitted through the target. The photon number was sufficient to record an image of the target in a single shot. The temporal overlap of the pump and the probe was confirmed through Spatio-temporal overlap on a second-harmonic crystal such as BBO on the target plane as shown in figure 5.1(c). This was achieved by removing the aluminum filter in the probe arm and allowing the NIR light to propagate in the probe arm onto the target surface while simultaneously allowing the attenuated pump pulse to propagate onto the BBO crystal. The two brighter spots of blue light correspond to the second-harmonic of the pump and probe arm while the central blue spot, which is generated through the temporal and spatial overlap of pump and probe NIR arm in BBO (see, figure



Spatial and temporal overlapping with BBO

Figure 5.1: (a) Schematic illustration of an experiment to generate and image HED states in Ti. (b) Probe XUV spectrum generated in Xenon gas. (c) Spatial and temporal overlap of pump and probe arms at Ti with the BBO. (d) Picture the chamber where HED states are created by heating the Ti target with NIR and imaged with the XUV pulses. XUV: extreme ultraviolet, NIR: near-infrared, L1: lens, TS: translation stage, KB: Kirkpatrick-Baez.

5.1(c).

Time resolved data in the solid to plasma transition

We show a typical XUV transmission image of the cold solid target (without the pump pulse) in figure 5.2(a). The image is slightly skewed and astigmatic due to the use of spherical mirrors at grazing angles. The horizontal magnification is ≈ 1.6 , and the vertical magnification is ≈ 1.9 . The photographs of plasma and plasma emission are shown in figure 5.2(b)—1200 fs delay XUV beam than with the NIR pump pulse. The dark lines are the target supports, and each target is 360 μ m × 360 μ m. The targets are square, and astigmatism comes from the use of the grazing incidence spherical mirrors. The dark area labeled "plasma" in (figure 5.2(b)) is approximately the area of the NIR heating pulse and is dark due to increased absorption relative to the surrounding areas. The area labelled "plasma emission" in (figure 5.2(b)) is due to the radiative emission from the hot plasma. The dashed line over the plasma region in (figure 5.2(b)) is where the profile of the plasma is taken, and the relative transmission measurement is taken.

The zoom-out transmission image of cold Ti and laser-heated Ti (transition from solid to plasma) with XUV is shown in figures 5.2(c) and 5.2(d). We have measured the transmission of the cold solid titanium target by comparing the transmitted intensity with and without the target in place. The average transmission is taken over multiple individual target areas and shots using the entire high-order harmonic spectrum for each image. We compare our values of absolute transmission of our 100 nm titanium foil coated with 5 nm of carbon on both sides. The time-resolved relative transmission (the relative change



Figure 5.2: (a) Transmission images are taken from the backside of the target (Ti) for XUV only. (b) XUV with the NIR pump pulse 1200 fs before the probe. The dark lines are the target supports, and each target is 360 μ m × 360 μ m. The targets are square, and astigmatism comes from the use of the grazing incidence spherical mirrors. The dark area labeled "plasma" in (b) is approximately the area of the NIR heating pulse and is dark due to increased absorption relative to the surrounding areas. The area labeled "plasma emission" in (b) is due to the radiative emission from the hot plasma. The dashed line over the plasma region in (b) is where the plasma profile is taken, and the relative transmission measurement is taken. (c) Typical transmission image of cold Ti with XUV.(d) Typical image of solid to plasma transition in Ti with XUV.



Figure 5.3: Relative transmission of XUV in laser-heated 100 nm Ti, (a) For 2 ps. (b) For 15 ps.
from the cold solid signal) as a function of time from the arrival of the pump pulse is shown in figure 5.3. We have designed a way to take photographs of a plasma with an XUV source on a femtosecond time scale as shown in figure 5.3. The ultrafast changes appear electronic, suggesting ionization occurring within the first 100 fs of the IR heating pulse.

The laser-induced changes from solid to plasma can only be resolved with femtosecond time resolution diagnostics, as the equilibration of the electronic and ion systems is on the scale of picoseconds. We present femtosecond time-resolved images of transmitted extreme ultra-violet (XUV) light from high harmonic generation. We use a grazing incidence focusing and imaging system that images in transmission a laserheated titanium foil of 100 nm in a single shot. We present the experimental setup and preliminary results of this ultrafast transition. Femtosecond time-resolved imaging of solid density titanium at 10 eV in a single shot showed a strong absorption of XUV pulses ($h\omega = 20 - 30 \text{ eV}$). The ultrafast changes appear electronic, suggesting ionization occurring within the first 100 fs of the IR heating pulse. This timescale seems long for electrons but short for ions, electron thermalization, or ultrafast melting. Future studies require which can improve the temporal resolution and reveal the delay (if any) between IR heating and probing of ionization of the bound electron states in solids through XUV source generated through gases. The solid-state HHG offered an alternate route for XUV pulses to probe HED states and image the ultrafast transitions from solid to plasma.

Appendix

Applied Physics B Lasers and Optics



Controlling the non-linear optical properties of MgO by tailoring the electronic structure

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Abstract

The study of the non-linear response of matter to high electric fields has recently encompassed harmonic generation in solids at near-infrared (NIR) driving wavelengths. Interest has been driven by the prospect of ultrafast signal processing and all-optical mapping of electron wave-functions in solids. Engineering solid-state band structures to control the non-linear process has already been highlighted theoretically. Here, we show experimentally for the first time that second harmonic generation (SHG) can be enhanced by doping crystals of magnesium oxide (MgO) with chromium (Cr) atoms. We show that the degree of enhancement depends non-linearly on dopant concentration. The SHG efficiency is shown to increase when Cr dopants are introduced into pure MgO. A physical picture of the effect of Cr dopants is aided by density functional theory (DFT) calculations of the electronic structure for pure and doped samples. This work shows an unambiguous enhancement of the SHG efficiency by modifying the electronic structure. The observed effects are consistent with an electronic structure that facilitates surface induced SHG and demonstrates a minimal angular dependence. This work highlights the potential of manipulating the electronic structure of solids to control, or test theories of, their non-linear optical response.

1 Introduction

Second harmonic generation (SHG) is the first perturbative non-linear response of solids at high driving fields. Efficient SHG is not possible in centrosymmetric solids due to symmetry conditions which forbid phase-matching. Near surfaces and interfaces, this symmetry is broken, and the phenomenon of SHG can occur. This process is termed as surface second-harmonic generation (SSHG). In centrosymmetric crystals such as MgO used in this study, phase matching conditions are not met, and the observed SHG

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produced is due to SSHG. For example, perturbative and non-perturbative high harmonics have been generated from the surface states of solids which shows the suppression of higher harmonics in bulk material due to lack of phase matching [1]. For an in-depth theoretical and experimental treatment of SHG, we refer the reader to the following works [2–7]. Practical uses of SSHG are widespread, including SHG spectroscopy for imaging to investigate the bio-molecular interactions at interfaces [8], optical imaging [9, 10], characterization of the interface of semiconductors [11], and near-field and far-field optical microscopy of microelectronics structures [12].

Here, we introduce Chromium (Cr) into pure MgO to experimentally investigate the role of doping in the SHG process. Cr is a transition metal, with higher energy occupied electron orbitals than MgO. Doping MgO with Cr will have the effect of adding electrons at normally unoccupied energy levels in the MgO energy states. Chromium atoms have been shown to replace Mg sites during the doping process [13, 14] and simulations showed the homogeneous distribution of Cr at the oxide lattice at low doping concentration [14]. The Cr dopants introduce electronic states in the MgO bandgap, which give rise to new optical transitions [15]. MgO doped with Cr, Cr: MgO, shows practical promise in a number of areas. It has been shown to generate less local stress compared to other transition metals when introduced into MgO, making it a good candidate for doping [16]. Crdoped MgO possesses long-range order and a number of active optical sites, which make it a good candidate for the optical measurements. The manipulation of the optical properties of MgO by introducing Cr dopants has been attributed to the new optical transitions made available from the Cr to the MgO orbitals [13]. The impact of doping concentration and crystal orientation on SHG is both a relevant scientific and practical question. By introducing dopants, we can alter the electronic structure and change the non-linear optical properties of the crystal. This could be used to tailor certain materials for strong field optoelectronics applications, for example a new degree of control in solid-state high harmonics [17].

In this work, we have generated the second harmonic in pure MgO and in Cr: MgO crystals. The impact of crystal orientation and doping concentration on the yield of SHG signal has been investigated. Experimental results have been explained by calculating the electronic structure using density functional theory (DFT) of pure MgO and Cr-doped MgO crystals.

In Sect. 2 we describe the experimental approach. The dependence of dopant concentration and crystal orientation on SHG are discussed in Sects. 3.1 and 3.2, respectively. We present DFT calculations of the electronic structure of the crystals and discuss our findings in Sect. 3.3. Finally, we give concluding remarks in Sect. 4.

2 Experimental setup

We used near-infrared (NIR) laser pulses of 40 fs at 800 nm operating at a repetition rate of 1 kHz, focused on the solid crystals to generate the second harmonic (SH). The schematic of the experimental setup is shown in Fig. 1a. The pulse duration of the driving field was measured by an autocorrelator, as shown in Fig. 1b, and the spectral profile of fundamental field measured by a UV-VIS spectrometer, as shown in Fig. 1c. Femtosecond laser pulses of ~20 µJ energy were focused on the 200 µm thick pure MgO and Cr-doped MgO bulk crystals to ~ 100 µm diameter by a convex lens of 750 mm focal length. The peak intensity of ~ 1.0×10^{13} W cm⁻² is below the damage threshold of MgO. The incident beam was kept normal to the surface plane of the crystal. The crystal was mounted on a threedimension translation stage as well as on a motorized rotational stage to keep the focal spot fixed at a point in the crystal during the rotation of the target.

The MgO crystals are cubic with 001-cut and (100) edge orientation. The pure MgO crystals were fabricated by a three-phase electric arc furnace as a single bulk crystal. The Cr powder is introduced directly into the MgO during the growth process and hence is uniformly distributed throughout the MgO. The fundamental and second harmonic pulses are separated using the chromatic dispersion of the side edge of a convex lens of a 100 mm focal length. The fundamental pulses are blocked by an iris and a short pass filter. The SH pulses are further focused by a 50-mm focal length into the optical fiber, which is connected to a UV–VIS spectrometer. The laser polarisation has been kept fixed while the target rotated about its axis to observe the orientation dependence of SHG in the pure and doped Cr: MgO crystals. The SHG spectrum is measured by a UV–VIS spectrometer. The SHG is first optimized by tuning the laser focus to maximize the SHG yield in pure MgO. These focusing parameters are then kept fixed for all the doped samples.

3 Results and discussion

3.1 Doping impact on the yield of SHG

In this section, we investigate the impact of Cr dopant concentration in pure MgO on the SHG efficiency. To validate the wavelength of the SH we present the spectral measurements of the SH at a fixed polarisation of the driving laser pulse, as shown in Fig. 2a. The spectral shape is identical for all dopant concentration, yet the intensity varies significantly. This is consistent with the different overall intensities presented in Fig. 3. About a twofold higher intensity of SHG is observed for a doping concentration of 740 parts per million (ppm) compared to the pure MgO crystal. Interestingly, as the concentration of Cr is increased further, the SHG intensity monotonically decreases, as shown in Fig. 2b. To observe the global dependence of Cr concentration we present total SHG yield accumulated over all angles for several dopant concentrations. The impact of doping on the yield of SHG is shown in Fig. 2b. The yield is measured as the average over one complete rotation of the crystal. This shows that at the lowest concentration of doping, which is 740 ppm here, the yield is highest. The yield of SHG decreases as the dopant concentration increases further.

To understand the dependence of efficiency on the Cr doping concentration, we now discuss the effect of Cr doping on the electronic, structural and optical properties of MgO, with reference to previous studies. At low dopant concentrations, most of the chromium ions take the position of the Mg ions [18]. Higher dopant concentrations of Cr have been shown to introduce different crystal phases, which may affect the SHG process [15]. Furthermore, it has been reported that by increasing the concentration of Cr doping, the number of atom-sized holes at the surface increases, which could also affect the efficiency of SHG [13]. The atom-sized hole may increase the symmetry breaking and thus enhance the SHG.



Fig. 1 a Schematic of second harmonic generation in MgO. The driving laser parameters: 40 fs, central wavelength 800 nm operating at 1 kHz. b The pulse duration of driving pulses measured from autocorrelator. c Spectrum of the driving pulses

At increasing levels of dopant concentration, structural changes occur, yet the influence of these new crystal phases on the optical properties is expected to be small. SSHG may not be strongly affected by the overall crystal structure, yet small imperfections at the crystal surface may play a role.

Doping common oxide crystals to alter their optical properties is a widely known and well-developed industrial technique [19, 20]. Here, we look at other works that have independently measured the effect of Cr doping in MgO on the optical properties. We are primarily concerned with our wavelengths of interest (800 nm and 400 nm). Cr: MgO has shown that transmission of optical light decreases overall with increasing doping concentration [21], relevant for both our wavelengths of interest.

The optical properties are a direct consequence of the electronic structure of the material. To clarify how the electronic structure changes in MgO when Cr atoms are introduced, we have conducted DFT simulations of pure and Cr-doped MgO. The results of these calculations, along with a discussion of how they explain the experimental results are presented in Sect. 3.3.

3.2 Orientation dependence of SHG

At a fixed polarisation of driving laser pulses, the crystals were rotated to observe the crystal orientation dependence of SHG with respect to the electric field. An anisotropic and chaotic dependence of SHG on the crystal orientation is observed in pure MgO as shown in Fig. 3. This polar graph has the linear axis in arbitrary units. The behaviour shown here underlines the complex dynamics of SHG in pure MgO and is attributed to the sensitivity of surface structural effects [22–24]. The exact shape of the orientation dependence of SHG may vary depending on crystal surface features or quality, as SH is generated due to the roughness of crystal



Fig. 2 a SHG spectrum at a given angle, θ , of rotation of pure MgO and MgO with different dopant concentrations of Cr. Pure MgO crystals (red), 740 ppm of Cr dopant in MgO crystal (blue), 1300 ppm of



Fig. 3 Orientation dependence of SHG in undoped and Cr-doped MgO crystal at fixed driving laser polarisation and rotation of crystal about its centre. Pure MgO crystal (red), 740 ppm of dopant (blue), 1300 ppm of dopant (green) and 9500 ppm of dopant (yellow)

surface. Conversely, isotropic emission is observed for all crystals containing Cr dopant, as shown in Fig. 3.

Furthermore, the Cr-doped MgO samples show a higher SH efficiency for all dopant concentrations. The angular anisotropy of the second harmonic emission relative to the crystal orientation present in pure MgO is lost when dopants are



Cr dopant in MgO crystal (green) and 9500 ppm dopant concentrations of Cr in MgO (yellow), \mathbf{b} angle averaged SHG intensity as a function of Cr dopant concentration

introduced. We have found that the exact angular dependence pattern of pure MgO to be sample dependent. Moreover, SHG was not observed from MgO samples with two polished surfaces, which shows that the disordered surface morphology is the source of SHG in this study. However, the overall efficiency of SHG is dependent on the doping concentration. This has been discussed in Sect. 3.1.

3.3 Electronic structure calculations from density functional theory

The SHG process has an inherent dependence on the allowed energy states and their corresponding occupation in the crystal. To better understand the role of the Cr doping, we have performed density functional theory (DFT) calculations of the pure and doped crystals (shown in Fig. 4a, b, respectively). The DFT calculations were performed using the VASP package [25-27]. Projected augmented wave (PAW) pseudo-potentials [28] and the generalised gradient approximation (GGA) for the exchange-correlation functional were used in combination with 300 bands and a $12 \times 12 \times 12$ automatically generated k-point mesh. The recently measured valence band structure of MgO agrees with our DFT calculations [29]. The single difference in the calculations of the pure MgO and doped Cr: MgO cases here was the inclusion of a Cr atom at the central site normally occupied by Mg. The cell size was 64 atoms in total, therefore, introducing a Cr atom at the centre of this cell would correspond to a $\sim 1.6\%$ dopant concentration. This is higher than our maximum





Fig. 4 The band dispersion plots using DFT, calculated in the Γ -X direction for **a** pure, and **b** chromium-doped, MgO. The lattice constant of MgO is 4.2 Å, however the supercell lattice constant of a=8.4 Å used in the calcuations results in the bands being folded four

times in the figure. The red arrows indicate the driving laser photon energy, and the blue arrows show the photon energy of the second harmonic. The occupation of the various bands is indicated in the respective legends

dopant concentration of ~ 1% in the experiment. However, the increase in cell size necessary for calculations with lower dopant concentrations becomes computationally prohibitive. Nonetheless, the physical effect of the dopant on the electronic structure remains qualitatively valid. A further increase in dopant concentration would increase the occupation of higher energy states and ultimately converge to the electronic structure of metallic Cr.

We present calculations of the band dispersion in the Γ -X direction of pure and Cr-doped MgO in Fig. 4a and b, respectively. In pure MgO (Fig. 4a), we note an optical band gap of bulk MgO of around 4.7 eV. This lies in clear contrast to the accepted band-gap of around 7.8 eV [30]. The discrepancy between the accepted band-gap and the value reported here is due to the choice of xc functional used. Here we use the GGA to the xc functional, which is known to underestimate the band-gap. In fact, calculations similar to those presented here have yielded similar bulk band-gaps from 4.6 to 5 eV for bulk MgO [30, 31]. It should be noted that surface band gaps of MgO have been shown elsewhere to be in the 5-eV range. Coincidentally, the bulk DFT band-gaps reported here are closer to the measured surface MgO band-gaps, where the SHG process reported here largely occurs.

It has been shown elsewhere that band-gaps of MgO can be well reproduced with other, more computationally expensive methods [30]. Calculations of the band-structure of MgO have been shown to match experimental values when more complex approaches (using hybrid Hartree–Fock methods) to the xc functional have been employed [31]. However, these approaches have the downside of often been computationally more intensive. Since our cell size is already at the limit of our computational resources, we restrict our calculations to the more efficient, but less accurate GGA approach. Despite the expected underestimation of the optical band-gap in bulk MgO reported here, we maintain that this difference does not affect our conclusions: the reduced the band-gap by introducing Cr dopants increases the photon absorption process, thereby increasing the SHG efficiency.

In Fig. 5 the highest occupied energy level (Fermi energy) is indicated by the vertical dash-dot line around 3 eV in Fig. 5a. There are no available energy levels for blue (SHG) photon transitions to occur around the Fermi energy for pure MgO. Therefore, a multi-photon absorption process must occur to drive electrons to the higher energy states (red arrows in Fig. 5a). Conversely, the Cr: MgO has higher lying occupied (defect) states, due



Fig. 5 The density of states of states of MgO (a) and Cr: MgO (b) calculated with DFT. The red arrows indicate the energy of a photon of the fundamental IR driving laser field. The blue arrows indicate the energy of a second harmonic photon

to the Cr doping (sharp peak around 8 eV). This higher lying occupied (defect) state allows for direct driving and recombination of electrons, without the need for prior multi-photon absorption processes to occur. This increase efficiency by allowing a more probable two-photon process to excite the electrons, as shown in Fig. 2. The dependence of SHG efficiency on the direction of the driving field is minimal, as the highest occupied state (dashed line in Fig. 5b is a narrow, atomic-like line that varies little in energy with respect to crystal orientation (as shown in Fig. 3). This lack of angular dependence on the initial and final state in the electronic structure translates to a lack of observed angular dependence with Cr: MgO, as shown in Fig. 3.

Hence, by manipulating the electronic structure, we can tailor the efficiency and polarisation dependence of non-linear processes in crystals. The efficiency, however, can be limited by the changing optical properties, as the dopant concentration is increased. This shows a delicate balance of the element and concentration of the dopant is essential for improving solid-state SHG in terms of yield.

4 Conclusion

We have generated the second harmonic in pure and Cr-doped MgO with a NIR driving field. On rotating the crystal relative to the driving field polarisation, an anisotropic and chaotic behaviour of SHG efficiency in pure MgO is observed. This is attributed to the complex interplay between surface and nonlinear effects for SHG in MgO. Conversely, the SHG signal was isotropic and symmetrical in Cr-doped MgO crystals. This isotropic emission of SHG is attributed to the minimal angular dependence of the Cr valence band, which we identify as the most probable initial energy state of the multi-photon IR absorption process through DFT calculations. The effect of doping concentration on the yield of SHG signal has been investigated, showing that the lowest (740 ppm) concentration of Cr gives a twofold increase in SHG efficiency relative to pure MgO. At higher doping concentrations the SHG yield is reduced. This reduction in SHG yield at higher dopant concentrations is attributed to the changing linear optical properties of doped MgO. In particular, increased re-absorption of the SH increases with Cr dopant concentration and, therefore, limits the overall achievable SHG efficiency.

This work has shown that, by introducing dopants into simple crystals, the electronic structure can be shaped to tailor the non-linear optical response in terms of efficiency and angular dependence. We show that Cr can increase the SHG efficiency and mitigate angular polarisation dependence when introduced to MgO, and that efficiency favors dopant concentration on the order of 740 ppm. This study paves the way for the merging of bandgap engineering and solid-state harmonic generation to tailor frequency up-conversion processes. Perhaps of equal importance is the prospect of experimentally testing theories of the solid-state high harmonic generation (HHG) mechanism with tailored electronic structures, with a final view towards all optical mapping of the band structure of solids.

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References

- J. Seres, E. Seres, C. Serrat, T. Schumm, Nonperturbative generation of DUV/VUV harmonics from crystal surfaces at 108 MHz repetition rate. Opt. Express 26, 21900–21909 (2018)
- S.M. Anderson, N. Tancogne-Dejean, B.S. Mendoza, V. Véniard, Theory of surface second-harmonic generation for semiconductors

including effects of nonlocal operators. Phys. Rev. B **91**, 075302 (2015)

- M.C. Downer, B.S. Mendoza, V.I. Gavrilenko, Optical second harmonic spectroscopy of semiconductor surfaces: advances in microscopic understanding. Surf. Interface Anal. 31, 966–986 (2001)
- W. Luis Mochán, J. A. Maytorena, Theory of surface second harmonic generation. In *EPIOPTICS-8* 17–45 (2006)
- K.L. Seyler, J.R. Schaibley, P. Gong, P. Rivera, A.M. Jones, S. Wu, J. Yan, D.G. Mandrus, W. Yao, X. Xu, Electrical control of second-harmonic generation in a WSe 2 monolayer transistor. Nat. Nanotechnol. 10, 407 (2015)
- T. Jiang, H. Liu, D. Huang, S. Zhang, Y. Li, X. Gong, Y.R. Shen, W.T. Liu, S. Wu, Valley and band structure engineering of folded MoS 2 bilayers. Nat. Nanotechnol. 9, 825 (2014)
- K.Q. Lin, S. Bange, J.M. Lupton, Quantum interference in secondharmonic generation from monolayer WSe2. Nat. Phys. 15, 242 (2019)
- R.J. Tran, K.L. Sly, J.C. Conboy, Applications of surface second harmonic generation in biological sensing. Ann. Rev. Anal. Chem. 10, 387–414 (2017)
- L. Mennel, M.M. Furchi, S. Wachter, M. Paur, D.K. Polyushkin, T. Mueller, Optical imaging of strain in two-dimensional crystals. Nat. Commun. 9, 516 (2018)
- J.Y. Chauleau, E. Haltz, C. Carrétéro, S. Fusil, M. Viret, Multistimuli manipulation of antiferromagnetic domains assessed by second harmonic imaging. Nat. Mater. 16, 803 (2017)
- G. Lüke, Characterization of semiconductor interfaces by secondharmonic generation. Surf. Sci. Rep. 35, 75–161 (1999)
- A.M. Zheltikov, G. Ferrante, M. Zarcone, On the far-and near-field optical microscopy of microelectronics structures using secondharmonic and sum-frequency generation. Laser Phys. 10, 600–602 (2000)
- F. Stavale, N. Nilius, H.J. Freund, Cathodoluminescence of nearsurface centres in Cr-doped MgO (001) thin films probed by scanning tunnelling microscopy. New J. Phys. 14, 033006 (2012)
- S. Benedetti, N. Nilius, S. Valeri, Chromium-doped MgO thin films: morphology, electronic structure, and segregation effects. J. Phys. Chem. C 119, 25469–25475 (2015)
- L.N. Kantorovich, A.L. Shluger, A.M. Stoneham, Recognition of surface species in atomic force microscopy: optical properties of a Cr³⁺ defect at the MgO (001) surface. Phys. Rev. B 63, 184111 (2001)
- J.W. Lee, J.H. Ko, Defect states of transition metal-doped MgO for secondary electron emission of plasma display panel. J. Inf. Display 15, 157–161 (2014)
- C. Yu, K.K. Hansen, L.B. Madsen, Enhanced high order harmonic generation in donor-doped band-gap materials. Phys. Rev. A 99, 013435 (2019)

- M.O. Henry, J.P. Larkin, G.F. Imbusch, Nature of the broadband luminescence center in MgO: Cr³⁺. Phys. Rev. B 13, 1893 (1976)
- H. Eskalen, Ş. Özğan, Ü. Alver, S. Kerli, Electro-Optical properties of liquid crystals composite with zinc oxide nanoparticles. Acta Phys. Polon. A. 127, (2015).
- C.W. Oh, E.G. Park, H.G. Park, Enhanced electrooptical properties in titanium silicon oxide nanoparticle doped nematic liquid crystal system. Surf. Coat. Technol. 360, 50–55 (2019)
- T. Kato, G. Okada, T. Yanagida, Optical, scintillation and dosimeter properties of MgO translucent ceramic doped with Cr³⁺. Opt. Mater. 54, 134–138 (2016)
- D. Guidotti, T.A. Driscoll, H.J. Gerritsen, Second harmonic generation in centro-symmetric semiconductors. Solid State Commun. 46, 337–340 (1983)
- T.A. Driscoll, D. Guidotti, Symmetry analysis of second-harmonic generation in silicon. Phys. Rev. B 28, 1171 (1983)
- O.A. Aktsipetrov, I.M. Baranova, Y.A. Il'inskii, Surface contribution to the generation of reflected second-harmonic light for centrosymmetric semiconductors. Zh. Eksp. Teor. Fiz **91**, 287–297 (1986).
- G. Kresse, J. Hafner, Ab initio molecular dynamics for liquid metals. Phys. Rev. B 47, 558–561 (1993)
- G. Kresse, J. Furthmuller, Efficient iterative schemes for ab initio total energy calculations using a plane-wave basis set. Phys. Rev. B 54, 11169–11186 (1996)
- G. Kresse, J. Furthmuller, Efficiency of ab-initio total energy calculations for metals and semiconductors using a plane-wave basis set. Comput. Mater. Sci. 6, 15–50 (1996)
- G. Kresse, D. Joubert, From ultrasoft pseudopotentials to the projector augmented-wave method. Phys. Rev. B 59, 1758–1775 (1999)
- H.S. Uhm, E.H. Choi, Measurement of valence band structure in arbitrary dielectric films. Mater. Res. Bull. 47, 2906–2910 (2012)
- S. Heo, E. Cho, H.I. Lee, G.S. Park, H.J. Kang, T. Nagatomi, P. Choi, B.D. Choi, Band gap and defect states of MgO thin films investigated using reflection electron energy loss spectroscopy. AIP Adv. 5, 077167 (2015)
- 31. M. Gerosa, C.E. Bottani, L. Caramella, G. Onida, C. Di Valentin, G. Pacchioni, Electronic structure and phase stability of oxide semiconductors: Performance of dielectric-dependent hybrid functional DFT, benchmarked against G W band structure calculations and experiments. Phys. Rev. B **91**, 155201 (2015)

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ABSTRACT

High harmonic generation (HHG) in crystals has revealed a wealth of perspectives such as all-optical mapping of the electronic band structure, ultrafast quantum information, and the creation of all-solid-state attosecond sources. Significant efforts have been made to understand the microscopic aspects of HHG in crystals, whereas the macroscopic effects, such as non-linear propagation of the driving pulse and its impact on the HHG process, are often overlooked. In this work, we study macroscopic effects by comparing two materials with distinct optical properties, silicon (Si) and zinc oxide (ZnO). By scanning the focal position of 85 fs duration and 2.123 μ m wavelength pulses inside the crystals, (Z-scan) we reveal spectral shifts in the generated harmonics. We interpret the overall blueshift of the emitted harmonic spectrum as an imprint of the spectral modulation of the driving field on the high harmonics. This process is supported with numerical simulations. This study demonstrates that through manipulation of the fundamental driving field through non-linear propagation effects, precise control of the emitted HHG spectrum in solids can be realized. This method could offer a robust way to tailor HHG spectra for a range of applications.

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In the recent decade, solid-state HHG has been studied in a wide variety of crystals and amorphous solids.^{1–3} The physical picture of solid-state HHG is in its infancy and is the subject of ongoing discussion.^{4–9} A better understanding of the physical process of solid-state HHG will not only lead to improved secondary sources but also to an ability to map the nonlinear properties and possibly allow all-optical mapping of the electronic structure of solids.^{10–15} HHG in solids can be realized in materials transparent to the driving laser pulse wavelength. As femtosecond duration pulses are normally generated in the near to mid-infrared region, insulating and semi-conducting solids are the materials of choice for HHG. The HHG process in solids shares

some similarities with HHG in gases, at least conceptually.^{14,16} The first step is an inter-band transition in the material that promotes a charge carrier to the conduction band. Once there, this electron is driven by the fundamental field and can emit harmonics due to oscillations within a band (intra-band) or excitation and relaxation between bands (inter-band).^{15,17}

The initial inter-band excitation requires a tunneling or a multiphoton absorption process, and the rate of free carrier generation is, therefore, inversely proportional to the bandgap. Apart from the microscopic physics of carrier generation and motion, the properties of the HHG emission can be influenced by the propagation of the

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electric fields inside the crystal. This macroscopic propagation is highly nonlinear for the driving field and linear for the harmonics, owing to their much lower intensity. This makes the HHG spectrum an intricate fingerprint of the complex interplay of microscopic and macroscopic processes. For example, HHG in ZnO^{1,18,19} has been shown to reveal both the inter and intra-band mechanisms. Similarly, harmonics have been generated in the most widely used material in electronics, silicon (Si), at 2.1 μ m driving wavelength²⁰ and used to disentangle the surface and bulk contributions in Si²¹ and topological insulators.²² It has also been shown that HHG in Si and ZnO can be controlled and monitored by manipulating the crystal surfaces.^{23,24} For example, spatial shaping of the crystal surface has been used to create HHG beams that carry an orbital angular momentum (OAM)²⁵ without the need of costly devices for spatial phase control. These generated OAM beams have many applications varying from the manipulation of nanoparticles to quantum cryptography.

Microscopic processes have previously attributed to spectral shifts during HHG. The propagation of the intense driving field has been linked with redshifts in the HHG spectrum in plasmas and gases.^{27–29} This effect is attributed to the delayed emission of HHG from excited states or resonant states³⁰ or dislocation of molecules.³¹ In solids, numerically computed HHG spectra have shown redshifts in the "higher plateaus" due to higher band transitions.³² In sapphire, intensity-dependent redshifts and blue-shifts were observed in the spectrum of harmonics and attributed to the long and short electron/ hole trajectories, respectively.³³

Other works have quantified the macroscopic propagation effects in the HHG process.^{34–36} Ghimire *et al.* showed theoretically that the efficiency of below bandgap harmonics is modulated mainly by phasematching conditions, and the above bandgap harmonics are limited by re-absorption in the material itself.³⁷ Similarly, numerical simulations of the propagation effects in semiconductors have shown that the dephasing of harmonics reduced the HHG signal.³⁸ Vampa *et al.* experimentally demonstrated HHG in a reflection geometry with the aim to avoid propagation effects.³⁹ Propagation effects have shown to impact the HHG process in solids, yet some studies report efficient harmonics are generated from only a few-tens of nanometers,^{40,41} whereas the driving field usually propagates within the solid for hundreds of micrometers. These studies highlight the importance of the non-linear driving field propagation and its impact on the HHG process in solids.

In this Letter, we have generated third (H3), fifth (H5), and seventh (H7) order-harmonics in Si and ZnO crystals with a driving central wavelength of 2.123 μ m in the sub-TW cm⁻² intensity regime. We have investigated the impact of the non-linear macroscopic beam propagation on the HHG process in Si and ZnO, particularly to anticipate the role of the non-linear propagation of the driving pulse and the effect on the spectrum of the harmonics. Although the tuning of the driving laser wavelength can allow tuning of the HHG, commercial laser systems traditionally operate with a fixed central laser wavelength, making tuning impossible. Alternatively, the non-linear propagation of intense driving pulses in solids offers a route to control the spectral profile of harmonics. By tailoring the generation scheme, in terms of the generating medium, crystal thickness, and laser focusing geometry, we show that it can offer a flexible and precise control over the HHG frequency comb, while using a fixed driving laser frequency.

A schematic representation of the experimental setup is shown in Fig. 1. We have employed a fiber laser (NOVAE Company) operating



FIG. 1. Schematic representation of the experimental setup to generate high order harmonics (H3, H5, and H7) in the 300 μ m thick silicon (Si) and 200 μ m thick-(100) oriented ZnO crystal. The convention for the Z-scan notation is explained in the inset. Note that P: polarizer; L: lens; T: telescope; S: sample; HF: harmonic filters; FM: flip mirror; CCD: charged coupled device.

at 2.123 μ m with a pulse energy of $\simeq 8$ nJ and a repetition rate of 19 MHz. To enable a tighter focus and, thus, achieve higher intensities, the size of the laser beam is magnified by a factor of 3.75 times using a telescope (T). The 85 fs duration pulses are focused on the crystals by a convex lens of 3 cm focal length, up to a maximum peak intensity of $\simeq 0.38$ TW cm⁻², which is well below the damage threshold of the crystals. The generated diverging harmonics are focused by a convex lens of 15 cm focal length either on a UV-enhanced CCD camera or a UV-VIS spectrometer (with a pixel resolution of \pm 0.2 nm) for spatial and spectral beam characterization, respectively. Band-pass filters centered at each harmonic wavelength are used to separate and characterize the HHG properties. We perform Z-scans by translating the crystal in the direction of laser propagation, as shown in Fig. 1 (inset).

We have generated harmonics in a 300 μ m thick, (100) oriented, Si crystal. The spectral and spatial profiles of H3, H5, and H7 harmonics are shown in Fig. 2(a). The z-scans for H3 and H5 are recorded with steps of 10 μ m as shown in Fig. 2(b). The signal of H7 is very weak and is, therefore, excluded from the Z-scan study. The yield of H3 and H5 reaches their maximum when the focus position of the driving field is on the back surface of the Si crystal. This is attributed to the absorption of the harmonics generated at the front surface and inside the bulk of the Si crystal. Compared to H3, the efficient generation region of H5 is translated $\simeq 5 \,\mu$ m toward the back surface [see Fig. 2(b)] due to its stronger absorption in the crystal. In parallel, we have measured the spectral of the harmonics generated in the Si crystal as a function of the focus position of the driving laser.

The driving intensity (I_z) at the surface of the crystal is estimated as $I_z = 2P/\pi w_z^2$, where w_z is the beam waist at *z* calculated using a hyperbolic function⁴² by considering the non-linear refractive indices of crystals with a confocal parameter $b = 46 \,\mu\text{m}$ and *P* is the peak power that is 0.05 MW (as shown in Fig. 3). A spectral shift of about 3.4 nm for H3 and 3.9 nm for H5 is observed in Si (see Fig. 3). As the laser focus is scanned from outside the crystal (at the position $-60 \,\mu\text{m}$) to inside the bulk (at the position of $+60 \,\mu\text{m}$), a spectral blue shift in H3 and H5 is observed. Indeed, when the laser focus is outside the crystal, the spectrum of H3 is centered at 704 nm, while



FIG. 2. Spectral and spatial measurement of high order harmonics in a 300 μ m thick Si crystal. The spectral and spatial profiles of each harmonic measured separately with the corresponding harmonic filters for different acquisition times. (a) H5 multiplied by 100 and H7 by 1000 to make them visible in the combined graph. (b) Z-scan measurements of H3 (red dots) and H5 (blue dots) in the Si crystal.

that of H5 is centered at 425 nm, corresponding to harmonics of the central driving wavelength in vacuum. In this configuration, we expect that nonlinear propagation effects are minimal. However, when the laser is focused inside the crystal ($+60 \mu$ m), the spectrum of H3 shifts to 701 nm, while that of H5 shifts to 421 nm (see Fig. 3).

The combined harmonic spectrum (H3, H5, and H7) generated in ZnO and the corresponding spatial profiles are shown in Fig. 4(a). The measured harmonic signal (H3, H5, and H7) as a function of the focus position of the driving beam in the ZnO crystal is shown in Fig. 4(b). The Z-scan of H3 exhibits a double peak structure corresponding to the



FIG. 3. Spectral shifting of the harmonic signal generated in the 300 μ m thick Si crystal with the focus position. The driving intensity evolution (I_z) at the rear face of the crystal with the focus position *z* (green squares). Spectral shift in H3 (red squares) and spectral shift in H5 (blue squares).

front and back of the crystal. The signal of H3 is reduced when the focus position is in the center of the crystal. H3 generated before and after the focus point in the bulk contribute destructively due to the phase mismatch of H3 pulses at the exit of the crystal. As a result, the signal of H3 drops when the laser focus position is at the center of the crystal, while the signal of H3 is maximum when the laser is focused near the surfaces. Such behavior has been reported elsewhere. $^{43-45}$

We observe a single peak for H5 and H7, which shows the detected harmonics originate from the rear surface of the crystal. As the harmonic order increases, the region of efficient harmonic generation moves closer to the back surface of the crystal. This is likely due to longer phase matching conditions for the lower order harmonics.

Figure 5(a) shows the spectral response of H3 for different focus positions. A spectral modulation and splitting of the H3 peak is observed, showing two peaks that are separated by up to 12 nm when the focus of the driving field is in the middle of the ZnO crystal. The first peak of H3 begins to decrease while the second peak of H3 builds up with the translation of the driving focus toward the front surface. The reduction in the harmonics intensity when the driving field is focused inside the bulk crystal has been reported elsewhere and attributed to phase mismatch between two harmonic sources, from the front surface and bulk,^{43,45} and in sapphire crystals due to phase mismatch in the bulk due to geometrical focusing effects.⁴⁴ The effective Rayleigh length here is long enough to generate H3 from the surface of the crystal, even when the focal point is near the center of the ZnO crystal [see Fig. 4(b)]. This creates a pulse of H3 from the surface that propagates at its group velocity in the crystal. The main driving envelope propagates at a different group velocity and drives H3 generation throughout the bulk of the crystal. The different group velocities of these two H3 pulses can cause overall destructive interference of the H3 signal, as seen in Fig. 4(b). This interference effect is highlighted by our spectral measurements of H3 as a function of the focus position in



FIG. 4. (a) Spectrum of the harmonic emission in ZnO at Z = 0 for different acquisition times with the harmonic beam profiles in insets. (b) Z-scan measurements of H3 (red dots), H5 (blue diamonds), and H7 (violet hexagons) order harmonics.

Fig. 4(b). Such spectral modulations have been attributed to such interference effects elsewhere. 33,46

The intensity of H3 increases with the spectral blueshift as we move the focus from outside the crystal toward the crystal [from $z = -60 \,\mu\text{m}$ to z = 0, triangle data points of Fig. 5(b)] and reach a maximum at z = 0, which corresponds to the rear surface of the ZnO crystal. When further translating the laser focus inside the crystal ($z = +40 \,\mu\text{m}$), the intensity of H3 decreases. However, the width of

the spectral shift increases even more. H3 generated from the front surface (red rectangles) and back surface (black triangles) of the crystal undergoes blueshifts (8 and 12 nm, respectively) as shown in Fig. 5(b).

We have also observed the spectral blueshifts in the spectrum of H5 and H7 in ZnO as shown in Fig. 5(b). There were no spectral modulations and splitting as observed for H3. The signals of H5 and H7 have increased when translating the laser focus position toward the rear surface. By further translating the focus of the driving field inside



FIG. 5. (a) Spectral shifting and splitting of H3 in ZnO. (b) The evolution of the driving intensity (I_z) at the rear surface of the crystal for different focus positions z (green dots). H3 generated from the front surface (red data points) and at a back surface (triangle data points) of the ZnO crystal. H3 exhibits a blueshift as the focus of the driving field translates toward the back and front surfaces. The z = 0 corresponds to the front surface for the red square data points and the back surface of crystal for the black triangle data points. Spectral shift in H5 (blue diamonds) and spectral shift in H7 (violet diamonds).

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the crystal, the signal of H5 and H7 decreases. The total spectral blueshift across our measurement range is of about 3.9 nm for H5 and H7 as shown in Fig. 5(b).

To understand the physical processes that give rise to the harmonic spectral shift, we model the propagation of the driving field inside the Si and ZnO crystals. We restrict the calculation to $z \gg z_R$, where z is the focus position inside the crystal and z_R is the Rayleigh length. We have used the model described in Ref. 47 with the exception that only the instantaneous Kerr effect is taken into account in our model. The group velocity dispersion and higher-order dispersion are calculated using a Taylor expansion in $\omega - \omega_0$ up to the fifth order of the frequency-dependent wavevector, $k(\omega) = n(\omega)\omega_0/c$, where ω_0 is the central driving frequency, ω is the shifted frequency, $n(\omega)$ is the index of refraction, and *c* is the speed of light. We then solve the paraxial wave equation in a cylindrical geometry, coupled to the equation that describes the evolution of the electron density. The laser parameters used were an 85 fs pulse duration, $\simeq 7 \text{ mm}$ Gaussian beam diameter focused onto the 300 μ m Si and 200 μ m ZnO crystals to a beam waist of 0.83 and 1.45 μ m, respectively, by a 3 cm focal length lens. Initially, we have assumed that the conduction band is empty. Figure 6(a) quantifies the (absolute) shift of the central driving wavelength for both crystals. The maximum shift, reached inside the crystal, is 54.0 nm for Si and 17.4 nm for ZnO. The spectral blue shift as well as the absorption are larger in Si than for ZnO due to the smaller bandgap that facilitates free carrier generation. When focusing behind the crystal, the shift rapidly drops to zero in both cases as seen in Fig. 6(a).

The macroscopic non-linear propagation of the laser pulses in the crystal induces a spectral blueshift in the driving field. This shift results in a shift of the central wavelength of any high order harmonics generated at the rear side of the crystal. Figure 6(b) compares the measured spectral shift at z = 0 for the different harmonic orders with the expected HHG wavelengths from the numerical propagation of the fundamental pulses.

Qualitatively, the direction of the spectral shift (blue) is correctly predicted by the model for all high harmonics. However, the measured shift for harmonics in Si and ZnO is less shifted as predicted by the modeling values [see Fig. 6(b)]. The model considers only the driving pulse and does not include the complex dynamics involved in the HHG process itself. Therefore, we do not expect an exact agreement between the HHG central wavelength and that of the propagated driving wavelength.

We attribute the HHG spectral shifts to the non-linear propagation of the intense driving field inside the crystal. Photo-ionization drives the generation of free-electrons in the optical transition from the valence band to the conduction band. The increased free carrier density induces a time and space dependant refractive index change that up-shifts the driving laser frequency. This is a well-documented effect observed in short pulse laser ionization in gasses.⁴⁸⁻⁵⁰ In turn, this up-shift in driving frequency results in an up-shift of the harmonic frequencies, which we observe as an overall blue-shift in HH wavelengths. Through modeling of the non-linear propagation, we find that increased free-carrier density through photo-ionization is the principle physical mechanism causing these shifts [Fig. 6(a)]. This is consistent with our general experimental observations, in that the blue-shift increases when the distance of the driving pulse propagation inside the crystal is greater, resulting in the generation of more free carriers [Figs. 3 and 5(b)]. The bandgap of the material is also shown to play a crucial role. Above bandgap harmonics are limited to the last few micrometers of the material, where spectral control is possible but limited due to re-absorption. Below bandgap harmonics (such as H3 in ZnO) can be created from the surfaces and bulk of the material, allowing not only blue-shifted but also strongly modulated spectra [Fig. 5(a)].

We have observed front and back surface emission due to phase matching of H3 in ZnO while back surface emission observed due to re-absorption of over bandgap harmonics in Si and ZnO. In ZnO, the generation of H3 is efficient from the front and rear surfaces of the crystal and a modulated spectrum observed when focusing at the center of the crystal. We attribute this spectral modulation to the groupvelocity mismatch of surface and driven part of H3 pulses during propagation, indicating the interference pattern of the temporal



FIG. 6. (a) Spectral shift of the driving wavelength with the focus position in Si (black squares) and ZnO (red dots) for the focus position $z = -60 \ \mu m$ (moving from vacuum toward the back surface) to $+60 \ \mu m$ (inside crystals), respectively. (b) The spectral shift in HHG when the focus of the laser is at z = 0 (back side of crystals), non-shifted (blue diamonds), Si (black empty squares), ZnO (black empty circles), and as per modeling in Si (black squares) and ZnO (red empty circles).

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separated H3 pulses. We have demonstrated the changes in the emitted harmonic spectrum as a function of the driving laser focal position in the crystals. We observed that all the harmonic peaks are blueshifted as the focus position is translated into the crystals. Due to the dependence on the focal position, and hence the propagation length in the crystal, we attribute the observed blueshifts to non-linear propagation effects of the driving laser. This is supported by calculations of the non-linear propagation of the driving field in Si and ZnO, which exhibits a blueshift of the central frequency, attributed to the photoionization of valence band electrons. Even in samples that strongly absorb the HHG spectrum, we show that since the emitted harmonics come from a small region at the end of the crystal, modulation of the driving pulse prior to the point of generation can be used to control the HHG spectrum. For materials with bandgaps higher than the harmonic photon energy, further control of the spectrum can be obtained from front and back surface emission, as we have demonstrated with the third harmonic in ZnO. This study reveals the fine control of the HHG emission spectrum through macroscopic non-linear effects in the bulk crystal alone. This technique could be used for tailoring frequencies for ultrafast spectroscopic techniques or spectral shaping for attosecond pulse generation.

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DATA AVAILABILITY

The data that support the findings of this study are openly available in the Cornell University data catalog at arXiv:2103.11479, Ref. 51.

REFERENCES

- ¹S. Ghimire, A. D. DiChiara, E. Sistrunk, P. Agostini, L. F. DiMauro, and D. A. Reis, "Observation of high-order harmonic generation in a bulk crystal," Nat. Phys. 7, 138 (2011).
- ²Y. S. You, D. A. Reis, and S. Ghimire, "Anisotropic high-harmonic generation in bulk crystals," Nat. Phys. 13, 345 (2017).
- ³Y. S. You, Y. Yin, Y. Wu, A. Chew, X. Ren, F. Zhuang, S. Gholam-Mirzaei, M. Chini, Z. Chang, and S. Ghimire, "High-harmonic generation in amorphous solids," Nat. Commun. **8**, 724 (2017).
- ⁴D. Golde, T. Meier, and S. W. Koch, "High harmonics generated in semiconductor nanostructures by the coupled dynamics of optical inter-and intraband excitations," Phys. Rev. B 77, 075330 (2008).
- ⁵T. Higuchi, M. I. Stockman, and P. Hommelhoff, "Strong-field perspective on high-harmonic radiation from bulk solids," Phys. Rev. Lett. **113**, 213901 (2014).

- ⁶P. G. Hawkins, M. Y. Ivanov, and V. S. Yakovlev, "Effect of multiple conduction bands on high-harmonic emission from dielectrics," Phys. Rev. A 91, 013405 (2015).
- ⁷M. Wu, D. A. Browne, K. J. Schafer, and M. B. Gaarde, "Multilevel perspective
- on high-order harmonic generation in solids," Phys. Rev. A 94, 063403 (2016).
 ⁸N. Tancogne-Dejean, O. D. Mücke, F. X. Kärtner, and A. Rubio, "Impact of the electronic band structure in high-harmonic generation spectra of solids," Phys. Rev. Lett. 118, 087403 (2017).
- ⁹I. Floss, C. Lemell, G. Wachter, V. Smejkal, S. A. Sato, X.-M. Tong, K. Yabana, and J. Burgdörfer, "Ab initio multiscale simulation of high-order harmonic generation in solids," Phys. Rev. A **97**, 011401 (2018).
- ¹⁰J. P. Marangos, "High-harmonic generation: Solid progress," Nat. Phys. 7, 97 (2011).
- ¹¹O. Schubert, M. Hohenleutner, F. Langer, B. Urbanek, C. Lange, U. Huttner, D. Golde, T. Meier, M. Kira, S. W. Koch *et al.*, "Sub-cycle control of terahertz high-harmonic generation by dynamical Bloch oscillations," Nat. Photonics 8, 119 (2014).
- ¹²M. Hohenleutner, F. Langer, O. Schubert, M. Knorr, U. Huttner, S. Koch, M. Kira, and R. Huber, "Real-time observation of interfering crystal electrons in high-harmonic generation," Nature 523, 572 (2015).
- ¹³T. T. Luu, M. Garg, S. Y. Kruchinin, A. Moulet, M. T. Hassan, and E. Goulielmakis, "Extreme ultraviolet high-harmonic spectroscopy of solids," Nature 521, 498 (2015).
- ¹⁴G. Vampa, T. Hammond, N. Thiré, B. Schmidt, F. Légaré, C. McDonald, T. Brabec, D. Klug, and P. Corkum, "All-optical reconstruction of crystal band structure," Phys. Rev. Lett. 115, 193603 (2015).
- ¹⁵S. Ghimire and D. A. Reis, "High-harmonic generation from solids," Nat. Phys. 15, 10 (2019).
- ¹⁶G. Vampa and T. Brabec, "Merge of high harmonic generation from gases and solids and its implications for attosecond science," J. Phys. B: At., Mol. Opt. Phys. **50**, 083001 (2017).
- ¹⁷G. Vampa, C. McDonald, G. Orlando, P. Corkum, and T. Brabec, "Semiclassical analysis of high harmonic generation in bulk crystals," Phys. Rev. B **91**, 064302 (2015).
- ¹⁸S. Gholam-Mirzaei, J. Beetar, and M. Chini, "High harmonic generation in ZnO with a high-power mid-IR OPA," Appl. Phys. Lett. **110**, 061101 (2017).
- ¹⁹S. Gholam-Mirzaei, J. E. Beetar, A. Chacón, and M. Chini, "High-harmonic generation in ZnO driven by self-compressed mid-infrared pulses," J. Opt. Soc. Am., B 35, A27–A31 (2018).
- ²⁰G. Vampa, B. Ghamsari, S. S. Mousavi, T. Hammond, A. Olivieri, E. Lisicka-Skrek, A. Y. Naumov, D. Villeneuve, A. Staudte, P. Berini *et al.*, "Plasmonenhanced high-harmonic generation from silicon," Nat. Phys. **13**, 659–662 (2017).
- ²¹G. Vampa, H. Liu, T. F. Heinz, and D. A. Reis, "Disentangling interface and bulk contributions to high-harmonic emission from solids," Optica 6, 553–556 (2019).
- ²²D. Baykusheva, A. Chacón, D. Kim, D. E. Kim, D. A. Reis, and S. Ghimire, "Strong-field physics in three-dimensional topological insulators," Phys. Rev. A 103, 023101 (2021).
- ²³M. Sivis, M. Taucer, G. Vampa, K. Johnston, A. Staudte, A. Y. Naumov, D. Villeneuve, C. Ropers, and P. Corkum, "Tailored semiconductors for high-harmonic optoelectronics," Science 357, 303–306 (2017).
- ²⁴D. Franz, S. Kaassamani, D. Gauthier, R. Nicolas, M. Kholodtsova, L. Douillard, J.-T. Gomes, L. Lavoute, D. Gaponov, N. Ducros *et al.*, "All semi-conductor enhanced high-harmonic generation from a single nanostructured cone," Sci. Rep. **9**, 5663 (2019).
- ²⁵D. Gauthier, S. Kaassamani, D. Franz, R. Nicolas, J.-T. Gomes, L. Lavoute, D. Gaponov, S. Février, G. Jargot, M. Hanna *et al.*, "Orbital angular momentum from semiconductor high-order harmonics," Opt. Lett. **44**, 546–549 (2019).
- ²⁶J. P. Torres and L. Torner, Twisted Photons: Applications of Light with Orbital Angular Momentum (John Wiley & Sons, 2011).
- ²⁷F. Brandi, F. Giammanco, and W. Ubachs, "Spectral redshift in harmonic generation from plasma dynamics in the laser focus," Phys. Rev. Lett. **96**, 123904 (2006).
- ²⁸X.-B. Bian and A. D. Bandrauk, "Spectral shifts of nonadiabatic high-order harmonic generation," Appl. Sci. 3, 267–277 (2013).

Applied Physics Letters

ARTICLE

scitation.org/journal/apl

- ²⁹H. Du, S. Xue, H. Wang, Z. Zhang, and B. Hu, "Nonadiabatic spectral redshift of high-order harmonics with the help of a VUV pulse," Phys. Rev. A 91, 063844 (2015).
- ³⁰X.-B. Bian and A. D. Bandrauk, "Nonadiabatic molecular high-order harmonic generation from polar molecules: Spectral redshift," Phys. Rev. A 83, 041403 (2011).
- ³¹X.-B. Bian and A. D. Bandrauk, "Probing nuclear motion by frequency modulation of molecular high-order harmonic generation," Phys. Rev. Lett. 113, 193901 (2014).
- ³²G.-R. Jia, X.-H. Huang, and X.-B. Bian, "Nonadiabatic redshifts in high-order harmonic generation from solids," Opt. Express 25, 23654–23662 (2017).
- ³³Y. W. Kim, T.-J. Shao, H. Kim, S. Han, S. Kim, M. Ciappina, X.-B. Bian, and S.-W. Kim, "Spectral interference in high harmonic generation from solids," ACS Photonics 6, 851–857 (2019).
- ³⁴J. Lu, E. F. Cunningham, Y. S. You, D. A. Reis, and S. Ghimire, "Interferometry of dipole phase in high harmonics from solids," Nat. Photonics 13, 96–100 (2019).
- ³⁵G. Vampa, J. Lu, Y. S. You, D. R. Baykusheva, M. Wu, H. Liu, K. J. Schafer, M. B. Gaarde, D. A. Reis, and S. Ghimire, "Attosecond synchronization of extreme ultraviolet high harmonics from crystals," J. Phys. B: At., Mol. Opt. Phys. 53, 144003 (2020).
- ³⁶J. Li, J. Lu, A. Chew, S. Han, J. Li, Y. Wu, H. Wang, S. Ghimire, and Z. Chang, "Attosecond science based on high harmonic generation from gases and solids," Nat. Commun. 11, 2748 (2020).
- ³⁷S. Ghimire, A. D. DiChiara, E. Sistrunk, G. Ndabashimiye, U. B. Szafruga, A. Mohammad, P. Agostini, L. F. DiMauro, and D. A. Reis, "Generation and propagation of high-order harmonics in crystals," Phys. Rev. A 85, 043836 (2012).
- ³⁸I. Kilen, M. Kolesik, J. Hader, J. V. Moloney, U. Huttner, M. K. Hagen, and S. W. Koch, "Propagation induced dephasing in semiconductor high-harmonic generation," Phys. Rev. Lett. **125**, 083901 (2020).
- ³⁹G. Vampa, Y. You, H. Liu, S. Ghimire, and D. Reis, "Observation of backward high-harmonic emission from solids," Opt. Express 26, 12210–12218 (2018).

- ⁴⁰S. Yamada and K. Yabana, "Determining the optimum thickness for high harmonic generation from nanoscale thin films: An ab initio computational study," Phys. Rev. B 103, 155426 (2021).
- ⁴¹M. Uemoto, S. Kurata, N. Kawaguchi, and K. Yabana, "First-principles study of ultrafast and nonlinear optical properties of graphite thin films," Phys. Rev. B 103, 085433 (2021).
- ⁴²M. A. Bandres and J. C. Gutiérrez-Vega, "Ince-gaussian beams," Opt. Lett. 29, 144-146 (2004).
- ⁴³N. Garejev, I. Gražulevičiūtė, D. Majus, G. Tamošauskas, V. Jukna, A. Couairon, and A. Dubietis, "Third-and fifth-harmonic generation in transparent solids with few-optical-cycle midinfrared pulses," Phys. Rev. A 89, 033846 (2014).
- ⁴⁴G, Yi, H. Lee, J. Jiannan, B. J. Chun, S. Han, H. Kim, Y. W. Kim, D. Kim, S.-W. Kim, and Y.-J. Kim, "Nonlinear third harmonic generation at crystalline sapphires," Opt. Express 25, 26002–26010 (2017).
- ⁴⁵J. Seres, E. Seres, C. Serrat, and T. Schumm, "Non-perturbative generation of duv/vuv harmonics from crystal surfaces at 108 mhz repetition rate," Opt. Express 26, 21900–21909 (2018).
- ⁴⁶S. Odoulov, A. Shumelyuk, H. Badorreck, S. Nolte, K.-M. Voit, and M. Imlau, "Interference and holography with femtosecond laser pulses of different colours," Nat. Commun. 6, 5866 (2015).
- ⁴⁷A. Couairon, L. Sudrie, M. Franco, B. Prade, and A. Mysyrowicz, "Filamentation and damage in fused silica induced by tightly focused femtosecond laser pulses," Phys. Rev. B 71, 125435 (2005).
- ⁴⁸E. Yablonovitch, "Self-phase modulation and short-pulse generation from laser-breakdown plasmas," Phys. Rev. A 10, 1888 (1974).
- ⁴⁹S. Wilks, J. Dawson, and W. Mori, "Frequency up-conversion of electromagnetic radiation with use of an overdense plasma," Phys. Rev. Lett. 61, 337 (1988).
- ⁵⁰W. M. Wood, C. Siders, and M. Downer, "Measurement of femtosecond ionization dynamics of atmospheric density gases by spectral blueshifting," Phys. Rev. Lett. 67, 3523 (1991).
- ⁵¹M. Hussain, S. Kaassamani, T. Auguste, W. Boutu, D. Gauthier, M. Kholodtsova, J. Gomes, L. Lavoute, D. Gaponov, N. Ducros *et al.*, "Spectral control of high order harmonics through non-linear propagation effects," arXiv:2103.11479 (2021).





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OPTICAL PHYSICS

Lithium fluoride detectors for high spatial resolution imaging of tabletop XUV from high harmonic generation in gases

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As high harmonic generation (HHG) sources have proliferated, the need for high resolution, affordable extreme ultraviolet (XUV) detectors has become ubiquitous. We studied lithium fluoride (LiF) crystals, traditionally used for x rays, as a detector for a tabletop XUV source from high harmonic generation in gases. The LiF response curve showed a dynamic range of 10^3 (not saturated), with a minimum threshold fluence of 66μ J/cm². Imaging tests were performed revealing sub-micrometer spatial resolution. We successfully recorded a scan of the focal plane of a Fresnel zone plate with high dynamic range. With this study, we showed that LiF can be used as a detector for HHG XUV, with a high potential to do near field imaging of complex objects such as the focus of structured light. © 2021 Optical Society of America

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1. INTRODUCTION

High resolution imaging with soft x rays is a very promising route for wide-field microscopy with nanometer resolution. With recently developed high repetition rate, high average power tabletop laser technology, extreme ultraviolet (XUV) sources from high harmonic generation (HHG) have become widespread [1]. One barrier to the uptake of XUV radiation imaging is the difficulty in detection. Soft x ray detectors are fragile and expensive equipment, limiting use of XUV diagnostics in laser laboratories.

An ideal detector has high sensitivity, small pixel size, and a large dynamic range. Spatial resolution is typically dependent both on the optics and detection systems. In the case of lensless imaging, pixel resolution and detector size are key limiting factors. Typical XUV sensors [2] are limited in pixel size, while older technology of XUV films is limited by the grain size of the Ag emulsion ($\sim \mu m$). Their poor sensitivity and small dynamic range caused them to be abandoned in favor of charge coupled devices (CCDs) [3].

The difficulty in XUV detection comes from the small absorption length in most materials, requiring use of back-thinned solid state photodetector material. For back-thinned CCDs, the smallest pixel is around 10 μ m. However, thanks to their high sensitivity and high quantum efficiency, an individual photon counting is possible in each pixel, which drives the widespread use of CCDs. Methods to bypass this limitation in

pixel size have been designed to decrease numerically the pixel size using sub-pixel displacements of the detection chip for super-resolution [4].

In recent years an alternative detection method has been proposed and demonstrated for x ray imaging. This method consists on the creation of color centers (CCs) in lithium fluoride (LiF) crystals [2,5,6]. The simplest CCs are point defects where anion vacancies are filled by electrons. These defects, and more complex ones, can be produced by irradiating the crystals with ionizing radiation, such as x rays. For imaging applications, only F2 and F_3^+ CCs are relevant [2]. Once these types of CCs are created in LiF crystals, they are stable for long periods of time (at room temperature) and can be observed easily with an optical microscope since they have an absorption band around 450 nm and emit in the visible spectra (F2 around 680 nm and F_3^+ around 540 nm).

Since these pioneering studies, LiF crystals were used as a detector in large-scale x ray facilities such as XFEL at Riken [7], where single-shot measurements were made thanks to the high peak brightness of the source. There are some key differences when considering typical x ray and HHG sources. Harmonics are generated with ultrashort pulses, and CC temporal response has shown dependence on the source pulse width. It has been demonstrated [6] that F2 CCs are predominant for continuous or nanosecond pulse duration whereas F_3^+ are predominant for femtosecond soft X ray pulses. This temporal dependence

also seems to dictate the minimum threshold fluence for image recording on LiF, which apparently is much smaller for picoand femtosecond pulse width sources, with a 10 μ J/cm² threshold reported for a 100 fs source [6] and 70 μ J/cm² reported for 7 ps [8].

The first demonstration of the usage of LiF for HHG was reported in [9], using relativistic HHG in the range of 80– 150 eV. While the relatively low signal-to-noise ratio due to the XUV energy per shot and source stability was not enough to demonstrate high resolution imaging, this study showed single-shot acquisition was possible in the XUV.

Here, we have investigated LiF crystals as a detector for a tabletop XUV source from HHG in gases. We have studied the response of LiF, specifically F_3^+ type CCs, to XUV radiation in terms of its dynamic range and imaging capability using contact masks and diffractive optics [Fresnel zone plate (FZP)]. We found LiF to be suitable for the XUV HHG source since the minimum threshold fluence was of 66 μ J/cm².

2. EXPERIMENTAL SETUP

We used a commercial Ti:sapphire laser to obtain IR pulses at 800 nm of 35 fs duration at 1 kHz repetition rate. The IR was focused by a lens (focal length of 75 cm) at a gas cell filled



Fig. 1. (a) and (b) Fluorescence images taken by the Leica TCS-SP5 confocal optical microscope in fluorescence mode of the LiF crystal exposed at XUV radiation through a contact copper mesh. Gray regions are the luminescent areas where active CCs have been generated by the EUV radiation produced by 3.6×10^6 shots of HHG in Ar at 11 mbar (fluence of 6.5 mJ/cm^2); the black regions represent the shadow of the mesh having a period of $125 \,\mu\text{m}$. (c) Fluorescence image of a recorded mesh square where the diffraction pattern is visible, taken with Zeiss LSM 710, with objective Plan-Apochromat $63 \times /1.40$ Oil DIC M27 (~200 nm resolution). The XUV irradiation conditions are the same as in (a) and (b) images. (d) Profile from the region marked in (c). (e) Zoom in of the profile with a diffraction pattern with a minimum FWHM of 600 nm. (f) Setup for LiF response calibration.

with argon (Ar) at 11–14 mbar. The generated high harmonics (HHs) were directed straight to a vacuum chamber while the remaining IR was blocked by two aluminum filters (150 nm Al). The HHG spectrum comprises wavelengths between 27.6 and 47.1 nm, corresponding to harmonics orders between 29th to 17th.

The LiF samples consisted in a UV grade LiF crystal with a diameter of 25.4 mm and thickness of 3 mm. The CCs were observed using confocal microscopes with an Ar excitation laser of 458 nm and spectral detection interval between 470 and 650 nm, in order to detect the F_3^+ CC. We used the Leica TCS SP5 confocal microscope to acquire most of the images presented in this work. The detection system of this microscope consist of an 8-bit hybrid photodetector (HyD). A different confocal microscope—Zeiss LSM 710 with an 8-bit photomultiplier tube (PMT) detector was used to acquire higher resolution images.

For the LiF response analysis, the crystal was mounted on vacuum motors, recording each irradiation in a different position in the crystal. Copper gratings with 125 μ m pitch (hole 85 μ m, bar 40 μ m) and 20 μ m thickness were loosely mounted on the surface of this crystal so that we could identify clearly each irradiation position, as represented in Fig. 1(f).

We used the same HHG and confocal microscope acquisition setups to image the focus of a FZP lens. The lens was fabricated in 100 nm gold (Au) and 10 nm chromium (Cr) layers on top of a 30 nm silicon nitride (Si₃N₄) membrane and was designed to have 612 zones, an outermost zone width of 340 nm, a diameter of 800 μ m, and a nominal focal distance of 8.15 mm at 32 nm.

3. LIF RESPONSE TO XUVS FROM HIGH HARMONIC GENERATION

We performed the LiF response calibration by irradiating copper gratings with increasing XUV fluence, obtained with increasing the number of shots from 5×10^4 to 3.6×10^6 . The HHG energy was estimated from the number of counts obtained in the CCD for one shot, for which we obtained 2 ± 1 nJ/cm²/shot. The resulting photoluminescence (PL) intensities, represented in Fig. 2 as "grid calibration," were measured by averaging the



Fig. 2. Photoluminescence intensity dependence (at $\lambda = 458$ nm) from the fluence of HHG beam irradiation. We calculated the uncertainty in fluence based on the minimum and maximum HHG energy observed at the laboratory. The uncertainty in PL is larger for FZP focus points due to the high standard deviation in each area caused by the beam profile. All the PL intensities were obtained with Leica TCS-SP5.



Fig. 3. (a) Schematic of the experimental setup of LiF crystal illumination by XUV radiation focused by a FZP. Here is also represented the superposition of the nondiffracted (zero-order) radiation on the LiF crystal. (b)–(d) Images obtained on LiF of the PL intensity distribution of the XUV beam near the FZP focus position for each of the harmonics (artificially colored). Scan positions are relative to the distance between the lens and crystal (z = 0 mm corresponds to the lens position). Scan position z = 7 mm obtained with 9×10^5 shots, and the rest obtained with 3×10^5 shots. The confocal fluorescent microscope Leica TCS SP5 was used for the readout process with a $10 \times$ magnification objective (± 700 nm resolution). For each image we optimized the acquisition conditions in order to not saturate the peak intensity. (e) Schematic of the HHG near the focus positions of the three strongest harmonics—HH₂₁, HH₂₅—whose focus is represented by f_{21} , f_{25} , f_{25} , respectively.

counts inside each grid square. As it is shown in Fig. 1(a), the intensity profile is not homogeneous, so for each irradiation we measured the intensities in the brightest and most uniform area [Fig. 1(b)].

The PL intensities measured from the FZP focus imaging were added to the plot in Fig. 2 to complement the fluence range. The FZP focus points correspond to the intensities measured for each focused harmonic at different positions along the beam path as it is shown in the next section in Fig. 3. The 0th order points, in the low fluence range of the plot, correspond to the intensities measured in the zero-order images (Fig. 4).

While the direct irradiation fluence was obtained by direct comparison with CCD signal, the fluence after the FZP was calculated by taking into account the well-known transmission efficiencies for each diffraction order and the Si_3N_4 membrane transmission, as well as the focusing effect and energy percentage of each harmonic in the case of focused radiation.

It was reported in [6] that the LiF response curve for soft x rays follows a square root law. The data from the grids calibration



Fig. 4. (a) PL image of the LiF irradiated area. In the center we can distinguish the images for each scan position (we repeated some of the scan positions, hence there are seven visible "focus") saturated due to the high exposure on microscope. (b) Schematic of the areas irradiated due to 0th order transmission and their superpositions.

does not have enough fluence range to confirm this behavior. Considering the addition of the data from the FZP focus imaging, it seems that the LiF response is following a square root behavior. However, we must note that the intensities measured in the focus images have too much uncertainty to provide a strong conclusion about the LiF response.

Nevertheless, these results showed that we did not reach saturation of the crystal, which is also in accordance with other reports where for similar sources a saturation was not achieved even for fluence values as high as 260 mJ/cm^2 [6]. The data from the focus images showed also that we could see images with lower fluence, where we have observed a minimum required fluence of $66 \mu \text{J/cm}^2$.

All of the PL intensities present in Fig. 2 were obtained with the Leica TCS-SP5 confocal optical microscope with the acquisition conditions described in Section 2. However, due to the low 8-bit dynamic range of the readout system, some images were acquired with different exposures, and then the intensities were scaled to the same conditions.

4. IMAGING HHG USING LIF

A. Wide Field Imaging with High Resolution

Figure 1 shows the images of one of the calibration grids irradiated with 3.6×10^6 shots. In these images we observed interference fringes on the edges of the squares. Since HHG is a highly coherent source, edge diffraction occurs, and due to the nonperfect contact between the grid and the crystal surface these patterns appeared [10].

The minimum feature observed in these patterns had a FWHM of 600 nm, which corresponds to a distance of around 200 μ m between the grid and the surface. Note that the confocal microscope resolution was ~200 nm [2]. With this imaging

test, we verified that, as expected, our source could produce large field images with high spatial resolution in LiF.

B. Direct Detection of Zone Plate Micro-focus

FZP lenses are widely used with soft x ray radiation, but usually it is difficult to image the focus of these lenses for several reasons. With soft x rays, the focus length is usually very short, so it is difficult to place a detector such as a CCD near the focus plane. Besides this, their large pixel size makes it difficult to image the focus points, which is often smaller than the pixel size of the CCDs. LiF crystals have been used to image soft X ray focus [8], but to our knowledge LiF has never been used to image the focus of FZP lenses in XUV.

In this work we used a LiF crystal to image the focus of a FZP lens. We scanned the beam path near the region where we could find the focus of each strongest harmonics with orders: 21st, 23rd, and 25th, represented by HH21, HH23, and HH25 with focus at $f_{21} = 7$ mm, $f_{23} = 7.6$, and $f_{25} = 8.2$ mm, respectively. The harmonics have 600 µm separation between each focus, so we recorded five different positions moving the LiF crystal along the z axis with 300 μ m and 600 μ m of step size, with a total distance of 1.2 mm. Hence, we recorded images for scan positions z = 7, 7.6, 7.9, 8.2, and 8.8 mm (distance from FZP lens). The initial scan position was determined by measuring the distance between LiF crystal and lens, and the rest were determined by the vacuum motor step size. This represents a low precision for the initial scan position (\sim 500 µm) and a much higher precision between each scan position ($\sim 1 \, \mu m$, from vacuum motor precision).

We estimated the exposure time from the results obtained with the grid irradiations, where we concluded the minimum exposure time to provide a fluence sufficient to separate the signal from the background noise was equivalent to 5×10^5 shots. As the beam focusing results in a much higher fluence, we irradiated each position with 3×10^5 shots. In order to obtain a brighter and easier-to-detect PL pattern, we repeated in a "*L*" shape scan position with z = 7 mm with a $3 \times$ higher number of shots of 9×10^5 . Between each irradiation we also moved the LiF crystal in *x* and *y* directions [Fig. 3(a)], keeping an interval of 200 µm between the centers of each image.

In the sequence of images presented in Figs. 3(b)-3(d), we can distinguish different levels of PL intensities. In the center of each image, we can see brighter regions that correspond to the focus of each harmonic. Around these centers we can observe disks with lower PL intensities, which correspond to the harmonics out of focus on that scan position, as represented in Fig. 3(e). Therefore, in Fig. 3(b), HH₂₁ focus is visible in the center, and the disk around this center corresponds to HH_{23} . In Fig. 3(c), HH₂₃ is in focus, the disk around this center corresponds to HH₂₁ and HH₂₅, and, with much lower PL intensity, a second disk is visible with a larger diameter corresponding to HH₂₇. In Fig. 3(d), HH₂₅ is in focus, and around the peak there is a smaller disk (indistinguishable) corresponding to HH₂₃ and HH₂₇ and then a larger disk from HH₂₁. In order to verify the measured scan positions, all the disk and focus sizes were compared to the theoretically expected values, and the PL intensities from each harmonic were compared to the relative intensity of each harmonic in the HHG spectrum. With this comparison we

concluded that the scan positions had a small offset of ${\sim}50~\mu m$ from the real focus positions.

The focus spot produced by this FZP lens has a minimum diameter of 1.6 μ m (independent of the wavelength). We detected a minimum focus size with FWHM of 2.45 μ m for the scan position z = 7.6 mm, which corresponds to the focus position of 23rd harmonic. We would like to stress that in contrary to experiments with hard x rays [7], here the attenuation length of the harmonics inside the LiF crystal is around 20 nm. Since the lens depth of focus is 7 μ m, we can neglect the beam propagation inside the crystal. Taking this into account, we can conclude that the difference between the expected focus size and the recorded one is due to the small offset of the scan position.

Figure 4(a) shows the images of the nondiffracted (zeroorder) radiation transmitted through the FZP lens. In the middle we can see the focused images for each position of scan. These centers appear saturated in this image because the microscope was set to a high exposure mode so that the zero orders are visible. As illustrated in Fig. 4(b), some areas of the zero-order images are superimposed. The zero orders correspondent to the scan positions with 3×10^5 shots are not visible in Fig. 4 because their exposure time was 3 times smaller than the one used for scan position z = 7 mm.

C. Dynamic Range

Besides resolution and sensor size, a key feature of a detector is its dynamic range. A detector with a large dynamic range allows for a high γ of detection, enabling the imaging of multiple phenomena with different intensities at the same time. LiF crystals have demonstrated high dynamic ranges; however, in this work, we were limited by the dynamic range of the microscope readout system of only 8 bit. This limitation can be surpassed by using different conditions of the confocal microscope [11], such as different values for the laser output power, detector gain, and acousto-optic tunable filter (AOTF).

The plot in Fig. 5 shows the minimum and maximum of PL detected for the scan position of z = 7 mm. We used three different AOTFs and laser output power values and kept all



Fig. 5. Lineout (a) and (b) shown in Fig. 4, combining different microscope conditions that show the minimum and maximum photoluminescence along the beam profile. AOTF 60 corresponds to the lowest exposure and AOTF 86 to the highest. On the left side, marked with 1, 2, 3, we can see the limits of each plateau corresponding to the areas illuminated with $1 \times 2 \times 3 \times 4 \times 2$ zero orders, as seen in Fig. 4.

the other acquisition parameters constant. In the center we can see the peak originated by the focusing of the 21st harmonic ($\lambda = 38.1$ nm) on top of a flat plateau originated from the superposition of four zero-order images as shown in the Fig. 4(b). As can be seen in the zoom of the peak, with different microscope exposures, we can distinguish features that were previously saturated and indistinguishable.

In this plot, the calculated fluence values for each zerothorder plateau are also represented; the disk originated from the HH₂₃, and the peak originated from the focus of the HH₂₁. The minimum fluence detected was 95 μ J/cm² from one 0th order (marked in the plot with 1), and the maximum fluence detected was ~100 mJ/cm² for the focus point, which corresponds to a total dynamic range of ~10³.

From the results in this experiment, we consider that this dynamic range is underestimated since it appears that the LiF crystal did not saturate. We can then presume that if higher intensities were achieved we could still discriminate them in this crystal.

5. CONCLUSION

In this work we showed that LiF crystals can be effectively used as an XUV detector for the gas based HHG tabletop sources, allowing an accessible imaging method with high spatial resolution for these widely available sources.

The LiF crystal response curve showed that the minimum XUV fluence required was bellow 100 μ J/cm², and we observed PL intensities for a maximum fluence around 100 mJ/cm² without any sign of saturation in the crystal. These values translate into a large dynamic range in the LiF crystal of 10³. Since there was no saturation, we can presume that this crystal is capable of larger dynamic ranges, at least of 10⁴ as reported by [6]. We note that most modern confocal microscopes already have a 16-bit readout system that facilitates the PL measurements.

As imaging tests, we analyzed a grating diffraction pattern recorded in the LiF where the minimum feature size observed was around 600 nm and recorded the beam structure around the focal plane of a FZP.

With these tests we were not able to demonstrate the viability of single-shot imaging with LiF for our source. In fact we only used long exposure times, which are equivalent to more than 10⁵ shots. Nevertheless, LiF crystals still provide a high resolution detector for near field imaging, which is very promising for the study of structured light, such as beams with orbital angular momentum.

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Data Availability. Data underlying the results presented in this paper are not publicly available at this time but may be obtained from the authors upon reasonable request.

REFERENCES

- J. Li, J. Lu, A. Chew, S. Han, J. Li, Y. Wu, H. Wang, S. Ghimire, and Z. Chang, "Attosecond science based on high harmonic generation from gases and solids," Nat. Commun. 11, 2748 (2020).
- G. Baldacchini, S. Bollanti, F. Bonfigli, F. Flora, P. Di Lazzaro, A. Lai, T. Marolo, R. M. Montereali, D. Murra, A. Faenov, T. Pikuz, E. Nichelatti, G. Tomassetti, A. Reale, L. Reale, A. Ritucci, T. Limongi, L. Palladino, M. Francucci, S. Martellucci, and G. Petrocelli, "Soft x-ray submicron imaging detector based on point defects in LiF," Rev. Sci. Instrum. 76, 113104 (2005).
- S. M. Gruner, M. W. Tate, and E. F. Eikenberry, "Charge-coupled device area x-ray detectors," Rev. Sci. Instrum. 73, 2815–2842 (2002).
- A. Lübcke, J. Braenzel, A. Dehlinger, M. Schnürer, P. Guttmann, S. Rehbein, G. Schneider, S. Werner, R. Kemmler, S. Ritter, M. Raugust, T. Wende, M. Behrendt, and M. Regehly, "Soft X-ray nanoscale imaging using a sub-pixel resolution charge coupled device (CCD) camera," Rev. Sci. Instrum. 90, 043111 (2019).
- G. Tomassetti, A. Ritucci, A. Reale, L. Palladino, L. Reale, L. Arrizza, G. Baldacchini, F. Bonfigli, F. Flora, L. Mezi, R. Montereali, S. Kukhlevsky, A. Faenov, T. Pikuz, and J. Kaiser, "High-resolution imaging of soft-X-ray laser beam by color-centers excitation in lithium fluoride crystals," Europhys. Lett. 63, 681–686 (2003).
- T. Pikuz, A. Faenov, Y. Fukuda, M. Kando, P. Bolton, A. Mitrofanov, A. Vinogradov, M. Nagasono, H. Ohashi, M. Yabashi, K. Tono, Y. Senba, T. Togashi, and T. Ishikawa, "Optical features of a LiF crystal soft x-ray imaging detector irradiated by free electron laser pulses," Opt. Express 20, 3424–3433 (2012).
- T. Pikuz, A. Faenov, T. Matsuoka, S. Matsuyama, K. Yamauchi, N. Ozaki, B. Albertazzi, Y. Inubushi, M. Yabashi, K. Tono, Y. Sato, H. Yumoto, H. Ohashi, S. Pikuz, A. N. Grum-Grzhimailo, M. Nishikino, T. Kawachi, T. Ishikawa, and R. Kodama, "3D visualization of XFEL beam focusing properties using LiF crystal X-ray detector," Sci. Rep. 5, 17713 (2015).
- A. Y. Faenov, Y. Kato, M. Tanaka, T. A. Pikuz, M. Kishimoto, M. Ishino, M. Nishikino, Y. Fukuda, S. V. Bulanov, and T. Kawachi, "Submicrometer-resolution *in situ* imaging of the focus pattern of a soft x-ray laser by color center formation in LiF crystal," Opt. Lett. 34, 941–943 (2009).
- T. Pikuz, A. Faenov, A. Pirozhkov, A. Astapov, G. Klushin, S. Pikuz, N. Nagorskiy, S. Magnitskiy, T. Esirkepov, J. Koga, T. Nakamura, S. Bulanov, Y. Fukuda, Y. Hayashi, H. Kotaki, Y. Kato, and M. Kando, "High performance imaging of relativistic soft X-ray harmonics by sub-micron resolution lif film detectors," Phys. Status Solidi C 9, 2331–2335 (2012).
- T. A. Pikuz, A. Y. Faenov, Y. Fukuda, M. Kando, P. Bolton, A. Mitrofanov, A. V. Vinogradov, M. Nagasono, H. Ohashi, M. Yabashi, K. Tono, Y. Senba, T. Togashi, and T. Ishikawa, "Soft x-ray free-electron laser imaging by lif crystal and film detectors over a wide range of fluences," Appl. Opt. 52, 509–515 (2013).
- P. Mabey, B. Albertazzi, T. Michel, G. Rigon, S. Makarov, N. Ozaki, T. Matsuoka, S. Pikuz, T. Pikuz, and M. Koenig, "Characterization of high spatial resolution lithium fluoride X-ray detectors," Rev. Sci. Instrum. **90**, 063702 (2019).

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High-harmonic generation wave front dependence on a driving infrared wave front

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With high-harmonic generation (HHG), spatially and temporally coherent XUV to soft x-ray (100 nm to 10 nm) table-top sources can be realized by focusing a driving infrared (IR) laser on a gas target. For applications such as coherent diffraction imaging, holography, plasma diagnostics, or pump-probe experiments, it is desirable to have control over the wave front (WF) of the HHs to maximize the number of XUV photons on target or to tailor the WF. Here, we demonstrate control of the XUV WF by tailoring the driving IR WF with a deformable mirror. The WFs of both IR and XUV beams are monitored with WF sensors. We present a systematic study of the dependence of the aberrations of the HHs on the aberrations of the driving IR laser and explain the observations with propagation simulations. We show that we can control the astigmatism of the HHs by changing the astigmatism of the driving IR laser without compromising the HH generation efficiency with a WF quality from $\lambda/8$ to $\lambda/13.3$. This allows us to shape the XUV beam without changing any XUV optical element. @ 2020 Optical Society of America

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1. INTRODUCTION

Radiation with wavelengths of 10 nm to 100 nm, also known as extreme ultraviolet (XUV), can be generated in a table-top setup by focusing a driving infrared (IR) laser on a gas target. This process known as high-harmonic generation (HHG) produces spatially and temporally coherent pulses that are used to perform coherent diffraction imaging [1,2], holography [3,4], plasma diagnostics [5,6], or pump–probe experiments for sub-femtosecond microscopy to study ultra-fast processes [7,8].

For the most demanding applications, it is desirable to have control over the wave front (WF) of the HHs to maximize the number of XUV photons on target. A flat WF would allow tight focusing on target, and a deformed WF would allow to adapt the beam to a favorable shape on target. The use of additional XUV optics such as mirrors in grazing incidence would introduce losses to the signal. Adaptive XUV optics are technically very challenging and expensive [9] and therefore implemented only at facilities such as synchrotrons or with free-electron lasers. An alternative to reflective optics and diffractive Fresnel zone plates in the XUV was recently developed by Drescher *et al.* [10] and Quintard *et al.* [11] using a density gradient in a gas jet to create a deformable refractive lens with low absorption. The losses inherent to XUV optics could be avoided if the generated XUV beam could be shaped in the required way during its generation process. Instead of using challenging gas jet systems or adaptive XUV optics under grazing incidence to shape the HHs under high losses, our approach is to imprint the WF aberrations in the IR using a deformable mirror (DM).

Yoshitomi *et al.* [12] used for the first time a DM to control the WF of a high-repetition IR driving laser to optimize the phase-matching conditions and therefore enhance the signal of the HHs. Wang *et al.* [13] recently used a DM to reduce the driving IR laser WF root-mean-square (rms) deformation to $\lambda/32$ [measured with a Shack–Hartmann WF sensor (WFS)].

An imprinting of an astigmatism from the driving IR to the generated HHs was found by Gautier *et al.* [14]. Valentin *et al.* [15] changed the astigmatism at 0°/90° of the driving high-repetition IR laser and measured the WF of the HHs and IR with a Hartmann and a Shack–Hartmann sensor, respectively. A minimization of the HH rms deformation was achieved with a spurious astigmatism in the IR still present, not with the astigmatism minimized. They were able to reduce the rms of the HHs down to $\lambda/7$, twice the diffraction limit.

Dacasa *et al.* [16] were recently able to achieve a WF quality of up to $\lambda/11$ of single-shot high-order harmonics by reducing the rms deformations of the driving IR laser. They observed an astigmatic HH WF (rms = $\lambda_{HH}/11$) at 0° with the IR WF (rms = $\lambda_{IR}/53$) having an astigmatism at 45°. However, so far, no systematic study has shown direct correlations between the IR and the XUV WFs. The main interest of studies so far has been to achieve the flattest WF possible by correcting the aberrations.

In this work, we present a systematic study of the dependence of the aberrations of the HHs on the aberrations of the driving IR laser. We show that we can control the astigmatism of the HHs by changing the astigmatism of the driving IR laser while keeping the HH photon number controlled within 20% depending on the chosen astigmatism, furthering the capability of all optical control of XUV WFs.

2. EXPERIMENTAL SETUP

A sketch of the experimental setup is shown in Fig. 1 and described in the following. The commercial Ti:sapphire laser system Astrella by Coherent, Inc. generates IR pulses at 800 nm of 35 fs duration at 1 kHz repetition rate with energies of 7.5 mJ per shot. An attenuator reduces them to 4.2 mJ. The IR beam is directed to a commercial DM with 40 piezo actuators produced by Thorlabs (model DMP40) with a 10 mm diameter and protected silver coating. The transmission of the DM is measured to be 83%. After passing an aperture with a diameter of 9.5 mm, the pulse has an energy of 2.6 mJ and is focused with a lens of 75 cm focal length at the downstream end of a gas cell that is 15 mm long. HHs in the XUV with a center wavelength of 32 nm are generated with argon gas at a pressure of 21 mbar. Two aluminum filters with a thickness of 300 nm block out the residual IR. We measure a superposition of all five HH orders present in our experiment. However, the individual WFs can differ from each other [11,17-20]. The WFs and intensities of both the HHs and IR laser are measured with WFSs built in partnership between Laser-Laboratorium Göttingen e.V. (LLG) and DESY [21]. The XUV WFS is placed 350 cm downstream of the gas cell. After each XUV acquisition, a wedge is inserted into the IR beam path downstream of the lens to deflect the beam towards the IR WFS. The fraction of ionization in

our experimental conditions being less than 1% [22], we can measure the IR beam WF before interaction.

The XUV WFS uses a Hartmann plate with 57 × 57 holes having diameters of 75 μ m and a pitch of 250 μ m, enabling a measurement of the WF to an accuracy of $\lambda/30$ [23]. The IR WFS has a WF resolution at 633 nm with an absolute accuracy of $\lambda/50$ to $\lambda/150$. A modal reconstruction of the WF with a Born–Wolf expansion of the Zernike coefficients is used (as described in ISO 15367 [24]). The analysis grid and circular aperture are set to contain intensities above 13.5% (1/ e^2) of the peak intensity in both IR and XUV.

The control software of the DM allows a manipulation of the IR WF by changing its Zernike coefficients. The WF rms of the IR beam is minimized manually. From this neutral setting, aberrations such as astigmatism, coma, and spherical aberration are introduced. The corresponding changes in the XUV WFs are recorded. With a shutter working at 1 Hz, the exposure times of a measurement of the IR WFS is set to 100 ms and for the XUV WFS to 400 ms to 500 ms. For the IR, an average of 30 measurements is recorded, and for the XUV, 30 measurements are recorded in sequence and later averaged.

3. RESULTS

Astigmatism as a lower-order aberration has a strong correlation between IR and XUV [Fig. 2(a)] translating with a factor of about 1:2.5.

Higher-order aberrations such as coma and spherical aberration do not show a clear correlation as in the case for astigmatism. The change of coma does not translate into the HHs [see Fig. 2(b)]. One can instead see an influence on the diagonal astigmatism [see Fig. 2(c)], although at a lower degree than for pure astigmatism.

Exemplary, we present the intensity and WF in the case of changing astigmatism $\pm 45^{\circ}$ in Fig. 3 and in the case of changing vertical coma in Fig. 4. Each figure shows a neutral setting of the DM labeled (B) in the center of the figure together with a most negative setting (C) below and a most positive setting (A) above. The leftmost and second to left columns show the averaged recorded normalized intensity and WF (normalized to the wavelength) for IR and XUV, respectively. The chosen aperture on the IR WFS has a diameter of 4.5 mm and on the XUV WFS of 10 mm. The color maps of the WF are normalized to $+0.2\lambda$



Fig. 1. Experimental setup in the VOXEL metrology station at IST/Lisbon (DM, deformable mirror; WFS, wave front sensor). Inset shows the HH spectrum of argon. Harmonic orders indicated on graph.



Fig. 2. Dependence of XUV aberrations on introduced IR aberrations for lower-order astigmatism and higher-order coma. The change of coma also influences astigmatism $\pm 45^{\circ}$. (a) Astigmatism, (b) coma, and (c) astigmatism $\pm 45^{\circ}$ versus coma.



Fig. 3. Astigmatism $\pm 45^{\circ}$ of the driving IR beam is changed. The generated HHs have similar aberrations. (A) Most positive setting of the DM leading to astigmatism $\pm 45^{\circ}$, (B) neutral setting of the DM, and (C) most negative setting creating astigmatism -45° . Leftmost column: averaged recorded intensity at the WFS (normalized to 1). Second to left column: averaged recorded WF at the WFS [normalized to $+0.2\lambda$ (red), -0.2λ (blue)], with $\lambda_{IR} = 800$ nm and $\lambda_{XUV} = 32$ nm. Aperture diameter on the IR-WFS is 4.5 mm and on the XUV-WFS 10 mm. Center and second to right columns: horizontal and vertical caustic around the gas cell end position. Beam direction is from left to right. The gas cell end is highlighted with white dashed lines. The height of the profiles is 300 µm. Rightmost column: Propagated intensity at the downstream end of the gas cell (300 µm × 300 µm). The IR color map is normalized to 10^{15} W cm⁻², and XUV intensity color map is normalized to 3.7×10^{16} counts cm⁻². Black and white contour lines represent 50% and 13.5% of the peak intensity, respectively. Yellow contour lines show 10^{14} W cm⁻² for the IR and 10^{14} counts cm⁻² for the XUV.

(red) and -0.2λ (blue) with $\lambda_{IR} = 800$ nm and $\lambda_{XUV} = 32$ nm. The center and second to right columns show the horizontal and vertical caustic along the gas cell position calculated using numerical Fresnel propagation [21,25] in a window of 300 $\mu m \times 300 \, \mu m.$ The caustic stretches from 10 mm upstream to 25 mm downstream of the gas cell end in step sizes of 0.5 mm, resulting in 72 images. The rightmost column shows the propagated intensity at the end of the gas cell for IR and XUV, respectively. Beam direction is from left to right. The gas cell end is highlighted with white dashed lines. The beam width was determined using $D4\sigma$ fits [26,27]. Under the assumption of a Gaussian beam, the corresponding peak intensity was calculated with the knowledge of the energy of the IR beam and the recorded counts on the XUV WFS in units of W cm⁻² and counts cm^{-2} , respectively. In order to compare the measurements, the color maps of the intensities are normalized to the same value. The IR color map is normalized to $10^{15} \,\mathrm{W \, cm^{-2}}$

and the XUV color map to 3.7×10^{16} counts cm⁻². Black and white contour lines represent 50% and 13.5% of the peak intensity, respectively. Yellow contour lines show 10^{14} W cm⁻² for the IR and 10^{14} counts cm⁻² for the XUV. The HH beam is approximately half as large as the driving IR beam. On average, the IR beam has a full width at half maximum (FWHM) of 71 µm and the XUV beam a FWHM of 36 µm at the end of the gas cell.

A. HHs Photon Number Dependence on Introduced Aberrations

Focusing an XUV beam can be achieved, for example, with mirrors in grazing incidence. A common configuration used is the Kirkpatrick–Baez mirror pair [28], where two line-foci are overlapped to produce a focus. A downside of this approach is that the focus is astigmatic. Pre-compensating the beam's



Fig. 4. Vertical coma of the driving IR beam is changed. The generated HHs show a change in astigmatism $\pm 45^{\circ}$ and only a weak change in vertical coma. (A) Most positive setting of the DM, (B) neutral setting of the DM, and (C) most negative setting. Leftmost column: averaged recorded intensity at the WFS (normalized to 1). Second to left column: averaged recorded WF at the WFS [normalized to $+0.2\lambda$ (red), -0.2λ (blue)], with $\lambda_{IR} = 800$ nm and $\lambda_{XUV} = 32$ nm. Aperture diameter on the IR-WFS is 4.5 mm and on the XUV-WFS 10 mm. Center and second to right columns: horizontal and vertical caustic around the gas cell position. Beam direction is from left to right. The gas cell end is highlighted with white dashed lines. The height of the profiles is 300 µm. Rightmost column: Propagated intensity at the downstream end of the gas cell (300 µm × 300 µm). The IR color map is normalized to 10^{15} W cm⁻², and XUV intensity color map is normalized to 3.7×10^{16} counts cm⁻². Black and white contour lines represent 50% and 13.5% of the peak intensity. Yellow contour lines show 10^{14} W cm⁻² for the IR and 10^{14} counts cm⁻² for the XUV.



Fig. 5. XUV photon number depending on rms deformation of the IR (red circles) and XUV beam (blue squares), respectively. The dashed line marks the rms deformation of a diffraction-limited beam according to Marcheal's criterion being $\lambda/14$. The XUV photon number is normalized to the neutral setting of the DM. (IR measurements do not have error bars because they were recorded as averages of 30 measurements. Unlike in the XUV case, there were no individual measurements recorded to calculate averages and corresponding errors.). (a) Astigmatism at 0°/90°, (b) astigmatism $\pm 45^{\circ}$, (c) vertical coma, and (d) horizontal coma.

aberrations by introducing an astigmatism in order to achieve a tight focus on target requires that it is not detrimental to the number of HH photons per shot. Maréchal's criterion [29] for a diffraction-limited beam says that the rms deformation of the WF has to be below $\lambda/14 = 0.071\lambda$. In the neutral setting (B), the XUV beam is close to diffraction limited with a rms deformation of $\lambda/10.2 \pm \lambda/200$ ((0.098 ± 0.005) λ) [Fig. 5(a)] and $\lambda/12.7 \pm \lambda/200$ ((0.079 ± 0.005) λ) [Fig. 5(b)]. When astigmatism at 0°/90° is introduced, the XUV photon number either does not change significantly [setting (C) in Fig. 5(a), with a rms deformation of $\lambda/8.62 \pm \lambda/56$] or even increases by $\sim 12\%$ [setting (A) in Fig. 5(a), with a rms deformation of $\lambda/9.34 \pm \lambda/91$]. Diagonal astigmatism leads to a reduction of the photon number of up to $\sim 20\%$ [setting (C) in Fig. 5(b), with a rms deformation of $\lambda/8 \pm \lambda/59$]. In the other setting (A), we lose less energy, although we have a worse rms deformation of $\lambda/7.24 \pm \lambda/200$). The maximum observed aberration coefficient of astigmatism without losing the HH photon number is about 0.4λ [Fig. 2(a)]. This corresponds to a Strehl ratio of 0.67 [30]. A pre-compensation of astigmatism with the DM to achieve a Strehl ratio of 1 would therefore allow an increase of the peak intensity of up to 50%.

Introducing coma to the IR beam can lead to higher photon number losses than for astigmatism. A change of coma in the negative direction (B)–(C) leads to a decrease in rms deformation for both horizontal and vertical comas and an increase in the photon number by ~ 5% [Fig. 5(d)] to ~ 15% [Fig. 5(c)]. In the positive direction (B)–(A), the photon number can drop by up to ~ 35%.

4. DISCUSSION

Our measurements clearly show strong correlations between HHs and IR for low-order aberrations such as astigmatism (as well as defocus and tilt), but not for higher-order ones.

A. HH Reconstruction from Recorded IR WF and Intensity

In order to understand why the IR beam's astigmatism is imprinted in the generated HHs but not the coma, we use a simple semi-classical model describing the generation of HHs. We reconstruct the HH intensity and WF from the recorded IR data. This approach was used recently by Dacasa *et al.* [16]. The IR field is propagated to a generation position z_G at the gas cell end where the field E_q of the q-th harmonic is approximated with the expression



Fig. 6. HH intensity and WF reconstruction from driving IR beam with astigmatism $\pm 45^{\circ}$. (A) Most positive setting of the DM leading to astigmatism at $+45^{\circ}$, (B) neutral setting of the DM, and (C) most negative setting creating astigmatism at -45° . First column: weighted sum of both intensity and phase according to the individual intensities in the spectrum. Second column: recorded data as comparison. The individual reconstructed harmonic signals are shown in the columns to the right. All images are on the same scale showing a window of 10 mm \times 10 mm.



Fig. 7. HH intensity and WF reconstruction from driving IR beam with vertical coma. (A) Most positive setting of the DM, (B) neutral setting of the DM and, (C) most negative setting. First column: weighted sum of both intensity and phase according to the individual intensities in the spectrum. Second column: recorded data as comparison. The individual reconstructed harmonic signals are shown in the columns to the right. All images are on the same scale showing a window of 10 mm \times 10 mm.

$$E_q(x, y, z_G) \propto |E(x, y, z_G)|^4 \exp[-i(q \cdot \phi + \phi_d)],$$
 (1)

with the phase being composed of q times the field ϕ of the driving IR beam and a dipole phase ϕ_d determined by the

inverse of the intensity $I(x, y, z_G)$ of the IR beam (for details, see [16]):

$$\phi_d(x, y, z_G) = \frac{\gamma_s (q - q_p)^2 \omega^2}{I(x, y, z_G)},$$
(2)

with $\gamma_s = 1.030 \times 10^{-18} \text{ s}^2 \text{ Wcm}^{-2}$, $q_p = I_p / \hbar \omega$, I_p : ionization potential of Argon, and ω : IR frequency.

The fields of harmonic orders 21-29 present under the experimental conditions are generated and propagated to the position of the XUV WFS. The spectrum was measured before (see inset in Fig. 1). The individual relative intensities of HH orders 21, 23, 25, 27, and 29 are 30%, 60%, 100%, 80%, and 20%, respectively. The first column in Figs. 6 and 7 shows the weighted sum of both intensity and phase according to the individual intensities in the spectrum. The second column shows the recorded data as comparison. The individual reconstructed harmonic signals are shown in the columns to the right. All images are on the same scale showing a window of 10 mm \times 10 mm. Figure 6 shows that we can successfully reproduce the measured intensities and shapes. The simulated HHs for IR beams with coma (Fig. 7) do not show any coma and confirm the measurements, given our experimental conditions.

In order to check other settings that could result in coma in HHs, we investigated various simulation conditions of the driving IR beam. We varied the intensity's shape, introduced flat-top beams, changed the beam's size and strengthened the coma values in the IR. We could not find any coma in the HHs. The nonlinear HH process acts as a filter for areas of higher intensity in the beam. Although the phase term in the exponential of Eq. (1) does affect the shape of the reconstructed WF as shown by Dacasa [16], we have identified the main filtering effect to be due to the E^4 dependence of the HH generation on the beam. Trimming the outer parts of the WF results in a shape resembling astigmatism, which we have observed [see Fig. 2(c)], effectively reducing the order of aberration.

5. CONCLUSION

We show that we can control the astigmatism of the HHs by changing the astigmatism of the driving IR laser with a change of the HH photon number of up to +12% and -20% with a WF quality from $\lambda/8$ to $\lambda/13.3$. Having control over the astigmatism of the XUV allows us to shape it to the individual requirements of each application. Elongated targets could be illuminated without the use of additional optics that would introduce losses or having to implement challenging gas jet systems. With a WF rms deformation of $\lambda/8 \pm \lambda/59$ close to Marcheal's criterion $\lambda/14$, the ability to change the astigmatism would allow to improve the focus and Strehl ratio of XUV optics in grazing incidence like Kirkpatrick-Baez mirror pairs. The observed Strehl ratio in the XUV for the strongest possible astigmatism was below 0.67. A pre-compensation of astigmatism with the DM would increase the peak intensity at the focus up to 50%.

We successfully demonstrate the manipulation of the WF and intensity of HHs by manipulation of the WF of the driving IR laser with a DM. In our experiment, astigmatism was particularly susceptible to control. No corresponding correlations can be found for higher-order aberrations such as coma. Instead, a correlation between coma and astigmatism exists, however minor. Propagation of the beam using a simple semi-classical HHG model confirms the observed aberrations in the XUV and can explain the observed effective aberration filter for higher orders due to the E^4 dependence of the HH generation on the driving IR beam.

Future work could entail the implementation of an adaptive closed-loop system between an XUV WFS and an IR DM with a finer control to produce beam shapes and WFs on target according to experiment needs with increased number of XUV photons.

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REFERENCES

- B. Chen, R. A. Dilanian, S. Teichmann, B. Abbey, A. G. Peele, G. J. Williams, P. Hannaford, L. Van Dao, H. M. Quiney, and K. A. Nugent, "Multiple wavelength diffractive imaging," Phys. Rev. A 79, 023809 (2009).
- H. N. Chapman and K. A. Nugent, "Coherent lensless x-ray imaging," Nat. Photonics 4, 833–839 (2010).
- D. Gauthier, M. Guizar-Sicairos, X. Ge, W. Boutu, B. Carré, J. R. Fienup, and H. Merdji, "Single-shot femtosecond x-ray holography using extended references," Phys. Rev. Lett. **105**, 093901 (2010).
- A.-S. Morlens, J. Gautier, G. Rey, P. Zeitoun, J.-P. Caumes, M. Kos-Rosset, H. Merdji, S. Kazamias, K. Cassou, and M. Fajardo, "Submicrometer digital in-line holographic microscopy at 32 nm with high-order harmonics," Opt. Lett. 31, 3095–3097 (2006).
- S. Dobosz, G. Doumy, H. Stabile, P. D'Oliveira, P. Monot, F. Réau, S. Hüller, and P. Martin, "Probing hot and dense laser-induced plasmas with ultrafast XUV pulses," Phys. Rev. Lett. 95, 025001 (2005).
- J.-F. Hergott, "XUV interferometry using high order harmonics: application to plasma diagnostics," in *Atoms, Solids, and Plasmas in Super-Intense Laser Fields* (Springer, 2001), pp. 401–406.
- B. Vodungbo, J. Gautier, G. Lambert, A. B. Sardinha, M. Lozano, S. Sebban, M. Ducousso, W. Boutu, K. Li, B. Tudu, M. Tortarolo, R. Hawaldar, R. Delaunay, V. López-Flores, J. Arabski, C. Boeglin, H. Merdji, P. Zeitoun, and J. Lüning, "Laser-induced ultrafast demagnetization in the presence of a nanoscale magnetic domain network," Nat. Commun. 3, 999 (2012).
- A. Schiffrin, T. Paasch-Colberg, N. Karpowicz, V. Apalkov, D. Gerster, S. Muhlbrandt, M. Korbman, J. Reichert, M. Schultze, S. Holzner, J. V. Barth, R. Kienberger, R. Ernstorfer, V. S. Yakovlev, M. I. Stockman, and F. Krausz, "Optical-field-induced current in dielectrics," Nature 493, 70–74 (2013).
- L. Raimondi, C. Svetina, N. Mahne, D. Cocco, F. Capotondi, E. Pedersoli, M. Manfredda, M. Kiskinova, B. Keitel, G. Brenner, E. Plönjes, T. Mey, K. Mann, and M. Zangrando, "Status of the k-b bendable optics at FERMI@elettra FEL," Proc. SPIE **9208**, 920804 (2014).
- L. Drescher, O. Kornilov, T. Witting, G. Reitsma, N. Monserud, A. Rouzée, J. Mikosch, M. J. J. Vrakking, and B. Schütte, "Extreme-ultraviolet refractive optics," Nature 564, 91–94 (2018).
- L. Quintard, V. Strelkov, J. Vabek, O. Hort, A. Dubrouil, D. Descamps, F. Burgy, C. Péjot, E. Mével, F. Catoire, and E. Constant, "Opticsless focusing of XUV high-order harmonics," Sci. Adv. 5, eaau7175 (2019).
- D. Yoshitomi, J. Nees, N. Miyamoto, T. Sekikawa, T. Kanai, G. Mourou, and S. Watanabe, "Phase-matched enhancements of high-harmonic soft x-rays by adaptive wave-front control with a genetic algorithm," Appl. Phys. B 78, 275–280 (2004).
- Y. Wang, T. Guo, J. Li, J. Zhao, Y. Yin, X. Ren, J. Li, Y. Wu, M. Weidman, Z. Chang, M. F. Jager, C. J. Kaplan, R. Geneaux, C. Ott,

D. M. Neumark, and S. R. Leone, "Enhanced high-order harmonic generation driven by a wavefront corrected high-energy laser," J. Phys. B **51**, 134005 (2018).

- 14. J. Gautier, P. Zeitoun, C. Hauri, A.-S. Morlens, G. Rey, C. Valentin, E. Papalarazou, J.-P. Goddet, S. Sebban, F. Burgy, P. Mercère, M. Idir, G. Dovillaire, X. Levecq, S. Bucourt, M. Fajardo, H. Merdji, and J.-P. Caumes, "Optimization of the wave front of high order harmonics," Eur. Phys. J. D 48, 459–463 (2008).
- C. Valentin, J. Gautier, J.-P. Goddet, C. Hauri, T. Marchenko, E. Papalazarou, G. Rey, S. Sebban, O. Scrick, P. Zeitoun, G. Dovillaire, X. Levecq, S. Bucourt, and M. Fajardo, "High-order harmonic wave fronts generated with controlled astigmatic infrared laser," J. Opt. Soc. Am. B 25, B161–B166 (2008).
- H. Dacasa, H. Coudert-Alteirac, C. Guo, E. Kueny, F. Campi, J. Lahl, J. Peschel, H. Wikmark, B. Major, E. Malm, D. Alj, K. Varjú, C. L. Arnold, G. Dovillaire, P. Johnsson, A. L'Huillier, S. Maclot, P. Rudawski, and P. Zeitoun, "Single-shot extreme-ultraviolet wavefront measurements of high-order harmonics," Opt. Express 27, 2656–2670 (2019).
- E. Frumker, G. G. Paulus, H. Niikura, D. M. Villeneuve, and P. B. Corkum, "Frequency-resolved high-harmonic wavefront characterization," Opt. Lett. 34, 3026–3028 (2009).
- E. Frumker, G. G. Paulus, H. Niikura, A. Naumov, D. M. Villeneuve, and P. B. Corkum, "Order-dependent structure of high harmonic wavefronts," Opt. Express 20, 13870–13877 (2012).
- L. Freisem, G. S. M. Jansen, D. Rudolf, K. S. E. Eikema, and S. Witte, "Spectrally resolved single-shot wavefront sensing of broadband high-harmonic sources," Opt. Express 26, 6860–6871 (2018).
- H. Wikmark, C. Guo, J. Vogelsang, P. W. Smorenburg, H. Coudert-Alteirac, J. Lahl, J. Peschel, P. Rudawski, H. Dacasa, S. Carlström, S. Maclot, M. B. Gaarde, P. Johnsson, C. L. Arnold, and A. L'Huillier,

"Spatiotemporal coupling of attosecond pulses," Proc. Natl. Acad. Sci. USA **116**, 4779–4787 (2019).

- B. Keitel, E. Plönjes, S. Kreis, M. Kuhlmann, K. Tiedtke, T. Mey, B. Schäfer, and K. Mann, "Hartmann wavefront sensors and their application at FLASH," J. Synchrotron Radiat. 23, 43–49 (2016).
- D. T. Lloyd, K. O'Keeffe, and S. M. Hooker, "Comparison of strongfield ionization models in the wavelength-scaling of high harmonic generation," Opt. Express 27, 6925–6935 (2019).
- J. Koliyadu, S. Künzel, T. Wodzinski, B. Keitel, J. Duarte, G. Williams, C. João, H. Pires, V. Hariton, M. Galletti, N. Gomes, G. Figueira, J. Dias, N. Lopes, P. Zeitoun, E. Plönjes, and M. Fajardo, "Optimization and characterization of high-harmonic generation for probing solid density plasmas," Photonics 4, 25 (2017).
- "Test methods for laser beam wavefronts-Part I: Terminology and fundamental aspects (2000), Part II: Phase gradient methods," ISO 15367 (2002).
- G. Vdovin and F. van Goor, "Lightpipes: beam propagation toolbox," 1999, https://opticspy.github.io/lightpipes/.
- "Lasers and laser-related equipment-test methods for laser beam widths, divergence angles and beam propagation ratios," ISO 11146 (2005).
- S. Prahl, "Laserbeamsize," 2018, https://github.com/scottprahl/laser beamsize.
- P. Kirkpatrick and A. V. Baez, "Formation of optical images by x-rays," J. Opt. Soc. Am. A 38, 766–773 (1948).
- 29. J. W. Goodman, Introduction to Fourier Optics (W.H. Freeman & Co Ltd., 2005).
- V. N. Mahajan, "Strehl ratio for primary aberrations: some analytical results for circular and annular pupils," J. Opt. Soc. Am. 72, 1258–1266 (1982).

Bibliography

- [1] P. á. Corkum and F. Krausz. Attosecond science. Nature physics, 3(6):381–387, 2007.
- [2] A. McPherson, G. Gibson, H. Jara, U. Johann, T. S. Luk, I. McIntyre, K. Boyer, and C. K. Rhodes. Studies of multiphoton production of vacuum-ultraviolet radiation in the rare gases. *JOSA B*, 4 (4):595–601, 1987.
- [3] P. B. Corkum. Plasma perspective on strong field multiphoton ionization. *Physical review letters*, 71(13):1994, 1993.
- [4] P. Antoine, A. L'huillier, and M. Lewenstein. Attosecond pulse trains using high-order harmonics. *Physical Review Letters*, 77(7):1234, 1996.
- [5] F. Calegari, G. Sansone, S. Stagira, C. Vozzi, and M. Nisoli. Advances in attosecond science. Journal of Physics B: Atomic, Molecular and Optical Physics, 49(6):062001, 2016.
- [6] M. C. Kohler, T. Pfeifer, K. Z. Hatsagortsyan, and C. H. Keitel. Frontiers of atomic high-harmonic generation. In Advances in Atomic, Molecular, and Optical Physics, volume 61, pages 159–208. Elsevier, 2012.
- T. Popmintchev, M.-C. Chen, D. Popmintchev, P. Arpin, S. Brown, S. Ališauskas, G. Andriukaitis,
 T. Balčiunas, O. D. Mücke, A. Pugzlys, et al. Bright coherent ultrahigh harmonics in the kev x-ray regime from mid-infrared femtosecond lasers. *science*, 336(6086):1287–1291, 2012.
- [8] A. L. Cavalieri, N. Müller, T. Uphues, V. S. Yakovlev, A. Baltuška, B. Horvath, B. Schmidt, L. Blümel, R. Holzwarth, S. Hendel, et al. Attosecond spectroscopy in condensed matter. *Nature*, 449(7165):1029–1032, 2007.
- [9] P. Peng, C. Marceau, and D. M. Villeneuve. Attosecond imaging of molecules using high harmonic spectroscopy. *Nature Reviews Physics*, 1(2):144–155, 2019.
- [10] Z. Tao, C. Chen, T. Szilvási, M. Keller, M. Mavrikakis, H. Kapteyn, and M. Murnane. Direct time-domain observation of attosecond final-state lifetimes in photoemission from solids. *Science*, 353(6294):62–67, 2016.
- M. Schultze, E. M. Bothschafter, A. Sommer, S. Holzner, W. Schweinberger, M. Fiess, M. Hofstetter, R. Kienberger, V. Apalkov, V. S. Yakovlev, et al. Controlling dielectrics with the electric field of light. *Nature*, 493(7430):75–78, 2013.

- [12] J. Itatani, J. Levesque, D. Zeidler, H. Niikura, H. Pépin, J.-C. Kieffer, P. B. Corkum, and D. M. Villeneuve. Tomographic imaging of molecular orbitals. *Nature*, 432(7019):867–871, 2004.
- [13] M. Uiberacker, T. Uphues, M. Schultze, A. J. Verhoef, V. Yakovlev, M. F. Kling, J. Rauschenberger, N. M. Kabachnik, H. Schröder, M. Lezius, et al. Attosecond real-time observation of electron tunnelling in atoms. *Nature*, 446(7136):627–632, 2007.
- [14] J. Li, J. Lu, A. Chew, S. Han, J. Li, Y. Wu, H. Wang, S. Ghimire, and Z. Chang. Attosecond science based on high harmonic generation from gases and solids. *Nature Communications*, 11(1): 1–13, 2020.
- S. Haessler, J. Caillat, W. Boutu, C. Giovanetti-Teixeira, T. Ruchon, T. Auguste, Z. Diveki,
 P. Breger, A. Maquet, B. Carré, et al. Attosecond imaging of molecular electronic wavepackets. *Nature Physics*, 6(3):200–206, 2010.
- [16] K. T. Kim, C. Zhang, T. Ruchon, J.-F. Hergott, T. Auguste, D. Villeneuve, P. Corkum, and F. Quéré. Photonic streaking of attosecond pulse trains. *Nature Photonics*, 7(8):651, 2013.
- [17] T. Kanai, S. Minemoto, and H. Sakai. Quantum interference during high-order harmonic generation from aligned molecules. *Nature*, 435(7041):470–474, 2005.
- [18] B. Dromey, M. Zepf, A. Gopal, K. Lancaster, M. Wei, K. Krushelnick, M. Tatarakis, N. Vakakis, S. Moustaizis, R. Kodama, et al. High harmonic generation in the relativistic limit. *Nature physics*, 2(7):456–459, 2006.
- [19] e. P. Franken, A. E. Hill, C. Peters, and G. Weinreich. Generation of optical harmonics. *Physical Review Letters*, 7(4):118, 1961.
- [20] J. Wildenauer. Generation of the ninth, eleventh, and fifteenth harmonics of iodine laser radiation. Journal of applied physics, 62(1):41–48, 1987.
- [21] M. Downer, B. S. Mendoza, and V. Gavrilenko. Optical second harmonic spectroscopy of semiconductor surfaces: advances in microscopic understanding. Surface and Interface Analysis: An International Journal devoted to the development and application of techniques for the analysis of surfaces, interfaces and thin films, 31(10):966–986, 2001.
- [22] S. M. Anderson, N. Tancogne-Dejean, B. S. Mendoza, and V. Véniard. Theory of surface secondharmonic generation for semiconductors including effects of nonlocal operators. *Physical Review B*, 91(7):075302, 2015.
- [23] K. L. Seyler, J. R. Schaibley, P. Gong, P. Rivera, A. M. Jones, S. Wu, J. Yan, D. G. Mandrus, W. Yao, and X. Xu. Electrical control of second-harmonic generation in a wse 2 monolayer transistor. *Nature nanotechnology*, 10(5):407–411, 2015.
- [24] T. Jiang, H. Liu, D. Huang, S. Zhang, Y. Li, X. Gong, Y.-R. Shen, W.-T. Liu, and S. Wu. Valley and band structure engineering of folded mos 2 bilayers. *Nature nanotechnology*, 9(10):825–829, 2014.

- [25] K.-Q. Lin, S. Bange, and J. M. Lupton. Quantum interference in second-harmonic generation from monolayer wse 2. Nature Physics, 15(3):242–246, 2019.
- [26] M. Hussain, H. Pires, W. Boutu, D. Franz, R. Nicolas, T. Imran, H. Merdji, M. Fajardo, and G. O. Williams. Controlling the non-linear optical properties of mgo by tailoring the electronic structure. *Applied Physics B*, 126(3):1–7, 2020.
- [27] W. Seka, S. Jacobs, J. Rizzo, R. Boni, and R. Craxton. Demonstration of high efficiency third harmonic conversion of high power nd-glass laser radiation. *Optics Communications*, 34(3):469– 473, 1980.
- [28] R. Craxton. High efficiency frequency tripling schemes for high-power nd: glass lasers. IEEE Journal of Quantum Electronics, 17(9):1771–1782, 1981.
- [29] L. Goldberg and D. A. Kliner. Tunable uv generation at 286 nm by frequency tripling of a high-power mode-locked semiconductor laser. Optics letters, 20(15):1640–1642, 1995.
- [30] J. Seres, E. Seres, C. Serrat, and T. Schumm. Non-perturbative generation of duv/vuv harmonics from crystal surfaces at 108 mhz repetition rate. *Optics express*, 26(17):21900–21909, 2018.
- [31] Y. S. You, D. A. Reis, and S. Ghimire. Anisotropic high-harmonic generation in bulk crystals. *Nature physics*, 13(4):345–349, 2017.
- [32] L. Keldysh et al. Ionization in the field of a strong electromagnetic wave. Sov. Phys. JETP, 20(5): 1307–1314, 1965.
- [33] S. Ghimire, A. D. DiChiara, E. Sistrunk, P. Agostini, L. F. DiMauro, and D. A. Reis. Observation of high-order harmonic generation in a bulk crystal. *Nature physics*, 7(2):138, 2011.
- [34] G. Vampa, C. McDonald, G. Orlando, P. Corkum, and T. Brabec. Semiclassical analysis of high harmonic generation in bulk crystals. *Physical Review B*, 91(6):064302, 2015.
- [35] G. Ndabashimiye, S. Ghimire, M. Wu, D. A. Browne, K. J. Schafer, M. B. Gaarde, and D. A. Reis. Solid-state harmonics beyond the atomic limit. *Nature*, 534(7608):520–523, 2016.
- [36] G.-R. Jia, X.-H. Huang, and X.-B. Bian. Nonadiabatic redshifts in high-order harmonic generation from solids. *Optics express*, 25(20):23654–23662, 2017.
- [37] Y. S. You, Y. Yin, Y. Wu, A. Chew, X. Ren, F. Zhuang, S. Gholam-Mirzaei, M. Chini, Z. Chang, and S. Ghimire. High-harmonic generation in amorphous solids. *Nature communications*, 8(1):724, 2017.
- [38] S. Ghimire and D. A. Reis. High-harmonic generation from solids. *Nature Physics*, page 1, 2018.
- [39] S. Gholam-Mirzaei, J. Beetar, and M. Chini. High harmonic generation in zno with a high-power mid-ir opa. Applied Physics Letters, 110(6):061101, 2017.

- [40] S. Gholam-Mirzaei, J. E. Beetar, A. Chacón, and M. Chini. High-harmonic generation in zno driven by self-compressed mid-infrared pulses. JOSA B, 35(4):A27–A31, 2018.
- [41] G. Vampa, Y. You, H. Liu, S. Ghimire, and D. Reis. Observation of backward high-harmonic emission from solids. *Optics express*, 26(9):12210–12218, 2018.
- [42] H. Liu, Y. Li, Y. S. You, S. Ghimire, T. F. Heinz, and D. A. Reis. High-harmonic generation from an atomically thin semiconductor. *Nature Physics*, 13(3):262–265, 2017.
- [43] Y. Wang, T. Guo, J. Li, J. Zhao, Y. Yin, X. Ren, J. Li, Y. Wu, M. Weidman, Z. Chang, et al. Enhanced high-order harmonic generation driven by a wavefront corrected high-energy laser. *Journal* of Physics B: Atomic, Molecular and Optical Physics, 51(13):134005, 2018.
- [44] D. Franz, S. Kaassamani, D. Gauthier, R. Nicolas, M. Kholodtsova, L. Douillard, J.-T. Gomes, L. Lavoute, D. Gaponov, N. Ducros, et al. All semiconductor enhanced high-harmonic generation from a single nanostructured cone. *Scientific reports*, 9(1):5663, 2019.
- [45] T. Apostolova and B. Obreshkov. High harmonic generation from bulk diamond driven by intense femtosecond laser pulse. *Diamond and Related Materials*, 82:165–172, 2018.
- [46] V. E. Nefedova, S. Fröhlich, F. Navarrete, N. Tancogne-Dejean, D. Franz, A. Hamdou, S. Kaassamani, D. Gauthier, R. Nicolas, G. Jargot, M. Hanna, P. Georges, M. F. Ciappina, U. Thumm, W. Boutu, and H. Merdji. Enhanced extreme ultraviolet high-harmonic generation from chromiumdoped magnesium oxide. *Applied Physics Letters*, 118(20):201103, 2021. doi: 10.1063/5.0047421. URL https://doi.org/10.1063/5.0047421.
- [47] D. Golde, T. Meier, and S. W. Koch. High harmonics generated in semiconductor nanostructures by the coupled dynamics of optical inter-and intraband excitations. *Physical Review B*, 77(7):075330, 2008.
- [48] T. Higuchi, M. I. Stockman, and P. Hommelhoff. Strong-field perspective on high-harmonic radiation from bulk solids. *Physical review letters*, 113(21):213901, 2014.
- [49] P. G. Hawkins, M. Y. Ivanov, and V. S. Yakovlev. Effect of multiple conduction bands on highharmonic emission from dielectrics. *Physical Review A*, 91(1):013405, 2015.
- [50] M. Wu, D. A. Browne, K. J. Schafer, and M. B. Gaarde. Multilevel perspective on high-order harmonic generation in solids. *Physical Review A*, 94(6):063403, 2016.
- [51] N. Tancogne-Dejean, O. D. Mücke, F. X. Kärtner, and A. Rubio. Impact of the electronic band structure in high-harmonic generation spectra of solids. *Physical review letters*, 118(8):087403, 2017.
- [52] I. Floss, C. Lemell, G. Wachter, V. Smejkal, S. A. Sato, X.-M. Tong, K. Yabana, and J. Burgdörfer. Ab initio multiscale simulation of high-order harmonic generation in solids. *Physical Review A*, 97 (1):011401, 2018.
- [53] J. P. Marangos. High-harmonic generation: Solid progress. Nature Physics, 7(2):97, 2011.

- [54] O. Schubert, M. Hohenleutner, F. Langer, B. Urbanek, C. Lange, U. Huttner, D. Golde, T. Meier, M. Kira, S. W. Koch, et al. Sub-cycle control of terahertz high-harmonic generation by dynamical bloch oscillations. *Nature Photonics*, 8(2):119, 2014.
- [55] M. Hohenleutner, F. Langer, O. Schubert, M. Knorr, U. Huttner, S. Koch, M. Kira, and R. Huber. Real-time observation of interfering crystal electrons in high-harmonic generation. *Nature*, 523 (7562):572, 2015.
- [56] T. T. Luu, M. Garg, S. Y. Kruchinin, A. Moulet, M. T. Hassan, and E. Goulielmakis. Extreme ultraviolet high-harmonic spectroscopy of solids. *Nature*, 521(7553):498, 2015.
- [57] G. Vampa, T. Hammond, N. Thiré, B. Schmidt, F. Légaré, C. McDonald, T. Brabec, D. Klug, and P. Corkum. All-optical reconstruction of crystal band structure. *Physical review letters*, 115(19): 193603, 2015.
- [58] N. Tancogne-Dejean, O. D. Mücke, F. X. Kärtner, and A. Rubio. Ellipticity dependence of highharmonic generation in solids originating from coupled intraband and interband dynamics. *Nature* communications, 8(1):1–10, 2017.
- [59] M. Wu, Y. You, S. Ghimire, D. A. Reis, D. A. Browne, K. J. Schafer, and M. B. Gaarde. Orientation dependence of temporal and spectral properties of high-order harmonics in solids. *Physical Review* A, 96(6):063412, 2017.
- [60] Y. S. You, J. Lu, E. F. Cunningham, C. Roedel, and S. Ghimire. Crystal orientation-dependent polarization state of high-order harmonics. *Optics letters*, 44(3):530–533, 2019.
- [61] G. Vampa and T. Brabec. Merge of high harmonic generation from gases and solids and its implications for attosecond science. *Journal of Physics B: Atomic, Molecular and Optical Physics*, 50(8):083001, 2017.
- [62] M. Wu, S. Ghimire, D. A. Reis, K. J. Schafer, and M. B. Gaarde. High-harmonic generation from bloch electrons in solids. *Physical Review A*, 91(4):043839, 2015.
- [63] L. Plaja and L. Roso-Franco. High-order harmonic generation in a crystalline solid. *Physical Review B*, 45(15):8334, 1992.
- [64] T.-Y. Du, X.-H. Huang, and X.-B. Bian. High-order-harmonic generation from solids: The contributions of the bloch wave packets moving at the group and phase velocities. *Physical Review A*, 97 (1):013403, 2018.
- [65] M. Lindberg and S. W. Koch. Effective bloch equations for semiconductors. *Physical Review B*, 38 (5):3342, 1988.
- [66] M. Garg, M. Zhan, T. T. Luu, H. Lakhotia, T. Klostermann, A. Guggenmos, and E. Goulielmakis. Multi-petahertz electronic metrology. *Nature*, 538(7625):359–363, 2016.

- [67] F. Langer, M. Hohenleutner, C. P. Schmid, C. Pöllmann, P. Nagler, T. Korn, C. Schüller, M. Sherwin, U. Huttner, J. Steiner, et al. Lightwave-driven quasiparticle collisions on a subcycle timescale. *Nature*, 533(7602):225–229, 2016.
- [68] G. Vampa, C. McDonald, G. Orlando, D. Klug, P. Corkum, and T. Brabec. Theoretical analysis of high-harmonic generation in solids. *Physical review letters*, 113(7):073901, 2014.
- [69] D. Golde, M. Kira, T. Meier, and S. W. Koch. Microscopic theory of the extremely nonlinear terahertz response of semiconductors. *physica status solidi* (b), 248(4):863–866, 2011.
- [70] C. McDonald, K. Amin, S. Aalmalki, and T. Brabec. Enhancing high harmonic output in solids through quantum confinement. *Physical review letters*, 119(18):183902, 2017.
- [71] T. Tamaya, A. Ishikawa, T. Ogawa, and K. Tanaka. Diabatic mechanisms of higher-order harmonic generation in solid-state materials under high-intensity electric fields. *Physical review letters*, 116 (1):016601, 2016.
- [72] D. Bauer and K. K. Hansen. High-harmonic generation in solids with and without topological edge states. *Physical review letters*, 120(17):177401, 2018.
- [73] N. Tancogne-Dejean, M. A. Sentef, and A. Rubio. Ultrafast modification of hubbard u in a strongly correlated material: Ab initio high-harmonic generation in nio. *Physical review letters*, 121(9): 097402, 2018.
- [74] K. K. Hansen, T. Deffge, and D. Bauer. High-order harmonic generation in solid slabs beyond the single-active-electron approximation. *Physical Review A*, 96(5):053418, 2017.
- [75] F. Brandi, F. Giammanco, and W. Ubachs. Spectral redshift in harmonic generation from plasma dynamics in the laser focus. *Physical review letters*, 96(12):123904, 2006.
- [76] X.-B. Bian and A. D. Bandrauk. Spectral shifts of nonadiabatic high-order harmonic generation. Applied Sciences, 3(1):267–277, 2013.
- [77] H. Du, S. Xue, H. Wang, Z. Zhang, and B. Hu. Nonadiabatic spectral redshift of high-order harmonics with the help of a vuv pulse. *Physical Review A*, 91(6):063844, 2015.
- [78] X.-B. Bian and A. D. Bandrauk. Nonadiabatic molecular high-order harmonic generation from polar molecules: Spectral redshift. *Physical Review A*, 83(4):041403, 2011.
- [79] X.-B. Bian and A. D. Bandrauk. Probing nuclear motion by frequency modulation of molecular high-order harmonic generation. *Physical review letters*, 113(19):193901, 2014.
- [80] Y. W. Kim, T.-J. Shao, H. Kim, S. Han, S. Kim, M. Ciappina, X.-B. Bian, and S.-W. Kim. Spectral interference in high harmonic generation from solids. ACS Photonics, 6(4):851–857, 2019.
- [81] M. Hussain, S. Kaassamani, T. Auguste, W. Boutu, D. Gauthier, M. Kholodtsova, J.-T. Gomes, L. Lavoute, D. Gaponov, N. Ducros, et al. Spectral control of high order harmonics through non-linear propagation effects. *Applied Physics Letters*, 119(7):071101, 2021.
- [82] S. Ghimire, A. D. DiChiara, E. Sistrunk, G. Ndabashimiye, U. B. Szafruga, A. Mohammad, P. Agostini, L. F. DiMauro, and D. A. Reis. Generation and propagation of high-order harmonics in crystals. *Physical Review A*, 85(4):043836, 2012.
- [83] J. Lu, E. F. Cunningham, Y. S. You, D. A. Reis, and S. Ghimire. Interferometry of dipole phase in high harmonics from solids. *Nature Photonics*, 13(2):96–100, 2019.
- [84] G. Vampa, J. Lu, Y. S. You, D. R. Baykusheva, M. Wu, H. Liu, K. J. Schafer, M. B. Gaarde, D. A. Reis, and S. Ghimire. Attosecond synchronization of extreme ultraviolet high harmonics from crystals. *Journal of Physics B: Atomic, Molecular and Optical Physics*, 53(14):144003, 2020.
- [85] S. Yamada and K. Yabana. Determining the optimum thickness for high harmonic generation from nanoscale thin films: An ab initio computational study. *Physical Review B*, 103(15):155426, 2021.
- [86] M. Uemoto, S. Kurata, N. Kawaguchi, and K. Yabana. First-principles study of ultrafast and nonlinear optical properties of graphite thin films. *Physical Review B*, 103(8):085433, 2021.
- [87] A. Korobenko, S. Saha, A. T. Godfrey, M. Gertsvolf, A. Y. Naumov, D. M. Villeneuve, A. Boltasseva, V. M. Shalaev, and P. B. Corkum. High-harmonic generation in metallic titanium nitride. *Nature communications*, 12(1):1–6, 2021.
- [88] G. Vampa, B. Ghamsari, S. S. Mousavi, T. Hammond, A. Olivieri, E. Lisicka-Skrek, A. Y. Naumov, D. Villeneuve, A. Staudte, P. Berini, et al. Plasmon-enhanced high-harmonic generation from silicon. *Nature Physics*, 13(7):659–662, 2017.
- [89] S. Kim, J. Jin, Y.-J. Kim, I.-Y. Park, Y. Kim, and S.-W. Kim. High-harmonic generation by resonant plasmon field enhancement. *Nature*, 453(7196):757–760, 2008.
- [90] R. J. Jones, K. D. Moll, M. J. Thorpe, and J. Ye. Phase-coherent frequency combs in the vacuum ultraviolet via high-harmonic generation inside a femtosecond enhancement cavity. *Physical Review Letters*, 94(19):193201, 2005.
- [91] H. Agueny. Tuning the electronic band structure of metal surfaces for enhancing high-order harmonic generation. The Journal of Chemical Physics, 154(24):244702, 2021.
- [92] Z. Nourbakhsh, N. Tancogne-Dejean, H. Merdji, and A. Rubio. High harmonics and isolated attosecond pulses from mg o. *Physical Review Applied*, 15(1):014013, 2021.
- [93] A. Korobenko, S. Rashid, C. Heide, A. Y. Naumov, D. Reis, P. Berini, P. Corkum, and G. Vampa. Generation of structured coherent extreme ultraviolet beams from an mgo crystal. *Optics Express*, 29(15):24161–24168, 2021.
- [94] C. Marceau, T. Hammond, A. Y. Naumov, P. Corkum, and D. Villeneuve. Wavelength scaling of high harmonic generation for 267 nm, 400 nm and 800 nm driving laser pulses. *Journal of Physics Communications*, 1(1):015009, 2017.

- [95] F. Krausz and M. I. Stockman. Attosecond metrology: from electron capture to future signal processing. *Nature Photonics*, 8(3):205, 2014.
- [96] M. Hussain, G. O. Williams, T. Imran, and M. Fajardo. Non-linear propagation effects of intense femtosecond pulses on low order harmonics in solids. arXiv preprint arXiv:2104.10629, 2021.
- [97] S. Augst, D. D. Meyerhofer, D. Strickland, and S.-L. Chin. Laser ionization of noble gases by coulomb-barrier suppression. JOSA B, 8(4):858–867, 1991.
- [98] M. V. Ammosov. Tunnel ionization of complex atoms and of atomic ions in an alternating electromagnetic field. Sov. Phys. JETP, 64:1191, 1987.
- [99] N. Bloembergen and P. Pershan. Light waves at the boundary of nonlinear media. *Physical review*, 128(2):606, 1962.
- [100] R. Boyd. Nonlinear optics third ed, 2007.
- [101] T. F. Heinz, C. Chen, D. Ricard, and Y. Shen. Spectroscopy of molecular monolayers by resonant second-harmonic generation. *Physical Review Letters*, 48(7):478, 1982.
- [102] J. Sipe, D. Moss, and H. Van Driel. Phenomenological theory of optical second-and third-harmonic generation from cubic centrosymmetric crystals. *Physical Review B*, 35(3):1129, 1987.
- [103] R. W. Boyd. Nonlinear optics. Elsevier, 2003.
- [104] T. Y. Tsang. Optical third-harmonic generation at interfaces. *Physical Review A*, 52(5):4116, 1995.
- [105] H. Kim, S. Han, Y. W. Kim, S. Kim, and S.-W. Kim. Generation of coherent extreme-ultraviolet radiation from bulk sapphire crystal. ACS Photonics, 4(7):1627–1632, 2017.
- [106] G. Yi, H. Lee, J. Jiannan, B. J. Chun, S. Han, H. Kim, Y. W. Kim, D. Kim, S.-W. Kim, and Y.-J. Kim. Nonlinear third harmonic generation at crystalline sapphires. *Optics express*, 25(21): 26002–26010, 2017.
- [107] W. Glenn. Second-harmonic generation by picosecond optical pulses. IEEE Journal of Quantum Electronics, 5(6):284–290, 1969.
- [108] D. N. Nikogosyan. Nonlinear optical crystals: a complete survey. Springer Science & Business Media, 2006.
- [109] H. Liu, J. Yao, and A. Puri. Second and third harmonic generation in bbo by femtosecond ti: sapphire laser pulses. Optics communications, 109(1-2):139–144, 1994.
- [110] T. Y. Fan, C. Huang, B. Hu, R. C. Eckardt, Y. Fan, R. L. Byer, and R. Feigelson. Second harmonic generation and accurate index of refraction measurements in flux-grown ktiopo 4. *Applied optics*, 26(12):2390–2394, 1987.
- [111] H. Hellwig, J. Liebertz, and L. Bohatỳ. Linear optical properties of the monoclinic bismuth borate bib 3 o 6. Journal of Applied Physics, 88(1):240–244, 2000.

- [112] M. Galletti, H. Pires, V. Hariton, C. P. Joao, S. Künzel, M. Galimberti, and G. Figueira. High efficiency second harmonic generation of nanojoule-level femtosecond pulses in the visible based on bibo. *High Power Laser Science and Engineering*, 7, 2019.
- [113] M. Ferray, A. L'Huillier, X. Li, L. Lompre, G. Mainfray, and C. Manus. Multiple-harmonic conversion of 1064 nm radiation in rare gases. *Journal of Physics B: Atomic, Molecular and Optical Physics*, 21(3):L31, 1988.
- [114] J. L. Krause, K. J. Schafer, and K. C. Kulander. High-order harmonic generation from atoms and ions in the high intensity regime. *Physical Review Letters*, 68(24):3535, 1992.
- [115] G. Cirmi, C.-J. Lai, E. Granados, S.-W. Huang, A. Sell, K.-H. Hong, J. Moses, P. Keathley, and F. X. Kärtner. Cut-off scaling of high-harmonic generation driven by a femtosecond visible optical parametric amplifier. *Journal of Physics B: Atomic, Molecular and Optical Physics*, 45(20):205601, 2012.
- [116] J. Tate, T. Auguste, H. Muller, P. Salières, P. Agostini, and L. DiMauro. Scaling of wave-packet dynamics in an intense midinfrared field. *Physical Review Letters*, 98(1):013901, 2007.
- [117] A. Shiner, C. Trallero-Herrero, N. Kajumba, H.-C. Bandulet, D. Comtois, F. Légaré, M. Giguère, J. Kieffer, P. Corkum, and D. Villeneuve. Wavelength scaling of high harmonic generation efficiency. *Physical Review Letters*, 103(7):073902, 2009.
- [118] M. Fedorov and J. Peatross. Strong-field photoionization and emission of light in the wave-packetspreading regime. *Physical Review A*, 52(1):504, 1995.
- [119] A. Emelina, M. Y. Emelin, and M. Y. Ryabikin. Wavelength scaling laws for high-order harmonic yield from atoms driven by mid-and long-wave infrared laser fields. JOSA B, 36(11):3236–3245, 2019.
- [120] E. J. Takahashi, Y. Nabekawa, and K. Midorikawa. Low-divergence coherent soft x-ray source at 13 nm by high-order harmonics. *Applied physics letters*, 84(1):4–6, 2004.
- [121] E. Constant, D. Garzella, P. Breger, E. Mével, C. Dorrer, C. Le Blanc, F. Salin, and P. Agostini. Optimizing high harmonic generation in absorbing gases: Model and experiment. *Physical Review Letters*, 82(8):1668, 1999.
- [122] J.-F. Hergott, M. Kovacev, H. Merdji, C. Hubert, Y. Mairesse, E. Jean, P. Breger, P. Agostini,
 B. Carré, and P. Salières. Extreme-ultraviolet high-order harmonic pulses in the microjoule range. *Physical Review A*, 66(2):021801, 2002.
- [123] P. Rudawski, C. Heyl, F. Brizuela, J. Schwenke, A. Persson, E. Mansten, R. Rakowski, L. Rading, F. Campi, B. Kim, et al. A high-flux high-order harmonic source. *Review of Scientific Instruments*, 84(7):073103, 2013.
- [124] K. Budil, P. Salières, A. L'Huillier, T. Ditmire, and M. Perry. Influence of ellipticity on harmonic generation. *Physical Review A*, 48(5):R3437, 1993.

- [125] C. V. Vuong, K. B. Dinh, P. Hannaford, and L. V. Dao. Phase-matched high-order harmonic generation in a semi-infinite gas cell with absorbing gaseous media. *Journal of Nonlinear Optical Physics & Materials*, 24(03):1550031, 2015.
- [126] A. Rundquist, C. G. Durfee, Z. Chang, C. Herne, S. Backus, M. M. Murnane, and H. C. Kapteyn. Phase-matched generation of coherent soft x-rays. *Science*, 280(5368):1412–1415, 1998.
- [127] C. G. Durfee III, A. R. Rundquist, S. Backus, C. Herne, M. M. Murnane, and H. C. Kapteyn. Phase matching of high-order harmonics in hollow waveguides. *Physical Review Letters*, 83(11): 2187, 1999.
- [128] J. C. Koliyadu, S. Künzel, T. Wodzinski, B. Keitel, J. Duarte, G. O. Williams, C. P. João, H. Pires, V. Hariton, M. Galletti, et al. Optimization and characterization of high-harmonic generation for probing solid density plasmas. In *Photonics*, volume 4, page 25. Multidisciplinary Digital Publishing Institute, 2017.
- [129] T. Wodzinski, S. Künzel, J. C. Koliyadu, M. Hussain, B. Keitel, G. O. Williams, P. Zeitoun, E. Plönjes, and M. Fajardo. High-harmonic generation wave front dependence on a driving infrared wave front. *Applied Optics*, 59(5):1363–1370, 2020.
- [130] P. Estrela, E. Maçôas, G. Williams, M. Hussain, and M. Fajardo. Lithium fluoride detectors for high spatial resolution imaging of tabletop xuv from high harmonic generation in gases. JOSA B, 38(7):2234–2238, 2021.
- [131] N. Yoshikawa, T. Tamaya, and K. Tanaka. High-harmonic generation in graphene enhanced by elliptically polarized light excitation. *Science*, 356(6339):736–738, 2017.
- [132] Y. S. You, E. Cunningham, D. A. Reis, and S. Ghimire. Probing periodic potential of crystals via strong-field re-scattering. *Journal of Physics B: Atomic, Molecular and Optical Physics*, 51(11): 114002, 2018.
- [133] M. Sivis, M. Taucer, G. Vampa, K. Johnston, A. Staudte, A. Y. Naumov, D. Villeneuve, C. Ropers, and P. Corkum. Tailored semiconductors for high-harmonic optoelectronics. *Science*, 357(6348): 303–306, 2017.
- [134] R. Silva, I. V. Blinov, A. N. Rubtsov, O. Smirnova, and M. Ivanov. High-harmonic spectroscopy of ultrafast many-body dynamics in strongly correlated systems. *Nature Photonics*, 12(5):266–270, 2018.
- [135] G. Vampa, T. Hammond, N. Thiré, B. Schmidt, F. Légaré, C. McDonald, T. Brabec, and P. Corkum. Linking high harmonics from gases and solids. *Nature*, 522(7557):462, 2015.
- [136] G. Vampa, H. Liu, T. F. Heinz, and D. A. Reis. Disentangling interface and bulk contributions to high-harmonic emission from solids. *Optica*, 6(5):553–556, 2019.
- [137] W. Houston. Acceleration of electrons in a crystal lattice. *Physical Review*, 57(3):184, 1940.

- [138] Y. S. You, M. Wu, Y. Yin, A. Chew, X. Ren, S. Gholam-Mirzaei, D. A. Browne, M. Chini, Z. Chang, K. J. Schafer, et al. Laser waveform control of extreme ultraviolet high harmonics from solids. *Optics letters*, 42(9):1816–1819, 2017.
- [139] A. Lanin, E. Stepanov, A. Fedotov, and A. Zheltikov. Mapping the electron band structure by intraband high-harmonic generation in solids. *Optica*, 4(5):516–519, 2017.
- [140] Z. Wang, H. Park, Y. H. Lai, J. Xu, C. I. Blaga, F. Yang, P. Agostini, and L. F. DiMauro. The roles of photo-carrier doping and driving wavelength in high harmonic generation from a semiconductor. *Nature communications*, 8(1):1–7, 2017.
- [141] G. Vampa and P. B. Corkum. Apparatus and method for generation of high harmonics from silicon, Aug. 29 2017. US Patent 9,746,748.
- [142] N. Klemke, G. Di Sciacca, Y. Yang, G. M. Rossi, R. Mainz, N. Tancogne-Dejean, A. Rubio, F. Kärtner, and O. Mücke. Circularly polarized high-order harmonics from solids driven by single-color infrared pulses. *Talk presented at ATTO*, pages 2–7, 2017.
- [143] N. Klemke, G. Di Sciacca, Y. Yang, G. Rossi, R. Mainz, N. Tancogne-Dejean, A. Rubio, F. Kärtner, and O. Mücke. Ellipticity dependence of higher-order harmonics in solids: unraveling the coupled intraband and interband dynamics. In *CLEO: QELS_Fundamental Science*, pages JTh5B–10. Optical Society of America, 2017.
- [144] N. Klemke, N. Tancogne-Dejean, A. Rubio, F. X. Kärtner, and O. D. Mücke. The role of intraband dynamics in the generation of circularly polarized high harmonics from solids, 2020.
- [145] D. E. Aspnes and A. Studna. Dielectric functions and optical parameters of si, ge, gap, gaas, gasb, inp, inas, and insb from 1.5 to 6.0 ev. *Physical review B*, 27(2):985, 1983.
- [146] W. Bond. Measurement of the refractive indices of several crystals. Journal of Applied Physics, 36 (5):1674–1677, 1965.
- [147] C. D. Salzberg and J. J. Villa. Infrared refractive indexes of silicon germanium and modified selenium glass. JOSA, 47(3):244–246, 1957.
- [148] R. E. Stephens and I. H. Malitson. Index of refraction of magnesium oxide. J. Res. Natl. Bur. Stand., 49(4):249–252, 1952.
- [149] F. Loesel, J. Fischer, M. Götz, C. Horvath, T. Juhasz, F. Noack, N. Suhm, and J. Bille. Non-thermal ablation of neural tissue with femtosecond laser pulses. *Applied Physics B: Lasers & Optics*, 66(1), 1998.
- [150] M. Lenzner, J. Krüger, W. Kautek, and F. Krausz. Precision laser ablation of dielectrics in the 10-fs regime. Applied Physics A: Materials Science & Processing, 68(3), 1999.
- [151] K. M. Davis, K. Miura, N. Sugimoto, and K. Hirao. Writing waveguides in glass with a femtosecond laser. Optics letters, 21(21):1729–1731, 1996.

- [152] C. B. Schaffer, A. Brodeur, J. F. García, and E. Mazur. Micromachining bulk glass by use of femtosecond laser pulses with nanojoule energy. *Optics letters*, 26(2):93–95, 2001.
- [153] E. Glezer, M. Milosavljevic, L. Huang, R. Finlay, T.-H. Her, J. P. Callan, and E. Mazur. Threedimensional optical storage inside transparent materials. *Optics letters*, 21(24):2023–2025, 1996.
- [154] T. Imran and G. Figueira. Intensity-phase characterization of white-light continuum generated in sapphire by 280 fs laser pulses at 1053 nm. *Journal of Optics*, 14(3):035201, 2012.
- [155] T. Imran, M. Hussain, and G. Figueira. Cross-correlation frequency-resolved optical gating of white-light continuum (500–900 nm) generated in bulk media by 1053 nm laser pulses. Laser Physics Letters, 13(6):066101, 2016.
- [156] W. Luis Mochán and J. A. Maytorena. Theory of surface second harmonic generation. In EPIOPTICS-8, pages 17–45. World Scientific, 2006.
- [157] R. J. Tran, K. L. Sly, and J. C. Conboy. Applications of surface second harmonic generation in biological sensing. Annual Review of Analytical Chemistry, 10:387–414, 2017.
- [158] L. Mennel, M. M. Furchi, S. Wachter, M. Paur, D. K. Polyushkin, and T. Mueller. Optical imaging of strain in two-dimensional crystals. *Nature communications*, 9(1):1–6, 2018.
- [159] J.-Y. Chauleau, E. Haltz, C. Carrétéro, S. Fusil, and M. Viret. Multi-stimuli manipulation of antiferromagnetic domains assessed by second-harmonic imaging. *Nature materials*, 16(8):803–807, 2017.
- [160] G. Lüpke. Characterization of semiconductor interfaces by second-harmonic generation. Surface Science Reports, 35(3-4):75–161, 1999.
- [161] A. Zheltikov, G. Ferrante, and M. Zarcone. On the far-and near-field optical microscopy of microelectronics structures using second-harmonic and sum-frequency generation. *Laser physics*, 10(2): 600–602, 2000.
- [162] F. Stavale, N. Nilius, and H.-J. Freund. Cathodoluminescence of near-surface centres in cr-doped mgo (001) thin films probed by scanning tunnelling microscopy. New Journal of Physics, 14(3): 033006, 2012.
- [163] S. Benedetti, N. Nilius, and S. Valeri. Chromium-doped mgo thin films: Morphology, electronic structure, and segregation effects. *The Journal of Physical Chemistry C*, 119(45):25469–25475, 2015.
- [164] J. W. Lee and J.-H. Ko. Defect states of transition metal-doped mgo for secondary electron emission of plasma display panel. *Journal of Information Display*, 15(4):157–161, 2014.
- [165] L. Kantorovich, A. Shluger, and A. Stoneham. Recognition of surface species in atomic force microscopy: optical properties of a cr 3+ defect at the mgo (001) surface. *Physical Review B*, 63 (18):184111, 2001.

- [166] C. Yu, K. K. Hansen, and L. B. Madsen. Enhanced high-order harmonic generation in donor-doped band-gap materials. *Physical Review A*, 99(1):013435, 2019.
- [167] M. Henry, J. Larkin, and G. Imbusch. Nature of the broadband luminescence center in mgo: Cr 3+. *Physical Review B*, 13(5):1893, 1976.
- [168] H. Eskalen, Ş. Özğan, Ü. Alver, and S. Kerli. Electro-optical properties of liquid crystals composite with zinc oxide nanoparticles. Acta Physica Polonica, A., 127(3), 2015.
- [169] C.-W. Oh, E.-G. Park, and H.-G. Park. Enhanced electro-optical properties in titanium silicon oxide nanoparticle doped nematic liquid crystal system. Surface and Coatings Technology, 360: 50-55, 2019.
- [170] T. Kato, G. Okada, and T. Yanagida. Optical, scintillation and dosimeter properties of mgo translucent ceramic doped with cr3+. Optical Materials, 54:134–138, 2016.
- [171] D. Guidotti, T. Driscoll, and H. Gerritsen. Second harmonic generation in centro-symmetric semiconductors. Solid state communications, 46(4):337–340, 1983.
- [172] T. Driscoll and D. Guidotti. Symmetry analysis of second-harmonic generation in silicon. *Physical Review B*, 28(2):1171, 1983.
- [173] O. Aktsipetrov, I. Baranova, and Y. A. Il'inskii. Surface contribution to the generation of reflected second harmonic light for centrosymmetric semiconductors. *Zh. Eksp. Teor. Fiz*, 91:287–297, 1986.
- [174] G. Kresse and J. Hafner. Ab initio molecular dynamics for liquid metals. *Physical Review B*, 47 (1):558, 1993.
- [175] G. Kresse and J. Furthmüller. Efficient iterative schemes for ab initio total-energy calculations using a plane-wave basis set. *Physical review B*, 54(16):11169, 1996.
- [176] G. Kresse and J. Furthmüller. Efficiency of ab-initio total energy calculations for metals and semiconductors using a plane-wave basis set. *Computational materials science*, 6(1):15–50, 1996.
- [177] G. Kresse and D. Joubert. From ultrasoft pseudopotentials to the projector augmented-wave method. *Physical review b*, 59(3):1758, 1999.
- [178] H. S. Uhm and E. H. Choi. Measurement of valence band structure in arbitrary dielectric films. Materials Research Bulletin, 47(10):2906–2910, 2012.
- [179] S. Heo, E. Cho, H.-I. Lee, G. S. Park, H. J. Kang, T. Nagatomi, P. Choi, and B.-D. Choi. Band gap and defect states of mgo thin films investigated using reflection electron energy loss spectroscopy. *AIP Advances*, 5(7):077167, 2015.
- [180] M. Gerosa, C. E. Bottani, L. Caramella, G. Onida, C. Di Valentin, and G. Pacchioni. Electronic structure and phase stability of oxide semiconductors: Performance of dielectric-dependent hybrid functional dft, benchmarked against g w band structure calculations and experiments. *Physical Review B*, 91(15):155201, 2015.

- [181] V. Nefedova, S. Fröhlich, F. Navarrete, N. Tancogne-Dejean, D. Franz, A. Hamdou, S. Kaassamani, D. Gauthier, R. Nicolas, G. Jargot, et al. Enhanced extreme ultraviolet high-harmonic generation from chromium-doped magnesium oxide. *Applied Physics Letters*, 118(20):201103, 2021.
- [182] C. Kittel. Quantum theory of solids, 1987.
- [183] G. Petrocelli, E. Pichini, F. Scudieri, and S. Martellucci. Anisotropic effects in the third-harmonicgeneration process in cubic crystals. JOSA B, 10(5):918–923, 1993.
- [184] W. Burns and N. Bloembergen. Third-harmonic generation in absorbing media of cubic or isotropic symmetry. *Physical Review B*, 4(10):3437, 1971.
- [185] G. Zhang and T. F. George. Ellipticity dependence of optical harmonic generation in c 60. Physical Review A, 74(2):023811, 2006.
- [186] Y. Tan, M. Povolotskyi, T. Kubis, Y. He, Z. Jiang, G. Klimeck, and T. B. Boykin. Empirical tight binding parameters for gaas and mgo with explicit basis through dft mapping. *Journal of Computational Electronics*, 12(1):56–60, 2013.
- [187] X. Yong-Nian. Self-consistent band structures, charge distributions, and optical-absorption spectra in mgo, α-al2o3, and mgal2o4/y.-n. xu, w. ching. *Phys. Rev. B*, 43(5):4461–4472, 1991.
- [188] N. Klemke, N. Tancogne-Dejean, G. M. Rossi, Y. Yang, F. Scheiba, R. Mainz, G. Di Sciacca, A. Rubio, F. Kärtner, and O. Mücke. Polarization-state-resolved high-harmonic spectroscopy of solids. *Nature communications*, 10(1):1–7, 2019.
- [189] A. Couairon, L. Sudrie, M. Franco, B. Prade, and A. Mysyrowicz. Filamentation and damage in fused silica induced by tightly focused femtosecond laser pulses. *Physical Review B*, 71(12):125435, 2005.
- [190] P. Koonath, D. R. Solli, and B. Jalali. Limiting nature of continuum generation in silicon. Applied Physics Letters, 93(9):091114, 2008.
- [191] S. Kaassamani. Polarization spectroscopy of high harmonic generation in semiconductors. 2020.
- [192] B. Chimier, O. Utéza, N. Sanner, M. Sentis, T. Itina, P. Lassonde, F. Légaré, F. Vidal, and J. Kieffer. Damage and ablation thresholds of fused-silica in femtosecond regime. *Physical Review* B, 84(9):094104, 2011.
- [193] D. Franz. High harmonic generation in crystals assisted by local field enhancement in nanostructures. PhD thesis, Paris Saclay, 2018.
- [194] M. Mlejnek, E. M. Wright, J. V. Moloney, and N. Bloembergen. Second harmonic generation of femtosecond pulses at the boundary of a nonlinear dielectric. *Physical review letters*, 83(15):2934, 1999.

- [195] N. Garejev, I. Gražulevičiūtė, D. Majus, G. Tamošauskas, V. Jukna, A. Couairon, and A. Dubietis. Third-and fifth-harmonic generation in transparent solids with few-optical-cycle midinfrared pulses. *Physical Review A*, 89(3):033846, 2014.
- [196] A. H. Chin, O. G. Calderón, and J. Kono. Extreme midinfrared nonlinear optics in semiconductors. *Physical review letters*, 86(15):3292, 2001.
- [197] B. Bussière, F. Canova, J.-P. Chambaret, P. Delaporte, T. Itina, and M. Sentis. Damage threshold of sapphire in short and long pulse regime. In *International Conference on Lasers, Applications,* and Technologies 2007: Laser-assisted Micro-and Nanotechnologies, volume 6732, page 67321P. International Society for Optics and Photonics, 2007.
- [198] S. Han, L. Ortmann, H. Kim, Y. W. Kim, T. Oka, A. Chacon, B. Doran, M. Ciappina, M. Lewenstein, S.-W. Kim, et al. Extraction of higher-order nonlinear electronic response in solids using high harmonic generation. *Nature communications*, 10(1):1–6, 2019.
- [199] H. Deng, K. J. Leedle, Y. Miao, D. S. Black, K. E. Urbanek, J. McNeur, M. Kozák, A. Ceballos, P. Hommelhoff, O. Solgaard, et al. Gallium oxide for high-power optical applications. *Advanced Optical Materials*, 8(7):1901522, 2020.
- [200] J. Zhang, J. Shi, D.-C. Qi, L. Chen, and K. H. Zhang. Recent progress on the electronic structure, defect, and doping properties of ga2o3. APL Materials, 8(2):020906, 2020.
- [201] W. Mu, Y. Yin, Z. Jia, L. Wang, J. Sun, M. Wang, C. Tang, Q. Hu, Z. Gao, J. Zhang, et al. An extended application of β-ga 2 o 3 single crystals to the laser field: Cr 4+: β-ga 2 o 3 utilized as a new promising saturable absorber. *RSC Advances*, 7(35):21815–21819, 2017.
- [202] I. Cora, F. Mezzadri, F. Boschi, M. Bosi, M. Čaplovičová, G. Calestani, I. Dódony, B. Pécz, and R. Fornari. The real structure of ε-ga 2 o 3 and its relation to κ-phase. *CrystEngComm*, 19(11): 1509–1516, 2017.
- [203] O. Bordun, I. Y. Kukharskyy, B. Bordun, and V. Lushchanets. Dispersion of refractive index of β-ga 2 o 3 thin films. Journal of Applied Spectroscopy, 81(5):771–775, 2014.
- [204] C. Tang and H. Rabin. Selection rules for circularly polarized waves in nonlinear optics. *Physical Review B*, 3(12):4025, 1971.
- [205] M. Rebien, W. Henrion, M. Hong, J. Mannaerts, and M. Fleischer. Optical properties of gallium oxide thin films. *Applied physics letters*, 81(2):250–252, 2002.
- [206] F. Preusch, B. Adelmann, and R. Hellmann. Micromachining of aln and al2o3 using fiber laser. Micromachines, 5(4):1051–1060, 2014.
- [207] J. Seres, E. Seres, C. Serrat, E. Young, J. Speck, and T. Schumm. All-solid-state vuv frequency comb at 160 nm using high-harmonic generation in nonlinear femtosecond enhancement cavity. *Optics express*, 27(5):6618–6628, 2019.

- [208] J. Seres, E. Seres, C. Serrat, and T. Schumm. High harmonic generation in all due to out-of-surface electron orbitals. OSA Continuum, 4(1):47–54, 2021.
- [209] W. Sun, J. Zhang, V. Adivarahan, A. Chitnis, M. Shatalov, S. Wu, V. Mandavilli, J. Yang, and M. A. Khan. Algan-based 280 nm light-emitting diodes with continuous wave powers in excess of 1.5 mw. Applied Physics Letters, 85(4):531–533, 2004.
- [210] V. Adivarahan, W. H. Sun, A. Chitnis, M. Shatalov, S. Wu, H. Maruska, and M. A. Khan. 250 nm algan light-emitting diodes. *Applied physics letters*, 85(12):2175–2177, 2004.
- [211] D. Passeri, M. Larciprete, A. Belardini, S. Paoloni, A. Passaseo, C. Sibilia, and F. Michelotti. Second harmonic generation in algan, gan and al x ga 1-x n/gan multiple quantum well structures. *Applied Physics B*, 79(5):611–615, 2004.
- [212] W. S. Yoo, H. Harima, and M. Yoshimoto. Polarized raman signals from si wafers: dependence of in-plane incident orientation of probing light. ECS Journal of Solid State Science and Technology, 4(9):P356–P363, 2015.
- [213] G. Wang, G. Kiehne, G. Wong, J. B. Ketterson, X. Liu, and R. Chang. Large second harmonic response in zno thin films. *Applied physics letters*, 80(3):401–403, 2002.
- [214] R. Panda, A. Singh, R. Samal, S. Bhattacharya, P. K. Sahoo, P. K. Datta, and S. K. Das. Femtosecond laser excited second harmonic and multiphoton absorption induced uv luminescence generation behaviour of zno nanofibers. *Optik*, 154:320–324, 2018.
- [215] U. Neumann, R. Grunwald, U. Griebner, G. Steinmeyer, M. Schmidbauer, and W. Seeber. Secondharmonic performance of a-axis-oriented zno nanolayers on sapphire substrates. *Applied Physics Letters*, 87(17):171108, 2005.
- [216] K. Y. Lo, Y. J. Huang, J. Y. Huang, Z. C. Feng, W. E. Fenwick, M. Pan, and I. T. Ferguson. Reflective second harmonic generation from zno thin films: A study on the zn–o bonding. *Applied physics letters*, 90(16):161904, 2007.
- [217] J. Ye, S. Gu, S. Zhu, and S. Liu. Jd ye, sl gu, sm zhu, sm liu, yd zheng, r. zhang, y. shi, q. chen, hq yu, and yd ye, appl. phys. lett. 88, 101905 (2006). Appl. Phys. Lett., 88:101905, 2006.
- [218] U. Özgür, Y. I. Alivov, C. Liu, A. Teke, M. Reshchikov, S. Doğan, V. Avrutin, S.-J. Cho, and H. Morkoç. A comprehensive review of zno materials and devices. *Journal of applied physics*, 98 (4):11, 2005.
- [219] S. Jiang, S. Gholam-Mirzaei, E. Crites, J. E. Beetar, M. Singh, R. Lu, M. Chini, and C. Lin. Crystal symmetry and polarization of high-order harmonics in zno. *Journal of Physics B: Atomic, Molecular and Optical Physics*, 52(22):225601, 2019.
- [220] M. Cardona. Optical properties and band structure of srti o 3 and bati o 3. Physical Review, 140 (2A):A651, 1965.

- [221] D. Baykusheva, A. Chacón, D. Kim, D. E. Kim, D. A. Reis, and S. Ghimire. Strong-field physics in three-dimensional topological insulators. *Physical Review A*, 103(2):023101, 2021.
- [222] D. Gauthier, S. Kaassamani, D. Franz, R. Nicolas, J.-T. Gomes, L. Lavoute, D. Gaponov, S. Février, G. Jargot, M. Hanna, et al. Orbital angular momentum from semiconductor high-order harmonics. *Optics letters*, 44(3):546–549, 2019.
- [223] J. P. Torres and L. Torner. Twisted photons: applications of light with orbital angular momentum. John Wiley & Sons, 2011.
- [224] I. Kilen, M. Kolesik, J. Hader, J. V. Moloney, U. Huttner, M. K. Hagen, and S. W. Koch. Propagation induced dephasing in semiconductor high-harmonic generation. *Physical review letters*, 125 (8):083901, 2020.
- [225] M. A. Bandres and J. C. Gutiérrez-Vega. Ince-gaussian beams. Optics letters, 29(2):144-146, 2004.
- [226] S. Odoulov, A. Shumelyuk, H. Badorreck, S. Nolte, K.-M. Voit, and M. Imlau. Interference and holography with femtosecond laser pulses of different colours. *Nature communications*, 6(1):1–8, 2015.
- [227] T. Brabec and F. Krausz. Nonlinear optical pulse propagation in the single-cycle regime. *Physical Review Letters*, 78(17):3282, 1997.
- [228] E. Yablonovitch and N. Bloembergen. Avalanche ionization and the limiting diameter of filaments induced by light pulses in transparent media. *Physical Review Letters*, 29(14):907, 1972.
- [229] T. Jia, H. Chen, M. Huang, F. Zhao, X. Li, S. Xu, H. Sun, D. Feng, C. Li, X. Wang, et al. Ultraviolet-infrared femtosecond laser-induced damage in fused silica and caf 2 crystals. *Physical Review B*, 73(5):054105, 2006.
- [230] D. Simanovskii, H. Schwettman, H. Lee, and A. Welch. Midinfrared optical breakdown in transparent dielectrics. *Physical review letters*, 91(10):107601, 2003.
- [231] D. Grojo, S. Leyder, P. Delaporte, W. Marine, M. Sentis, and O. Utéza. Long-wavelength multiphoton ionization inside band-gap solids. *Physical Review B*, 88(19):195135, 2013.
- [232] L. Gallais, D.-B. Douti, M. Commandre, G. Batavičiūtė, E. Pupka, M. Ščiuka, L. Smalakys, V. Sirutkaitis, and A. Melninkaitis. Wavelength dependence of femtosecond laser-induced damage threshold of optical materials. *Journal of Applied Physics*, 117(22):223103, 2015.
- [233] M. Li, S. Menon, J. P. Nibarger, and G. N. Gibson. Ultrafast electron dynamics in femtosecond optical breakdown of dielectrics. *Physical review letters*, 82(11):2394, 1999.
- [234] P. Audebert, P. Daguzan, A. Dos Santos, J. Gauthier, J. Geindre, S. Guizard, G. Hamoniaux, K. Krastev, P. Martin, G. Petite, et al. Space-time observation of an electron gas in si o 2. *Physical Review Letters*, 73(14):1990, 1994.

- [235] A. Couairon, E. Brambilla, T. Corti, D. Majus, O. d. J. Ramírez-Góngora, and M. Kolesik. Practitioner's guide to laser pulse propagation models and simulation. *The European Physical Journal Special Topics*, 199(1):5–76, 2011.
- [236] G. P. Agrawal. Nonlinear fiber optics. In Nonlinear Science at the Dawn of the 21st Century, pages 195–211. Springer, 2000.
- [237] W. T. Vetterling, S. A. Teukolsky, W. H. Press, and B. P. Flannery. Numerical recipes in Fortran. Number BOOK. Cambridge University Press, 1992.
- [238] S. M. Sze, Y. Li, and K. K. Ng. Physics of semiconductor devices. John wiley & sons, 2021.
- [239] K. Sokolowski-Tinten, J. Białkowski, and D. von der Linde. Ultrafast laser-induced order-disorder transitions in semiconductors. *Physical review B*, 51(20):14186, 1995.
- [240] A. D. Bristow, N. Rotenberg, and H. M. Van Driel. Two-photon absorption and kerr coefficients of silicon for 850–2200 nm. Applied Physics Letters, 90(19):191104, 2007.
- [241] K. Sokolowski-Tinten and D. von der Linde. Generation of dense electron-hole plasmas in silicon. *Physical Review B*, 61(4):2643, 2000.
- [242] R. Adair, L. Chase, and S. A. Payne. Nonlinear refractive index of optical crystals. *Physical Review B*, 39(5):3337, 1989.
- [243] V. Dimitrov and S. Sakka. Electronic oxide polarizability and optical basicity of simple oxides. i. Journal of Applied Physics, 79(3):1736–1740, 1996.
- [244] J. B. Baxter and C. A. Schmuttenmaer. Carrier dynamics in bulk zno. i. intrinsic conductivity measured by terahertz time-domain spectroscopy. *Physical Review B*, 80(23):235205, 2009.
- [245] E. Yablonovitch. Self-phase modulation and short-pulse generation from laser-breakdown plasmas. *Physical review A*, 10(5):1888, 1974.
- [246] S. Wilks, J. Dawson, and W. Mori. Frequency up-conversion of electromagnetic radiation with use of an overdense plasma. *Physical review letters*, 61(3):337, 1988.
- [247] W. M. Wood, C. Siders, and M. Downer. Measurement of femtosecond ionization dynamics of atmospheric density gases by spectral blueshifting. *Physical review letters*, 67(25):3523, 1991.
- [248] F. Pfeiffer. X-ray ptychography. Nature Photonics, 12(1):9–17, 2018.
- [249] R. Hollinger, D. Hoff, P. Wustelt, S. Skruszewicz, Y. Zhang, H. Kang, D. Würzler, T. Jungnickel,
 M. Dumergue, A. Nayak, et al. Carrier-envelope-phase measurement of few-cycle mid-infrared laser
 pulses using high harmonic generation in zno. *Optics Express*, 28(5):7314–7322, 2020.
- [250] H. N. Chapman, A. Barty, M. J. Bogan, S. Boutet, M. Frank, S. P. Hau-Riege, S. Marchesini, B. W. Woods, S. Bajt, W. H. Benner, et al. Femtosecond diffractive imaging with a soft-x-ray free-electron laser. *Nature Physics*, 2(12):839–843, 2006.

- [251] A. Ravasio, D. Gauthier, F. Maia, M. Billon, J. Caumes, D. Garzella, M. Géléoc, O. Gobert, J.-F. Hergott, A. Pena, et al. Single-shot diffractive imaging with a table-top femtosecond soft x-ray laser-harmonics source. *Physical review letters*, 103(2):028104, 2009.
- [252] T. Gorkhover, S. Schorb, R. Coffee, M. Adolph, L. Foucar, D. Rupp, A. Aquila, J. D. Bozek, S. W. Epp, B. Erk, et al. Femtosecond and nanometre visualization of structural dynamics in superheated nanoparticles. *Nature photonics*, 10(2):93–97, 2016.
- [253] J. Huijts, S. Fernandez, D. Gauthier, M. Kholodtsova, A. Maghraoui, K. Medjoubi, A. Somogyi, W. Boutu, and H. Merdji. Broadband coherent diffractive imaging. *Nature Photonics*, pages 1–5, 2020.
- [254] J. Rodenburg, A. Hurst, A. Cullis, B. Dobson, F. Pfeiffer, O. Bunk, C. David, K. Jefimovs, and I. Johnson. Hard-x-ray lensless imaging of extended objects. *Physical review letters*, 98(3):034801, 2007.
- [255] P. Thibault, M. Dierolf, A. Menzel, O. Bunk, C. David, and F. Pfeiffer. High-resolution scanning x-ray diffraction microscopy. *Science*, 321(5887):379–382, 2008.
- [256] M. Guizar-Sicairos, I. Johnson, A. Diaz, M. Holler, P. Karvinen, H.-C. Stadler, R. Dinapoli, O. Bunk, and A. Menzel. High-throughput ptychography using eiger: scanning x-ray nano-imaging of extended regions. *Optics express*, 22(12):14859–14870, 2014.
- [257] D. A. Shapiro, Y.-S. Yu, T. Tyliszczak, J. Cabana, R. Celestre, W. Chao, K. Kaznatcheev, A. D. Kilcoyne, F. Maia, S. Marchesini, et al. Chemical composition mapping with nanometre resolution by soft x-ray microscopy. *Nature Photonics*, 8(10):765–769, 2014.
- [258] J. Rodenburg, A. Hurst, and A. Cullis. Transmission microscopy without lenses for objects of unlimited size. Ultramicroscopy, 107(2-3):227–231, 2007.
- [259] P. Thibault, M. Dierolf, O. Bunk, A. Menzel, and F. Pfeiffer. Probe retrieval in ptychographic coherent diffractive imaging. *Ultramicroscopy*, 109(4):338–343, 2009.
- [260] A. M. Maiden and J. M. Rodenburg. An improved ptychographical phase retrieval algorithm for diffractive imaging. *Ultramicroscopy*, 109(10):1256–1262, 2009.
- [261] B. Enders and P. Thibault. A computational framework for ptychographic reconstructions. Proceedings of the Royal Society A: Mathematical, Physical and Engineering Sciences, 472(2196):20160640, 2016.
- [262] S. Marchesini, H. Krishnan, B. J. Daurer, D. A. Shapiro, T. Perciano, J. A. Sethian, and F. R. Maia. Sharp: a distributed gpu-based ptychographic solver. *Journal of applied crystallography*, 49 (4):1245–1252, 2016.
- [263] V. Favre-Nicolin, J. Coraux, M.-I. Richard, and H. Renevier. Fast computation of scattering maps of nanostructures using graphical processing units. *Journal of Applied Crystallography*, 44(3):635–640, 2011.

- [264] V. Favre-Nicolin, G. Girard, S. Leake, J. Carnis, Y. Chushkin, J. Kieffer, P. Paleo, and M.-I. Richard. Pynx: high-performance computing toolkit for coherent x-ray imaging based on operators. *Journal of Applied Crystallography*, 53(5):1404–1413, 2020.
- [265] O. Mandula, M. Elzo Aizarna, J. Eymery, M. Burghammer, and V. Favre-Nicolin. Pynx. ptycho: a computing library for x-ray coherent diffraction imaging of nanostructures. *Journal of Applied Crystallography*, 49(5):1842–1848, 2016.
- [266] J. Vila-Comamala, A. Sakdinawat, and M. Guizar-Sicairos. Characterization of x-ray phase vortices by ptychographic coherent diffractive imaging. *Optics letters*, 39(18):5281–5284, 2014.
- [267] N. X. Truong, R. Safaei, V. Cardin, S. M. Lewis, X. L. Zhong, F. Légaré, and M. A. Denecke. Coherent tabletop euv ptychography of nanopatterns. *Scientific reports*, 8(1):1–9, 2018.
- [268] M. Dierolf, A. Menzel, P. Thibault, P. Schneider, C. M. Kewish, R. Wepf, O. Bunk, and F. Pfeiffer. Ptychographic x-ray computed tomography at the nanoscale. *Nature*, 467(7314):436–439, 2010.
- [269] V. Elser. Phase retrieval by iterated projections. JOSA A, 20(1):40–55, 2003.
- [270] S. Marchesini, Y.-C. Tu, and H.-t. Wu. Alternating projection, ptychographic imaging and phase synchronization. Applied and Computational Harmonic Analysis, 41(3):815–851, 2016.
- [271] P. Thibault and M. Guizar-Sicairos. Maximum-likelihood refinement for coherent diffractive imaging. New Journal of Physics, 14(6):063004, 2012.
- [272] J. Vieira, R. M. Trines, E. P. Alves, R. Fonseca, J. Mendonça, R. Bingham, P. Norreys, and L. Silva. High orbital angular momentum harmonic generation. *Physical review letters*, 117(26):265001, 2016.
- [273] C. Hernández-García, J. Vieira, J. T. Mendonca, L. Rego, J. San Román, L. Plaja, P. R. Ribic, D. Gauthier, and A. Picón. Generation and applications of extreme-ultraviolet vortices. In *Photonics*, volume 4, page 28. Multidisciplinary Digital Publishing Institute, 2017.
- [274] D. Gauthier, P. R. Ribič, G. Adhikary, A. Camper, C. Chappuis, R. Cucini, L. DiMauro, G. Dovillaire, F. Frassetto, R. Géneaux, et al. Tunable orbital angular momentum in high-harmonic generation. *Nature communications*, 8(1):1–7, 2017.
- [275] G. Gariepy, J. Leach, K. T. Kim, T. J. Hammond, E. Frumker, R. W. Boyd, and P. B. Corkum. Creating high-harmonic beams with controlled orbital angular momentum. *Physical review letters*, 113(15):153901, 2014.
- [276] R. Géneaux, A. Camper, T. Auguste, O. Gobert, J. Caillat, R. Taïeb, and T. Ruchon. Synthesis and characterization of attosecond light vortices in the extreme ultraviolet. *Nature communications*, 7(1):1–6, 2016.
- [277] G. K. Tadesse, W. Eschen, R. Klas, M. Tschernajew, F. Tuitje, M. Steinert, M. Zilk, V. Schuster, M. Zürch, T. Pertsch, et al. Wavelength-scale ptychographic coherent diffractive imaging using a high-order harmonic source. *Scientific reports*, 9(1):1–7, 2019.

- [278] Y. V. Bludov, N. M. Peres, and M. I. Vasilevskiy. Excitation of localized graphene plasmons by a metallic slit. *Physical Review B*, 101(7):075415, 2020.
- [279] L. Zhang, A. Kubo, L. Wang, H. Petek, and T. Seideman. Imaging of surface plasmon polariton fields excited at a nanometer-scale slit. *Physical review B*, 84(24):245442, 2011.
- [280] F. Graziani, M. P. Desjarlais, R. Redmer, and S. B. Trickey. Frontiers and challenges in warm dense matter, volume 96. Springer Science & Business, 2014.
- [281] A. Levy, P. Audebert, R. Shepherd, J. Dunn, M. Cammarata, O. Ciricosta, F. Deneuville,
 F. Dorchies, M. Fajardo, C. Fourment, et al. The creation of large-volume, gradient-free warm dense matter with an x-ray free-electron laser. *Physics of Plasmas*, 22(3):030703, 2015.
- [282] R. Ernstorfer, M. Harb, C. T. Hebeisen, G. Sciaini, T. Dartigalongue, and R. D. Miller. The formation of warm dense matter: experimental evidence for electronic bond hardening in gold. *Science*, 323(5917):1033–1037, 2009.
- [283] B. I. Cho, T. Ogitsu, K. Engelhorn, A. Correa, Y. Ping, J. Lee, L. J. Bae, D. Prendergast, R. Falcone, and P. Heimann. Measurement of electron-ion relaxation in warm dense copper. *Scientific reports*, 6(1):1–7, 2016.
- [284] B. J. Siwick, J. R. Dwyer, R. E. Jordan, and R. D. Miller. An atomic-level view of melting using femtosecond electron diffraction. *Science*, 302(5649):1382–1385, 2003.
- [285] R. Huber, F. Tauser, A. Brodschelm, M. Bichler, G. Abstreiter, and A. Leitenstorfer. How manyparticle interactions develop after ultrafast excitation of an electron-hole plasma. *Nature*, 414 (6861):286–289, 2001.
- [286] T. White, J. Vorberger, C. Brown, B. Crowley, P. Davis, S. Glenzer, J. Harris, D. Hochhaus, S. Le Pape, T. Ma, et al. Observation of inhibited electron-ion coupling in strongly heated graphite. *Scientific reports*, 2(1):1–5, 2012.