

RESEARCH ARTICLE | JUNE 01 1981

Vibrational spectra and structure of fluorozirconate glasses



Rui M. Almeida; John D. Mackenzie

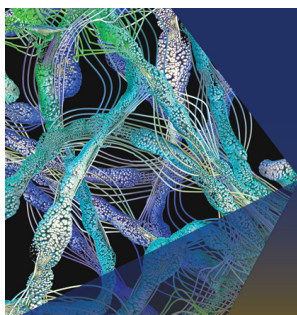


J. Chem. Phys. 74, 5954–5961 (1981)

<https://doi.org/10.1063/1.441033>



25 June 2024 11:51:50



The Journal of Chemical Physics

Special Topic:

Machine Learning for Biomolecular Modeling

Guest Editors: Pratyush Tiwary, Francesca Grisoni, Pilar Cossio

Submit Today!

Vibrational spectra and structure of fluorozirconate glasses

Rui M. Almeida^{a)} and John D. Mackenzie

Materials Science and Engineering Department, University of California, Los Angeles, California 90024
(Received 17 November 1980; accepted 13 February 1981)

A series of binary fluorozirconate glasses have been prepared in the $\text{ZrF}_4\text{--BaF}_2$ system, containing between 52–74 mol % ZrF_4 . Their infrared and polarized Raman spectra are reported for the first time, down to 33 cm^{-1} . The glass transition and crystallization temperatures were also measured. The vibrational modes have been assigned to different types of atomic motions in the glass network. The basic structure of the fluorozirconate glasses is proposed to consist of zigzag chains of ZrF_6 octahedra, cross linked by Ba–F ionic bands. The interoctahedral Zr–F–Zr angle distribution was estimated to peak at $\sim 136^\circ$, based on the analysis of the two highest frequency Raman modes.

I. INTRODUCTION

Glass formation in ZrF_4 -based systems was first reported by Poulain *et al.*¹ in 1975. Since then, these glasses have received increasing attention due to their somewhat unusual properties, namely, a relatively high anionic electrical conductivity^{2,3} and their optical transparency,⁴ extending from the near UV (~ 230 nm) to the middle IR (~ 8000 nm), which makes them good candidates for laser windows and optical waveguide materials. Fluorozirconate glasses are also interesting from a scientific point of view, since their structure appears to be markedly different from that of other known glass systems.

So far, only the structure of a few multicomponent systems has been discussed, such as $\text{ZrF}_4\text{--BaF}_2\text{--ThF}_4$ ⁴ and $\text{ZrF}_4\text{--BaF}_2\text{--LaF}_3\text{--NdF}_3$.⁵ Such glasses have been proposed to consist of a random association of six-, seven-, and eight-coordinated fluorozirconate polyhedra.^{4,5} Nothing has yet been said about their geometry or arrangement in space, in part because a more direct probing of the glass structure, for example by vibrational spectroscopy, x-ray or neutron diffraction, or NMR, has not yet been undertaken. In this paper, we report the IR and Raman spectra of binary $\text{ZrF}_4\text{--BaF}_2$ glasses, a system whose properties have not been studied before.

II. EXPERIMENTAL PROCEDURE

A series of fluorozirconate glasses were prepared in the $\text{ZrF}_4\text{--BaF}_2$ system and a $\text{ZrF}_4\text{--SrF}_2$ sample was also synthesized. Commercial ZrF_4 of 99% purity (Alfa Inorganics) was unacceptable for Raman spectroscopy due to the high level of luminescence observed. Therefore, the commercial product was purified by double distillation, which reduced the initial Fe content (~ 1000 ppm) by a factor of about 5. Ultrapure BaF_2 and SrF_2 were used (Alfa Inorganics). Batches of ~ 6 g were melted in platinum crucibles in a dry box filled with high purity nitrogen (O_2 and H_2O contents at ~ 1 ppm). The

binary mixtures were heated in an electric furnace from room temperature up to 900°C , kept for 10 min at this temperature for homogenization, and then cast. The compositions of the glasses prepared are shown in Table I. From the IR absorption spectra recorded for a few bulk samples (1–2 mm thick), no evidence was found for the presence of residual water in the glasses.

The glass transition and crystallization temperatures were measured by differential thermal analysis, with a heating rate of $7.5^\circ\text{C min}^{-1}$.

Infrared absorption spectra were recorded for all samples by the KBr disc method, between $4000\text{--}300$ cm^{-1} , in a Perkin-Elmer 457, grating, double-beam spectrophotometer. IR absorption was also recorded for three different glasses between $500\text{--}33$ cm^{-1} , using polyethylene pellets, in a Perkin-Elmer 180, grating, double-beam spectrophotometer. The pressed-disc technique was used, since all attempts to blow thin films from the binary melts failed (this was actually possible for ternary melts containing ThF_4 or LaF_3). Polarized Raman spectra were recorded for all samples down to ~ 30 cm^{-1} , in the 90° scattering configuration. The Raman spectrometer consisted of a Spectra Physics model 165 Ar^+ laser, a Spex double monochromator, and photon-counting electronics. The spectrum of glass #3 was taken with the Spex 1401, which was linear in frequency, whereas all other spectra were taken with the Spex 1400-II model, which was linear in wavelength. The spectra recorded with the two instruments were identical. The 514.5 nm laser line was used in all experiments and the slits were opened to 250 μm . All spectra were recorded in both the $HH(II)$ configuration, where the scattered light was analyzed for electric vector parallel to that of the incident radiation, and the $VH(I)$ configuration, where the scattered light was analyzed for electric vector perpendicular to that of the incident laser. The polished glass samples were in the form of small rectangular plates, with thicknesses between 0.8 and 1.5 mm. The largest sample corresponded to the most stable composition (#3 in Table I). For calculating the depolarization ratios ρ , the Raman spectrometer was standardized against the polarized (459 cm^{-1}) and the depolarized (314 cm^{-1}) bands of liquid CCl_4 . All spectra were taken at room temperature.

^{a)}Present address: Complexo Interdisciplinar, Instituto Superior Técnico, Av. Rovisco Pais, 1096 Lisboa Codex, Portugal.

TABLE I. Composition and characteristic temperatures of fluorozirconate glasses.

Batch composition (mol %)			Analyzed composition (mol %)			Glass #	T_g (°C)	T_{cryst} (°C)
ZrF ₄	BaF ₂	SrF ₂	ZrF ₄	BaF ₂	SrF ₂			
50	50		52	48		1		
60	40		...	...		2	298	338
65	35		64	36		3	300	352
66.7	33.3		67	33		4	291	332
85	15		...	...		5	293	345
90	10		...	...		6	289	344
80	20		74	26		7	288	335
70		30	...		...	8	290	340

III. RESULTS AND DISCUSSION

A. Glass transition and crystallization temperatures

Poulain *et al.*⁶ prepared binary ZrF₄-BaF₂ glasses with ZrF₄ contents between 60–70 mol%, using the same quenching rate as in the present work. In our work, the glass-forming region of the ZrF₄-BaF₂ system was found to lie between ~52–74 mol% ZrF₄.

The glass transition (T_g) and crystallization (T_{cryst}) temperatures are given in Table I. They showed little variation over the composition range that was tested (60–74 mol% ZrF₄).

B. IR spectra

The IR spectral data of the fluorozirconate glasses studied are given in Table II. The middle and far IR spectra of glasses #3, #7, and #8 are shown in Fig. 1. The spectra of all glasses consisted of three main peaks: a strong band at ~472–520 cm⁻¹, a medium band at ~270–250 cm⁻¹, and a weak band at ~115–130 cm⁻¹. There was also a weak shoulder at ~625 cm⁻¹ for most samples, but this was not structure sensitive, since its frequency did not vary with composition.

C. Raman spectra

The Raman spectral data of the eight fluorozirconate glasses studied are given in Table III. The spectra of glasses #1, #3, #7, and #8 are shown in Figs. 2, 3, 4,

and 5, respectively. The depolarization ratio was computed for each band by the formula

$$\rho = I_{VH}/I_{HH}, \quad (1)$$

where I_{VH} and I_{HH} are the intensities of the VH and HH spectra, respectively, above the base line. In those cases where the position of the base line was uncertain, ρ was not computed, although it is sometimes indicated that the band was depolarized (ρ clearly larger than 0.75).

All glasses exhibited a depolarized band at ~50 cm⁻¹, which is characteristic of the Raman spectra of most known glasses. This peak may be due to the combined effects of the Bose-Einstein thermal population and the λ^{-4} dependence of the Raman scattering intensity⁷ and also due to the existence of optical modes of low frequency that are Raman active.⁸ Since the nature of these modes is still uncertain, we will not assign this feature. Most glasses had five main peaks: two polarized, high energy peaks at ~565–598 and ~468–500 cm⁻¹ and three

TABLE II. Frequencies and intensities of the IR bands of fluorozirconate glasses.

Glass sample ^a	IR absorption bands (cm ⁻¹)			
	KBr pellets		Polyethylene pellets	
#1	625 wsh	472 s		
#2	620 wsh	487 s		
#3	...	490 s	270 m	120 w
#4	630 wsh	490 s		
#5	625 wsh	505 s		
#6	625 wsh	505 s		
#7	620 wsh	520 s	250 ms	115 wsh
#8	620 wsh	510 s	250 m	130 wsh

^aFor glass compositions, refer to Table I. Nomenclature: w—weak; m—medium; s—strong; sh—shoulder.

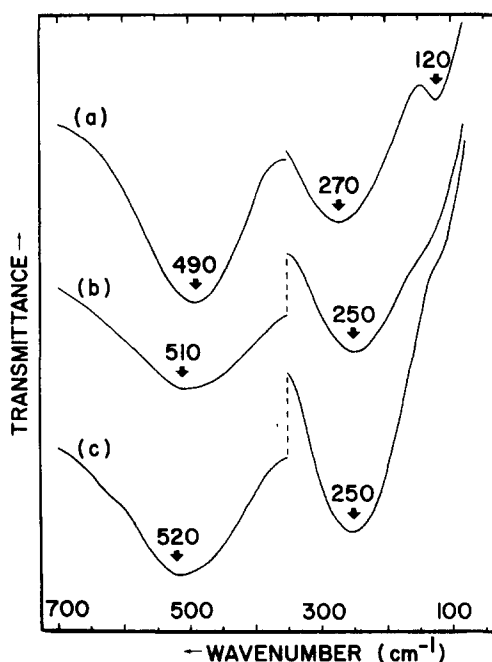


FIG. 1. Middle and far IR absorption spectra of (a) 64 ZrF₄-36 BaF₂ glass, (b) 67 ZrF₄-33 SrF₂ glass, and (c) 74 ZrF₄-26 BaF₂ glass.

TABLE III. Frequencies, intensities, and depolarization ratios in the Raman spectra of fluoro-zirconate glasses.

Spectral data	Glass ^a sample							
	#1	#2	#3	#4	#5	#6	#7	#8
$\bar{\nu}$					629 sh	629 sh	630 sh	637 sh
$\bar{\nu}$	565 s	577 vs	580 vs	583 vs	584 vs	592 vs	598 vs	595 vs
ρ	0.03	0.01	0.00	0.03	0.06	0.06	0.03	0.07
$\bar{\nu}_h$		53	56	57	62	58	70	74
$\bar{\nu}$	468 m	478 m	485 m	490 m	490 m	492 m	500 m	500 m
ρ	0.33	0.26	0.28	0.26	0.23	0.20	0.13	0.19
$\bar{\nu}$	386 mw	397 vw	400 vw	398 w	404 vw	403 w	406 w	416 vw
ρ	0.69	1.05	0.79	0.53	1.10	0.81	0.86	0.75
$\bar{\nu}$	322 mw	324 wb	324 w	340 m	341 w	341 m	348 mw	340 mw
ρ	1.09	0.75	0.81	0.59	1.2	dep	0.53	0.80
$\bar{\nu}$	230 w	196 w	196 mb	194 m	194 m	183 mw	183 m	194 mb
ρ	0.72	1.00	0.75	0.43	1.0	dep	0.90	0.97
$\bar{\nu}$	139 w					92 w	104 w	101 w
ρ							dep	dep
$\bar{\nu}$	53 vw	51 vw	50 ms	50 w	50 vw	49 vw	52 w	52 mw
ρ		dep	0.84	dep	dep			dep

^aFor glass compositions, refer to Table I. Nomenclature: $\bar{\nu}$ —frequency in cm^{-1} ; ρ —depolarization ratio; $\bar{\nu}_h$ —width at half-height in cm^{-1} ; s—strong; m—medium; w—weak; v—very; sh—shoulder; b—broad; dep—depolarized.

weaker, depolarized bands at ~ 386 – 416 , ~ 322 – 348 , and ~ 183 – 196 cm^{-1} . For compositions with $\geq 67 \text{ mol\% ZrF}_4$, a shoulder appeared at ~ 629 – 637 cm^{-1} . All these modes will be assigned in the next section. Some glasses also had a weak band in the neighborhood of 100 cm^{-1} , which we will not attempt to assign.

D. Vibrational modes of fluorozirconate glasses

No study has yet been published dealing with the vibrational spectra of a fluorozirconate glass. Besides, only a small number of studies have appeared concerning vi-

brational spectra of related molten or crystalline fluorozirconates. Toth *et al.*⁹ have shown that in the absence of bridging there is an inverse correlation between the symmetric stretching (which we will call ν^s or SS frequency and the coordination number (CN) of Zr in the complex ions present in the structure of a number of crystalline compounds. These included Li_2ZrF_6 and Cs_2ZrF_6 , both containing free ZrF_6^{2-} octahedral ions, where the highest energy (ν^s) Raman peaks occurred at

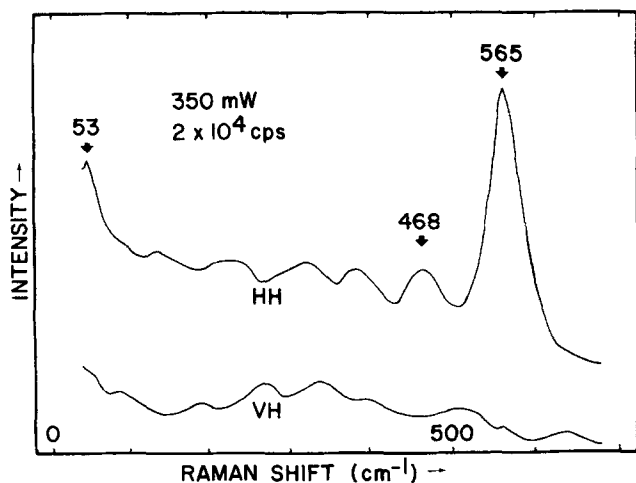


FIG. 2. Raman spectrum of the 52 ZrF_4 –48 BaF_2 glass in the polarized (HH) and depolarized (VH) configurations.

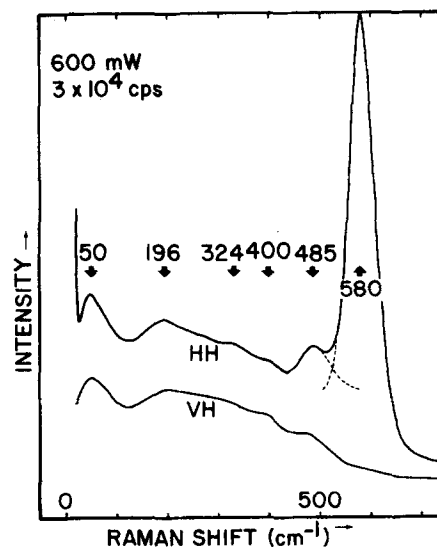


FIG. 3. Raman spectrum of the 64 ZrF_4 –36 BaF_2 glass in the polarized (HH) and depolarized (VH) configurations.

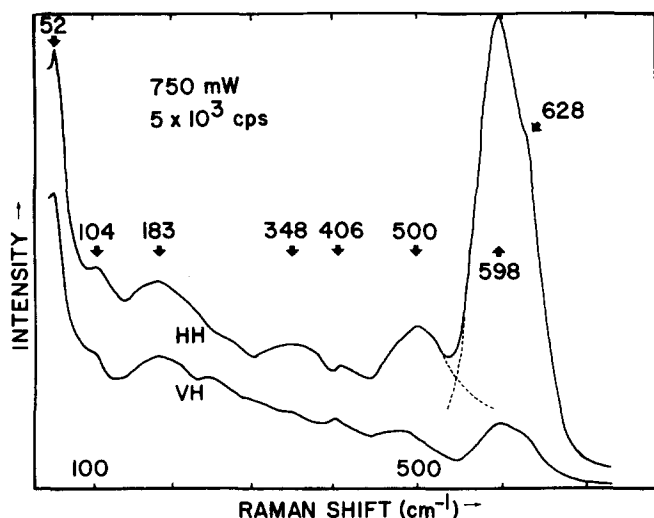


FIG. 4. Raman spectrum of the 74 ZrF₄-26 BaF₂ glass in the polarized (HH) and depolarized (VH) configurations.

585 and 577 cm⁻¹, respectively; Na₃ZrF₇, containing free ZrF₆³⁻ ions, with the ν^s band at 556 cm⁻¹; finally, K₂ZrF₆—composed of chains of ZrF₆ polyhedra sharing two edges each—had the ν^s peak at 525 cm⁻¹. Based on these results, Toth *et al.*⁹ studied the Raman spectra of LiF-NaF-ZrF₄ molten salt mixtures and proposed that the CN of Zr varied between eight and four for ZrF₄ contents between 14–40 mol%; here the ν^s frequency correspondingly varied between 555–593 cm⁻¹ and octahedral coordination was proposed for the 33 mol% ZrF₄ mixture, with ν^s at 577 cm⁻¹.

In order to assign the vibrational modes of the fluorozirconate glasses, we will postulate a structural model *ab initio*. The 64 ZrF₄-36 BaF₂ glass was the most stable and its composition, lying approximately in the center of the glass-forming region, coincides with 2ZrF₄·BaF₂, within the experimental error of the chemical analysis. Therefore, this will be taken as the *dizirconate* model glass and its spectra will be analyzed first. The relative simplicity of the IR and Raman spectra and the observed symmetry (geometric) of the dominant bands indicate that essentially there is only one CN for the Zr atoms. The dizirconate glass has an F/Zr ratio of 5.0; if all F atoms are bounded to Zr atoms—we have no evidence for the occurrence of “ionic fluorine”—the minimum CN possible is five. If this were the case, the glass would be formed by isolated ZrF₅⁻ ions and it would probably not be very stable, due to the absence of bridging. The two possible types of polyhedra would be the tetragonal pyramid (C_{4v}) and the trigonal bipyramid (D_{3h}); the first one should exhibit six IR and nine Raman bands, three of which are polarized, whereas for the second one, one would predict five IR and six Raman bands, two of which are polarized. Our experimental results (a stable glass with three IR and five Raman bands) seem to rule out the five-coordinated geometries. On the other hand, since the ν^s frequency of eight-coordinated K₂ZrF₆ occurs at 525 cm⁻¹, which is much lower than the highest frequency of the dizirconate glass at 580 cm⁻¹, we will assume that the highest CN possible

is seven. The seven-coordinated geometry of highest symmetry is the pentagonal bipyramid (D_{5h}), and a fairly realistic model in this case, such as the “bound bipyramidal unit”¹⁰ vibrating against a fixed network of infinite mass, would predict the occurrence of seven IR and seven Raman bands. The fact that the glass spectra have a considerably smaller number of bands and particularly the fact that seven-coordinated Na₃ZrF₇ has the ν^s peak at 556 cm⁻¹ < 580 cm⁻¹ indicate that the CN is not seven either. Therefore, it has to be six, which is strongly supported by the occurrence of the ν^s peaks of six-coordinated Li₂ZrF₆ and Cs₂ZrF₆ at ~580 cm⁻¹ as well.

Since trigonal prisms are less stable than octahedra and have not yet been found in crystalline fluorozirconates, we will propose that the glass contains ZrF₆ octahedra, sharing two corners each in order to satisfy the F/Zr ratio of 5.0. Our model for the dizirconate glass structure is that of an inorganic polymer, formed by zigzag chains of octahedra, as shown in Fig. 6. Theoretically, such chains would be infinite but, in practice, the low viscosity of the glass-forming melt¹¹ suggests that the lengths are relatively short, although we cannot quantify. Some rings are also expected to exist, as in the case of the isostructural metasilicate and metaphosphate glasses.

A mode assignment can now be made consistent with the proposed structure. The highest frequency mode (580 cm⁻¹, Raman active) is a very strong, sharp (half-width = 56 cm⁻¹), and completely polarized ($\rho \approx 0$) band. The zero depolarization ratio shows that this is a totally symmetric vibration and its sharpness indicates that it is highly localized and must depend very little on the distribution of interoctahedral angles. We assign this mode to the symmetric stretching vibration of the four Zr-F_{nb} bands of the octahedron (where F_{nb} designates a nonbridging fluorine atom). It will be called $\nu^s(\text{Zr-F}_{nb})$ and it is equivalent to the $\nu_1(A_{1g})$ mode of the square planar Zr-(F_{nb})₄ structure (D_{4h} group) shown in Fig. 7.

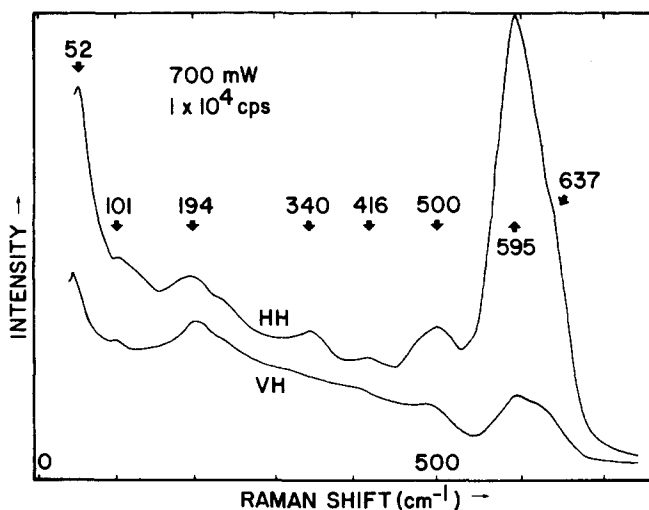


FIG. 5. Raman spectrum of the 67 ZrF₄-33 SrF₂ glass in the polarized (HH) and depolarized (VH) configurations.

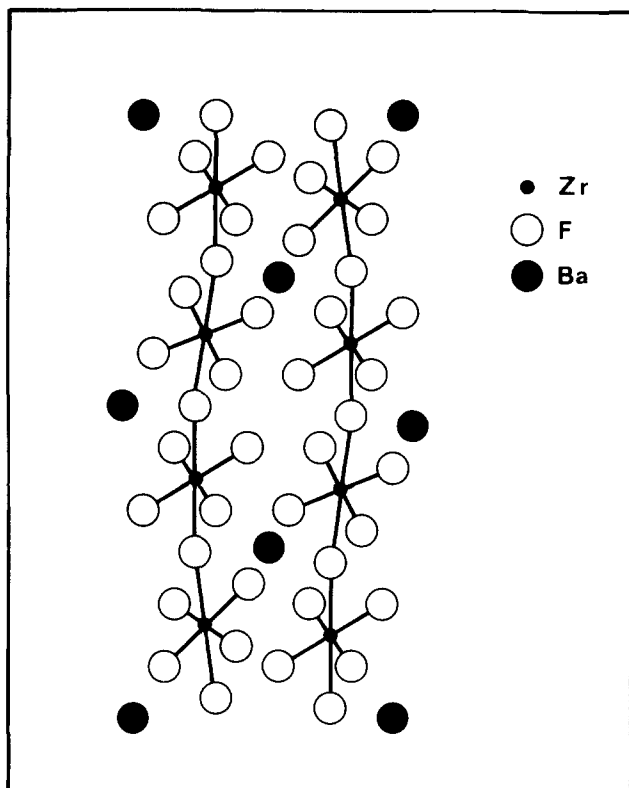


FIG. 6. Structure of barium dizirconate glass $2\text{ZrF}_4 \cdot \text{BaF}_2$, composed of zigzag chains of ZrF_6 octahedra, cross linked by Ba-F ionic bonds.

The stretching force constant k_1 , in this case, is given by

$$k_1 = \omega_1^2 m_F, \quad (2)$$

where $\omega_1^2 = 4\pi^2 c^2 \bar{\nu}_1^2$, ω_1 is the angular frequency of the mode, c is the speed of light, $\bar{\nu}_1$ is the wave number, and m_F is the mass of the fluorine atom. Therefore, the nonbridging force constant $k_1 = 376.6 \text{ N m}^{-1}$.

The second highest frequency mode (490 cm^{-1} , IR active) is a strong, high energy band, which is also expected to involve motion of the F_{nb} atoms. However, a simple antisymmetric stretching (AS) of the F_{nb} atoms would only be Raman active [$\nu_4(B_{2g})$ mode of D_{4h} group] and the glass mode has to be of a more complex nature. At this frequency, and given the large value of the Zr/F mass ratio (4.80), appreciable Zr cation motion (called C) is not likely. Such an argument for unlikely cationic motion has been used for both oxide and fluoride glasses.^{12,13} According to Galeener,¹³ the highest frequency IR active mode of a tetrahedral AX_2 glass such as SiO_2 (which is the highest frequency LO-TO pair in

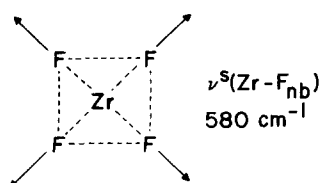


FIG. 7. $\nu_1(A_{1g})$ mode of the square planar structure $\text{Zr}-(\text{F}_{\text{nb}})_4$.

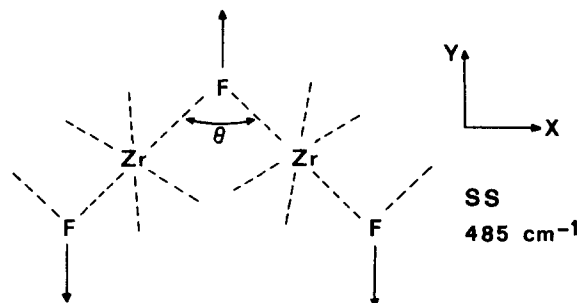


FIG. 8. Symmetric stretching vibration of bridging fluorine atoms along the bisector of the Zr-F-Zr angle, with fixed Zr atoms.

the Raman spectrum) corresponds to an AS motion of the bridging X_b atoms along a line parallel to A-A. From this we infer that the 490 cm^{-1} mode involves antisymmetric stretching motion of the bridging fluorine atoms (F_b) as well and we will tentatively assign this mode to an antisymmetric stretching of both the F_{nb} and F_b atoms in unspecified directions, which we call AS ($\text{F}_{\text{nb}}, \text{F}_b$).

The next mode (485 cm^{-1} , Raman active) is a medium, relatively sharp, and polarized ($\rho = 0.28$) mode, corresponding, therefore, to a totally symmetric vibration. (One could associate this band with the possibility of the 490 cm^{-1} IR mode being weakly allowed in Raman, but the Raman peak appears too strong and its polarized character seems to rule out this interpretation). This high frequency band is assigned to a symmetric stretching (SS) mode and the fact that its frequency is lower than that of the $\nu^s(\text{Zr-F}_{\text{nb}})$ band suggests that motion of the F_b atoms is now involved. Therefore, we assign this mode to the SS vibration of the F_b atoms and, by analogy with the dominant Raman band (ω_1) of tetrahedral AX_2 glasses,^{13,14} we assume that the F_b atoms move along the bisector of the Zr-F-Zr angle θ , while the Zr atoms remain fixed, as shown in Fig. 8. We will now develop an equation relating the frequency ω_{ss} of the mode to the angle θ , which is different from the one developed by Sen and Thorpe¹⁴ for fully bridged tetrahedral networks.

In our model, the stretching force constant k associated with the Zr-F_b bonds, which is somewhat smaller than k_1 , is considered to be independent of θ (Fig. 8). The force f acting along a Zr-F_b bond may be decomposed into two components, along the X and Y directions. There are two such bonds involved in the movement of one F_b atom and thus there are two equal forces f , whose X components cancel and whose Y components add, such that the total force F acting on a F_b atom may be expressed as

$$F = 2f \cos \frac{\theta}{2}. \quad (3)$$

Therefore, the angular frequency ω_{ss} of the SS motion will be given by

$$\omega_{\text{ss}}^2 = \frac{2k}{m_F} \cos \frac{\theta}{2}. \quad (4)$$

In order to derive a relationship between ω_{ss} and θ , valid

for the dizirconate glass, one has to estimate k . One way of doing this is by relating it to k_1 , whose value is already known. We expect the k/k_1 ratio to be a function of the $\text{Zr}-\text{F}_b/\text{Zr}-\text{F}_{nb}$ bond length ratio (BLR). Furthermore, since nothing is known about the actual $\text{Zr}-\text{F}_b$ and $\text{Zr}-\text{F}_{nb}$ distances in fluorozirconate chains (either in glasses or in crystals), we will estimate the BLR from crystalline metasilicates, which have a chain structure similar to that of the dizirconate glass and for which the $\text{Si}-\text{O}_b$ and $\text{Si}-\text{O}_{nb}$ bond lengths are known. We use a simplified electric point charge model in which the charges along $\text{Si}-\text{O}_b$ and $\text{Si}-\text{O}_{nb}$ bonds are assumed to be the same, so that the ratio of the electric force f_{e1}^b along $\text{Si}-\text{O}_b$ to the electric force f_{e1}^{nb} along $\text{Si}-\text{O}_{nb}$ is given, from Coulomb's law, by

$$f_{e1}^b/f_{e1}^{nb} = [d(\text{Si}-\text{O}_b)/d(\text{Si}-\text{O}_{nb})]^2, \quad (5)$$

and we assume that

$$k/k_1 = f_{e1}^b/f_{e1}^{nb}. \quad (6)$$

Then, from the values of the bond lengths given by Balta and Balta¹⁵ for Na and Ca crystalline metasilicates, an average estimate is made of $k/k_1 \approx 0.92$, such that $k \approx 351 \text{ Nm}^{-1}$. Therefore, from Eqs. (4)–(6), the following relation is obtained:

$$\bar{\nu}_{ss} = 791.93 \cos^{1/2} \frac{\theta}{2}, \quad (7)$$

where $\bar{\nu}_{ss}$ is the wave number of the SS mode.

The actual value of $\bar{\nu}_{ss} = 485 \text{ cm}^{-1}$ gives directly an estimate of the interoctahedral angle θ at $\sim 136^\circ$. For example, in crystalline $\text{SiO}_2 \cdot \text{Na}_2\text{O}$, the $\text{Si}-\text{O}-\text{Si}$ angle is 137° . If the k/k_1 ratio were, for example, only 0.89, θ would be 133.7° , whereas for $k/k_1 = 0.95$, θ would be 136.8° . Therefore, according to the present model, we may assume with a fair degree of confidence, that there is a distribution of angles θ in the glass, with a maximum at $\sim 133^\circ$ – 138° . This also means that the most likely number of Zr atoms which occur in the rings of octahedra present in the glass is probably eight or nine, since the $\text{Zr}-\text{F}-\text{Zr}$ angle is 135° for a planar eight-membered ring and 140° for a nine-membered one.

In the present model, for $\theta = 120^\circ$ Eq. (4) becomes

$$\omega_{ss}^2 = k/m_F, \quad (8)$$

which is the formula for the frequency of the harmonic motion of an isolated F atom vibrating against a fixed Zr atom. Therefore, for $\theta = 120^\circ$, the octahedral units become effectively uncoupled and the corresponding $\bar{\nu}_{ss} = 560 \text{ cm}^{-1}$ is the vibrational frequency of the $\nu^s(\text{Zr}-\text{F})$ symmetric stretching mode of an isolated ZrF_6^{2-} octahedral ion in the glass. This frequency (whose value depends on the estimate of k) should correspond to a weak band in the Raman spectrum that may be hidden under the strong peak at 580 cm^{-1} (Fig. 3); we believe this to be the case, since the low viscosity of the glass-forming melt¹¹ suggests the occurrence of isolated octahedral ions in the glass structure. In the model of Sen and Thorpe,¹⁴ uncoupling of the tetrahedral units occurred at $\theta = 90^\circ$, rather than 120° .

The next two Raman active modes (400 and 324 cm^{-1})

TABLE IV. Vibrational mode assignment for the barium dizirconate model glass.^a

Frequency (cm ⁻¹)	Activity	Type of vibration	Alternative designation
580	R	$\nu^s(\text{Zr}-\text{F}_{nb})$	$\nu_1(A_{1g})D_{4h}$
490	IR	AS(F_{nb} , F_b)	
485	R	SS	SS(F_b)
400	R	$\nu^{AS}(\text{Zr}-\text{F})$ in free ZrF_6^{2-}	$\nu_2(E_g)O_h$
324	R	$\delta(\text{F}-\text{Zr}-\text{F})$ in free ZrF_6^{2-}	$\nu_5(F_{2g})O_h$
270	IR	AS + C	AS(F_b) + C
196	R	B	
120	IR	C	

^aNonmenclature: ν^s , SS—symmetric stretch; ν^{AS} , AS—antisymmetric stretch; δ , B—bending; C—cation motion; R—Raman; IR—infrared.

are very weak, depolarized ($\rho > 0.75$) bands and we will tentatively assign them to the antisymmetric stretching and bending modes of isolated ZrF_6^{2-} octahedra, which we will call $\nu^{AS}(\text{Zr}-\text{F})$ and $\delta(\text{F}-\text{Zr}-\text{F})$, respectively. These are also the $\nu_2(E_g)$ and $\nu_5(F_{2g})$ modes of an octahedron (O_h group).

The next mode (270 cm^{-1} IR active) is of medium intensity and low frequency, suggesting that there is not appreciable motion of the F_{nb} atoms. We will tentatively assign this mode to antisymmetric stretching of the F_b atoms plus Zr cation motion and we will designate it AS + C. At a lower frequency, there is the 196 cm^{-1} Raman mode, which is a broad and depolarized ($\rho \approx 0.75$) band. Both this and the 485 cm^{-1} SS mode were observed in all the glasses (cf. Table III) and also in the Raman spectra of crystalline systems containing between 50–100 mol% ZrF_4 , as shown elsewhere.¹⁶ These crystals included α - BaZrF_6 and ZrF_4 , where $\text{Zr}-\text{F}-\text{Zr}$ bridging sequences are known to occur. Therefore, the 196 cm^{-1} band is assigned to in-chain bending and it will be called B.

Finally, the 120 cm^{-1} mode (IR active) is a weak, relatively sharp band. Alkali and alkaline-earth cation site vibrational bands have been observed previously in metaphosphate glasses,¹⁷ whose structure is analogous to that of the dizirconate glass, namely, Ba^{2+} cation motions occurred at $\sim 145 \text{ cm}^{-1}$, which is close to 120 cm^{-1} . Exarhos and Risen¹⁷ observed a cation mass (m_c) dependence of the frequency of roughly $m_c^{-1/2}$, which in the present case would lead to Sr^{2+} cation motion at $\sim 150 \text{ cm}^{-1}$. In glass #8, the shoulder is located at $\sim 130 \text{ cm}^{-1}$, but the exact frequency cannot be determined from the spectrum (Fig. 1). Therefore, the 120 cm^{-1} band is tentatively assigned to localized vibrations of the Ba^{2+} cations in their network sites, which we will call C. The different band assignments are given in Table IV.

E. Structure

The structure of ZrF_4 -based glasses has not been studied by vibrational spectroscopy, RDF, or NMR tech-

niques. The only known fact from crystal structure determinations is that six-, seven-, and eight-coordinated Zr atoms can occur, sometimes in the same compound, such as in $\text{Rb}_5\text{Zr}_4\text{F}_{21}$.¹⁸ Complex anionic dimers with seven-coordinated Zr atoms are also common, such as in $\alpha\text{-BaZrF}_6$,¹⁹ in $\text{Na}_5\text{Zr}_2\text{F}_{13}$ ²⁰ and in $\text{K}_2\text{Cu}(\text{ZrF}_6)_2 \cdot 6\text{H}_2\text{O}$.²¹ Coordination numbers as small as five and four have also been proposed for melts.⁸

The structure of the barium dizirconate model glass $2\text{ZrF}_4 \cdot \text{BaF}_2$ has already been discussed: it consists of zigzag chains of ZrF_6 octahedra, cross linked by Ba-F ionic bonds (Fig. 6). A small number of rings, mostly with eight or nine Zr atoms, may also occur. The in-chain Zr-F-Zr angle has its most likely value at $\sim 136^\circ$. There are $\sim 80\%$ F_{nb} atoms, whereas the similar structures of metasilicate or metaphosphate glasses contain only 66.6% O_{nb} . The Sr-containing glass, with an estimated composition of $67 \text{ ZrF}_4\text{-}33 \text{ SrF}_2$, has IR and Raman spectra [Figs. 1(b) and 5] very similar to those of the Ba dizirconate glass, except for small upward frequency shifts of most bands, due to the effect of the modifying cation size or mass (130 cm^{-1} band) and the 637 cm^{-1} Raman shoulder in the Sr glass, which occurred in all glasses with $> 67 \text{ mol}\%$ ZrF_4 . Therefore, the structure of the Sr and Ba dizirconate glasses are assumed to be analogous.

Within the experimental error in the chemical analysis, the composition of glass #1 ($52 \text{ ZrF}_4\text{-}48 \text{ BaF}_2$) coincides with $\text{ZrF}_4 \cdot \text{BaF}_2$ and this will be taken as the *metazirconate* model glass. The crystallized product was shown to be $\alpha\text{-BaZrF}_6$,¹⁶ which is a seven-coordinated crystal formed by $\text{Zr}_2\text{F}_{12}^{4-}$ dimers, and its Raman spectrum was characterized by a very strong peak at 562 cm^{-1} , probably polarized.¹⁶ The Raman spectrum of glass #1 is of questionable quality in the low frequency region, since only very small pieces of glass could be prepared due to its strong crystallization tendency. However, the highest frequency band is clearly identified: This is the $\nu^s(\text{Zr-F}_{\text{nb}})$ vibration, which is strongly polarized ($\rho = 0.03$) and occurs at 565 cm^{-1} , very close to the corresponding crystal peak¹⁶ at 562 cm^{-1} , and 15 cm^{-1} below the same peak in the dizirconate glass. Therefore, we suggest that the barium metazirconate glass contains seven-coordinated Zr atoms, like the $\alpha\text{-BaZrF}_6$ crystalline compound. The glass contains 83% F_{nb} atoms.

Finally, the $74 \text{ ZrF}_4\text{-}26 \text{ BaF}_2$ composition will be taken as the barium *trizirconate* model glass $3\text{ZrF}_4 \cdot \text{BaF}_2$. Compared to the dizirconate, this glass has higher vibrational frequencies—namely, the $\nu^s(\text{Zr-F}_{\text{nb}})$ is 18 cm^{-1} higher. Since the general appearance of the two spectra is still the same, we believe that $\text{CN} = 6$ is still predominant in the trizirconate glass and the higher frequency of the dominant Raman band indicates, therefore, the occurrence of increased bridging (or branching). This was also suggested by the fact that the ratio of the areas of the $\nu^s(\text{Zr-F}_{\text{nb}})$ and SS bands (graphically resolved for glasses #3 and #7 in Figs. 3 and 4, respectively), was ~ 8.1 in the dizirconate glass but only ~ 3.9 in the trizirconate glass, indicating that the later composition has a lower $\text{F}_{\text{nb}}/\text{F}_b$ atomic ratio. Finally, it was also confirmed by the fact that the electrical con-

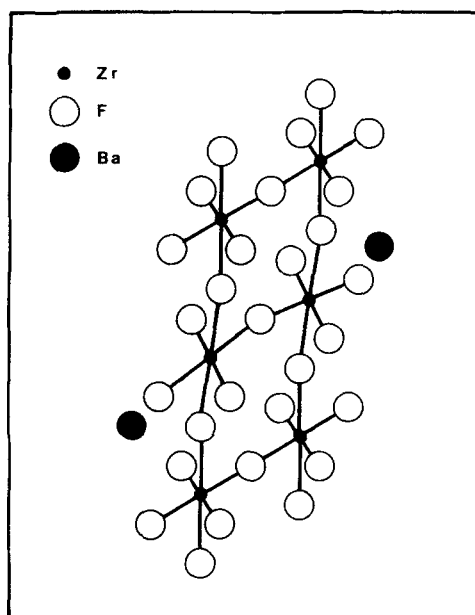


FIG. 9. Example of a double chain of ZrF_6 octahedra, in the structure of barium trizirconate glass $3\text{ZrF}_4 \cdot \text{BaF}_2$. Such chains are cross linked by Ba-F ionic bands.

ductivity of this glass was ~ 2.8 times lower than that of the dizirconate composition.²² On the other hand, the half-width of the dominant Raman band of the trizirconate glass (70 cm^{-1}) is 14 cm^{-1} larger than that of the dizirconate, due to the occurrence of a shoulder at $\sim 630 \text{ cm}^{-1}$. This may be associated with the $\nu^s(\text{Zr-F}_{\text{nb}})$ vibrations of five-coordinated polyhedra in the glass. Therefore, we propose that the trizirconate glass has a more two-dimensional structure when compared with the dizirconate model glass such that, for example, double and triple chains of octahedra are now likely to occur and maybe even sheetlike units with more extensive bridging. A certain amount of five-coordinated fluorozirconate polyhedra are also likely to occur, as well as some isolated ZrF_6^{2-} octahedral ions, as indicated by the 406 and 348 cm^{-1} bands in the Raman spectrum. An example of a double chain of octahedra is shown in Fig. 9.

With the exception of the 196 cm^{-1} mode, as the ZrF_4 content increases from 52 to 74 mol%, there is a gradual increase in the vibrational frequencies of the glasses, indicating a gradual decrease in the average CN or Zr and a steady increase in the degree of bridging. This suggests that the glass structure is progressively converted from metazirconate-like up to trizirconate-like, without the occurrence of any abrupt changes. As for the 196 cm^{-1} bending mode, its frequency decreases with the ZrF_4 content; this fact may be due to an increase in the overall size of the structural units as the degree of bridging increases, in agreement with the proposed model.

IV. CONCLUSIONS

A series of glasses were studied in the binary system $\text{ZrF}_4\text{-BaF}_2$ by vibrational spectroscopy. Their vibrational modes has been assigned. The structure was characterized for three different model glasses. The

metazirconate glass $\text{ZrF}_4 \cdot \text{BaF}_2$ is suggested to contain seven-coordinated Zr atoms. The dizirconate glass $2\text{ZrF}_4 \cdot \text{BaF}_2$ —the basic structure in the glass-forming region—is formed by chains of ZrF_6 octahedra sharing two corners each, plus a smaller amount of rings, mostly eight- and nine membered. The interoctahedral angle distribution has a maximum estimated at $\sim 136^\circ$. The structure of the trizirconate glass $3\text{ZrF}_4 \cdot \text{BaF}_2$ is proposed to have a more two-dimensional character when compared with the dizirconate model, and also to contain a smaller amount of five-coordinated fluorozirconate polyhedra. All glasses appear to have a small number of isolated ZrF_6^{2-} octahedral ions. The structure of the fluorozirconate glasses was found to vary gradually with the ZrF_4 content.

ACKNOWLEDGMENTS

This research was supported by the Air Force Office of Scientific Research, under grant AFOSR-80-0059. We are grateful to Professor Malcolm F. Nicol of UCLA for the use of the Raman spectrometer and also for useful discussions of portions of this work. We are also indebted to Dr. Frank L. Galeener of the Xerox Palo Alto Research Center and Dr. Shiv K. Sharma of the Hawaii Institute of Geophysics for helpful discussions of the Raman spectra of the glasses. The laboratory assistance of Mrs. Ramona G. Pond is also greatly appreciated.

¹M. Poulain, M. Poulain, and J. Lucas, *Mater. Res. Bull.* 10, 243 (1975).

- ²D. Leroy, J. Lucas, M. Poulain, and D. Ravaine, *Mater. Res. Bull.* 13, 1125 (1978).
- ³D. Leroy and D. Ravaine, *C. R. Acad. Sci. Ser. C* 286, 413 (1978).
- ⁴M. Poulain, M. Chanthanasinh, and J. Lucas, *Mater. Res. Bull.* 12, 151 (1977).
- ⁵J. Lucas, M. Chanthanasinh, M. Poulain, M. Poulain, P. Brun, and M. G. Weber, *J. Non-Cryst. Solids* 27, 273 (1978).
- ⁶M. Poulain, M. Poulain, and J. Lucas, *Rev. Chim. Miner.* 16, 267 (1979).
- ⁷F. L. Galeener and P. N. Sen, *Phys. Rev. B* 17, 1928 (1978).
- ⁸R. H. Stolen, *Phys. Chem. Glasses* 11, 83 (1970).
- ⁹L. M. Toth, A. S. Quist, and G. E. Boyd, *J. Phys. Chem.* 77, 1384 (1973).
- ¹⁰G. J. Su, N. F. Borrelli, and A. R. Miller, *Phys. Chem. Glasses* 3, 167 (1962).
- ¹¹R. M. Almeida, J. D. Mackenzie, and R. G. Pond (to be published).
- ¹²F. L. Galeener, G. Lucovsky, and R. H. Geils, *Phys. Rev. B* 19, 4251 (1979).
- ¹³F. L. Galeener, *Phys. Rev. B* 19, 4292 (1979).
- ¹⁴P. N. Sen and M. F. Thorpe, *Phys. Rev. B* 15, 4030 (1977).
- ¹⁵P. Balta and E. Balta, *Introduction to the Physical Chemistry of the Vitreous State* (Abacus, Kent, England, 1976).
- ¹⁶R. M. Almeida and J. D. Mackenzie (to be published).
- ¹⁷G. J. Exarhos and W. M. Risen, Jr., *Chem. Phys. Lett.* 10, 484 (1971).
- ¹⁸G. Brunton, *Acta Crystallogr. Sect. B* 27, 1944 (1971).
- ¹⁹J. P. Laval, R. Papiernik, and B. Frit, *Acta Crystallogr. Sect. B* 34, 1070 (1978).
- ²⁰R. M. Herak, S. S. Malic, and Lj. M. Manojlovic, *Acta Crystallogr.* 18, 520 (1965).
- ²¹J. Fisher and R. Weiss, *Chem. Commun.* 1968, 1137.
- ²²R. M. Almeida and J. D. Mackenzie (to be published).