Structure of Fluorozirconate Glasses and Melts*

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We present a thermodynamic model for fluorozirconate melts which takes into consideration the strong negative deviation from ideality manifested by deep eutectic wells in phase diagrams and exothermic heats of mixing. The model is based on chemical equilibria between complexes with 6—8-fold coordination of Zr. Only 6-coordinated complexes are present in the glass-forming regions. The results of the thermodynamic model are related to structural data obtained by infrared and Raman spectroscopy. Frequencies of Zr—F stretching vibrations have been found to decrease with increasing $n(\mathrm{F})/n(\mathrm{Zr})$ ratio for both melts and glasses, which indicates either an increasing Zr coordination number or decreased connectivity between ZrF_n polyhedra. At constant $n(\mathrm{F})/n(\mathrm{Zr})$ ratio the stretching frequencies increase significantly going from the glass to the melt. We propose that the coordination number of Zr in fluorozirconate glasses is decreasing significantly when heating above the glass transition temperature. The fragility of fluorozirconate glasses shown by the non-Arrhenius behaviour of the viscosity is thereby explained by a decreasing coordination number of Zr causing the connectivity between ZrF_n polyhedra to decrease. The viscosity of fluorozirconate melts demonstrates that the fragility is not very sensitive to changes in composition. However, both the glass transition temperature and the viscosity increase with increasing charge of the counter-cations.

The heavy metal fluorides based on ZrF_4 belong to the most remarkable ionic glasses. The coordination number of the major cation Zr is around 7—8 which is quite unusual compared to traditional oxide glasses. Such high coordination numbers in glasses were relatively unknown before the discovery of the fluorozirconate glasses in 1974 [1]. The heavy metal fluoride glasses (HMFG) based on ZrF_4 have a broad optical transmission window extending into the near IR region and thereby a potential for ultra-low optical losses [2]. The fluorozirconate glasses are also known as ones of the most fragile high T_g (glass transition temperature) glasses, which is shown by the extreme non-Arrhenius temperature dependence of the viscosity and the large change in the heat capacity going through the glass transition region [3, 4]. These properties make the fluorozirconate glasses a unique class of inorganic vitreous materials.

The coordination of fluorine around zirconium has been regarded as an important parameter for the understanding of the structure and properties of the fluorozirconate glasses. In crystalline fluorozirconates the coordination number (CN) of Zr is 6—8 [5]. Similar CN of Zr has been suggested in fluorozirconate melts based on Raman spectroscopy and thermodynamic investigations [6, 7]. It is generally agreed that the coordination number of Zr in the fluorozirconate glasses is in the region 7—8 [8]. However, so far there is no general agreement on how the fluorozirconate glass structure changes upon variation in composition or heating above T_g. *Phifer et al.* have considered the effect of coordination environments (including the effect of the counter-cations) on the Zr—F symmetric stretching frequency of fluorozirconate crystals, glasses, and melts [9]. The proposed dependence of this frequency on composition was based on data for a few fluorozirconate crystalline compounds.

We have recently carried out an experimental program in order to study the structure and properties of both melts and glasses of binary and ternary fluorozirconate systems which compose the main part of the well known ZBLAN/Li (ZrF_4—BaF_2—LaF_3—AlF_3—NaF/LiF) fluorozirconate glasses. The structural aspects of both fluorozirconate melts and glasses obtained by the experimental program are summarized in the present paper. First, the thermodynamic investigations of binary and ternary fluorozirconate melts are presented including liquid-liquid heats of mixing, phase diagrams, and a physical thermodynamic model for fluorozirconate melts containing alkali and alka-

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line earth fluorides [7, 10—14]. Secondly, the observed correlation between composition and viscosity/T_g of some of the most important glasses is presented [4, 5, 14, 15]. Finally, infrared and Raman spectroscopic studies of the structure of ternary ZrF_4—BaF_2—NaF (ZBN) and ZrF_4—BaF_2—LiF (ZBLi) glasses are summarized [16, 17]. A correlation between the vibrational data and the $n(F)/n(Zr)$ ratio in melts and glasses is presented. Based on all these data we propose a structural model which takes into consideration the known fragility of the fluorozirconate glasses.

Physical Thermodynamic Model for Fluorozirconate Melts

The phase diagrams of a number of binary and ternary fluorozirconate systems have been studied by differential thermal analysis and X-ray diffraction [10—15]. Deep eutectic wells are found in all these phase diagrams containing alkali and alkaline earth fluorides, as shown for the important binary system ZrF_4—BaF_2 in Fig. 1. The solidus temperatures are about 370 °C and 470 °C lower than the melting point of ZrF_4 in the important binary ZrF_4—BaF_2 and ternary ZrF_4—BaF_2—NaF systems, respectively. The composition of the glass-forming melts can be described by the $n(F)/n(Zr)$ ratio between 4.5 and 6, independent of the composition of the counter-cations

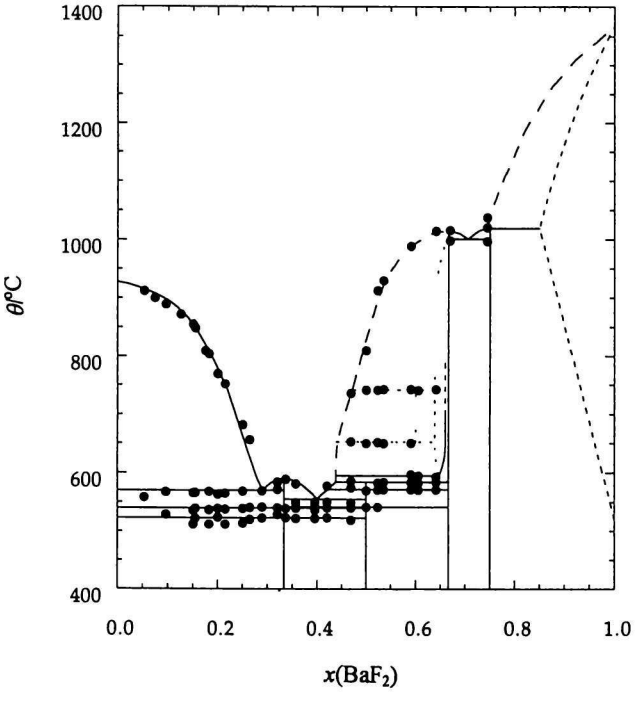

Fig. 1. The phase diagram of the binary system ZrF_4—BaF_2. Experimental observations shown are reported by *Grande* [10, 14]. The solid lines representing the liquidus temperatures are calculated by the thermodynamical model [7]. The dotted liquidus lines are reported by *Grande* [10, 14].

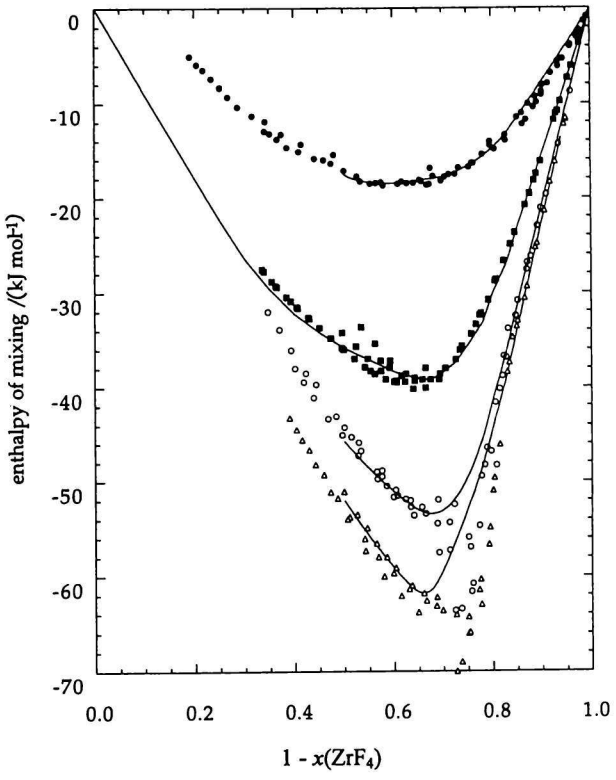

Fig. 2. Experimental and calculated liquid-liquid heats of mixing in ZrF_4—alkali fluoride systems: ● ZrF_4—LiF, ■ ZrF_4—NaF, ○ ZrF_4—KF, Δ ZrF_4—RbF. Experimental data reported by *Hatem et al.* [18, 19] and *Grande* [14] (ZrF_4—NaF).

of the glass. The glass-forming regions of fluorozirconate systems are always located within these deep eutectic wells which are limited by the liquidus surfaces for ZrF_4 on the ZrF_4-rich side and the liquidus surface for refractory fluorozirconates like Ba_2ZrF_8 at high $n(F)/n(Zr)$ ratios.

Hatem et al. [18, 19] and *Grande* [14] have measured the liquid-liquid heats of mixing for a number of binary and ternary fluorozirconate systems, as shown for the binary zirconium fluoride—alkali fluoride systems in Fig. 2. The liquid-liquid heats of mixing of fluorozirconate melts are strongly exothermic reaching a value of about $-(40—60)$ kJ mol^{-1} at the minimum where the $n(F)/n(Zr)$ ratio is near 6. The exothermic heats of mixing are a clear evidence for local order in the melts and have been interpreted as the signature of the particular stability of isolated ZrF_6^{2-} complexes [7, 14] which also have been found in crystals [20, 21]. Octahedral coordination of zirconium is also supported by the spectroscopic investigations of ZrF_4-based melts [6, 22]. In alkali fluoride-rich melts with $n(F)/n(Zr)$ ratio > 6 the interpretation of vibrational data gives support to the formation of ZrF_7^{3-} and ZrF_8^{4-} anions [6, 22]. At $n(F)/n(Zr)$ ratio < 6 the coordination number of Zr is proposed to be 6 based on the high entropy of melting of ZrF_4 [14]. The num-

ber of bridging Zr—F—Zr and terminal Zr—F fluorine bonds in the melts is dependent on the proposed CN of Zr and the $n(\mathrm{F})/n(\mathrm{Zr})$ ratio in the melt. Based on these arguments a physical model for fluorozirconate melts consisting of complex anions with 6-fold coordination of Zr, together with ZrF_7^{3-} and ZrF_8^{4-} at high concentrations of alkali and alkaline earth fluorides has been developed [7, 14]. The stoichiometry of the 6-coordinated anions in the model is $Zr_mF_{4m+2}^{2-}$ ($m \geq 1$). Models consisting of complexes with 5-, 7- or 8-fold coordination of Zr could not fit the thermodynamic data at high concentrations of ZrF_4. The formation of these complexes in ZrF_4—BF_2—AF melts (A = alkali metal, B = alkaline earth metal) is described by the following chemical equilibria shown for the binary ZrF_4—AF system

$$ZrF_4(l) + n\ AF(l) = A_nZrF_{4+n}(l)$$

$$m\ ZrF_4(l) + 2\ AF(l) = A_2Zr_mF_{4m+2}(l)$$

where $n = 2, 3, 4$ and $m = 2, 3, 4, 5$ ($m > 5$ has been neglected). The complexes are assumed to dissociate to A^+ and B^{2+} cations and $Zr_mF_{4m+2}^{2-}$ and ZrF_{4+n}^{n-} anions in the molten state. The chemical activities of the complexes were described by a Temkin model [23], assuming random mixing of cations in a cation "sublattice" and random mixing of anions in the corresponding anion "sublattice" [7]. Molecular $ZrF_4(l)$ was defined as an anion in the Temkin model.

Liquid-liquid heats of mixing of binary and ternary fluorozirconate systems were calculated by the model and are compared to experimental data as shown in Fig. 2. The experimental data are well reproduced by the thermodynamical model. The model was also observed to agree well with the chemical activities defined by solid-liquid phase relations [7]. This is shown in Fig. 1, where the estimated phase diagram for the binary system ZrF_4—BaF_2 is compared to experimental observations. The calculated heats of fusion of binary compounds were also in reasonable agreement with experimental values (± 5 %) [14].

The calculated distribution of anions in the molten system ZrF_4—BaF_2 is shown in Fig. 3. All the species introduced in the model are present as major species and have a significant contribution to the free energy of mixing. $Zr_2F_{10}^{2-}$ and ZrF_6^{2-} are the major complex species in the glass-forming region of the system ZrF_4—BaF_2—NaF ($n(\mathrm{F})/n(\mathrm{Zr})$ ratio = 4.5—6) [24]. Based on the model considerations six-fold coordination of Zr in the glass-forming regions of fluorozirconate melts can therefore be assumed as most likely. At higher $n(\mathrm{F})/n(\mathrm{Zr})$ ratios the model melt consists of the complexes ZrF_6^{2-}, ZrF_7^{3-}, and ZrF_8^{4-} which is consistent with the interpretation of the vibrational data of molten fluorozirconates [6, 22]. The number of fluorines around Zr is increasing with the $n(\mathrm{F})/n(\mathrm{Zr})$ ratio in this region which probably causes an increasing Zr—F bond length. An increasing bond length with increasing $n(\mathrm{F})/n(\mathrm{Zr})$ ratio agrees nicely with the reported decreasing frequency of the Zr—F bond with increasing $n(\mathrm{F})/n(\mathrm{Zr})$ ratio [6, 22]. At high contents of ZrF_4 in the melts, larger anionic complexes are present together with pure ZrF_4. The model proposes six-coordination of Zr in pure molten ZrF_4. Chains or rings formed by edge-sharing ZrF_6 octahedra is one possible structure of this liquid. The entropy of fusion of ZrF_4 is large [25] and a change from 8- to 6-fold coordination of Zr upon melting is therefore reasonable. In the glass-forming region ($n(\mathrm{F})/n(\mathrm{Zr})$ ratio 4.5—6), the model for the melt consists only of complexes with six-coordinated Zr.

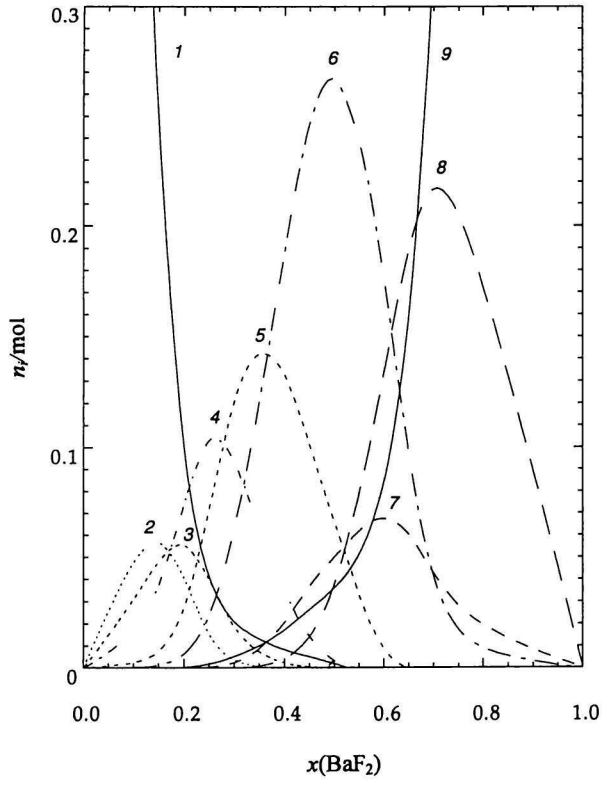

Fig. 3. The calculated distribution of the complex anions in the molten system ZrF_4—BaF_2 [7]. The species are: ZrF_4 (*1*), $BaZr_5F_{22}$ (*2*), $BaZr_4F_{18}$ (*3*), $BaZr_3F_{14}$ (*4*), $BaZr_2F_{10}$ (*5*), $BaZrF_6$ (*6*), $Ba_{1.5}ZrF_7$ (*7*), Ba_2ZrF_8 (*8*), $Ba_{0.5}F$ (*9*).

Viscosity and Glass Transition Temperature

The fluorozirconate melts exhibit one of the most fragile viscosity—temperature dependences among high T_g glasses as shown in Fig. 4. The fragile nature of the fluorozirconates is compared to the viscosity of BeF_2 which is the fluoride analogue to the strong SiO_2. One of us has previously measured the viscosity of some binary and ternary fluorozirconate melts in the glass-forming ZBLAN system [4]. At constant $n(\mathrm{F})/n(\mathrm{Zr})$ ratio, the viscosity is found to increase

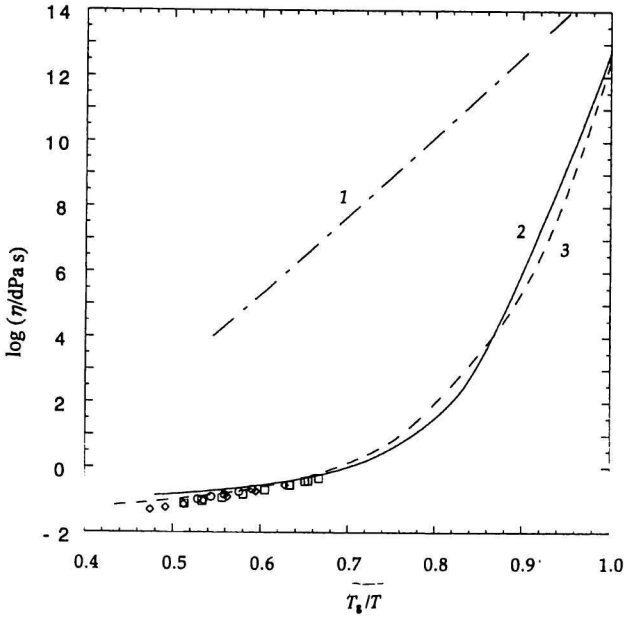

Fig. 4. T_g-Scaled Arrhenius plots for the viscosity of some fluoride glass-forming melts: ◊ $BaZrF_6$ [14], □ $BaZr_2F_{10}$ [14], ○ $NaBaZr_3F_{15}$ [14]. *1.* BeF_2 [33], *2.* ZBLA [3], and *3.* ZBLAN [3].

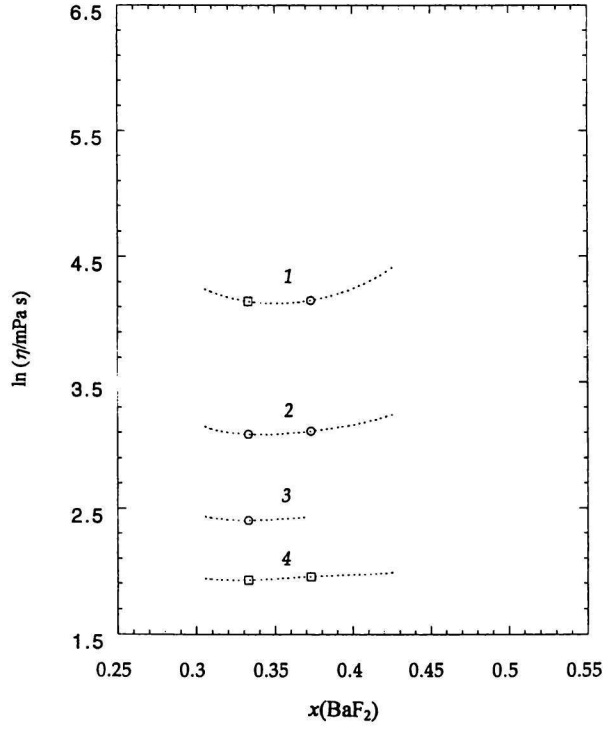

Fig. 5. The viscosity in the system ZrF_4—BaF_2 as a function of composition and temperature. The extrapolated (□) and interpolated (○) values are given by Fulcher fits to experimental data reported by *Grande* [14]. Temperatures: *1.* 850 °C, *2.* 750 °C, *3.* 650 °C, *4.* 550 °C. The dotted lines are drawn as a guide to the eye.

markedly with increasing ionic charge (ionic potential, Z/r) of the counter-cations (Na, Ba, La) in the

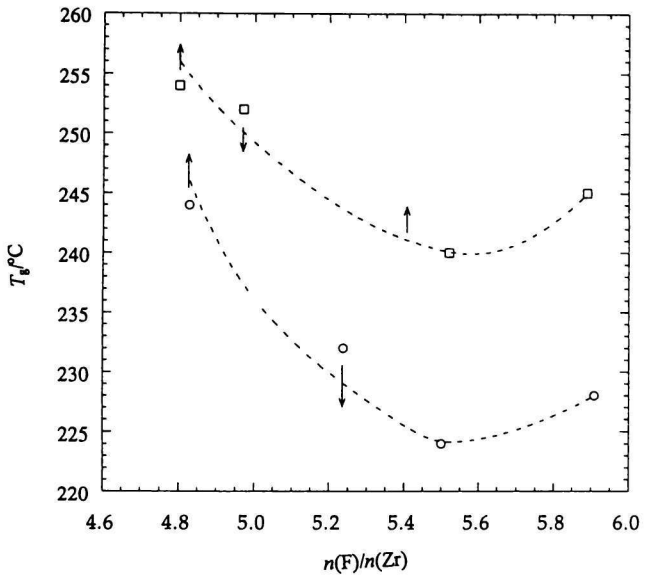

Fig. 6. Glass transition temperatures in ZBN (○) and ZBLi (□) systems along joins with the A/Ba ratio equal to one (A = Na or Li) [15]. The arrows indicate the expected direction of a correction in the T_g value due to a deviation from the A/Ba = 1 joins in the ternary phase diagrams. The lines are drawn as a guide to the eye.

fluorozirconate melts [4]. The glass transition temperature has also been found to increase with increasing charge on the counter-cations in the ternary ZBN system [15, 24]. When the logarithm of the viscosity of the melts is plotted *vs.* the reduced inverse temperature T_g/T, curves for different compositions superimpose as shown in Fig. 4.

Moderate changes in composition do not have any significant influence on the temperature dependence of the structural relaxation in the fluorozirconate melts as shown in Fig. 4. It is rather the thermodynamical properties that change drastically with composition as shown in the preceding chapter. Across the glass formation field in the system ZrF_4—BaF_2 the viscosity varies by less than one order of magnitude [4]. In fact, it has been manifested that it is a minimum in the isothermal viscosity at the $n(F)/n(Zr)$ ratio near 5.5 in the system ZrF_4—BaF_2 as shown in Fig. 5. Similarly, a minimum in the glass transition temperature as a function of the $n(F)/n(Zr)$ ratio is shown for the ternary ZBN and ZBLi glasses at constant $n(Na)/n(Ba)$ ($n(Li)/n(Ba)$) ratios in Fig. 6. Glass transition data reported by other groups support these findings [24, 26, 30, 31]. The minima in T_g and viscosity are both located in the composition region where the fluorozirconate glasses are reported to be the most stable. The minimum in the glass transition temperature itself does not seem to have a determining effect on the stability of the glasses. We propose a very simple explanation of the minimum in the glass transition temperature. The initial decrease in T_g with increas-

ing $n(F)/n(Zr)$ ratio is probably due to a decreasing number of bridging fluorine bonds as suggested by *Aasland et al.* [16]. However, at sufficiently high $n(F)/n(Zr)$ ratio the proportion of counter-cations in the structure is large enough that the effect of cation—cation repulsions starts to dominate over the role of the connectivity of the ZrF_n polyhedra. Our argument is reflected in the solid state by the large difference between the melting points of crystalline compounds in the ZrF_4—BaF_2 system (Fig. 1). The congruent melting points of Ba_2ZrF_8 and Ba_3ZrF_{10} are both more than 400 °C higher than the melting point of the glass-forming compound $BaZr_2F_{10}$. Using the empirical relationship $T_g/T_l \approx 2/3$, one would predict that the glass transition temperature should increase by about 300 °C on going from $BaZr_2F_{10}$ to Ba_2ZrF_8.

The glass transition temperature for ternary ZBA (A = alkali) and other alkali-containing multicomponent fluorozirconate systems has been found to decrease with decreasing size of the alkali ions as shown for ZBN and ZBLi in Fig. 6 [15]. The lowered T_g and viscosity when BaF_2 is substituted by alkali fluorides in ternary ZBA systems at constant $n(F)/n(Zr)$ ratio can be explained by a weaker ability of the alkali ions to cross-link the Zr polyhedra due to their lower ionic potential. However, the observed increase in T_g with increasing size of the alkali ions is somewhat surprising as the ionic potential is decreasing in this case. This observation could then indicate different coordinations for the alkali cations in fluorozirconate glasses, as higher coordinated alkalies may have a higher ability to cross-link the Zr—F polyhedra. Indeed, the smaller sized alkali ions are found to have lower coordination numbers than the larger alkali ions in alkali fluorozirconate crystals. Rb and Cs have 12-coordination of fluorine while Li has only 6-coordination in the binary alkali fluorozirconate crystals A_2ZrF_6 (A = Li, Rb or Cs) with six-coordinated Zr [21, 27]. In the ternary $ABaZr_2F_{11}$ (A = Li or Na), Li is 4-coordinated while Na is 6-coordinated [28, 29].

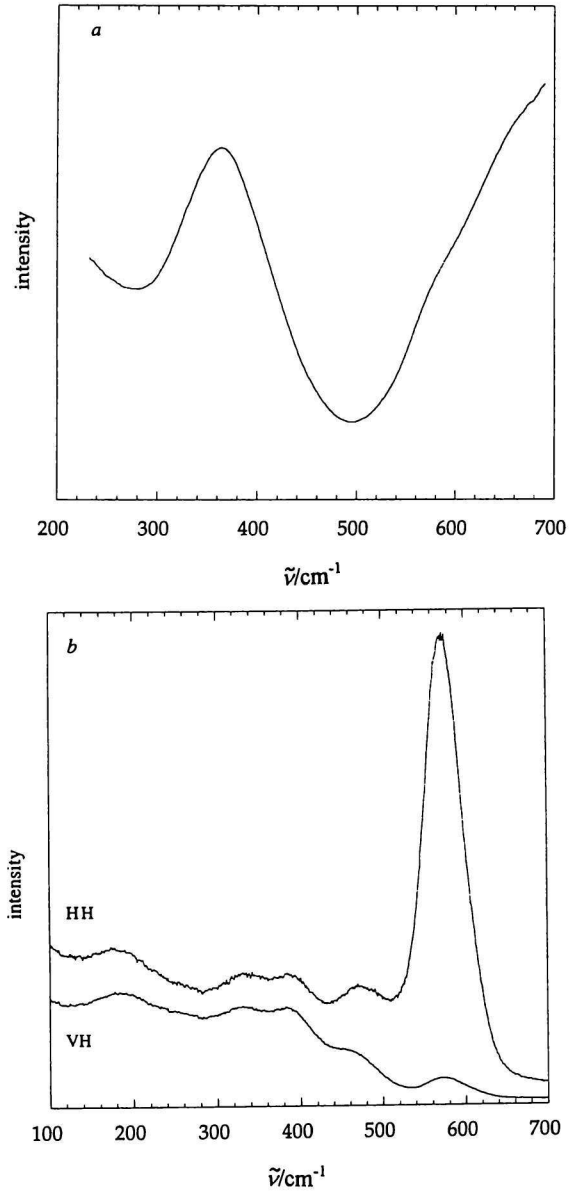

Fig. 7. *a*) Infrared and *b*) Raman spectra of a fluorozirconate glass with composition 50 mole % ZrF_4, 25 mole % BaF_2, and 25 mole % NaF. Both polarized and depolarized Raman spectra are shown in *b*).

The Structure of Binary and Ternary Fluorozirconate Glasses

The structure of binary and ternary fluorozirconate glasses has been studied by Raman and IR spectroscopy [16, 17, 26]. Infrared and Raman spectra of a ternary ZrF_4—BaF_2—NaF glass (50 mole %—25 mole %—25 mole %) are shown in Fig. 7. The spectral features are similar for all the reported binary and ternary alkali and alkaline earth fluorozirconate glasses. The most intense Raman band at $\tilde{\nu}$ = 569—592 cm^{-1} (denoted ν_s) and the weaker band around 480 cm^{-1} are interpreted as symmetric stretching vibrations of terminal and bridging Zr—F bonds, respectively [16, 26]. Two broad bands at 260—270 cm^{-1} and 480—516 cm^{-1} (denoted ν_{as}) are observed in the IR spectra. The most intense infrared band at 480—516 cm^{-1} is assigned to asymmetric stretching vibrations of bridging and nonbridging Zr—F bonds [16].

The observed ν_s and ν_{as} stretching frequencies for binary and ternary fluorozirconate glasses are compared in Fig. 8. The stretching frequencies are seen to decrease with increasing $n(F)/n(Zr)$ ratio for all the fluorozirconate glasses. This observation is consistent with an increase in the average Zr—F bond length, giving rise to a decrease in Zr—F stretching force constant. *Phifer et al.* have reported such a general decrease in the ν_s frequency with increasing terminal bond length for isostructural series of crystals, for in-

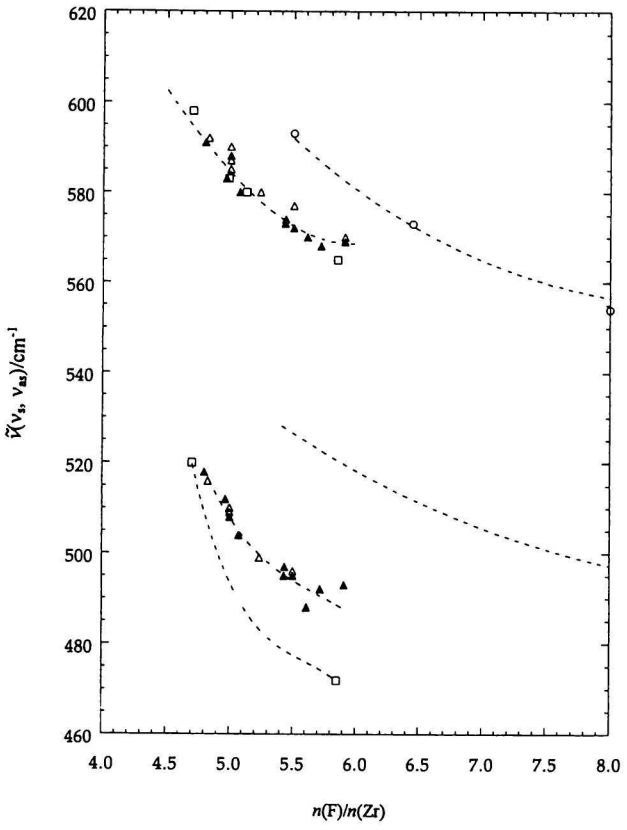

Fig. 8. IR ($\tilde{\nu} \leq 530$ cm^{-1}) and Raman ($\tilde{\nu} > 550$ cm^{-1}) frequencies observed for fluorozirconate melts and glasses as a function of the $n(F)/n(Zr)$ ratio; ○, ●, ■ ternary fluorozirconate melts [6, 16, 22], □ binary ZrF_4—BaF_2 glasses [26], ▲ ternary ZBN glasses [16], Δ ternary ZBLi glasses [16, 17]. The lines are drawn as a guide to the eye.

stance β-$BaZrF_6$, α-$SrZrF_6$, and α-$PbZrF_6$ [9]. The nonbridging Zr—F bond lengths also increase with increasing coordination number of terminal fluorines around Zr, as the bond valence is decreased. In addition, a shortening of the nonbridging Zr—F bond is expected if the number of (longer and weaker) bridging Zr—F(—Zr) bonds increases at constant CN of Zr [14]. Thus the observed decrease in the stretching frequencies of fluorozirconate glasses and melts with $n(F)/n(Zr)$ ratio can be explained by increased CN of Zr and/or decreased bridging of the Zr polyhedra. An increase in the relative intensity of the ν_s band to the band at 480 cm^{-1} (stretching of bridging bonds) with $n(F)/n(Zr)$ ratio observed in the Raman spectra for the ZBLi and the ZBN glasses [16, 17] indicates an increasing proportion of terminal fluorines as the $n(F)/n(Zr)$ ratio is increased.

The effect of different counter-cations (Li, Na, and Ba) on the ν_s and ν_{as} frequencies of the fluorozirconate glasses can be seen from Fig. 8. The ν_s frequency (Raman) decreases smoothly with increasing $n(F)/n(Zr)$ ratio, and is nearly independent of the nature of the counter-cations. However, the ν_{as} frequencies (IR) change markedly between the ZB and the ZBN and ZBLi glasses, for a similar $n(F)/n(Zr)$ ratio. One reason for this is that the dominant high-frequency Raman band of symmetric ZrF_n structural units is always singly degenerated, while the high-frequency IR band is usually triply or doubly degenerated. Perturbation of the ZrF_n species by interaction with counter-cations will cause distortion and splitting of the IR mode, resulting in a broadened band, which will shift the position of the transmission minimum. In addition, the width and position of the IR band will also be more affected by changes in effective partial charges, because of the highly polar nature of the Zr—F asymmetric stretching vibration.

Structural Changes above T_g – an Explanation of the Fluorozirconates Fragility

Continuous structural studies of the transition between fluorozirconate melts and glasses are difficult due to the high quenching rate needed to avoid crystallization. The fluorozirconate glasses will also crystallize when heated above T_g. However, a few spectroscopic studies of fluorozirconate melts have previously been reported [6, 22], and we recently managed to obtain infrared spectra of both glass and melt for one ZBN composition [16]. The ν_s and ν_{as} frequencies observed for the melts are always significantly higher than the corresponding frequencies of the fluorozirconate glasses with the same $n(F)/n(Zr)$ ratio, even if the effects of counter-cations are taken into account as shown in Fig. 8. For example, the ν_{as} wavenumber reported for the one ZBN melt is 30—40 cm^{-1} *higher* than that for the corresponding glass. This change cannot be due to inharmonic effects, which would be expected to *decrease* the observed frequencies at high temperature. We therefore conclude that the difference in the ν_s and ν_{as} frequencies of room-temperature glass and high-temperature melt is due to some structural effect.

The ν_s and ν_{as} frequencies can be correlated with the average terminal Zr—F bond strength, which decreases on increasing the Zr coordination and/or with decreased number of Zr—F—Zr bridges. We propose that this type of structural change is responsible for the large shift in the ν_s and ν_{as} frequencies going from the glass to the melt. Although it is still not clear how the structure of fluorozirconate glasses changes with variations in composition, it is generally agreed that CN of Zr in *glasses* is in the region 7—8 [2, 8, 16]. The number of bridging Zr—F—Zr bonds in the glasses is large (*i.e.* at $n/(F)/n(Zr) = 5$ with CN of Zr = 7 the fraction of bridging bonds is 4/7), and a three-dimensional network is probably formed. We predicted a coordination number of 6 in the glass-forming region of fluorozirconate *melts* based on the thermodynamic model described above. The dominating complexes are ZrF_6^{2-} and $Zr_2F_{10}^{2-}$ as shown in Fig. 3. A substantial

decrease in the coordination number of Zr going from the glass to the melt is in agreement with the large increase in the Zr—F frequency shown in Fig. 8. The reduction in Zr coordination at constant $n(\mathrm{F})/n(\mathrm{Zr})$ ratio with increasing temperature (above T_g) will cause a lowering of the number of bridging Zr—F—Zr bonds in the melt. The connectivity between the ZrF_n polyhedra is therefore much more pronounced in the glassy state compared to the molten state. Upon cooling the melt through the supercooled region, we propose that the ZrF_6 polyhedra present in the melt begin to polymerize by formation of Zr—F—Zr bridging bonds. The formation of bridging bonds simultaneously results in an increased coordination number of zirconium.

The prediction of a low content of bridging Zr—F—Zr bonds in molten fluorozirconates agrees with the viscosity of sodium and barium fluorozirconate melts being approximately one order of magnitude higher than the viscosity of simple molten salts, but several orders of magnitude lower than most glass-forming oxide melts [4]. Fluorozirconate glasses belong to the most fragile inorganic glasses known due to the low viscosity of the molten state as shown in Fig. 4. The proposed structural rearrangement upon heating of the fluorozirconate glasses, which involves a decreasing number of bridging fluorines, may explain the rapid decrease in the viscosity above the glass transition temperature. The significant change in the heat capacity of fluorozirconate glasses going through the glass transition region is firmly established [2]. The high heat capacity of the supercooled melt is probably due to a decreasing coordination number of Zr and thereby a reduction of the number of bridging fluorines. Assuming the heat capacity of the crystalline ground state to be of the same order as for the glasses, the configurational entropy will rapidly increase with increasing temperature due to the large heat capacity of the supercooled melts relative to the ground state. The structural relaxation time and hence the viscosity will therefore show a non-Arrhenius temperature dependence in the supercooled region due to the rapid change in the configurational entropy in accordance with the model analysis of *Adam* and *Gibbs* [32].

CONCLUSION

A physical thermodynamical model for fluorozirconate melts based on chemical equilibrium between the anionic complexes $Zr_mF^{2-}_{4m+2}$ and ZrF^{n-}_{4+n} has been developed. The model takes into account the strong negative deviation from ideality manifested by deep eutectic wells in the phase diagrams and strong exothermic liquid-liquid heats of mixing. In the glass-forming region ($n(\mathrm{F})/n(\mathrm{Zr})$ ratio between 4.5 and 6) which is located in the deep eutectic wells, the model consists mainly of complexes with six-fold coordination of fluorine around zirconium. Both the viscosity and the glass transition temperature show a minimum in the middle of the glass-forming region. Thus we propose that it is the thermodynamics rather than viscosity which determines the glass-forming properties of fluorozirconate systems.

The frequencies of infrared and Raman bands assigned to stretching of Zr—F bonds were observed to decrease with increasing $n(\mathrm{F})/n(\mathrm{Zr})$ ratio in the fluorozirconate glasses. Structural changes involving increased coordination number of zirconium and decreased bridging between the Zr polyhedra are proposed. Structural dependence on the counter-cations (La, Ba, Na, Li) was demonstrated in the high-frequency infrared band and in the viscosity and T_g data. An increasing ability to cross-link the Zr polyhedra, and thus influence the intermediate range of structural order, with increasing charge on the counter-cations was proposed.

On going from the glass to the melt at constant $n(\mathrm{F})/n(\mathrm{Zr})$ ratio, a remarkable increase in the intense Raman and infrared frequencies has been manifested. We propose a structural model involving a significant decrease in the coordination of Zr from 7—8 in the glasses to 6 in the melts. The proposed coordination change upon heating above T_g can also explain the fragile behaviour of these melts. The bond breaking process leading to increasing coordination number of Zr and a decreasing connectivity between the ZrF_n polyhedra may explain the high heat capacity of the supercooled fluorozirconate melts due to increasing configurational entropy. The rapidly decreasing viscosity, shown by the extreme fragility of these supercooled melts, is also reasonable as the Zr—F—Zr bridges disappear with increasing temperature.

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