Molecular dynamics simulations of halide glasses

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SUMMARY

Halide glasses have been extensively studied in recent years because of their potential application as infrared transmitting fibre optic materials. They are believed to be more ionic than glasses based on silica and should therefore be more amenable to molecular dynamics simulation using simple two-body potentials. Here the main features of structural models derived using such techniques are described and compared with available structural data. Possible future applications of this approach are outlined.

INTRODUCTION

One reason for the current interest in halide melts is that many will form glasses on cooling to room temperature under laboratory conditions. The principal glass forming systems identified to date are based on BeF_2, $ZnCl_2$, $(Zr,Hf,Th,U)F_4$, $(Al,Sc,In)F_3$, various transition metal fluorides, $BiCl_3$, (Cd,Zn,Pb) $(F,Cl,Br,I)_2$, and (Ag,Cu) (Cl,Br,I), although most require the addition of further components, often in significant proportions, for the requisite stability.

BeF_2 is structurally analogous to silica and is particularly easy to make in a vitreous form. The resulting glass has exceptional optical properties but is extremely toxic and hygroscopic. $ZnCl_2$ is another good glass former, but is also very hygroscopic. The glass-forming ability of these single component halides has been known for many years and their structures fit into the traditional picture of glasses. Both of these systems have been previously studied by molecular dynamics [1,2]; like silica, they are based on networks of tetrahedral units linked by sharing corners.

Glasses based on AlF_3 have also been known for some time but are unusual in having a structure based on a network of linked octahedra. Unlike BeF_2 and $ZnCl_2$, they require at least two components for glasses to be made and even so early compositions crystallised easily during fabrication. Recently glasses based on the ZrF_4-BaF_2-NaF system were discovered by Poulain et al. [3] and could be made as relatively large, crystal-free samples of acceptable chemical durability in normal atmospheres. Over the last fifteen years this has led to an extensive investigation of halide glass-forming systems. Many new compositions have been identified as already listed and the

ZrF_4-based systems have had their properties optimised. Most of these new systems fit only poorly into the normal picture of network structures used by glass technologists, which is based on cations of small coordination number, and this fact alone has created considerable interest.

In addition however, a number of potentially very significant applications for these new materials, particularly the fluorozirconates, have been identified. While these include bulk optics because of their extended IR and UV transmission combined with a moderate refractive index, the same properties make them suitable for IR transmitting fibres in sensor applications; further, their unusually high transparency at their optimum transmission window makes them potential materials to replace silica in telecommunications networks, with the possibility of transmitting signals over 1000 km without amplification. The same glasses are resistant to attack by fluorine and dry HF, and selected compositions display exceptional electrical behaviour such as high fluoride ion and lithium conductivities. While many of the same properties are also observed in the related crystalline phases, the advantage of glassy materials is that they are easily fabricated into the required shapes.

The reason for simulating the structures of these glasses is to provide a framework which will enhance understanding of their nature and will allow significant properties to be related to composition. Although kinetic factors such as nucleation and crystal growth rates provide the immediate reason why some compositions form glasses and others do not, nevertheless these will relate to underlying structural factors; a further aim of the glass technologist therefore is to attempt to understand why halide glasses can be formed and what factors are likely to influence their stability. The models obtained from such simulations also can provide a basis for analysis of structural data such as that obtained by diffraction experiments. In the following, fluorozirconate glasses based on the ZrF_4-BaF_2 system will form the basis of the discussion.

METHOD

In molecular dynamics simulations the trajectories of the ions in an ionic melt or solid are calculated by summing the forces on each ion as a result of all neighbouring ions and solving Newton's equations of motions numerically at time intervals which are short compared with the normal atomic vibrational frequencies, typically 2–10×10^{-15} s.

The normal approach to simulating glass structures is to start in the molten state where the ions are free to diffuse. The models used consist of 200 or more ions initially randomised in a cubic box, which is surrounded by images of itself in order to eliminate edge effects. The box density is normally fixed at the experimental value but can be varied to give zero pressure. The ions present are given random velocities appropriate to a Boltzmann distribution for the chosen temperature. The system is allowed to evolve until it achieves equilibrium (e.g. the net kinetic energy remains constant with time). The resulting ionic arrangement should then represent the melt structure if the interionic forces have been correctly defined. The system is quenched to a temperature where long-range ionic motion no longer occurs within a normal time scale i.e. it is in a glassy state. The model is allowed to evolve for several hundred more time steps for it to re-equilibrate, before a final run of approximately 1 ps for property determination. By averaging the ionic positions during this latter period or by following any net drift, structural characteristics can be observed and diffusion coefficients can be determined. Equilibrium properties such as density, elastic moduli and lattice energies can also be calculated from the model.

To obtain a sensible model for a glass structure an accurate parametric form for the interionic potential between the ions is needed. In the present work a Born–Huggins–Mayer (BHM) form for the potential has been chosen, with the van der Waals interaction terms set to zero. The BHM potential assumes a simple two-body ionic interaction. For vitreous silica where bonding has a strongly covalent character three-body potentials give a better fit to the observed structures [4]. Several factors justify the simpler form of the potential in fluorozirconates at least as a first step. For example the difference in electronegativities between Si and O is only (3.5–1.8) whereas the difference between Zr and F is (4.0–1.55) and between Al and F is (4.0–1.5). Table 1 lists the Racah B parameters obtained by fitting optical spectra for transition metals in oxide and fluoride glass hosts [5]. The values obtained for the fluoride host are closer to the free ion values. Since the parameter B is a measure of the extent of orbital overlap between transition metal and ligand ions, the implication is that the bonding is more nearly ionic at least for these ions. The viscosities at the liquids are also very low for fluorozirconate melts and much closer to those of typical ionic materials than to silicate melts, although the observed values of 1–0.1 poise suggest that some association occurs. On the other hand the difference in the effect on physical properties of apparently almost identical ions such as Hf and Zr can be greater than would be expected assuming simple ionic potentials [6]. Since ionic potentials are long range, an Ewald summation method has been used to aid convergence, with use of tabulation techniques to minimise the computational time involved. All calculations have been made on a Control Data Cyber 205 vector processor.

In the standard BHM potential the repulsive part of the potential is expressed by a function of the form $b_{ij} \exp[(\sigma_i + \sigma_j - r_{ij})/\rho]$ where r_{ij} represents the distance between the atoms i and j, σ_i and σ_j represent size parameters for the individual ions and b_{ij}, ρ are constants for particular ion-pairs. The parameters chosen for the present model were obtained originally by fitting physical property data for various simple crystalline species [7]. Little information is available on the physical properties of more complex compounds so there has been no opportunity to test the chosen parameters for crystalline phases corresponding more closely to the glass compositions. We have varied the size parameters slightly in order to fit the basic near-neighbour distances (in particular the Zr-F distance) as determined by X-ray and neutron diffraction experiments. More effort is still needed to test the ability of the potentials used in the model to fit observed physical properties such as the elastic moduli.

The molecular dynamics technique has a number of limitations which must be borne in mind when interpreting the results obtained. Firstly the unit of structure simulated is small, typically a few hundred atoms. With network structures particularly, this may impose unrealistic constraints and there is the additional statistical problem that the effect of dopant atoms at low concentra-

TABLE 1

RACAH PARAMETER, B, OBTAINED FROM FITS TO OPTICAL ABSORPTION DATA

Dopant ion	B, fluoride glass (cm^{-1})	B, oxide glass (cm^{-1})	B, free ion (cm^{-1})
Co (II)	923	872	971
Ni (II)	1016	903	1030
V (III)	671	617	861
Cr (III)	801	736	918

tions is difficult to assess. The effective quench rates used in the simulation correspond typically to 10^3 °C/10^{-12} s or 10^{15} °C/s. In a laboratory situation a quench rate of 10^2 °C/s or less would be typical for a halide melt. At a cooling rate of 0.1 °C/s the melt viscosity corresponding to the glass transition is near 10^{13} dPa s. Assuming that the time constants for appropriate structural relaxations vary inversely with the melt viscosity, this difference of a factor of 10^{16} in quench rates suggests that the corresponding glass transition in the simulation will be at a viscosity of 10^{-3} dPa s. As a result, observed physical properties such as density will differ significantly from those obtained by modelling because the transition from melt to glass will occur at a much higher temperature. As a practical example of this effect, fluoride glass fibres are quoted as having densities some 1.3 % lower than those of bulk glasses simply because of the difference in cooling rates; this change in quench rates is very much smaller than observed in a simulation. Finally there is always the limitation of using a too simple potential to simulate the interionic interactions. For example any tendency for specific molecular orbitals to form with particular spatial orientations means that three-body potentials are strictly necessary.

RESULTS

Having obtained reasonable parameters for the form of the various interionic potentials in a fluorozirconate glass we have compared the results of extended simulations with those of structural studies [7]. Significant results of the model include the Zr coordination which varies between 7 and 8 depending on precise composition. This agrees with typical results from diffraction experiments [8] although some analyses of Raman spectra have suggested that the coordination is six [9]. The coordination numbers of Zr in ZrF_4 and those barium fluorozirconates whose structures are known are also 7 or 8. The similarity in densities of glass and these crystalline species suggests that coordination numbers should change little. Recent molecular dynamics simulations have also

TABLE 2

DIMENSIONS OF Zr-F POLYHEDRA IN CRYSTALS AND SIMULATED GLASSES

	Coordination	$\bar{r}$ (F–F)/r(Zr–F)
MD simulation	8	1.201
Crystals		
$\beta BaF_2 \cdot ZrF_4$	8	1.265
$\alpha BaF_2 \cdot ZrF_4$	7	1.271
$2LiF \cdot ZrF_4$	6	1.414
$7NaF \cdot ZrF_4$	8	1.247
Theory		
Octahedron	6	1.414
Cube	8	1.155
Square antiprism	8	1.215
Triangular dodecahedron	8	1.199 or 1.265

The $\bar{r}$ (F–F) value for the triangular dodecahedron depends on which near-neighbour F–F distances are included in the calculation.

been able to associate the observed Raman spectra with structural vibrational frequencies for the higher coordination structures [10]. Ba ions are found to have coordination numbers near 10–11.

Since the mean Zr-F distance has been used as a parameter in fitting the form of the potential it cannot be used as a check on the model. Nevertheless an interesting feature is the difference in mean Zr-F distance according to whether the fluorine is bridging (i.e. coordinated to two zirconiums) or non-bridging, which broadens the first peak on radial distribution functions (rdf) and makes it slightly asymmetric. The observed half-height full width on the calculated rdf is 0.023 nm while the observed value is 0.024 nm. The asymmetry points to the extra care experimentalists need to take in fitting Gaussian profiles in order to determine peak areas. Interestingly the experimental mean Zr-F nearest-neighbour distance is closer to that found in 8-fold coordinated crystalline fluorozirconate structures than for those which are 6-fold coordinated.

The shape of the average coordination polyhedron around the cation can be determined by examining the ratio of the F-F and Zr-F distances and the F-F distance distributions. The former parameter varies significantly according to the mean coordination number but also according to the shape of the polyhedron as shown in Table 2. Further evidence can be obtained from the form of the F-F distribution as illustrated in the histogram given in Fig. 1. These results suggest that the fluorines are arranged principally as triangular dodecahedra as in αZrF_4 rather than as the Archi-
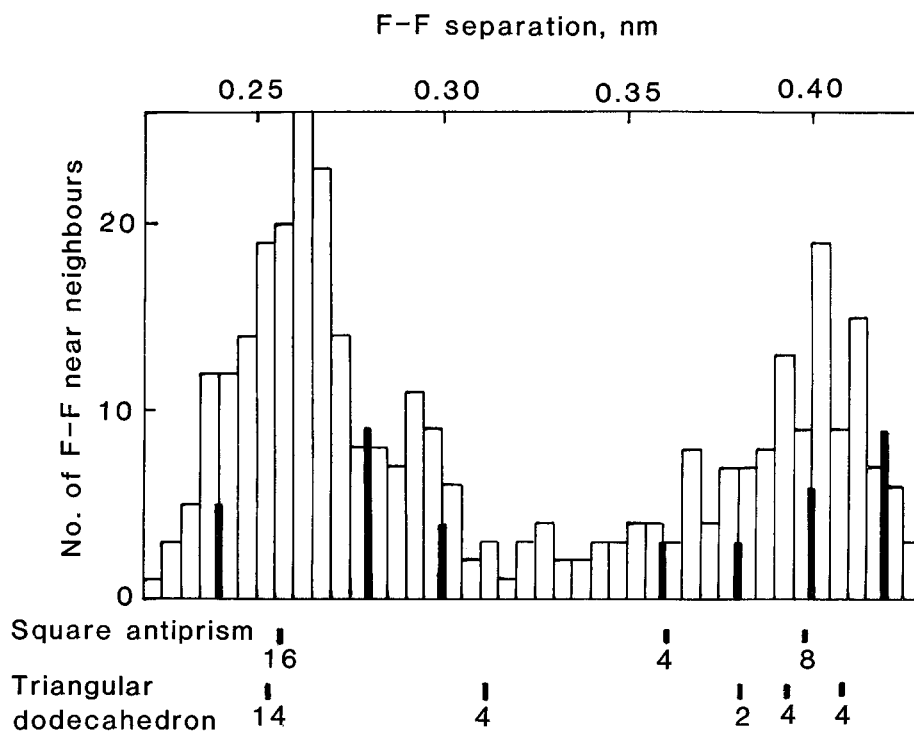

Fig. 1. The average F–F distribution around a Zr atom as determined in a molecular dynamics simulation is shown and compared with the results for $\beta BaF_2 \cdot ZrF_4$ where the ZrF_8 coordination polyhedra approximate to triangular dodecahedra (crystal data as black bars). Data for ideal Archimidean antiprisms and triangular dodecahedra are also indicated.

midean antiprisms found in pure βZrF_4, although the difference in energies between these arrangements is small.

The linkage of the polyhedra found in the simulation is via edge and corner sharing. Similar schemes occur in crystalline barium fluorozirconates. Interestingly the proportion of edge sharing linkages found in molecular dynamics simulations by different workers has varied according to the precise parameters used in the analysis. Analysis of the mean F-F distance in edge-shared linkages shows that it is significantly less than the first peak in the F-F radial distribution function at 0.256 nm and the average value of 0.226 nm found agrees well with that observed in crystalline species (e.g. 0.236 nm in $\alpha BaF_2 \cdot ZrF_4$, 0.223 nm in $\beta BaF_2 \cdot ZrF_4$ [7]).

Unfortunately experimentalists who have obtained diffraction data and those authors who have simulated structures have selected slightly different compositions for their work. Nevertheless the results presented in Fig. 2 show a comparison between our own measurements and those
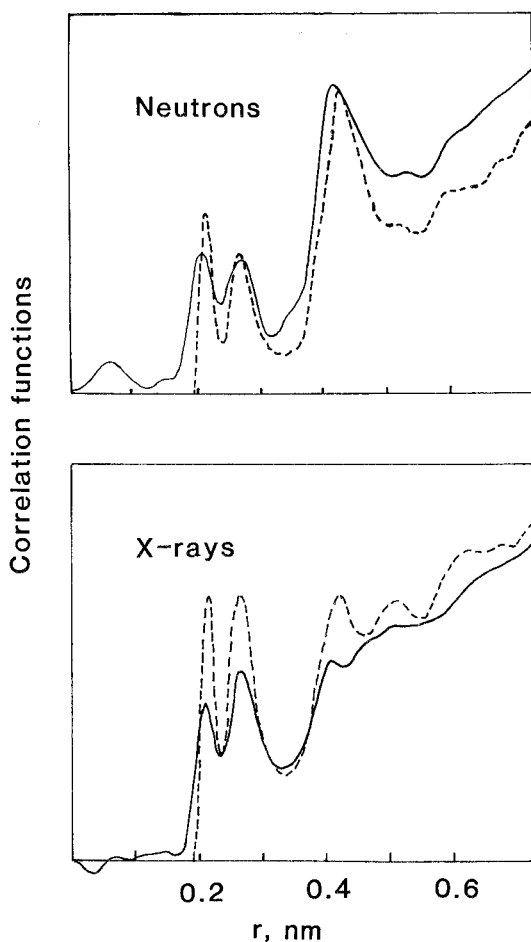

Fig. 2. Total correlation functions as determined by Wright [8] from our simulations of vitreous $2BaF_2 \cdot 3ZrF_4$ and weighted according to the appropriate scattering factors (dashed curves) compared with X-ray and neutron difrraction scattering data (continuous curves) for the composition $BaF_2 \cdot 2ZrF_4$.

of several authors using both X-ray and neutron diffraction techniques for slightly different compositions [8]. The agreement is good and provides further confirmation of the method.

The significance of the coordination number of the Zr ion arises from the link between structure and properties made by many authors. If the Zr coordination is six in simple fluorozirconate glasses then the stoichiometry demands that each unit is linked to at most two others and a chain-like structure is implied. Indeed observations of rubber-like behaviour in these glasses have been attributed to the presence of such polymeric units [11]. During optical fibre pulling at high viscosity, anisotropy in the final fibre might also be expected if such structures occurred. As indicated here, however, the weight of evidence points to a higher coordination.

We have used our model to examine the effect of a number of added ions on the glass structure [7]. For example small ions of low charge can be shown to act in the traditional sense as network modifiers sitting in a cage surrounded by both bridging and non-bridging fluoride ions (fluoride ions linked to 2 or 1 Zr, respectively). Thus in a simulated glass of composition $2LiF \cdot 40ZrF_4$, the average Li coordination was found to be 7.4 with 23% of the fluoride ions being non-bridging compared with an average number in the whole glass of only 1.2%. The coordination numbers for both Li and Na ions fell slightly as their concentration increased, probably as a result of the greater proportion of non-bridging anions available. Early experiments of property-composition trends had suggested a well defined coordination change for Li from octahedral to tetrahedral at approximately 20 mol% concentration but with no such change for NaF additions. Recent, more detailed analyses of compositional trends are consistent with the results of the simulations, however.

Transition metals ions such as manganese (chosen because it is a d^5 ion and therefore has no crystal field stabilisation energy) adopt a coordination of six in model simulations which is consistent with interpretations of the optical absorption spectra [5]. Aluminium also surrounds itself by a regular octahedron of fluoride ions although in reality sp^3d^2 octahedral molecular orbitals may also be formed; it adopts a network-forming role being surrounded only by non-bridging anions and this is consistent with its role as an ion which stabilises the glass. Other authors have examined the environment of rare earth ions in such fluoride glasses with the ultimate aim of improving understanding of the splitting of energy levels and its effect on lasing characteristics [2].

Our models also predict that oxygen impurity ions will sit between two zirconiums and this again is consistent with observed changes in the IR absorption spectrum.

In spite of the rapid quenching rate the glass transition temperatures observed for the model, for example by extrapolating the diffusion coefficients of the principal network forming ions to zero, are typically only 100–200°C above those observed experimentally. In silicates that is not the case [4] probably because the temperature–viscosity curve is relatively shallow whereas in fluoride melts the structure breaks up quickly with rising temperature.

A significant problem with silica optical fibres has been the diffusion of hydrogen into the core through interstices in the network. Again examination of the MD model suggests that such holes are not present in fluoride glasses [12].

By following the mean square displacement of ions in the molten fluoride near the glass transition temperature the fluoride ions can be shown to be relatively mobile. Measurements of electrical conductivity confirm that the glasses are fluoride ion conductors in the glassy state. Activation energies determined from Arrhenius plots of diffusion coefficients above T_g are near 40 kJ/mol [7] while measured values are higher, being typically 80 kJ/mol. This apparent discrepancy could be

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related to the lower temperature used for the experimental measurement. Inoue and Yasui have gone further and attempted to determine the activation energy barriers for such processes in halide glasses by modelling the activated state. Typical values were near 75 kJ/mol. They also found that non-bridging fluoride ions had a much lower activation energy for diffusion than bridging ions [13].

An interesting recent development has been an attempt by Inoue and MacFarlane to relate structural trends across a composition series to glass-forming ability [14]. The parameter examined was the ordering tendency of anions around the glass-forming cation. The initial results have been very encouraging and suggest that the glass-forming regions are associated with the most disordered arrangements of anions.

CONCLUSIONS

Early results suggest that molecular dynamics models of fluoride melts correctly fit a number of structural properties both qualitatively and even quantitatively in some cases. Nevertheless model parameters used have been obtained by fitting to simple crystalline solids and there is a need to validate these models by modelling thermodynamic quantities and physical properties such as thermal conductivity and Young's modulus.

In the longer term temperature–viscosity relationships, the nature of β-relaxations below the glass transformation temperature, the surface energies of melt-crystal boundaries which are of importance in the crystallisation behaviour, the determination of those thermodynamic properties which affect glass stability and phase equilibria are all likely to be fruitful areas of study. Determining vibrational densities of state may well be able to resolve some of the difficulties inherent in interpreting Raman and infrared absorption spectra of glasses.

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