

The electrical conductivity of fluorozirconate and chloro-fluorozirconate glasses

RUI M. ALMEIDA

*Centro di Fisica Molecular, Instituto Superior Tecnico, Av. Rovisco Pais,
1096 Lisboa-Codex, Portugal*

JOHN D. MACKENZIE

*Materials Science and Engineering Department, University of California, Los Angeles,
CA 90024, USA*

The electrical conductivities of glasses in the ZrF_4 - BaF_2 and ZrF_4 - BaF_2 - $BaCl_2$ systems have been measured as a function of temperature. The conductivities of binary fluorozirconate glasses had values comparable to those previously measured for ternary systems. The introduction of chlorine in the glass network markedly decreased the electrical conductivity and increased the activation energy for conduction. The decrease in conductivity could not be explained exclusively on the basis of zero mobility for the Cl atoms; it is proposed that these atoms effectively hinder the motion of the conducting fluorine ions. The activation energy for electrical conduction in fluorozirconate glasses was analysed via a modification of the Anderson and Stuart model for anionically conducting glasses, in which the "electrostatic energy" was found to predominate. In chloro-fluorozirconate glasses, this term appears to be less predominant.

1. Introduction

Fluorozirconate glasses were first prepared in 1975 by Poulain *et al.* [1] and their electrical properties have been studied for a few multi-component systems. Leroy *et al.* [2] measured the electrical conductivity of a number of glasses in the ZrF_4 - BaF_2 - ThF_4 and ZrF_4 - BaF_2 - LF_3 systems, where $L = La, Pr$ or Nd . Their d.c. values of conductivity at 200°C (obtained by extrapolation of a.c. measurements to zero frequency) were in the neighbourhood of $4 \times 10^{-6} \Omega^{-1} \text{cm}^{-1}$ and the activation energies varied from 0.75 to 0.89 eV.

Both Leroy *et al.* [2] and Leroy and Ravaine [3] have shown, by using the Tubandt test, that fluorozirconate glasses are essentially F^- ion conductor materials. In a latter paper, Ravaine and Leroy [4] studied several glass compositions among those previously prepared in [2]: e.m.f. measurements of sodium amalgam cells gave a mean ionic transport number of 0.999 ± 0.004 and the blocking electrode method showed that the electronic transport number did not exceed

6.8×10^{-3} . Therefore, fluorozirconate glasses may be treated as exclusively anionic conductors. Anionic conduction in glasses has been reported so far only in a few cases [5-7]; on the other hand, BaF_2 is known to be an anionic conductor [8] and the same is probably true for $BaCl_2$ [9].

The effect of the concentration of the network former on the glass conductivity appears to be weak in the range of compositions that has been studied. On the other hand, the results of Leroy *et al.* [2] showed that the conductivity increased substantially with the BaF_2 content, indicating that the electrolytic mobility of the non-bridging fluorine atoms (F_{nb}) was larger than that of the bridging ones (F_b). In a study of glasses in the ZrF_4 - BaF_2 - NaF - ThF_4 system, Chandrashekar and Shafer [10] did not detect any measurable Na^+ ion conductivity, when using molten $NaNO_3 + NaNO_2$ electrodes reversible to sodium ions.

2. Experimental procedure

Two fluorozirconate and two chloro-fluorozirconate

TABLE I Physical properties of fluorozirconate and chloro-fluorozirconate glasses

Glass sample	Analysed composition (mol%)			Density (g cm ⁻³)	T _g (°C)	Electrical conductivity at 25° C (Ω ⁻¹ cm ⁻¹)	Activation energy E _σ (eV)
	ZrF ₄	BaF ₂	BaCl ₂				
FZ-1	64	36	—	4.662	300	1.19 × 10 ⁻¹⁰	0.70
FZ-2	74	26	—	4.501	288	4.19 × 10 ⁻¹¹	0.70
CFZ-1	72	25	3	4.466	274	1.96 × 10 ⁻¹¹	0.78
CFZ-2	60	22	18	4.312	261	7.09 × 10 ⁻¹³	0.97

glass samples were evaluated. The raw materials were ZrF₄ purified by double-distillation and Ultrapure BaF₂ and BaCl₂ (obtained from Alfa Inorganics); the preparation method has been described elsewhere [11, 12]. The analysed glass compositions are given in Table I. Infra-red absorption spectroscopy showed that the fluorozirconate glasses were water-free, whereas a small amount of residual water remained in the chloro-fluorozirconate glasses. Due to the high tendency for crystallization, only sample FZ-1 was annealed. The densities were measured at 24° C by buoyancy in toluene. Glass transition temperatures, T_g, were measured by differential thermal analysis with a heating rate of 7.5° C min⁻¹.

The d.c. electrical conductivity was measured for all samples by a three-probe technique (according to ASTM Standard D 257-78) with sputtered gold electrodes. The samples were disc-shaped and had thicknesses between 0.3 and 1.5 mm. Measurements were made in vacuum, as a function of temperature, with a picoameter at a field strength of about 670 V cm⁻¹. A steady-state d.c. current was reached instantaneously, following application of the voltage. The dielectric constant of Sample FZ-1 was measured using an impedance bridge.

3. Results and discussion

3.1. Electrical conductivity of fluorozirconate glasses

The room temperature conductivities and activation energies of the binary fluorozirconate glasses, given in Table I, are similar to those reported for ternary fluorozirconates [2]; on the other hand, the conductivity was generally higher and the activation energy was lower than those of binary fluoroberyllate glasses [13]. The measured conductivities are shown in Fig. 1 as a function of temperature. If one assumes the glasses to be purely anionic conductors in which only the F_{nb} atoms have appreciable mobility below T_g, their electrical conductivity, σ, will be given by

$$\sigma = [F_{nb}] z_{F_{nb}} e \mu_{F_{nb}}, \quad (1)$$

where [F_{nb}] is the concentration of mobile F_{nb} atoms z_{F_{nb}} is their formal charge, μ_{F_{nb}} is their drift mobility and e is the electronic charge.

The conductivity of Sample FZ-1 was about 1.47 times that of Sample FZ-2, but the actual factor is somewhat higher since Sample FZ-2 was not annealed (the conductivity of a ternary fluorozirconate glass dropped by a factor of almost two after it was annealed [10]). Although nothing is known about the absolute values of mobility in either glass, a structural model was recently proposed by the present authors [11], in which Sample FZ-1 was mostly chain-like and 6-co-ordinated (see Fig. 2), whereas Sample FZ-2 had a larger degree of bridging and a certain fraction of 5-co-ordinated Zr atoms. We believe that these structural differences should not significantly affect the mobilities, a reasoning which is con-

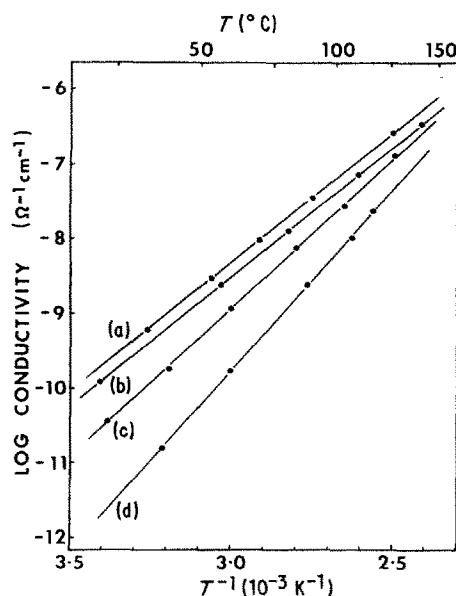


Figure 1 Arrhenius plot of the electrical conductivity of four different glass samples: (a) FZ-1, (b) FZ-2, (c) CFZ-1 and (d) CFZ-2.

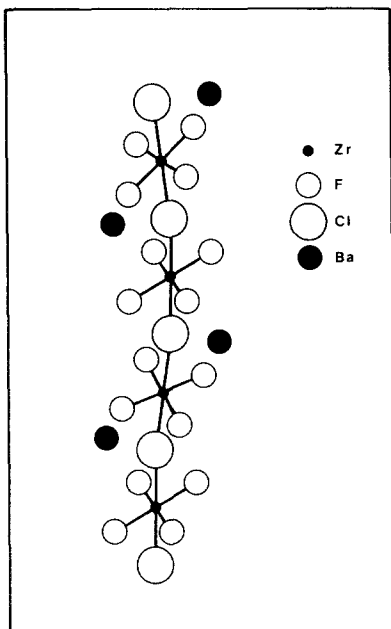


Figure 2 Structure of barium dizirconate glass $2\text{ZrF}_4 \cdot \text{BaF}_2$, composed of zig-zag chains of ZrF_6 octahedra, cross-linked by Ba-F ionic bonds. The arrows represent possible jumping paths of the F_{nb} ions. (Adapted from [11].)

firmed by the equal values of the activation energies of the two glasses (0.70 eV). Therefore, the above difference in conductivities is ascribed mostly to a change in $[\text{F}_{\text{nb}}]$. The concentration of F_{nb} atoms, relative to the total fluorine content of the glass, was about 80% for the “dizirconate”, glass Sample FZ-1 [11], whereas it was considered to be somewhat lower for the “trizirconate” glass Sample FZ-2, in the neighbourhood of 70%, but depending on the actual structure [14]. Therefore, the change in the total concentration of F_{nb} atoms (of about $80\%/70\% = 1.14$) explains in part only the observed conductivity difference. We conclude that only a certain fraction of the F_{nb} atoms are simultaneously mobile at a given temperature, in qualitative agreement with the “weak-electrolyte” model for ionic conduction in glass [15].

3.2. Electrical conductivity of chloro-fluorozirconate glasses

The room-temperature conductivities of the Cl-containing glasses, given in Table I, were lower than those of pure fluorozirconate glasses and decreased with the BaCl_2 content. The conductivities are shown as a function of temperature in Fig. 1 and the activation energy is seen to be higher for the mixed-anion glasses. Let us now

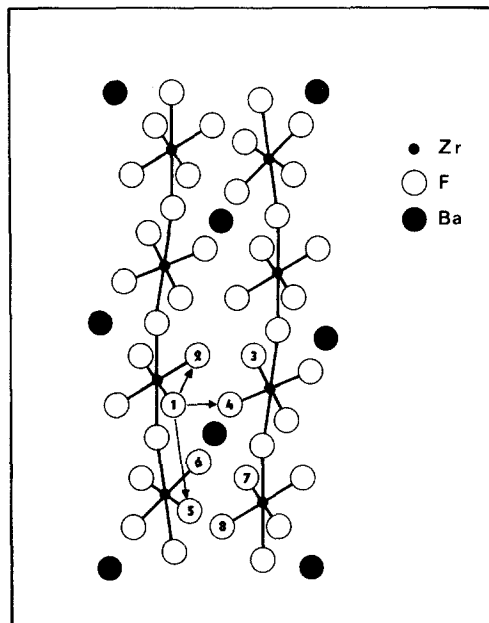


Figure 3 Mixed-halide chain of ZrCl_2F_4 octahedra in the structure of a chloro-fluorozirconate glass. The chains are cross-linked by Ba-F ionic bonds. (After [12].)

compare glass Samples FZ-1 and CFZ-2, for which the electrical parameters differ most. We have proposed [12] that the basic structure of the mixed-anion glass consists of zig-zag chains of ZrCl_2F_4 octahedra (Fig. 3) plus a pure fluorozirconate matrix formed mostly by chains of ZrF_6 octahedra (Fig. 2); the Cl atoms were shown to preferentially occupy the two bridging positions of each octahedron along the chain axis. Therefore, the Cl atoms are not expected to give any significant contribution to the total ionic conductivity and Equation 1 is assumed to be still valid. Since Sample CFZ-2 had a slightly lower ZrF_4 content than Sample FZ-1, the total concentrations of F_{nb} atoms in both glasses are expected to be similar [14]. On the other hand, since their structure is not very different [11, 12], the mobilities of the F_{nb} atoms would, in principle, be comparable. However, the electrical conductivity of Sample CFZ-2 is considerably lower than that of Sample FZ-1, except at the higher temperatures (at 25°C it is smaller by a factor of about 85.3). Therefore, it is possible that the bridging Cl atoms have a “blocking” effect on the movement of the F_{nb} ions, acting as traps due to their large size and polarizability. It is conceivable that the jumps of F_{nb} ions along the chains (from Position 1 to 5 or 6, in Fig. 2) are considerably hindered by

the presence of the large Cl atoms in bridging positions.

The packing density of the glasses may be computed as the ratio between the volume of ions in one mole and the molar volume. Using the experimental densities (given in Table I) and published values of the ionic radii, this found that the packing densities of Samples FZ-1 and CFZ-2 are both about 62%; if Sample CFZ-2 were annealed, its packing density would probably be somewhat higher. This would have only a small effect in lowering the conductivity of Sample CFZ-2, relative to that of Sample FZ-1. Finally, the present results could be the consequence of yet another effect. In alkali oxide glasses, when one alkali oxide is progressively substituted for another, the electrical conductivity goes through a deep minimum in a manifestation of the "mixed alkali effect" [16]. On the other hand, in alkali-free fluorophosphate glasses of the systems $\text{Ba}(\text{PO}_3)_2\text{-BaF}_2\text{-BaX}_2$ (where $X = \text{Cl}, \text{Br}$) with a total of 20 mol% barium halide, a "mixed anion effect" has been reported for the electrical conductivity [17]. Therefore, the present results may be the consequence of a "mixed halide effect" in mixed anion zirconate glasses, but a confirmation of this must await further studies, particularly in systems where the Cl/F ratio reaches a value large enough (≥ 0.5) for the possible minimum in electrical conductivity to be detected. In the chloro-fluorozirconate system, the limit of the glass formation region occurred at $\text{Cl}/\text{F} \approx 0.23$.

3.3. Activation energy for conduction

The activation energies for conduction, E_σ , of the binary fluorozirconate glasses studied are somewhat lower than those of ternary fluorozirconate glasses [2], whereas those of the chloro-fluorozirconates are higher. On the other hand, the absolute values of E_σ for the two types of glasses studied are similar to those measured for binary alkali silicate glasses. We will start by attempting a semi-quantitative interpretation of the E_σ values of the fluorozirconate glasses (0.70 eV).

The classical Anderson and Stuart model [18] for the calculation of the activation energy for conduction in silicate glasses considers this energy as the sum of the elastic strain energy, E_S , and the electrostatic energy, E_E :

$$E_\sigma = E_S + E_E. \quad (2)$$

The strain energy is the energy required to enlarge the radius of a spherical cavity from r_D (the "doorway" radius) to r (the radius of a diffusing ion):

$$E_S = 4\pi G r_D (r - r_D)^2, \quad (3)$$

where G is the shear modulus of the glass. The electrostatic energy is the difference in energy between the static equilibrium configuration (where the distance between a conducting alkali cation and the nearest non-bridging oxygen is equal to the sum of the two radii) and the transition state (where the interionic separation, R , is the distance between the ions when the alkali ion is half way between adjacent equilibrium positions):

$$E_E = \left| \frac{z_{\text{Cl}} z_{\text{O}_{\text{nb}}} e^2}{\epsilon} \left(\frac{1}{r_{\text{Cl}} + r_{\text{O}_{\text{nb}}}} - \frac{1}{R} \right) \right|, \quad (4)$$

where Cl and O_{nb} represent the conducting ion and a non-bridging oxygen, respectively, whose oxidation states and ionic radii are represented by z and r and ϵ is the high-frequency dielectric constant.

When one tries to apply this mode to anionically conducting fluorozirconate glasses, the conducting ions will be F_{nb}^- and the role of the O_{nb} atoms will be played by Zr atoms. In the absence of noble gas diffusion data for fluorozirconate glasses, the value of r_D is unknown and the analysis of the E_S term will be left for a later stage. In order to make a semi-quantitative analysis of the E_E term of Sample FZ-1, we will use the ionic model for the Zr- F_{nb} bonds, which is only an approximation [19], although Pauling [20] has predicted 82% of ionic character for the Zr-F bond. When this is done, the E_E term may be written:

$$E_E = \left| \frac{z_{\text{F}} - z_{\text{Zr}^{4+}} e^2}{\epsilon} \left(\frac{1}{d(\text{Zr}-\text{F}_{\text{nb}})} - \frac{1}{R} \right) \right|, \quad (5)$$

where $d(\text{Zr}-\text{F}_{\text{nb}})$ represents the average Zr- F_{nb} bond length in the glass. This may be estimated from the Zr- F_{nb} bond lengths of isolated ZrF_6^{2-} octahedral ions in Li_2ZrF_6 [21] and $\text{Rb}_5\text{Zr}_4\text{F}_{21}$ [22] at about 0.200 nm. The jump distance, $2R$, can be estimated for Sample FZ-1 from the structural model of Fig. 2 and the interatomic distances determined by Laval *et al.* [23] in crystalline $\alpha\text{-BaZrF}_6$. In this compound, each Ba^{2+} ion has 8 nearest-neighbour F atoms at an average distance

of about 0.277 nm, which we will assume to be the average Ba–F_{nb} distance in the glass, where each Ba²⁺ ion probably has also 8 nearest-neighbour F_{nb} ions, as represented in Fig. 2. Here, if one assumes that the F_{nb} atoms numbered 1 to 8 roughly form a cube, the F_{nb}–F_{nb} nearest-neighbour distance will be about 0.320 nm. Therefore, considering that the most probable ionic jumps will be the shortest, i.e., from Position 1 to Positions 2, 4 or 5 in Fig. 2, one obtains an estimate of R at about 0.256 nm. Finally, the dielectric constant of Sample FZ-1 was found to vary asymptotically between 16.4 and 13.9 from 1 kHz to 3 MHz, respectively, contrary to the behaviour previously reported for ternary fluorozirconates, whose dielectric constant was independent of frequency [2]. The high frequency value of 13.9 (28° C) will be used. When the above parameters are introduced in Equation 5, one gets a value of $E_E = 0.46$ eV. This result is strongly dependent on the values of ϵ and R (assuming that 0.200 nm is already a fairly good estimate of $d(\text{Zr}-\text{F}_{\text{nb}})$). The dielectric constant of Sample FZ-1 was somewhat higher than those previously measured for ternary fluorozirconate glasses, which varied from 6.8 to 11.9; a high value of ϵ yields a low value of E_E . There is a relatively large uncertainty in the jump distance: a value of R higher than 0.256 nm would give a higher E_E term, whereas any value of R between 0.164 nm and 0.256 nm would give a value of $E_E < 0.46$ eV. It should also be noted that the attraction exerted by the Ba²⁺ ions on the F_{nb}⁻ ions is negligible in the present model, since the Ba–F_{nb} distances remain approximately constant between the initial state and the transition state.

Given the fact that the “doorway radius”, r_D , of Sample FZ-1 or any other fluorozirconate glass is unknown, it is better to estimate E_S from Equation 2 rather than from Equation 3. Thus, $E_S = 0.70 - 0.46 = 0.24$ eV. If one applies the present modification of the Anderson and Stuart model to a ternary glass such as 56.2 mol% ZrF₄–36.3 mol% BaF₂–7.5 mol% ThF₄, studied in [2], whose structure will be similar to that of Sample FZ-1 as long as we assume that ThF₄ plays the same role as ZrF₄ [19], one obtains $E_S = 0.19$ eV, with $E_\sigma = 0.78$ eV. This behaviour, similar to that observed in light alkali–silicate glasses [18], suggests that, although the electrostatic energy term is predominant, the strain energy is not negligible. Our calculations do not

support the claim that the activation energy for formation of “point defects” is zero in fluorozirconate systems [2, 10].

The presence of Cl atoms significantly increases the E_σ values, as seen in Table I. This may be due to a substantial increase in the jump distance, particularly for the most probable in-chain jumps, which increases E_E . On the other hand, it is also possible that, due to the larger size and polarizability of the Cl atoms compared to the F atoms, the E_S term is larger for the mixed-anion glasses, probably because r_D is considerably smaller than r in this case. Finally, if a “mixed halide effect” actually occurs (compare with Section 3.2.), it would manifest itself in increased values of E_σ .

4. Conclusions

The electrical conductivity was measured as a function of temperature for fluorozirconate and chloro-fluorozirconate glasses. The conductivity of binary fluorozirconates was comparable to that of ternary fluorozirconate glasses previously studied. The conductivity decreased substantially with the introduction of chlorine anions into the network, which appeared to have a “blocking effect” on the movement of the F_{nb} ions. The values of the activation energy for conduction were analysed according to a modified version of the Anderson and Stuart model. This indicated that the electrostatic energy term was generally predominant over the strain energy term, but more so in the case of the pure fluorozirconate glasses.

Acknowledgements

This research was supported by the Air Force Office of Scientific Research, under grant number AFOSR-80-0059. We are grateful to Mr Toshiyasu Kawaguchi, for his assistance with the electrical measurements. The laboratory assistance of Mrs Ramona G. Pond is also appreciated.

References

1. M. POULAIN, M. POULIN and J. LUCAS, *Mat. Res. Bull.* **10** (1975) 243.
2. D. LEROY, J. LUCAS, M. POULAIN and D. RAVAINÉ, *ibid.* **13** (1978) 1125.
3. D. LEROY and D. RAVAINÉ, *Compt. Rend. Acad. Sci. Paris, Serie C* **286** (1978) 413.
4. D. RAVAINÉ and D. LEROY, *J. Non-Cryst. Sol.* **38/39** (1980) 575.
5. G. T. PETROVSKII, E. K. LEKO and O. V. MAZURIN in “Structure of Glass” Vol. 4, edited by

- O. V. Mazurin (Consultants Bureau, New York, 1965) pp. 88–92.
6. J. KUMMER and M. E. MILBERG, *Chem. Eng. News* 47 (1969) 90.
 7. P. C. SCHULTZ and M. S. MIZZONI, *J. Amer. Ceram. Soc.* 56 (1973) 65.
 8. H. MATZKE, *J. Mater. Sci.* 5 (1970) 831.
 9. C. E. DERRINGTON and M. O'KEEFFE, *Sol. Stat. Commun.* 15 (1974) 1175.
 10. G. V. CHANDRASHEKHAR and M. W. SHAFER, *Mat. Res. Bull.* 15 (1980) 221.
 11. R. M. ALMEIDA and J. D. MACKENZIE, *J. Chem. Phys.* 74 (1981) 5954.
 12. *Idem*, unpublished work (1981).
 13. C. M. BALDWIN and J. D. MACKENZIE, *J. Non-Cryst. Sol.* 42 (1980) 455.
 14. R. M. A. ALMEIDA, PhD thesis, University of California, Los Angeles (1980).
 15. D. RAVAINÉ and J. L. SOUQUET, *Phys. Chem. Glasses* 18 (1977) 27.
 16. J. O. ISARD, *J. Non-Cryst. Sol.* 1 (1969) 235.
 17. A. A. PRONKIN and K. K. EVSTROP'EV, *Sov. J. Glass Phys. Chem.* 4 (1979) 209.
 18. O. L. ANDERSON and D. A. STUART, *J. Amer. Ceram. Soc.* 37 (1954) 573.
 19. C. M. BALDWIN, R. M. ALMEIDA and J. D. MACKENZIE, *J. Non-Cryst. Sol.* 43 (1981) 309.
 20. L. PAULING, "The Nature of the Chemical Bond" 3rd edn (Cornell University Press, Ithaca, New York, 1960) pp. 69–75.
 21. R. HOPPE and W. DAHNE, *Naturwissenschaften* 17 (1960) 397.
 22. G. BRUNTON, *Acta Cryst.* B27 (1971) 1944.
 23. J. P. LAVAL, R. PAPIERNIK and B. FRIT, *Acta Cryst.* B34 (1978) 1070.

*Received 23 November 1981
and accepted 29 January 1982*