JOURNAL OF MATERIALS SCIENCE 26 (1991) 3159–3164

Electrical properties of ZrF_4–BaF_2–GdF_3–AlF_3–glass

N. MAFFEI, S. E. PRASAD
B.M. Hi-Tech Inc. PO Box 97, Collingwood, Ontario, Canada L9Y 3Z4
T. A. WHEAT
Energy, Mines and Resources, CANMET, Ceramic Section, Ottawa, Ontario, Canada K1A 0G1

The electrical and dielectric behaviour of a gadolinium-based zirconium fluoride glass have been studied over a wide temperature (23–275 °C) and frequency (100 Hz – 1 MHz) range. The conductivity at 200 °C was of the order of 10^{-6} (ohm-cm)$^{-1}$ and the activation energy was 0.75 eV. The dielectric constant measured at 1 kHz was 14 and was independent of frequency at low temperatures. The observed dielectric dispersion has been attributed to the conduction mechanism.

1. Introduction

Zirconium-based fluoride glasses have tremendous potential as infrared (IR) transmitters in such diverse applications as laser hosts and windows, IR domes, lenses and IR optical fibres, and as a result the optical properties of these systems have been extensively studied [1]. The outstanding characteristic of fluoride glasses is their ultra-transparency and excellent transmission well into the infrared (approximately 8 micrometres). The theoretical attenuation of these systems would allow repeaterless transoceanic cables to become a reality. Extensive research has not yet been able to produce materials of sufficient quality to allow this application to be realized.

Fluorozirconate glasses, in particular zirconium–barium–lanthanum–aluminum (ZBLA) and zirconium–barium–gadolinium–aluminum (ZBGA) compositions, are the most promising of the fluoride glasses. Poor glass-forming ability (due to the low viscosity of these systems) and undesirable scattering due to impurities and macro/microcrystallites have limited their commercial exploitation.

The ionic conducting nature of these glasses and their electrical properties have been investigated by several groups [2–8]. The ionic conductivity at 200 °C compares favourably with β-alumina (a well-known ionic conductor). Their low softening temperature has, however, restricted their application to devices such as gas sensors, solid-state batteries, fuel cells, thermoelectric generators, etc. [9]. Device exploitation requires an extensive data-base in order to optimize device performance. As a result, the electrical and dielectric behaviour of a ZBGA glass system has been studied over a wide temperature and frequency range to gain a better understanding of the physical characteristics of the glass. Another advantage of electrical measurements, in particular impedance measurements, is that the presence of different phases and/or electrode contributions can be detected.

This study forms part of a larger project concerned with materials processing in space (MPS). The advent of prolonged periods of microgravity on board the space transportation system (STS, commonly referred to as the space shuttle) has sparked renewed interest in the field of MPS. Among the unique characteristics of low-earth orbit the condition of 'zero gravity' has been extensively exploited. Under this condition containerless processing of materials is possible, and hence high-purity low-loss vitreous materials can be produced because of the reduced nucleation sites (heterogenous nucleation). This processing technique would allow the preparation of new materials which has not been possible due to the lack of suitable containers. Other factors including critical cooling rates required to form vitreous components have been shown to be less severe in the microgravity environment thus allowing new and reluctant glass-forming systems such as the fluoride glasses to be investigated. The elimination of sedimentation, convection currents, etc. should alleviate troublesome aspects such as crystallization and phase separation.

Investigation of several fluoride glass compositions, in the ZBGA family, is continuing in the hopes of identifying compositions which would benefit from MPS.

2. Experimental procedure

Glasses were prepared from fluoride precursors purchased from Cerac. The purity of ZrF_4 was 99.5%, while the other precursors were 99.9% pure. A 10-gram batch of component fluorides was mixed with excess ammonium bifluoride and melted at 800 °C for 1 h in a platinum crucible under an argon atmosphere. The melt was cast in a preheated carbon mould, annealed for half an hour just below the glass transition temperature and cooled slowly to ambient temperature.

0022–2461/91 $03.00 + .12

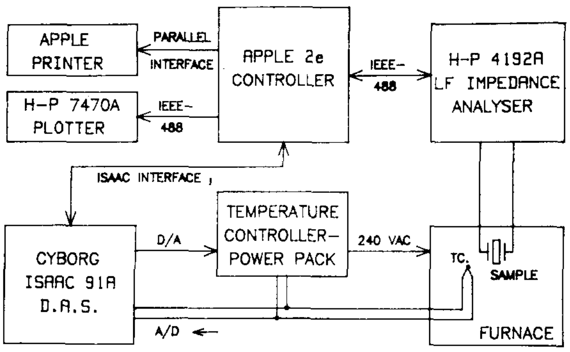

Figure 1 Experimental arrangement used for measuring the impedance of the sample.

The density of the glass was determined by the pycnometer technique, using toluene. The glass transition temperature T_g, crystallization temperature T_x and melting temperature T_m were determined by differential thermal analysis (DTA) using a DuPont 1090 instrument and a heating rate of 15 °C/min. The index of refraction of the glass was determined by the Becke line method. IR absorption of polished glass samples was measured on a Beckman IR 4260 Research Spectrometer. These samples were prepared by dry polishing to a 10 micrometre finish with SiC paper and wet polished with 3 micrometre diamond paste on a lap using a mixture of mineral oil and kerosene as lubricant. The samples were cleaned with petroleum ether.

The direct current (d.c.) conductivity was determined by two techniques. The first method used a Keithley 619 electrometer/multimeter to directly measure the current from which the conductivity was calculated. The second method used the alternating current (a.c.) technique, Fig. 1 [10, 11]. An Apple IIe microcomputer was used to control the Hewlett–Packard 4192 Impedance Analyser via the IEEE-488 bus. The temperature was set and monitored by using a Cyborg data acquisition system. This configuration was used to determine the real and imaginary components of impedance from which the resistance at d.c. could be calculated. The present apparatus is very versatile and allows one to determine the capacitance and dissipation from which the dielectric behaviour of the glass may be studied. The electrodes used were air-drying silver paint.

3. Results and discussion

Table I summarizes the properties of the glass composition studied. The IR transmission characteristics for a 2.74 centimetre thick glass are shown in Fig. 2, and confirm the high transmission in the range 1500–4000 cm^{-1} and the absence of significant absorption due to hydroxyl ions in the region 3300–3600 cm^{-1}. The density and index of refraction for this glass are comparable to those of similar composition [12]. The glasses were transparent but had small areas of inclusions principally at the surface of the glass. This colour inclusion has been attributed to the presence of different oxidation states of zirconium [13].

TABLE I Physical properties of glass studied: composition 60% ZrF_4–32% BaF_2–4% GdF_3–4% AlF_3 (mol %)

Density	4.62 $\mathrm{gm/cm^3}$
T_g	314
T_x	386
T_m	538
η	1.519 (measured with sodium D line)
ε	14 at 1 kHz
	11 at 1 MHz
σ (25 °C)	3.7×10^{-11} $(\mathrm{ohm\text{-}cm})^{-1}$
σ (200 °C)	1.2×10^{-6} $(\mathrm{ohm\text{-}cm})^{-1}$
E	0.75 eV

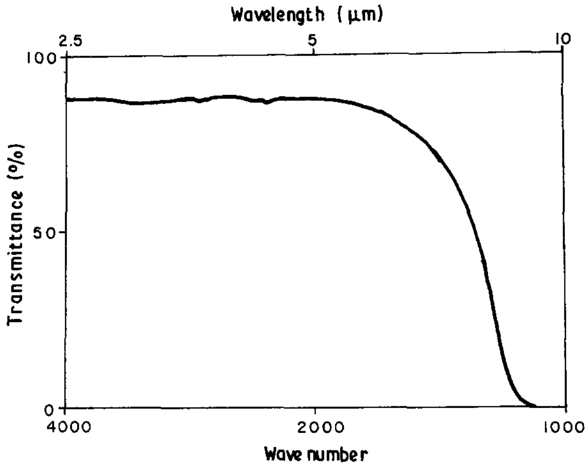

Figure 2 Infrared transmittance of a typical ZBGA glass.

3.1. D.c. conductivity

The conductivity obtained by the d.c. technique is shown in Fig. 3. The glass exhibited ionic conductivity which obeyed an Arrhenius law with

$$\sigma = \sigma_0 \exp(-E/kT)$$

in the temperature range 25–275 °C. The activation energy was determined to be 0.76 eV.

3.2. A.c. Conductivity

To avoid polarization effects, a.c. conductivity measurements were also carried out to determine the activation energy for the system. The oscillator level of the 4192 was varied from 10 mV, 50 mV, 100 mV, and 1 V. The measured impedance values showed little variation with oscillator level; as a result all a.c. measurements were taken at the default value (1 V).

A typical impedance diagram for the sample is shown in Fig. 4. The intercept with the real axis (resistance at d.c.) was determined by a circular regression programme. The impedance diagrams show no component due to the electrode at low temperatures. At higher temperatures however there is evidence of another circle indicating an electrode contribution to the system. The contribution may be due to the formation of a surface layer resulting from polarization of the electrode at these higher temperatures.

The conductivity as a function of temperature obtained from the impedance plots is shown in Fig. 5. The extraneous points at low temperatures are due to

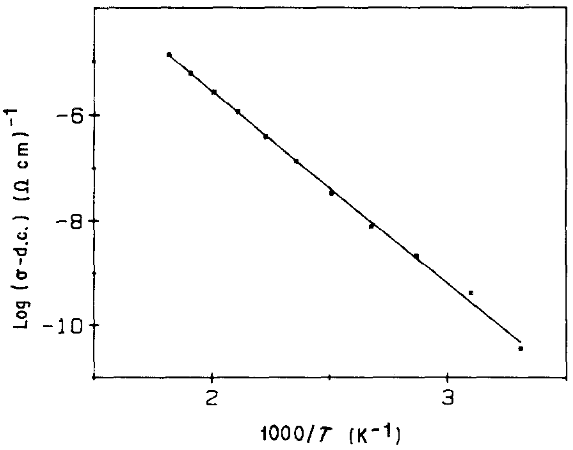

Figure 3 D.c. conductivity of the sample as determined by the d.c. measuring technique.

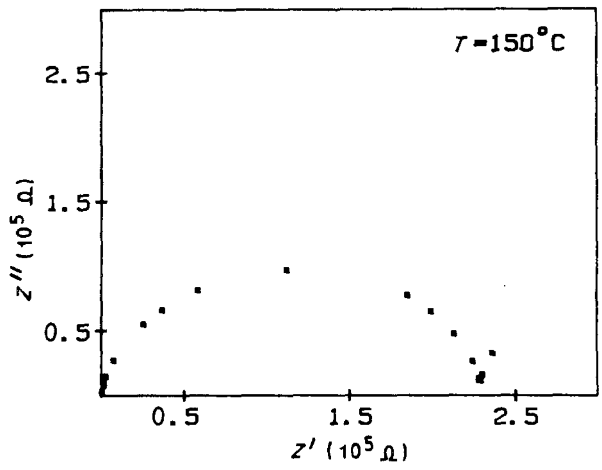

Figure 4 Typical impedance plot for the ZBGA glass sample.

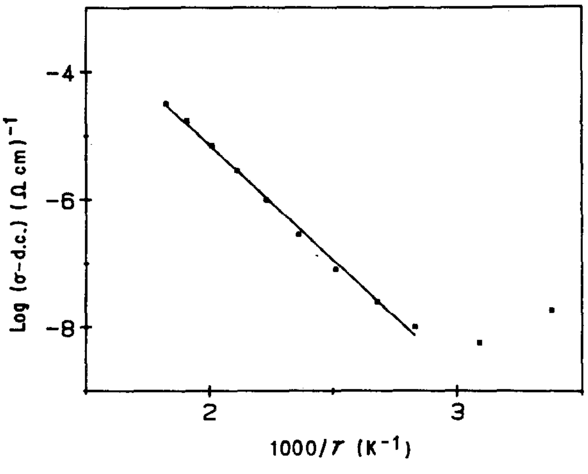

Figure 5 D.C. conductivity of the sample as determined from the impedance diagrams.

the error involved in determining the intercept. Again the variation of conductivity with temperature followed an Arrhenius relationship with an activation energy of 0.74 eV which is in excellent agreement with the value determined by the d.c. technique and is consistent with values determined for other zirconium-based fluoride glasses. The d.c. conductivity at room temperature was of the order of 10^{-10} (ohm-cm)$^{-1}$ and increased to approximately 10^{-6} (ohm-cm)$^{-1}$ at 200 °C.

The variation in conductivity with frequency, Fig. 6, shows a slight dependency on frequency at low temperatures but becomes frequency-independent at higher temperatures which is typical for ionic conductors. This behaviour also indicates the development of good electrical contacts to the sample [14].

The variation in a.c. conductivity with temperature is shown in Fig. 7. At higher temperatures the a.c. conductivity approaches the d.c. conductivity; the temperature at which the a.c. conductivity approaches the d.c. value increases with frequency. The d.c. value is never approached which could indicate polarization effects in the d.c.-measuring techniques. The slight difference in activation energy determined by the two techniques may also be a result of polarization.

The dielectric constant was independent of frequency below 100 °C indicating that the measured value is due to bulk and not surface effects (Fig. 8). At higher temperatures, the considerable dispersion at low frequency is due to polarization effects whereas the slight dispersion at high frequency is due to ionic conduction [15]. The variation in dielectric constant

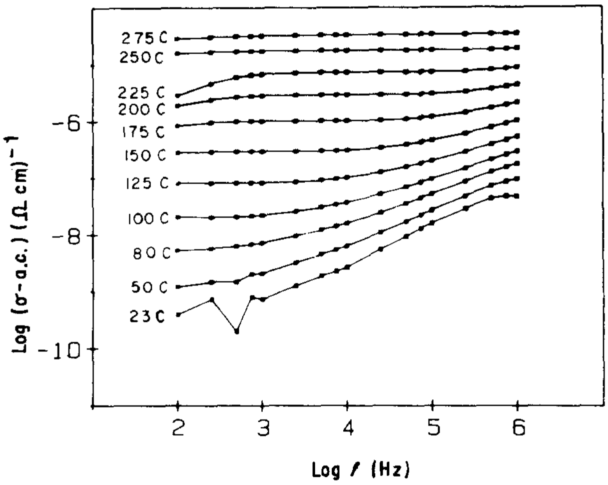

Figure 6 Variation of a.c. conductivity as a function of frequency.

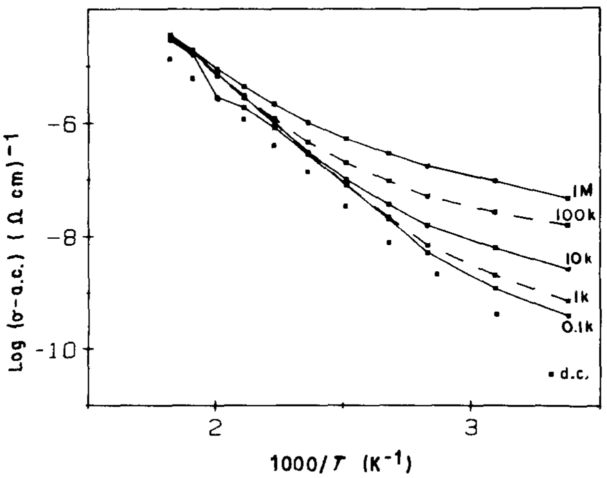

Figure 7 Plot of a.c. conductivity as a function of temperature.

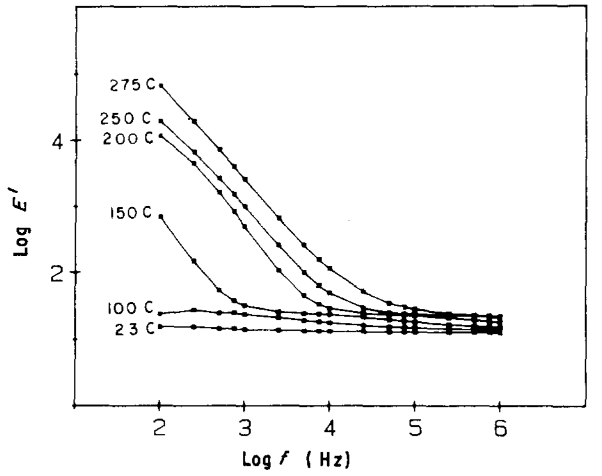

Figure 8 Variation of the dielectric constant as a function of frequency.

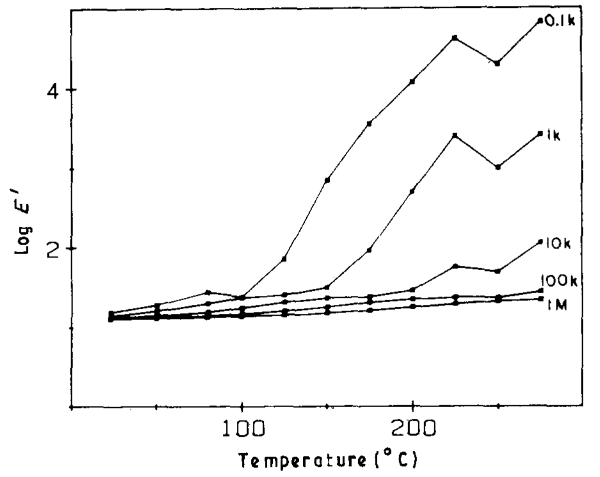

Figure 9 Variation of the dielectric constant as a function of temperature.

with temperature is shown in Fig. 9. At low frequencies, the dielectric constant increases with temperature due to polarization whereas the high-frequency dielectric constant varies little with temperature.

Relaxation times obtained from Cole–Cole plots are given in Fig. 10. The dielectric relaxation times follow an expression of the form

$$\tau = \tau_0 \exp(U/kT)$$

The value obtained for U was 0.64 eV which is similar to the value obtained from d.c. conductivity measurements indicating that the d.c. conductivity mechanism may be responsible for the dispersion in relaxation time. The spread in relaxation time was quite high: the value of the spreading parameter was of the order of 0.8 for temperatures above 200 °C, while below this temperature the dispersion was much lower being typically 0.1 between 125 °C and 175 °C.

An alternative approach to dispersion in vitreous systems is the modulus formulation [16]. The advantage of this approach is that electrode effects are supposedly eliminated. A typical modulus plot for the sample is given in Fig. 11. The width of the peak is quite large indicating a spread in relaxation time, and

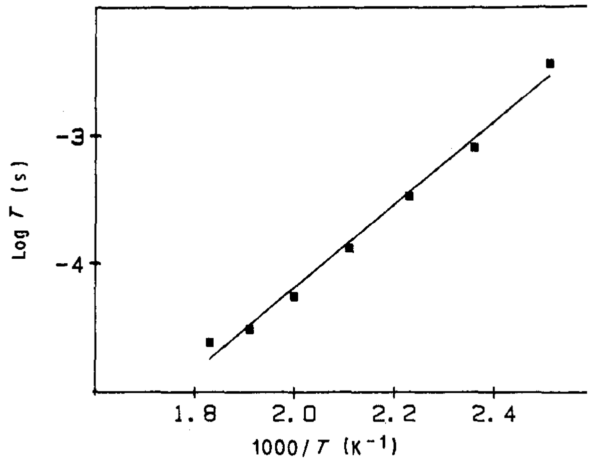

Figure 10 Variation of relaxation time as a function of temperatur

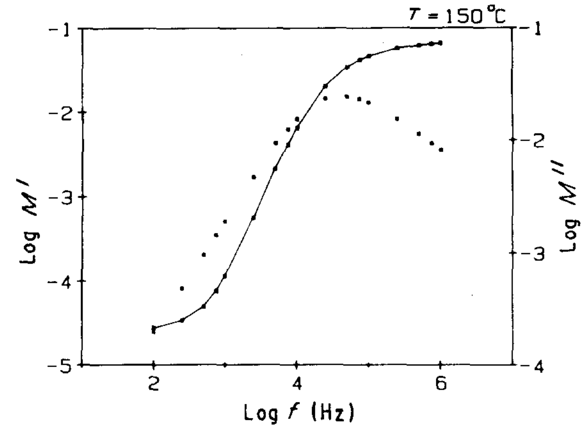

Figure 11 Typical modulus plot for the ZBGA sample.

increased with temperature indicating an increase i dispersion. The broadening of the peak has bee attributed to the presence of other phases and wate contamination [17]. The variation in relaxation tim with temperature (calculated from the modulus plot is shown in Fig. 12. The value of U was 0.79 eV whic is in close agreement with the value of 0.76 eV ot tained from d.c. conductivity.

The variation in dissipation with temperature i shown in Fig. 13. The peak in dissipation is shifted t higher temperature for higher frequencies which i typical for Debye-type dispersion. Fig. 14 shows th variation of dissipation with frequencies. The peak i shifted to higher frequency with increasing temper ature as expected.

The variation in peak frequency with temperature i shown in Fig. 15. The activation energy from pea frequency has been found to be similar to the d. conduction activation energy for many glass system The activation energy from Fig. 15 was 0.69 eV whic is similar to the activation energy found for d. conduction suggesting that the dispersion is due to th conduction process and seems to be a bulk phenom enon rather than surface polarization. The observe dispersion may also be affected by impurities and/o defects.

The electrical properties of the ZBGA compositio studied are similar to compositions reported by other

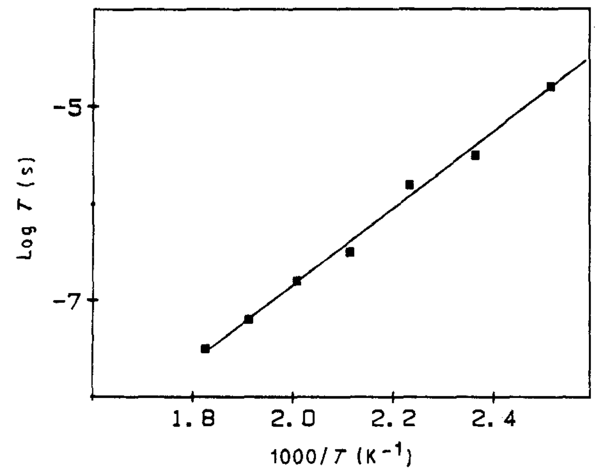

Figure 12 Variation of relaxation time as a function of temperature.

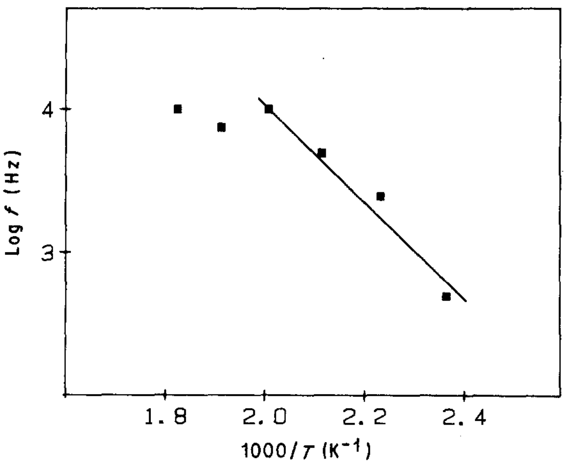

Figure 15 Variation of peak frequency with temperature.

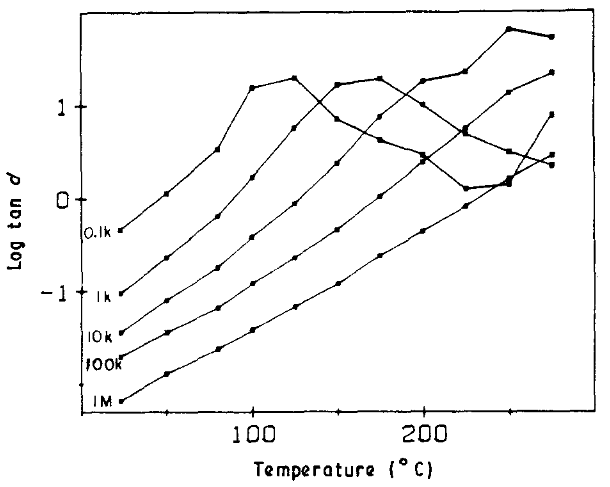

Figure 13 Variation of dissipation with temperature.

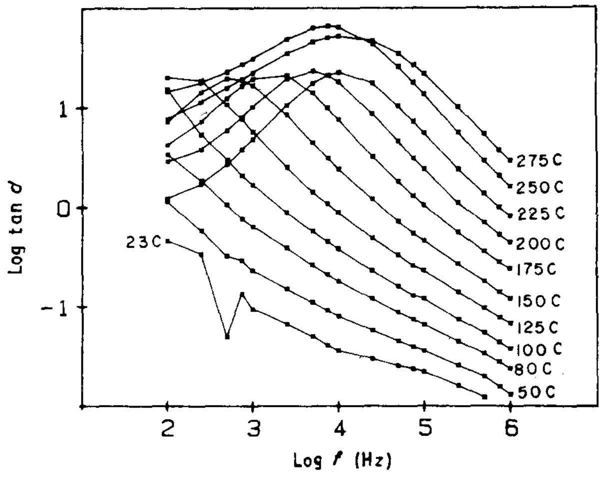

Figure 14 Variation of dissipation with frequency.

but the magnitude of conductivity needs to be increased to be useful in device applications. The conductivity in other systems has been shown to vary only slightly with composition. It would be interesting to determine if the conductivity of ZBGA glasses could be modified by the addition of alkali fluorides such as NaF.

The dielectric studies indicate that the conduction process is due to the bulk and does not seem to be masked by surface polarization. No evidence of second phases was observed in the a.c. impedance diagrams suggesting that the composition of the glass is uniform and that the crystallization present was too small to be detected. The observed dispersion seems to be Debye-like with a large spread in relaxation times. The glass in the present study was produced from raw materials obtained commercially. It would be interesting to examine the effects of impurities on the glass system as they may give rise to dispersion. The dispersion in the modulus peaks could be due to the presence of water and/or hydroxyl ions since no evidence of phase separation was apparent in the impedance diagrams. The effect of hydroxyl ions on the conductivity has not been investigated but could yield significant information on the conduction mechanism in these glasses.

4. Conclusions

The electrical properties of a zirconium-based glass were measured over a wide frequency and temperature range. The conductivity obeyed an Arrhenius law and had an activation energy of 0.75 eV. The conductivity at 200 °C was of the order of 10^{-6} (ohm-cm)$^{-1}$. The dielectric constant of the glass was 14 at 1 kHz. The observed dispersion seems to be due to the bulk and has been attributed to the conduction mechanism. The significant d.c. conductivity and low operating temperature make utilization of the glass in a device application impractical.

Acknowledgement

Financial assistance for this project was provided by the Space Station User Development Programme, Space Division, National Research Council of Canada and administered by Dr P. Kumar to B.M. Hi-Tech Inc. This assistance is gratefully acknowledged.

References

1. D. C. TRAN, G. H. SIGEL and B. BENDOW, *J. Lightwave Tech.* **LT-2** (1984) 566.

2. D. RAVAINE and D. LEROY, *J. Non-Cryst. Solids* **38–39** (1980) 575.
3. G. V. CHANDRASHEKHAR and M. W. SHAFER, *Mater. Res. Bull.* **15** (1980) 221
4. D. LEROY, J. LUCAS, M. POULAIN and D. RAVAINE, *ibid.* **13** (1978) 1125.
5. J. SENEGAS, J. M. REAU, H. AOMI, P. HAGENMULLER and M. POULAIN, *J. Non-Cryst. Solids* **85** (1986) 315.
6. R. M. ALMEIDA and J. D. MACKENZIE, *J. Mater. Sci.* **17** (1982) 2533.
7. Y. KAWAMOTO and I. NOHARE, *Solid State Ionics* **22** (1987) 207.
8. Z. XIUJIAN, T. KOKUBO and S. SAKKA, *J. Mater. Sci. Lett.* **6** (1987) 143.
9. R. A. HUGGINS, *Solid State Ionics* **5** (1981) 15.
10. J. E. BAUERLE, *J. Phys. Chem. Solids* **30** (1969) 2637.
11. I. M. HODGE, M. D. INGRAM and A. R. WEST, *J. Electroanal. Chem.* **74** (1976) 125.
12. S. MITACHI, *Phys. Chem. Glasses* **23** (1982) 190.
13. M. ROBINSON, R. C. PASTOR, R. R. TURK, D. P. DEVOR and M. BRAUNSTEIN, *Mater. Res. Bull.* **15** (1980) 735.
14. S. W. MARTIN and C. A. ANGELL, *J. Non-Cryst. Solids* **83** (1986) 185.
15. M. TOMOZAWA, "Treatise on Materials Science and Technology", **12** (1977) 283.
16. P. B. MACEDO, C. T. MOYNIHAN and R. BOSE, *Phys. Chem. Glasses* **13** (1972) 171.
17. I. M. HODGE, M. D. INGRAM and A. R. WEST, *J. Electroanal. Chem.* **74** (1976) 125.

Received 19 September 1989
and accepted 9 April 1990