JOURNAL OF MATERIALS SCIENCE 26 (1991) 6271–6274

Electrical properties of barium–borosilicate glasses

G. R. MORIDI
Department of Physics, University of the South Pacific, Suva, Fiji
A. NOURUZI
Department of Physics, Al-Zahra University, Vanak, Tehran, Iran
C. A. HOGARTH
Department of Physics, Brunel University, Uxbridge, Middlesex UB8 3PH, UK

Bulk and thin-blown films of barium–borosilicate glass were prepared and their electrical conduction properties at high and low fields were measured as functions of temperature. The electrical conductivity is an exponential function of inverse temperature at high temperatures with an activation energy in the range 1.0 to 1.4 eV, depending on composition. The conduction process is believed to involve polarons hopping in the adiabatic regime. Some high-field electroforming effects are observed.

1. Introduction

Studies of the electrical and optical properties of amorphous materials have been carried out extensively, both theoretically and experimentally, by many workers in the past. Oxide glasses containing significant concentrations of transition-metal ions or low mobility metal ions such as Zn^{2+} or Ba^{2+} [1, 2] exhibit electronic conductivity and may be regarded as high-resistivity semiconductors. As far as the electrical properties of amorphous materials are concerned, three distinctive characteristics were observed within the wide range of applied electric field: low-field ohmic conductivity, high-field conductivity, and switching. Certain physical mechanisms are believed to be responsible for each of these characteristics. In this paper we shall report experimental data on the low-field conductivity of barium–borosilicate glasses. It has been generally accepted that in highly disordered systems, where the states are localized, an electron moves from one site to another by a thermally activated hopping mechanism. This is accompanied by the emission or absorption of a phonon. The jump probability p is given by [3].

$$p = \nu_0 \exp(-2\alpha R - W/kT) \quad (1)$$

where ν_0 is the phonon frequency; R, site separation; α, overlap integral; and W, activation energy. This leads to a conductivity formula of the form

$$\sigma = \sigma_0 \exp(-W/kT) \quad (2)$$

A low-mobility electron strongly distorts the surrounding lattice and forms a bound state with the potential well due to its own lattice displacement. This dynamic electron–lattice interaction is referred to as a polaron, having a binding energy W_p resulting from the polarization of the surrounding ions. This energy is given by [3]

$$W_p = \frac{1}{2}\frac{e^2}{\varepsilon_p r_\pi} \quad (3)$$

where

$$\frac{1}{\varepsilon_p} = \frac{1}{\varepsilon_\infty} - \frac{1}{\varepsilon_o} \quad (4)$$

where ε_∞ and ε_o are the high- and low-frequency relative dielectric constants respectively, ε_p is the effective dielectric constant, and r_p is the polaron radius. For narrow band materials, r_p is given by [4]

$$r_p = 1/2(\pi/6N)^{1/3} \quad (5)$$

where N is the concentration of sites. The activation energy in Equation 1, W, consists of the activation energy for hopping, W_H, and the energy difference between the initial and the final sites, W_D.

$$W = W_H + \tfrac{1}{2}W_D + W_D^2/16W_H \quad (6)$$

where $W_H = \frac{1}{2}W_p$. In materials where the potential wells overlap, and the site separation is not large compared with r_p [3, 5], W_H is given by

$$W_H = \frac{e^2}{4\varepsilon_p}\left(\frac{1}{r_p} - \frac{1}{R}\right) \quad (7)$$

This is the adiabatic case in which, due to the overlap of wells, an electron makes many transitions between two sites within a period of 10^{-12} s. In this case the exponential term $\exp(-2\alpha R)$ does not appear in the jump probability, and therefore it is expected that σ_0, the pre-exponential factor in the conductivity formula, does not vary exponentially with R. Such an exponential term is included in σ_0 for the non-adiabatic regime.

0022–2461/91 $03.00 + .12

The activation energy, W, is dependent upon temperature [6]. At temperatures above $\frac{1}{2}\theta_D$, where θ_D is the Debye temperature and given by $\theta_D = \hbar\omega_o$, where ω_o is the radial optical phonon frequency and $\hbar$ is Planck's constant,

$$W = W_H + \tfrac{1}{2}W_D \quad (8)$$

and at $T < \frac{1}{4}\theta_D$

$$W = W_D \quad (9)$$

In a more detailed treatment of the polaron model, Emin and Holstein [7] show that in the adiabatic regime the activation energy is given by

$$W = W_H - J \quad (10)$$

where J is the polaron band width, related to the overlapping of wave functions of adjacent sites. The condition for adiabatic hopping is that [7]

$$J \geq \left(\frac{2kTW_H}{\pi}\right)^{1/4}\left(\frac{\hbar\omega_o}{\pi}\right)^{1/2} \quad (11)$$

and the condition for a small polaron to exist is that [7]

$$J \leq \tfrac{1}{3}W_H \quad (12)$$

2. Experimental procedure

A series of barium–borosilicate glasses, having the composition 30% SiO_2–(70–x)% B_2O_3–x% BaO, where $50 \geq x \geq 25$, were made. Table I shows the glass composition. The glass preparation method has been given elsewhere [8]. As the glass preparation history has a significant effect on the electrical properties of the glass, parameters such as melting temperature, melting time, annealing temperature and so forth were kept uniform for all the glasses examined. Both bulk and thin blown film specimens were used for the conductivity measurements. A guard-ring electrode system was used in order to eliminate the surface resistance. Silver, gold and copper were evaporated in vacuum on to glass surfaces and good ohmic contacts were obtained. The current was measured by a Keithley 610C electrometer sufficiently sensitive for measuring currents down to 10^{-14} A. The power supply was a Keithley 240 stabilized high-voltage supply. The current–voltage characteristics of the specimens were measured under a vacuum of 10^{-5} torr. The conductivity values were calculated from the ohmic region of the I–V curves at different temperatures.

3. Results and discussion

The d.c. electrical conductivity of barium–borosilicate glasses was measured in the temperature range 20 to 400 °C. Fig. 1 shows typical plots of log σ against $1/T$ for glasses containing different barium concentrations. The curves obtained for all the glasses fitted Equation 2 at high temperatures. Within experimental error, the low-field conductivity values of blown films were found to be similar to those of the bulk glass specimens. The conductivity values were reproducible for glasses of different thicknesses taken from the same batch. Fig. 2 shows log σ at 667 K as a function of the BaO content of the glasses. The value of the pre-exponential factor in the conductivity formula σ_o was found to be in the range of 10–100 $\Omega^{-1}\,cm^{-1}$, dependent on the glass composition. Such a dependence of σ_o on R is not of an exponential form, as was predicted by Equation 1 for the carriers hopping in a non-adiabatic regime. The effect of the replacement of SiO_2 by B_2O_3 (another glass-forming oxide) on the electrical conductivity of a series of barium–borosilicate glasses containing 20 mol % BaO was examined and no significant changes were recorded. However, a partial replacement of a glass-forming oxide by BaO (a glass-modifying oxide) shows a considerable effect on the electrical properties of the glass. It was suggested [8] that barium is breaking the chemical bonds and filling the voids in the glass structure, hence increasing the concentration of the defect centres D. Such an increase will certainly affect the activation energy as well as the conductivity itself. Fig. 3 shows the variation of high temperature activation energy as a function of barium oxide content of the glass. Similar relationships have also been reported for glasses containing transition-metal ions [2, 9–11]. Fig. 4 shows the variation of W with the site separation R. As may be seen, a fairly good straight line was obtained. Following the small polaron model such a dependence of W on site separation R would be expected if the polarons are hopping in the adiabatic regime, (Equation 10). This model predicts that the thermal activation energy is a temperature dependent quantity and a break in linearity of the log σ against $1/T$ curves at $T = \frac{1}{2}\theta_D$ is expected. Supposing that the optical phonon frequency does not appreciably differ between BaO alone and the glass, and taking the infrared frequency of BaO to be 503 cm^{-1}, the Debye temperature θ_D for these glasses was estimated to be 724 K. A departure from linearity in the log σ against $1/T$ curves for glasses containing 40 and 45 mol % BaO is evident at a

TABLE I Composition and some properties of barium–borosilicate glasses

Glass no.	Glass composition (mol%)			R (nm)	r_p (exp) (nm)	r_p (theory) (nm)	ε_0	ε_∞	ε_p	W (eV)	W_H (eV)	W_D (eV)
	SiO_2	B_2O_3	BaO									
S-50	30	20	50	0.436	0.176	0.152	17.0	2.0	2.27	1.04	0.54	1.00
S-45	30	25	45	0.462	0.186	0.159	15.3	1.8	2.04	1.11	0.56	1.10
S-40	30	30	40	0.489	0.197	0.168	13.8	1.6	1.81	1.18	0.60	1.16
S-35	30	35	35	0.517	0.208	0.180	11.9	1.4	1.58	1.26	0.65	1.22
S-30	30	40	30	0.556	0.224	0.199	10.2	1.2	1.36	1.33	0.70	1.26
S-25	30	45	25	0.601	0.242	0.227	8.5	1.0	1.13	1.40	0.76	1.28

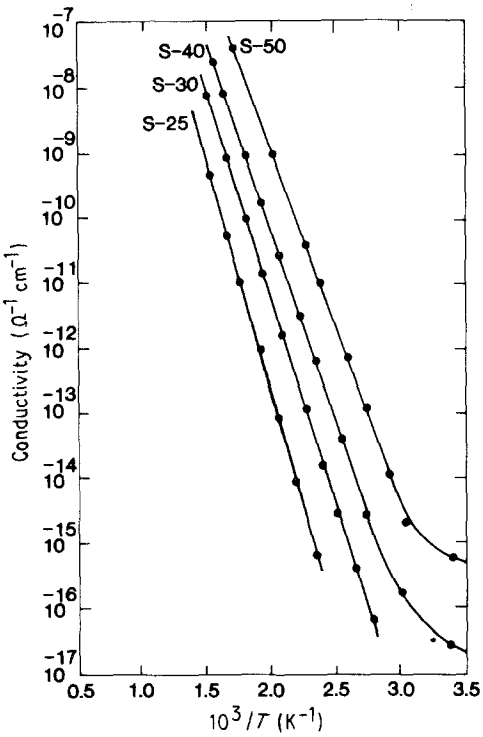

Figure 1 Conductivity of barium–borosilicate glasses as a function of inverse temperature.

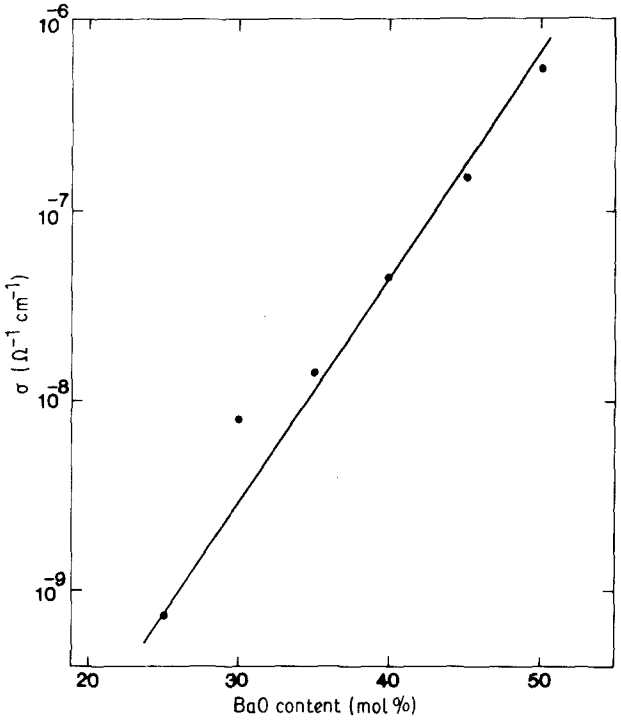

Figure 2 Conductivity of barium–borosilicate glasses as a function of BaO content.

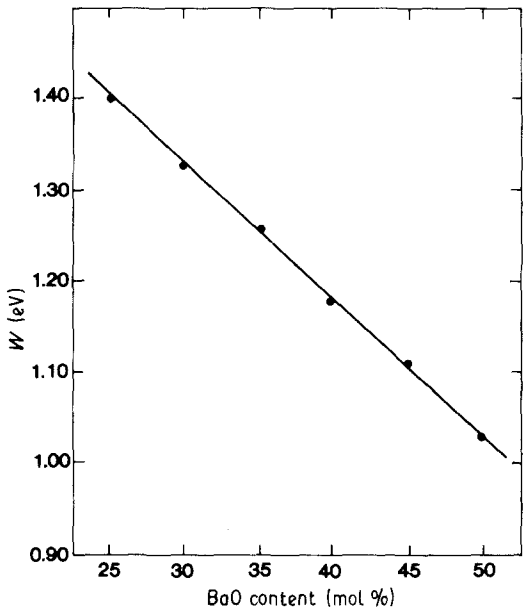

Figure 3 Activation energy of barium–borosilicate glasses as a function of BaO content.

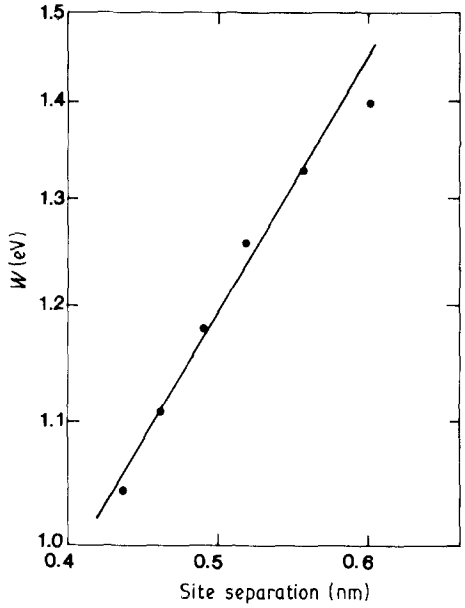

Figure 4 Activation energy as a function of site separation for a series of barium–borosilicate glasses.

temperature about 350 K (Fig. 1) which is in reasonable agreement with the value predicted by the polaron theory.

Assuming that at $T > \frac{1}{2}\theta_D$ and $W \approx W_H$, an estimate of the value of J for the glass S-50 can be made using Equation 11. The limiting value of the polaron bandwidth was found to be $J \geq 0.1$ eV at 600 K. The upper limit of J can be calculated using Equation 12, which gives the value of $J \leq 0.35$ eV. The limiting values of J satisfy the condition for carriers hopping in the adiabatic regime.

The concentration of barium ions in the glass was calculated using the formula

$$N = \frac{\rho M N_A}{AW \times 100} \tag{13}$$

where ρ is the density, M is the weight percent of barium in glass, N_A is the Avogadro number, AW is the atomic weight of barium. The average site spacing R of barium was calculated, supposing a uniform distribution of barium ions in the glass as $R = (1/N)^{1/3}$. The values of polaron radius r_p were calculated from Equation 5 for all samples and are given in Table I. An experimental estimate of polaron radius

was obtained from Equation 3 and making the assumption $W = W_H = \frac{1}{2}W_P$. These values are listed in Table I. The discrepancy between the two values of r_p may be due to the simplified assumption made about the distribution of barium ions in the glass. The polaron radius decreases as the barium content of the glass increases, and it is considerably less than the site separation R. The small values of r_p suggest that the polarons are strongly localized. Static and high frequency dielectric constants of the glasses were measured and are listed in Table I. The effective dielectric constant ε_p was calculated using Equation 4.

However, the above observation clearly shows that the conduction mechanism in barium–borosilicate glasses is due to small polarons hopping from one site to another in the adiabatic regime. Having accepted this, one may calculate the polaron hopping energy W_H using Equation 7. The estimated values of W_H, as well as the disorder energy W_D, are listed in Table I. The disorder energy seems to be approximately equal to the polaron binding energy. Such a large disorder energy has been reported for glasses containing vanadium [12] and tungsten [13].

The effect of forming on the electrical conductivity of glass S-50 was investigated. Thin blown films of a glass sample were formed by the application of a given voltage. Some preliminary results on switching in simple borosilicate glasses have been published [14]. Further details of the forming process and subsequent switching mechanism in our present glasses are to be published. The conductivity of the formed specimen is plotted as a function of $1/T$ in Fig. 5. The conductance characteristic has two regions with different slopes corresponding to activation energies of 0.52 eV and 0.28 eV, respectively. It seems reasonable to consider the two linear regions of the log σ against $1/T$ graphs as being associated with the two different conductive paths through the specimen, that is to say, a high conductive filament produced after forming, and the material surrounding the filament extending out to the electrodes on the glass surface. At lower temperatures ($T < 300$ K), the formed specimen shows a departure from linearity in the log σ against $1/T$ curve with a very low activation energy. This low activation energy was not observed in unformed specimens at these temperatures. The small value of activation energy at relatively low temperatures seems to suggest that forming the specimen has probably increased the density of the localized states, and the conductivity is then due to hopping of carriers between localized states near the Fermi energy.

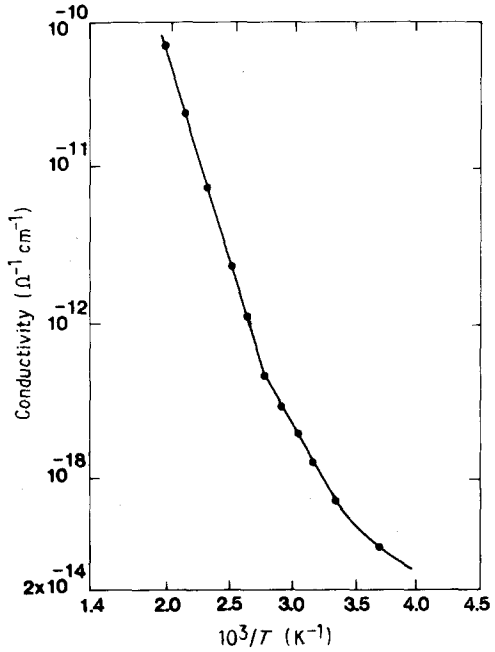

Figure 5 Conductivity of thin blown glass film (glass S-50) as a function of inverse temperature after forming.

4. Conclusion

The electrical conductivity of barium–borosilicate glasses was studied using both bulk and thin-blown glass specimens. The conductivity of all glasses at high temperatures followed a usual exponential relationship with $1/T$, with an activation energy in the range 1.0–4.1 eV, depending on glass composition. The activation energy decreases with temperature and is dependent on barium separation in the glass. The results were discussed in terms of a polaron model and it was found that the conduction mechanism suits the requirements for carriers hopping in the adiabatic regime. The effect of the forming process on the conductivity was investigated. Three regions of conductance were noted. It was suggested that at low temperatures forming leads to an increase in the density of localized states at the Fermi level, and at high temperatures the highly conductive filament and its surrounding material are responsible for a change of slope in the log σ against $1/T$ plot.

References

1. M. A. GHAURI, A. R. MIR, C. A. HOGARTH and M. AHMED, *Int. J. Electron.* **53** (1982) 311.
2. S. F. ANVARY, C. A. HOGARTH and G. R. MORIDI, to be published.
3. I. G. AUSTIN and M. F. MOTT, *Adv. Phys.* **18** (1969) 41.
4. V. N. BOGOMOLOV, E. K. KUDINOV and Yu. A. FIRSOV, *Sov. Phys. Solid State*, **9** (1968) 2502.
5. H. R. KILLIAS, *Phys. Lett.* **20** (1966) 5.
6. N. F. MOTT, *Adv. Phys.* **16** (1967) 49.
7. D. EMIN and T. HOLSTEIN, *Ann. Phys.* **53** (1969) 439.
8. G. R. MORIDI, A. NOURUZI and C. A. HOGARTH, to be published.
9. G. R. MORIDI and C. A. HOGARTH, "Proceedings of 4th Conference on Non-Crystalline Solids", Clausthal-Zellerfield, 1976, edited by G. H. Frischat, (Trans. Tech Publications, Aadermannsdorf, 1977) p. 254.
10. M. H. HEKMAT-SHOAR, C. A. HOGARTH and G. R. MORIDI, *J. Mater. Sci.* **20** (1985) 889.
11. A. DURAN, J. R. JURADO and J. M. F. NAVARRO, *J. Non-Crystalline Solids* **79** (1986) 333.
12. G. N. GREAVES, *ibid.* **11** (1973) 427.
13. F. P. KOFFYBERG and F. A. BENKO, *ibid.* **40** (1980) 7.
14. C. A. HOGARTH, G. R. MORIDI and A. NOURUZI-KHORASSANI, *Phys. Status Solidi (a)* **30** (1975) K189.

Received 29 March
and accepted 20 April 1990