Electrical properties of barium–borosilicate glasses

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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].

$$p = v_o \exp(-2\alpha R - W/kT)$$

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

$$\sigma = \sigma_o \exp(-W/kT)$$

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].

$$W_p = \frac{1}{2} \frac{e^2}{\varepsilon_p \varepsilon_0}$$

where

$$\frac{1}{\varepsilon_p} = \frac{1}{\varepsilon_\infty} - \frac{1}{\varepsilon_0}$$

where $\varepsilon_\infty$ and $\varepsilon_0$ are the high- and low-frequency relative dielectric constants respectively, $\varepsilon_p$ is the effective dielectric constant, and $r_p$ is the polaron radius. For narrow band materials, $r_p$ is given by [4].

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

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, $W_D$.

$$W = W_H + \frac{1}{2}W_D + \frac{W_D^2}{16W_H}$$

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

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

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 $\sigma_o$, the pre-exponential factor in the conductivity formula, does not vary exponentially with $R$. Such an exponential term is included in $\sigma_o$ for the non-adiabatic regime.
The activation energy, $W$, is dependent upon temperature [6]. At temperatures above $\frac{1}{2} \theta_D$, where $\theta_D$ is the Debye temperature and given by $\theta_D = \frac{h \omega_o}{k}$, where $\omega_o$ is the radial optical phonon frequency and $h$ is Planck's constant,

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

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]

$$J \geq \left( \frac{2 k T W_H}{\pi} \right)^{1/4} \left( \frac{h \omega_0}{\pi} \right)^{1/2} \quad (11)$$

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

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

2. Experimental procedure

A series of barium-borosilicate glasses, having the composition 30% SiO$_2$-(70-x)% B$_2$O$_3$-x% BaO, where 50 $\geq$ x $\geq$ 25, were made. Table 1 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 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 $\sigma$ 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 $\sigma$ at 667 K as a function of the BaO content of the glasses. The value of the pre-exponential factor in the conductivity formula $\sigma_o$ was found to be in the range of 10$^{-100}$ Ω$^{-1}$ cm$^{-1}$, dependent on the glass composition. Such a dependence of $\sigma_o$ 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$_2$O$_3$ (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 $\sigma$ against $1/T$ curves at $T \geq \frac{1}{2} \theta_D$ 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 $\theta_D$ for these glasses was estimated to be 724 K. A departure from linearity in the log $\sigma$ against $1/T$ curves for glasses containing 40 and 45 mol % BaO is evident at a

<table>
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<th>Glass no.</th>
<th>SiO$_2$ (nm)</th>
<th>B$_2$O$_3$ (nm)</th>
<th>BaO (nm)</th>
<th>$r_p$ (exp) (nm)</th>
<th>$r_p$ (theory) (nm)</th>
<th>$e_o$ (eV)</th>
<th>$e_x$ (eV)</th>
<th>$e_p$ (eV)</th>
<th>$W_H$ (eV)</th>
<th>$W_D$ (eV)</th>
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