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AC conductivity of unconventional bismuth cuprate glass

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Abstract. The frequency dependence of the AC electrical conductivity of different compositions of bismuth cuprate glasses has been presented in the temperature range 80–400 K. The conductivity data have been analysed in terms of different theoretical models to determine the possible conduction mechanism. Analysis of the conductivity data and the frequency exponent shows that the correlated barrier hopping of electrons between Cu^{+} and Cu^{2+} ions in the glasses is the most favourable mechanism for AC conduction. The different parameters obtained from the fits of this model to the experimental data are reasonable. The high value of the dielectric constant observed in this glass system can be attributed to the influence of the high polarizability of the Bi^{3+} ions of the unconventional network former Bi_2O_3 on the AC response.

1. Introduction

Oxide glasses containing transition-metal (TM) ions are interesting because of their possible applications in threshold and memory switching, etc [1, 2]. Study of the electrical conductivity of these glasses shows their semiconducting nature, which arises from the presence of more than one valence state of the TM ions (such as Cu^{+} and Cu^{2+} for cuprate glasses). However, the position of the copper ions is important in that case. Extensive studies have been made of cuprate glasses based on conventional network formers such as P_2O_5 and B_2O_3 [3–7]. The high activation energy (about 1 eV) observed in these glasses has been explained assuming a hopping of electrons between non-identical copper sites [5]. Some workers [3] have observed mixed electronic and ionic conduction in copper phosphate glasses and have interpreted the results assuming that the Cu^{+} ions exist in sites with different bending forces. Cuprate glasses based on an unconventional network former such as Bi_2O_3 have not been studied extensively [8]. The glasses based on this type of heavy-metal oxide are, however, interesting because they can be used to produce glass ceramics, reflecting windows, layers for optical and optoelectronic devices, etc [9, 10]. Recently, structural studies of the cuprate glasses based on Bi_2O_3 and PbO as unique network formers have been reported [11, 12]. The study of the DC conductivity of bismuth cuprate glasses [13] reveals that electronic hopping is the dominant conduction mechanism in this glass system. The structural studies [11] show that the copper ions occupy the network forming position and thus are unable to diffuse through the host matrix, confirming the absence of ionic conduction in these cuprate glasses.

The purpose of the present paper is to study the AC conduction mechanism of the different glass compositions and also to study the influence of the heavy-metal network former on the AC electrical properties of unconventional bismuth cuprate glasses over wide temperature and frequency ranges.

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2. Experimental procedure

The preparation of bismuth cuprate glasses has been described in detail elsewhere [11]. In brief, glasses of compositions xCuO–$(100 - x)$$Bi_2O_3$ with $x = 27$–68 mol% (table 1) were prepared from reagent grade chemicals, Bi_2O_3 and CuO. The appropriate mixtures of these chemicals were melted in alumina crucibles in an electrical furnace for 1 h in the temperature range 1000–1200 °C depending on composition. The melts were then quenched by pouring onto a twin roller. The amorphous nature of the samples was confirmed by x-ray diffraction, while their homogeneity was ascertained from scanning electron microscopy. Structural characterization of the samples was made using different techniques [11].

Table 1. Parameters obtained by fitting the experimental data to the correlated barrier hopping (CBH) model for bismuth cuprate glasses.

Glass composition (mol%)					
CuO	Bi_2O_3	W_M (eV)	τ_0 (s)	N (cm^{-3})	e
27.15	72.85	1.42	0.55×10^{-13}	2.10×10^{21}	24
35.35	64.65	1.18	0.11×10^{-13}	3.20×10^{21}	26
45.70	54.30	0.89	1.90×10^{-13}	0.80×10^{21}	29
55.60	44.40	0.68	0.34×10^{-13}	4.55×10^{21}	31
67.60	32.40	0.58	1.45×10^{-13}	5.10×10^{21}	33

For electrical measurements, gold electrodes were deposited on both surfaces of the samples by vacuum evaporation. The AC conductivity was measured using a capacitance bridge (Gen Rad, model 1615A) in the frequency range 10^2–10^5 Hz. The measurement of the DC conductivity was carried out using an electrometer (Keithley model 617). All the measurements were made in the temperature range 80–400 K. For low-temperature measurements, the sample cell was inserted in a cryostat, while for measurements above room temperatures the cell was placed in an electric oven.

3. Results and discussion

The measured AC conductivity as a function of reciprocal temperature for the 35.35CuO–64.65Bi_2O_3 glass composition is shown in figure 1 at three frequencies. The DC conductivity is also included in figure 1 for comparison. It is clear in figure 1 that in the low-temperature region the AC conductivity is substantially higher than the DC conductivity and shows a weak temperature dependence but a strong frequency dependence, while in the high-temperature region the AC conductivity shows a strong temperature dependence but is almost frequency independent. The temperature and frequency dependences of the AC conductivity for the other glass compositions are qualitatively similar. It is worth mentioning that, at low frequencies and high temperatures, electrode polarization might make a significant contribution to the dielectric constant. However, for the present glass compositions, the dielectric constant is found to be independent of the thickness of the samples and the electrode area for all frequencies and temperatures, indicating that the bulk effect is dominant and the electrode polarization makes no contribution to the dielectric properties.

The AC conductivity as a function of angular frequency is plotted in figure 2 for the 45.70CuO–54.30Bi_2O_3 glass composition at various low temperatures where the DC

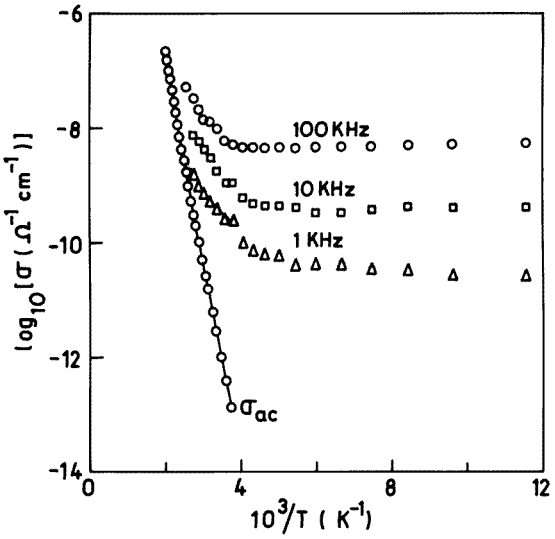

Figure 1. The temperature dependences of the measured AC conductivity at three different frequencies and of the DC conductivity for the 35.25CuO–64.65Bi_2O_3 glass composition.

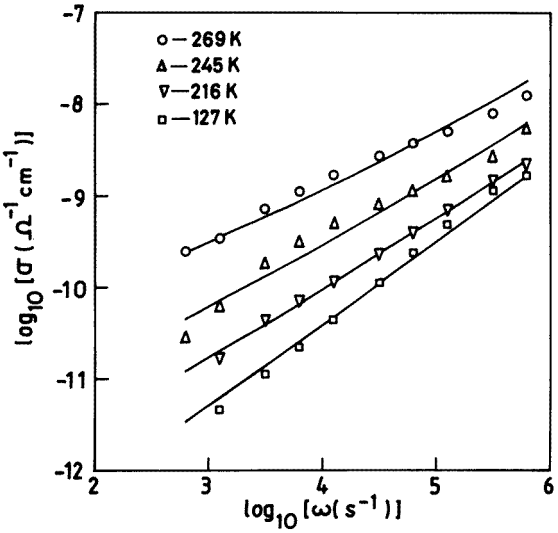

Figure 2. Variation in the measured AC conductivity with frequency at different temperatures for the 45.70CuO–54.30Bi_2O_3 glass composition. The solid curves are the best fit to the CBH model.

contribution is negligible. The log–log plots in figure 2 are nearly straight lines, indicating that the AC conductivity obeys the power law

$$\sigma(\omega) = A\omega^s \tag{1}$$

where A is a constant dependent on temperature and s is a frequency exponent whose value is generally less than or equal to unity. The values of s obtained from the least-squares straight-line fit of the conductivity versus frequency data are presented as a function of

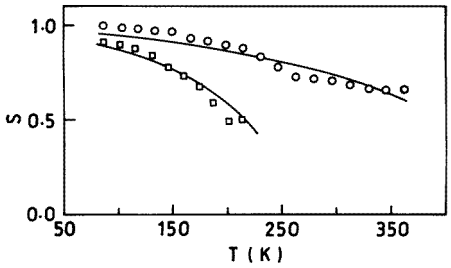

Figure 3. Frequency exponent s shown as a function of temperature for two glass compositions of the bismuth cuprate system: ○, 35.35 mol% CuO; □, 55.60 mol% CuO. The solid curves are the best fit to the CBH model.

temperature in figure 3 for two glass compositions of the bismuth cuprate system. It is observed from figure 3 that s increases with the decrease in temperature. A consistent decrease in s is also observed with increase in the CuO content of the glass compositions.

It is well known [14] that the AC conductivity of a system is governed by the relaxation mechanism. In the TM ion glasses the dipole formed between two different valence states acts as relaxing species, which have a distribution of relaxation time as its length changes with the distribution of sites. It is generally assumed [14] that a Debye-type dielectric response with a distribution of relaxation times is responsible for electrical conduction. The overall conductivity is then the summation of individual microscopic processes acting in parallel. However, two distinct models, namely quantum-mechanical tunnelling (QMT) through the barrier separating two equilibrium sites and classical hopping over the barrier, have been proposed [14] to account for the relaxation of dipoles. In the following sections, the frequency and temperature dependences of the AC conductivity and frequency exponent data have been analysed in terms of these models to determine the possible conduction mechanism of the bismuth cuprate glass system.

3.1. Quantum-mechanical tunnelling models

In TM oxide glasses, the conductivity may arise from the tunnelling of electrons between different valence states of TM ions. In the QMT model, the relaxation time is given by $\tau \propto \exp(2\alpha R)$ where α is the decay constant for the s-like wavefunction assumed to describe the localized states and R is the distance separating localized states. The real part of the AC conductivity due to electron tunnelling can be calculated [15, 16] using

$$\sigma(\omega) = \frac{\pi^4}{384}\frac{e^2kT}{\alpha^5}N^2(E_F)\omega\left[\ln\left(\frac{1}{\omega\tau_0}\right)\right]^4 \tag{2}$$

where $N(E_F)$ is the density of states at the Fermi level. The frequency exponent s predicted by this model is given by

$$S = 1 - \frac{4}{\ln(1/\omega\tau_0)}. \tag{3}$$

Equation (3) predicts that $s \approx 0.81$ independent of temperature, for $\omega = 10^4$ rad s^{-1} and $\tau_0 = 10^{-13}$ s, while s decreases as ω increases. However, the experimental values of s shown in figure 3 decrease as the temperature increases. This is in marked disagreement with the QMT model.

In most amorphous materials a polaron is formed due to the lattice distortion [17] which was ignored in the previous approach. If small polarons are formed, the tunnelling model [14] predicts a decrease in s with decrease in temperature. On the other hand, if overlapping large polarons are formed, the tunnelling model [15] predicts a decrease in s with increase in temperature up to a certain range and then an increase in s with a further increase in temperature. Our experimental results (figure 3) disagree with the predictions of both these models. Thus the possibility of polaron tunnelling as a possible conduction mechanism is ruled out for the bismuth cuprate glass system.

3.2. Classical hopping models

Alternatively, hopping between two energetically favourable sites over a potential barrier may take place in TM oxide glasses. The relaxation time for the classical hopping is given by $\tau = \tau_0 \exp(W/kT)/\cosh(\Delta/2kT)$, where Δ is the energy difference between two sites [18]. If two favourable sites having separation R are correlated then there is a lowering of the barrier height due to Coulomb interaction [19], from W_M to $W = W_M - (e^2/\pi\varepsilon_0\epsilon R)$, where ε_0 is the free-space dielectric permittivity and ϵ is the dielectric constant. The AC conductivity due to CBH of an electron in the narrow band limit is given by [14]

$$\sigma(\omega) = \frac{\pi^3}{24} N^2 \varepsilon_0 \epsilon \omega R_\omega^6 \tag{4}$$

where N is the density of pair of sites and R_ω is the hopping length at frequency ω, which is given by

$$R_\omega = \frac{e^2}{\pi\varepsilon_0\epsilon[W_M - kT(1/\omega\tau_0)]}. \tag{5}$$

Correspondingly the frequency exponent s can be estimated [15] as

$$s = 1 - \frac{6kT}{W_M - kT\ln(1/\omega\tau_0)}. \tag{6}$$

The conductivity data at different temperatures were fitted to equation (4) for all compositions of the bismuth cuprate glass system. The solid lines in figure 2 represent some of these best-fit curves for the $45.70CuO–54.30Bi_2O_3$ glass composition. Similar reasonable fits were also obtained for other glass compositions in the temperature range where the DC contribution is negligible, indicating CBH as the likely conduction mechanism. The frequency exponent s plotted against T in figure 3 was also fitted to equation (6) by the best-fit procedure. Again a reasonable good fit was observed, strengthening the applicability of the CBH mechanism in the bismuth cuprate glasses. The different values of the parameters obtained from the best fits are shown in table 1. It may be noted that the values of W_M decrease with increase in the CuO content of the glass compositions and are consistent with the dc activation energy [13]. The values of τ_0 are also reasonable and consistent with the values estimated from IR measurements [11]. The values of N are of the same order of magnitude as those for the copper ion concentrations in the glass compositions, indicating that almost all sites take part in the conduction mechanism. It is noteworthy that the values of the dielectric constant ϵ are higher than those of the oxide glasses formed with conventional network formers [6]. The high values of ϵ can be attributed to the influence of the high polarizability of the Bi^{3+} ions of the unconventional network former Bi_2O_3 on the AC response.

4. Conclusions

The AC conductivity of the cuprate glasses based on unconventional bismuth oxide for a wide composition range has been measured in the frequency range 10^2–10^5 Hz and in the temperature range 80–400 K. The AC conductivity increases consistently with increase in the CuO content of the glass compositions, and at low temperatures the AC conductivity is substantially higher than the DC conductivity. The frequency dependence of the AC conductivity obeys a power law behaviour. It appears that the CBH of electrons between different valence states take place in the present glass system. Values of the parameters τ_0, W_M and N obtained from the fits of the CBH model to the experimental data are reasonable. The value of the dielectric constant observed in this glass system is higher than that of the glasses based on conventional network formers, which may be due to the influence of the high polarizability of the heavy-metal glass-forming cations (Bi^{3+}) on the AC response.

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