PHILOSOPHICAL MAGAZINE B, 1996, VOL. 74, NO. 3, 235–241

Hopping conduction in unconventional lead cuprate glass

By S. HAZRA and A. GHOSH†

Solid State Physics Department, Indian Association for the Cultivation of Science, Calcutta 700 032, India

[*Received 13 November 1995 and accepted 3 April 1996*]

ABSTRACT

The ac conductivity of cuprate glasses based on the unconventional network former PbO is reported in the frequency range 10^2–10^5 Hz and in the temperature range 80–450 K. Analysis of the conductivity data has been made in the light of different existing theoretical models. It is observed that, among them, the correlated barrier hopping model can best explain the conductivity and frequency exponent data. The values of the different parameters obtained from this model are reasonable. The high values of the dielectric constant observed in this system are attributed to the high polarizability of the unconventional network former PbO.

§ 1. INTRODUCTION

The transition-metal (TM) oxide glasses based on conventional network formers like P_2O_5, GeO_2, etc., have been studied extensively (Owen and Robertson 1970, Linsley, Owen and Hayatee 1970, Sayer and Mansingh 1972, 1982, Mansingh, Dhawan and Sayer 1983, Ghosh 1990a, b, 1992). The TM oxide glasses show semiconducting behaviour which arises from the presence of the TM ions in multivalent states (such as V^{4+} and V^{5+} in vanadate glasses). The conduction process in the copper phosphate and copper borate glasses are characterized by a high activation energy which is mainly governed by an electron hopping mechanism between non-identical copper sites (Sayer and Mansingh 1972, Austin and Sayer 1974). Austin and Mott (1969) pointed out that the ligand field environment is different for Cu^+ and Cu^{2+} ions and thus part of the activation energy can be a carrier-excitation energy from one site to another. Drake and Scanlan (1970) proposed that Cu^+ and Cu^{2+} ions exist in different coordination spheres in copper phosphate glass. Some authors (Tsuchiya and Moriya 1975) have postulated a mixed electronic and ionic conduction in copper phosphate glasses and this behaviour is interpreted assuming that the Cu^+ ion exists in sites with different bonding forces. Recently, glass formation and structure of the TM oxide glasses based on the unconventional network formers Bi_2O_3 and PbO have been reported (Hazra and Ghosh 1995a, b). Structural studies (Hazra and Ghosh 1995b) reveal that the copper ions in the lead cuprate glasses occupy network-forming positions and thus are unable to diffuse through the host matrix, unlike the alkali ions in most conventional network-modified glasses (Martin 1991, Sidebottom, Green and Brow 1995). Studies of the dc conductivity of the lead cuprate glasses (Hazra and Ghosh 1995c) show that the dc electrical conduction occurs by the hopping of electrons between Cu^+ and Cu^{2+} ions in

†Author for correspondence.

the nonadiabatic regime, similar to the precursor glasses of high-T_c cuprate superconductors (Ghosh and Chakravorty 1990, Ghosh 1993).

The purpose of the present paper is to study the ac conduction mechanism of unconventional lead cuprate glasses in the frequency range 10^2–10^5 Hz.

§ 2. Experimental procedure

The details of preparation of the glass samples of compositions xCuO–$(100 - x)$ PbO, where $x = 15$–50 mol.%, have been reported earlier (Hazra and Ghosh 1995b). In brief, mixtures of reagent grade CuO (Loba, India) and PbO (Koch Light, UK) were melted for 1 h in alumina crucibles in an electric furnace at a temperature in the range 1100–1250°C depending on the composition. Glassy samples were obtained by subsequent twin-roller quenching of the melts. The amorphous nature of the samples was confirmed by X-ray diffraction. The homogeneous nature of the samples was also verified from SEM micrographs. The prepared glasses were well characterized by a variety of techniques, such as differential thermal analysis, density and molar volume, atomic absorption, infrared absorption, electron spin resonance, magnetic measurements, etc. (Hazra and Ghosh 1995b).

The ac measurements were carried out using a GenRad (model-1615A) Capacitance Bridge in the frequency range 10^2–10^5 Hz, using gold as the electrode material. The dc measurements were made using a Keithley (model-617) electrometer. All measurements were taken in the temperature range 80–450 K. The sample cell was placed in an electric furnace and in a cryostat for measurements above and below room temperature, respectively. To ascertain the bulk properties, measurements were also made for samples with different thicknesses and electrode areas.

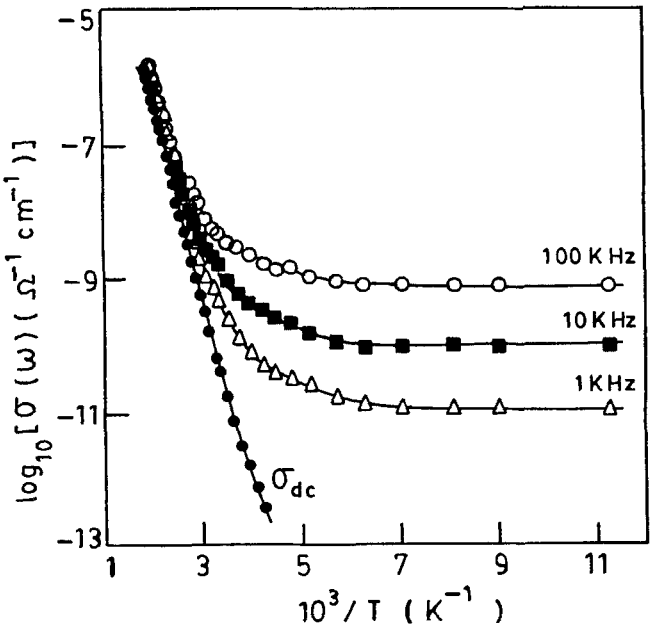
§ 3. Results and discussion

Figure 1 shows the variation of the measured total conductivity, $\sigma(\omega)$ with the inverse temperature at three frequencies for a typical glass composition. The dc conductivity is also included in the figure for comparison. In fig. 1, it is clear that in common with other amorphous semiconductors, the temperature dependence of the measured conductivity is much less than the dc conductivity at low temperatures, and it is not activated in behaviour. However, at higher temperatures, the temperature dependence of the conductivity becomes strong and its frequency dependence becomes small. Ultimately the measured conductivities at all frequencies coincide with the dc conductivity at higher temperature. Similar behaviour is also observed for the other glass compositions, the only difference being the temperature at which the measured conductivity becomes equal to the dc conductivity.

The measured conductivity as a function of frequency at various temperatures is shown in fig. 2 (*a*) for the same glass composition as in fig. 1. It is also evident from the figure that the dc contribution is significant at high temperatures, while the frequency-dependent term dominates at low temperatures. Figure 2 (*b*) shows the frequency-dependent conductivity, $\sigma_1(\omega)$, obtained by subtracting the dc conductivity from the measured ac conductivity as a function of frequency at the same temperatures and for the same glass composition as in fig. 2 (*a*). It is clear from fig. 2 (*b*) that the $\sigma_1(\omega)$ obeys the power law

$$\sigma_1(\omega) = A\omega^s, \tag{1}$$

Fig. 1



The temperature dependence of the measured total conductivity at three different frequencies and the dc conductivity for the 30CuO–70PbO glass composition. Solid curves through the data are to guide the eye.

where A is a temperature-dependent constant and the frequency exponent s is generally less than or equal to unity. The exponent s was obtained from least-square straight-line fits of the data of fig. 2 (*b*). The variation of s with temperature is shown in fig. 3 for two glass compositions. Figure 3 shows that s increases as the temperature decreases. It may be noted that s decreases as the CuO content increases in the glass compositions.

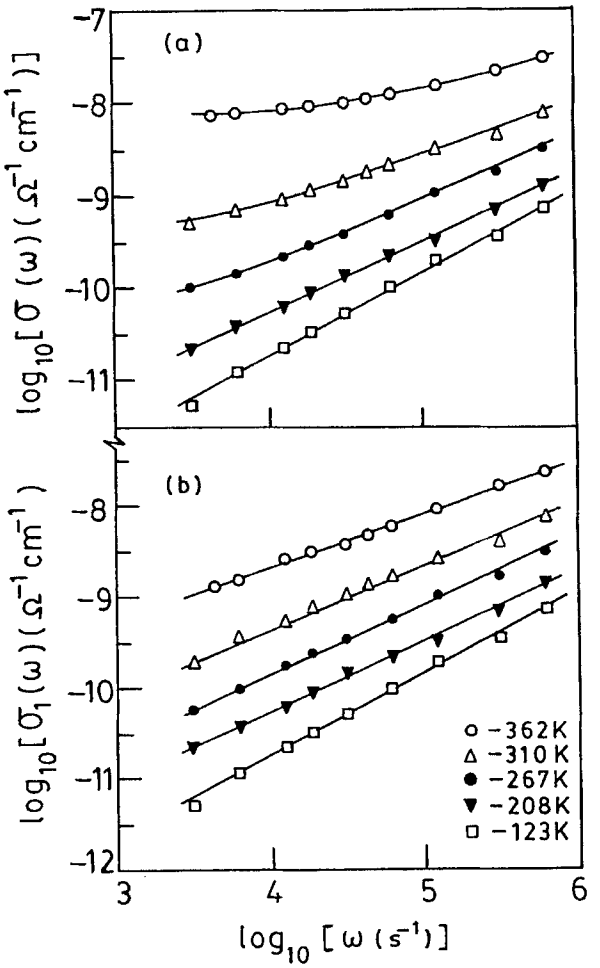
Different theoretical models (Elliott 1987, Long 1982) have been developed to account for the frequency and temperature dependence of $\sigma_1(\omega)$ and s. In essence, two distinct models have been proposed: (i) quantum mechanical tunnelling through the barrier separating two equilibrium sites, and (ii) classical hopping over a barrier. The results presented above for the lead cuprate glasses are discussed below in terms of these models.

3.1. *Quantum mechanical tunnelling (QMT) models*

Several authors (Böttger and Bryksin 1976, Long 1982) have evaluated, within the pair approximation, the ac conductivity for single-electron motion undergoing tunnelling and obtained the following expression,

$$\sigma_1(\omega) = \frac{\pi}{3} e^2 kTN^2(E_F)\alpha^{-5}\omega[\ln(1/\omega\tau_0)]^4, \tag{2}$$

Fig. 2



(*a*) Variation of measured total conductivity with frequency at different temperatures for the 30CuO–70PbO glass composition. Solid curves are the best fit to eqn. (5) plus the measured dc conductivity. (*b*) Corresponding ac conductivity obtained by subtracting the dc contribution. The solid lines are straight-line fits obtained by a least-squares fitting procedure.

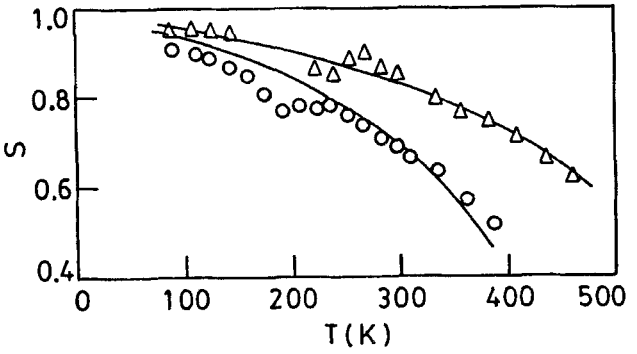
where $N(E_F)$ is the density of states at the Fermi level and α^{-1} is the localization length. The frequency exponent s is given by

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

Equation (3) predicts that s is independent of temperature. For $\omega = 10^4\,s^{-1}$ and $\tau_0 = 10^{-13}$ s, eqn. (3) gives $s = 0{\cdot}81$. However, the experimental values of s shown in fig. 3 decrease as the temperature increases. This is in marked disagreement with the QMT model.

In the above approach, it was assumed that no lattice distortion was taking place. But in most amorphous materials lattice distortion takes place, i.e. polarons

Fig. 3



Frequency exponent s shown as a function of temperature for two glass compositions: △, 21 mol.% CuO; ○, 30 mol.% CuO. Solid curves are the best fit to eqn. (7).

are formed (Mott and Davis 1979). However, the small-polaron tunnelling model predicts a decrease of s with a decrease of temperature (Elliott 1987) and thus is not consistent with the experimental data. On the other hand, if overlapping large polarons are formed (Long 1982), then the frequency exponent s decreases with an increase of temperature up to a certain temperature and then increases with further increase of temperature. However, the data for s (fig. 3) do not exhibit such a temperature dependence, thus ruling out the applicability of large-polaron tunnelling as a possible conduction mechanism in the present glass system.

3.2. *Classical hopping models*

The other type of process which has been proposed for the ac conduction mechanism is classical hopping over a barrier. A model for ac conduction, which correlates the relaxation variable W with the intersite separation R, has been developed by Pike (1972) for single-electron hopping and extended by Elliott (1977) for simultaneous two electron hopping. If two favourable sites having a separation R are correlated, then there is a lowering of the barrier height due to the Coulomb interaction, from W_M to W, given by (Pike 1972)

$$W = W_M - e^2/\pi\epsilon\epsilon_0 R, \tag{4}$$

where ε_0 is the dielectric permittivity of free space and ϵ is the dielectric constant of the material.

The ac conductivity due to correlated barrier hopping (CBH) of an electron in the narrow-band limit is given by (Pike 1972, Elliott 1977, Long 1982)

$$\sigma_1(\omega) = \frac{\pi^3}{24} N^2 \epsilon\epsilon_0 \omega R_\omega^6, \tag{5}$$

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

$$R_\omega = e^2/\pi\epsilon\epsilon_0[W_M - kT \ln (1/\omega\tau_0)]. \tag{6}$$

Table 1. Parameters obtained by fitting the experimental data to the CBH model for the lead cuprate glass system.

Glass composition (mol.%)	W_M (eV)	τ_0 (s)	N (cm^{-3})	ϵ
15CuO–85PbO	1·45	$1{\cdot}70 \times 10^{-13}$	$2{\cdot}00 \times 10^{21}$	19
21CuO–79PbO	1·38	$1{\cdot}90 \times 10^{-13}$	$2{\cdot}85 \times 10^{21}$	20
30CuO–70PbO	0·98	$2{\cdot}00 \times 10^{-13}$	$0{\cdot}80 \times 10^{21}$	21
36CuO–64PbO	0·90	$1{\cdot}45 \times 10^{-13}$	$7{\cdot}10 \times 10^{21}$	27

The exponent s in the theory is estimated as (Long 1982)

$$s = 1 - 6kT/[W_M - kT \ln (1/\omega\tau_0)]. \quad (7)$$

Equation (7) shows that the exponent s decreases wth an increase of temperature consistent with the experimental data (fig. 3). The conductivity data at different temperatures were fitted to eqn. (5) plus the dc conductivity for the present glass system. The solid lines in fig. 2 (*a*) represent some of these best-fit curves for a glass composition. A good fit is observed, indicating CBH to be the possible conduction mechanism. The frequency exponent s plotted against T was also fitted to eqn. (7) by the best-fit procedure. Again a reasonably good fit was observed, strengthening the case for the CBH mechanism. The different values of the parameters obtained from the fits are shown in table 1. The values of W_M are consistent with the glass compositions, while the values of τ_0 are reasonable and consistent with the values estimated from IR measurements (Hazra and Ghosh 1995b). The values of N are of the same order of magnitude as the copper ion concentrations (Hazra and Ghosh 1995b) in the glass compositions. The values of ϵ are high when compared with those of other oxide glasses formed with conventional network formers (Mansingh *et al.* 1983). The high values of ϵ can be attributed to the influence of the high polarizability of the Pb^{2+} ions of the unconventional network former PbO on the ac response.

§ 4. Conclusions

The ac conductivity of the unconventional lead cuprate glass system in the composition range 15–50 mol.% CuO was analysed over the frequency range 10^2–10^5 Hz. The ac conductivity at low temperatures is substantially higher than the dc conductivity and shows a weak temperature dependence but a strong frequency dependence. Analysis of the conductivity data, and also the frequency exponent, shows that CBH is the most favourable model to describe the conduction mechanism in the present glass system. The values of different parameters obtained from this model are reasonable. The value of the dielectric constant is large compared to that of conventional glasses, which may be due to the influence of the highly polarizable network former PbO.

Acknowledgment

S. H. acknowledges the University Grants Commission (India) for providing financial support.

References

Austin, I. G., and Mott, N. F., 1969, *Adv. Phys.*, **18**, 41.

Austin, I. G., and Sayer, M., 1974, *J. Phys*: C, 7, 905.

Böttger, H., and Bryksin, V. V., 1976, *Phys. Status solidi*, B, **78**, 415.

Drake, C. F., and Scanlan, I. F., 1970, *J. non-crystalline Solids*, 4, 234.

Elliott, S. R., 1977, *Phil. Mag.*, **36**, 1291; 1987, *Adv. Phys.*, **36**, 135.

Ghosh, A., 1990a, *Phys. Rev.* B, **41**, 1479; 1990b, *Phys. Rev.* B, **42**, 5665; 1992, *Phys. Rev.* B, **45**, 11318; 1993, *Phys. Rev.* B, **48**, 16081.

Ghosh, A., and Chakravorty, D., 1990, *J. Phys.: condens. Matter*, **2**, 649.

Hazra, S., and Ghosh, A., 1995a, *Phys. Rev.* B, **51**, 851; 1995b, *J. mater. Res.*, **10**, 2374; 1995c, *J. chem. Phys.*, **103**, 6270.

Linsley, G. S., Owen, A. E., and Hayatee, F. M., 1970, *J. non-crystalline Solids*, **4**, 208.

Long, A. R., 1982, *Adv. Phys.*, **31**, 553.

Mansingh, A., Dhawan, V. K., and Sayer, M., 1983, *Phil. Mag.* B, **48**, 215.

Martin, S. W., 1991, *J. Am. Ceram. Soc.*, **74**, 1767.

Mott, N. F., and Davis, E. A., 1979, *Electronic Processes in Non-Crystalline Materials*, 2nd edition (Oxford: Clarendon Press), p. 225.

Owen, A. E., and Robertson, J. M., 1970, *J. non-crystalline Solids*, **2**, 40.

Pike, G. E., 1972, *Phys. Rev.* B, **6**, 1572.

Sayer, M., and Mansingh, A., 1972, *Phys. Rev.* B, **6**, 4629; 1982, *Phys. Chem. Glasses*, **23**, 83.

Sidebottom, D. L., Green, P. F., and Brow, R. K., 1995, *Phys. Rev.* B, **51**, 2770.

Tsuchiya, T., and Moriya, T., 1975, *Cent. Glass Ceram. Res. Institute Bull.*, **22**, 55.