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AC conduction in semiconducting $CuO–Bi_2O_3–P_2O_5$ glasses

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Abstract. The first measurements are reported for the AC conductivity (real and imaginary parts) of the semiconducting $CuO–Bi_2O_3–P_2O_5$ glasses in the frequency range 10^2–10^5 Hz and in the temperature range 80–4000 K. The experimental results have been analysed in the light of various theoretical models proposed for amorphous semiconductors such as quantum mechanical tunnelling and classical hopping over the barrier of a charge carrier. The analysis shows that the correlated barrier-hopping model predicts the correct temperature and frequency dependence of the AC conductivity and its frequency exponent. This model provides reasonable values of the maximum barrier height and characteristic relaxation time.

1. Introduction

The DC electrical properties of a new semiconducting glass system $CuO–Bi_2O_3–P_2O_5$ have been reported recently (Ghosh and Chakravorty 1990). These glasses are characterised by rather high values of the ratio $C \equiv [Cu^+]/[Cu_{total}]$. They have fairly high room-temperature conductivity of the order of $10^{-5}\ \Omega^{-1}\ cm^{-1}$ and exhibit phonon-assisted hopping conduction at high temperatures. A variable-range hopping mechanism seems to dominate the low-temperature behaviour.

AC conductivity of glasses containing transition-metal oxides has been extensively investigated and various theoretical models have been proposed to explain the behaviour in different glass systems (Sayer and Mansingh 1972, Owen 1977, Long 1982, Murawski 1984). The AC electrical behaviour in the system $CuO–Bi_2O_3–P_2O_5$ has been studied in the present work over a frequency range 10^2–10^5 Hz and a temperature range 80–400 K. The data have been examined on the basis of various theoretical models. The results are reported in this paper.

2. Experiment

Glass samples of three compositions (table 1) are prepared from the reagent grade chemicals CuO, Bi_2O_3 and $(NH_4)_2HPO_4$ respectively. The mixtures of these chemicals in 15 g batches are melted in a platinum crucible at 1273 K in air for 2 h. The amorphous nature of the samples is confirmed from the x-ray diffraction pattern. The density of the samples is measured by Archimedes' principle.

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Table 1. Some physical parameters of the $CuO–Bi_2O_3–P_2O_5$ glasses.

Glass composition (mol%)			Density	N	
CuO	Bi_2O_3	P_2O_5	($g\,cm^{-3}$)	(cm^{-3})	R(Å)
60	20	20	5.12	4.74×10^{21}	5.95
70	10	20	6.01	1.04×10^{22}	4.58
80	5	15	6.12	2.31×10^{22}	3.51

The concentrations N of the total copper ions present in the samples are estimated from atomic absorption spectroscopy (Varian model AA 1735). The average intersite separation R is determined from the total copper ion concentration. The values are given in table 1.

For electrical measurements, disk-shaped samples of diameter about 8 mm and thickness about 0.5 mm are cut and polished. Gold electrodes are vacuum evaporated on two parallel faces. The AC measurements are carried out in a General Radio (model GR-1615A) capacitance bridge which measures equivalent parallel conductance and capacitance of a sample at frequencies ranging from 20 to 10^5 Hz in a three-terminal arrangement. For low-temperature measurement the sample cell is inserted in a cryostat. Measurements are made in the temperature range 80–400 K with a stability of ±0.5 K.

3. Results

Figure 1 shows the total measured conductivity $\sigma_{tot}(\omega)$ along with the DC conductivity σ_{DC} as a function of inverse temperature at various frequencies for one glass composition. It is evident from the figure that the temperature dependence of $\sigma_{tot}(\omega)$ is much less than that of σ_{DC} at low temperatures and high frequencies and is not activated in behaviour while the DC contribution is significant at low frequencies and high temperatures. Similar behaviour is also observed for the other glass compositions.

Figure 2 shows the AC conductivity $\sigma(\omega)$ (real part) obtained by subtracting the DC conductivity from the measured conductivity as a function of frequency at various temperatures for the same glass composition as in figure 1. The full lines in the figure are the straight-line fits obtained by the least-squares fitting procedure. It is evident that $\sigma(\omega)$ obeys the relation (Mott and Davis 1979)

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

where A and s are constants.

4. Discussion

The AC conductivity data obtained in the present glass system are examined on the basis of the different theoretical models in the following sections.

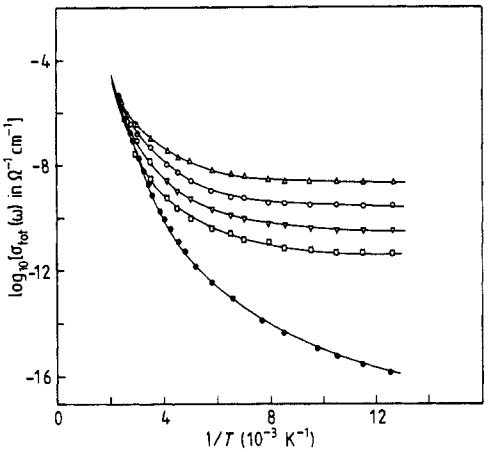

Figure 1. The measured total conductivity for glass composition containing 80 mol% CuO shown as a function of inverse temperature at four frequencies: △, 10^5 Hz; ○, 10^4 Hz; ▽, 10^3 Hz; □, 10^2 Hz; ——, fits using the CBH model. The measured DC conductivity (●) is also shown (Ghosh and Chakravorty 1989).

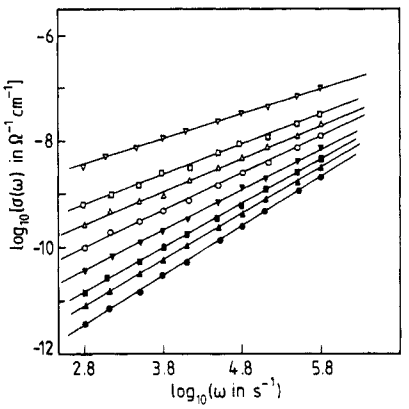

Figure 2. The frequency-dependent conductivity, obtained by subtracting the DC conductivity from the measured total conductivity for the glass composition as in figure 1: ——, straight-line fits; ▽, 305 K; □, 250 K; △, 224 K; ○, 197 K; ▼, 176 K; ■, 135 K; ▲, 124 K; ●, 80 K.

4.1. Quantum mechanical tunnelling model

The AC conductivity $\sigma(\omega)$ has been shown (Long 1982, Austin and Mott 1969, Pollak 1971, Bottger and Bryskin 1976, Butcher and Hayden 1977) to be given by

$$\sigma(\omega) = Ce^2kT\alpha^{-1}[N(E_F)]^2\omega R_\omega^4 \tag{2}$$

where C is a numerical constant, α^{-1} the spatial decay constant for the localised electron wavefunction, $N(E_F)$ the density of states at the Fermi level and R_ω the hopping distance at frequency ω (circular). R_ω is given by

$$R_\omega = -(2\alpha)^{-1}\ln(\omega\tau_0) \tag{3}$$

where τ_0 is a characteristic relaxation time.

The frequency exponent s in the quantum mechanical tunnelling (QMT) model has been deduced as

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

A temperature-dependent frequency exponent can be predicted within the framework of the QMT model by assuming the carrier to form non-overlapping small polarons. In the latter case the frequency exponent s has the variation

$$s = 1 + 4/[\ln(\omega\tau_0) + W_H/kT]. \tag{5}$$

The behaviour of the present glass system cannot be reconciled with the predictions of the QMT model. Perhaps the most obvious discrepancy between theory and experiment concerns the temperature dependence of the frequency exponent s of the AC conductivity $\sigma(\omega)$. The QMT model (equation (4)) predicts, in its simplest form, a value of $s \simeq 0.81$ (assuming that $\tau_0 = 10^{-13}$ s and $\omega = 10^4$ s^{-1}), independent of temperature. However,

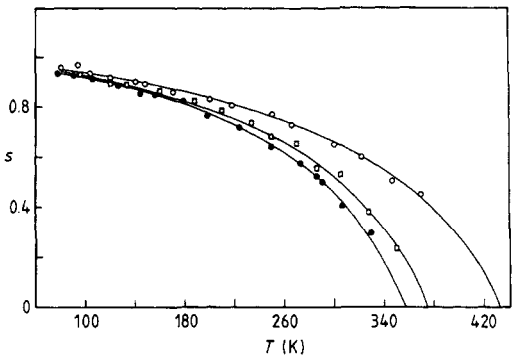

Figure 3. The temperature dependence of the frequency exponent s for the different glass compositions: ——, calculated using the CBH model; ●, 80 mol% CuO; □, 70 mol% CuO; ○, 60 mol% CuO.

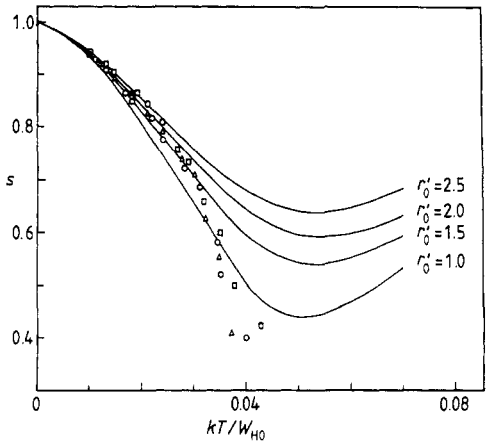

Figure 4. The frequency exponent s shown as a function of kT/W_{H0} for various values of the normalised polaron radius r_0': ○, 80 mol% CuO; △, 70 mol% CuO; □, 60 mol% CuO; ——, calculated from the OLPT model for a fixed value of $\omega = 10^4\ s^{-1}$ and $\tau_0 \simeq 10^{-13}$ s.

Table 2. Parameters obtained from the OLPT model at low temperatures.

CuO content (mol%)	r_0'	W_{H0} (eV)	W_H[a] (eV)	r_0 (Å)
60	1.5	0.85	0.66	1.33
70	1.7	0.78	0.60	1.06
80	2.0	0.70	0.54	0.80

[a] From Ghosh and Chakravorty (1990).

figure 3 indicates that the general trend for s is to decrease with increasing temperature, which is at variance with the prediction of the simple QMT model. For the small-polaron QMT model, a temperature dependence of s is expected, but it is of opposite sign (equation (5)). The wide variation in the experimental values of s (figure 3) can be explained in terms of the simple QMT model only if the characteristic relaxation time τ_0 varies by many orders of magnitude. The experimental results are particularly difficult to match with this theory for values of $s \simeq 1$ measured at lower temperatures, because this requires unrealistically small values of $\tau_0 \simeq 10^{-25}$ s. The simple QMT model predicts that s should decrease appreciably with increasing frequency. No such variation has been observed in the present glasses. The QMT model also predicts that $\sigma(\omega)$ should have a linear temperature dependence (equation (2)). However, the data presented in figures 1 and 2 show a stronger temperature dependence than that predicted by the QMT model, even at low temperatures.

4.2. Overlapping large-polaron tunnelling model

According to the overlapping large-polaron tunnelling (OLPT) model (Long 1982) the large-polaron wells of two sites overlap which reduces the polaron hopping energy (Austin and Mott 1969, Pollak 1965) as follows:

Table 3. Parameters obtained from the CBH model.

CuO content (mol%)	τ_0 (s)	W_M (eV)
60	2×10^{-13}	0.98
70	1×10^{-13}	0.86
80	1×10^{-13}	0.82

$$W_H = W_{H0}(1 - r_0/R) \tag{6}$$

where r_0 is the large-polaron radius and W_{H0} is a constant for all sites. The intersite distance R is a random variable. The conductivity $\sigma(\omega)$ is given by

$$\sigma(\omega) = (\pi^4/12)e^2(kT)^2[N(E_F)]^2\omega R_\omega^4/(2\alpha kT + W_{H0}r_0/R_\omega^2). \tag{7}$$

R_ω is determined by the quadratic equation

$$(R'_\omega)^2 + [\beta W_{H0} + \ln(\omega\tau_0)]R'_\omega - \beta W_{H0}r'_0 = 0 \tag{8}$$

where $R'_\omega = 2\alpha R_\omega$, $r'_0 = 2\alpha r_0$ and $\beta = 1/kT$. The frequency exponent s in this model given by

$$s = 1 - (8\alpha R_\omega + 6W_{H0}r_0/R_\omega kT)/(2\alpha R_\omega + W_{H0}r_0/R_\omega kT)^2 \tag{9}$$

The OLPT model predicts that $\sigma(\omega)$ should have a negative temperature dependence of s at least at low temperatures (equation (9)). Thus, at first sight, it appears that the OLPT model might be a possible mechanism for AC conduction in the present glasses. In figure 4 the theoretical curves for s given by equation (9) are plotted versus reduced temperature kT/W_{H0} as a function of r'_0. These curves are universal, i.e. changes in W_{H0} result in rescaling of the temperature axis. The experimental values for s are also plotted in figure 4, rescaling the temperature axis (i.e. varying W_{H0}) for different glass compositions. The best fits of the low-temperature data to the theoretical curves are obtained for the values of W_{H0} and r'_0 shown in table 2. On the assumption that the polaron hopping energy W_H is approximately equal to the high-temperature activation energy (table 2) for DC conduction (Ghosh and Chakravorty 1990), the polaron radius r_0 (table 2) has been estimated from equation (6). It might be noted that the values of r_0 are smaller than the intersite separation R. This is inconsistent with the basic premise of the OLPT model. Also no sign of a minimum is observed in the experimental plots of s versus T curves (figures 3 and 4), suggesting that the OLPT model is not likely to be valid for the present glasses.

The OLPT model (equation (9)) also predicts the frequency dependence of s. In the present experiment, the change in frequency does not exceed three orders of magnitude and the frequency dependence of s is not observed.

The other feature which casts doubts on the applicability of the OLPT model concerns the temperature dependence of $\sigma(\omega)$. The temperature dependence of $\sigma(\omega)$ may, in general, be expressed in the form of power law, i.e. $\sigma(\omega) \propto T^n$ where the exponent n need not be constant (Elliott 1987). Figure 5, which is a plot of $\log_{10}\sigma(\omega)$ versus $\log_{10} T$ for one glass composition, shows that n is equal to 1.25 in the low-temperature region and its value increases rapidly at higher temperatures. The functional form of the temperature dependence of $\sigma(\omega)$ predicted by the OLPT model (equation (7)) is complicated and cannot be expressed simply as $\sigma(\omega) \propto T^n$ with n constant over a wide temperature

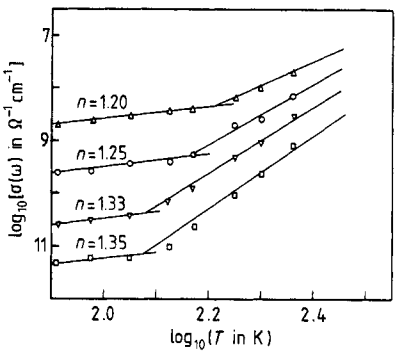

Figure 5. The temperature dependence of the AC conductivity plotted double-logarithmically for the glass composition containing 70 mol% CuO: △, 10^5 Hz; ○, 10^4 Hz; ▽, 10^3 Hz; □, 10^2 Hz.

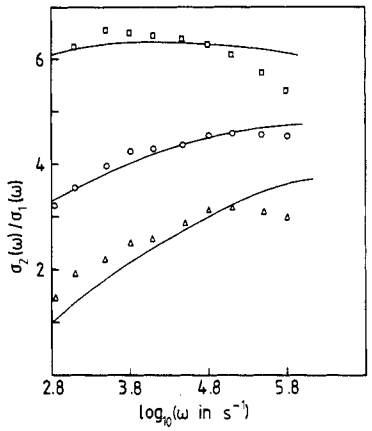

Figure 6. The ratio of the imaginary to the real parts of the AC conductivity plotted as a function of frequency at three temperatures for the glass containing 80 mol% CuO: □, 80 K; ○, 105 K; △, 146 K; ——, obtained from the CBH model.

range. Nevertheless at lower temperatures the hopping length R_ω has an approximately constant temperature dependence, $R_\omega \sim T^{1.25}$ (for $r_0' = 2.5$) and hence $\sigma(\omega) \sim T^6$ for the uncorrelated case. This is certainly at variance with the much weaker temperature dependence exhibited by the low-temperature data of the present work (figure 5) and, even if the correlated form (Long 1982) of the OLPT model is used, the dependence is predicted to decrease only to $\sigma(\omega) \sim T^4$. Thus the temperature dependence of $\sigma(\omega)$ also is not consistent with the predictions of the OLPT model.

4.3. Correlated barrier-hopping model

The correlated barrier-hopping (CBH) model correlates the relaxation variable W with the intersite separation R for single-electron hopping (Pike 1972) and extended subsequently (Elliott 1977, 1978, 1987) for two electrons hopping simultaneously. For neighbouring sites at separation R the Coulomb wells overlap resulting in a lowering of the effective barrier height which for the single-electron CBH is given by (Elliott 1987)

$$W = W_M - e^2/\pi\varepsilon\varepsilon_0 R \tag{10}$$

where W_M is the maximum barrier height, ε the dielectric constant of the material and ε_0 that of free space. The AC conductivity $\sigma(\omega)$ has the following expression:

$$\sigma(\omega) = (\pi^3/24)N^2\varepsilon\varepsilon_0\omega R_\omega^6 \tag{11}$$

where N is the concentration of localised sites and R_ω is given by

$$R_\omega = e^2/\pi\varepsilon\varepsilon_0[W_M + kT\ln(\omega\tau_0)]. \tag{12}$$

The frequency exponent s is evaluated as (Elliott 1987)

$$s = 1 - 6kT/[W_M + kT\ln(\omega\tau_0)]. \tag{13}$$

Thus the CBH model (equation (13)) predicts that s should decrease with increasing

temperature and therefore it might be a possible contending theory for AC conductivity of the present glass system. Fits of the experimental values of s to the theoretical curve calculated from equation (13) are shown in figure 3, using W_M and τ_0 as variable parameters. In all cases, a fixed frequency $\omega = 10^4\ s^{-1}$ has been assumed. The values of W_M and τ_0 obtained from the least-squares fitting procedure are shown in table 3. It is observed in figure 3 that the fits appear to be reasonable over the entire temperature range of measurements. In figure 1 the total AC conductivity $\sigma_{tot}(\omega)$ is fitted to the AC conductivity calculated from equation (11) plus the measured values of the DC conductivity. In calculating the AC conductivity the same values of the parameters W_M and τ_0 (table 3) are used. The calculated curves are scaled so as to fit the value of $\sigma_{tot}(\omega)$ at $\omega = 2\pi \times 10^5\ s^{-1}$ for the lowest temperatures (thereby effectively fixing the value of N). Figure 1 shows that the fits are reasonable. It should be noted that the values of W_M are greater than the high-temperature activation energy for DC conduction (Ghosh and Chakravorty 1990) as expected and the values of τ_0 are in reasonable agreement with typical inverse phonon frequency ν_0 (Ghosh and Chakravorty 1990).

We have also tried to analyse the AC data assuming $W_M = 2W_H$, where W_H is the DC activation energy at high temperatures. From equation (11) we then obtain a value of $N = 10^{21}\ cm^{-3}$ over the entire temperature range for the glass containing 80 mol% CuO. It implies that not all the copper sites within the glass are contributing to the AC conduction.

4.4. *Imaginary part of the AC conductivity*

Thus far the real part of the AC conductivity (henceforth denoted by $\sigma_1(\omega)$) has been considered, neglecting its imaginary part (denoted by $\sigma_2(\omega)$) which is related to the dielectric constant. The models for AC conduction also make specific predictions concerning $\sigma_2(\omega)$ which is discussed below.

The total measured capacitance $C_{tot}(\omega)$, like conductance, can be decomposed into two components: a dispersive term $C(\omega)$ and a non-dispersive term C_α, i.e.

$$C_{tot}(\omega) = C(\omega) + C_\alpha. \tag{14}$$

The non-dispersive component C_α can be eliminated by adjustment of C_α until the resulting $C(\omega)$ obeys a power law dependence on ω (Long 1982). The ratio of the imaginary to the real part of the AC conductivity is then calculated from the relation

$$\sigma_2(\omega)/\sigma_1(\omega) = \omega C(\omega)/G(\omega) \tag{15}$$

where $G(\omega)$ is the conductance at frequency ω.

It has been shown (Long 1982) that the quantity $\sigma_2(\omega)/\sigma_1(\omega)$ has characteristically different functional forms for the various mechanisms of dielectric relaxation. For the QMT model,

$$\sigma_2(\omega)/\sigma(\omega) = -(2/5\pi)\ln(\omega\tau_0) \tag{16}$$

and, for the CBH model, to a first approximation,

$$\sigma_2(\omega)/\sigma_1(\omega) = -(2/\pi)\ln(\omega\tau_0)[1 + (3kT/W_M)\ln(\omega\tau_0)]. \tag{17}$$

For the OLPT model $\sigma_2(\omega)/\sigma_1(\omega)$ behaves like that for the simple QMT model at high temperatures, whereas at low temperatures the behaviour is similar to that exhibited by the CBH model. It may be noted that equation (17) predicts a temperature dependence for $\sigma_2(\omega)/\sigma_1(\omega)$, while equation (16) does not.

In figure 6, the experimental data for $\sigma_2(\omega)/\sigma_1(\omega)$ calculated using equation (15) are plotted versus $\log_{10}\omega$ at various temperatures. It is observed that $\sigma_2(\omega)/\sigma_1(\omega)$ is temperature dependent, implying that the QMT model is not applicable to the present system. The theoretical curves predicted by the CBH model (equation (17)) are drawn in figure 6, using the same values of the parameters W_M and τ_0 used for fitting the real parts of the AC conductivity and as given in table 3. The fit between theory and experiment may be regarded as good, bearing in mind that no extra variable parameters are used in the calculation of $\sigma_2(\omega)/\sigma_1(\omega)$ from equation (17). The observed discrepancy is ascribed to the fact that equation (17) is approximate and higher-order terms become important at high temperatures. Also it should be noted that the fitting to $\sigma_2(\omega)/\sigma_1(\omega)$ is much more sensitive to the parameters used (such as W_M and τ_0) than when the fitting is done for $\sigma_1(\omega)$ only.

5. Conclusions

Analysis of the AC conductivity data of the semiconducting $CuO–Bi_2O_3–P_2O_5$ glasses in the light of various theoretical models shows that the CBH model is the most appropriate to predict quantitatively the frequency and temperature dependences of the AC conductivity and its frequency exponent. The parameters such as the maximum barrier height and relaxation time obtained by fitting this model to the experimental data appear reasonable. The QMT model fails completely to predict the observed temperature and frequency dependences of the AC conductivity. Similarly, the OLPT model predicts a much stronger temperature dependence of the AC conductivity, although the low-temperature data for the frequency exponent are somewhat consistent with this model.

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