Transport mechanism in nonconventional bismuth cuprate glass

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Temperature and compositional dependence of the electrical transport properties of the nonconventional binary bismuth cuprate glasses are reported for the first time. It has been observed that the phonon assisted small polaron hopping model in the nonadiabatic regime is consistent with the data only at high temperatures. The variable range hopping model can fit the low temperature data qualitatively. The polaron hopping models proposed by Schnakenberg [Phys. Status Solidi **28**, 623 (1968)] and Emin [Phys. Rev. Lett. **32**, 303 (1974)] can predict quantitatively the conductivity data in the entire temperature range of measurement for all glass compositions. The physical parameters obtained from the best fits of these models are found reasonable and consistent with the glass compositions. © *1996 American Institute of Physics.* [S0021-9606(96)51223-7]

I. INTRODUCTION

The cuprate glasses formed with conventional glass formers as P_2O_5, TeO_2, etc., have been reported.[1,2] The electrical conduction in these glasses arises from the hopping of electrons or polarons between two different valence states of the copper ions, e.g., Cu^{2+} and Cu^{+}. The multicomponent glasses based on nonconventional network formers PbO and Bi_2O_3, are of considerable interest because they can be used to produce glass ceramics, layers for optical and optoelectronic devices, thermal and mechanical sensors, reflecting windows, etc.[3–7] Although these multicomponent cuprate glasses have been studied extensively,[3–9] the binary cuprate glasses based on PbO and Bi_2O_3, have been paid little attention.[10–12] The electrical properties of the binary lead cuprate glasses show that the electrical conduction in these glasses occurs by the small polaron hopping in the nonadiabatic regime.[12] The studies of the binary bismuth cuprate glasses are interesting because of its glass forming ability, in which Bi_2O_3 acts as a nonconventional unique network former in a wide composition range.[11] The glass formation domain of the binary system is also found to be much wider than that of the multicomponent systems.[6,8,9] The structural studies of these glasses[11] indicate that the copper ions occupy the network forming positions.

In this paper, the temperature and compositional dependence of the electrical properties of the binary bismuth cuprate glasses is reported. The experimental data have been analyzed in terms of different theories of polaronic conduction.

II. EXPERIMENTAL PROCEDURE

Glasses of compositions $(Bi_2O_3)_{100-x}(CuO)_x$, with $x=25-70$ mol % (Table I) were prepared from the reagent grade chemicals, Bi_2O_3 and CuO. The appropriate mixtures of these chemicals were melted in alumina crucibles in an electrical furnace at 1000 °C for 1 h. The melts were then quenched by pouring onto a twin roller. Amorphous character of the samples was confirmed by x-ray diffraction. The final chemical compositions of samples and the concentration of Cu^{2+} ions were determined by the atomic absorption and magnetic measurements, respectively. Density of the samples was measured by Archimedes' principle using acetone as an immersion liquid. The average intersite separation between Cu ions was obtained from estimated glass compositions. The different physical parameters of the glass samples are shown in Table I. For electrical measurements, gold electrodes were deposited on both surfaces of the samples by vacuum evaporation. Electrical measurements were carried out in a Keithley electrometer (Model 617). The absence of barrier layers at the contacts was confirmed by linear $I-V$ characteristics. After application of the electric field, the resistances of the samples were independent of time. This indicates that the electronic transport is dominant in these glasses. For low temperature measurements, the sample cell was inserted in a cryostat. Measurements were made in the temperature range 150–500 K.

III. RESULTS AND DISCUSSION

The electrical conductivity for several glass compositions is shown in Figs. 1 and 2 as a function of T^{-1} and $T^{-1/4}$, respectively. Figure 1 shows that the conductivity exhibits nonlinear behavior below the temperature range of 285–320 K depending on glass compositions, indicating temperature dependent activation energy, which decreases with decreasing temperature, characteristic of small polaron hopping conduction.[13–18] However, above this temperature range, the variation of activation energy with temperature is negligibly small so that the behavior may be treated as activated. The activation energy and pre-exponential factor were obtained from the least square straight line fits of the data above 320 K. The compositional dependence of the conductivity at 400 K and the activation energy are shown in Fig. 3. A striking feature of the binary cuprate glasses is that the conductivity is about an order of magnitude higher than that of the multicomponent cuprate glasses with the similar copper ion content.[6] Figure 2 shows linearity in the $\log_{10}\sigma$ vs $T^{-1/4}$ plot below about 300 K, indicative of variable range hopping[19] for a considerable temperature range. The above results are analyzed below in the light of small polaron hopping conductivity theories.[13–19]

TABLE I. Different physical parameters estimated from atomic absorption, density and magnetic measurements for the bismuth cuprate glasses.

Analyzed glass composition						
Bi_2O_3 (mol %)	CuO	Density ($g\,cm^{-3}$)	N ($10^{21}\,cm^{-3}$)	$[Cu^+]$ ($10^{21}\,cm^{-3}$)	C $[Cu^+]/N$	R (Å)
72.85	27.15	8.29	3.70	2.72	0.74	6.47
64.65	35.35	8.20	5.30	3.39	0.64	5.73
54.30	45.70	7.99	7.60	4.87	0.64	5.09
44.38	55.62	7.75	10.35	6.79	0.66	4.59
32.40	67.60	7.54	14.98	10.94	0.73	4.06

Mott[13] has investigated theoretically the hopping conductivity in oxide glasses containing transition metal ions. The conductivity of the nearest neighbor hopping of small polaron in the nonadiabatic regime at high temperatures ($T>\Theta_D/2$) is given by[13]

$$\sigma=\nu_0\frac{e^2C(1-C)}{kTR}\exp(-2\alpha R)\exp(-W/kT), \tag{1}$$

where ν_0 is the optical phonon frequency, α is the inverse localization length of the s-like wave function assumed to describe the localized states (at the transition metal ion sites), C is the fraction of sites occupied by an electron or polaron and is thus the ratio of the concentrations of the reduced states to that of the total transition metal ions, and W is the activation energy for hopping conduction. Assuming a strong electron–phonon interaction, Austin and Mott[14] have shown that

$$\begin{aligned} W&=W_H+W_D/2 \quad \text{for } T>\Theta_D/2 \\ &=W_D \quad \text{for } T<\Theta_D/4, \end{aligned} \tag{2}$$

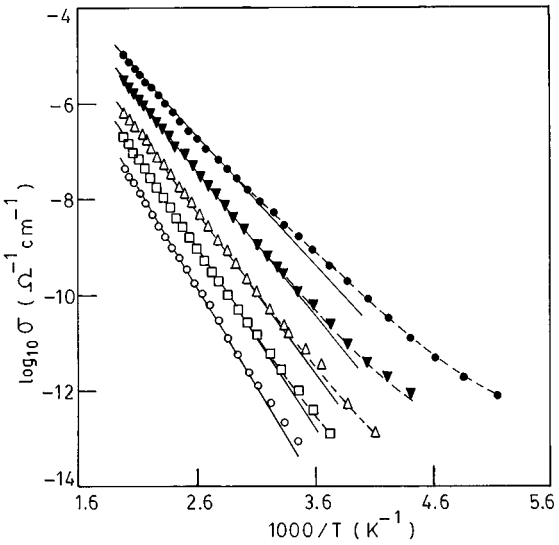

FIG. 1. Temperature dependence of the dc conductivity for bismuth cuprate glasses: ○, 27.15 mol % CuO; □, 35.35 mol % CuO; △, 45.70 mol % CuO; ▼, 55.62 mol % CuO; ●, 67.60 mol % CuO. The solid lines are the best fits of the data above 300 K to Eq. (1). The dashed curves are drawn through the data to guide the eye.

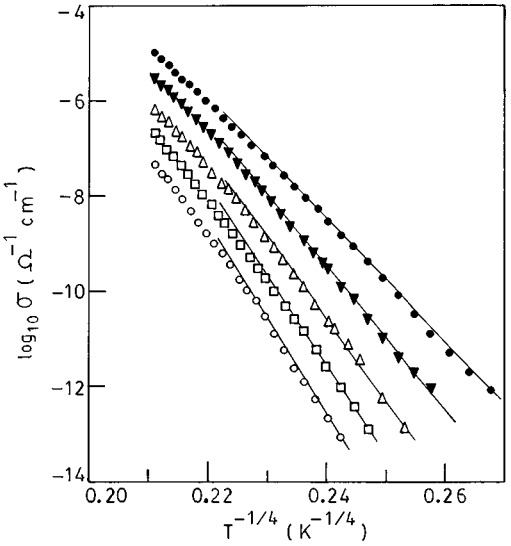

FIG. 2. Logarithmic conductivity shown as a function of $T^{-1/4}$ for the same bismuth cuprate glass compositions as in Fig. 1. The solid straight lines are the fits to Eq. (5).

where W_H is the polaron hopping energy, W_D is the disorder energy resulting from the variation of local environments of ions, and Θ_D is the characteristic Debye temperature. It should be noted that the tunneling term, $\exp(-2\alpha R)$ in expression (1) reduces to unity for the hopping in the adiabatic limit.

A general trend observed in Fig. 1 is that the magnitude of the conductivity at any temperature tends to be highest in those compositions having smallest activation energy, which is consistent with Eq. (1). However, Eq. (1) cannot predict temperature dependence of the activation energy observed below about 300 K. As shown in Fig. 4, a semilogarithmic plot of the conductivity measured at an arbitrarily chosen temperature (400 K) versus the activation energy at 400 K for all glass compositions is a straight line with a slope corresponding to a measurement temperature of 440 K. As suggested earlier,[1] it thus appears that the pre-exponential term

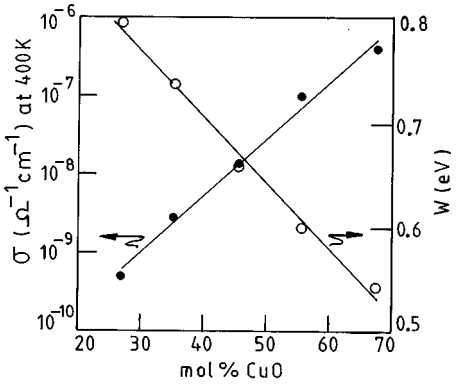

FIG. 3. Composition dependence of the conductivity at 400 K (●) and high temperature activation energy (○) for the bismuth cuprate glasses.

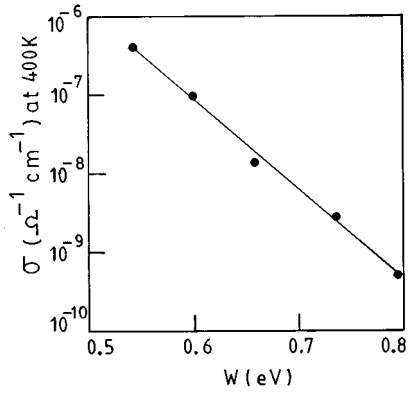

FIG. 4. Plots of $\log_{10}\sigma$ vs W at 400 K for different compositions of the bismuth cuprate glasses. The solid straight line is the least square fit to the data yielding a temperature of 440 K.

in Eq. (1), including $\exp(-2\alpha R)$, depends on the glass compositions. The thermal activation energy, therefore, cannot determine the conductivity. In particular, the tunneling term $\exp(-2\alpha R)$ needs vary rapidly with intersite separation R in order to account for the variation of the conductivity with CuO content.

Austin and Mott[14] have showed that the polaron hopping energy W_H can be estimated using the following expression:

$$W_H = e^2/2\varepsilon_0\epsilon_p r_p, \tag{3}$$

where ε_0 is the free space dielectric permittivity, ϵ_p is an effective dielectric constant which was calculated from the dielectric data[20] and are shown in Table II, and r_p is the polaron radius which can be calculated from the following expression suggested for a nondispersive system:[21]

$$r_p = (\pi/6)^{1/3}(R/2). \tag{4}$$

The estimated values of r_p from Eq. (4), using the values of R from Table I, are shown in Table II. The small values of the polaron radius suggest strong localization in the glass compositions. The values of W_H were calculated from Eq. (3) and are shown in Table II. Equation (2) was then used to calculate the disorder energy (Table II). It may be noted that the hopping energy decreases with the increase of the CuO content in the glass compositions consistent with the activation energy. However, the values of the disorder energy for the glasses with lower CuO content are comparable with the hopping energy which is unlikely as evidenced from the subsequent discussion.

TABLE II. Parameters obtained from polaron hopping models.

Glass composition (mol % CuO)	W (eV)	r_p (Å)	ϵ_p[a]	W_H (eV)	W_D (eV)	$N(E_F)$ ($\mathrm{eV^{-1}\,cm^{-3}}$)
27.15	0.84	2.61	31	0.56	0.56	5.79×10^{18}
35.35	0.79	2.31	36	0.54	0.50	6.98×10^{18}
45.70	0.70	2.05	39	0.57	0.26	9.36×10^{18}
55.62	0.64	1.85	41	0.60	0.08	1.60×10^{19}
67.60	0.60	1.64	51	0.54	0.12	2.54×10^{19}

[a]From Ref. 20.

At lower temperatures ($T<\theta_D/4$), where the polaron binding energy is small, Mott[19] has proposed that hops may occur preferentially beyond nearest neighbors. The conductivity for the variable range hopping is then given by[19]

$$\sigma = \sigma_0 \exp[-(T_0/T)^{1/4}], \tag{5}$$

where the constants σ_0 and T_0 are given by

$$\sigma_0 = \nu_0 e^2[3N(E_F)/2\pi\alpha kT]^{1/2},$$
$$T_0 = 19.44\alpha^3/kN(E_F), \tag{6}$$

where $N(E_F)$ is the density of states at the Fermi level. The values of σ_0 and T_0 were obtained from the least squares straight line fits of the data presented in Fig. 2 below 300 K. Assuming a reasonable value of $\alpha=1$ $\mathrm{Å}^{-1}$ for localized states,[22] the values of $N(E_F)$ were calculated from both σ_0 and T_0. Although the values of $N(E_F)$ (Table II) calculated from T_0 are reasonable for localized states,[22] those obtained from σ_0 are unreasonably high ($\sim10^{60}$ $\mathrm{eV^{-1}\,cm^{-3}}$). The reason for this discrepancy may be due to the assumption of the constant density of states. Thus the variable range hopping model can predict the data below 300 K only qualitatively.

A polaron hopping model has been investigated by Holstein and co-workers[15] considering zero disorder energy and covering both the adiabatic and nonadiabatic hopping processes. On the basis of molecular crystal model, Friedman and Holstein[15] have derived an expression for the dc conductivity

$$\sigma = (3e^2NR^2J^2/2kT)(\pi/kTW_H)^{1/2}\exp(-W_H/kT), \tag{7}$$

for the case of nonadiabatic hopping, while Emin and Holstein[15] have shown that for the case of adiabatic hopping

$$\sigma = (8\pi e^2NR^2\nu_0/3kT)\exp[-(W_H-J)/kT), \tag{8}$$

where N is the site concentration and J is a polaron band width related to electron wave function overlap on the adjacent sites.

The present experimental results follow Eq. (7) much more closely, with a thermal activation energy W_H, which varies with the CuO content. This model also provides an independent way of ascertaining the nature of hopping mechanism at high temperatures. The condition for the nature of hopping can be expressed by[15]

$$J \gtrless (2kTW_H/\pi)^{1/4}(h\nu_0/\pi)^{1/2}, \tag{9}$$

where the signs $>$ and $<$ indicate adiabatic and nonadiabatic hopping, respectively. The condition for the formation of small polaron is, however, given by $J \leqslant W_H/3$. The limiting value of J calculated from the right-hand side of expression (9) at 400 K is of the order of 0.04–0.05 eV, depending on compositions and therefore the condition for the existence of small polaron is satisfied. An unambiguous decision as to whether the polaron is actually in the adiabatic or in the nonadiabatic regime requires an estimate of the value of J, which can be obtained from[15]

$$J \approx e^3[N(E_F)/(\varepsilon_0\epsilon_p)^3]^{1/2}. \tag{10}$$

Using the values of $N(E_F)\sim10^{19}$ $\mathrm{eV^{-1}\,cm^{-3}}$ (Ref. 22) and ϵ_p from Table II, Eq. (10) gives $J=0.03$ eV and thus the

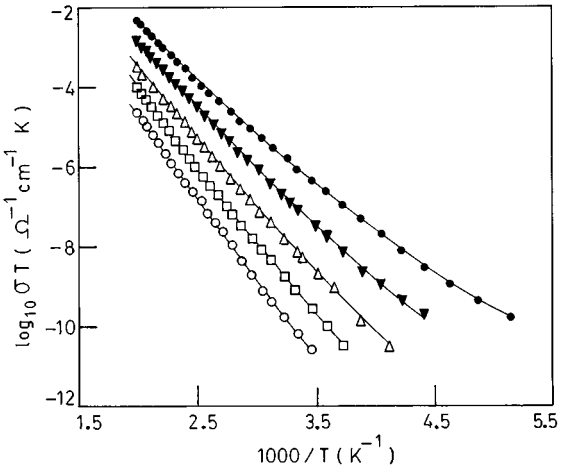

FIG. 5. Plots of $\log_{10}(\sigma T)$ vs $10^3/T$ for the same bismuth cuprate glass compositions as in Fig. 1. The solid curves are the best fits to Eq. (11).

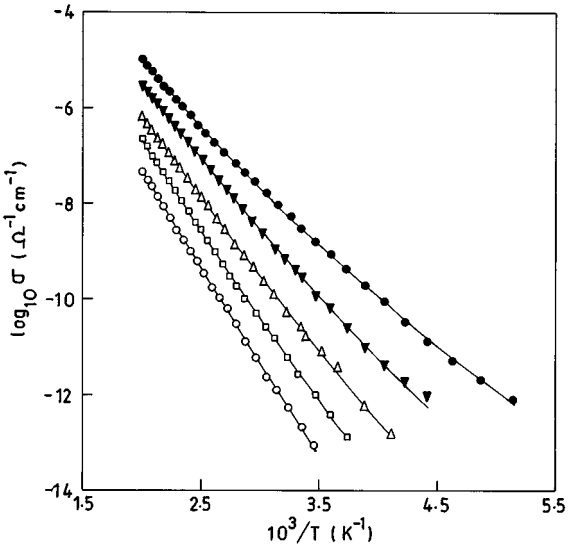

FIG. 6. The fits of the measured dc conductivity to the prediction of Emin's model [Eqs. (12) and (13)]. The solid curves represent the best fits for the same sample compositions as in Fig. 1.

nonadiabatic hopping theory is most appropriate to describe the polaronic conduction at high temperatures in bismuth cuprate glasses in sharp contrast with the conventional cuprate glasses.[1,2]

Schnakenberg[16] has considered a polaron hopping model, in which optical multiphonon process determines the dc conductivity at high temperatures, while at low temperatures charge transport is considered to be an acoustical one-phonon-assisted hopping process. The temperature dependence of the conductivity in this model has the form

$$\sigma \sim T^{-1}[\sinh(h\nu_0/kT)]^{1/2}\exp[-(4W_H/h\nu_0) \times \tanh(h\nu_0/4kT)]\exp(-W_D/kT). \quad (11)$$

It may be noted that Eq. (11) predicts a temperature dependent hopping energy which decreases with the decrease in temperature in consistence with the experimental data (Fig. 1). In Fig. 5, experimental data are fitted to Eq. (11) by the best fit method, and it is noted that the agreement between the theory and experiment is very good. The best fits yield the values of parameters ν_0, W_H, and W_D which are shown in Table III for different glass compositions. It is noted that the values of ν_0 are close to the estimates of ν_0 from infrared data.[11] The values of hopping energy W_H increases with the decrease of CuO content in the glass compositions in consistence with the activation energy. However, the disorder energy W_D does not vary much with compositions in consistent with the fact that the structural units in the binary glasses do not change significantly with compositions.[11] It may be noted that the values of W_D for the bismuth cuprate glasses are comparable to those of the lead cuprate glasses.[12]

Emin and co-workers[17,18] have discussed a phonon assisted hopping model in which electrons (polarons) could couple with either optical or acoustical phonons or both. Considering interaction of electrons with both acoustical and optical phonons, the dc conductivity for the nonadiabatic multiphonon hopping of small polarons has been calculated as[18]

$$\sigma = \frac{Ne^2R^2}{6kT}(J/\hbar)^2\left[\frac{\pi\hbar^2}{2(E_c^{\rm op}+E_c^{\rm ac})kT}\right]^{1/2} \times \exp\left[-\frac{W_D^2}{8(E_c^{\rm op}+E_c^{\rm ac})kT}\right]\exp\left[-\frac{W_D}{2kT}\right] \times \exp\left[-\frac{E_A^{\rm op}}{kT}-\frac{E_A^{\rm ac}}{kT}\right], \quad (12)$$

where $E_c^{\rm op}$, $E_c^{\rm ac}$, $E_A^{\rm op}$, and $E_A^{\rm ac}$ are defined as

$$E_c^{\rm op} = E_b^{\rm op}(1/N_p)\sum_q [h\nu_{0,q}/2kT]\,\mathrm{cosech}(h\nu_{0,q}/2kT),$$

TABLE III. Parameters obtained from the fits of Schnakenberg's model to the experimental data of bismuth cuprate glasses.

Glass composition (mol % CuO)	ν_0 (10^{13} s^{-1})	W_H (eV)	W_D (eV)
27.15	1.03	0.82	0.18
35.35	1.17	0.76	0.18
45.70	1.30	0.71	0.18
55.62	1.46	0.65	0.19
67.60	1.73	0.57	0.20

TABLE IV. Parameters obtained from the fits of Emin's model to the experimental data of bismuth cuprate glasses.

Glass composition (mol % CuO)	ν_0 (10^{13} s^{-1})	$E_b^{\rm op}$ (eV)	$E_b^{\rm ac}$ (eV)	W_D (eV)	J (eV)
27.15	1.50	0.94	0.75	0.20	0.040
35.35	1.67	0.89	0.68	0.20	0.035
45.70	1.84	0.84	0.63	0.20	0.034
55.62	2.10	0.74	0.60	0.20	0.028
67.60	2.40	0.69	0.56	0.20	0.025

$$E_c^{ac}=E_b^{ac}(1/N_p)\sum_q\ [h\nu_{a,q}/2kT]\text{cosech}(h\nu_{a,q}/2kT),$$
$$E_A^{op}=E_b^{op}(1/N_p)\sum_q\ [h\nu_{0,q}/2kT]^{-1}\ \tanh(h\nu_{0,q}/2kT), \quad (13)$$
$$E_A^{ac}=E_b^{ac}(1/N_p)\sum_q\ [h\nu_{a,q}/2kT]^{-1}\ \tanh(h\nu_{a,q}/2kT),$$

where $\nu_{0,q}$ and $\nu_{a,q}$ are the optical and acoustical phonon frequencies, respectively, at wave vector q, N_p is the number of phonon modes, E_b^{op} and E_b^{ac} are the polaron binding energies related to optical and acoustical phonons, respectively. Equations (12) and (13) have been utilized in calculating the dc conductivity, assuming that the acoustic phonon density of states is approximately given by $g(\omega)\propto\omega^2$ and that the mean optical phonon frequency, ν_0 is constant and also the acoustical phonon frequency is related to optical phonon frequency as $\nu_a=\nu_0/3$. The best fits to the experimental data for the bismuth cuprate glasses are shown in Fig. 6. The corresponding values of the parameters E_b^{op}, E_b^{ac}, W_D, J, and ν_0 are shown in Table IV. The values of these parameters obtained from the fits are reasonable. It may be noted that the values of the disorder energy obtained from this model are similar to those obtained from Schnakenberg's model. Also the values of the overlap integral J, estimated from this model are reasonable for small polaron hopping in the nonadiabatic regime.

IV. CONCLUSIONS

Temperature dependent electrical conductivity of the nonconventional binary bismuth cuprate glasses is presented for the first time for a wide composition range. Analysis of the conductivity data shows that the conductivity at high temperatures is consistent with the polaron hopping model in the nonadiabatic regime. The low temperature data are qualitatively consistent with the variable range hopping model. The temperature dependence of the conductivity is predicted by the polaron hopping models of Schnakenberg and Emin in the entire temperature range of measurement. The physical parameters obtained from the best fits of these models are found reasonable and consistent with the glass compositions.

ACKNOWLEDGMENT

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