

Transport properties of nonconventional lead cuprate glass

S. Hazra and A. Ghosh^{a)}

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

(Received 6 March 1995; accepted 6 July 1995)

The dc electrical transport properties of the nonconventional lead cuprate glasses of compositions $(\text{CuO})_x(\text{PbO})_{100-x}$ for $x = 15-50$ mol % are reported in the temperature range 150–500 K. The experimental results have been analyzed in the light of existing theoretical models. It has been observed that the high-temperature conductivity data are consistent with Mott's nearest-neighbor hopping model, while at low temperatures Mott's variable-range-hopping model fits the data very well. The polaron hopping models of Schnakenberg and Emin can predict the conductivity data in the entire temperature range of measurement. The percolation model of Triberis and Friedman is not consistent with the experimental results. © 1995 American Institute of Physics.

I. INTRODUCTION

Electrical properties of the semiconducting transition metal oxide glasses formed with conventional glass formers like P_2O_5 , TeO_2 , etc. have been studied extensively.^{1,2} It is generally accepted that the electrical conduction in these glasses occurs by the hopping of electrons or polarons between two different valence states of transition metal ions (e.g., Cu^+ and Cu^{2+} in cuprate glasses).^{1,2} It has been alternatively suggested³ that dc electrical transport in these glasses could be due to multiphonon tunneling of localized electrons with weak electron-phonon coupling. The vanadate glasses have been observed to have lower activation energy compared to the other transition metal oxide glasses.^{1,2} However, little attention has been paid to the study of the electrical properties of the binary cuprate glasses formed with nonconventional glass formers. Recently, nonconventional binary bismuth cuprate glasses,⁴ in which Bi_2O_3 acts as a glass former, have been characterized. These glasses exhibit adiabatic small polaron hopping between Cu^+ and Cu^{2+} states, in contrast with the nonadiabatic small polaron hopping observed in the multicomponent bismuth cuprate glasses.⁵ Multicomponent glasses based on PbO are of great interest because they can be used to produce glass ceramics, layer for optical and optoelectronic devices, thermal and mechanical sensors, reflecting windows, etc.⁶⁻⁸ It has been pointed out⁹ that the Pb^{2+} ions are highly polarizable and the asymmetry of their polyhedra inhibits crystallization process in the melts in which they participate. Recently, glasses in which PbO acts as a main glassy network former have been synthesized and their structure has been studied.⁶⁻¹⁰ The purpose of the present work is to study the temperature dependence of the dc electrical conductivity of the binary lead cuprate glasses for a wide composition range. The experimental results are analyzed with the help of existing theoretical models.

II. EXPERIMENTAL PROCEDURE

Glassy samples of compositions $(\text{CuO})_x(\text{PbO})_{100-x}$ were prepared (Table I) from the reagent grade chemicals CuO and PbO, for $x = 15-50$ mol %. The appropriate mixtures of

these chemicals in 20 g batch were melted in alumina crucibles in an electrical furnace at temperatures in the range 1100–1250 °C depending on compositions for 1 h. Glassy samples were obtained by quenching the melts in a twin roller. Amorphous nature of the samples was confirmed by differential thermal analysis, scanning electron microscopy, infrared spectroscopy and x-ray diffraction studies. Density of the samples was measured by Archimedes' principle using acetone as an immersion liquid. The total copper ion concentrations as well as final chemical compositions of the samples were determined by the atomic absorption (Varian, model AA 1745), while the concentrations of Cu^{2+} ions, $[\text{Cu}^{2+}]$ were determined by magnetic measurements (Parc, model 155). The average intersite separation between copper ions was obtained from estimated glass compositions and density. The various physical parameters of the glass compositions are shown in Table I. Electrical measurements were carried out in the temperature range 150–500 K by a Keithley electrometer (model 617). For electrical measurements, gold electrodes were deposited on both surfaces of the samples by vacuum evaporation technique and the absence of barrier layers at the contacts was confirmed by linear I-V characteristics before measurements. For low-temperature measurements, the sample cell was inserted in a liquid nitrogen cryostat. The time independence of the resistance observed after application of the dc voltage suggests that the electronic transport is dominant in these glass compositions.

III. RESULTS AND DISCUSSION

Logarithmic conductivity as a function of inverse temperature for different lead cuprate glass compositions is plotted in Fig. 1, which shows nonlinearity below the temperature range 250–350 K, depending on glass compositions, indicating temperature dependent activation energy. It is evident from Fig. 1 that above this temperature range the activation energy is nearly constant. This activation energy and the conductivity at 400 K are plotted as a function of glass composition in Fig. 2. The conductivity increases and the activation energy decreases with the increase of CuO content in the glass compositions, consistent with other cuprate glasses in which the electrical conduction has been observed to arise from the hopping of electrons or polarons between

^{a)}Corresponding author.

TABLE I. Physical parameters of the lead cuprate glasses.

Analyzed glass composition (mol %)		Density (g cm^{-3})	N (10^{21} cm^{-3})	$[\text{Cu}^+]^a$ (10^{21} cm^{-3})	C^b	R (\AA)
PbO	CuO					
84.93	15.07	9.39	4.22	3.10	0.74	6.18
78.87	21.13	8.90	5.87	4.37	0.74	5.54
70.47	29.53	8.28	8.15	5.75	0.70	4.97
64.24	35.76	7.76	9.73	7.13	0.73	4.68
49.45	50.55	6.67	13.44	9.88	0.73	4.21

^a $[\text{Cu}^+] = N - [\text{Cu}^{2+}]$.

^b $C = [\text{Cu}^+]/N$.

Cu^+ and Cu^{2+} states.^{1,2} In the following, the conductivity data have been analyzed with reference to different theoretical models^{11–19} in order to extract dominant transport mechanism.

The semiconducting behavior of the transition metal oxide glasses has been described by Mott¹¹ in terms of phonon-assisted hopping of small polarons between localized states. At high temperatures ($T > \theta_D/2$), the following expression for the electrical conductivity has been proposed for the nearest-neighbor hopping in the nonadiabatic regime:

$$\sigma = \nu_0 [e^2 C(1-C)/kTR] \exp(-2\alpha R) \exp(-W/kT), \quad (1)$$

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, R is the average intersite separation, C is the fraction of sites occupied by an electron or polaron and is thus a fraction of reduced transition metal ion, and W is the activation energy for hopping conduction. Assuming a strong electron-phonon interaction, Austin and Mott¹² have shown that

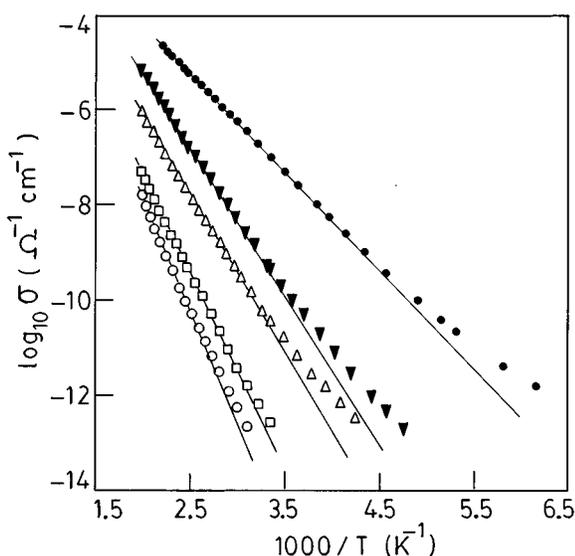


FIG. 1. Logarithmic conductivity as a function of inverse temperature for lead cuprate glasses: \circ , 15.07 mol % CuO; \square , 21.13 mol % CuO; \triangle , 29.53 mol % CuO; ∇ , 35.76 mol % CuO; \bullet , 50.55 mol % CuO. The solid lines are the best fits to Eq. (1).

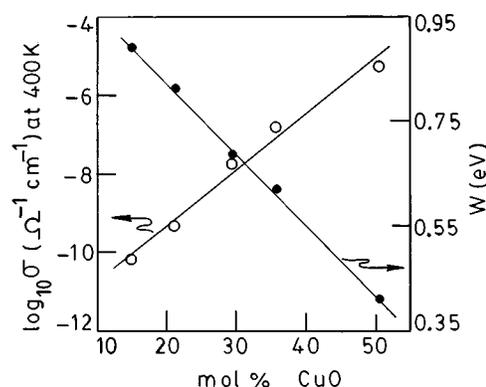


FIG. 2. Conductivity at 400 K (\circ) and activation energy (\bullet) at high temperature as a function of CuO content in the lead cuprate glasses.

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

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 Debye temperature.

In Fig. 1, experimental data above 250–350 K depending on glass compositions is fitted consistently to Eq. (1) by the least-square fitting procedure. The values of the parameters W and α obtained from the best fits, utilizing values of ν_0 estimated from infrared spectra²⁰ and C from Table I, are shown in Table II. The values of W decrease with the increase of CuO content in the glass compositions similar to other conventional cuprate glasses.^{1,2} The values of α obtained are reasonable for localized states and indicate strong localization in the lead cuprate glasses.²¹ The value of α increases with the increase of CuO content in the glass compositions similar to the other cuprate glasses.²

Bogomolov and co-workers²² have derived an expression for the polaron radius r_p for a nondispersive system and is given by

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

The values of r_p , obtained by using the values of N from Table I, in Eq. (3), are shown in Table II. The small values of r_p also suggest strong localization in the lead cuprate glasses.

At low temperatures, where the polaron binding energy is small, Mott¹⁵ has proposed that optimization is achieved

TABLE II. Parameters obtained by fitting the high-temperature conductivity data to Mott's model.

Glass composition (mol % CuO)	W (eV)	α (\AA^{-1})	r_p (\AA)
15.07	0.90	0.52	2.49
21.13	0.82	0.60	2.23
29.53	0.69	0.70	2.00
35.76	0.63	0.75	1.89
50.55	0.42	0.95	1.69

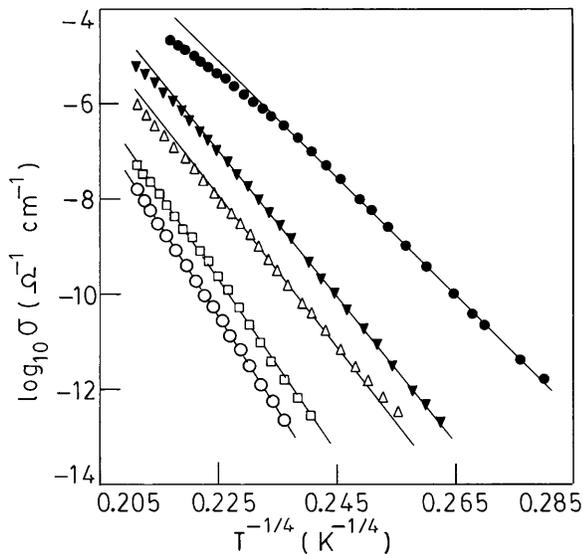


FIG. 3. Logarithmic conductivity as a function of $T^{-1/4}$ for the same lead cuprate glass compositions as in Fig. 1. The solid straight lines are the fits to Eq. (4).

between R and W in Eq. (1) so that hops may occur preferentially beyond nearest neighbors. The variable-range-hopping conductivity is then given by¹⁵

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

where σ_0 and T_0 are constants, and T_0 is given by

$$T_0 = 19.44\alpha^3/kN(E_F), \quad (5)$$

where $N(E_F)$ is the density of states at the Fermi level. On the other hand, variable-range-hopping conductivity derived by Efros and Shklovskii,¹⁶ taking correlation effects between the carriers into account, is given by

$$\sigma = \sigma_0 \exp[-(T_0/T)^{1/2}]. \quad (6)$$

A semilogarithmic plot of the conductivity versus $T^{-1/4}$ is shown in Fig. 3 for the lead cuprate glasses, in which Eq. (4) is fitted to the experimental data for temperatures below ~ 325 K. The data were also separately fitted to Eq. (6). Considering the quality of the fits, it is concluded that Mott's variable-range-hopping model is operative in these glasses for a considerable temperature range below ~ 325 K. The values of $N(E_F)$ obtained from the fits using the values of α from Table II in Eq. (5), are shown in Table III. These values of $N(E_F)$ are reasonable for localized

TABLE III. Parameters obtained by fitting the data to variable range hopping and percolation models.

Glass composition (mol % CuO)	$N(E_F)$ ($\text{eV}^{-1} \text{cm}^{-3}$)	N_0 ($\text{eV}^{-1} \text{cm}^{-3}$)
15.07	8.70×10^{17}	7.97×10^{17}
21.13	1.50×10^{18}	1.37×10^{18}
29.53	4.16×10^{18}	3.81×10^{18}
35.76	6.07×10^{18}	5.56×10^{18}
50.55	3.02×10^{19}	2.76×10^{19}

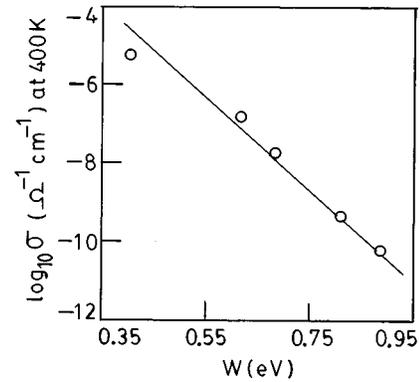


FIG. 4. Logarithmic conductivity as a function of activation energy at 400 K for lead cuprate glasses. The solid straight line is the least square fit to the data yielding a temperature of 430 K.

states²¹ and increase in consistence with the increase of copper ion content in the glass compositions. It may be noted that the values of $N(E_F)$ for the binary lead cuprate glasses are of the same order for the binary bismuth cuprate glasses,⁴ but these values are less by two orders of magnitude than those for the multicomponent cuprate glasses⁵ with comparable CuO content.

The nature of the hopping mechanism at high temperatures might be ascertained from the semilogarithmic plot of the conductivity versus activation energy at an experimental temperature for all glass compositions.¹ If the slope of such a plot yields a temperature which is of the order of experimental temperature, then the hopping will be adiabatic, otherwise, hopping will be nonadiabatic. Such a plot for the lead cuprate glasses is shown in Fig. 4 at an experimental temperature of 400 K and the straight line obtained by least-square fit yields a temperature of the order of 430 K. It is difficult to reach a conclusion on the basis of this value. The nature of hopping mechanism is determined from the other theory described in the next paragraph.

A polaron hopping model proposed by Holstein and co-workers¹³ can be employed independently to check the nature of the hopping mechanism. The criterion for the nature of hopping is

$$J \geq (2kTW_H/\pi)^{1/4}(h\nu_0/\pi)^{1/2}, \quad (7)$$

where J is the transfer integral between adjacent sites and the signs $>$ and $<$ indicate adiabatic and nonadiabatic hopping, respectively. The condition for the formation of small polaron is also given by $J \leq W_H/3$. The values of the right-hand side of Eq. (7) at 400 K, using the values of ν_0 and $W_H \approx W$ from Table II, are in the range 0.04–0.05 eV. On the other hand, an upper limit of J can be deduced by assuming that the entire concentration dependence of the activation energy is due to the variation in J . In the present glass system, this corresponds to a change in W from 0.42 to 0.90 eV, a possible variation in J being ~ 0.48 eV. However, since W is likely to change with compositions, the true value is probably smaller than this. The values of J can also be estimated from the formula²¹

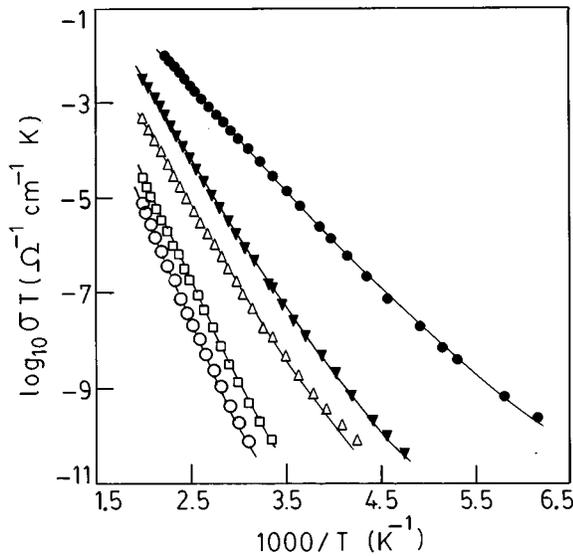


FIG. 5. Plots of $\log_{10}(\sigma T)$ as a function of inverse temperature for the same lead cuprate glass compositions as in Fig. 1. The solid curves are the best fits to Eq. (9).

$$J \sim e^3 [N(E_F)/\epsilon_p^3]^{1/2}. \quad (8)$$

The value of J obtained from Eq. (8) by using the value of ϵ_p estimated from ac measurement²⁰ and $N(E_F)$ from Table III, is of the order of 0.02 eV. Thus, the nonadiabatic hopping theory is likely to describe the polaronic conduction in lead cuprate glasses at high temperatures.

A polaron hopping model has been considered by Schnakenberg,¹⁴ in which an optical multiphonon process determines the conductivity at high temperatures, while an acoustical one-phonon-assisted hopping process is operative at low temperatures. According to this model the temperature dependence of the conductivity is given by

$$\sigma \sim T^{-1} [\sinh(h\nu_0/kT)]^{1/2} \exp[-(4W_H/h\nu_0)] \times \tanh(h\nu_0/4kT) \exp(-W_D/kT). \quad (9)$$

It may be noted that Eq. (9) predicts a temperature-dependent hopping energy which decreases with decreasing temperature consistent with the experimental data (Fig. 1). The experimental points fitted to Eq. (9) by the best fit method are shown in Fig. 5. The values of parameters ν_0 , W_H , and W_D obtained from the best fits are shown in Table IV. It is noted that the values of ν_0 are close to the estimates

TABLE IV. Parameters obtained from the fits of Schnakenberg's model [Eq. (9)] to the experimental data.

Glass composition (mol % CuO)	ν_0 (s^{-1})	W_H (eV)	W_D (eV)
15.07	0.88×10^{13}	0.86	0.16
21.13	1.07×10^{13}	0.79	0.20
29.53	1.30×10^{13}	0.66	0.24
35.76	1.67×10^{13}	0.60	0.26
50.55	1.18×10^{13}	0.39	0.21

of ν_0 from infrared data.²⁰ The value of hopping energy W_H increases with the decrease of CuO content in the glass compositions consistent with the activation energy. The disorder energy W_D varies slightly with compositions consistent with the fact that the structural units in the binary glasses do not change significantly with compositions.⁴ It may be noted that the values of the disorder energy obtained from this model are comparable with those for other cuprate glasses.⁵

Emin and co-workers^{17,18} have discussed phonon-assisted hopping models in which electrons 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 polaron has been calculated as¹⁸

$$\sigma = \frac{Ne^2R^2}{6kT} (J/\hbar)^2 \left[\frac{\pi\hbar^2}{2(E_c^{\text{op}} + E_c^{\text{ac}})kT} \right]^{1/2} \times \exp\left[-\frac{W_D^2}{8(E_c^{\text{op}} + E_c^{\text{ac}})kT}\right] \exp\left[-\frac{W_D}{2kT}\right] \times \exp\left[-\frac{E_A^{\text{op}}}{kT} - \frac{E_A^{\text{ac}}}{kT}\right], \quad (10)$$

where J is, as before, the transfer integral between adjacent sites and $\hbar = h/2\pi$. E_c^{op} , E_c^{ac} , E_A^{op} , and E_A^{ac} are defined as

$$E_c^{\text{op}} = \frac{\hbar^2}{4kT} \frac{1}{N_p} \sum_q \left(\frac{2E_b^{\text{op}}}{\hbar\omega_{q,0}} \right) \text{cosech}\left(\frac{\hbar\omega_{q,0}}{2kT}\right) \omega_{q,0}^2, \\ E_c^{\text{ac}} = \frac{\hbar^2}{4kT} \frac{1}{N_p} \sum_q \left(\frac{2E_b^{\text{ac}}}{\hbar\omega_{q,a}} \right) \text{cosech}\left(\frac{\hbar\omega_{q,a}}{2kT}\right) \omega_{q,a}^2, \quad (11) \\ E_A^{\text{op}} = kT \left(\frac{2E_b^{\text{op}}}{\hbar\omega_0} \right) \tanh\left(\frac{\hbar\omega_0}{2kT}\right), \\ E_A^{\text{ac}} = kT \frac{1}{N_p} \sum_q \left(\frac{2E_b^{\text{ac}}}{\hbar\omega_{q,a}} \right) \tanh\left(\frac{\hbar\omega_{q,a}}{2kT}\right),$$

where $\omega_0 = 2\pi\nu_0$ is the mean optical-phonon frequency, $\omega_{q,0}$ and $\omega_{q,a}$ 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.

The dc conductivity given by Eqs. (10) and (11) is calculated, assuming that the acoustic phonon density of states is approximately given by $g(\omega) \propto \omega^2$ and that the mean optical phonon frequency is constant. The best fits to the experimental data are shown in Fig. 6. The values of the parameters E_b^{op} , E_b^{ac} , W_D , J , and ν_0 are shown in Table V. It may be noted that the values of these parameters obtained from the fits are reasonable.

Triberis and Friedman¹⁹ have applied percolation theory to the small polaron hopping regime. Considering correlation due to energy of a common site in a percolation cluster, they have obtained

$$\sigma = \sigma'_0 \exp[-(T'_0/T)^{1/4}], \quad (12)$$

where σ'_0 and T'_0 are constants. T'_0 is given by

$$T'_0 = C\alpha^3/kN_0, \quad (13)$$

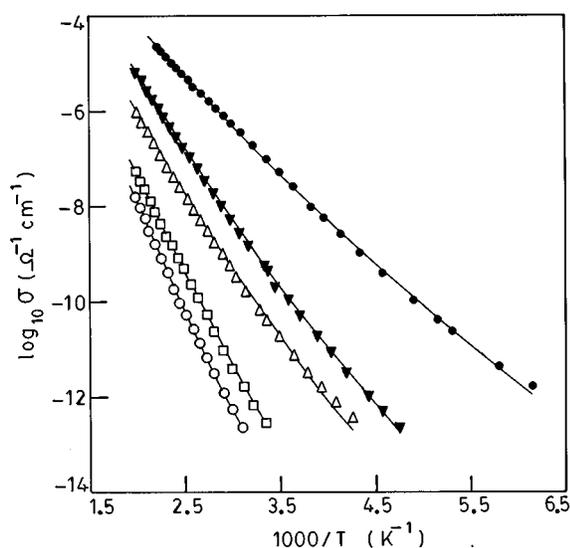


FIG. 6. The fits of the measured dc conductivity to the prediction of Emin's model [Eqs. (10) and (11)]. The solid curves represent the best fits for the same sample compositions as in Fig. 1.

where N_0 is the constant density of states in the mobility gap, and the constant C has two different values 12.5 and 17.8 in the high- and low-temperature regimes, respectively. It may be noted that Eq. (12) is similar to that of Mott's variable-range-hopping model [Eq. (4)] with slightly different values of T'_0 . In Fig. 3, two different slopes are observed in the $\log_{10}\sigma$ vs $T^{-1/4}$ plot for the glass compositions with higher CuO content. The other glass compositions might have showed two slopes at temperatures which are higher than our experimental limit. It may be noted that the ratio of two slopes observed experimentally at low and high temperatures is higher than that predicted by this model. However, the

TABLE V. Parameters obtained from the fits of Emin's model [Eqs. (10) and (11)] to the experimental data.

Glass composition (mol % CuO)	ν_0 (10^{13} s^{-1})	E_b^{op} (eV)	E_b^{ac} (eV)	W_D (eV)	J (eV)
15.07	1.90	0.98	0.75	0.35	0.05
21.13	1.25	0.92	0.72	0.18	0.03
29.53	2.21	0.86	0.76	0.10	0.04
35.76	1.90	0.68	0.60	0.20	0.03
50.55	2.95	0.49	0.49	0.28	0.03

value of N_0 can be obtained from Eq. (13), considering the straight line fits at low temperatures. The values of N_0 shown in Table III are very close to the values of $N(E_F)$ estimated from Mott's variable-range-hopping model.

IV. CONCLUSIONS

The temperature dependence of the dc electrical conductivity of the binary nonconventional lead cuprate glasses is presented for a wide glass composition range. Analysis of the experimental data shows that Mott's models of nearest-neighbor hopping and variable-range hopping can explain the experimental data at high and low temperatures, respectively. The polaron hopping models of Schnakenberg and Emin can fit the conductivity data in the entire temperature range of measurement. These models yield reasonable values of various physical parameters consistent with glass compositions. The percolation model applied to hopping regime is not consistent with the data.

ACKNOWLEDGMENT

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

- M. Sayer and A. Mansingh, Phys. Rev. B **6**, 4629 (1972).
- A. Ghosh, J. Phys.: Condens. Matter **1**, 7819 (1989); A. Ghosh and D. Chakravorty, Phys. Rev. B **48**, 5167 (1993).
- K. Shimakawa, Philos. Mag. B **60**, 377 (1989).
- S. Hazra and A. Ghosh, Phys. Rev. B **51**, 851 (1995).
- A. Ghosh, Phys. Rev. B **48**, 16 081 (1993).
- Y. Dimitriev, V. Mihailova, and E. Gattaf, Phys. Chem. Glasses **34**, 114 (1986).
- W. Mianxve and Z. Peinan, J. Non-Cryst. Solids **84**, 344 (1986).
- Y. Takahashi and K. Yamaguchi, J. Mater. Sci. **25**, 3950 (1990).
- K. Fajans and N. Kreidl, J. Am. Ceram. Soc. **31**, 105 (1948).
- K. J. Rao, Phys. Chem. Glasses **25**, 57 (1984).
- N. F. Mott, J. Non-Cryst. Solids **1**, 1 (1968).
- I. G. Austin and N. F. Mott, Adv. Phys. **18**, 41 (1969).
- T. Holstein, Ann. Phys. (NY) **8**, 343 (1959); L. Friedman and T. Holstein, Ann. Phys. (NY) **21**, 494 (1963).
- J. Schnakenberg, Phys. Status Solidi **28**, 623 (1968).
- N. F. Mott, Philos. Mag. **19**, 835 (1969).
- A. L. Efros and B. I. Shklovskii, J. Phys. C **8**, L49 (1975).
- D. Emin, Phys. Rev. Lett. **32**, 303 (1974); Adv. Phys. **24**, 305 (1975).
- E. Gorham-Bergeron and D. Emin, Phys. Rev. B **15**, 3667 (1977).
- G. P. Triberis and L. Friedman, J. Phys. C **18**, 2281 (1985); G. P. Triberis, J. Non-Cryst. Solids **74**, 1 (1985).
- S. Hazra and A. Ghosh, J. Mat. Res. (in press).
- N. F. Mott and E. A. Davis, *Electronic Processes in Non-Crystalline Materials*, 2nd ed. (Clarendon, Oxford, 1979).
- V. N. Bolomolov, E. K. Kudinov, and Y. A. Firsov, Sov. Phys. Solid State **9**, 2502 (1968).