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Nonadiabatic small-polaron hopping conduction in Li-doped and undoped $Bi_4Sr_3Ca_3Cu_yO_x$ $(0 \le y \le 5)$

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Detailed experimental results of temperature- and CuO-concentration-dependent dc conductivities of semiconducting $Bi_4Sr_3Ca_3Cu_yO_x$ ($y=0$ to 5) and Li-doped $Bi_4Sr_3Ca_{3-z}Li_zCu_4O_x$ ($z=0.1$, 0.5, and 1.0) glasses are reported. The variation of activation energy with glass compositions dominates the conductivity. Unlike many glasses with transition-metal ions, a strong preexponential factor containing the "small-polaron" tunneling term $[\exp(-2\alpha R)]$ is observed. Nonadiabatic small-polaron hopping mechanism is found to be appropriate for explaining the conductivity data of both glass systems. Addition of alkali-metal ions decreases the conductivities and causes appreciable change of some model parameters obtained from least-squares fittings of the experimental data. The overall thermal behavior of the electrical conductivities of the glasses, however, remains unaltered. This indicates that small (less than 10 wt.%) amount of Li or other alkali-metal ions in these glasses acts as a flux to keep the oxygen content fixed in the corresponding glass-ceramic (superconducting) phases. This in turn helps increase the superconducting transition temperature of the glass ceramics and also lower the sintering and melting temperatures of the glasses.

I. INTRODUCTION

The study of transition-metal oxide glasses are of particular importance for many technological applications.[1] Recently several transition-metal oxide glasses, such as $YBa_2Cu_3O_x$,[2] (Bi,Pb)-Sr-Ca-Cu-O,[3] etc., have been discovered, which become superconductors in their glass-ceramic phases. These glasses with transition-metal ions (TMI) are very useful precursor materials for making high-temperature superconducting oxide wires, tapes, or thick films.[4] The room-temperature electrical conductivities of these glasses are, however, two to three orders of magnitude lower than those of iron, vanadium, or other TMI glasses.[5,6] The glasses of our present investigation, such as $Bi_4Ca_3Sr_3Cu_yO_x$ (hereafter referred to as 4:3:3:y, glasses) have already been found[7,8] to show interesting nonlinear variations of glass transition temperature (T_g), density (ρ), mean molar oxygen volume (V_0^*), etc., as a function of CuO or Bi_2O_3 concentrations. The 4:3:3:4 glass is especially important as it acts as a precursor for making single phase $Bi_2Sr_2Ca_1Cu_2O_8$ (2:2:1:2) superconductors with T_c between 80 and 84 K.[9] It has also been reported[10-13] that addition of some alkaline oxides in this system improves the superconducting behavior of the glass ceramics (increase of T_c) and also lowers the ceramic sintering temperature. However, detailed investigation of the electrical properties of both Li-doped and undoped Bi-Sr-Ca-Cu-O glasses for different CuO concentrations has not yet been reported.

Since the superconducting behavior of the present glass ceramics depends on the CuO concentrations,[7,8] our plan is to study the CuO- and Li-concentration-dependent electrical and other properties of the $Bi_4Ca_3Sr_3Cu_yO_x$ (with $y=0$–5) and $Bi_4Sr_3Ca_{3-z}Li_zCu_4O_x$ (with $z=0.1$, 0.5, and 1.0) glasses, respectively. An attempt has also been made to study the effects of Li ions on the superconducting transition temperatures (T_c) of the corresponding Li-doped 4:3:$(3-z)$:4 glass ceramics. Such studies would elucidate the differences in the properties of these and other transition-metal oxide (TMO) glasses, which do not become superconductors in their glass-ceramic phases. Furthermore, the model parameters like Debye temperature, electron-phonon interaction constant, polaron radius, etc., obtained from the electrical conductivities of these glasses might be useful to a deeper understanding of the mechanism of superconductivity in the corresponding glass ceramics.

In Sec. II we have discussed in brief the preparation and characterization of the glasses. In Sec. III results of dc conductivities of both 4:3:3:y and Li-doped 4:3:$(3-z)$:4 glasses have been discussed with small-polaron hopping models. The different model parameters calculated for both the glass systems are reported. Finally, the paper ends with a conclusion in Sec. IV.

II. PREPARATION AND CHARACTERIZATION OF THE GLASSES

The method of preparation of the $Bi_4Ca_3Sr_3Cu_yO_x$ glasses have already been discussed earlier.[7,8,14] A similar method has also been used to prepare the lithium-doped 4:3:$(3-z)$:4, or $Bi_4Sr_3Ca_{3-z}Li_zCu_4O_x$, glasses. Three Li-doped 4:3:$(3-z)$:4 glass samples studied are for $z=0.1$ (sample No. 9), 0.5 (sample No. 10), and 1.0 (sample No. 11). The oxide materials, viz., Bi_2O_3, $CaCO_3$, $SrCO_3$, CuO, and $LiOH\cdot H_2O$ used for the preparation of the glasses are of 99.99% purity. Since the ratio $C=[Cu^{1+}]/[Cu(total)]$ depends on the glass making temperature, all the glasses were made by quick quenching from their respective melts at 1200 °C to room temperature (303 K). Each melt was kept at this temperature for one hour. The amorphous character of these glasses were confirmed by x-ray diffraction (Philips, Model PW 1050/1051) and scanning electron microscopic (Hitachi, Model S-415A) studies as before.[7,14] The scattering wave vector k calculated from the relation $k = 4\pi \sin\theta/\lambda$ gives a value of 2.11 Å^{-1}, which is typical for an amorphous material. Annealing the samples up to 200 °C for 2 h did not induce any crystallinity. Figure 1 shows the differential thermal analysis (DTA) (Shimadzu DT-30) curves of different glasses. Each curve shows an endothermic peak around 400–425 °C that corresponds to the glass transition temperature (T_g). Most of the TMO glasses, however, show lower (around 350 °C) T_g values. We did not observe, unlike Zheng and co-workers,[4] a systematic variation of T_g with CuO concentration as shown in Table I. There are number of exothermic crystallization peaks followed by endothermic glass transition peaks some of which are only prominent (Fig. 1). The difference ($T_{cr} - T_g$) between crystallization temperature (T_{cr}) and T_g for the 4:3:3:y glasses vary from 60 °C to 115 °C (Table I) indicating that the glasses are fairly stable. Some important parameters obtained from DTA (for determining T_g and T_{cr}), density measurement, atomic absorption, and chemical analysis are shown in Tables I and II, respectively, for the 4:3:3:y and Li-doped 4:3:(3−z):4 glasses. Slightly higher values of the final wt% of Cu than the corresponding starting value (Table I) is considered to be mainly due to the loss of oxygen from the melt. However, evaporation loss of Bi_2O_3, in particular, should also be taken into account. It is further observed from Table I that a majority of the copper atoms exist in the glasses as Cu^{1+} ions. Addition of Li ions does not appreciably change the value of Cu concentration in the Li-doped 4:3:(3−z):4 glasses. Little increase in the T_g values of the Li-doped 4:3:(3−z):4 glasses than those of the corresponding base glass, viz., $Bi_4Sr_3Ca_3Cu_4O_x$ (4:3:3:4, for which $z = 0$) is also noticed from Table II.

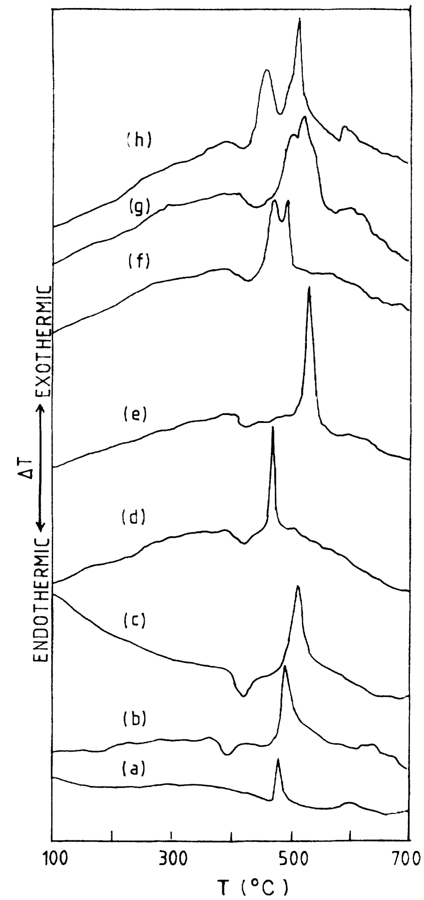

FIG. 1. DTA curves of $Bi_4Sr_3Ca_3Cu_yO_x$ glasses with (a) $y = 0$, (b) $y = 1$, (c) $y = 2$, (d) $y = 3$, (e) $y = 3.5$, (f) $y = 4$, (g) $y = 4.5$, and (h) $y = 5$.

III. RESULTS AND DISCUSSION

Figure 2(a) shows the logarithm of dc conductivity (σ_{dc}) of the $Bi_4Sr_3Ca_3Cu_yO_x$ glasses for different y (CuO

TABLE I. Some important parameters for the $Bi_4Sr_3Ca_3Cu_yO_x$ glasses.

Sample	No. 1	No. 2	No. 3	No. 4	No. 5	No. 6	No. 7	No. 8
Values of y	0	1	2	3	3.5	4	4.5	5
Starting Cu content (wt%)	0	4.26	8.09	11.56	13.17	14.70	16.17	17.57
Final Cu content (wt%)[a]	0	4.63	8.21	11.64	14.05	15.90	17.22	18.08
Density (ρ) (g cm^{-3})	5.97	5.95	5.93	5.92	5.89	5.89	5.88	5.86
N (10^{21} cm^{-3})		2.61	4.61	6.53	7.84	8.87	9.59	10.04
$C = [Cu^+/Cu(total)]$		0.79	0.75	0.70	0.75	0.78	0.80	0.79
R (Å)		7.26	6.01	5.35	5.03	4.83	4.71	4.64
r_p (Å)		2.93	2.42	2.16	2.03	1.95	1.90	1.87
T_g (°C)	408	402	422	422	440	426	446	431
$T_{cr} - T_g$ (°C)	97	110	112	73	115	106	86	60
T_c (K)[b]				70	79	85	85.5	76

[a] Obtained from atomic absorption spectroscopy.

[b] Superconducting transition temperature of the glass ceramics obtained from resistivity measurement.

TABLE II. Some important parameters for the $Bi_4Sr_3Ca_{3-z}Cu_4Li_zO_x$ glasses.

Sample	No. 9	No. 10	No. 11
Values of z	0.1	0.5	1.0
Density (ρ) ($g\ cm^{-3}$)	5.82	6.02	6.59
N ($10^{21}\ cm^{-3}$)	8.24	8.62	9.54
R (Å)	4.95	4.88	4.71
r_p (Å)	1.99	1.96	1.89
T_g (°C)	428	433	436
T_c (K)[a]	86.0	88.5	89.5

[a] Superconducting transition temperature of the glass ceramics obtained from resistivity measurement.

concentration) values as a function of $10^3/T$ (T is the absolute temperature). The slopes of the curves change slightly with T in the high-temperature region indicating slow variation of activation energy (W). The corresponding dc conductivity curves for lithium-doped $Bi_4Sr_3Ca_{3-z}Li_zCu_4O_x$ samples are shown in Fig. 3(a). The nature of the curves (with $z=0.1$, 0.5, and 1.0) are almost similar to those of the pure 4:3:3:y glasses shown in Fig. 2(a). However, the magnitude of dc conductivity at any temperature (say at room temperature) is lower in the Li-doped 4:3:(3$-z$):4 glasses. A plot of excess conductivity $\Delta\sigma_{dc}$ [$=\sigma_{dc}$ (undoped 4:3:3:4 glasses) $-\sigma_{dc}$ (Li-doped 4:3:(3$-z$):4 glasses)] as a function of temperature for different Li concentrations (shown in Fig. 4) distinguishes the low- and high-temperature regions of the thermal variations of σ_{dc}. The low-temperature conductivities are almost independent of temperature in the Li-doped glasses. Below a certain temperature, which varies from 240 to 200 K (for different 4:3:3:y glasses) the change of slopes are more pronounced in the glasses with higher values of y having higher conductivity at low temperature. Such a behavior of σ_{dc} is typical for "small-polaron" hopping conduction in transition-metal oxide glasses.[15] The variation of conductivity and activation energy W with y are shown in Fig. 5, which indicates that at any fixed temperature, σ_{dc} increases with increasing CuO concentration. This increase is, however, nonlinear,[7,8] unlike iron-bismuth,[6] vanadate,[5] or Cu-Te-O-type[16] glasses. The magnitude of activation energy at higher temperatures (above $\Theta_D/2$, Θ_D being the Debye temperature) decreases with the increase of CuO content in the glasses. Similar variation of σ_{dc} and W are also observed for Li-doped 4:3:(3$-z$):4 glasses as shown in Fig. 5.

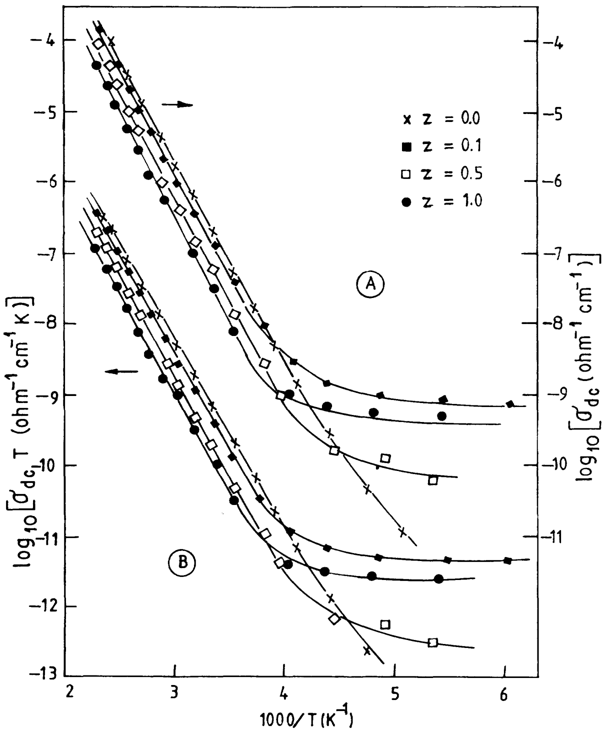

FIG. 3. (a) Thermal variation of dc conductivity (σ_{dc}) of different $Bi_4Sr_3Ca_{3-z}Li_zCu_4O_x$ glasses. (b) Variation of $\log_{10}[(\sigma_{dc}T)]$ vs $10^3/T$ curves for different 4:3:3:y glasses.

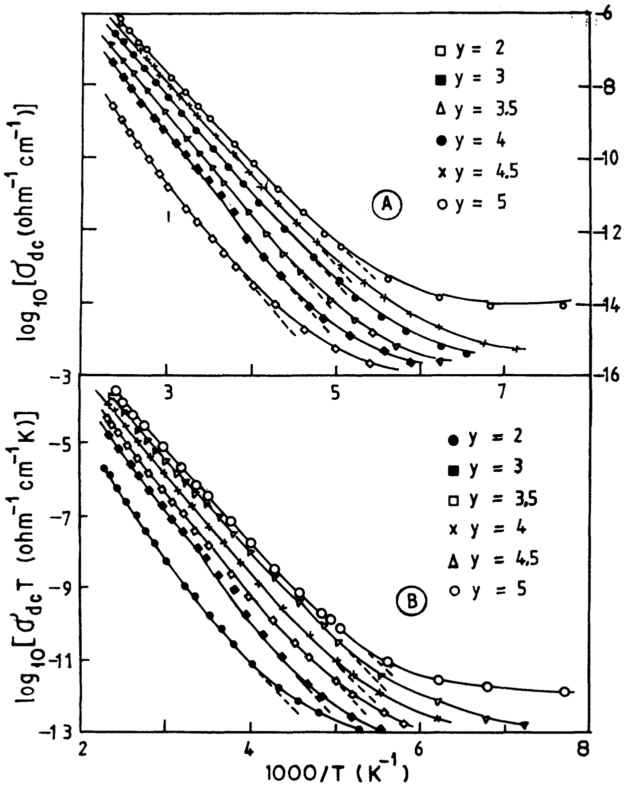

FIG. 2. (a) Thermal variation of dc conductivity (σ_{dc}) of different $Bi_4Sr_3Ca_3Cu_yO_x$ glasses. (b) Variation of $\log_{10}[(\sigma_{dc}T)]$ vs $10^3/T$ curves for different 4:3:3:y glasses.

Using a polaron hopping mechanism, the experimental conductivity data of these glasses could be explained[14,17] with an equation (in the nonadiabatic approximation) of the form[15]

$$\sigma_{dc}=\sigma_0\exp(-2\alpha R)\exp(-W/k_B T)\ , \qquad (1)$$

where $\sigma_0 = \nu_{\text{ph}} e^2 C(1-C)/k_B TR$, ν_{ph} is the optical phonon frequency, R is the average Cu-Cu spacing, k_B is Boltzmann's constant, and α is the wave-function decay constant. The activation energy W can be written as[15]

$$W = \begin{cases} W_h + W_d/2 \ , & (\text{for } T > \Theta_D/2) \\ W_d \ , & (\text{for } T < \Theta_D/4) \ , \end{cases} \tag{2}$$

where W_h and W_d are, respectively, the polaron hopping energy and disorder energy arising from the energy difference of the neighboring sites.

The presence of T^{-1} term in the preexponential factor of Eq. (1) suggests that a plot of $\log_{10}(\sigma_{\text{dc}} T)$ as a function of T^{-1} would be more appropriate to distinguish between the high- and the low-temperature region. Figures 2(b) and 3(b) show such curves, respectively, for the 4:3:3:y and Li-doped 4:3:$(3-z)$:4 glasses. The values of Θ_D determined from the departure from the linearity of these curves are shown in Table III. The values of Θ_D calculated for the Li-doped 4:3:$(3-z)$:4 glasses are higher than those of the 4:3:3:y glasses. The values of phonon frequency (ν_{ph}) calculated from different curves in Figs. 2 and 3 are in good agreement as shown in Table III. The values of ν_{ph} calculated from the infrared spectra corresponding to the characteristic absorption band[7,17] at 505–510 cm^{-1} is 1.53×10^{13} Hz, which is slightly higher but almost constant for all the glass samples studied (Table III). Both ν_{ph} and Θ_D of the Li-doped 4:3:$(3-z)$:4 glasses are higher than those of the pure 4:3:3:y glasses. The higher values of Θ_D and ν_{ph} are found to give higher values of T_c in the Li-doped superconducting glass ceramics.

The dc conductivity of semiconducting TMO glasses, such as 4:3:3:y and Li-doped 4:3:$(3-z)$:4 can be explained by considering hopping of polarons (electrons) between localized states. The values of different parameters like W, α, r_p (polaron radius), W_h, C, etc., as calculated from the σ_{dc} values following Eqs. (1) and (2) are shown in Tables I–IV. The value of W_h is calculated from the relation

$$W_h = W_p/2 = (e^2/4\epsilon_p)(r_p^{-1} - R^{-1}) \ , \tag{3}$$

where r_p is the polaron radius and ϵ_p is the effective dielectric constant ($\epsilon_p = \epsilon_\infty = n^2$, n is the refractive index of the glass). Since dielectric constant[17] of the 4:3:3:y glasses do not change much with CuO concentrations, the value of n, for all the 4:3:3:y glasses, is taken to be equal to 1.995, which was determined from the measurements of Brewster's angle.[14,17] W_h obtained from the slopes of the curves of Figs. 2 and 3 at two fixed temperatures (300 and 410 K) are shown in Table IV. The disorder energy (W_d) is calculated from the Miller-Abrahams theory.[18] The difference between W and W_h arises from the disorder term $W_d/2$ [Eq. (2)]. The values of W_d cal-

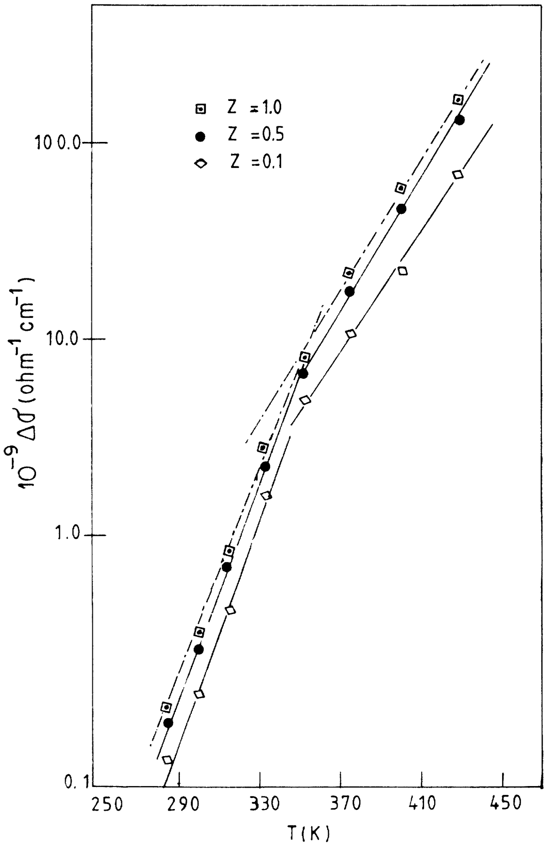

FIG. 4. Variation of excess conductivity $\Delta\sigma_{\text{dc}} = \sigma_{\text{dc}}$ (for 4:3:3:4 base glass) $-\sigma_{\text{dc}}$ (for the Li-doped 4:3:$(3-z)$:4 glass).

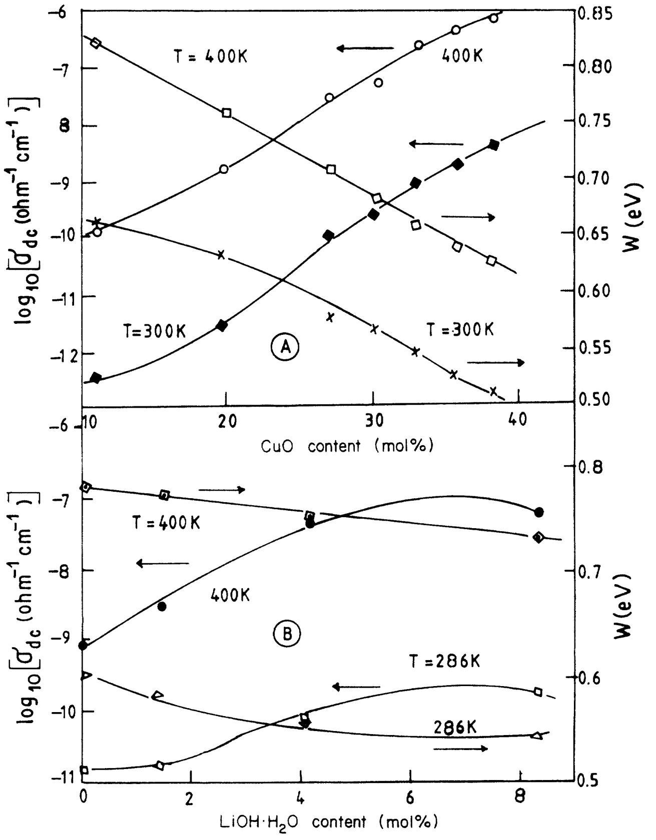

FIG. 5. Variation of dc conductivity (σ_{dc}) and activation energy (W) with Cu (a) and Li (b) concentrations in the 4:3:3:y and Li-doped 4:3:$(3-z)$:4 glasses, respectively, at two different fixed temperatures.

TABLE III. Some important parameters for the 4:3:3:y and Li-doped 4:3:(3$-z$):4 glasses obtained from the dc conductivity data.

	Debye temperature Θ_D (K)		Phonon frequency ν_{ph} (Hz)		
Sample	(a)	(b)	(a)	(b)	(c)
No. 3	484	480	1.01×10^{13}	1.00×10^{13}	1.11×10^{13}
No. 4	452	444	9.41×10^{12}	9.25×10^{12}	9.89×10^{12}
No. 5	444	424	9.25×10^{12}	8.83×10^{12}	9.31×10^{12}
No. 6	428	412	8.91×10^{12}	8.58×10^{12}	8.93×10^{12}
No. 7	420	396	8.75×10^{12}	8.25×10^{12}	8.70×10^{12}
No. 8	400	388	8.33×10^{12}	8.08×10^{12}	8.58×10^{12}
(Li-doped) No. 9	510		1.06×10^{13}		
(Li-doped) No. 10	500		1.04×10^{13}		
(Li-doped) No. 11	490		1.03×10^{13}		

[a] Calculated from the $\log_{10}(\sigma_{\mathrm{dc}})$ versus $10^3/T$ curve [Figs. 2(a) and 3(a)].

[b] Obtained from the $\log_{10}(\sigma_{\mathrm{dc}}T)$ versus $10^3/T$ curve [Fig. 2(b)].

[c] Obtained from the intercept of the $\log_{10}[\sigma_0/C(1-C)]$ versus R curve [Fig. 6(a)].

culated[18] from $W_d=0.3e^2/\epsilon_s R$ (where ϵ_s is the static dielectric constant) varies from 0.062 to 0.029 eV for the 4:3:3:y glasses. It is found that the disorder energy decreases with increase of CuO concentrations. This is also true for the other TMO glasses. We notice from Table IV that the values of ΔW ($=W-W_h$, at 300 K, say) vary in the range of 0.48–0.22 eV, which is much higher than the theoretically calculated values of $W_d/2$. Similar results have also been reported for the Fe_2O_3-Bi_2O_3 and vanadate glasses.[5,6] Since the C values {the ratio $[Cu^{1+}]/[Cu(total)]$} do not change much (see Table I) in the 4:3:3:y glasses for different CuO contents, this discrepancy in activation energy might be described as the effect of the partial charge of the cations of the glass forming oxides (Bi_2O_3, CaO, etc.).[19]

The importance of the tunneling term [$\exp(-2\alpha R)$] in Eq. (1) for the glasses could be understood[20] by plotting $\log_{10}\sigma_{\mathrm{dc}}$ against W at a fixed temperature. The temperature T_e estimated from the slope of such a plot would be close to the experimental temperature when the hopping is considered to be in the adiabatic regime.[20] On the other hand, T_e would be very different from the experimental temperature if the hopping is considered to be in the nonadiabatic regime. Such a plot for two fixed temperatures ($T=300$ and 410 K) is shown in Fig. 6(a). The temperatures estimated from the slopes of the curves are 195 and 260 K, respectively. Similarly for the Li-doped 4:3:(3$-z$):4 glasses such a plot for two fixed temperatures (286 and 400 K) the corresponding T_e values estimated are 647 and 915 K, respectively. Thus, the higher values of T_e from the corresponding experimental temperatures suggest nonadiabatic polaron hopping conduction in the 4:3:3:y and Li-doped 4:3:(3$-z$):4 glasses. The nonadiabatic hopping character is also supported from the validity of Holstein's condition[21] as discussed below.

For adiabatic hopping the polaron bandwidth J should satisfy the following condition,[21] viz.,

$$J>H\ , \tag{4}$$

where

TABLE IV. Some electrical parameters of the 4:3:3:y and Li-doped 4:3:(3$-z$):4 obtained from the conductivity data.

	σ_{dc} (ohm^{-1} cm^{-1})		W (eV)		W_h^{a}	ΔW	W_d^{b}
Sample	at 300 K	at 410 K	300 K	410 K	(eV)	(eV)	(eV)
No. 2	1.03×10^{12}	8.70×10^{-10}	0.660	0.820	0.18	0.480	0.062
No. 3	2.42×10^{-12}	1.50×10^{-9}	0.634	0.760	0.22	0.414	0.043
No. 4	9.00×10^{-11}	2.53×10^{-8}	0.580	0.709	0.25	0.330	0.050
No. 5	2.05×10^{-10}	4.71×10^{-8}	0.568	0.684	0.26	0.308	0.030
No. 6	7.70×10^{-10}	2.31×10^{-7}	0.544	0.656	0.28	0.264	0.029
No. 7	1.70×10^{-9}	3.80×10^{-7}	0.526	0.637	0.28	0.246	0.037
No. 8	3.90×10^{-9}	6.95×10^{-7}	0.510	0.625	0.29	0.220	0.029
(Li-doped) No. 9	4.29×10^{-10}	1.46×10^{-7}	0.561	0.643	0.28	0.281	0.029
(Li-doped) No. 10	2.15×10^{-10}	8.57×10^{-8}	0.588	0.664	0.29	0.298	0.029
(Li-doped) No. 11	1.25×10^{-10}	4.29×10^{-8}	0.591	0.682	0.30	0.291	0.030

[a] Calculated from Eq. (3) assuming $\epsilon_p=\epsilon_\infty=n^2$ (with $n=1.995$).

[b] Calculated from $W_d=0.03e^2/\epsilon_s R$. The values of ϵ_s were estimated from the experimental dielectric constant data of the samples (Ref. 17).

$$H = (2k_B T W_h/\pi)^{1/4}(\hbar\omega_{\mathrm{ph}}/\pi)^{1/2} \, .$$

Similarly for nonadiabatic hopping one has $J < H$. The condition for the formation of small polaron is $J < W_h/3$. An estimation of J can be made from the approximate relation

$$J \approx e^3[N(E_F)]^{1/2}/\epsilon_p^{3/2} \, . \tag{5}$$

The right-hand side of Eq. (4) gives a value of 0.03–0.04 eV. From Eq. (5) one finds $J = 0.02$ eV for a value of $N(E_F) = 10^{20}$ eV^{-1}cm^{-3} [$N(E_F)$ is the density of states at the Fermi level obtained from the ac conductivity data of the 4:3:3:y glasses[17]]. The condition for small-polaron formation ($J < W_h/3$) is also satisfied. The estimated value of J obtained from Eq. (5) is slightly less than the right-hand side of Eq. (4), which indicates that the small-polaron hopping occurs in the nonadiabatic regime. Nonadiabatic hopping conduction in the present glass systems is also supported from other facts as illustrated below.

The wave-function decay constant (α) can be obtained experimentally from the slope of $\log_{10}[\sigma_0/C(1-C)]$ versus R curve [Fig. 6(a)]. Murawski and Gzowski[22] have shown that $\log_{10}\sigma_0$ is a linear function of R in iron-phosphate glasses and σ_0 [Eq. (1)] should be divided by $[C(1-C)]$ as the value of C may vary for different glass compositions. From the slope of the linear curve [Fig. 6(a)] the value of α is found to be 0.67 Å^{-1}. This value of α is well within the limit suggested by Austin and Garbett[23] and also satisfies the requirement for applying small-polaron theory, viz., $\alpha^{-1} < r_p < R$. Murawski, Chung, and Mackenzie[24] have shown that the value of α ranges from 0.4–4 Å^{-1} for a series of TMO glasses. The values of α can also be calculated from Eq. (1) by inserting the values of N, R, and C from Tables I and II and assuming a reasonable value of $\nu_{\mathrm{ph}} = 10^{13}$ Hz. We have already estimated from IR spectra a value of $\nu_{\mathrm{ph}} = 1.53 \times 10^{13}$ Hz for the 4:3:3:y-type glasses. The values of $\nu_{\mathrm{ph}}\exp(-2\alpha R)$ calculated from the conductivity data is shown in Table V. It is noticed from Table V that the values of $\nu_{\mathrm{ph}}\exp(-2\alpha R)$ varying from 2.92×10^9 to 1.69×10^{10} Hz are much less than the corresponding values of the TMO glasses obeying adiabatic hopping conduction. This also suggests that the nonadiabatic conduction mechanism is valid for the 4:3:3:y and Li-doped 4:3:$(3-z)$:4 glasses. The values of ν_{ph} have also been calculated from the conductivity data assuming $\alpha = 0.67$ Å^{-1} as obtained from the slope of Fig. 6(a) and using the values of R, N, and C from Table I. These values of ν_{ph} (shown in Table V) are little less than those obtained from the IR absorption spectra. The IR spectra, as mentioned above, gives more or less constant values of ν_{ph} for all 4:3:3:y glasses, whereas the values of ν_{ph} obtained from the conductivity data of the glasses decreases with the increase of CuO concentrations of the glasses. The values of ν_{ph} calculated from Θ_D values (Table III) also show this trend of variation of ν_{ph} (see Table III).

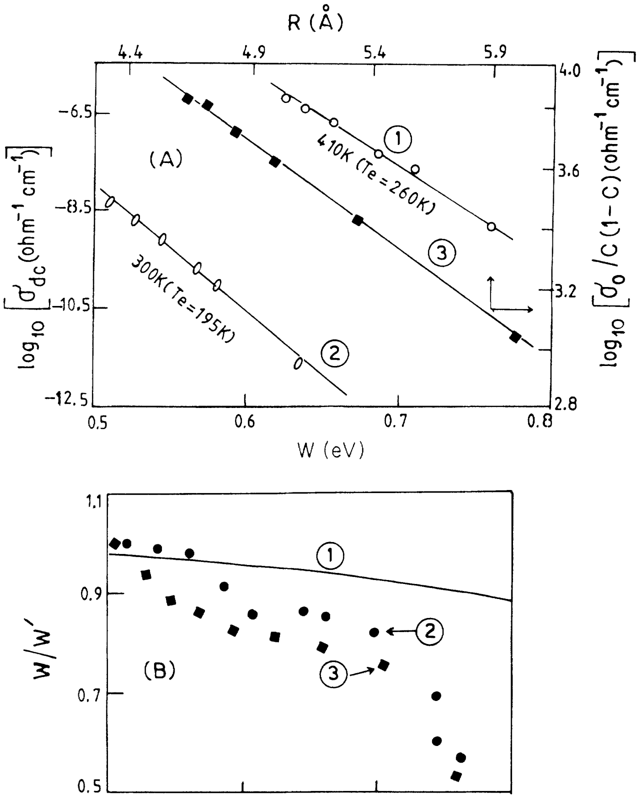

FIG. 6. (a) Plot of $\log_{10}(\sigma_{dc})$ vs activation energy (W) for the 4:3:3:y glasses at two fixed experimental temperatures, 410 K (1) and 300 K (2). The temperatures T_e within the parentheses are obtained from the slopes of the curves; variation of $\log_{10}[\sigma_0/C(1-C)]$ with R (mean separation between Cu sites) for the 4:3:3:y glasses (3). (b) Plot of W/W' vs $10^3/T$ for the $\mathrm{Bi_4Sr_3Ca_3Cu_4O_x}$ (3) and $\mathrm{Bi_4Sr_3Ca_{3-z}Li_zCu_4O_x}$ (for $z = 1.0$ only) (2) glasses. The theoretical curve (1) is obtained from Eq. (7).

The values of small-polaron coupling constant (γ_p), which is a measure of electron-phonon interaction in the glasses, can be estimated from the relation[15] $\gamma_p = 2W_h/h\nu_{\mathrm{ph}}$. Using the values of W_h from Table IV and $\nu_{\mathrm{ph}} = 10^{13}$ Hz, the calculated values of γ_p listed in Table V are found to vary from 8.69 to 14 for the 4:3:3:y-type glasses. Austin and Mott[15] suggested that a value of $\gamma_p > 4$ usually indicates strong electron-phonon interaction in solids. From the values of γ_p, we have evaluated the effective mass (m_p) of the polaron in the glasses using the relation[15]

$$m_p = (h/2JR^2)\exp(\gamma_p) = m^*\exp(\gamma_p) \, , \tag{6}$$

where m^* is the rigid-lattice effective mass. The calculated values of γ_p and m_p/m^* are found to be quite large indicating strong electron-phonon interaction in these glasses, which also supports the formation of small polarons in them.[25] The values of m_p/m^* for the Li-doped 4:3:$(3-z)$:4 glasses are a little bit higher (see Table V) than those of the Li-free glasses.

Schnakenberg[26] suggested that with the lowering of temperature the multiphonon processes are replaced by a single phonon (optical) process and the activation energy for conduction should follow the relation

TABLE V. Some electrical parameters characterizing the 4:3:3:y and Li-doped 4:3:(3$-z$):4 glasses.

Sample	$\nu_{ph}\exp(-2\alpha R)$ (Hz)	ν_{ph}^{a} (Hz)	α^{b} (Å^{-1})	α^{c} (Å^{-1})	$\gamma_p^{d}=2W_h/\hbar\omega_{ph}$	$m_p/m^*=\exp(\gamma_p)$
No. 2	2.92×10^{9}	1.34×10^{13}	0.47	0.98	8.69	5.9×10^{3}
No. 3	4.00×10^{9}	1.25×10^{13}	0.46	0.92	10.62	4.1×10^{4}
No. 4	7.78×10^{9}	1.01×10^{13}	0.45	1.23	12.07	1.7×10^{5}
No. 5	1.13×10^{10}	9.57×10^{12}	0.45	0.99	12.56	2.8×10^{5}
No. 6	1.38×10^{10}	8.88×10^{12}	0.44	0.97	13.52	7.5×10^{5}
No. 7	1.64×10^{10}	8.94×10^{12}	0.44	0.75	13.52	7.5×10^{5}
No. 8	1.69×10^{10}	8.40×10^{12}	0.44	0.87	14.00	1.2×10^{6}
(Li-doped) No. 9	3.28×10^{10}	1.06×10^{13}	0.58		13.61	8.1×10^{5}
(Li-doped) No. 10	2.20×10^{10}	1.04×10^{13}	0.63		13.81	1.0×10^{6}
(Li-doped) No. 11	1.15×10^{10}	1.02×10^{13}	0.71		14.29	1.6×10^{6}

[a] Calculated from $\nu_{ph}\exp(-2\alpha R)$ assuming $\alpha=0.67\ \text{Å}^{-1}$ as obtained from the slope of $\log_{10}[\sigma_0/C(1-C)]$ versus R curve [Fig. 6(a)].

[b] Calculated from the values of $\nu_{ph}\exp(-2\alpha R)$ assuming $\nu_{ph}=10^{13}$ Hz.

[c] Obtained from the slope of $\log_{10}(\sigma_{dc}T^{1/2})$ versus $T^{-1/4}$ curve (Fig. 7).

[d] Assuming $\omega_{ph}/2\pi=10^{13}$ Hz.

$$W/W'=\tanh(\hbar\omega_{ph}/4k_BT)/(\hbar\omega_{ph}/4k_BT)\ , \qquad (7)$$

where W' is the high-temperature activation energy. In Fig. 6(b), the experimental as well as theoretical values of W/W' for one typical glass sample ($Bi_4Sr_3Ca_3Cu_4O_x$) are plotted as a function of temperature. All the other members of the 4:3:3:y glasses also behave almost similarly. It is observed from Fig. 6(b) that both the experimental and theoretical values of W/W' decrease with the decrease of temperature but the quantitative fit is rather poor. Almost similar is the case with Li-doped glasses [Fig. 6(b)]. It should be mentioned here that the fall in activation energy with temperature is quite consistent in the light of polaron hopping model of dc conductivity.

At sufficiently low temperature where the polaron binding energy is small and static disorder energy of the glass plays a dominant role in the conduction process, Mott's $T^{-1/4}$ analysis for the variable range hopping (VRH) can in general be applied for the TMO glasses. But for the 4:3:3:y and Li-doped 4:3:(3$-z$):4 glasses sufficient data at low temperature is not available due to experimental limitations and very high resistivity of the samples. An attempt to verify the applicability of this law gives unacceptably large values of α and W_d. In an alternative way, Greaves[27] suggested a variable range hopping conduction in the intermediate temperature range and derived an expression for the conductivity as

$$\sigma_{dc}T^{1/2}=L\exp(-B/T^{1/4})\ , \qquad (8)$$

where B and L are constants. The slope (B) of $\log_{10}(\sigma_{dc}T^{1/2})$, versus $T^{-1/4}$ curve is given by

$$B=2.1[\alpha^3/k_BN(E_F)]^{1/4}=2.4[W_d(\alpha R)^3/K_B]^{1/4}\ . \qquad (9)$$

Figure 7 shows the plot of $\log_{10}(\alpha_{dc}T^{1/2})$ as a function of $T^{-1/4}$ for some of the 4:3:3:y and Li-doped 4:3:(3$-z$):4

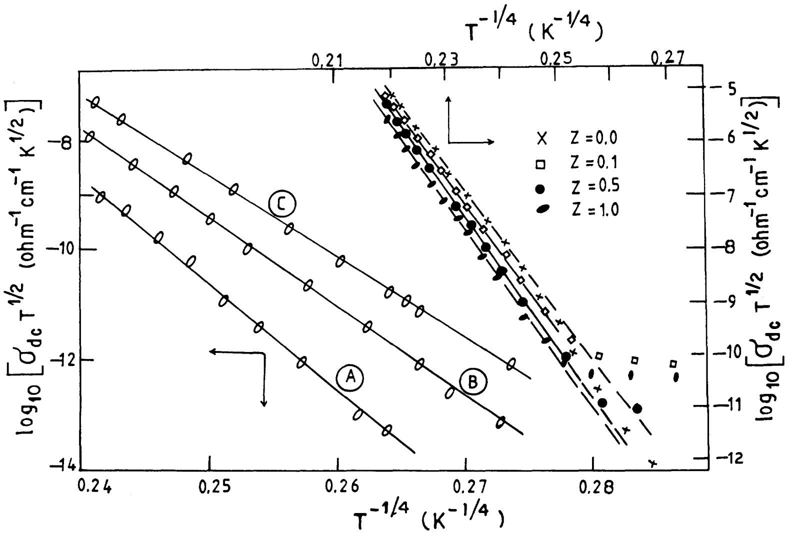

FIG. 7. Plot of $\log_{10}[(\sigma_{dc}T^{1/2})]$ vs $T^{-1/4}$ for the $Bi_4Sr_3Ca_3Cu_yO_x$ [$y=3$ (A), $y=4$ (B), $y=5$ (C)] and $Bi_4Sr_3Ca_{3-z}Li_zCu_4O_x$ glasses.

glasses. Other members also follow similar behavior. From the slopes (B) of the curves the values of α and W_d have been calculated using Eq. (9). The calculated values of α from Greaves' $T^{-1/4}$ plot shown in Table V are higher than those obtained from the dc conductivity data at higher temperatures but still they are well within the limit suggested by Austin and Garbett.[23] The calculated values of W_d from Eq. (9) are unacceptably large. This type of large value of W_d was also reported for the vanadate[28] and $\mathrm{Bi_2O_3}$-$\mathrm{Fe_2O_3}$ glasses.[6]

IV. CONCLUSION

The dc conductivities of the Li-doped $4{:}3{:}(3-z){:}4$ glasses are lower than those of the undoped 4:3:3:y glasses. Electrical conduction in both the glasses are found to be, due to hopping of small polarons between localized sites and the hopping process occurs, unlike many other TMO glasses, in the nonadiabatic regime. In the high-temperature region the activation energy W decreases slowly with the decrease of temperature and the conduction process is dominated by the thermally activated nearest-neighbor hopping of small polarons. In the intermediate- and low-temperature regions the VRH conduction appears to be more appropriate. The fitting of the experimental conductivity data with Greaves' relation[27] [Eq. (8)] at intermediate temperature shows qualitative agreement but the quantitative fit is not very good. An attempt to fit the low-temperature conductivity data of some glasses with Mott's VRH (Refs. 15 and 25) gives unacceptably large values of the disorder energy W_d and wave-function decay constant α.

Partial replacement of Ca by Li is found to increase the superconducting transition temperatures (T_c) by 4–5 K in the corresponding glass ceramics (see Table II). Since the electrical conductivities of both 4:3:3:y and Li-doped $4{:}3(3-z){:}4$ glasses behave similarly it appears that Li or another alkali metal acts as a flux in the glass matrix to lower the melting point of the glasses and finally to increase the superconducting T_c by reducing the possibility of oxygen loss in the glass ceramics. Recent experimental results on alkali-metal doped superconducting ceramics[29] indicate that Li gets some preferred position in the Cu sites in the three-dimensional lattice. Addition of Li has, however, little effect on the overall microstructural behavior of the Li-doped $4{:}3{:}(3-z){:}4$ glasses, which is also indicated from the similar nature of the temperature dependent electrical and other properties of 4:3:3:y and Li-doped $4{:}3{:}(3-z){:}4$ glasses.

Finally, it would be worthwhile to point out that the theoretical discussion made in this paper could also be extended for explaining the conductivity of polymers and ionic conductors.

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