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1998 J. Phys.: Condens. Matter 10 9413

(http://iopscience.iop.org/0953-8984/10/42/007)

J. Phys.: Condens. Matter **10** (1998) 9413–9418. Printed in the UK PII: S0953-8984(98)93828-0

Transport properties of semiconducting $Pb_2Sr_2CaCu_3O_8$ glass

M Sural and A Ghosh†

Department of Solid State Physics, Indian Association for the Cultivation of Science, Jadavpur, Calcutta 700032, India

Received 1 May 1998

Abstract. The dc electrical transport in the semiconducting $Pb_2Sr_2CaCu_3O_8$ glass has been investigated in the temperature range 80–400 K. The analysis of the dc conductivity in terms of different hopping models shows that the multiphonon hopping of localized electrons with weak electron–phonon interaction is the dominant charge transport mechanism in this multicomponent glass. The physical parameters obtained from the best fit of the data to this theory are reasonable for the weak coupling regime. It has been observed that the variable range and the small polaron hopping theories cannot interpret the observed conductivity data quantitatively.

1. Introduction

The multicomponent oxide glasses based on the unconventional network former PbO are of great interest because they form amorphous materials without traditional network formers such as SiO_2 and they can be used in optical and optoelectronic devices, reflecting windows, etc [1–4]. However, a few studies have been reported on the PbO based glasses. It has been reported [5] that Pb^{2+} ions are highly polarizable and the asymmetry of their polyhedra inhibits the crystallization process in the melts in which they participate. In silicate glasses, when PbO is added, it acts as a network modifier for low concentration, while at high concentration it is capable of participating in the network [6]. Recently, glasses in which PbO acts as a main network former have been synthesized and their structures have been studied [7–10]. The electrical properties of these glasses have not been reported so far, except a few reports [11, 12] on some binary cuprate glasses based on the network former PbO. In the present paper we have studied the electrical properties of the multicomponent $Pb_2Sr_2CaCu_3O_8$ glass in which PbO acts as a glass network former. This material is of interest, because its crystalline form exhibits superconducting properties when 20–80% of the divalent Ca ions is replaced by trivalent rare earth ions except Ce [13–15]. It has been observed that the multiphonon hopping of electrons with weak electron–phonon interaction is the dominant conduction mechanism in this multicomponent cuprate glass.

2. Experiment

The $Pb_2Sr_2CaCu_3O_8$ glass sample was prepared from high purity PbO, $SrCO_3$, $CaCO_3$ and CuO. The appropriate mixture of these chemicals in a 10 g batch was melted in a platinum

† Author to whom all correspondence should be addressed.

0953-8984/98/429413+06$19.50

crucible at 1200 °C in an electric furnace for 2 h and then poured onto a twin roller. Glass flakes of area ∼1.0–1.6 cm^2 and thickness ∼0.01 cm were obtained. The amorphous nature of the sample was confirmed from x-ray diffraction studies (Siefert, model C-3000). The density of the sample was measured by Archimedes' principle using acetone as an immersion liquid. The concentration of the total Cu ions present in the sample was estimated from the glass composition and density. An ESR spectrum was take at room temperature to determine the carrier density. An FT–IR spectrum of the powdered sample in KBr matrix was taken in the range 400–4000 cm^{-1} (Nicolet, model IR 700) to determine the phonon frequency. For electrical measurement gold electrodes (of area ∼1 cm^2 and thickness ∼200 Å) were deposited on both surfaces of the sample by vacuum evaporation. The gold coated sample was heat treated at 150 °C for stabilization of the gold electrode. The electrical measurements were carried out in the temperature range 80–400 K by a Keithley electrometer (model 617). Before measurement, absence of barrier layers at the contacts was confirmed from linear I–V characteristics. For low temperature measurements, the sample cell was inserted in a cryogenic unit.

3. Results and discussion

The dc conductivity (σ) of the $Pb_2Sr_2CaCu_3O_8$ glass is shown in figure 1 as a function of reciprocal temperature. It is clear from the figure that the sample behaves as a semiconductor and the conductivity exhibits a nonactivated behaviour. The activation energy decreases continuously with the decrease of temperature. These results are analysed below in terms of different theories.

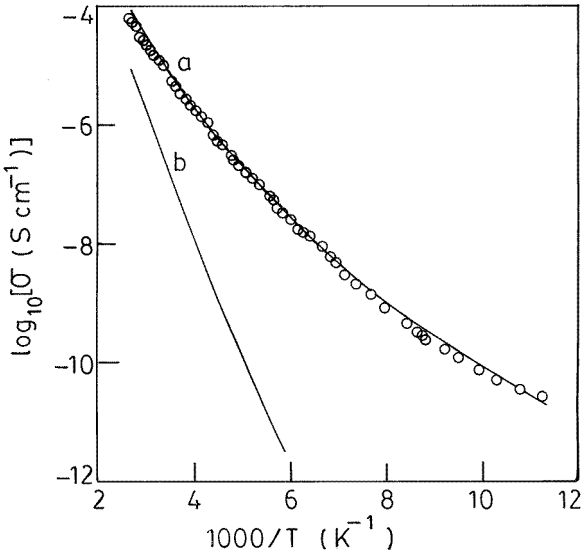

Figure 1. Logarithmic conductivity shown as function of reciprocal temperature. The solid curves a and b are best fits of the small polaron theory (equations (2)–(4)) to the data for the parameters shown in the text.

It is well known [16–18] that the nonactivated transport can be described by the variable range hopping of charge carriers between localized states. In fact, the variable range hopping has been observed in a large number of materials such as semiconducting glasses [19, 20],

superconducting cuprates and their parent compounds etc [21–25]. The variable range hopping theory [16–18] in three dimensional cases predicts

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

where the exponent T_0 is given by $T_0 = 16\alpha^3/kN(E_F)$. Here α^{-1} is the Bohr radius of the localized states and $N(E_F)$ is the density of states at the Fermi level. The conductivity data presented in figure 1 are shown in figure 2 as a function of $T^{-1/4}$. It is noted that the data can be described by a single straight line in the entire temperature range of measurements. The least squares straight line fit yields $\sigma_0 = 1.82 \times 10^{11}$ S cm^{-1} and $T_0 = 5.9 \times 10^8$ K. Both the exponent T_0 and the preexponential factor σ_0 can be used to extract $N(E_F)$. However, $N(E_F)$ cannot be obtained independently of α. Assuming a value of $\alpha^{-1} = 10$ Å (which is the usual practice for strong localization [26]) a value of $N(E_F) = 3.14 \times 10^{17}$ eV^{-1} cm^{-3} is obtained from $T_0 = 16\alpha^3/N(E_F)$. This value of $N(E_F)$ is lower than the values (10^{18}–10^{19} eV^{-1} cm^{-3}) observed for the semiconducting glasses [17, 26]. It may be noted that preexponential term σ_0 is anomalously high and yields an unphysically large value of $N(E_F)$. This behaviour is not fully understood, but may be due to the assumption of a single phonon in the development of the theory [26]. This theory has been criticized recently [27]. It is thus suspected that the dc transport in the $Pb_2Sr_2CaCu_3O_8$ glass cannot be dominated by the variable range hopping theory.

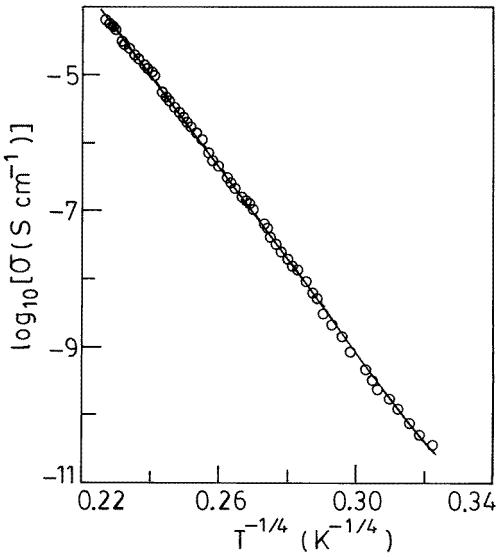

Figure 2. Logarithmic conductivity shown as a function of $T^{-1/4}$. The solid line is the least squares straight line fit to the data.

It may be noted that the nonactivated dc transport observed in figure 1 is similar to that observed for small polarons [28–32]. A small polaron is formed when electron–phonon interaction is strong enough [28]. In polaron formation electrons could couple strongly with both the acoustic and optical phonons. Different small polaron hopping theories have been proposed in the literature [29]. We shall consider here a small polaron theory [31] that takes the acoustic as well as optical phonons into consideration.

The dc hopping conductivity, in general, can be written as [17]

$$\sigma = n_c e^2 R^2 \Gamma / 6kT \tag{2}$$

where n_c is the carrier density, R is the hopping distance and Γ is the hopping rate. Following Holstein [28], Gorham-Bergeron and Emin [31] have calculated the nonadiabatic multiphonon hopping rate for small polarons considering both acoustic and optical phonon coupling. The hopping rate in their theory is given by

$$\Gamma = (J/\hbar)^2[\hbar^2\pi/2(E_C^{op}+E_C^{ac})kT]^{1/2}\exp[-\Delta^2/8(E_C^{op}+E_C^{ac})]\exp(-\Delta/2kT) \times \exp(-E_A^{op}/kT - E_A^{ac}/kT] \tag{3}$$

where J and Δ are the transfer integral and the energy difference between two sites respectively. E_C^{op}, E_C^{ac}, E_A^{op} and E_A^{ac} are defined as follows:

$$\begin{aligned} E_C^{op} &= (h^2/4kT)(2E_b/\hbar\omega_0)\mathrm{cosec}(\hbar\omega_0/2kT)\omega_0^2 \\ E_C^{ac} &= (\hbar^2/4kT)(1/N)\sum_g (E_b^{ac}/h\omega_{g,ac})\mathrm{cosec}(\hbar\omega_{g,ac})\omega_{g,ac}^2 \\ E_A^{op} &= (2kT/\hbar\omega_0)E_b^{op}\tanh(\hbar\omega_0/4kT) \\ E_A^{ac} &= (1/N)\sum_g (2kT/\hbar\omega_{g,ac})E_b^{ac}\tanh(\hbar\omega_{g,ac}/4kT) \end{aligned} \tag{4}$$

where $\omega_0 = 2\pi\nu_0$ is the mean optical frequency, $\omega_{g,ac}$ is the acoustic phonon frequency at wavevector g and N is the number of phonon modes. E_b^{op} and E_b^{ac} are the polaronic binding energies related to optical and acoustic phonons respectively.

The calculated best fit results using equations (2)–(4) are shown in figure 1 by the solid curve a. The phonon density of states was approximated to be $g(\omega) \propto \omega^2$ for acoustic phonons and the mean optical phonon frequency ν_0 was assumed constant. The physical parameters required for the best fit are $E_b^{op} = 0.56$ eV, $E_b^{ac} = 0.48$ eV, $\Delta = 0.097$ eV, $\nu_0 = 3.57 \times 10^{13}$ s^{-1}, $J = 0.038$ eV and $R = 12.5$ Å. In the calculation, the value of the carrier density $n_c \cong 1\times10^{21}$ cm^{-3} obtained from the ESR measurement was used. It may be noted that the value of $J = 0.038$ eV obtained from the fit is reasonable for the small polaron hopping in the nonadiabatic regime. However, the value of the optical phonon frequency is higher than the phonon frequency $\nu_0 = 1.5 \times 10^{13}$ s^{-1} corresponding to a absorption band at 500 cm^{-1} observed in the FT–IR spectrum of the glass. Using the experimental value of $\nu_0 = 1.5 \times 10^{13}$ s^{-1}, the curve b in figure 1 was calculated. Clearly there is no fit of the data to the theory in this case. Thus the small polaron hopping theory cannot predict quantitatively the temperature dependence of the conductivity. It is worth noting that the temperature dependence of the electrical conductivity for the binary cuprate glasses [11] based on the same glass former PbO as for the present multicomponent glass was adequately explained by the small polaron hopping theory in sharp contrast to the present glass system. It may be mentioned that the failure of the small polaron hopping in the multicomponent glass might be due to difference in the structure of the multicomponent glass from that of the binary glasses [10]. The small value of the intersite separation R ($\sim$5 Å) of the binary glasses [11] favours the formation of small polarons. The intersite separation ($\sim$12.5 Å) for the multicomponent glass is comparatively large and is not favourable for small polaron formation.

The dc conductivity data are replotted in figure 3 as a function of logarithmic temperature. The figure also shows that the conductivity is proportional to T^n for a considerable temperature range. A value of $n = 11.3$ was calculated from the least squares straight line fit. As shown below the results can be interpreted in terms of multiphonon hopping of charge carriers with weak electron–phonon interaction.

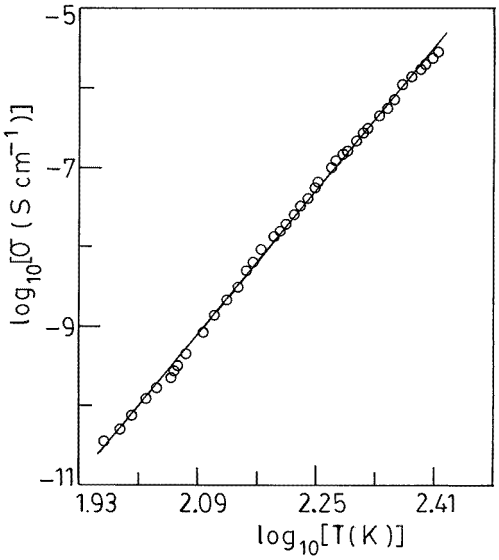

Figure 3. Logarithmic conductivity shown as a function of logarithmic temperature. The solid line is the least squares straight line fit to the data.

Different authors [17, 30, 33] have calculated the hopping rate for the multiphonon hopping processes with weak electron–phonon interaction, that can be written as

$$\Gamma = C\exp(-\gamma p)[kT/h\nu_0]^p \tag{5}$$

where $C \sim \nu_0$, $p = \Delta/h\nu_0$ and $\gamma = \ln(\Delta/E_m) - 1$. ν_0 is a phonon frequency which is most effectively coupled to weakly localized electrons. An electron overlap term, $\exp(-2\alpha R)$, is implicitly involved in the constant C. The parameter γ or E_m is a measure of the electron–phonon coupling strength. The multiphonon processes involve absorption and emission of p phonons and thus p is an integral number. However if Δ or ν_0 is distributed around a certain value, p may have a finite distribution and its mean value will be nonintegral. The experimentally observed non-integral value of p indicates such a situation in the present case. As the carrier density n_c in equation (2) must be given by $N(E_F)kT$, the conductivity obtained from equations (2) and (5) is proportional to T^p, which is observed experimentally in figure 3.

The validity of the multiphonon hopping model with weak electron–phonon coupling requires an estimation of the parameter γ in equation (5). Using the value of $\nu_0 = 1.5 \times 10^{13}$ s^{-1} obtained from infrared data and the measured value of the dc conductivity, γ was estimated from equations (2) and (5). In calculation, the carrier density n_c obtained from ESR measurement was used. The estimated γ values at $T = 100$ K and 304 K are 0.66 and 0.61 respectively. These values of γ are reasonable for weak coupling regime [17, 33]. Robertson and Friedman [33] have shown that the condition for the weak coupling regime is $E_m/h\nu_0 \ll 1$. Englman and Jortner [34] have shown that weak coupling regime should satisfy the condition $G = (E_m/h\nu_0)(kT/h\nu_0) < 1$. We have obtained $G = 0.3$ for measurement at $T = 100$ K and $G = 0.7$ for measurement at 304 K. These values clearly satisfy the condition for the weak coupling regime. Thus the multiphonon hopping with weak electron–phonon coupling dominates the dc transport in the $Pb_2Sr_2CaCu_3O_8$ glass.

4. Conclusion

We have investigated the temperature dependence of the dc electrical conductivity of the $Pb_2Sr_2CaCu_3O_8$ glass in the temperature range 80–400 K. It is observed that charge transport is nonactivated and cannot be explained quantitatively by variable range hopping or small polaron hopping theories. The multiphonon hopping theory with weak electron–phonon interaction can predict the temperature dependence of the conductivity data quantitatively. The parameters obtained from this model are reasonable and satisfy the condition for the weak coupling regime.

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