Asian Journal of Chemistry Vol. 18, No. 5 (2006), 3321-3324

DC Conductivity of Copper-Bismuth Glasses Doped with TiO_2 and ZnO

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The dc electrical conductivity of glasses with composition 40CuO-40Bi_2O_3-20TiO_2 and 40CuO-40Bi_2O_3-20ZnO prepared by rapid quenching method has been investigated over the temperature range 300-600 K. The glassy phase is confirmed from X-ray diffraction (XRD) pattern which shows a broad hump around $2\theta = 30°$. The dc conductivity of ZnO doped glass at all the temperatures is higher than that of the corresponding composition doped with TiO_2 but the general trend of the increase or decrease of conductivity and activation energy are similar in both the glasses. Holstein's relation suggests that hopping conduction is in non-adiabatic region for both the glasses.

Key Words: Glass, DC conductivity, Small polarons.

INTRODUCTION

Transition metal oxide (TMO) glasses are being investigated since three-four decades due to their technological importance[1]. P_2O_5, TeO_2 are known as conventional glass network formers whereas Bi_2O_3, PbO *i.e.,* heavy metal oxides are in the category of unconventional glass network formers being very important due to their various important applications[2]. Dc conductivity in copper-bismuth glasses is explained by small-polaron hopping[3] (SPH) model. This is observed in many TMO glasses[4-6]. The conduction in these glasses takes place by the transfer of electrons from lower to higher valency transition metal ions. Again, TiO_2 and ZnO are very important candidates for future technology such as spintronics, diluted magnetic semiconductors (DMS) technology, etc. They easily produce the electron-hole pairs by the exposure of ultra violet (UV) light which is necessary for photo processes[7]. Herein, the comparison of dc conductivity incorporated with the presence of guests TiO_2 and ZnO in copper-bismuth glasses is reported.

EXPERIMENTAL

Reagent grade chemicals of CuO, Bi_2O_3, TiO_2 and ZnO (with purity more than 99%) were mixed at stoichiometric ratio (*i.e.* 40 mol % CuO, 40 mol % Bi_2O_3 and 20 mol % TiO_2 for sample A and 40 mol % CuO, 40 mol % Bi_2O_3 and 20 mol % ZnO for sample B) and grinded in an agate mortar for two hours. The mixture was heated at 500°C for two hours to evaporate the moisture (if any), cooled and again grinded. It was once more sintered at 800°C for 4 h. Finally, the grinded mixed

oxide was melted at a temperature of 1100°C in a high temperature programmable muffle furnace for one hour and stirred several times for better mixing. The melt was then poured on a highly polished copper block in air and quenched by another highly polished copper block. This gave the opaque glass with shining surfaces. The sample was then annealed at 250°C to remove the micro-cracks (if any) during the glass formation. A small amount of the glass was powdered for the measurement of X-ray diffraction pattern. Glassy phase of the sample was confirmed by XRD pattern as it showed a broad hump at 2θ *ca.* 30°. Both surfaces of a properly shaped glass were highly polished and cleaned by acetone. Then the surfaces were coated with silver paste and heat-treated at 100°C for four hours to stabilize the electrodes. The dc conductivity of the sample was measured by using a Keithley Digital Multimeter (Model 2000) in the temperature range 300-600 K.

RESULTS AND DISCUSSION

DC conductivity (σ_{dc}) of these glasses can be explained by a polaron hopping mechanism (in the non-adiabatic approximation) with the following formula[3], $\sigma_{dc} = (\sigma_o/T) \exp(-W/k_BT)$, where $\sigma_o = \nu_{ph}Ne^2R^2C_v(1-C_v) \exp(-2\alpha R)/k_B$, T is the absolute temperature and W is the activation energy. Here, ν_{ph} is an optical-phonon frequency (*ca.* 10^{13} Hz), N is the number of transition-metal ions (TMIs) per unit volume, e is the electronic charge, R is the average Cu-Cu spacing (*ca.* $N^{-1/3}$), C_v is the ratio of the TMI concentration in the low valence state to the total TMI concentration, α is the wave function decay constant and k_B is the Boltzmann constant. It should be mentioned here that the integral $I = \exp(-2\alpha R)$ reduces to 1.0 in the adiabatic case. The activation energy W is given by[3] $W = W_h + W_d/2$ for $T > \theta_D/2$ and, $W = W_d$ for $T < \theta_D/4$, where θ_D is the Debye temperature and is given by $h\nu_{ph} = k_B\theta_D$, h being the Planck constant, W_h is the polaron-hopping energy equal to $W_p/2$, W_p is the polaron binding energy and W_d is the disorder energy arising from the energy difference of the neighbouring sites. W_h is estimated from the relation[3] $W_h = W_p/2 = (e^2/4\varepsilon_p)(r_p^{-1} - R^{-1})$, where r_p ($\sim \frac{1}{2}(\pi/6)^{1/3}R$) is the polaron radius and ε_p is the effective dielectric constant ($\varepsilon_p = \varepsilon_\infty = n^2$, n is the refractive index of the glass). The value of n is *ca.* 1.995, which can be determined from the measurement of Brewster's angle. The calculated value of W_h are then found to be *ca.* 0.3507 eV for sample A and 0.3601 eV for sample B. Fig. 1 shows the Arrhenius plots of $\log_{10}(\sigma_{dc})$ and $\log_{10}(\sigma_{dc}T)$ for the glasses. At 410, 450, 500 and 560 K temperatures, the estimated dc conductivities are 3.93×10^{-8}, 6.27×10^{-8}, 1.32×10^{-7} and 4.60×10^{-7} ohm^{-1} cm^{-1} for sample A and 5.94×10^{-7}, 1.22×10^{-6}, 2.90×10^{-6} and 6.44×10^{-6} ohm^{-1} cm^{-1} for sample B, the activation energies at the above temperautres are 0.36, 0.385, 0.408 and 0.421 eV

for sample A and 0.303, 0.316, 0.328 and 0.345 eV for sample B, respectively. It is clear from the above that the conductivity of ZnO doped copper-bismuth glass is higher than that of the TiO_2 doped one at all the temperatures, which can be attributed to the the higher polaron mobility of the former compared to the latter due to smaller polaronic radius. The slopes of the curves (Fig. 1) change slightly with T at high temperatures, indicating little modification of the activation energy W in both the glasses in the similar manner. The temperature where the linearity of the Arrhenius plot (Fig. 1) deviates are taken as $\theta_D/2$ where θ_D *ca.* 787 K for sample A and 689 K for sample B and consistent with other cuprate glasses.

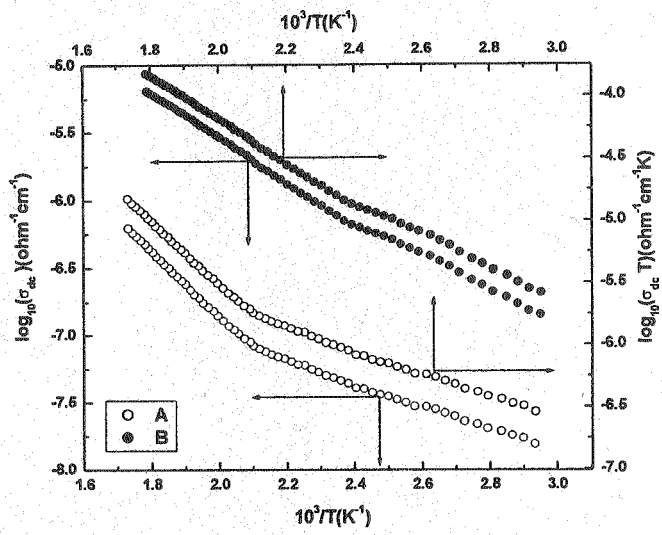

Fig. 1. Inverse temperature variation of $\log_{10}(\sigma_{dc})$ and $\log_{10}(\sigma_{dc}T)$ of $CuO\text{-}Bi_2O_3\text{-}TiO_2$ (A) and $CuO\text{-}Bi_2O_3\text{-}ZnO$ (B) glasses

From Holstein's relation[8], one can infer whether the hopping conduction is in the adiabatic or non-adiabatic region. According to that relation, the polaron bandwidth J should obey the following conditions: $J > H$ for adiabatic hopping and $J < H$ for non-adiabatic hopping conduction, where $H = (2k_BTW_h/\pi)^{1/4}(h\nu_{ph}/\pi)^{1/2}$. The condition for small-polaron formation is $J < W_h/3$. An evaluation of J can be made from the approximate relation[8] for high- temperatures $J(T) \approx 0.67h\nu_{ph}(T/\theta_D)^{1/4} = 0.027(T/\theta_D)^{1/4}$ and for ground-state bandwidth $J(0) = 3h\nu_{ph} = 0.12$ eV. Taking $\nu_{ph} = 10^{13}$ Hz, it is found that H (500 K) *ca.* 0.034 eV for sample A and 0.035 eV for sample B and J (500 K) *ca.* 0.023 eV for sample A and 0.024 eV for sample B. Again, $W_h/3$ is *ca.* 0.1106 eV for sample A and 0.1109 eV for sample B. Since J (500 K) is less than both H (500 K) and $W_h/3$, we conclude that dc conduction in these glasses occur by small-polaron hopping in the non-adiabatic regime. Similar relation for H and J is also valid at other temperatures.

Conclusion

Copper-bismuth glasses doped with TiO_2 and ZnO have been prepared by rapid quenching method. At any fixed temperature, the dc conductivity of ZnO contained glass is higher than that of the TiO_2 which is attributed to be due to the smaller polaron radius of the former compared to that of the latter. By exercising Mott-Austin's SPH model[3] and the Holstein condition[8], it is suggested that conduction in these glasses is due to small-polaron hopping in the non-adiabatic regime for temperatures above $\theta_D/2$.

ACKNOWLEDGMENT

One of the authors (DKS) is thankful to Inter University Accelerator Centre, New Delhi, India for providing the financial support.

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