Transport properties of amorphous CuO-Bi$_2$O$_3$ semiconducting pellets

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The results of measurement of dc-electrical conductivity and activation energy have been reported for four different composition of CuO-Bi$_2$O$_3$ glass powder pellets pressed at 50°C in the temperature range of 300 – 493 K. A plot of $-\log \sigma$ versus $1/T$ shows two different regions of conduction suggesting two types of conduction mechanisms switching from one type to another occurring at knee temperature. The dc-conductivity increases with increase in temperature of the sample and also with increase of mol% of CuO. Activation energy calculated for both regions (LTR and HTR) is below 1 eV, thus the electrical conduction is electronic. Activation energy decreases with increase of mol% of CuO. Non-adiabatic hopping conduction was observed in the sample. A plot of dielectric constant versus log of frequency shows zig-zag nature. Dielectric constant decreases with increase in mol% of CuO.

In the recent years, there has been an increasing interest in the study of electrical, optical and structural properties of oxide glasses, because of their potential applications, such as switching and memory devices, thermistors and semiconductors. The transition metal oxide glasses shows semiconducting behaviour, because of transition metal ions. Ghosh and Chaudhury$^1$ discussed the dc-conductivity of semiconducting vanadium bismuth oxide glasses containing 80 – 95 mol% vanadium pentoxide in the temperature range of 300 – 500 K. They observed adiabatic hopping conduction and discussed the results of measurements on the basis of polaronic hopping model. The phenomena of adiabatic and/or non-adiabatic hopping conduction in various glass systems has been discussed by many research workers$^{2-6}$. The electrical conduction in CuO-Bi$_2$O$_3$ glass powder pellets of different compositions shows non-adiabatic hopping conduction$^7,8$. This phenomenon has been discussed on the basis of method suggested by Sayer and Mansingh$^9$ with the light of polaronic hopping model. Chakravorty$^9$ has reviewed the electrical, optical, magnetic and mechanical properties of the various bismuth glasses and observed that at high electric fields certain glasses containing bismuth granules show a memory switching effect.

The authors have studied the variation of dc-electrical conductivity of glass powder pellets pressed at 50°C of CuO-Bi$_2$O$_3$ in the temperature range of 300 – 493 K. Similarly the variation of dielectric constant with frequency is also studied at room temperature (300 K) only with an aim to know the conduction mechanism and relaxation effects. For studying the properties of amorphous material, the most straightforward approach is to prepare melt quenched glasses and then to make measurement on them. It is known that the density of pellets depend on the pressure used and sometimes also on temperature of pressing and thus their other physical and transport properties will be different from bulk properties. In the present study, pellets of glass powder of CuO-Bi$_2$O$_3$ pressed at 50°C and pressure $3 \times 10^3$ kg/cm$^2$ have been used with an intention to observe the change in the behaviour of transport properties of CuO-Bi$_2$O$_3$ bulk glass and pellet.

Experimental Procedure

Preparation of the samples—Pellet samples under investigation were prepared in the laboratory by mixing an appropriate amounts of CuO and Bi$_2$O$_3$ (mol%) (AR-grade). A homogeneous mixture of two powders was prepared and fired in a fire clay crucible at 1000 ± 10°C for half an hour in an automatically controlled muffle furnace. Then the molten mixture was taken out, allowed to cool and crushed into powder form. The glass powder was then agglomerated and pressed on
the pellet machine having pressure of $3 \times 10^3$ kg/cm² with the binding reagent euprol at 50°C in circular shapes having diameter 2 cm and thickness 0.2 cm.

A thin conducting silver paint in a circular form is pasted on the opposite sides of the sample for the purpose of electrical measurements. Heat treatment is given to all silver paint pasted samples at 100°C for fixing the paint and removing the air bubbles. The amorphous nature of the sample was checked by X-ray diffraction method. All the samples were amorphous in nature.

**Electrical measurements**—The resistance of the pellet was measured by voltage drop method given by Yawale et al. The voltage drop across the standard resistance of 1 MΩ was measured by using digital multimeter (DT-850 Japan having accuracy of ±0.1 mV and input impedance 1000 MΩ) at constant voltage. The resistance of the pellets of various compositions was measured in the temperature range of 300 - 493 K. The accuracy in the resistance measurement was less than 2%. The detail procedure is reported elsewhere. The dielectric constant of the pellets was measured by using a pellet machine having pressure of 3 x 10^3 kg/cm² with the binding reagent euprol at 50°C in the pellet machine having pressure of 3 x 10^3 kg/cm² with the binding reagent euprol at 50°C in circular shapes having diameter 2 cm and thickness 0.2 cm.

When the overlap integral between sites $J_o \exp(-2aR)$ approaches $J_o$, i.e., $\exp(-2aR) -> unity$, the hopping is adiabatic and it is mainly controlled by the activation energy.

Then the Eq.(1) reduces to

$$\sigma = \nu_o \frac{Ne^2 R^2}{kT} c(1-c) \exp \left( -\frac{\Delta E}{kT} \right)$$

To explore the nature of hopping conduction a plot of log $\sigma$ versus activation energy ($\Delta E$) at fixed temperature for the pellet of different compositions is plotted. The straight line nature of the plot indicate the validity of Eq. (3). The temperature $(T, K)$ at which the plot is drawn is determined from the slope of the plot, which decides the hopping conduction mechanism.

Nagels has considered the two channel model and suggested that with decreasing temperature the conduction changes from extended to localized tail states. Therefore, the shift in the Fermi and conduction band energy with temperature occurs. This has been observed from the plot of log $\sigma$ versus $1/T$, which shows kink at the temperature where slope changes and hence energy changes. Similar type of kink is observed in our glass pellets. According to this model

$$\sigma = \sigma_o \exp \left[ \frac{\delta \Delta E}{k(E_c - E_a)} \right]$$

where, $\sigma_o$ is the exponential factor from log $\sigma$ versus $1/T$ plot, $\delta$ is the linear temperature coefficient of the shift of conduction band $E_c$ and $E_a$ is the valence band edge.

This model leads to a linear dependence of log $\sigma_o$ versus activation energy $\Delta E$.

**Results and Discussion**

The conductivity of the pellet samples is found to be of the order of $10^{-12}$ (ohm cm)⁻¹ at room temperature (300 K). It is in the order of the glasses of CuO reported by Singh and Tarsikka. Fig. 1 shows the plot of $-\log \sigma$ versus $1/T$ for the different compositions of CuO and Bi₂O₃. This plot is divided into two linear regions. The activation energy is calculated for both the regions from Arrhenious. The behaviour of the plot in all the pellets is observed to be same, which suggests a similar conduction mechanism for the studied glass powder pellets. Similar type of behaviour is observed in the lead borate glasses by Burzo et al. As the temperature and CuO mol % increases the dc-conductivity of the
pellet increases (Figs 1 and 2). In high temperature region the electrical conductivity increases faster in 50, 60 and 70 CuO mol % whereas in 80 CuO mol % pellet the increase is slow.

The value of pre-exponential factor $-\log \sigma_0$ is found to be maximum for 70 mol % CuO pellet (Fig. 3). The value of $\sigma_0$ is the intercept on log $\sigma$ axis in log $\sigma$ versus $1/T$ plot. The change in the value of $\sigma_0$ is due to change in density of transition metal ions.

The electrical conductivity measurement show the presence of two activation energies for electrical conduction. This suggests the charge transfer between $\text{Cu}^+$ and $\text{Cu}^{++}$ ions in similar and different environment at lower temperature and higher temperature respectively.

The activation energy ($\Delta E$) is plotted against CuO mol % for the low temperature (LTR) and high temperature regions (HTR) (Fig. 4) which shows linear decrease with the increase in CuO mol %. The activation energy calculated in high temperature region is found to be of the order of borate oxide glasses. In LTR the activation energy is found to be of the order of 0.03 to 0.07 eV, which may be called disordered energy $\Delta E_D$. The activation energy calculated in LTR might be included in the range of $T < \theta_D/4$ in which case it is considered as disordered energy.

To examine the nature of hopping conduction, the method suggested by Sayer and Mansingh and Murawaski et al. is applied. The exploration
of Eq. (3) done by plotting the $-\log \sigma$ versus activation energy $\Delta E$ at fixed temperature in both the temperature regions, shows linear nature, but the temperature estimated (115 K) from the slope (Fig. 5a) is found to be very different from the fixed temperature taken (303 K) in LTR. Similarly for HTR (Fig. 5b) estimated temperature (231 K) is different from the fixed temperature (473 K). This indicates that the hopping conduction is non-adiabatic in LTR and HTR. Therefore, the conduction is not mainly controlled by the activation energy.

The plot of $-\log \sigma$ versus $1/T$ is divided into two linear regions from some fixed temperature called knee temperature ($\theta_k$). The value of knee temperature decreases with increase in CuO mol %. The kink in the dc-conductivity $-\log \sigma$ versus $1/T$ plot is explained on the basis of ‘two channel model’ for transport of carriers. According to this model the conduction path of carriers changes from extended to localized tail states with decreasing temperature. Fig. 6 shows the plot of $-\log \sigma_0$ versus activation energy ($\Delta E$). The nature of the graph is a straight line. The straight line drawn from the points is least square fitted giving $\sigma_0 = 2.519 \times 10^7$ (ohm. cm)$^{-1}$ and slope, $\delta_e/k(E_c - E_0) = 3.877$ (eV)$^{-1}$. This model suggests that the shifting of mobility edge $E_c$ with temperature occurs due to increase in overlap integral $I$, which keeps the localization condition constant by decreasing $E_c$.

The dielectric constant of three samples studied is found to be frequency and composition (CuO) dependent. Fig. 7 shows variation of dielectric constant with log of frequency at room temperature. The nature of the plot is zig-zag (non-linear). At 1 kHz frequency dielectric constant shows dip for all the samples. A gradual decrease of dielec-
tric constant with a point of inflexion in between of $\varepsilon$ versus $f$ plot represents the occurrence of relaxation phenomenon in the glasses. But the plot (Fig. 7) does not show similar type of behaviour, which suggest that some other phenomenon might be present in these pellets.

Fig. 8 shows the plot of dielectric constant versus mol % of CuO at three different frequencies (0.2, 1 and 10 kHz). These plots are linear in nature. It is observed that dielectric constant decreases with increase of CuO mol %.

**Conclusion**

The activation energy is found to be in the range of semiconducting glasses and the behaviour of $-\log \sigma$ versus $1/T$ is linear as observed in the case of many semiconducting glasses. Similarly, non-adiabatic hopping conduction is observed suggesting that the conductivity is not mainly controlled by activation energy. Linearity has been observed in the dielectric constant with composition of CuO mol %. It is concluded that the electrical conductivity data of CuO-Bi$_2$O$_3$ pellets is well explained by small polaron model.

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**References**