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Hopping Conduction Mechanism in Amorphous Cuo-Bi_2o_3 Semiconducting Pellets

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Abstract :

The results of measurement of dc-electrical conductivity and activation energy have been reported for three different composition of CuO-Bi_2O_3 glass powder pellets pressed at 100°C in the temperature range of 343 - 533 K. A plot of —log σ versus I/ *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. The activation energy is temperature independent but depends on composition. Activation energy increases with increase of mol% of CuO. Non-adiabatic hopping conduction was observed in the sample.

Keywords : CuO-Bi_2O_3 pellets, electrical properties

1. Introduction

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 phenomenon 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_2O_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[3] with the light of polaron 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 100°C of CuO-Bi_2O_3 in the temperature range of 343-533 K. For studying the properties of amorphous material, the most straight forward 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_2O_3 pressed at 100°C and pressure 3 x 10^3 kg/cm^2 have been used with an intention to observe the change in the behaviour of transport properties of CuO-Bi_2O_3 bulk glass and pellet.

2. Experimental Procedure :

2.1 Preparation of the samples—Pellet samples under investigation were prepared in the laboratory by mixing an appropriate amounts of CuO and Bi_2O_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 x 10^3 kg/ cm^2 with the binding reagent euprol at 100°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 Kher *et al*[18] and Yawale *et al*[2]. The voltage drop across the standard resistance of 1 M Ω was measured by using digital multimeter (DT-850 Japan having accuracy of ±0.1 mV and input impedance 1000 MΩ) at constant voltage 600 V. The resistance of the pellets of various compositions was measured in the temperature range of 343 - 533 K. The accuracy in the resistance measurement was less than 2%. The detail procedure is reported elsewhere[2].

3. Theory

The dc-electrical conductivity of semi conducting oxide glasses is expressed[11] as

$$\sigma = \nu_0 \frac{Ne^2R^2}{kT} c(1-c) \exp(-2\alpha R) \exp\left(-\frac{\Delta E}{kT}\right) \qquad \ldots\ldots. (1)$$

where, *c* is the fraction of reduced valence sites of the transition metal ions, ν_0 is the frequency factor, *R* is the intersite distance, N is the density of the transition metal ions, α is the spatial decay constant for the electron wave function and ΔE is the activation energy.

The activation energy is given by

$$\begin{aligned} \Delta E &= \Delta E_H \frac{\Delta E_D}{2} && \text{for } T > \theta_D / 2 \\ &= \Delta E_D && \text{for } T < \theta_D / 4 \end{aligned} \qquad \ldots\ldots. (2)$$

Where θ_D is Debye temperature, ΔE_H is polaron hopping energy, ΔE_D is the disorder energy.

Adiabatic or non-adiabatic hopping conduction is checked by adopting the method suggested by Sayer and Mansingh[3] and Murawaski *et al*[4].

When the overlap integral between sites $J_O \exp(-2\alpha R)$ approaches to J_O i.e., $\exp(-2\alpha R) \rightarrow$ unity, the hopping is adiabatic and it is mainly controlled by the activation energy.

Then the Eq. (1) reduces to

$$\sigma = \nu_0 \frac{Ne^2R^2}{kT} c(1-c) \exp\left(-\frac{\Delta E}{kT}\right) \qquad \ldots\ldots. (3)$$

To explore the nature of hopping conduction a plot of $-\log \sigma$ versus activation energy (ΔE) at fixed temperature for the pellet of different compositions is plotted. The straight line nature of the plot indicate the validity of equation (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[10] 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

$$\sigma_0 = \sigma_0' \exp\left[\frac{\delta_c \Delta E}{k(E_c - E_a)}\right] \qquad \ldots\ldots\ldots.. (4)$$

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

This model leads to a linear dependence of log σ_O versus activation energy ΔE.

4. Results and Discussion :

The conductivity of the pellet samples is found lo be of the order of 10^{-12} (ohm. cm)$^{-1}$ at room temperature (303 K). It is in the order of the glasses of CuO reported by Singh and Tarsikka [12]

Fig. 1 shows the plot of -log σ versus 1/T for the different compositions of CuO and Bi_2O_3. This plot is divided into two linear regions. LTR-343 K to 453 K and HTR -453 K to 533 K. 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 el al[15]. As the temperature and CuO mol % increases the dc-conductivity of the pellet increases.

The conductivity increases with increase in temperature and also with mol% to CuO. In LTR conductivity varies with temperature linearly but increase in conductivity with temperature as slow. In HTR the variation of conductivity with temperature is linear but conductivity increases rapidly with temperature. The activation energy from the slope of the straight line (figure 1) in both the regions is calculated and it is observed that activation energy is temperature independent but depends on composition.

The intercept of -log σ versus 1/T plot gives pre-exponential factor – log σ_0. Figure 2 shows the plot of -log σ_0 versus CuO mol%. For all the pellets the nature of the curve is linear and the pre-exponential factor increases with the increase of CuO mol%.

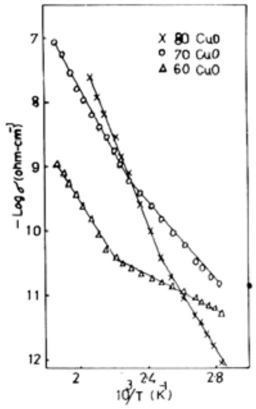

Fig. 1 – Variation of dc-conductivity (-log σ) versus 1/T, for the pellets of different composition of CuO-Bi_2-O_3

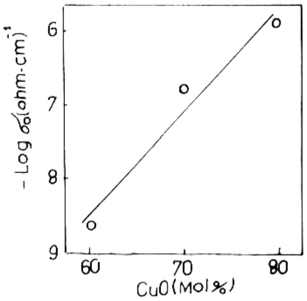

Fig. 2 – Variation of pre-exponential factor (-log σ_o) with composition of CuO mol%

The electrical conductivity measurement show the presence of two activation energies for electrical conduction. This suggests the charge transfer between Cu^+ and Cu^{++} ions in similar and different environment at lower temperature and higher temperature respectively[16-17].

The activation energy (ΔE) is plotted against CuO mol% for the low temperature (LTR) and high temperature regions (HTR) (Fig.. 3) which shows linear increase with the increase in CuO mol %. The activation energy calculated is found to be of the order of borate oxide glasses[13-14]. All the samples studied indicated a negative temperature coefficient as well as electronic conduction, since the activation energy is less than 1 eV.

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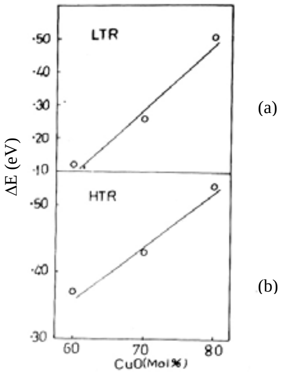

Fig. 3 – Dependence of activation energy (ΔE) on composition CuO mol% in LTR and HTR

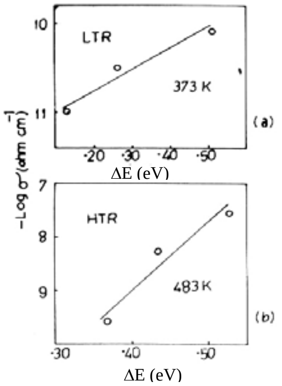

Fig. 4 – Plot of electrical conductivity (-log σ) versus activation energy (ΔE) at fixed temperature.

To examine the nature of hopping conduction, the method suggested by Sayer and Mansingh[3] and Murawaski *et al*[4]. is applied. The exploration of equation (3) done by plotting the -log σ versus activation energy ΔE at fixed temperature in both the temperature regions, shows linear nature, but the temperature estimated (476 K) from the slope (Fig. 4a) is found to be very different from the fixed temperature taken (373 K) in LTR. Similarly for HTR (Fig. 4b) estimated temperature (772 K) is different from the fixed temperature (483 K). This indicates that the hopping conduction is non-adiabatic in nature in both LTR and HTR. Therefore, the conduction is not mainly controlled by the activation energy.

5. Conclusion :

The activation energy is found to be in the range of semi conducting glasses and the behaviour of -log σ versus 1/Tis 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.

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