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RESEARCH ARTICLE

Physical and thermal properties of Cuo-B_2O_3 Glasses

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ABSTRACT

The thermal conductivity of CuO-B_2O_3 glass system has been experimentally determined in the temperature range 302-423 K. The data covered the glass composition range from 10 to 35 mol% of CuO. It has been observed that the thermal conductivity increases linearly with temperature. Thermal conductivity is composition dependent. The results obtained confirmed that the major contribution to the thermal conductivity of this glass system is due to lattice vibrations. The value of density, molar volume, lattice thermal conductivity (λ_L), melting temperature, electronic (λ_e) and bipolar component of thermal conductivity (λbp), band gap energy are also reported. The physical properties like density, molecular weight, molar volume, hopping distance, polaron radius and number of ions per cm^3 have been reported.

Keywords : CuO-B_2O_3 glasses, Thermal conductivity, Polarons, Phonons, Physical properties

INTRODUCTION

In the recent years, the interest in the study of electrical, optical and structural properties of glassy semiconductors has increased considerably (Mandal and Ghosh, 1993). The chalcogenide and oxide glasses, both have potential applications such as thermistors, catalysts, switching and memory devices Vanadium phosphate glasses are the most extensively studied transition metal oxide glasses. Herring (1954); Callaway (1959); Valeri and Rincon (1993) has studied the thermal conductivity of the materials in which heat is carried by phonons. A formula for thermal conductivity has been presented by Callaway Callaway (1959). The contribution of free electrons (Price 1955; Moreli *et al*., 1993) and holes to thermal conductivity is possible at high temperature. Nowadays the thermal conductivity has been used as an indicator on the amorphous to crystalline transformations (Holand, 1963; Omer and El-Zaidia, 1976; El-Mously and EL-Zaidia, 1978). Thermal conductivity of amorphous selenium has been measured by El-Zaidia *et al*. (1981) using longitudinal-bar method. DC conductivity, density and infra-red investigations have been carried out on ZnO-PbO-B_2O_3 glasses by Doweldar *et al*. (1994). In TeO_2-B_2O_3 glass system both the conductivity and activation energy were found to be a function of

added oxide type (Sabry and Bi-Samanoudy, 1994). An attempt has been made to measure the thermal conductivity of $CuO-B_2O_3$ semiconducting glass system. The effect of CuO mol% on the thermal conductivity of the semiconducting $CuO-B_2O_3$ glass system has also been studied. The thermal and electrical conductivity is measured with an aim to know the mechanism of heat transport and electrical transport in $CuO-B_2O_3$ glass system. Also the main contribution to the thermal mechanism is determined. Chaudhury (1995) have discussed in brief the general procedure for making glass ceramic superconductors and some of their physical properties. Dc-conducting and hopping mechanism in $Bi_2O_3-B_2O_3$ glasses has been studied by Yawale *et al*. (1993). The physical and transport properties such as density, hopping distance, polaron radius, dc-conductivity and activation energy are reported by them.

EXPERIMENTAL PROCEDURE

Preparation of glass samples

The glass samples under investigation were prepared in a fireclay crucible. The muffle furnace used was of Heatreat co. Ltd. (India) operating on 230 volts AC reaching upto a maximum temperature of 1500 ± 10°C. Glasses were prepared from AR grade chemicals. Homogeneous mixture of an appropriate amounts of CuO and B_2O_3 (mol%) in powder form was prepared. Then, it was transferred to fire-clay crucible, which was subjected to melting temperature (1300°C). The duration of melting was generally two hours. The homogenized molten glass was cast in steel disc of diameter 2 cm and thickness 0.7 cm. Samples were quenched at 200°C and obtained in glass state by sudden quenching method. All the samples were annealed at 350°C for two hours. More details regarding the preparation of glass samples has been reported elsewhere (Yawale and Pakade, 1993; Pakade *et al*., 1994; 1988). From XRD it was found that the nature of samples was amorphous. Differential thermal analysis (DTA) of the samples was done in the temperature range 303K-873K. The heating rate of sample was 10° C/min. The purpose of DTA analysis was to determine the melting temperature of the glass samples. The formula suggested by Kauzmann (1948), $T_m = 1.5\ T_g$, has been used to determine the melting temperature, T_m of the glass.

Density measurement

The densities of glass samples were measured using the Archimedes principle. Benzene was used as a buoyant liquid. The accuracy in the measurement of density was 0.001 g/cm^3. The densities obtained d_{exptl} were compared with corresponding theoretical values, d_{theor} calculated according to the additive rule given by Demkina (1960).

d_{theor} = (Mol% of CuO x density of CuO + Mol% of B_2O_3 x density of B_2O_3)/100.

Electrical measurement

The dc resistance of the glass sample was measured by using D.C. microvoltmeter, Systronics 412 India, having an accuracy of ± 1μV and input impedance 10 MΩ, by voltage drop method. Before electrical measurements all the samples were polished to smooth surfaces using fine quality emery paper. After application of conducting silver paint at either sides, the samples were used for electrical measurements. The silver paint acts like electrodes for all the samples.

Thermal conductivity apparatus

The apparatus used for the thermal conductivity measurement is shown in Fig. 1. This was fabricated in our laboratory. The thermal conductivity of the glasses was measured using steady-state axial heat flow divided bar method (Beck, 1957). The apparatus can be divided into two halves.

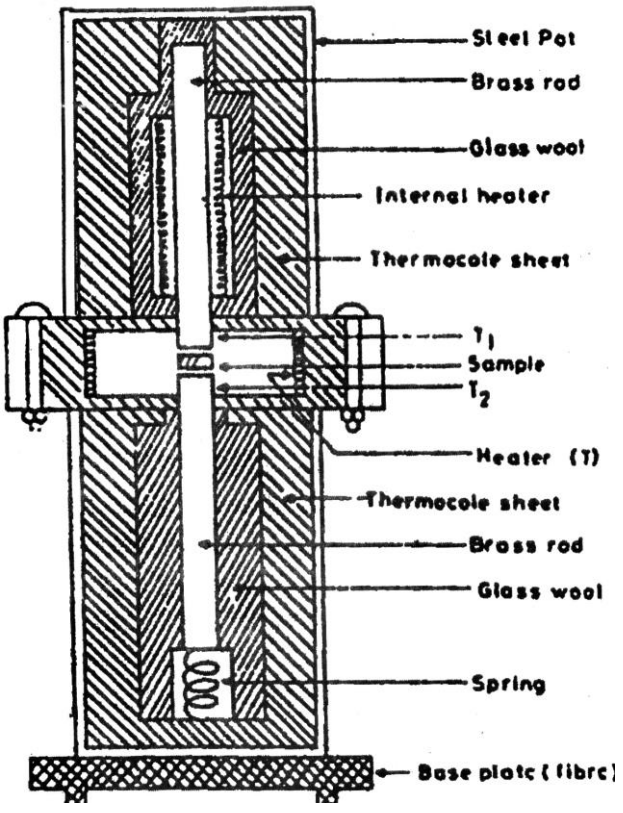

Fig.1-Diagram of apparatus for measurement of thermal conductivity

The sample was coaxially sandwiched between two brass rods. In the upper half the brass rod is surrounded by two cylindrical pots. The outer pot is of copper and inner one is of steel. Both the pots are separated by heat resistive material thermocole so that there should not be transfer of any heat between surrounding and the innerside of the apparatus. The space between the rod and pot was filled with glass wool for thermal insulation. For longitudinal heat flow through the sample, a heating element is wound around the upper brass rod on a ceramic cylinder. The two extreme ends of the heating element are connected to the secondary of the power transformer through diode rectifier and primary of the transformer is connected to dimmerstat. The other half of the apparatus consists of brass rod which is kept at room temperature and can be moved up or down by the spring as shown in Fig. 1. so that the sample can be properly gripped between lower and upper electrodes. The upper and lower electrodes are well insulated electrically and thermally from the upper and lower pots of the apparatus. To note the temperatures (T_1 and T_2) of sample faces two calibrated copper-constantan thermocouples, fixed in holes drilled in each rod are used along with digital microvoltmeters (Systronics - 412 India).

Heat losses from the sample sides were minimised by adjusting the temperature of the sample surrounding at a value $T = (T_1 + T_2) / 2$. Where T_1 and T_2 are the temperature of the sandwiched sample faces. The temperature of glass sample (T) was measured with the help of another thermocouple fitted near the sample. All the measurements were carried out in a dry atmosphere. All electrical leads were shielded and maintained at a constant temperature. Thermal conductivity was measured in the temperature range 302-423 K. After steady-state was reached the thermal conductivity (λ) was determined by measuring the rate of heat flow per unit area (Q) and the temperature gradient ($d\theta/dX$) through the brass bar, using the expression.

$$Q = \lambda \frac{d\theta}{dX}$$

Theory

The thermal transport behaviour of a pure (intrinsic) semiconductor is similar to that of an insulator with heat conduction due to lattice waves (phonons) at moderate temperature. To produce desired numbers of electrons or holes, controlled amount of suitable impurities (dopants) can be added to a semiconductor. These charge carriers gives rise to an electronic contribution to thermal conductivity. In semiconductor, at sufficiently high temperatures to excite the carriers across the energy band gap, electron hole pair can transport heat and give rise to bipolar contribution (i.e. due to electron and hole pair) to the thermal conductivity (Bhandari and Rawe, 1985; Mott, and Davis, 1979; Meckenzi, 1964). Therefore, the total thermal conductivity (λ) of a semiconductor may be expressed as

$$\lambda = \lambda_L + \lambda_e + \lambda_{bp} + \lambda_{ph}$$

where λ_L represents the lattice component, λ_e is the electronic (polar component) and λ_{bp} is the electron hole pairs (bipolar) component and λ_{ph} is the photon contribution.

The free electron thermal conductivity (λ_e) can be evaluated in terms of the total electrical conductivity (σ) from Wiedmann-Franz law (Doweldar *et al*.,1994).

$$\lambda_e = L \sigma T$$

where L is the Lorentz number $L = \left(\frac{\pi^2}{3}\right)\left(\frac{k}{e}\right)^2$

σ is the electrical conductivity and T is the absolute temperature.

The bipolar thermal conductivity (λ_{bp}) caused by electron-hole pairs with energy E_g diffusing down the temperature gradient, is given for a well-compensated intrinsic semiconductor with an ordinary parabolic band and current carriers scattering due to acoustic phonons, by the formula (Regel *et al*., 1972).

$$\lambda_{bp} = \frac{3}{4\pi^2} L \left(\frac{E_g}{kT} + 2\right)^2 \sigma.T \quad \ldots\ldots\ldots\ldots\ldots (3)$$

where E_g is the energy gap for the electron hole pairs. All the relevant data given by Regal *et al*.(1972), show that the value of molecular lattice component (λ_L) can be sufficiently well established by the formula which is suggested (Turnbull, 1961) for the salt melts.

$$\lambda_L = 2.88 \times 10^{-3} \left(\frac{T_m}{(M/n)\,(V/n)^{4/3}}\right)^{1/2} \quad \ldots\ldots\ldots\ldots\ldots (4)$$

where T_m is the melting temperature, M is the atomic weight, V is the molar volume and n is the number of

separate ions per molecule. In many cases, the mechanism of heat transfer may become significant due to photons. If the material is transparent for a particular photon it can pass through the material undisturbed, while if not, it will diffuse in the material and down a temperature gradient. In this case the photon thermal conductivity plays dominant role. The expression for photon conductivity (Genzel, 1953) is given by

$$\lambda_{ph} = (16 / 3)\ \sigma_0 n^2 T^3 \alpha^{-1}$$

where, σ_0 is the Stefan-Boltzman constant, n is the refractive index of the material and α is the absorption coefficient.

At high temperature photon thermal conductivity also becomes significant with lattice thermal conductivity. If the energy gap is small, the α^{-1} value becomes very low therefore λ_{ph} is small.

RESULTS AND DISCUSSION

Physical properties :

The physical parameters such as density (d), molecular weight (M), molar volume (V), hopping distance (R), polaron radius (r_p) and number of ions per unit volume (N) are reported in table 1 for CuO-B_2O_3 glasses. The density, molecular weight and number. of ions per cm^3 increases with increasing mol% of CuO but molar volume, hopping distance and polaron radius decreases with increasing mol% of CuO. In glasses the structure depends on the glass network in which the number of ions enter. In what way they entered and what is the nature of the ions, decides the density of the glass.

Table 1 : Physical parameters of CuO-B_2O_3 glasses

Glass No.	Composition (mol%) CuO-B_2O_3	Density		Molecular weight M(gm)	Molar volume V(cm^3/ mol)	No.of ions per cm^3 N(cm^{-3}) x 10^{22}	Hopping distance R(A^0)	Polaron radius r_p(A^0)
		d_{the} gm/cc	dexpt gm/cc					
G A1	10-90	1.91	2.254	63.75	28.28	2.14	3.60	1.45
G A2	15-85	2.16	2.413	64.63	26.78	2.28	3.54	1.42
G A3	20-80	2.40	2.515	65.51	26.04	2.33	3.51	1.41
G A4	25-75	2.64	2.655	66.39	25.00	2.43	3.46	1.39
G A5	30-70	2.89	2.836	67.27	23.72	2.54	3.40	1.37
G A6	35.65	3.13	2.891	68.14	23.56	2.56	3.39	1.36

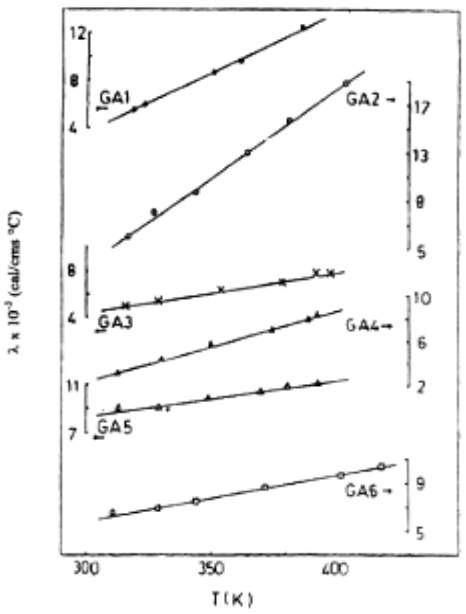

Fig.2 – Variation of thermal conductivity with temperature for CuO-B_2O_3 glass system
● - 10% CuO – 90% B_2O_3, O - 15% CuO–85% B_2O_3,
x - 20% CuO – 80% B_2O_3, ▲ - 25% CuO–75% B_2O_3,
Δ - 30% CuO – 70% B_2O_3, □ - 35% CuO–65% B_2O_3,

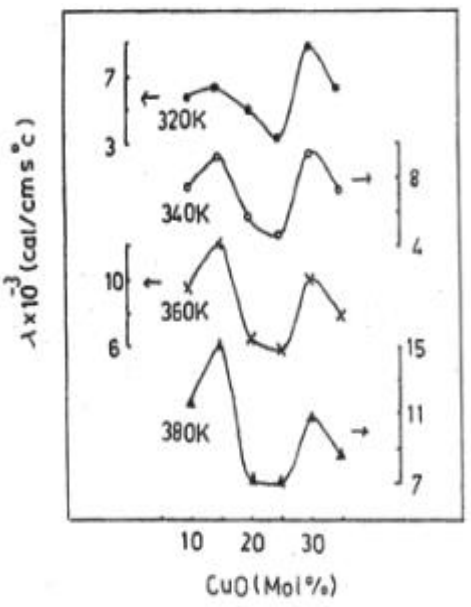

Fig.3 – Variation of thermal conductivity with CuO (mol%) for CuO-B_2O_3 glasses at various temperatures

The increase in the density with increasing mol% of CuO suggest the decrease in the number of non-bridging oxygen ions. The hopping distance is reduced with the increase in CuO mol% in the glass system. This indicates that the conduction processe becomes fast, because of the small hopping distance the polaron requires smaller time to hop between nearest neighbour place. The values of physical parameters reported are found to be of the order of glasses reported in literature (Soppe *et al*., 1988; Damodaram and Rao, 1989; Royle *et al*., 1994; Ghosh, 1995).

Thermal conductivity:

The thermal conductivity (λ) was measured for six glass samples as a function of temperature in the range 302-423 K. The measured thermal conductivity (λ) increases linearly with temperature (Fig. 2). Similar temperature dependence has been reported by many workers (El-Mously and El-Zaidia, 1978; El-Zaidia *et al*., 1981; Sabry and Bi-Samanoudy, 1995) in semiconducting glasses. The measured values of thermal conductivity are found to be of the order of phosphate glasses (Higazy, 1985).

The variation of thermal conductivity λ, with CuO(mol%) content at constant temperatures 320, 340, 360 and 380 K is shown in Fig.3. The thermal conductivity values are dependent on glass composition and change with CuO mol%, having a maximum value at 15 and 30 mol% CuO.

The values of density d_{theor}, d_{expt}, molar volume, lattice component of thermal conductivity (λ_L), band gap energy (Eg), melting temperature (T_m) of glasses are given in Table 2. The values of density calculated d_{exptl} and d_{theor} agree well, their nature has been found to be increasing with mol % of CuO. The density of the glass is due to the volume of the constituent ions, therefore it depends on the nature, the number and the way by which ions enter in the glass structure. It is known that the density of glass is additive (Demkina , 1960) and can be calculated on the basis of glass composition. However, this is not always true in many glass systems. Jen and Kalinowski (1980) suggested a model for the calculation of glass density on the basis of bridging to non-bridging oxygen ratio as a function of glass composition. The experimental values are in excellent agreement with those reported on this model. However, this model has not been applied to present glass system as the structure of CuO-B_2O_3 glass has not been discussed in detail.

The values of λ_e and λ_{bp} for different compositions of CuO and at different temperatures are given in Table 3(a) and 3(b).

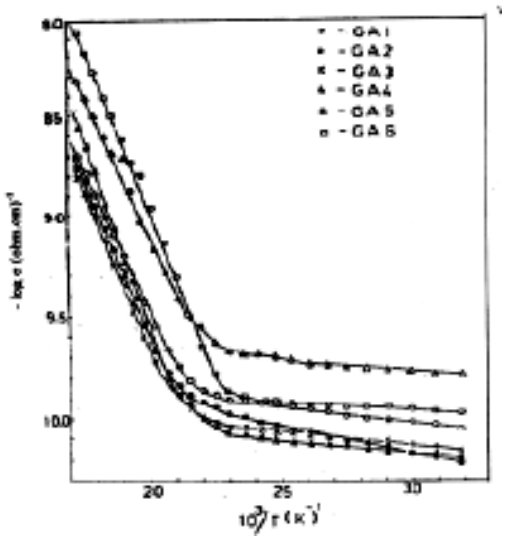

Fig.4 : Temperature Dependence of dc-electrical conductivity for the glasses of different compositions of CuO and B_2O_3

• - 10% CuO – 90% B_2O_3, O - 15% CuO–85% B_2O_3,
x - 20% CuO – 80% B_2O_3, ▲ - 25% CuO–75% B_2O_3,
Δ - 30% CuO – 70% B_2O_3, □ - 35% CuO–65% B_2O_3,

Table 2 :Density, molar volume, lattice thermal conductivity (λ_L), band gap energy and melting temperature of glass

Glass sample CuO-B_2O_3 Mol%	Density		Molar Volume cm^3	Lattice thermal cond. (λ_L) x10^{-3} (302K) cal/cm s deg	Band gap energy (E_g) eV	Melting temperature T_m K
	d_{theor} g/cm^3	d_{exptl} g/cm^3				
GA_1 10-90	1.91	2.254	28.28	3.626	0.0414	566
GA_2 15-85	2.15	2.413	26.78	4.406	0.0344	927
GA_3 20-80	2.40	2.515	26.04	4.558	0.0240	969
GA_4 25-75	2.64	2.655	25.00	4.623	0.0206	957
GA_5 30-70	2.89	2.836	23.72	4.771	0.0172	963
GA_6 35-65	3.13	2.891	23.56	4.795	0.0138	993

Table 3(a) - λ_e of $CuO\text{-}B_2O_3$ glass of different composition at different temperatures.

Temp T (K)	Electronic thermal conductivity λ_e (Cal/cm s^{0}C) x 10^{-16}					
	GA₁	**GA_2**	**GA_3**	**GA_4**	**GA_5**	**GA_6**
313	4.416	6.914	5.543	5.055	12.21	8.195
333	5.553	7.836	6.175	5.632	13.57	8.939
353	6.474	8.802	6.854	6.310	15.09	9.726
373	7.411	9.784	7.533	6.824	16.51	10.53
383	8.004	10.262	7.893	7.129	17.35	10.95
393	8.552	10.809	8.234	7.402	18.63	11.42

Table 3(b) λ_{bp} of $CuO\text{-}B_2O_3$ glass of different composition at different temperatures

Temp T (K)	Bipolar thermal conductivity λ_{bp} (Cal/cm s^{0}C) x 10^{-16}					
	GA₁	**GA_2**	**GA_3**	**GA_4**	**GA_5**	**GA_6**
313	1.048	1.348	0.841	0.702	1.54	0.950
333	1.196	1.458	0.903	0.756	1.67	1.000
353	1.329	1.569	0.969	0.822	1.80	1.065
373	1.457	1.677	1.033	0.865	1.93	1.130
383	1.541	1.727	1.067	0.893	2.086	1.165
393	1.615	1.787	1.098	0.916	2.131	1.204

The plot of -log σ versus 1/T is shown in Fig. 4. The measured value of room temperature dc electrical conductivity is found to be of the order of 10^{-11} $(ohm\text{-}cm)^{-1}$. The conductivity of all the studied glass samples increases linearly with increasing temperature. The dc conductivity of the glass samples is found to be compositional dependent. Band gap energy E_g is determined from the slope of -log σ versus 1/T plot (Fig. 4). The determined band gap energy values, agreed well with the values reported by Nassar *et al* (1982).

The calculated values of electron thermal conductivity (λ_e) for $CuO\text{-}B_2O_3$ glasses (Table 3a) increases with temperature and CuO content (of the order of 10^{-16} cal/cm s deg).

The calculated values of λ_{bp} for $CuO\text{-}B_2O_3$ glasses (Table 2b) increases with temperature (of the order of 10^{-16} cal/cm s deg). It is observed that the electronic and bipolar component of thermal conductivity become significant at high temperature. These values are increasing with the increase in temperature (Table 3a and 3b). Thus at high temperature the λ_e and λ_{bp} play dominant role in thermal conduction in addition to the lattice component also.

The calculated lattice thermal conductivity (λ_L) is found to be of the order of 3.626 x 10^{-3} – 6.795 x 10^{-3} cal/cm s deg (Table 2) which is of the same order of the measured values of total thermal conductivity (λ). Thus the two components λ_e and λ_{bp} may be neglected as compared with the measured values of thermal conductivity (λ). This shows that the main contribution to thermal conductivity of the studied glasses is only due to lattice component (λ_L).

Thus one may conclude that the main mechanism of heat transport through $CuO\text{-}B_2O_3$ glasses is by phonons (lattice). The increase of phonon conductivity (λ_L) may be explained by considering the increase of the number of scattering due to the dissolving of CuO atoms in the $CuO\text{-}B_2O_3$ glass. Regarding the photon contribution of thermal conductivity (λ_{ph}) in such glasses the band gap energy (E_g) is small, therefore the absorption coefficient is very small and hence the contribution of photon thermal conductivity is small. Hence the photon thermal conductivity plays negligible role. It is concluded that the lattice component plays dominant role in the thermal conduction of $CuO\text{-}B_2O_3$ glass.

CONCLUSION

Thermal conductivity of $CuO\text{-}B_2O_3$ glass system is studied in the temperature range 302-423 K. The thermal conductivity is CuO (mol%) dependent. The contribution of λ_e, λ_{bp} and λ_{ph} is negligible as compared with the lattice thermal conductivity (λ_L) component.

Hence, the main contribution to the thermal mechanism is due to lattice. The main mechanism of heat transport in such glasses is occurred by phonons.

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