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Physical and Thermal Properties of Cuo-Mno$_2$-B$_2$o$_3$ Glasses

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Abstract :

The thermal conductivity of CuO-MnO$_2$-B$_2$O$_3$ glass system has been experimentally determined in the temperature range 302-423 K. The data covered the glass composition range from 5 to 30 mol% of CuO. It has been observed that the thermal conductivity increases linearly with temperature. Thermal conductivity is composition dependent. The result obtained confirmed that the major contribution to the thermal conductivity of this glass system is due to lattice vibration. The value of density, molar volume, lattice thermal conductivity (λ_L), melting temperature, electronic (λ_e) and bipolar component of thermal conductivity (λ_{bp}), 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-MnO$_2$-B$_2$O$_3$ glasses, Thermal conductivity, physical properties.

In the recent years, the interest in the study of electrical, optical and structural properties of glassy semiconductors has increased [1] considerably. 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. Many investigators [2-4] have studied the thermal conductivity of the materials in which heat is carried by phonons. A formula for thermal conductivity has been presented by Callaway [3]. The contribution of free electrons [5,6] 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[7-9]. Thermal conductivity of amorphous selenium has been measured by El-Zaidia et al[10] using longitudinal-bar method. DC conductivity, density and infra-red investigations have been carried out on ZnO-PbO-B$_2$O$_3$ glasses by Doweldar et al [11]. In TeO$_2$-B$_2$O$_3$ glass system both the conductivity and activation energy were found to be a function of added oxide type [12]. An attempt has been made to measure the thermal conductivity of CuO-MnO$_2$-B$_2$O$_3$ semiconducting glass system. The effect of CuO mol% on the thermal conductivity of the semiconducting CuO-MnO$_2$-B$_2$O$_3$ 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-MnO$_2$-B$_2$O$_3$ glass system. Also the main contribution to the thermal mechanism is determined. Chaudhury et al [29] 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$_2$O$_3$-B$_2$O$_3$ glasses has been studied by Yawale et al [13]. The physical and transport properties such as density, hopping distance, polaron radius, dc-conductivity and activation energy are reported by them

2. Experimental Procedure :

2.1 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, MnO_2 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[13,25,26]. 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 [14], $T_m = 1.5\ T_g$, has been used to determine the melting temperature, T_m of the glass.

2.2 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[15].

$$d_{theor} = (\text{Mol\% of CuO x density of CuO + Mol\% of } MnO_2 \text{ x density of } MnO_2 + \text{Mol\% of } B_2O_3 \text{ x density of } B_2O_3)/100.$$

2.3 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.

2.4 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 [16]. The apparatus can be divided into two halves. 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

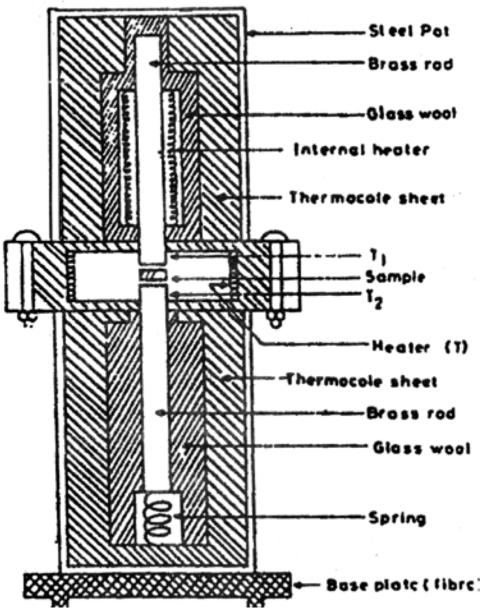

Fig.1-Diagram of apparatus for measurement of thermal conductivity

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.

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

3. 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. [21,23,24,28]. Therefore, the total thermal conductivity (λ) of a semiconductor may be expressed as

$$\lambda = \lambda_L + \lambda_e + \lambda_{bp} + \lambda_{ph} \qquad (1)$$

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 [11].

$$\lambda_e = L \sigma T \qquad (2)$$

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 formulas [17].

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

where E_g is the energy gap for the electron hole pairs. All the relevant data given by Regal et al [17], show that the value of molecular lattice component (λ_L) can be sufficiently well established by the formula which is suggested [18] for the salt melts.

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

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 transfer 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 [19] 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.

4. Results and Discussion :

4.1 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- MnO_2-B_2O_3 glasses. The density, molecular weight and number. of ions per cm^3increases 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. 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 processes 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 [30-33].

Glass No.	Composition (mol%) CuO-MnO_2-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^O)	Polaron radius r_p(A^O)
		d_{the} gm/cc	d_{expt} gm/cc					
G C1	5-20-75	2.38	2.991	66.86	22.68	2.66	3.35	1.35
G C2	10-20-70	2.63	3.093	68.74	22.22	2.732	3.32	1.3379
G C3	15-20-65	2.87	3.161	69.62	22.02	2.737	3.318	1.3371
G C5	25-20-55	3.36	3.360	71.37	21.24	2.86	3.27	1.31
G C6	30-20-50	3.60	3.477	72.25	20.77	2.91	3.25	1.30

Table 1 : Physical parameters of CuO- MnO_2-B_2O_3 glasses

4.2 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 [9,10,12] in semiconducting glasses. The measured values of thermal conductivity are found to be of the order of phosphate glasses[20].

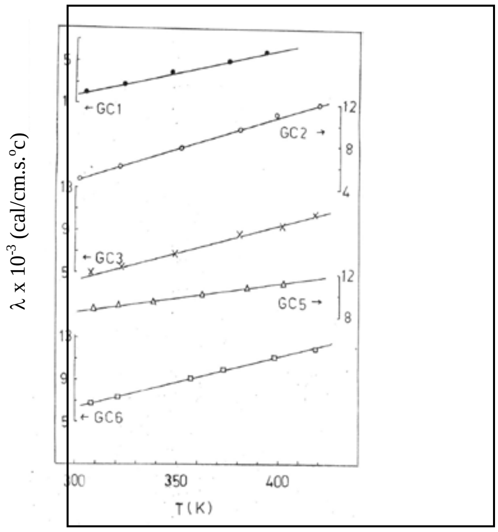

Fig.2 – Variation of thermal conductivity with temperature for CuO-MnO$_2$-B$_2$O$_3$ glass system

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 10 and 25 mol% CuO.

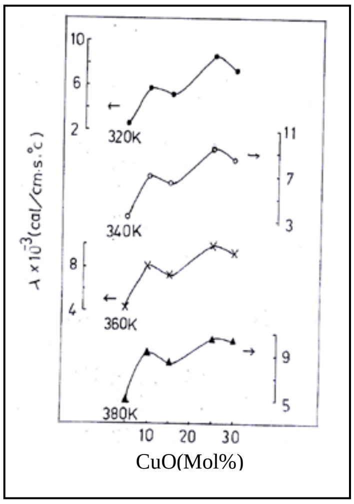

Fig.3 – Variation of thermal conductivity with CuO (mol%) for CuO-MnO$_2$-B$_2$O$_3$ glasses at various temperatures

The values of density d_{theor}, d_{expt}, molar volume, lattice component of thermal conductivity (λ_L) band gap energy (E_g), melting temperature (T_m) of glasses are given in Table2. 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 [15] and can be calculated on the basis of glass composition. However, this is not always true in many glass systems. Jen and Kalinosi[22] 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-MnO_2-B_2O_3 glass has not been discussed in detail.

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

Glass sample CuO-MnO_2-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				
GC_1 05-20-75	2.38	2.991	22.68	7.248	0.0172	1080
GC_2 10-20-70	2.63	3.093	22.22	7.259	0.0102	1068
GC_3 15-20-65	2.87	3.161	22.02	7.091	0.0138	1020
GC_5 25-20-55	3.36	3.360	21.24	7.036	0.0102	981
GC_6 30-20-50	3.60	3.477	20.77	7.237	0.0102	1020

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-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 [27] .

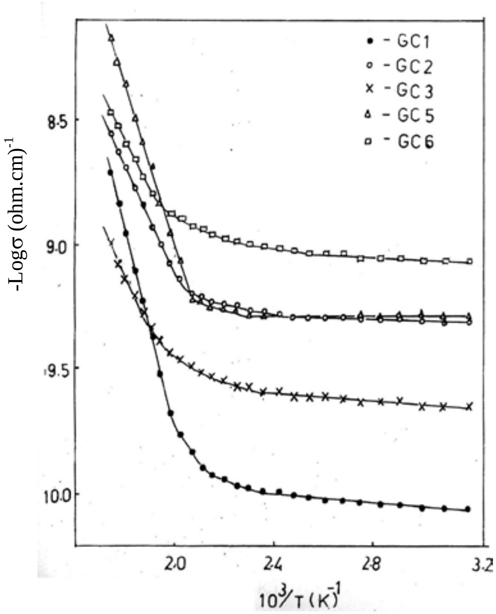

Fig.4 – Temperature Dependence of dc-electrical conductivity for the glasses of different compositions of CuO-MnO_2-B_2O_3

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).

Table 3(a) - λ_e of CuO-MnO_2-B_2O_3 glass of different composition at different temperatures.

Temp T (K)	Electronic thermal conductivity λ_e (Cal/cm s^OC) x 10^{-16}				
	GC1	GC2	GC3	GC5	GC6
313	6.685	36.79	16.81	38.75	65.54
323	7.024	38.31	17.41	39.98	67.96
353	7.814	42.84	19.89	43.79	76.41
383	8.925	47.27	22.56	47.61	86.57
403	9.704	50.43	24.08	50.20	92.91

Table 3(b) λ_{bp} of CuO-MnO_2-B_2O_3 glass of different composition at different temperatures

Temp T (K)	Bipolar thermal conductivity λ_{bp} (Cal/cm s^OC) x 10^{-16}				
	GC1	GC2	GC3	GC5	GC6
313	0.846	0.378	0.192	0.398	0.674
323	0.875	0.390	0.197	0.407	0.692
353	0.935	0.425	0.217	0.434	0.758
383	1.032	0.458	0.240	0.461	0.839
403	1.099	0.482	0.251	0.480	0.889

The calculated values of electron thermal conductivity (λ_e) for CuO-MnO_2-B_2O_3 glasses (Table 3a) increases with temperature and depends on CuO content (of the order of 10^{-16} cal/cm s deg).

The calculated values of λ_{bp} for CuO-MnO_2-B_2O_3 glasses (Table 3b) 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 7.248 x 10^{-3} – 7.237 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} maybe 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-MnO_2-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-MnO_2-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 thephoton thermal conductivity plays negligible role. It is concluded that the lattice component plays dominant role in the thermal conduction of CuO-MnO_2-B_2O_3 glass.

5. Conclusion :

Thermal conductivity of CuO-MnO_2-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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