Thermal conductivity of the vitreous system $(ZnO)_x$–$(P_2O_5)_{1-x}$

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Glasses of the system $(ZnO)_x$–$(P_2O_5)_{1-x}$ have been prepared by melting ZnO with anhydrous P_2O_5 in open crucibles. These glasses had compositions ranging from 20 to 70 mol % ZnO (chemically analysed ZnO mol %). Measurements of the thermal conductivity for the present glass system have been made in the temperature range 305 to 630 K. The thermal conductivity of this glass system is mainly due to lattice thermal vibrations. The thermal conductivity data are found to be fairly sensitive to the ZnO mol % content. It is observed from these data that the present glass system can be divided into three compositional regions. This behaviour is qualitatively explained in terms of changes in glass structure.

1. Introduction

In solids, thermal conductivities showed a great variability, both in magnitude and temperature dependence. This is because there are many different mechanisms contributing to the flow of heat through the solid materials. In fact there are two principal carriers of heat: (i) lattice waves, which are always present, and (ii) free electrons which are present in metals and semiconductors. However, the mean free path of these carriers is affected by various scattering processes. The lattice waves are scattered by each other owing to the anharmonicity of the lattice forces. They are also scattered by various defects and imperfections of the crystal lattice. The conduction electrons are scattered by the lattice waves, so that the mean free path of both electrons and lattice waves is reduced. One aspect is the fact that the carrier mean free path is affected by lattice defects, so that the measurements of thermal conductivity, λ, can, in some cases, be used as a tool in the study of these imperfections: it has been used as an indication of the amorphous–crystalline transformation [1, 2].

In semiconductor materials, the total thermal conductivity, λ_t, may be expressed as

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

where λ_L is the lattice component and λ_e and λ_{bp} represent the electronic components.

In most semiconductors, λ_L is very much greater than λ_e or λ_{bp} [3–8], i.e. in these materials the heat is carried by phonons. Detailed information about the phonon spectrum and phonon density of states distribution for several materials such as silicon and germanium are available [9–11]. Relatively little information is obtained about the semiconducting oxide glasses.

The aim of this investigation was to measure and analyse the thermal conductivity of the ZnO–P_2O_5 glass system from room temperature up to 600 K.

2. Experimental procedure

2.1. Preparation of glasses

ZnO–P_2O_5 glasses were prepared from laboratory reagent grades of Analar phosphorous pentoxide (P_2O_5, mol wt 141.95) and Analar zinc oxide (ZnO, mol wt 81.38), using alumina crucibles (100 cm^3 capacity) heated in an electric furnace open to the atmosphere. The reagents were mixed and placed for 2 h in a furnace held at between 850 and 1100 °C, the highest temperature being applicable to the mixes richest in ZnO. The preparation procedure was employed to prepare glasses with a glass formation range from 10 to 70 mol % ZnO (starting composition). Details about the preparation technique are presented elsewhere [12]. The samples were rod-shaped with diameter 1 cm and thickness about 1 cm.

Nine of these glasses, having densities evenly spread throughout the vitreous range obtained, were selected for chemical analysis [13].

2.2. Thermal conductivity measurements

The construction of the apparatus used for the thermal conductivity measurements of the present glass system is shown in Fig. 1. A steady-state axial heat flow method was used [14]. The glass sample was sandwiched between two brass rods (10 cm long, 1 cm diameter), surrounded by two guard brass tubes of 3 cm i.d. The heat flow was generated by means of a heater at the far end of the upper rod. The whole

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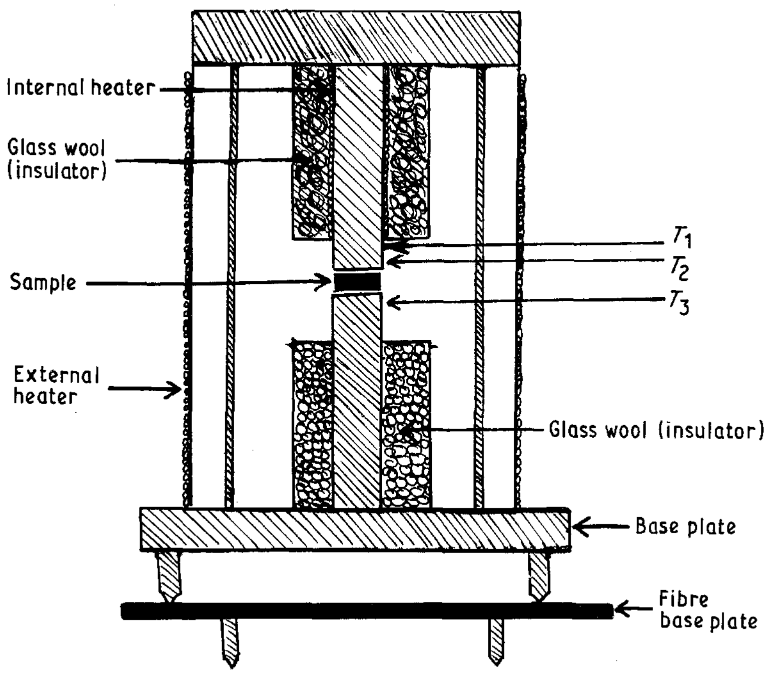

Figure 1 Apparatus used for thermal conductivity measurements by using steady-state axial heat flow comparative method.

system was put in an automatic temperature-regulated oven. Heat losses from sample sides was minimized by adjusting the temperature of the oven to a value $T = (T_1 + T_2)/2$ where T_1 and T_2 are the temperature of the sandwiched sample faces. The temperature gradient was measured by means of three copper–constantan thermocouples. The reproducibility of the results was quite satisfactory (within approximately $\pm$ 10%). The thermal conductivity of the present ZnO–P_2O_5 glasses was measured in the temperature range 300 to 630 K, using the expression

$$H = \lambda \frac{dT}{dX} \quad (2)$$

where H is the equilibrium heat flow per unit per unit time, λ is the measured thermal conductivity and dT/dX is the temperature gradient through the brass bar; λ is obtained with reference to the conductivity of the brass bars, which was previously determined, using the well-known thermal conductivity fused quartz ($0.0146\ \mathrm{cal\,cm^{-1}\,s^{-1}\,°C^{-1}}$ at 28 °C).

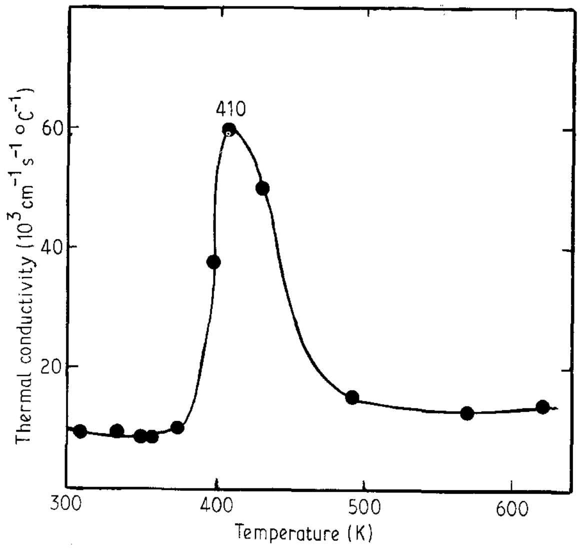

Figure 2 Variation of the thermal conductivity with temperature for ZnO–P_2O_5 glass having 20.05 mol % ZnO.

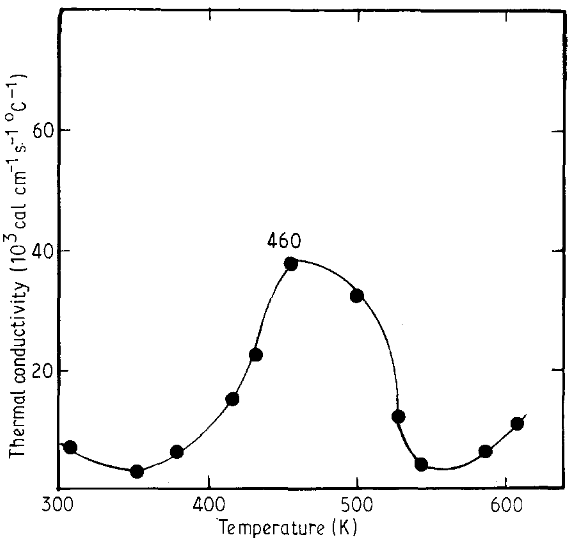

Figure 3 Temperature dependence of the thermal conductivity for ZnO–P_2O_5 glass having 28.62 mol % ZnO.

3. Results and discussion

The results from the measurement of thermal conductivity for our ZnO–P_2O_5 glasses are shown in Table I. Also collected in Table I are the ZnO mol % (chemically analysed with accuracy $\pm$ 1.5 mol % [13]), the free-electron thermal conductivity, λ_e, the bipolar thermal conductivity, λ_{bp}, and the Debye temperature, θ_D.

The electronic thermal conductivity, λ_e, for the present glasses is evaluated using the d.c. electrical conductivity, σ, obtained by Hussein *et al.* [15] and the Wiedemann–Franz law

$$\lambda_e = L_0 \sigma T \quad (2)$$

where T is the absolute temperature and L_0 is the

TABLE I Compositions, measured thermal conductivity, λ_t (cal cm^{-1} s^{-1} °C^{-1}), calculated electronic thermal conductivity, λ_e, and λ_{bp} (cal cm^{-1} s^{-1} °C^{-1}), and the Debye temperature, θ_D(K), for ZnO–P_2O_5 glass system

Sample no.	ZnO (mol %)	$T = 350$ K			$T = 400$ K			$T = 500$ K			$T = 550$ K			$T = 600$ K			θ_D(K)
		λ_t ($\times 10^{-3}$)	λ_e ($\times 10^{-19}$)	λ_{bp} ($\times 10^{-17}$)	λ_t ($\times 10^{-3}$)	λ_e ($\times 10^{-18}$)	λ_{bp} ($\times 10^{-16}$)	λ_t ($\times 10^{-3}$)	λ_e ($\times 10^{-16}$)	λ_{bp} ($\times 10^{-14}$)	λ_t ($\times 10^{-3}$)	λ_e ($\times 10^{-15}$)	λ_{bp} ($\times 10^{-13}$)	λ_t ($\times 10^{-3}$)	λ_e ($\times 10^{-14}$)	λ_{bp} ($\times 10^{-12}$)	
Z-1	20.1	9 ± 1	1020	2900	40 ± 2	1160	2600	15 ± 1	1860	2800	12 ± 1	540	480	13 ± 1	230	250	340
Z-2	28.6	3 ± 0.4	306	930	11 ± 1	233	560	32 ± 2	349	560	4 ± 0.4	240	310	9 ± 1	170	190	351
Z-3	36.0	7 ± 0.6	160	520	7 ± 0.8	150	380	4 ± 0.4	197	330	4 ± 0.4	160	220	4 ± 0.4	42	99	360
Z-4	43.2	13 ± 1	102	340	14 ± 1	81	180	20 ± 2	61	107	20 ± 2	38	55	24 ± 2	24	31	343
Z-5	47.6	31 ± 2	61.2	209	27 ± 2	27	74	27 ± 2	27	47	30 ± 2	25	37	38 ± 2	19	21	340
Z-6	50.2	39 ± 2	19.0	604	34 ± 2	18	51	46 ± 2	23	42	46 ± 2	21	31	35 ± 2	15	20	319
Z-7	65.3	16 ± 1	4.1	16	23 ± 2	2.2	6.8	29 ± 2	2.3	4.8	12 ± 1	2.5	4.4	11 ± 1	2.4	3.4	318
Z-8	70.0	10 ± 1	1.02	4.3	11 ± 1	1.16	3.8	20 ± 2	1.3	2.8	14 ± 1	1.7	3.2	2 ± 0.2	1.4	21	323

Lorentz number which is given by

$$L_0 = \frac{\pi^2}{3}\left(\frac{K}{e}\right)^2 \quad (3)$$

where K is the Boltzmann constant.

The bipolar thermal conductivity, λ_{bp}, is calculated according to the equation [16]

$$\lambda_{bp} = \frac{3}{4\pi^2} L_0 \left(\frac{E_g}{KT} + 4\right)^2 \sigma T \quad (4)$$

where E_g is the diffusing energy for the electron–hole pairs.

The calculated values of λ_e for the present glasses increase as temperature increases, i.e. λ_e changed from $\sim 10^{-19}$ cal cm^{-1} s^{-1} °C^{-1} at 350 K to $\sim 10^{-14}$ cal cm^{-1} s^{-1} °C^{-1} at 600 K (see Table I). Also, the calculated values of λ_{bp} show an increase as the temperature increases. The values changed from $\sim 10^{-17}$ cal cm^{-1}s^{-1} °C^{-1} at 350 K to $\sim 10^{-13}$ cal cm $^{-1}$s^{-1} °C^{-1} at 600 K (see Table I). It is obvious from the calculated values of λ_e and λ_{bp} and the values of the measured thermal conductivity λ($\sim 10^{-1}$ cal cm^{-1} s^{-1} °C^{-1}), that the main contribution of thermal conductivity of the studied glasses is mainly due to lattice thermal conductivity, λ_L, i.e. the flow of heat through such glasses is due to phonon propagation. Here the photon contribution is excluded in the measured temperature range.

The plots of the thermal conductivity, λ_L, against temperature for all glasses are shown in Figs 2 to 9. From these figures it is clear that the thermal conductivity of Z-3, Z-4, Z-6, Z-7 and Z-8 glass samples shows anomalous behaviour with temperature around $T = 1.6\theta_D$, where θ_D is the Debye temperature calculated from ultrasonic data [17] of the same glasses (see Figs 4, 5, 7 to 9). However, glass samples Z-1 and Z-2 show this anomalous behaviour at $T = 1.3\theta_D$ (see Figs 2 and 3). Glass sample Z-5 shows different behaviour to those glasses (see Fig. 6). Generally, the thermal conductivity, λ (for all glasses except Z-1, Z-2 and Z-5), shows increasing with temperatures at

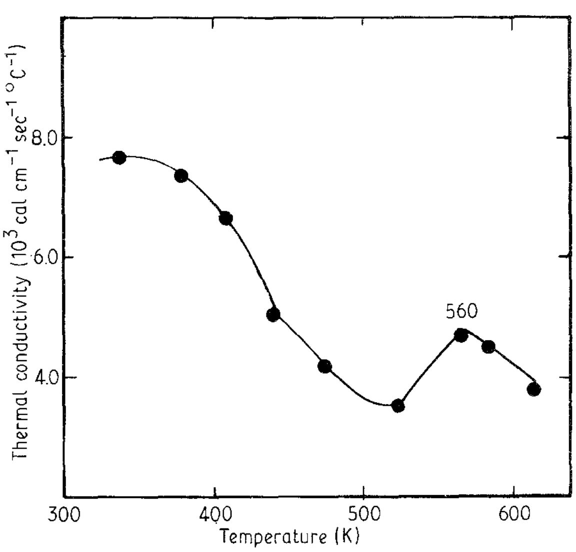

Figure 4 Thermal conductivity of ZnO–P_2O_5 glass having 36.01 mol % ZnO as a function of temperature.

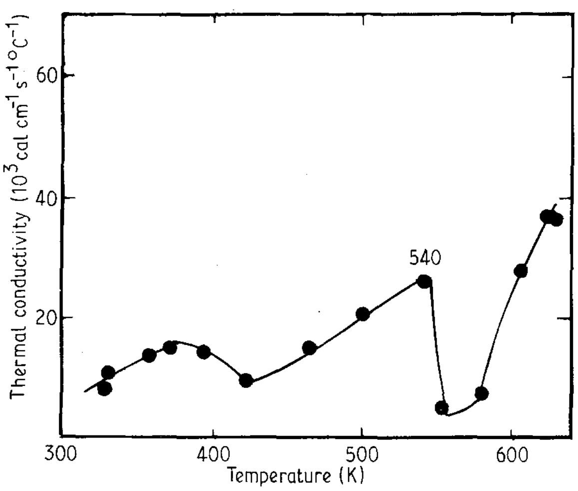

Figure 5 Variation of the thermal conductivity with temperature for $ZnO–P_2O_5$ glass having 43.20 mol % ZnO.

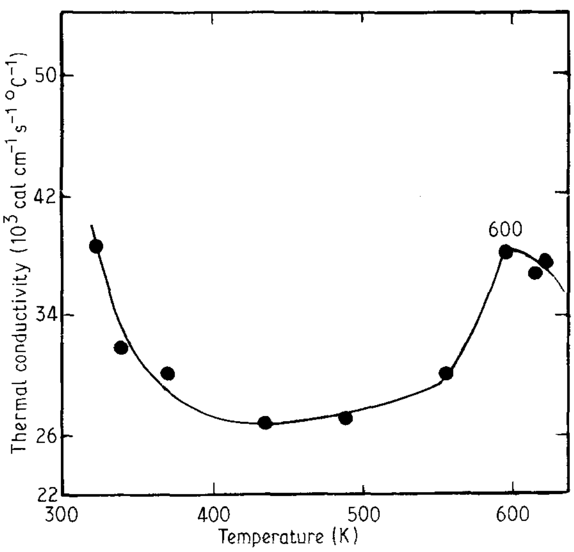

Figure 6 Temperature dependence of the thermal conductivity for $ZnO–P_2O_5$ glass having 47.55 mol % ZnO.

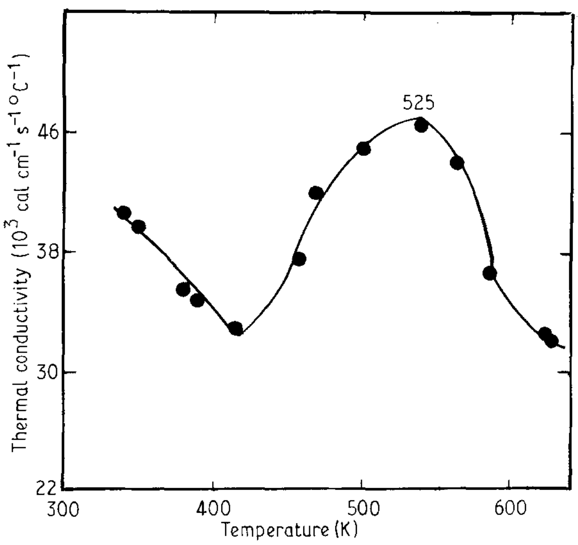

Figure 7 Variation of the thermal conductivity with temperature for $ZnO–P_2O_5$ glass having 50.23 mol % ZnO.

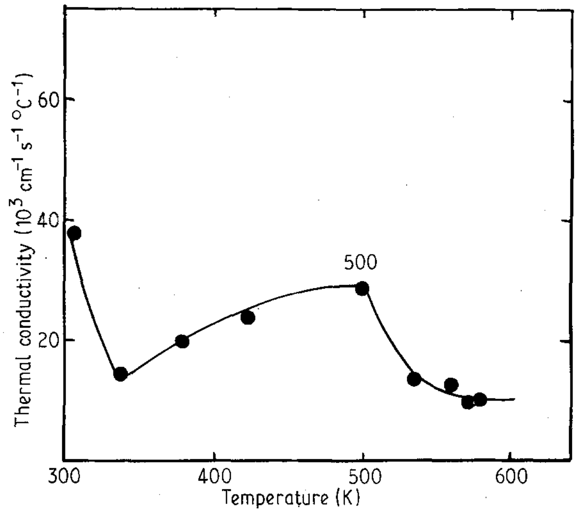

Figure 8 Variation of the thermal conductivity with temperature for $ZnO–P_2O_5$ glass having 65.25 mol % ZnO.

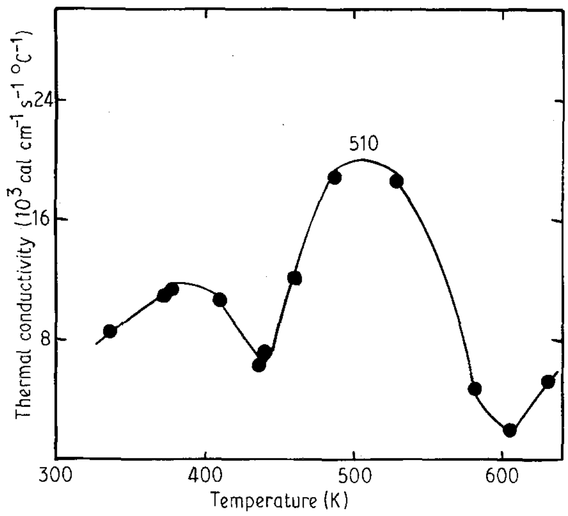

Figure 9 Temperature dependence of the thermal conductivity for $ZnO–P_2O_5$ glass having 70.0 mol % ZnO.

$T < 1.6\theta_D$ and decreasing at $T > 1.6\theta_D$. The same behaviour is shown for Z-1 and Z-2 samples at $T = 1.3\theta_D$. The variations of Debye temperature θ_D [17] and $1.6\theta_D$ with ZnO mol % for all glasses are shown in Fig. 10.

The decreases of phonon thermal conductivity, λ_L, beyond $1.3\theta_D$ for Z-1 and Z-2 samples and $1.6\theta_D$ for Z-3, Z-4, Z-6, Z-7 and Z-8 samples may be explained in terms of three-phonons and four-phonons Umklapp scattering which may take place. On investigating silicon and germanium, Glassbrenner and Slack [18] reported that, at higher temperature, λ_L decreases faster than T^{-1} as a sign that four-phonon processes are taking place. A similar conclusion has been arrived at by Stuckes [19] and by Steigmeier and Kudman [20] for various IV and III–V semiconductors. These investigations may support our explanation mentioned above.

The variations of the thermal conductivity, λ_L, as a function of ZnO mol % content for $ZnO–P_2O_5$ glasses at different temperatures are shown in Figs 11 to 13. It is observed from these figures that the thermal

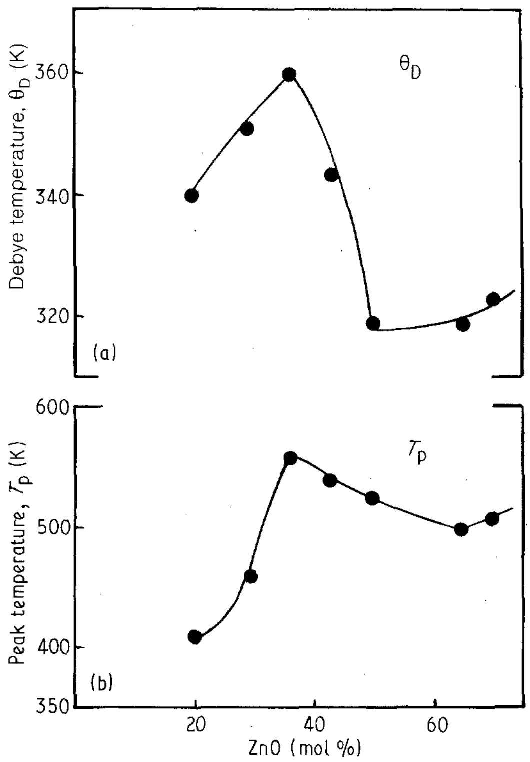

Figure 10 Variations of (a) Debye temperature, and (b) peak temperature ($\equiv 1.6\theta_D$) with ZnO mol % for $ZnO-P_2O_5$ glass system.

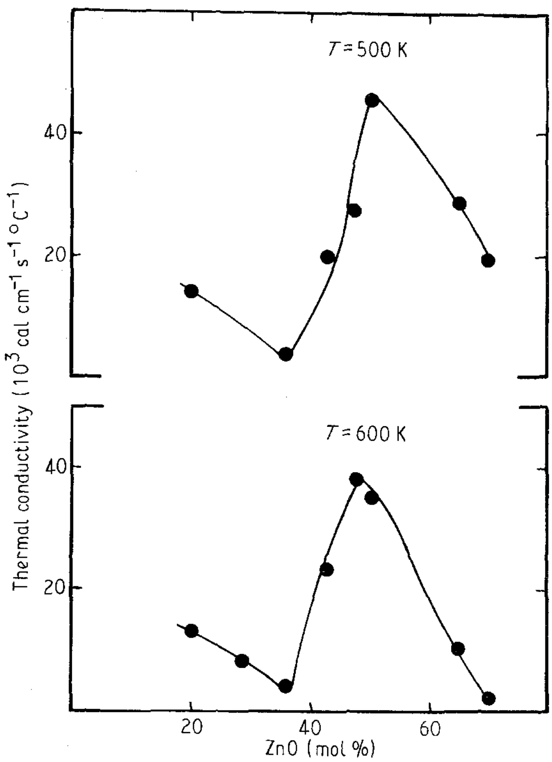

Figure 12 Compositional dependence of the thermal conductivity for $ZnO-P_2O_5$ glass system at $T = 500$ and 600 K.

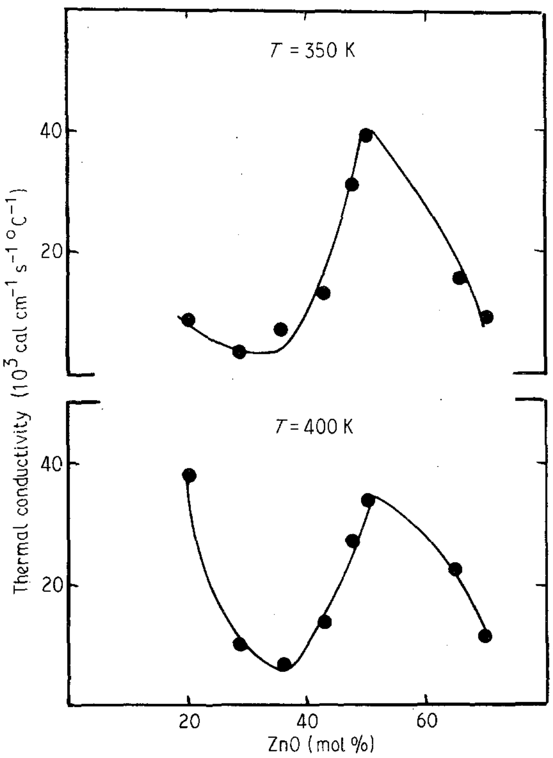

Figure 11 Variations of the thermal conductivity with ZnO mol % for $ZnO-P_2O_5$ glass system at $T = 350$ and 400 K.

conductivity data are sensitive to the glass structure. Three compositional regions can be shown for the present glass system. The addition of ZnO to the vitreous structure P_2O_5 decreases the thermal conductivity, which reaches minimum values at about 35 mol % ZnO. Then there is an increase in thermal

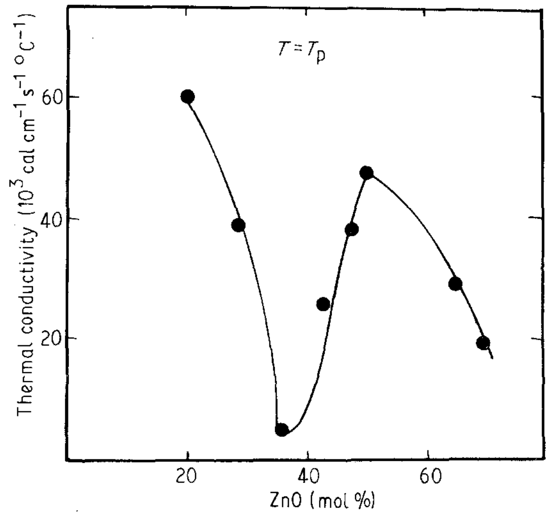

Figure 13 Variations of the thermal conductivity with ZnO mol % for $ZnO-P_2O_5$ glass system at $T =$ peak temperature, T_p ($\simeq 1.6\theta_D$).

conductivity until maximum values are reached at about 50 mol % ZnO content; beyond 50 mol % the thermal conductivity values decrease again.

The addition of ZnO_4 tetrahedra to the vitreous P_2O_5 network will transform P=O bonds into bridging bonds of the type P–O–Zn and P–O–P. This will lead to an increase in the average cross-link density of glasses from 0 up to 35 mol % ZnO content. The above effect will reduce the mean free path of lattice waves which causes the thermal conductivity, λ_L, to decrease. This is true for our $ZnO-P_2O_5$ glasses.

In the region 35 to 50 mol % ZnO content the thermal conductivity, λ_L, increases inspite of the fact that the cross-link density increases with ZnO content.

In this region perhaps the increase in the fraction of weaker Zn–O bonds compared to P–O bonds leads to an increase in λ. However, when the content of ZnO is > 50 mol %, the Zn^{2+} cations fill the octahedral vacancies [21], i.e. $Zn–O_4$ tetrahedra will transform into $Zn–O_6$ octahedra. This will reduce the mean free path of the lattice waves and increase the number of the scattering centres, thus the thermal conductivity, λ, will decrease (see Figs 11 to 13).

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