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Thermophysical properties of polycrystalline $ZnIn_2Se_4$

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Abstract. The specific heat capacity (C_p), thermal conductivity (λ), and thermal diffusivity (a) were measured for polycrystalline $ZnIn_2Se_4$ in the 300 to 600 K range. Measurements were performed using the flash method. The results showed that the mechanism of heat transfer is mainly due to phonons, whereas the contribution of electrons and dipoles are negligible.

Keywords. Thermophysical properties; polycrystalline $ZnIn_2Se_4$; thermal conductivity; anharmonicity.

1. Introduction

Some compounds such as the $A^{II}B^{III}C^{VI}$ ternary group, were studied by several authors [1–4]. The study was focused on the structure and optical properties of compounds like $ZnIn_2S_4$, $ZnIn_2Se_4$, $ZnIn_2Te_4$, $CdIn_2Se_4$ and $CdIn_2Te_4$ [1–7]. A very distinctive character was found in its photoelectric and luminescent properties. These findings made these materials promising for applications [8]. Needles to say, information about the thermophysical properties of these compounds which are presented in two forms, polycrystalline or thin films, is very limited. Most of the studies were conducted on polycrystalline and single crystalline samples of $ZnIn_2Se_4$ [3,4,5,9]. Previously few authors [10] had studied the preparation of polycrystalline $ZnIn_2Se_4$ by using the diffusion method to have pure ingot. Also, the crystal structure of both the powder and the thin films (as prepared and annealed) of these compounds had been examined by both the X-ray diffraction (XRD) and the electron microscopy. In addition, it was found that the optical properties of $ZnIn_2Se_4$ films depend on the heat treatment [10].

However, few studies [11] have been carried out on the thermophysical properties of these compounds. This is the first paper to deal with measuring the thermal conductivity (λ), specific heat capacity (C_p) and thermal diffusivity (a) of polycrystalline $ZnIn_2Se_4$ from 300 to 600 K.

2. Experimental

$ZnIn_2Se_4$ was prepared from mixtures of spectrally pure elements (SN Matthey Chemicals, Ltd.). The details of the preparation procedure are described in a previous work [10]. Discs of 2 cm diameter and 2 mm thickness were produced under pressure of about $9{\cdot}8 \times 10^3$ Pa. A pulse of radiant energy from an incandescent lamp is used to irradiate the front surface of the sample and the corresponding temperature at the lower surface is detected with a thermocouple. The pulse causes a rise in the mean

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temperature of the sample by only about 1 K above its initial value. The mean temperature is controlled by a suitable furnace. The thermal diffusivity and specific heat capacity of the sample material were deduced from the shape of the resulting temperature transient.

The theory of the pulse method for measuring the thermal diffusivity (a) is given in detail in reference [12]. The thermal diffusivity can be calculated by $a = 0{\cdot}139\ (I^2/t_{0.5})$, where $t_{0.5}$ (in s) is the time required for the lower surface of the sample to reach the half maximum in its small temperature rise and I (in m) is the sample thickness. The specific heat capacity C_p can be measured by the following relation,

$$C_p = q/MT_m \tag{1}$$

where q is the power dissipated through the sample, M the mass of the sample and T_m the maximum temperature rise. The heat losses by radiation from the boundaries of the sample were taken into consideration. The ratio between the diameter of the sample and the thickness can be chosen $\geqslant 5$. The thermal conductivity λ can be calculated from the relation,

$$\lambda = QC_p a \tag{2}$$

where Q is the density of the sample.

A sample in the form of a disc of diameter 1 to 2 cm and thickness 1 to 3 mm is mounted in a vacuum chamber. The surfaces of the specimen were coated with graphite as a highly absorbing medium. The sample is heated by a furnace to achieve the mean temperature of the sample. The radiation pulse from the flash lamp was chosen to be of negligible duration in comparison with the characteristic rise time of the sample. The transient response of the lower surface is then measured and detected by means of a nickel-chrome-nickel thermocouple (diameter 0·1 mm) amplifier, and a Y-t plotter. The optical flux from the powerful incandescent lamp (2000 W) was focused on the upper surface of the sample by means of an elliptic reflector through a fused quartz window.

The short duration of the radiant flux was achieved by an electronically controlled shutter. The heat losses by radiation from the surfaces of the samples are minimized by making the measurements in a very short time (8 ms). The mean temperature of the sample is compensated by means of a bias circuit in order to detect only the temperature rise due to the pulse on the lower surface of the sample. The thermal inertia of the detecting circuit is also considered.

The duration of the pulse was recorded by means of a photodiode viewing the upper surface of the sample and it appears on the oscillogram as a small ramp. The $t_{0.5}$ values were measured from the starting time of the photodiode response up to the time when the lower surface attained half its maximum temperature rise. The heat losses by radiation are minimized by making the measurements in a short period of time.

Various experimental conditions and different factors affecting the results are analyzed and considered. Accordingly, a certain accuracy is claimed, 5% systematic error in thermal diffusivity, 4% in heat capacity, and 5·5% in the thermal conductivity are to be expected.

3. Results and discussion

Typical results of specific heat capacity (C_p), thermal conductivity (λ), and thermal diffusivity (a) in the temperature range 300 K to 600 K of $ZnIn_2Se_4$ compounds are

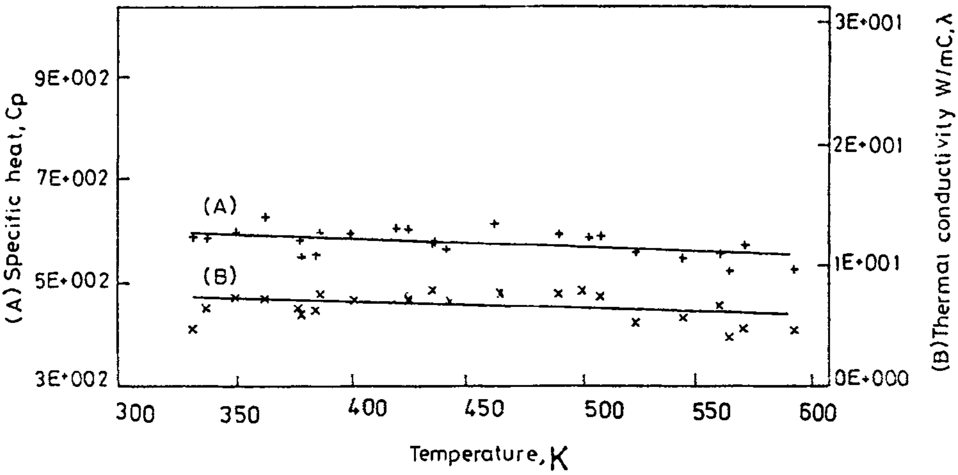

Figure 1. The temperature dependence of (A) The specific heat capacity C_p and (B) thermal conductivity λ for $ZnIn_2Se_4$.

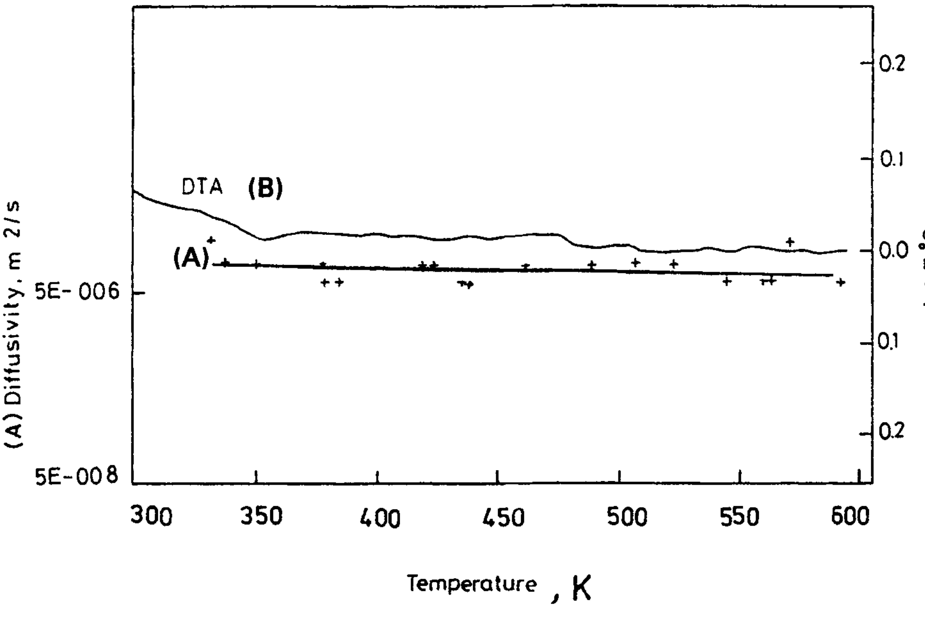

Figure 2. (A) Thermal diffusivity (A) and (B) the temperature dependence of differential analysis DTA for $ZnIn_2Se_4$.

shown in figures (1A&B) and figure (2A). From figure (1A), it was found that the specific heat capacity (C_p) decreases slightly with temperature indicating that there is no considerable change in its crystal structure in the temperature range of measurements which is confirmed by DTA measurements as shown in figure (2B). Anharmonicity may be responsible for the decrease of C_p with temperature. It is known that the change of specific heat of a semiconductor has two components, one due to lattice vibrations

Table 1. Calculated values of the electronic contribution C_e to the specific heat capacity C_p, E_f is the Fermi energy, the electrical conductivity σ and the calculated values of the electronic part λe and bipolar part λbp for $ZnIn_2Se_4$ at 300 and 500 K.

Temperature	E_f (eV)	Ce $JKg^{-1}K^{-1}$	σ $(\Omega^{-1}Cm^{-1})$	λe $(Wm^{-1}K^{-1})$	λbp $(Wm^{-1}K^{-1})$
300 K	1·691	$4{\cdot}92 \times 10^{-5}$	0·417	$3{\cdot}062 \times 10^{-9}$	$4{\cdot}116 \times 10^{-7}$
500 K	1·559	$7{\cdot}231 \times 10^{-3}$	0·344	$10{\cdot}007 \times 10^{-4}$	$6{\cdot}234 \times 10^{-3}$

C_L and the other is due to electrons Ce, therefore, $C = Cr + Ce$. The electronic contribution Ce of specific heat was calculated from the relation,

$$Ce = \frac{\pi^2 K^2 T}{2E_F} \times \left[\frac{2\pi \mathrm{mok} T}{h^2}\right]^{3/2}, \tag{3}$$

where k is the Boltzmann constant, h the Planck constant, and E_F the Fermi energy. The calculated values of Ce and E_F at 300 and 500 K are given in table 1. It is clear that the values of (Ce) are negligible compared to the specific heat due to lattice vibrations.

From figure (1B), it can be seen that the value of the thermal conductivity λ_T decreases slightly with temperature. The mechanism of heat transfer in such materials is due to phonons, electrons, and a bipolar contribution. The heat transfer by electromagnetic radiation can be written as,

$$\lambda \text{photon} = \frac{16}{3} \times \frac{\sigma n^2 T^2}{\alpha}, \tag{4}$$

where σ is the Stefan–Boltzmann constant, n the refractive index, and α is the absorptance. $ZnIn_2Se_4$ compounds are opaque materials, so the role of photons in the heat transfer mechanism is negligible in the measured temperature range. Figure 3b shows the dependence of λph on temperature Tk. The electronic part of thermal conductivity λe was calculated using the Wiedemann–Franz ($\lambda e = L_0 \sigma T$), where σ is the electric conductivity, L_0 the Lorentz number, and T the absolute temperature. Figure 3c, represents the relation between λe and T. The electron-hole thermal conductivity λ_{bp} can be calculated according to

$$\lambda 6p = \frac{3L_0 \sigma T}{4\pi^2} \times \left[\frac{Eg}{KT} + 4\right]^2 \tag{5}$$

and is tabulated in table (1) at 300 and 500 K. The values of λe ande λbp are very small and are negligible in the measured temperature range. For $ZnIn_2Se_4$ samples, any deviation from the T^{-1} law is due to defects of the crystal lattice which affect the phonon-phonon interaction in these materials. Such an effect was found to increase with the increase in temperature. This behaviour is related to umklapp processes of phonon-phonon interaction [13]. So one may conclude that the main mechanism of heat transfer in the studied samples is due to phonons. Figure 2A shows that the thermal diffusivity (a) decreases as the temperature increases.

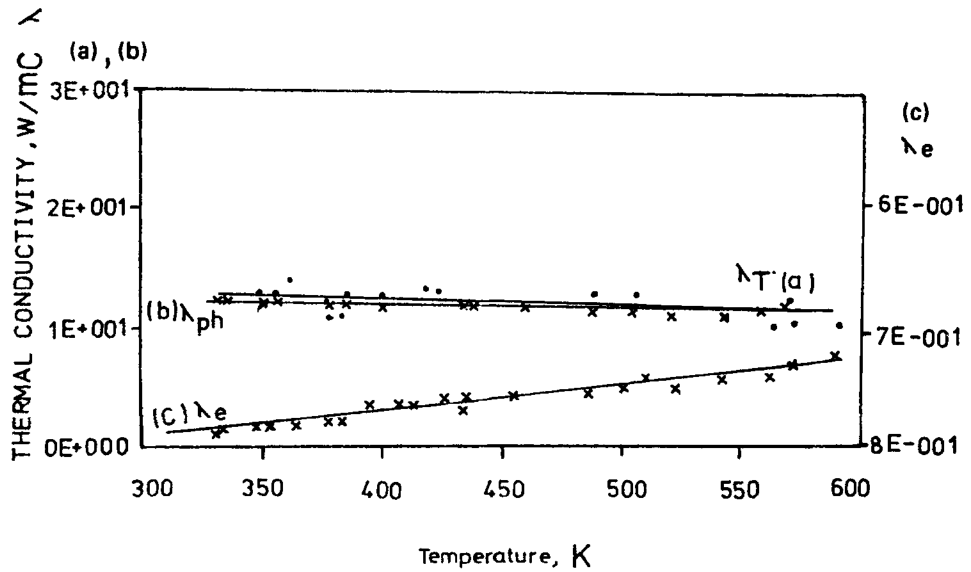

Figure 3. The temperature dependence of (**a**) total thermal conductivity λT, (**b**) thermal conductivity due to photon λPh and (**c**) the electronic part of thermal conductivity λe for $ZnIn_2Se_4$.

Conclusions

The specific heat capacity and thermal diffusivity for $ZnIn_2Se_4$ samples were measured in the temperature range 300–600 K. It was found that the electrical properties (σ) of the samples were agreeable with our previous work on thin films. In addition, the results showed that in polycrystalline $ZnIn_2Se_4$ electrons, dipoles and photons did not contribute to total thermal conductivity at the temperature range of our measurements and the mechanism of heat transfer is due to phonons only.

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