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THERMAL PROPERTIES OF POLYCRYSTALLINE $ZnIn_2Se_4$

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Abstract

A pulse method was used to measure the thermal conductivity λ, specific heat capacity C_p and thermal diffusivity ξ of polycrystalline $ZnIn_2Se_4$ in the temperature range 300–600 K.

The temperature dependence of λ, C_p and ξ demonstrated a light decrease for this material in the temperature range 300–600 K, indicating that there is not a significant change in the structure in this temperature range; this was confirmed by DTA measurements. The results showed that the mechanism of heat transfer is due mainly to phonons; the contributions of electrons and dipoles are very small.

Keywords: heat capacity, polycrystalline $ZnIn_2Se_4$, thermal conductivity, thermal diffusivity

Introduction

Some ternary compounds $A^{II}B^{III}C^{VI}$ have been studied by various authors [1–4], focusing on the structures and optical properties of materials such as $ZnIn_2S_4$, $ZnIn_2Se_4$, $ZnIn_2Te_4$, $CdIn_2Se_4$ and $CdIn_2Te_4$ [1–7]. A very distinctive character was found in their photoelectric and luminescent properties. These findings made these materials promising for certain applications [8]. Needless to say, information concerning the thermophysical properties of these materials, which can exist 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]. The preparation of polycrystalline $ZnIn_2Se_4$ by using a diffusion method to obtain a pure ingot was studied previously [10]. These studies were followed by X-ray diffraction and electron microscopic examinations of samples in both powder and thin film forms. It was found that the optical properties of $ZnIn_2Se_4$ films depend on the heat treatment [10].

However, few studied [11] have been carried out on the thermophysical properties of these materials. This paper deals with measurements of the thermal conductivity (λ), specific heat capacity (C_p) and thermal diffusivity (ξ) of polycrystalline $ZnIn_2Se_4$ from 300 to 600 K.

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Experimental

$ZnIn_2Se_4$ was prepared from mixtures of the spectroscopically pure elements (5 N Matthey Chemicals, Ltd.). The details of the preparation procedure were described in a previous work [10]. The sample was mixed thoroughly in a porcelain ball mill for 5 h (dry mixing) and sieved completely through a 200 mesh sieve. Compact discs approximately 2 cm in thickness and approximately 2 cm in diameter were made by compressing the powder in a cylindrical mould under a pressure of 10^4 Pa. A pulse of radiant energy from an incandescent lamp was used to irradiate the upper surface of the sample, and the corresponding temperature at the lower surface was detected with a nickel chrome-nickel thermocouple. The pulse caused a rise in the mean temperature of the sample by only about 1 K above its initial value. The mean temperature was controlled by a suitable furnace. The thermal diffusivity and specific heat capacity of the sample were deduced from the shape of the resulting temperature transient.

The theory of the pulse method for measuring ξ was given in detail in reference [12]. Accordingly, it can be calculated by using the following empirical formula:

$$\xi = 0.139(I^2/t_{0.5})$$

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 determined from the following relation:

$$C_p = q/MT_m$$

where q is the power dissipated through the sample, M is the mass of the sample and T_m is the maximum temperature rise.

The ratio between the diameter of the sample and its thickness was chosen to be ≥ 5 in order to minimize the heat losses by radiation from the boundaries. Accordingly, the heat losses by radiation from the boundaries of the sample can be neglected. The thermal conductivity λ can be calculated from the relation

$$\lambda = \rho C_p \xi$$

where ρ is the density of the sample.

A sample in the form of a disc of diameter approximately 2 cm and thickness approximately 2 mm was mounted in a vacuum chamber. The surfaces of the specimen were coated with graphite as a highly absorbing medium. The sample was 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 was then measured by means of a nickel chrome-nickel thermocouple, an amplifier and a Y-t plotter. The optical flux from a powerful incandescent lamp (2000 W) was focussed 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 with an electronically controlled shutter. The heat losses by radiation from the surface of the sample were minimized by making the measurements in a very short time (8 ms). The mean temperature of the sample was 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 duration of the pulse was recorded by means of a photodiode viewing the upper surface of the sample, and appeared 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.

Various experimental conditions and different factors affecting the results were analysed and considered. Accordingly, a certain accuracy was attained: a 5% systematic error in thermal diffusivity, 4% in heat capacity, and 5.5% in thermal conductivity are to be expected.

Results and discussion

Typical results on the specific heat capacity C_p, thermal conductivity λ and thermal diffusivity ξ of $ZnIn_2Se_4$ in the temperature range 300–600 K are presented in Fig. 1A, B and C, respectively. It was found that C_p decreases slightly with temperature, indicating that there is no significant change in its crystal structure in the temperature range of measurements; this was confirmed by DTA measurements, which revealed no detectable phase change. The values of C_p indicate that the sample obeys the Debye theory of specific heat at high temperature. Anharmonicity may be responsible for the decrease in C_p with temperature. It is known that the change in specific heat of a semiconductor has two components, one due to lattice vibrations C_L, and the other due to electrons C_e, with $C=C_L+C_e$. The electronic contribution C_e was calculated from the relation [13]

$$C_e=\frac{\pi^2 k^2 T}{2E_F}\left[\frac{2\pi m_o kT}{h^2}\right]^{3/2}$$

where k is the Boltzmann constant, m_o is the electron mass, h is Planck's constant, and E_F is the Fermi energy:

$$E_F=E_{F(o)}\left[1-\frac{\pi^2}{12}\frac{kT}{E_{F(o)}}\right]^2$$

where $E_{F(o)}$ is the Fermi energy at absolute zero.

We earlier measured the electrical properties of $ZnIn_2Se_4$ [14] in the temperature range 300–600 K [14]. The values of the electrical conductivity σ allowed estimation of the electronic and bipolar contributions of thermal conductivity at 300 and 500 K. The calculated values of C_e, E_F and σ at 300 and 500 K are given in Table 1. It is clear that the values of C_e are negligible as compared with the specific heat due to lattice vibrations.

Table 1 Calculated values of the electronic contribution C_e to the specific heat capacity C_p, the Fermi energy E_F, the electrical conductivity σ and the calculated values of the electronic part λ_e and the bipolar part λ_{bp} for $ZnIn_2Se_4$ at 300 and 500 K

Temperature/ K	E_F/ eV	C_e/ J kg^{-1} K^{-1}	σ/ Ω^{-1} cm^{-1}	λ_e/ W m^{-1} K^{-1}	λ_{bp}/ W m^{-1} K^{-1}
300	1.7	$4.9\cdot10^{-5}$	0.34	$3\cdot10^{-9}$	$10\cdot10^{-4}$
500	1.6	$7.2\cdot10^{-3}$	0.42	$4\cdot10^{-7}$	$6\cdot10^{-3}$

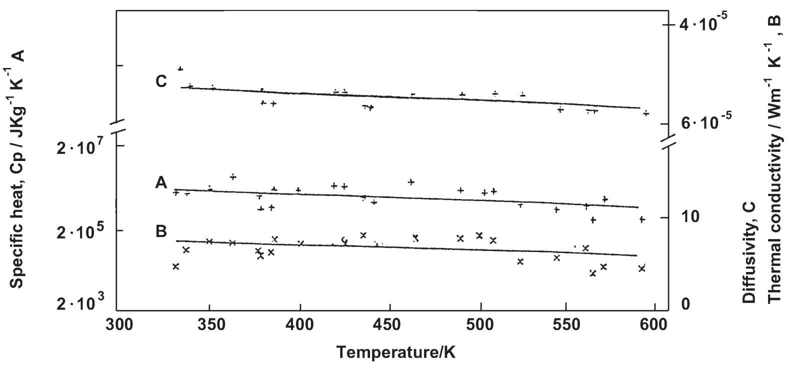

Fig. 1 Temperature dependence of (A) specific heat capacity C_p, (B) thermal conductivity λ and (C) thermal diffusivity ξ for $ZnIn_2Se_4$

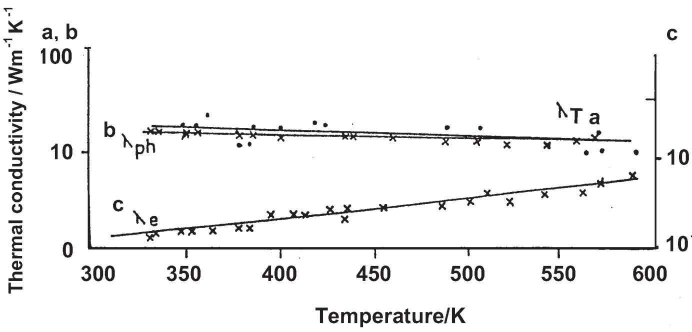

Fig. 2 Temperature dependence of (a) total thermal conductivity λ_T, (b) thermal conductivity due to photons λ_{Ph} and (c) electronic part of thermal conductivity λ_e for $ZnIn_2Se_4$

Figure 1B reveals that the thermal conductivity λ 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 [13]

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

where σ is the Stefan-Boltzmann constant, n is the refractive index, and α is the absorbance. The $ZnIn_2Se_4$ sample is opaque, so the role of photons in the heat transfer mechanism is negligible in the measured temperature range. Figure 2b shows the dependence of λ_{ph} on $T(K)$. The electronic part of the thermal conductivity λ_e was calculated by using Wiedemann-Franz law ($\lambda_e = L_o \sigma T$), where σ is the electric conductivity, L_o is the Lorentz number ($L_o = k/q)^2$, and T is the absolute temperature. Figure 2c depicts the relation between λ_e and T.

The electron-hole thermal conductivity λ_{bp} can be calculated according to [13]

$$\lambda_{pb} = \frac{3L_o \sigma T}{4\pi^2}\left[\frac{E_g}{kT}+4\right]^2$$

and is tabulated in Table 1 at 300 and 500 K. The values of λ_e and λ_{bp} are very small and are negligible in the measured temperature range. For $ZnIn_2Se_4$, any deviation from the T^{-1} law is due to defects in the crystal lattice, which affect the phonon-phonon interaction in this material. Such an effect was found to increase with increase of temperature. This behaviour is related to umklapp processes of phonon-phonon interaction [13]. Thus, it may be concluded that the main mechanism of heat transfer in the studied sample is due to phonons. Figure 1C demonstrates that the thermal diffusivity ξ decreases as the temperature is increased.

Conclusions

Measurements of thermal conductivity λ, specific heat capacity C_p and thermal diffusivity ξ were performed by using a pulse method in the temperature range 300–600 K. The temperature dependence of λ, C_p and ξ indicated a slight decrease for this material, in agreement with our previous results on the electrical conductivity $\sigma(T)$ for this sample under the same conditions. DTA measurements confirmed these results.

The results showed that the mechanism of heat transfer is due mainly to phonons, the contributions of electrons and dipoles being very small.

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