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TEMPERATURE DEPENDENCE OF THE THERMOPHYSICAL PROPERTIES OF POLYCRYSTALLINE CHALCOGENIDE GLASSES

Mercury and antimony sulphides

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Abstract

The specific heat (C_p), thermal conductivity (λ), thermal diffusivity (a), and electrical conductivity (σ) were measured for polycrystalline HgS and Sb_2S_3 in the temperature range 300–600 K. The measurements were performed with an experimental apparatus based on a so-called flash method. The results showed that the mechanism of heat transfer is mainly due to phonons, whereas the contribution of electrons and bipolars is very small indeed. The energy gap of the samples was also calculated.

Keywords: HgS, Sb_2S_3, thermophysical properties

Introduction

Chalcogenide glasses possess thermoelectric and photoelectric properties which are of practical importance. These have been studied in the solid phase at different temperatures [1–3]. Mercury and antimony sulfides (HgS and Sb_2S_3) have been studied very little in the solid state at low temperatures [4, 5]. The present study of pure HgS and Sb_2S_3 chalcogenide glasses was made in order to determine the effect of temperature on the specific heat, thermal conductivity and thermal diffusivity in the temperature range 20–300°C. These measurements were performed using a technique based on a so-called flash method. This technique was explained and published elsewhere [6] and was used for measuring the thermal properties of different materials [7, 8].

Mercury and antimony sulfides used in the present study were 99.999% pure materials supplied by Aldrich Chemical Company, Inc., Wisconsin, Mil-

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waukee USA. The crystal structure was studied using X-ray diffraction. DTA was used to determine any phase changes in the measured temperature range.

Experimental

The pulse of radiant energy from an optical incandescent lamp was used to irradiate the front surface of a sample and the corresponding temperature at the lower surface was detected with a thermocouple. The pulse causes a rise in the mean temperature of the sample only about 1 K above its initial value. The mean temperature is controlled by a suitable furnace. The thermal diffusivity and specific heat of the sample material were deduced from the shape of the resulting temperature tansient.

The theory of the pulse method for measuring the thermal diffusivity a was given in detail in [9]. The thermal diffusivity a can be calculated as

$$a = 0.139 \frac{l^2}{t_{0.5}} \text{ m}^2 \text{ s}^{-1}$$

where $t_{0.5}$ is the time required for the lower surface of the sample to reach half the maximum in its small temperature rise, and l is the sample thickness. The specific heat C_p can be determined using the following relationship:

$$C_p = \frac{q}{MT_m}$$

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 heat losses caused by radiation from the boundaries of the samples were taken into consideration. The ratio between the diameter of the sample Φ and thickness l can be chosen >5. The thermal conductivity can be calculated from the relationship

$$\lambda = \rho C_p a$$

where ρ is the density of the sample.

The calculated values of the density were 3.65×10^3 kg m^{-3} for Sb_2S_3 and 3.35×10^3 kg m^{-3} for HgS.

The sample in the form of a disc of 1–2 cm diameter and 1–3 mm thickness was mounted in a vacuum chamber. The surfaces of the specimen were coated with graphite as a highly absorbent 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 and detected by means of NiCr/Ni thermocouple (diameter 0.1 mm), an amplifier, and an y–t plotter. The optical flux from the powerful incandescent lamp (2000 watt) 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 by an electronically controlled shutter. The heat losses caused by radiation from the surfaces 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 thermal inertia of the detecting circuit was considered.

The duration of the pulse was detected by means of a photodiode viewing the upper surface of the sample and appeared on the oscillogram as a small ramp. $t_{0.5}$ values were measured from the starting time of the photodiode response to the point of time at which the lower surface attained one half of its maximum temperature rise.

Various experimental conditions and different factors affecting the results were analyzed and considered. Accordingly, a certain accuracy is claimed, 3% systematic error in thermal diffusivity, 2% in heat capacity and 5.5% in the thermal conductivity is to be expected.

Results and discussion

Figure 1 shows the DTA curves recorded for polycrystalline HgS and Sb_2S_3 samples, which show that there is no transition of any kind in the investigated temperature interval (300–600 K).

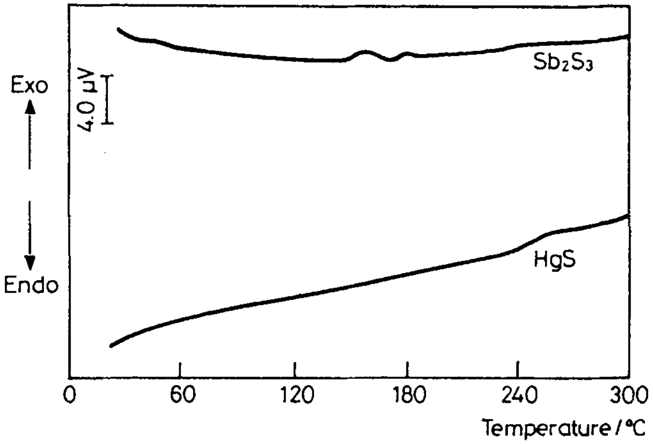

Fig. 1 DTA curves of HgS and Sb_2S_3

X-ray powder diffraction patterns of the investigated samples using CuK$_\alpha$ as an incident radiation are presented in Figs 2 and 3. It was found that HgS has a hexagonal structure while Sb_2S_3 is orthorhombic with lattice parameters; a=11.23 Å, b=11.31 Å, and c=3.8 Å. All reflection lines observed are characteristic of the two samples and no indication of strange reflections was found.

Electrical conductivity σ

The measured temperature dependence of the electrical conductivity of Sb_2S_3 and HgS samples in the temperature range 300–600 K are shown in

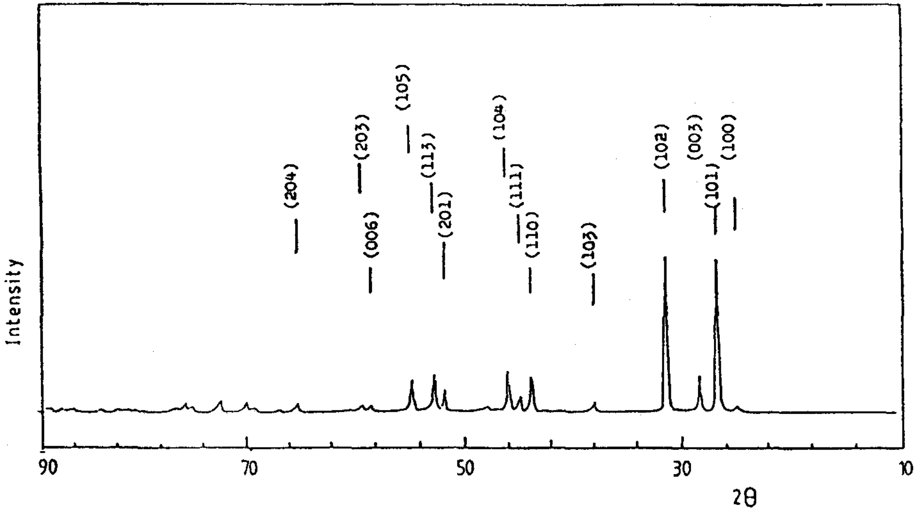

Fig. 2 X-ray diffraction patterns of HgS

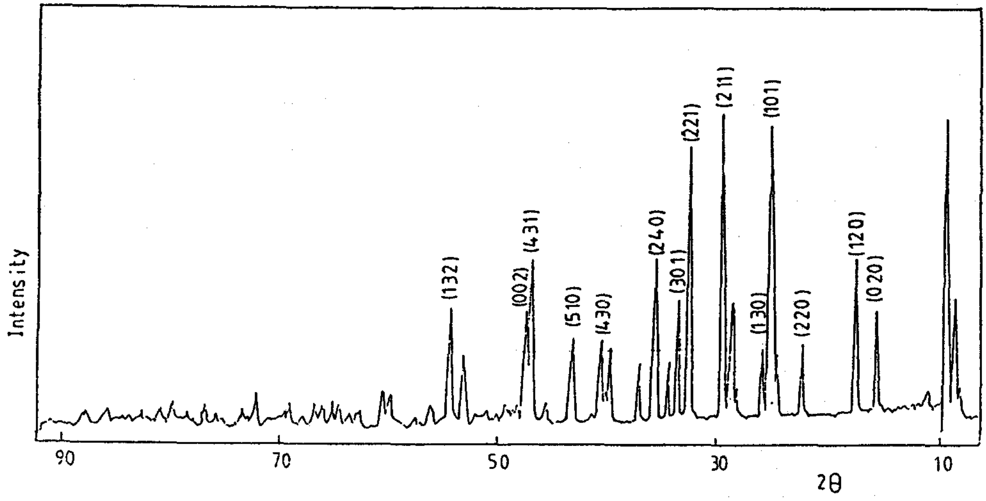

Fig. 3 X-ray diffraction patterns of Sb_2S_3

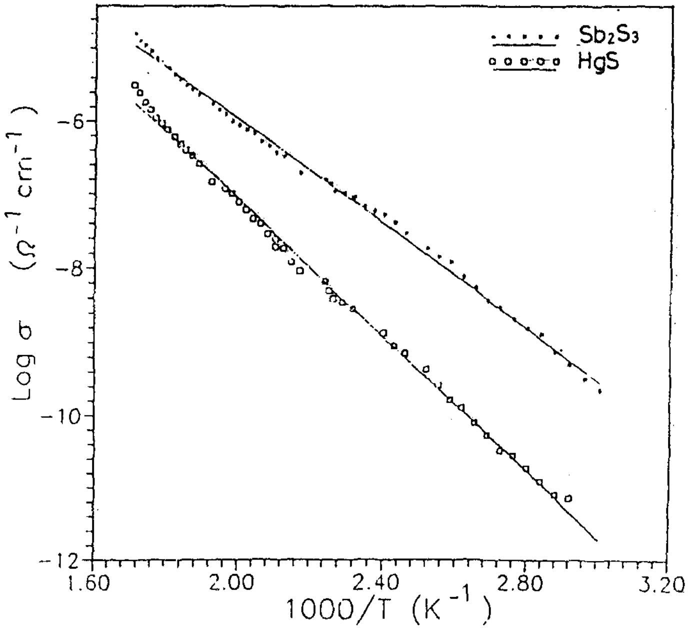

Fig. 4 The dependence of electrical conductivity σ on temperature for HgS and Sb_2S_3

Table 1 Calculated values of the energy gap E_g of polycrystalline Sb_2S_3 and HgS

Sample	E_g/eV
Sb_2S_3	0.70
HgS	0.91

Fig. 4. The weighted least squares fit to all data points yields the energy gap, E_g of polycrystalline Sb_2S_3, and HgS samples as presented in Table [1].

Examples of the measured temperature dependence of the electrical conductivity for Sb_2S_3 are 15.5×10^{-4} $\Omega^{-1}m^{-1}$ at 584.8 K, 87.1×10^{-6} $\Omega^{-1}m^{-1}$ at 500 K, and 51.3×10^{-9} $\Omega^{-1}m^{-1}$at 342.8 K, and for HgS, 75.9×10^{-7} $\Omega^{-1}m^{-1}$ at 500 K, and 72.4×10^{-11} $\Omega^{-1}m^{-1}$ at 342.5 K. These results indicate that Sb_2S_3 and HgS have semiconducting properties.

Specific heat capacity C_p

The measured temperature dependences of specific heats at constant pressure, C_p, for HgS and Sb_2S_3 in the temperature range 300–600 K are shown in Fig. 5. As can be seen from this graph, C_p for both samples increases slightly in a monotonous fashion with the temperature within experimental error. This behaviour of C_p suggests that the structures of these materials do not change sig-

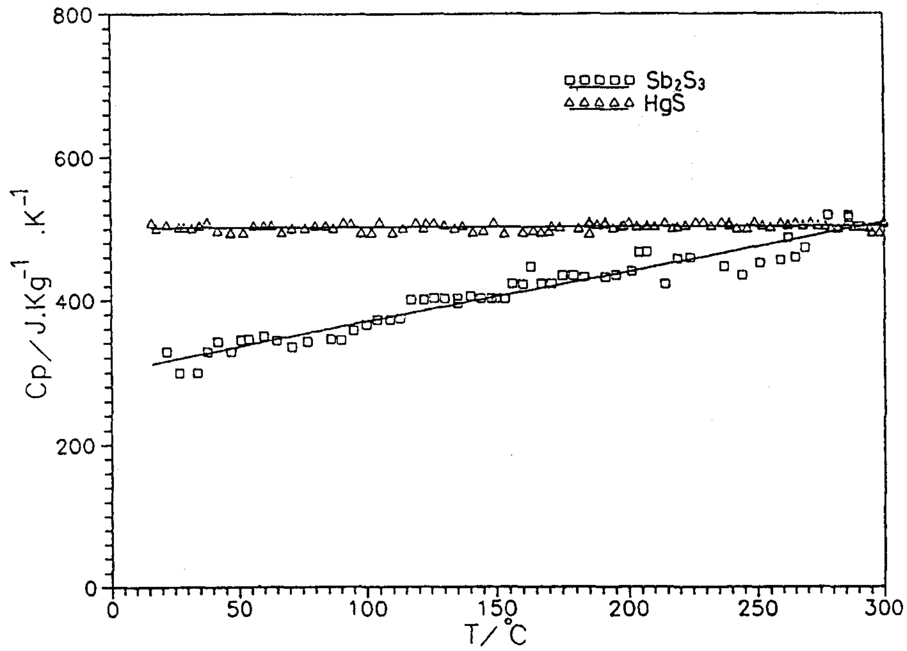

Fig. 5 The variation of C_p with temperature for HgS and Sb_2S_3

nificantly with temperature in the measured temperature range. This is in a good agreement with DTA data. Anharmonicity might be responsible for the slight increase of C_p with temperature. The specific heat of a typical semiconductor has two components, one due to lattice vibration, C_v (lattice), and the other is due to electronic contribution, therefore,

$$C_v = C_v(\text{electronic}) + C_v(\text{lattice})$$

The electronic specific heat can be calculated using the following expression:

$$C_v = C_v(\text{electronic}) = \frac{\pi^2}{2}\left(\frac{KT}{E_F}\right)N(T)K;$$

$$N(T) = 2\left(\frac{2\pi mKT}{h^2}\right)^{3/2}$$

where N is the number of electrons per unit volume, K is Boltzmann constant, m is the electron mass, h is Planck's constant and E_F is the Fermi energy at finite temperature which is expressed in terms of its value at the absolute zero temperature, $E_F(0)$, by:

$$E_F = E_F(0)\left(1 - \frac{\pi^2}{12}\right)(KT/E_F(0))^2$$

In the present work, and for simplicity the magnitude of the Fermi energy at absolute zero, $E_F(0)$, is considered to be half the energy gap.

Table 2 Calculated values of the Fermi energy E_F of polycrystalline Sb_2S_3 and HgS at absolute zero, 342.5 K, 500 K and 548.8 K

Sample	E_F(0 K)/eV	E_F(342.5 K)/eV	E_F(500 K)/eV	E_F(584.8 K)/eV
Sb_2S_3	0.351	0.349	0.347	0.345
HgS	0.457	0.455	0.454	0.452

Table 3 Calculated values of the electronic specific heat C_v (electronic), for Sb_2S_3 and HgS at 342.5 K, 500 K and 584.8 K

Sample	$C_v = C_v$(electronic)J kg^{-1} K^{-1}		
	342.5 K	500 K	584.8 K
Sb_2S_3	14.8	15.6	18.3
HgS	8.7	30.1	56.7

The temperature dependence of the Fermi energy of the present two compounds, determined in the way given above, are listed in Table 2. The calculated values of the electronic contribution to C_p for the two samples are presented in Table 3. It can be seen from Table 3 that the electronic part of C_v is insignificant compared with the specific heat component due to lattice vibration.

The specific heat at constant volume C_v was calculated using the relation

$$C_p - C_v = Ac^2\rho T \quad \text{since}$$

$$A = \frac{2.14\times10^{-2}}{T_{mp}}\text{mol cal}^{-1}$$

where T_{mp} is the melting point of the sample. The melting point of HgS is 583.5°C and 550°C for Sb_2S_3. It was found that the differences between C_p and C_v are very small ($C_p \sim C_v$) and the values of C_v indicate that the behaviour of C_v obeys the Debye theory of specific heat at high temperatures.

Thermal conductivity

Figure 6 shows the variation of thermal conductivity λ with temperature for HgS and Sb_2S_3. It was found that λ for HgS decreases as the temperature increases and the data obey λT=Constant, which means that the main mechanism of heat transfer in HgS is due to phonons only.

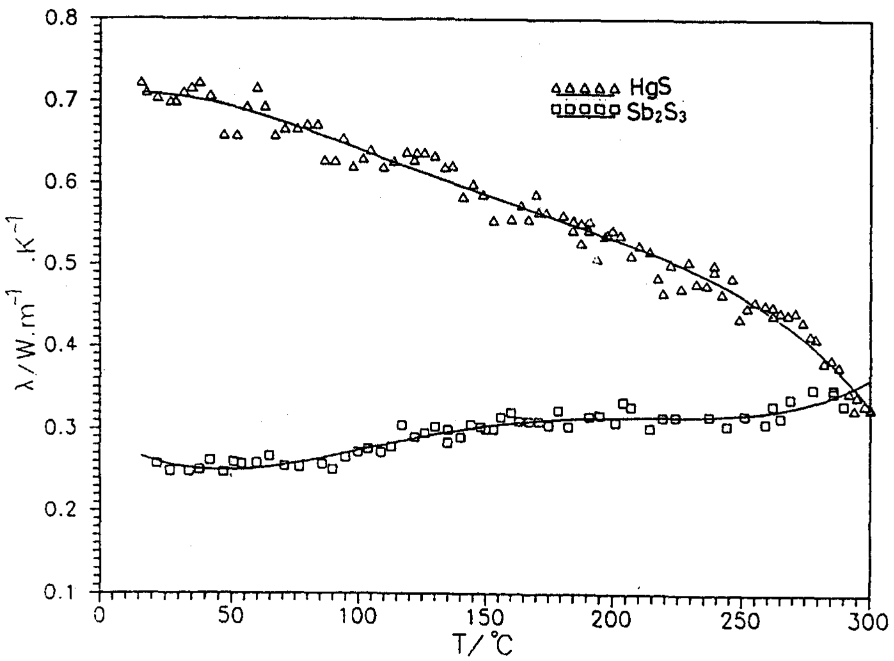

Fig. 6 The dependence of thermal conductivity λ on temperature for HgS and Sb_2S_3

The thermal conductivity λ for Sb_2S_3 was found to increase slightly with temperature. This indicates that there are more than one mechanisms responsible for heat transfer through this material in the temperature range investigated. The mechanism of heat transfer in such materials is due to electrons, photons and phonons. For the electronic part of the thermal conductivity λ_e, Muzhadaba and Shalyt [9] reported that the Wiedmann-Franz ratio can be used to calculate λ_e in a limited range of temperatures and carrier densities. This can be represented by the condition that λ_e/λ_T should be greater than 5% from our result. However, this condition cannot be satisfied by our results. Therefore, the electronic part of the thermal conductivity λ_e is negligible. The values of the electrical conductivities together with the energy gap permitted estimation of the electron and bipolar contribution to the thermal conductivity. The bipolar thermal conductivity λ_{bi} for both samples was calculated using the equation:

$$\lambda_{bi} = \frac{3\pi^2}{4} L\sigma T(E_g/KT + 4)^2$$

It was found that λ_{bi} for Sb_2S_3 at 342.4 K is 4.1×10^{-6} W $m^{-1}K^{-1}$, 3.2×10^{-6} W $m^{-1}K^{-1}$ at 500 K and 2.9×10^{-6} W $m^{-1}K^{-1}$ at 584.8 K. For HgS sample λ_{bi} at 342.5 K is 6.5×10^{-6} W $m^{-1}K^{-1}$, at 500 K, 4.9×10^{-6} W $m^{-1}K^{-1}$ and at

584.8 is 4.5×10^{-6} W $m^{-1}K^{-1}$. From the above disscussion it was found that the main mechanism of heat transfer is due to phonons.

The radiative part of thermal conductivity $\lambda_{photons}$ depends on the optical properties in the form of the refractive index n and the optical absorption coefficient α of the investigated material. The investigated materials are opaque and therefore $\lambda_{photons}$ should be negligible [10].

Thermal diffusivity a

Figure 7 shows the variation of the thermal diffusivity, a with temperature for HgS and Sb_2S_3. The thermal diffusivity is related to the total thermal conductivity by the relation:

$$a=\frac{\lambda}{\rho C_p}$$

where ρ is the density of the investigated material. The estimated values of a indicate that the materials under investigation are typical insulators in the temperature range of the measurements.

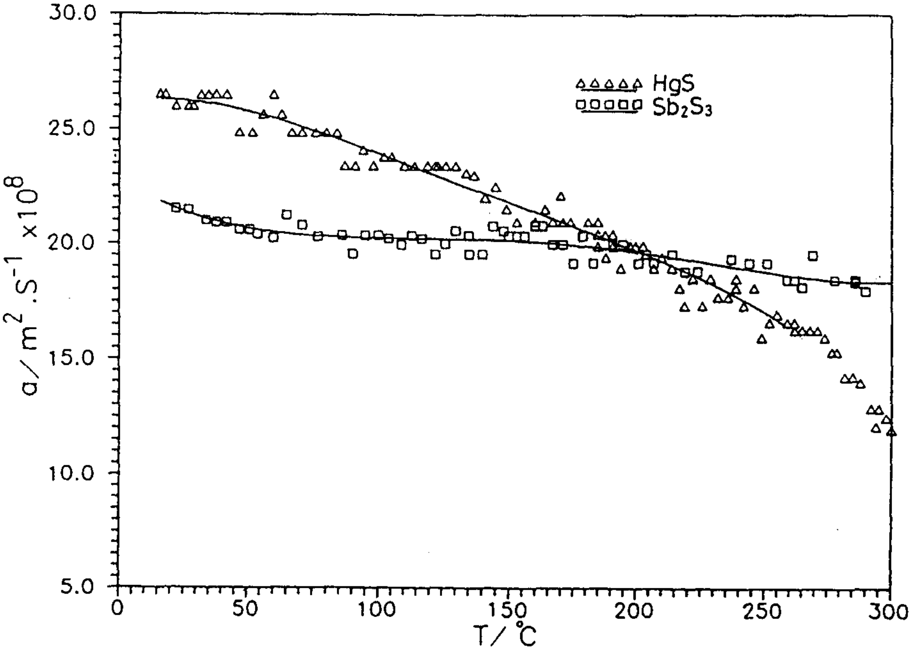

Fig. 7 The variation of thermal diffusivity a with temperature for HgS and Sb_2S_3

Conclusion

It was found that in these materials the main mechanism of heat transfer is due to phonons, and the role of electrons, bipolars and photons is negligible in the investigated temperature range. The results of specific heat measurements show that the electronic specific heat is very small compared with the lattice contribution, and the results obey the Debye theory of the specific heat. The thermal diffusivity results showed that the investigated materials are typical insulators and that there is no transition of any kind in this range of measurements.

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