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Optical investigation of SnS_2 single crystals

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The optical properties of the layered compound SnS_2 have been studied. Reflectivity spectra were measured at room temperature, in the energy region 1.8–5.6 eV. Optical transmission measurements were carried out in the temperature range 13–300 K, in order to evaluate the energy gaps and their temperature dependences. The spectra of the optical constants n, κ, ε_1 and ε_2 versus photon energy $h\nu$ have also been presented.

1. Introduction

SnS_2 is a layered semiconductor, with the CdI_2 structure. It belongs to the dichalcogenide MX_2 family compounds, which exhibits structural polytypism. M is an element of the IVth group of the Periodic Table and X is a chalcogen element. The most common space group of the SnS_2 polytypes is the D^3_{3d}, with one molecule in the hexagonal unit cell. The crystals are composed of thin layers, with hexagonal close-packed sulphur atoms and with tin atoms in octahedral co-ordination, stacked upon each other. On the layers, the tin and sulphur atoms are bound together by covalent forces; the bonds between successive layers are due to weak Van der Waals forces [1–14].

Until now, the temperature dependence of the energy gap of this material was measured in the range 350–80 K [15].

In this work, optical transmission measurements were made of SnS_2 single crystals in the temperature range 13–300 K. From the corresponding spectra, the absorption coefficient, α, was evaluated and then the existence of direct and indirect energy gaps (E^d_g and E^i_g), and their dependence on the temperature was examined. Reflectivity spectra are also presented from 1.8–5.6 eV recorded at room temperature, as are the evaluated spectra of the refractive index, $\tilde{n}$, and of the real and imaginary parts of the dielectric constant, ε_1 and ε_2, respectively.

2. Experimental procedure

SnS_2 crystals of dimensions $\sim 6.5 \times 7 \times 0.1\ \text{mm}^3$ were grown by the stoichiometric composition technique (total synthesis) in a constant temperature furnace (1000 °C) [14, 16, 17]. The crystals were flat, quite transparent , brilliant, of reddish colour. The structural characterization of the samples was performed by means of transmission and scanning electron microscopy. From the TEM investigation we determined the lattice parameters: $a = b = 0.3646$ nm and $c = 0.5879$ nm, which are in the range of those reported previously in the literature: $a = 0.3639$–0.3652 nm, $c = 0.5868$–0.5894 nm [18–20]. Scanning electron micrographs revealed the layered structure of the compound. An extended report concerning the growth and the morphology of the obtained crystals is given elsewhere [17].

To measure the optical transmission we properly prepared the samples by cleaving them repeatedly. With this procedure, thin samples ($\sim 10\ \mu$m) were obtained with flat surfaces oriented normal to the c-crystallographic axis. Special care was taken to avoid holes and scratches and to obtain samples with homogeneous thickness.

The optical transmission of the samples was measured using a Cary (model 14 double beam) spectrophotometer with a prism-grating combination. The incident unpolarized light beam was perpendicular to the surfaces of the samples. The apparatus was provided with tungsten and hydrogen lamps and photomultiplier detectors. A liquid helium cryogenic system was adapted to the spectrophotometer for low-temperature measurements (13–300 K). The cryostat was evacuated at $\sim 10^{-7}$ torr [21].

For the reflectivity measurements at 300 K, an automated apparatus was used, consisting of a spectrophotometer (Gilford model-250) and a lock-in amplifier (Stanford-Research-530). The spectrophotometer was operated with chopped radiation (186 Hz), in the range 220–800 nm, fitted with deuterium and halogen lamps and a photomultiplier detector.

3. Results and discussion

To find the absorption coefficient, the measured transmitivity values, T, were evaluated with the following equation

$$T = (1 - R)^2 \exp(-\alpha d) \qquad (1)$$

where d is the sample thickness, R the reflectivity and α the absorption coefficient. The absorption coefficient was determined for all temperatures using the values of R at room temperature and assuming that the temperature change from 13 K to 300 K produces only relative small changes in R [22, 23].

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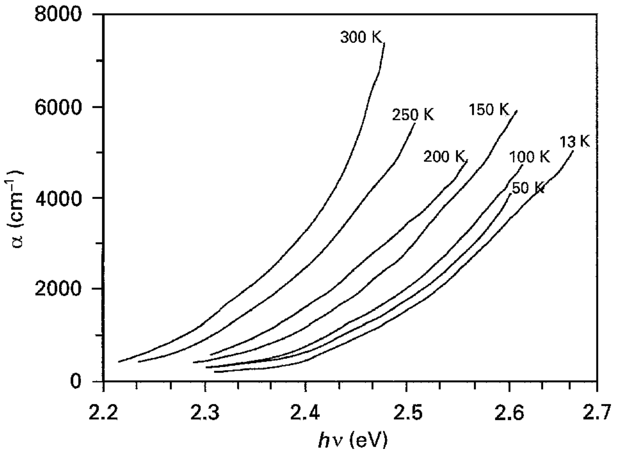

Figure 1 Absorption coefficient, α, of SnS_2 as a function of the photon energy, $h\nu$, for different temperatures.

The thickness of the sample was determined by the interference fringes in the region 1800–2000 nm, where the real part, n, of the refractive index, $\tilde{n}$, is almost constant [17, 24, 25].

Fig. 1 shows the absorption coefficient, α, plotted at seven different temperatures in the range 13–300 K. All experimental curves were recorded in the fundamental absorption region. It is obvious from these curves that as the temperature increases the absorption edge shifts to lower energy values.

The imaginary part, κ, of the refractive index, $\tilde{n}$, can be obtained from the absorption coefficient using the equation

$$\kappa = \frac{\alpha\lambda}{4\pi} \tag{2}$$

The values of κ varied from 0–0.03 in the energy region of the measurements (Fig. 2a). Thus, the real part, n, of the refractive index, $\tilde{n}$, was evaluated by the equation

$$R = \frac{(n-1)^2 + \kappa^2}{(n+1)^2 + \kappa^2} \tag{3}$$

where κ was not taken into account because of its very low values.

Fig. 2b shows n versus $h\nu$, and Fig. 3 the measured reflectivity R at 300 K in the range 1.8–5.6 eV. The measured reflectivity curve and the positions of the corresponding peaks agree with reports in the literature [18, 22]. Good agreement also exists for the corresponding plots of n and κ [26, 27].

The possible existence of different energy gaps is revealed using the fitting with the well-known equations

$$\alpha^r = A(h\nu - E_g) \quad \text{for direct transitions} \tag{4}$$

$$\alpha^{r'} = A'(h\nu - E_g \pm E_p) \quad \text{for indirect transitions} \tag{5}$$

where $r = 1/2$ or $3/2$ and $r' = 2$ or 3 for allowed and forbidden transitions respectively, $h\nu$ is the photon energy, E_p the phonon energy and A, A' constants.

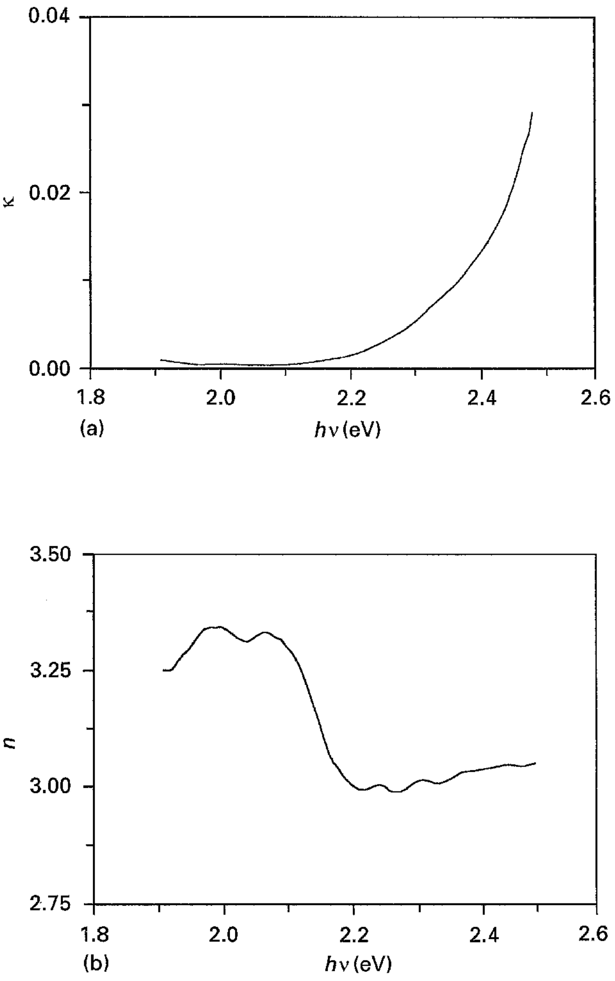

Figure 2 (a) Imaginary part, κ of the refractive index versus photon energy, $h\nu$, at 300 K. (b) Real part n of the refractive index versus photon energy $h\nu$ at 300 K.

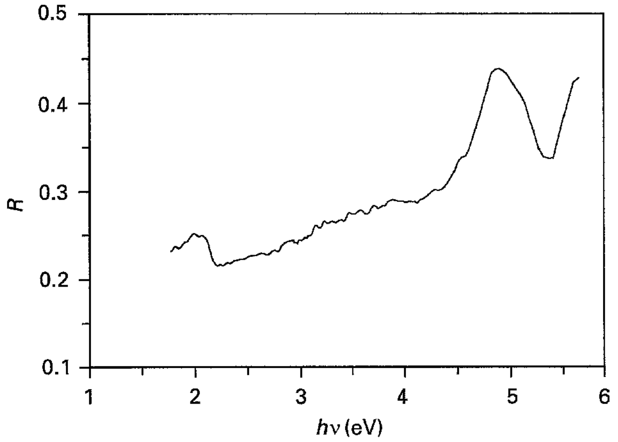

Figure 3 Reflectivity spectrum of SnS_2 at 300 K.

In Fig. 4a and b the $\alpha^{2/3}$ versus $h\nu$ and $\alpha^{1/2}$ versus $h\nu$ plots are shown at different temperatures. Extrapolations of the linear parts of the curves down to α^r, $\alpha^{r'} = 0$ provide the values of the direct forbidden and indirect allowed energy gaps, $E_g^{d,f}$ and $E_g^{i,al}$, respectively. The absorption edge again shifts to lower values as the temperature increases from 13 K to 300 K. The obtained values of the energy gaps are listed in Table I.

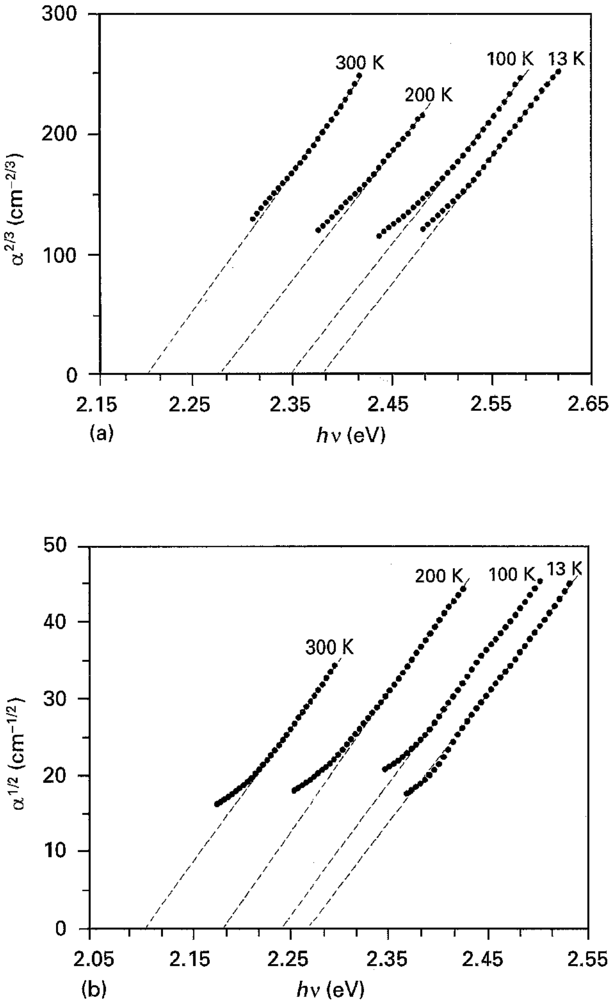

Figure 4(a) Plot of $\alpha^{2/3}$ and (b) plot of $\alpha^{1/2}$, versus $h\nu$ for some representative temperatures.

TABLE I The obtained values of the energy gaps for seven different temperatures

T (K)	$E_g^{d,f}$ (eV)	$E_g^{i,al}$ (eV)
13	2.380	2.265
50	2.370	2.260
100	2.350	2.240
150	2.320	2.210
200	2.275	2.180
250	2.240	2.140
300	2.203	2.100

The value of the allowed indirect gap at room temperature has been found to be 0.02–0.12 eV, lower than that reported in the literature [18, 23, 24, 28, 29]. The deviation does not exceed 5%. For the direct forbidden gap at room temperature, the closest reported values are 2.17, 2.31 and 2.40 eV [28, 30, 31], i.e. the deviation from the value of the present report is ~ 1.5%–10%.

The temperature dependence of the energy gaps can be described with the empirical formula of Varshni [32]

$$E_g(T) = E_g(0) - \frac{\delta T^2}{T + \beta} \qquad (6)$$

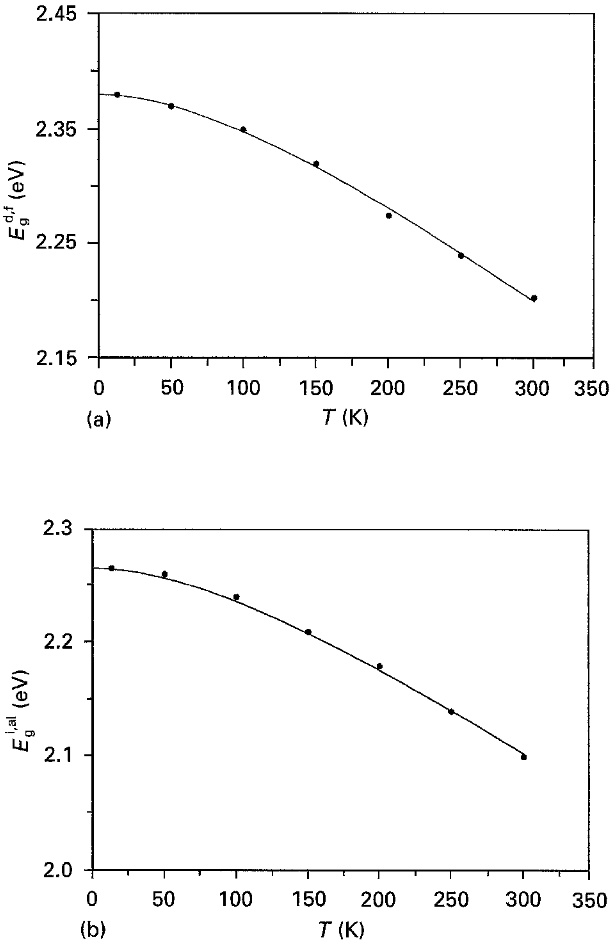

Figure 5 Temperature dependence of (a) the forbidden direct gap $E_g^{d,f}$ and (b) the allowed indirect gap $E_g^{i,al}$. (●) Experimental points, (——) fitting of experimental points using equation 6, and values of δ and β from Table II.

TABLE II The evaluated values of $E_g(0)$, δ and β as obtained from the fitting of the temperature dependence of the energy gaps $E_g^{d,f}$ and $E_g^{i,al}$ with Varshni's equation

Type of gap	$E_g(0)$ (eV)	δ (10^{-4} eV K^{-1})	β (K)
$E_g^{d,f}$	2.38	10.66	232
$E_g^{i,al}$	2.265	9.58	232

where $E_g(0)$ is the value of the energy gap at 0 K (direct or indirect), β is a constant, describing the Debye temperature, θ_D, and $\delta \approx dE_g/dT$ (for $T \gg \beta$).

Fig. 5a and b show the temperature dependence of the energy gaps. The experimental points are shown, with the fitting of the experimental points using Equation 6 and for δ and β the values listed in Table II.

From the linear parts of the temperature dependence of $E_g^{i,al}$, the following values for dE_g/dT are obtained [18, 23]: 8.6 and 9.8×10^{-4} eV K^{-1}, being not very different from the corresponding value of δ (Table II).

Finally, the real and imaginary parts of the dielectric constant, ε_1 and ε_2, respectively were evaluated. For this reason the following equations were used

$$\varepsilon_1 = n^2 - \kappa^2 \qquad (7)$$

$$\varepsilon_2 = 2n\kappa \qquad (8)$$

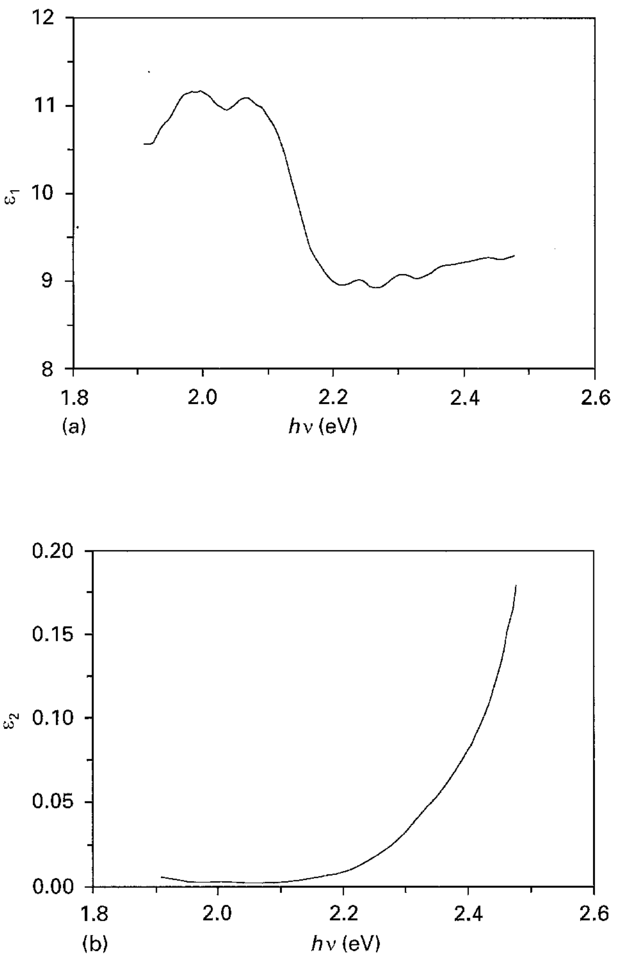

Figure 6 (a) Real part ε_1 and (b) imaginary part ε_2 of the dielectric constant versus $h\nu$ at 300 K.

In Figs. 6a and b the plots of ε_1 and ε_2 versus $h\nu$ are shown, respectively. As we can see from the plots, the values of the optical constants determined here do not differ much from those reported previously in the literature [26, 27].

4. Conclusion

In the present work, results concerning the energy gap values of SnS_2 between 300 and 13 K are reported, thus completing the existing reports in the range 350–80 K. For this reason absorption measurements were conducted on thin layered samples. As far as we know from the literature, it is the first time that the Debye temperature has been evaluated for SnS_2 with this procedure. Finally, the optical constants n, κ, ε_1 and ε_2 were evaluated, in good agreement with corresponding reports in the literature.

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