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Preparation and Fundamental Physical Properties of $\text{Sn}_2\text{SbS}_2\text{I}_3$ and $\text{Pb}_2\text{SbS}_2\text{I}_3$ Compounds

The oriented ingots of isostructural compounds $\text{Sn}_2\text{SbS}_2\text{I}_3$ and $\text{Pb}_2\text{SbS}_2\text{I}_3$ were prepared using a modified Bridgman method. The lattice parameters of the prepared orthorhombic compounds have been determined by a X-ray powder diffraction analysis. From the spectral response of the photoconductivity the following values for the forbidden zone of the prepared sulfides-iodides were found: $E_g(\text{Sn}_2\text{SbS}_2\text{I}_3)$ 1.5 eV, $E_g(\text{Pb}_2\text{SbS}_2\text{I}_3)$ = 2.0 eV.

1. Introduction

Chalcogenide-halides of the elements of the group Vb of the periodic system have become an object of considerable interest in the last twenty years, and that because of their significant semiconducting and ferroelectric properties. So far, little attention has been paid to the quaternary chalcogenide-halides of group IV and V elements. Preparation and basic structure data are reported by OLIVIER-FOURCADE et al.; the $\text{Sn}_2\text{SbS}_2\text{I}_3$ crystals exhibit orthorhombic structure corresponding to the Cmc₂m space group. The preparation of the isostructural $\text{Pb}_2\text{SbS}_2\text{I}_3$ compound is reported by DOLGIKH (1985a), where the authors investigated the dielectric properties, in particular the high-frequency permittivity.

In the present paper we describe the preparation of the $\text{Sn}_2\text{SbS}_2\text{I}_3$ and $\text{Pb}_2\text{SbS}_2\text{I}_3$ compounds, give the results of the enthalpy changes on melting the crystals, report the determination of precise lattice parameter values and compare the energy gap width, as determined from the spectral dependence of the photoconductivity.

2. Experimental

2.1. Preparation of $\text{Sn}_2\text{SbS}_2\text{I}_3$ and $\text{Pb}_2\text{SbS}_2\text{I}_3$

To synthesise polycrystalline quaternary compounds $\text{Sn}_2\text{SbS}_2\text{I}_3$ and $\text{Pb}_2\text{SbS}_2\text{I}_3$ we used elemental Sn, Sb, and Pb of 5 N purity, sulphur purified using a technique described by DOLGIKH (1985b) to a purity of 4.5 N, and resublimated iodine p.a. No heavy metals were identified by spectral analysis of the iodine used. The weighed quantities of the elements corresponding to stoichiometry were sealed into an evacuated quartz glass double ampoule (to a pressure lower than $3 \cdot 10^{-3}$ Pa). Iodine was contained in a special small glass tube sealed into the reaction ampoule in order to eliminate the problems of its volatility and the possibility of its contamination by moisture. After breaking the tube, iodine was resublimated into the reaction space and the reaction mixture was heated and left to react. The ampoule was maintained at 650 °C in a rocking furnace for 36 hours. Homogeneous polycrystalline $\text{Sn}_2\text{SbS}_2\text{I}_3$ and $\text{Pb}_2\text{SbS}_2\text{I}_3$ materials were obtained in this way.

The polycrystalline materials were used to grow oriented ingots by means of a modified Bridgman method. A polycrystalline sample of the quaternary compound was inserted into a conical quartz ampoule, which was then flushed with pure argon, evacuated to a pressure lower than $3 \cdot 10^{-3}$ Pa and

sealed off. After 48 hours of heat treatment at a temperature of 500 °C the ampoule was pulled at a rate of 1.0 mm/hour through a temperature gradient of 400 K/5 cm. In this way, oriented ingots of diameter $d = 10$ mm and length 50–60 mm were obtained and used for the preparation of the samples.

2.2. Determination of lattice parameters

Powder X-ray analysis was carried out on samples prepared by thorough grinding of the single crystals in a vibrating mill. A vertical X-ray diffractometer HZG-4B (VEB Freiburger Präzisionsmechanik, GDR) featuring a goniometer 25 cm in diameter was used for the measurements. The radiation used was $\text{CuK}\alpha$ ($\lambda = 0.154178$ nm) and $\text{CuK}\alpha_1$ ($\lambda = 0.154051$ nm) for angles $2\theta < 30^\circ$ and $2\theta > 30^\circ$, respectively. The $\text{K}\beta$ radiation was attenuated by means of a Ni filter and the diffraction was analysed with the proportional detector (X-ray analysis of $\text{Sn}_2\text{SbS}_2\text{I}_3$ and $\text{Pb}_2\text{SbS}_2\text{I}_3$ see Table 1)

2.3. Thermal analysis

The samples of the prepared $\text{Sn}_2\text{SbS}_2\text{I}_3$ and $\text{Pb}_2\text{SbS}_2\text{I}_3$ compounds were investigated using the technique of differential thermal analysis with the aid of a PERKIN-ELMER Thermal Analysis DTA 17000 System High Temperature Differential Thermal Analyser apparatus.

The measured sample, a quantity of 20–25 mg, sealed into quartz ampoules evacuated to a pressure of approx. 1 Pa was heated, together with Al_2O_3 standard sample, at a rate of 20 K/min, the accuracy of temperature reading being ± 2 K. The obtained DTA curves were used to determine the enthalpy changes and to characterize the solid-liquid phase transition.

2.4. Determination of photoelectric properties

In the aim to estimate the energy gap width E_g of the prepared quaternary compound crystals we measured the dependence of the photoconductivity on the wavelength of the incident radiation. The measurements were carried out on the samples $4 \times 1 \times 0.1 - 0.3$ mm³ in size, obtained by cleaving from the oriented ingots; the contacts were made with metallic indium. The dependence of the photoelectric current i_{ph} on the incident radiation wavelength was determined under conditions of chopping the light beam at a frequency of 6.25 s⁻¹, using the d.c. voltage 8.5 V, at room temperature. The plot of i_{ph} versus λ , corrected for intensity variation of the incident radiation, is shown in Figure 1. The energy gap width E_g was approximately determined from the value of $\lambda_{1/2}$ corresponding to the wavelength at which the photocurrent value in the long-wavelength region is equal to the half of the value of maximum photocurrent. Thus, the E_g value was calculated as $hc/\lambda_{1/2}$.

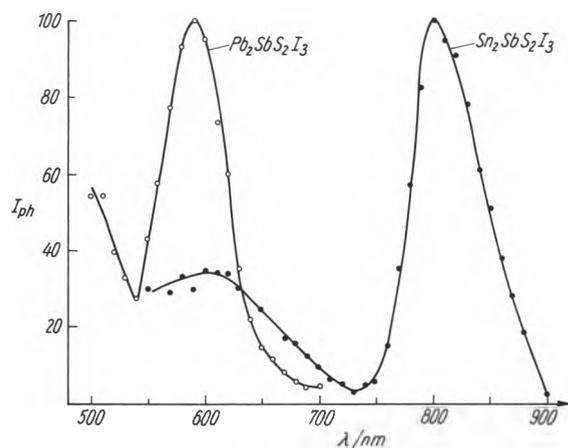


Fig. 1. Spectral response in the photoconductivity of the compounds $\text{Sn}_2\text{SbS}_2\text{I}_3$ and $\text{Pb}_2\text{SbS}_2\text{I}_3$. Photocurrent I_{ph} is expressed in arbitrary units

3. Results and discussion

The synthesis of the quaternary compounds was carried out maintaining strict stoichiometry of the elements corresponding to the chemical formula. The possibility of volatilisation of a small quantity of iodine, as a matter of fact, might influence not only the semiconducting properties of the quaternary compounds but also the values of the lattice parameters. The parameters a , b , c of the orthorhombic lattice of the quaternary compounds are given in Table 1 and are compared with the data obtained by OLIVIER-FOURCADE and DOLGIKH (1985a). It followed from the differential thermal analysis plots that both quaternary compounds studied exhibit congruent melting points. The data on the melting point and on the enthalpy changes at melting are given in Table 2. In agreement with the idea that, in the series of isostructure semiconducting compounds, the melting point decreases with increasing atomic mass of the elements, we found that $\text{Pb}_2\text{SbS}_2\text{I}_3$ has a somewhat lower melting point than $\text{Sn}_2\text{SbS}_2\text{I}_3$. Also the latent heat of melting is slightly lower for $\text{Pb}_2\text{SbS}_2\text{I}_3$. This can be accounted for by adopting the idea that the isostructure compound with a smaller bonding energy exhibits a lower melting point and that, at the same time, the energy required to pass from the crystalline to liquid state is lower, too.

Table 1
Lattice parameters, wavelength of the maximum photocurrent and energy gap width of $\text{Sn}_2\text{SbS}_2\text{I}_3$ and $\text{Pb}_2\text{SbS}_2\text{I}_3$ compounds

Compound	a nm	b nm	c nm	V nm^3	Z	ρ calc $\text{g} \cdot \text{cm}^{-3}$	$\lambda_0(i_{ph})$ nm	E_g eV
$\text{Sn}_2\text{SbS}_2\text{I}_3$ *)	0.4275(1)	1.4059(3)	1.6465(3)	0.9900	4	5.44	—	—
$\text{Sn}_2\text{SbS}_2\text{I}_3$	0.4272(1)	1.4075(2)	1.6460(3)	0.9898(4)	4	5.40	800	1.5
$\text{Pb}_2\text{SbS}_2\text{I}_3$ **)	0.4334	1.4195	1.6552	—	—	—	—	—
$\text{Pb}_2\text{SbS}_2\text{I}_3$	0.43179(6)	1.4160(2)	1.6523(2)	1.0102(2)	4	6.45	590	2.0

*) according to OLIVIER-FOURCADE et al.

***) according to DOLGIKH (1985a)

Table 2

Compound	Melting point $^{\circ}\text{C}$	Enthalpy of melting $\text{kJ} \cdot \text{mole}^{-1}$
$\text{Pb}_2\text{SbS}_2\text{I}_3$	410 410 ± 5 *)	53.4
$\text{Sn}_2\text{SbS}_2\text{I}_3$	415 400 ± 5 **)	

*) according to OLIVIER-FOURCADE et al.

***) according to DOLGIKH (1985a)

Table 1 further gives the values of the energy gap width determined from the spectral dependence of the photoelectric current. The value E_g ($\text{Sn}_2\text{SbS}_2\text{I}_3$) is 1.5 eV, whereas E_g ($\text{Pb}_2\text{SbS}_2\text{I}_3$) is 2.0 eV; in a series of isostructure elements or compounds with dominant covalent bonding we expect a lower value of the energy gap with increasing atomic or molecular mass. The results of our experiments are thus, from this viewpoint, anomalous.

The mentioned anomaly is, however, known in the series of isostructural compounds derived from group IVb elements of the periodic table. Lead iodide PbI_2 , of orange colour, has a larger energy gap width than tin iodide SnI_2 , which exhibits a grey metallic appearance; the maximum of the inner photoeffect on the wavelength scale is shifted for PbI_2 towards shorter wavelengths than for SnI_2 . In agreement with this effect, we found the value of E_g ($\text{Pb}_2\text{SbS}_2\text{I}_3$) to be higher than that of E_g ($\text{Sn}_2\text{SbS}_2\text{I}_3$).

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