PREPARATION AND SOME PHYSICAL PROPERTIES OF SINGLE CRYSTALS OF THE SEMICONDUCTING COMPOUND $PbSb_2Se_4$

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Employing the method of transport reactions, single crystals of $PbSb_2Se_4$ were obtained. The incongruent character of their melting point has been demonstrated by thermal and X-ray diffraction analyses. The electric conductivity $\sigma \approx 7 \cdot 10^{-5}\ \Omega^{-1}\ cm^{-1}$ is of the *p* type, the activation energy, ΔE, has been calculated from the temperature dependence of the electric conductivity as 0·8 eV. At the electric field strength about $10^4\ V\ cm^{-1}$ the electrical switching effect occurs in the crystals and the electric conductivity of the samples increases reversibly by orders of magnitude. With increasing temperature the switching voltage decreases. The crystals are photoelectrically sensitive in the range of 600—1 600 nm. The spectral distribution of photoconductivity depends on the way of preparation of the crystals and on the state of their surface.

Little attention has been paid to the chemical and physical properties of $PbSb_2Se_4$. Elagina[1] proposed a phase diagram of the system $PbSe$–Sb_2Se_3 and reported a congruent melting point of 618°C for the compound $PbSb_2Se_4$. Employing samples containing *c.* 0·1% of impurities, Elagina measured the electric conductivity ($\sigma \approx \approx 1 \cdot 10^{-6}\ \Omega^{-1}\ cm^{-1}$), thermoelectric power ($-870 \cdot 10^{-6}\ VK^{-1}$) and the width of the forbidden band (1·80 eV). Synthesis of $PbSb_2Se_4$ containing less than 10^{-3}% of impurities was described by Frumar and Chaloupka[2]. These authors have found that the compound is photoelectrically sensitive in a wide range of wave lengths with a maximum at 1 400—1 420 nm. From measurements of the light transmittance, diffuse reflectivity spectra, the electric conductivity and the spectral distribution of the photoconductivity, the width of the forbidden band was estimated as $E_g = 0{\cdot}8$ eV. Measurement of the thermoelectric power showed the electric conductivity to be of the *p*-type. All the data were obtained on polycrystalline samples. The present paper deals with the preparation of single crystals of $PbSb_2Se_4$ and characterization of their basic physical properties.

EXPERIMENTAL

Polycrystalline samples were synthetized from very pure (99·999%) elements in evacuated and sealed quartz ampoules. Spectral analysis showed that lead contained traces ($<10^{-3}$%) of Bi,

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Ca and Cu, antimony contained traces of Ca, As and Cd; selenium proved spectrally pure. The synthesis proceeded 4 to 5 h at 650—700°C. In the course of the synthesis the mixture in the ampoule was vigorously stirred. After solidification the ampoule was kept at 550°C for 10 to 60 h, then cooled down to 25°C. The polycrystalline block was crushed and the single crystals were grown in quartz ampoules placed in an oven with a suitable temperature gradient. The ampoules with $PbSb_2Se_4$ were evacuated, charged with a weighed amount or a measured volume of a transporter[3] and sealed under vacuum. The interplanar spacings were determined by the Debye-Scherrer method with an X-ray goniometer URS 50 — IM (Burevestnik, Leningrad), employing the radiation CuK_α. The radiation K_β was quenched with a nickel filter. From the measured diffraction angles, the interplanar spacings $d\alpha/n$ were calculated with the aid of Giller's tables[4]. The differential thermal analysis (DTA) was performed in thin-walled quartz ampoules with an apparatus Derivatograph, system Erdey-Paulik (MOM, Budapest). Prior to measurement the ampoules were filled with pure nitrogen ($p \approx 0{\cdot}1$ Torr, 25°C) and sealed. The data on the thermocouple were corrected according to the melting point of pure antimony. The photoconductivity was measured in an atmosphere of pure N_2 (0·1 Torr, 25°C) by the method of chopped irradiation of the sample. The chopping frequency of the irradiation was 125 Hz or 450 Hz; the duration of a light pulse was equal to the dark period between two light pulses. The source of radiation was a carefully stabilized tungsten lamp with a monochromator VSU (Zeiss, Jena). The incident energy was smaller than 10^{-4} Ws cm^{-2} (1400 nm). The alternating signal was amplified with a selective amplifier with an input impedance[2] of $\approx 10^9\ \Omega$. The curves of the spectral dependence of photoconductivity were corrected to the same intensity of the exciting radiation. The electric conductivity was measured with the Wheatstone bridge in pure nitrogen (0·1 Torr). This experimental set up was also used for measuring the thermoelectric power. The thermoelectric power was measured with a valve milivoltmeter with an input impedance of $10^{11}\ \Omega$. The volt-ampere characteristics were measured with an apparatus described elsewhere[5]. In series with the sample a load resistor of 0·5 to 2M Ω was connected. The content of Pb in the samples was determined by chelatometric titration according to Kotrlý and Vřeštál[6]. After dissolving a sample in a mixture of tartaric and nitric acids the moderately acid solution was buffered by urotropine under potentiometric indication. Xylene orange was then added and the solution was titrated with 0·001M-EDTA (sodium salt). The course of the titration was followed on a spectrophotometer Spekol (Zeiss, Jena). Antimony was distilled off in the form of $SbCl_3$ and determined bromatometrically.

RESULTS AND DISCUSSION

The thermal analysis shows that the compound $PbSb_2Se_4$ undergoes two phase changes at 590 ± 5°C and at 615 ± 5°C. Analogous changes are apparent on the cooling curves (Fig. 1). At 590°C the compound melts partially, the melting is complete at 615°C. The zone refining of a polycrystalline block of $PbSb_2Se_4$ resulted in the composition changes of the individual parts of the block. Whereas the first part after 10 passages of the molten zone contained 70 mol% of PbSe, the middle part contained 50 mol% of PbSe and the last one only 35 mol% of PbSe. The Debye–Scherrer analysis of the individual parts showed that the first part was rich in PbSe, the last one in Sb_2Se_3.

The presence of PbSe and Sb_2Se_3 in the products of zone refining of $PbSb_2Se_4$ and the results of thermal analysis clearly demonstrate the incongruent character of the melting point of $PbSb_2Se_4$. This conclusion has been confirmed by measuring

the homogeneity of the samples with an electron-probe microanalyser (JXA-5, Jeolco, Japan). Those samples which were rapidly cooled down from temperatures 20 to 30°C above the melting point proved heterogeneous. The Debye–Scherrer patterns of these samples clearly exhibited the diffraction lines of PbSe. These facts convincingly prove the incongruent character of the melting point of $PbSb_2Se_4$ at 590 ± 5°C. Thus the data in ref.[1] are probably erroneous.

The compound $PbSb_2Se_4$ is decomposed even when heated *in vacuo*. Sublimation of $PbSb_2Se_4$ at about 10^{-4} Torr afforded only crystals of Sb_2Se_3 with lead concentration $c_{Pb} < 2{\cdot}9$ weight%, which is evidently due to the much higher vapour pressure of Sb_2Se_3 than that of $PbSb_2Se_4$. The decomposition of $PbSb_2Se_4$ during the vacuum sublimation could not be suppressed even by the addition of an excess of PbSe (up to 80 mol%) to the sublimed sample. The Debye–Scherrer diffraction lines of polycrystalline blocks with an excess of PbSe show that in the system $PbSb_2Se_4$–PbSe no further compound was formed.

The incongruent melting point makes it difficult to prepare single crystals of $PbSb_2Se_4$ from their own melt. To avoid this obstacle we have studied chemical transport reactions yielding volatile halides of lead and antimony. As a transporter (Schäfer's definition[3]), I_2, HCl, NH_4I, or NH_4Cl was employed. For the growing of $PbSb_2Se_4$ single crystals by the transport reaction method with iodine as a transporter the most suitable concentration of I_2 was 5 to 7 mg per ml

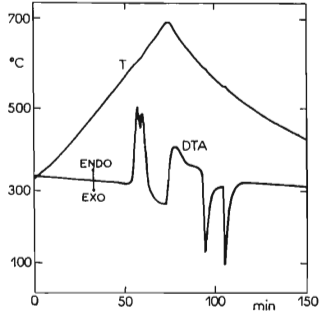

FIG. 1

Thermal Analysis of a Single Crystal of $PbSb_2Se_4$

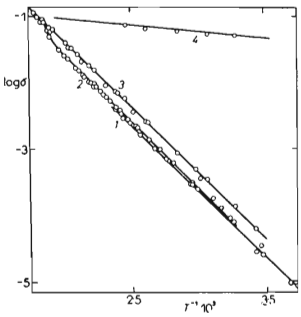

FIG. 2

Temperature Dependence of the Electric Conductivity ($\sigma, \Omega^{-1}\,cm^{-1}$) of a Single Crystal of $PbSb_2Se_4$

1, *2* Different samples, *3* sample *2* after heating to the temperature of beginning decomposition, *4* sample *3* after switching into a state of high conductivity.

and the optimum temperatures of the reaction vessels were t_1 550°C and t_2 420°C; for HCl as a transporter (200 Torr at 25°C) t_1 550–560°C and t_2 430 to 460°C; for NH_4I as a transporter (4 mg per ml) t_1 500 to 540°C and t_2 400 to 500°C.

In a simplified scheme it is possible to assume that the transport of the compound is controlled by the temperature shift of the reaction equilibrium

$$PbSb_2Se_4 + 8\,HX = PbX_2 + 2\,SbX_3 + 4\,H_2Se\,, \qquad (A)$$

where X designates a halogen, or by the shift of the reaction equilibrium

$$PbSb_2Se_4 + 4\,I_2 = PbI_2 + 2\,SbI_3 + 2\,Se_2\,. \qquad (B)$$

The single crystals of $PbSb_2Se_4$, 0·5 . 5 mm, have always grown in the colder part of the ampoule. This indicates that the isochoric reaction heat of the postulated transport reactions, ΔU, has a positive value and reactions A and B, are evidently endothermic. The single crystals of $PbSb_2Se_4$, 0·1 . 8 mm, were obtained even by a prolonged (1000 h) recrystallization heating of the compound in an evacuated ampoule at 540°C.

The temperature dependence of the electric conductivity of monocrystals of $PbSb_2Se_4$ has a form typical for semiconductors (Fig. 2). The activation energy calculated

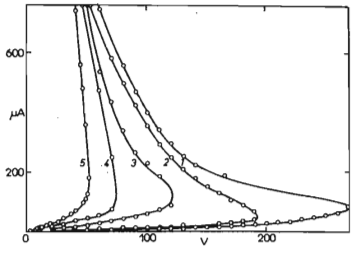

FIG. 3

Volt-Ampere Characteristics of a Single Crystal of $PbSb_2Se_4$

Temperature (°C) *1* 32°, *2* 53°, *3* 78°, *4* 110°, *5* 131°; the cross-sectional area of the sample 5·03 . 10^{-5} cm^2, thickness 8 . 10^{-3} cm.

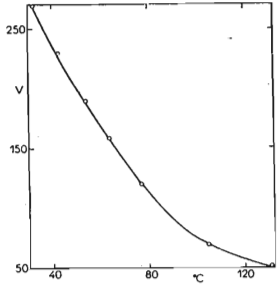

FIG. 4

Temperature Dependence of the Switching Voltage of a Single Crystal of $PbSb_2Se_4$

from the temperature dependence of the electric conductivity employing the relation $\sigma = \sigma_0 \exp(-\Delta E/2kT)$ was $\Delta E = 0{\cdot}8$ eV. This value is identical with the width of the forbidden band, estimated from measurements on the polycrystalline material[2].

The electric conductivity of the single crystals was $\approx 7 \cdot 10^{-5}\ \Omega^{-1}\ cm^{-1}$; the major current carriers were of the *p* type. At higher electric field strengths the electric conductivity of crystalline $PbSb_2Se_4$ crystals deviates from Ohm's law and in the equation $I = E^n/R$ the exponent n is greater than 1. On reaching a certain (threshold) voltage the so-called switching effect takes place in the crystals. The electric resistance of the crystal drops abruptly by orders of magnitude and the crystal acquires a semimetallic character (Fig. 2). The volt-ampere characteristics are symmetrical with regard the voltage polarity applied and their forms depend on the load resistor value. With a suitable value of this resistance the volt-ampere characteristic could be measured in a wide range of the current intensity, including the region of the negative electric resistance (Fig. 3). The shape of the curve is similar to that of a switching device based on amorphous semiconductors[5,7-9]. With increasing temperature the value of the switching voltage decreases (Fig. 4). The tran-

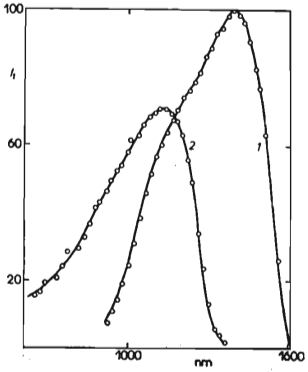

FIG. 5

Spectral Dependence of Photoelectric Conductivity of Single Crystals of $PbSb_2Se_4$

Crystal thickness: *1* 0·007 cm; *2* 0·004 cm. The single crystals were obtained without the use of a transporter. I_f designates the intensity of photoelectric current in relative units.

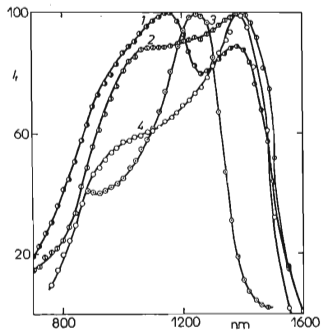

FIG. 6

Spectral Dependence of Photoelectric Conductivity of $PbSb_2Se_4$

The single crystals were obtained by a transport reaction with HCl *1*, *2* and iodine *3*; sample *4* was prepared from sample *1* by heating before the measurement *in vacuo* (170°C, 0·01 Torr, 2 h). I_f see Fig. 5.

sition into the physical state of high electric conductivity is reversible and occurs both with the d.c. and the a.c. voltage. With the samples studied the switching was reversible up to a current density of $5 \cdot 10^2$ A cm^{-2}. Beyond that value the samples were destroyed by overheating. The switching effect was observed both along and across the individual single crystal needles; it was also observed on polycrystalline samples and sintered pellets of $PbSb_2Se_4$.

In order to interpret the switching effect in amorphous semiconductors a number of hypotheses have been advanced[5,7–11]. In $PbSb_2Se_4$ the volt ampere characteristics, temperature dependence of the switching voltage V_B and the dependence of the electric conductivity σ on V_B are analogous to those observed with amorphous semiconductors. Hence it can be assumed that the processes will be essentially analogous. This analogy is most probably due to the similarity in the chemical properties and structure of antimonous and arsenic chalcogenides, which are the essential constituent of a number of semiconducting kinds of glass. The solid chalcogenides of arsenic and antimony are characterized by a high stability of the principal coordination polyhedra of As and Sb which can give rise to amorphous substances or crystals with a great number of atoms in a crystal unit cell. The periodicity in properties of such crystals does not appear until after translation of a very high number of interatomic distances. From the viewpoint of transport of an electric charge such a crystal resembles a set of relatively large blocks of an amorphous compound and a number of its properties can be similar to those of a semiconducting glass[12]. This suggests that the forbidden band of crystalline $PbSb_2Se_4$ contains a number of local levels which facilitate the regenerative electric breakdown. It is doubtless that the switching is strongly affected by the Joule heat[11,13,14]. The theory[15] interpreting the breakdown as due to heat only is based on the condition that in a steady state it holds $V_B = f(\sigma^{-1/2})$. In our experiments the exponent was $-0{\cdot}43$, which value is not far from $-1/2$.

The single crystals of $PbSb_2Se_4$ were photosensitive in a wide range of wavelengths from 600 to 1600 nm. Like on the polycrystalline samples[2] the spectral course of photoelectric conductivity of the crystals contained a band with a peak at 1400 nm and a shorter-wave band with a peak at 1200 nm (Fig. 5). The latter band was particularly marked on samples obtained by a transport reaction with hydrogen chloride or iodine (Fig. 6). We suppose that this band is associated with the surface properties of the crystals. With crystals grown without a foreign transporter the short-wave band of photoelectric conductivity was the more intense the thinner the needles, *i.e.* the relatively greater their surface. The crystals grown up by the transport reaction in the vapour of a halogen or a hydrogen halide can be supposed to contain chemisorbed halide ions on their surface or halide ions incorporated into a surface layer. These halide ions may considerably influence the spectral character of the light absorption and the surface recombination of the excited current carriers, and thus affect the spectral distribution of the photoelectric sensitivity. The halide

ions, whether chemisorbed or incorporated into a surface layer of the crystal, can probably be displaced by heating the sample *in vacuo* (170°C, 0·1 Torr, 2 h), in selenium vapour (300°C, p_{Se} = 0·16 Torr, 2 h) or in gaseous hydrogen (250°C, 760 Torr, 2 h). After such heat treatment the short-wave band of the spectral distribution of photoconductivity either disappears completely or is considerably diminished (Fig. 6).

To conclude it can be said that we have succeeded in the preparation of single crystals of a ternary semiconducting compound, $PbSb_2Se_4$, which has interesting photoelectric and electric properties. Owing to its switching effect it represents a new material for the study and use of this phenomenon.

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