

Crystallographic and Chemical Properties of Compounds of Indium, Sulfur, Selenium and Tellurium

HEINZ TITZE

Department of Solid State Physics, University of Lund, Box 725, S-220 07 Lund, Sweden

Compounds with various compositions, $\text{In}_2\text{S}_x\text{Se}_y$ and $\text{In}_2\text{Se}_x\text{Te}_y$, where $x+y=3$, have been synthesized by heating the elements in evacuated quartz ampoules and analyzed by electron probe microanalysis. Crystals of known compositions have also been investigated by X-ray diffraction methods. $\alpha\text{-In}_2\text{S}_3$ crystallizes in a defect spinel lattice and is able to take up Se in a continuous substitutional solid solution, $\text{In}_2\text{S}_{3-x}\text{Se}_x$ where $0 \leq x \leq 2$. In_2SSe_2 was sublimed in a monoclinic modification exhibiting order–disorder phenomena and a superstructure. Crystalline $\text{In}_2\text{Se}_2\text{Te}$ is related to a known modification of indium selenide with hexagonal symmetry and has slightly increased cell parameters compared with the latter. A new phase containing all three chalcogens, crystallizing with rhombohedral symmetry, has been prepared. Resistivity studies confirm that all these crystals are semiconductors.

Compounds of In, S, Se and Te of type In_2X_3 (where X is the chalcogen) have complex properties. The large number of papers published on this subject indicates that the compounds have been investigated thoroughly (e.g., Refs. 1–4 for In_2S_3 , Refs. 5–10 for In_2Se_3 and Refs. 11–14 for In_2Te_3). Going from sulfur to tellurium over selenium, the general trend is that the ionic character decreases, while the number of possible phases increases. Several phases of the selenide thus exist and the range of variation is increased further by the occurrence of order–disorder phenomena. The number of papers published on the selenides is large, and the confusion existing as to labelling, number and transformation temperatures of the various phases even larger. The number of papers on phases containing two or more chalcogens is smaller, only the partial replacement of sulfur by selenium having been investi-

gated.¹⁵ It is to be expected that gradual replacement of sulfur by selenium, and selenium by tellurium, would lead to the formation of stable ternary phases. In this investigation, such phases have been synthesized, analyzed and, as far as possible, characterized insofar as their crystallographic properties are concerned.

EXPERIMENTAL

Since the melting point of various compounds is about 1000 °C, they were grown in closed quartz ampoules, which also made it possible to maintain purity. The starting materials were elemental In, S, Se or Te of purity 5N. Weighed amounts of in all about 1–2 grams were used. The shapes and sizes of the ampoules are shown in Fig. 1. Before sealing the ampoule, a turbomolecular pumped system was used to obtain a good vacuum. Spontaneous exothermic reactions were prevented by separating indium from the rest of the elements. Successful results were obtained using the following procedure:

1. Place control thermocouple in position 1 (see Fig. 1). Increase the temperature to the boiling point of sulfur (selenium) at a rate of about 5 °C/min and then keep the temperature constant for a few hours.

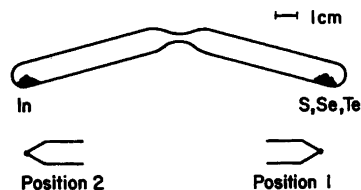


Fig. 1. The construction of the quartz ampoule with its separated melts. The positions of the thermocouple are indicated.

Table 1. Results of electron probe microanalysis.

Composition of starting materials	Composition of reaction products
$\text{In}_2\text{S}_2\text{Se}$	In_2S_3 (Se contaminated) $\text{In}_2\text{S}_2\text{Se}$ $\text{In}_4\text{S}_3\text{Se}_3$ In_2SSe_2
In_2SSe_2	In_2SSe_2
$\text{In}_2\text{S}_2\text{Te}$	In_2S_3 (Te contaminated) In_2STe_2 In_2Te_3 (S contaminated) In_2S_3 (Te contaminated) In_2STe_2
In_2STe_2	In_2Te_3 (S contaminated) $\text{In}_2\text{Se}_2\text{Te}$ In_2SeTe_2
$\text{In}_2\text{Se}_2\text{Te}$	$\text{In}_4\text{S}_3\text{Se}_3$ (Te contaminated) $\text{In}_4\text{SSe}_2\text{Te}_3$

2. Change the control thermocouple to position 2 and increase the temperature slowly at a rate of 0.2 to 0.5 °C/min to a peak temperature above the estimated melting temperature of the reaction product and then keep the temperature constant for several hours.

3. Cool slowly, *e.g.* 0.1–0.2 °C/min.

The reaction products were normally sublimed in evacuated quartz ampoules with a small temperature gradient. This method is better than using transport reactions which always lead to impure products.

ANALYSIS

Electron probe microanalysis of the products was carried out with the Tracor Northern system TN 2000 and a Cambridge S4 scanning electron microscope. The excitation voltage was 20 kV and the beam current 2×10^{-10} A. For the quantitative determination of composition, standards employing the pure elements, or the binary standards CdS and InP for S and In, respectively, were used. Similar results were obtained with both sets of standards. The ZAF corrections were made in the conventional manner using the commercial software. A typical standard deviation for the fit of the unknown spectrum was about one percent. All reaction products were analyzed. In most cases well-defined stoichiometric compositions were found. The results are shown in Table 1. From this table, it is apparent that In_2S_3 and In_2Te_3 are present in most samples, whereas In_2Se_3 is not formed. The binary compounds always contain

small amounts of the second chalcogen. This is understandable since, in the course of the synthesis, sulfur reacts at relatively low temperatures to form the sulfide, which is then contaminated by Se or Te before the other compounds are formed. In the first entry in Table 1, stepwise replacement of S by Se is seen to occur. This does not occur for the pair S–Te. Moreover no crystals of composition In_2STe_2 were found. Experiments with all three chalcogens present simultaneously resulted in a stable compound with no obvious stoichiometry. This phase differs from the other phases investigated.

CRYSTALLOGRAPHIC INVESTIGATIONS

Single crystal diffraction-photographs were taken with the Weissenberg method using $\text{CuK}\alpha$ or $\text{MoK}\alpha$ radiation. In addition, for many of the samples powder diffraction patterns were obtained with a Guinier-Hägg camera using $\text{CuK}\alpha$ radiation. Most of the powder films displayed diffuse patterns which made their evaluation difficult or impossible. The first synthesis in Table 1 resulted in three different cubic modifications. Weissenberg photographs of single crystals with compositions $(\text{In}_2\text{S}_2\text{Se}, \text{In}_4\text{S}_3\text{Se}_3$ and In_2SSe_2 showed no difference concerning the presence and the intensity distribution of the reflections. These compounds can therefore be regarded as a single phase, *i.e.* a continuous substitutional solid solution $\text{In}_2\text{S}_{3-x}\text{Se}_x$ with $0 \geq x \geq 2$. This means that up to two sulfur atoms in the sulfide can be replaced by selenium, this only resulting in a slight increase in the lattice parameters. The new monoclinic phase of In_2SSe_2 , obtained by sublimation at 800 °C, gave very diffuse powder diffraction patterns. A closer inspection of films obtained from single crystals indicated several possible reasons for this. Weissenberg photographs were taken for a large number of crystals. The results can be summarized as follows:

1. All the crystals investigated displayed more or less obvious reflections from a superstructure in rotation photographs taken with *a* and *b* as rotation axes.

2. Some of the crystals gave sharp reflections in the rotation and Weissenberg photographs. Rotation photographs obtained from these crystals showed obvious intensity differences between the same layer line in different crystals. In addition, determination of the parameters *a* and *b* from rotation photographs yielded different values for different crystals. Thus two modifications exist, only one sample of

Table 2. Summary of the crystallographic data of the phases found in this paper.

Formulae	Symmetry	Lattice Parameters	Space group, etc.
$\text{In}_2\text{S}_{3-x}\text{Se}_x$	cubic	for $x=0$: $a=10.88\text{\AA}$, $x=1$: $a=11.03\text{\AA}$, and $x=2$: $a=11.16\text{\AA}$	continuous substitutional solid solution from $X=0$ to 2
In_2SSe_2	monoclinic	modification 1: $a=6.86\text{\AA}$, $b=7.93\text{\AA}$, $c=18.69\text{\AA}$, $\beta=97^\circ$, $V=1009\text{\AA}^3$, $Z=8$ modification 2: $a=6.79\text{\AA}$, $b=7.83\text{\AA}$, $c=18.5\text{\AA}$, $\beta=93^\circ$, $V=982\text{\AA}^3$, $Z=8$	calculated density for modification 1 5.52, experimental density 5.53
$\text{In}_4\text{SSe}_2\text{Te}_3$	rhombohedral	$a=14.0028(10)\text{\AA}$, $c=35.2282(51)\text{\AA}$ (as hexagonal axes)	space group: $\bar{R}3$ (No. 148) complete structure determ. will be published later
$\text{In}_2\text{Se}_2\text{Te}$	hexagonal	$a=7.29\text{\AA}$, $c=19.81\text{\AA}$	space group $P6_1$ (No. 169)

the second having been found (Table 2 contains the lattice parameters for both modifications).

3. Other crystals gave noticeable diffuse streaks in addition to discrete reflections. This is a typical order-disorder phenomenon. The layers hll and $h3l$ consist only of diffuse streaks, of varying intensity and about 1 cm in length, whereas $0kl$, $1kl$ and $2kl$ consist of streaks with discrete intensity maxima.

Like all the other samples, $\text{In}_2\text{Se}_2\text{Te}$ and In_2SeTe_2 were black and shiny. Only the former could be obtained as crystals suitable for X-ray diffraction analysis. These crystals had hexagonal symmetry (see Fig. 2). It seems reasonable to assume that one

selenium atom of the compound In_2Se_3 is replaced by tellurium. A hexagonal phase designated β or sometimes $\gamma\text{-In}_2\text{Se}_3$ was first described by Semiletov.⁶ The structure was later determined by Likforman *et al.*⁹ The lattice parameters were found to be $a=7.11\text{\AA}$ and $c=19.34\text{\AA}$ and the space group $P6_1$, No. 169. $\text{In}_2\text{Se}_2\text{Te}$ was found to have the same space group with a slight increase in the lattice parameters according to the Weissenberg films. It is not evident whether the replacement of selenium by tellurium is random or ordered. Finally, a new phase has been found, the composition of which is not known exactly. It contains S, Se and Te in the approximate ratio 1:2:3 with formula $\text{In}_4\text{SSe}_2\text{Te}_3$. An analysis of the crystal structure will soon be published.

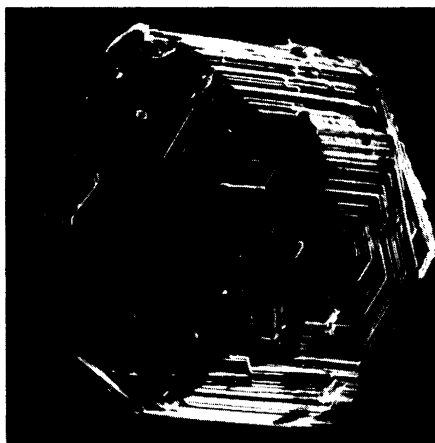


Fig. 2. An example of a small hexagonal crystal of $\text{In}_2\text{Se}_2\text{Te}$. The diameter is approximately 0.2 mm. Most analyzed crystals were considerably larger and of irregular shape.

PHYSICAL PROPERTIES

Some simple measurements were made in order to characterize the electrical properties of the materials. Ohmic contacts were made with liquid gallium on opposite sides of the crystals, which were mounted on TO-5 headers. The resistances of the samples varied between wide limits from less than 1 ohm to about 10^6 ohm, demonstrating that the materials are semiconductors. In addition In_2SSe_2 is photoconductive, and when illuminated with white light, its conductivity increased by more than three orders of magnitude.

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