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Growth and characterization of $SnSe_2$

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Tin diselenide single crystals were grown by direct synthesis using the Bridgman technique and were subsequently purified by successive recrystallizations. An X-ray powder diffraction study verified that the crystals obtained belong to the $D_{3d}^3 - P\bar{3}m1$ space group with lattice parameters $a = 0.3811$ nm and $c = 0.6137$ nm. A stoichiometric analysis gave a maximum deviation of their nominal $SnSe_2$ composition of $\sim 4\%$. Study of their morphology by scanning electron microscopy reveals the layered-type structure of the obtained material. Finally, the microhardness parallel and perpendicular to the layer planes was found to be strongly anisotropic, as expected from the layered structure of $SnSe_2$.

1. Introduction

Compounds with layered structure, particularly the transition metal dichalcogenides [1] (MX_2 in general) show a wide range of interesting electronic properties and are characterized by their anisotropic features along different crystallographic directions. The present work studied the growth conditions and characterization of $SnSe_2$ by X-ray diffraction, scanning electron microscopy and microhardness measurements.

The tin diselenide structure belongs to the hexagonal CdI_2-type lattice and is characterized by strongly bonded two-dimensional M–X–M (chalcogenide–metal–chalcogenide) sandwiches, which are weakly coupled by Van der Waals forces, thus having anisotropic properties [2]. In order to obtain single $SnSe_2$ crystals of better quality several methods of growth have been used.

During the last 30 years or so, $SnSe_2$ crystals have been usually grown by iodine phase transport (IPT) [3–8]. Because of the iodine contamination-affected crystal structure and the subsequently influenced semiconducting properties, efforts were undertaken to grow $SnSe_2$ by the vapour phase transport (VPT) method [4, 9–11]. The crystals obtained from these methods show a polytypism, i.e. simultaneous existence of 2H, 4H and 6H polytypes. It seems from the literature and also from our results, that the Bridgman–Stockbarger method gives better crystals, easily cleavable and quite thick [2, 12–15]. Therefore, in this work, the characterization of $SnSe_2$ concerns samples obtained by the vertical Bridgman technique.

2. Experimental procedure

$SnSe_2$ crystals were grown by the vertical Bridgman technique in a standard apparatus [2, 15–17]. As starting materials, 99.9999% pure Sn and 99.99% pure Se were used. The synthesis and the crystallization processes were carried out in quartz ampoules with an inner diameter of 12 mm and a wall thickness of 1.5 mm. The ampoules were cleaned with a solution of H_2SO_4 and HNO_3 in distilled water, and then washed successively with acetone, alcohol and distilled water. The ampoules were then evacuated at $\sim 10^{-5}$ torr (1 torr = 133.322 Pa) and flame heated for 0.5 h. The starting materials were put into the ampoules in stoichiometric amounts, then the ampoules were evacuated up to 10^{-6} torr and subsequently sealed. They were kept at $\sim 730\,^{\circ}C$ for 72 h. After homogenization of the melt, the crystal growth process was carried out. The ampoules, which had a pointed bottom (so that the crystal growth could start at a single point) were lowered vertically. The spatial temperature gradient was $10\,^{\circ}C\,cm^{-1}$, while the lowering speed of the ampoules was $0.47\,mm\,h^{-1}$. The final temperature reached was $50\,^{\circ}C$. The lowering rate was controlled by a clock work mechanism. The crystals obtained had a size of $\sim 10 \times 10 \times 1\,mm^3$, and were brilliant grey metallic colour with a pronounced layered structure, Fig. 1.

3. Characterization

3.1. X-ray characterization

To characterize the obtained crystals, first an X-ray powder diffraction analysis was undertaken by using an URD6 diffractometer. This analysis gave the spectrum shown in the upper part of Fig. 2. In the lower part of the same figure, a calculated spectrum is also shown. This spectrum was obtained assuming that $SnSe_2$ belongs to the $D_{3d}^3 - P\bar{3}m1$ space group [2], and the best fitting was obtained with the following

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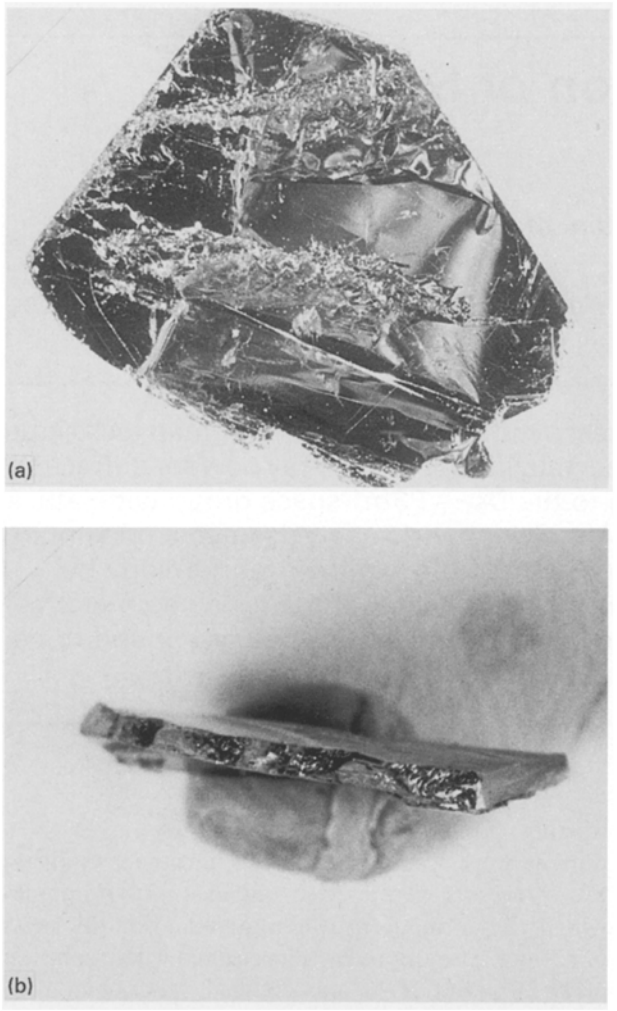

Figure 1 Photographs of grown $SnSe_2$ crystals: (a) view perpendicular to the layers, and (b) parallel to the layers.

lattice parameters: $a = 0.3811$ nm and $c = 0.6137$ nm. These results are in agreement with those reported previously in the literature [6, 15], $a = 0.384$ nm and $c = 0.613$ nm.

3.2. SEM investigations

To study the morphology of the crystals obtained and their stoichiometry, an examination was carried out using a scanning electron microscope (Jeol-type 100) and the corresponding attached unit (Superprobe 733) suitable for performing stoichiometric investigations. Fig. 3 shows scanning electron micrographs clearly displaying the layered structure of the $SnSe_2$-compound. According to Harbec *et al.* [2] and Domingo *et al.* [4], the crystallographic c-axis of $SnSe_2$ is always oriented perpendicular to the layers. The same is also true for the very similar compound SnS_2.

In Table I, the stoichiometric proportions of the constituent elements tin and selenium, as deduced from the stoichiometric analysis by the appropriate attached unit, are listed. They represent mean average values obtained at different positions on the same sample. The maximum deviations of the obtained results at the different positions are also given, as are the deviations of the obtained results from the stoichiometry corresponding to the formula $SnSe_2$. It can be deduced from Table I, that the obtained crystals are quite homogeneous and the deviations from the stoichiometry corresponding to the formula $SnSe_2$ do not exceed approximately $\pm$ 4%.

3.3. Microhardness

Microhardness measurements have been performed on the obtained $SnSe_2$ layered crystals. The samples were encapsulated in a dental resin (Kallocryl CP-rz) enabling easy handling. After a hardening process of 24 h, the capsules were mechanically polished with 5 mm diameter aluminia powder, until flat surfaces oriented perpendicular to the layer planes were obtained. For the microhardness measurements on the layer planes, this procedure was not necessary.

The measurements were carried out at 300 K, both on the layer planes and perpendicular to them using

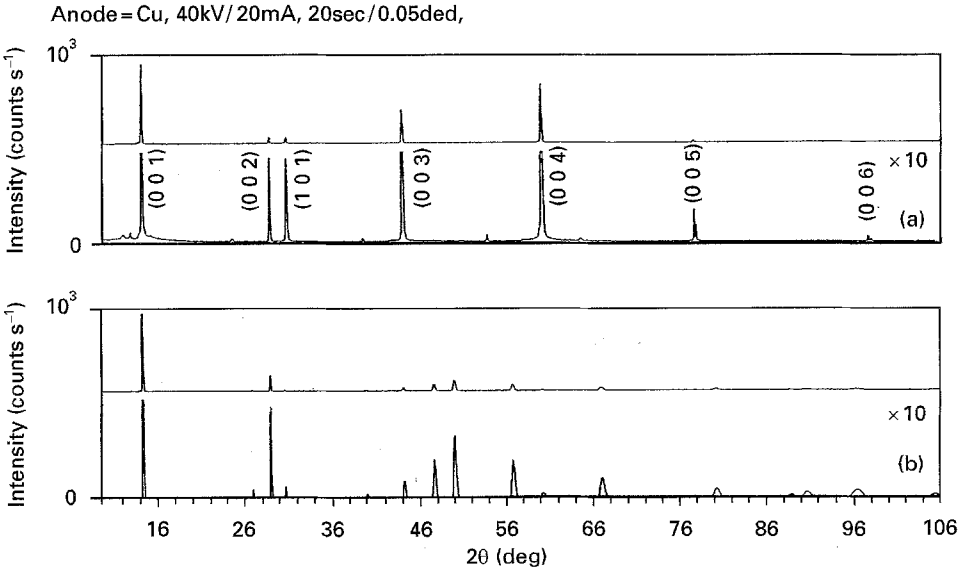

Figure 2 (a) X-ray spectrum obtained by a powder diffraction analysis. (b) A spectrum calculated assuming that $SnSe_2$ belongs to the $D_{3d}^3 - P\bar{3}m1$ space group and has the lattice parameters: $a = 0.3811$ nm and $c = 0.6137$ nm. There is satisfactory agreement between the two spectra.

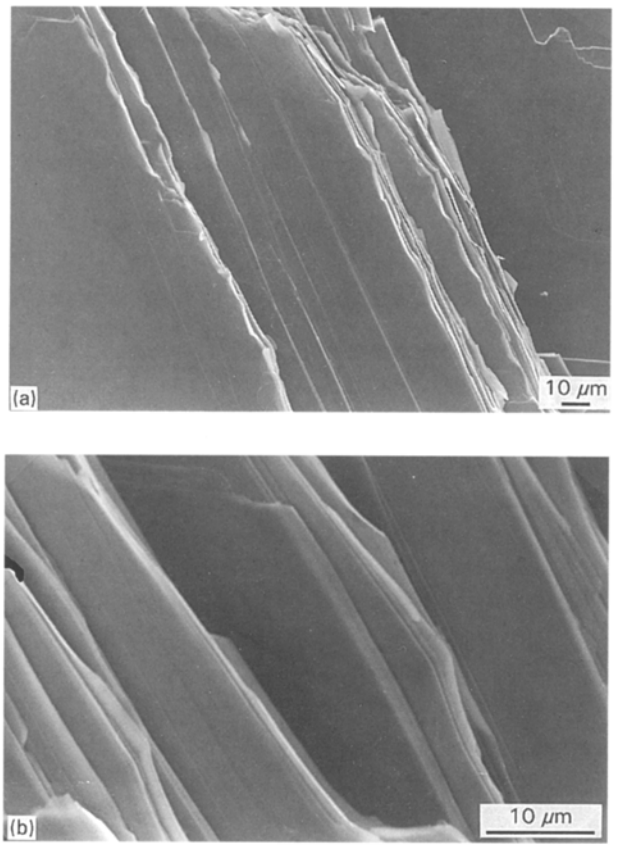

Figure 3 (a, b) Scanning electron micrographs of $SnSe_2$. The layered structure is obvious.

TABLE I Stoichiometric proportions of Sn and Se.

Element	Line	Atomic percentage	Max. local deviation (%)	Max. deviation from the normal values (%)
Sn	L	34.624	0.202	+ 3.87
Se	L	65.267	0.064	− 2.10

the PMT-3 microhardness tester [18]. A Vickers diamont indentor (a square-based pyramid) was applied. The average microhardness value obtained for measurements perpendicular to the layer planes was $72.80 \pm 6.88\ kg\,mm^{-2}$, while the corresponding value for measurements parallel to the layer planes was $35.42 \pm 2.46\ kg\,mm^{-2}$. This means that the microhardness of $SnSe_2$ is strongly anisotropic, as expected from the layered structure of this material.

For all measurements, the indentor was loaded with 1 g (much larger loads easily break the material). The contact time, i.e. the time under load, was 15 s. The above values are the mean arithmetic values of five measurements for each plane. The mean square error of the mean arithmetic value, i.e. the data scattering, was quite reasonable ($\sim 9\%$) [15].

4. Conclusion

Although, in the literature, the growth of $SnSe_2$ has already been reported [2, 4, 5, 9, 11, 12, 15–17, 19], the crystals obtained were in the form of layers, like mica. In addition, no reports about the stoichiometry and the homogeneity of $SnSe_2$ exist, or they are very rare. In the present paper, the growth of large $SnSe_2$ crystals is reported, with flat surfaces, and they are characterized by means of an X-ray and SEM study. The obtained results indicate that the lattice parameters do not differ from the corresponding values reported in the literature, while the stoichiometric analysis has shown that the samples are homogeneous, deviating from the nominal composition by no more than about $\pm 4\%$. On the other hand, scanning electron micrographs confirm the layered structure of $SnSe_2$ and the microhardness measurements reveal an anisotropy of the material, which has to be related to the layered form of $SnSe_2$. The values obtained for the microhardness, $35.42\ kg\,mm^{-2}$ parallel to the layers and $72.8\ kg\,mm^{-2}$ perpendicular to the layers, are also comparable with the average value of $30\ kg\,mm^{-2}$, reported by Busch *et al.* [15] for the same material.

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