Discussion. Recently 21 polytypes of SnS₂ were reported and a multiphase model for characterization of their structures was suggested (Patosz et al., 1985). The structural series of polytypes with intermediate structures 2H–18R, 4H–18R and 2H–4H–18R were derived theoretically with the use of a multiphase model of polytype structures (Patosz, 1983) and only polytypes of these three kinds were found in SnS₂ crystals. Most of the polytypes presented here also belong to these three main structural groups: 2H–18R: 42H, 44H, 36R, 54R, 84R, 96R, 114R, 132R, and 144R; 4H–18R: 22H, 40H, 30R, 48R, 138R; 2H–4H–18R: 12H. Besides these simple polytypes some polytypes were found to have a more complicated composition: they contain the stackings of layers not belonging to basic structures 2H (stackings o), 4H (t) or 18R (flf5fl), namely flf2 (8H, 10H, 12H, 14H) or f2f2 (24H, 24R, 42R, 72R). The stackings of layers (zig-zag sequences of S–Sn–S molecules) corresponding to simple mixed structures 2H–18R and 4H–18R are presented in Fig. 25. As has already been seen, structures of this kind may be considered to be composed of domains of pure basic structures. Here each molecular layer belongs to one of the simple phases: o,t,flf5fl. Note that in this case no faulted arrangements of layers occur in the interphase interfaces. Fig. 26 presents the stackings f1f2 and f2f2 found in polytypes of SnS₂. These two ‘faulted sequences’ may be considered as a kind of interdomain boundary occurring between neighbouring domains of the same structure: faults f1f2 occur in the 2H–2H interface (between the domains 2H having different orientations of molecules); faults f2f2 occur in the multidomain structure 18R. Note that the structures presented in Fig. 26 are similar to the multidomain structure 4H called structure D and occurring frequently in CdI₂ and PbI₂ crystals (Patosz, 1983). The layers f1 and f2 occur frequently in polytypes of CdI₂ and PbI₂, and, as discussed elsewhere (Patosz, 1983), these layers were found to be interdomain boundaries between domains 2H and 4H. The same layers occurring in SnS₂ polytypes, however, can in no case be regarded as 2H–4H boundaries. The 2H and 4H polytypes occur in SnS₂ as in CdI₂ and PbI₂, but no polytypes were found to be constructed of domains 2H (o layers) and 4H (t) with layers f1 and f2 occurring between the domains.

This work was sponsored by the Institute of Physics of the Polish Academy of Sciences.

References


Polytypism of SnSe₂ Crystals Grown by Chemical Transport: Structures of Six Large-Period Polytypes of SnSe₂

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(Received 30 August 1984; accepted 28 May 1985)

Abstract. The polytype structure of SnSe₂ single crystals grown by chemical transport is examined by X-rays. Frequencies of occurrence of different polytype structures are given and structures of six large-period polytypes are identified: 12H: f2(0)2f1f1f1/2(11)211; 48H: f1f5f1/2(2121)2121(11)2; 24R: f1f5f1/12222; 24R: f2f2f1/12211; 30R: f2o2f2f1/12211; 54R: f2(0)2f2f1/12211; 121.

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Introduction. Polytypism of SnSe₂ crystals has been reported several times in the literature, e.g. Minagawa (1980), Acharya & Srivastava (1981). It was established that the common structures of SnSe₂ were the polytypes 2H and 18R with Zhdanov sequences 11 and (1212), respectively. Minagawa (1980) reported that crystals grown from a melt always have the structure 18R and those grown by chemical transport have two alternative basic structures 2H and 18R. Also, some complex structures, large-period polytypes and disordered structures, were found in the crystals; their structures, however, have not been identified completely.

Below we present the results of a structural analysis of SnSe₂ crystals grown by chemical transport. The occurrence of 2H and 18R polytypes as basic structures is confirmed and the structures of six polytypes are given.

Experimental. Single crystalline samples were prepared by chemical transport reactions in closed silica glass crucibles and with several kinds of transport agents (I₂, ICl₅, Br₂). The compounds are prepared from the elements in growth ampoules that are usually 20–30 cm in length and about 2 cm in diameter. Before the growth reaction, the source material (reacted compound) was transported several times from one side of the ampoule to the other, with large temperature gradients. The growth temperatures for the crystals were around 873 K and the temperature gradients of the order of 50 K. Single crystals in the shape of flakes up to a few cm² could be grown. Small crystals were also easily obtained without a transport agent in somewhat larger temperature gradients.

Single crystals of SnSe₂ were examined by X-rays (Co K radiation) with a 43 mm radius camera and 0.7 mm collimator. Crystals were oscillated around ø*, where the angle between the c axis and incident beam varied between 18 and 33°. With the above conditions reflexions 10.l and 11.l are registered in the patterns for which l values satisfy the condition 1.5 ≤ l/N ≤ 2.5; N is the number of Se layers in the unit cell.

The method of layer-stacking identification in the polytype cell used here is the same as that used earlier for CdI₂ and SnS₂ polytypes (Palog, Gierlotka, 1984; Pałosz, Palosz & Gierlotka, 1985). In this method the reflexion intensities measured on the patterns by photometry are compared with the intensities calculated theoretically for structural models; cf. standard expression for MX₂ crystals (Gyaneshwar, Chada & Trigunayat, 1973). The lattice constants used for the calculations were a = 3.81, c₀ = 3.067 Å (after Minagawa, 1980); the fₜₙ and fₛₑ factors were approximated by the analytical function given by Lee & Pakes (1969); the reflexion intensities were multiplied by the Lorentz–polarization factor Lp⁻¹. The experimental and theoretical values of reflexion intensities were compared on intensity diagrams of 10.I/11.l reflexions (Figs. 1–6).*

The measurements of the reflexion intensities on the patterns for the SnSe₂ polytypes under investigation were very troublesome for several reasons: As discussed by Whitehouse & Balchin (1979), precise determination of intensity values requires the use of absorption coefficients. This factor strongly depends on the shape and dimensions of the sample and in the case of irregularly shaped crystals it cannot be calculated accurately. The crystals examined usually had irregular shapes and the polytypes were always observed in coexistence with basic structures and frequently with a certain disorder. Absorption has a very strong effect on small-angle reflexions (small values of l/N) and a comparatively small effect on the intensities of large-angle reflexions. So, we decided to ignore the absorption coefficient in the calculations of the theoretical values of the intensities and to use only reflexions for which 2.0 ≤ l/N ≤ 2.5. [Note: In our previous studies on MX₂ polytype identification we used the reflexions for which 1.5 ≤ l/N ≤ 2.5 or 2.5 ≤ l/N ≤ 3.5 (Palosz & Przedmojski, 1980).] The intensity diagrams prepared for these reflexions enable one to observe the special symmetry of the diagrams, cf. calculated intensities in Figs. 1–6. Using this symmetry and having intensities for 2.0 ≤ l/N ≤ 2.5, one can easily calculate reflexion intensities for the second part of the diagram, for 1.5 ≤ l/N ≤ 2.0. So, in fact, the measurements of reflexion intensities for 2.0 ≤ l/N ≤ 2.5 are enough for a unique determination of the structure of a polytype and this property of the 10.I/11.l reflexion diagrams is used here for SnSe₂ polytypes.

Discussion. The structures of more than 40 single crystals of SnSe₂ were examined and two basal faces of each sample were analysed independently. The frequencies of occurrence of different polytype structures found in the crystals are given in Table 1. In this table the present results are compared with those reported by Minagawa (1980) for the crystals grown at about 840 K. As already known, polytypism is a function of growth conditions: For CdI₂ and PbI₂ (Palosz, 1983) and for SnS₂ (Palosz, Palosz & Gierlotka, 1984) it has been found that the relative frequencies of occurrence of basic structures and the structures of polytypes strongly depend on temperature of crystallization. Similar relations probably occur for SnSe₂ but no experimental data concerning this problem have been published yet.
Structures of six new polytypes of SnSe$_2$ are listed in Table 2 where they are described in the t-o-f notation and in the Zhdanov notation. The intensity diagrams for the identified polytypes are given in Figs. 1–6 where reflection intensities calculated for $1.5 \leq I/N \leq 2.5$ and measured for $2.0 \leq I/N \leq 2.5$ are shown.

As we showed earlier for all known MX$_2$ polytype materials the polytypes may always be regarded as structures intermediate between basic polytypes (PaIosz, 1983; PaIosz et al., 1985). Depending on the basic structures of a material, specific arrangements of molecular layers occur in the crystals forming complex structures: these are multilayer polytypes. The basic structures of SnSe$_2$ are 2H and 18R polytypes and we expected that the large-period polytypes of SnSe$_2$ would be similar to the polytypes of SnS$_2$ identified recently and grown in coexistence with 2H and 18R (PaIosz et al., 1984). The latter consisted of two kinds of stacking of layers: f1–f5–f1 and f2–f2–f1–f1 and of basic layers o. So, in constructing models of SnSe$_2$ polytypes (stackings of layers in a cell) we considered only structures composed of two kinds of structures. For the identified polytypes the following models were considered:

12H$_1$ \[ (f'2o(f1)_2)_{0} \text{ and } f2(o)_{2}f'1f'2f1; \]
48H$_1$ \[ (f'1f5f1)_0(o)_{0}, (f'1f5f1)_2(o)_{0}, f'1f5f1(o)_{0}, (f'1f5f1)_4(o)_{0}, f'1f5f1(o)_{0}, (f'1f5f1)_6(o)_{0}, f'2o(f2)_{2}f'1f'1, (f'1f5f1)_2; \]
24R$_1$ and 24R$_2$ \[ f'1f5f1o and f'2f'2f1f1; \]
30R$_1$ \[ f'1f5f1(o)_{2}, f2o(f2)_{2}f1f1, f'2f2f1o_{1}, f2(o)_{2}f'2f1o_{1}, f'2o(f2)_{2}f1o_{1}, f2(o)_{2}f'2f1o_{1}, \]
and \[ f2(o)_{2}f'2f1(o)_{3}f1. \]

As seen from the above the assumption of multiphase character of polytype structures allowed a very simple determination of the structure of the polytypes.

The small number of known polytypes of SnSe$_2$ does not make it possible to derive rules governing the formation of the polytype structure of the crystals. The similarity between SnS$_2$ and SnSe$_2$ polytypes is evident. However, it should be noted that while the structures intermediate between 2H and 18R without faults \[ [(f1f5f1)_4(o)_{0}] \] are typical for SnS$_2$, among the six known polytypes of SnSe$_2$ only two are of this kind; four polytypes contain 'faulted layers' f2.

This work was sponsored by the Institute of Physics of the Polish Academy of Sciences.

### Table 1. Frequencies of occurrence of polytypes in SnSe$_2$ crystals grown by a chemical transport reaction at about 873 K

<table>
<thead>
<tr>
<th>Polytype</th>
<th>Number of samples</th>
<th>% of structure</th>
</tr>
</thead>
<tbody>
<tr>
<td>2H</td>
<td>69</td>
<td>70</td>
</tr>
<tr>
<td>18R (pure)</td>
<td>15</td>
<td>20</td>
</tr>
<tr>
<td>18R (reverse + obverse)</td>
<td>5</td>
<td>20</td>
</tr>
</tbody>
</table>

Polytypes:
- Structure determined: 6 (Table 2), 10
- Structure undetermined: 3 (54R, 60R, 108R)

Note: In two crystals only the polytype 18R was found to occur on both crystal faces. In most cases 18R and large-period polytypes occurred in coalescence with 2H.

### Table 2. Structures of known polytypes of SnSe$_2$

<table>
<thead>
<tr>
<th>Ramsdell symbol</th>
<th>t-o-f sequence</th>
<th>Zhdanov sequence</th>
</tr>
</thead>
<tbody>
<tr>
<td>Basic structures</td>
<td></td>
<td></td>
</tr>
<tr>
<td>2H</td>
<td>o</td>
<td>11</td>
</tr>
<tr>
<td>18R</td>
<td>f1f5f1</td>
<td>(2121)$_2$</td>
</tr>
</tbody>
</table>

Hexagonal polytypes:
- 12H$_1$ \[ f2(o)_{2}f'1f'2f1; \]
- 48H$_1$ \[ f1f5f1_0(o)_{0}, (f1f5f1)$_2(o)_{0}, f'1f5f1(o)_{0}, (f1f5f1)$_4(o)_{0}, f'1f5f1(o)_{0}, (f1f5f1)$_6(o)_{0}, f'2o(f2)_{2}f'1f'1, (f1f5f1)_2; \]
- 24R$_1$ and 24R$_2$ \[ f'1f5f1o and f'2f'2f1f1; \]
- 30R$_1$ \[ f'1f5f1(o)_{2}, f2o(f2)_{2}f1f1, f'2f2f1o_{1}, f2(o)_{2}f'2f1o_{1}, f'2o(f2)_{2}f1o_{1}, f2(o)_{2}f'2f1o_{1}, \]
and \[ f2(o)_{2}f'2f1(o)_{3}f1. \]

References


