The crystal structure of lead (II) indium (III) chalcogenide: PbIn$_2$S$_4$, a synthetic phase closely related to the lillianite group.

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SUMMARY

PbIn$_2$S$_4$, Mr. = 565.1, orthorhombic, Pnma, a = 11.675 (2), b = 3.848 (1), c = 13.754 (3) Å, Z = 4, D$_m$ = 6.1 g cm$^{-3}$, F(000) = 976, μ (Mokα) = 363 cm$^{-1}$. The structure was solved by heavy atom method and refined by block-diagonal least-squares method to a final R = 0.057 for all observed reflections. The lead and indium atoms have a distorted 8 and 6 coordination, respectively. This synthetic phase is closely related to the lillianite group. Average bond lengths in PbIn$_2$S$_4$ are: Pb-S 3.08 (3) and In-S 2.63 (4) Å.

RESUMEN

PbIn$_2$S$_4$, Mr = 565.1, ortorombico, Pnma, a = 11.675 (2), b = 3.848 (1), c = 13.754 (3) Å, Z = 4, D$_m$ = 6.1 g cm$^{-3}$, F(000) = 976, μ (Mokα) = 363 cm$^{-1}$. La estructura ha sido determinada por el método de Patterson y refinada por un método de mínimos cuadrados hasta un valor final R = 0.057. Los átomos de Pb presentan coordinación 8 y los átomos de In muestran coordinación 6. La estructura de esta fase se encuentra relacionada a la de los minerales del grupo de la lillianita. Las distancias medias de enlace en PbIn$_2$S$_4$ son: Pb-S 3.08 (3) y In-S 2.63 (4) Å.

INTRODUCTION

For many years a lot of attention has been devoted to the experimental synthesis of mineral chalcogenides of general formula A$_x$B$_y$X$_z$, where X = S, Se or Te in which one of the cations, A or B, is a transition metal, due to the fact that they can show magnetic properties.

Some ternary mineral chalcogenides of formula AB$_2$X$_4$ where A or B = Fe, Co, Ni, Cu, As, In, Sb, Pb, Bi and X = S, Se, have been studied by Itakata and Nowacki (1961, 1962), Le Bihan (1962, 1963) and Skinner et al. (1964). Other additional references about synthesis and crystal chemistry of related sulfides and sulfosalts can be found in Nowacki (1969), Povarennykh (1972) and Ribbe (1974).

In this work, PbIn$_2$S$_4$ was synthesised according to the method indicated by Arriortua, Iglesias and Amigó (1979) and Arriortua (1981), mixing stoichiometric quantities of the elements Pb, In and S placing them in Vycor tubes. The starting materials were obtained from commercial sources and they had a stated purity of 99.99%. The Vycor tubes were evacuated to a nominal pressure of 10$^{-3}$mmHg and sealed off. The samples were then raised to temperatures in the range 1000-6200°C and maintained below 700°C, approximately for 4 days. A needle shaped submetallic red single crystal (0.03x0.01x0.01 mm) was selected for X-ray crystal structure determination.

Independently, Kramer and Berroth (1980) have synthesised this ternary chalcogenide from the binary components PbS and In$_2$S$_3$ and determined its structure. When this structure appeared published, our crystal structure determination was at the refinement stage already. Yet the authors thought it would be worthy publicating the results for comparison purposes, as well as pointing out the structural relations between this synthetic phase and the lillianite homologues series.

EXPERIMENTAL

The unit-cell parameters were determined by automatically centring of 25 independent reflections and refinement of unit-cell parameters and orientation matrix by least-squares. The intensities of 1190 independent reflections (20 50°) were collected on a Philips PW1100 four-circle diffractometer using graphite-monochromated Mokα radiation (λ = 0.7107Å) and the ω scan technique. 841 reflections only were considered as observed applying the condition I ≥ 2σ(I) and included in the refinement. The relative intensities were corrected for the usual Lorentz and polarization factors. Absorption corrections were made using the ORABS program on the basis of a precise description of the crystal shape.

The crystal structure has been determined by the Patterson method. A synthesis of F$^2$ allowed us to locate the position of the Pb and In atoms, which atomic positions were isotropically refined by means of a diagonal block matrix until a R = 0.308. The mini-
### Table 1. Atomic coordinates (x10^5) and equivalent thermal parameter coefficients. (Ueq = (8\pi^2)^{-1}B_{ij}a_{ij})

<table>
<thead>
<tr>
<th></th>
<th>X</th>
<th>Y</th>
<th>Z</th>
<th>Ueq</th>
</tr>
</thead>
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<tr>
<td>Pb</td>
<td>255789</td>
<td>25000</td>
<td>16274</td>
<td>0.023</td>
</tr>
<tr>
<td>In(1)</td>
<td>93305</td>
<td>111</td>
<td>25000</td>
<td>10901</td>
</tr>
<tr>
<td>In(2)</td>
<td>57967</td>
<td>101</td>
<td>75000</td>
<td>10092</td>
</tr>
<tr>
<td>S(1)</td>
<td>8998</td>
<td>343</td>
<td>75000</td>
<td>7377</td>
</tr>
<tr>
<td>S(2)</td>
<td>52827</td>
<td>382</td>
<td>25000</td>
<td>21878</td>
</tr>
<tr>
<td>S(3)</td>
<td>29464</td>
<td>361</td>
<td>75000</td>
<td>33701</td>
</tr>
<tr>
<td>S(4)</td>
<td>37556</td>
<td>321</td>
<td>75000</td>
<td>2608</td>
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Symmetry operation code used in Table II and subsequent Tables:

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<th>Operation</th>
</tr>
</thead>
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<td>i</td>
<td>(=1+x,y,z)</td>
</tr>
<tr>
<td>ii</td>
<td>(=1+x,-1+y,z)</td>
</tr>
<tr>
<td>iii</td>
<td>(=x,1+y,z)</td>
</tr>
<tr>
<td>iv</td>
<td>(=-1+x,y,z)</td>
</tr>
<tr>
<td>v</td>
<td>(=-1+x,1+y,z)</td>
</tr>
<tr>
<td>vi</td>
<td>(=-1+x,y,z)</td>
</tr>
<tr>
<td>vii</td>
<td>(=-1+x,2-y,z)</td>
</tr>
</tbody>
</table>

### Table 2. Eight-Coordination for Pb atom

<table>
<thead>
<tr>
<th>Central atom</th>
<th>distances (Å)</th>
<th>Angles with central atom (°)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pb-S(1)</td>
<td>3.01</td>
<td>S(1) -- S(3\text{iv}) 79.6</td>
</tr>
<tr>
<td>-S(2)</td>
<td>3.25</td>
<td>S(3) -- S(3\text{iv}) 76.6</td>
</tr>
<tr>
<td>-S(3\text{iv})</td>
<td>3.10</td>
<td>S(4) -- S(4\text{iv}) 79.2</td>
</tr>
<tr>
<td>-S(4\text{iv})</td>
<td>3.02</td>
<td>Mean: 78.5°</td>
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</tbody>
</table>

### Table 3. Six-Coordination for In (1) atom

<table>
<thead>
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<th>Central atom</th>
<th>distances (Å)</th>
<th>Angles with central atom (°)</th>
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</thead>
<tbody>
<tr>
<td>In (1) -- S (1I)</td>
<td>2.70</td>
<td>S (1I) -- S (3\text{III}) 173</td>
</tr>
<tr>
<td>-S(1\text{III})</td>
<td>2.70</td>
<td>S (1I) -- S (3\text{III}) 173</td>
</tr>
<tr>
<td>-S(1\text{IVIII})</td>
<td>2.53</td>
<td>S(1\text{III}) -- S(2\text{III}) 161°</td>
</tr>
<tr>
<td>-S(2\text{III})</td>
<td>2.62</td>
<td>Mean: 169°</td>
</tr>
<tr>
<td>-S(3\text{III})</td>
<td>2.62</td>
<td>S(1\text{III}) -- S(1\text{VIII}) 83.9</td>
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<tr>
<td>Mean: 263 Å</td>
<td>82.8</td>
<td>-S(2\text{III}) 82.8</td>
</tr>
<tr>
<td>S(3\text{III}) -- S(1\text{VIII}) 102.5</td>
<td>-S(2\text{III}) 90.3</td>
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<tr>
<td>S(1I) -- S(1\text{I}) 90.3</td>
<td>-S(2\text{III}) 89.0</td>
<td></td>
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<tr>
<td>S(1\text{III}) -- S(1\text{I}) 89.0</td>
<td>-S(2\text{III}) 83.9</td>
<td></td>
</tr>
<tr>
<td>S(1\text{III}) -- S(2\text{III}) 82.8</td>
<td>-S(3\text{III}) 86.09</td>
<td></td>
</tr>
<tr>
<td>S(3\text{III}) -- S(1\text{I}) 86.09</td>
<td>-S(1\text{VIII}) 102.5</td>
<td></td>
</tr>
<tr>
<td>Mean: 89.6°</td>
<td>-S(1\text{VIII}) 90.3</td>
<td></td>
</tr>
<tr>
<td>-S(2\text{III}) 94.5</td>
<td>-S(3\text{III}) 94.5</td>
<td></td>
</tr>
</tbody>
</table>

### Table 4. Six-Coordination for In (2) atom

<table>
<thead>
<tr>
<th>Central atom</th>
<th>distances (Å)</th>
<th>Angles with central atom (°)</th>
</tr>
</thead>
<tbody>
<tr>
<td>In (2) -- S (2)</td>
<td>2.59</td>
<td>S (2) -- S (4\text{vii}) 177.1</td>
</tr>
<tr>
<td>-S(2\text{vii})</td>
<td>2.60</td>
<td>S (2\text{vii}) -- S (4\text{vii}) 177.1</td>
</tr>
<tr>
<td>-S(4\text{vii})</td>
<td>2.59</td>
<td>S (4\text{vii}) -- S (3\text{iii}) 175.4</td>
</tr>
<tr>
<td>Mean: 2.62 Å</td>
<td>2.65</td>
<td>S (2\text{vii}) -- S (4\text{vii}) 177.1</td>
</tr>
<tr>
<td>S(2\text{vii}) -- S(3\text{iii}) 91.5</td>
<td>S (4\text{vii}) -- S (3\text{iii}) 91.05</td>
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</tr>
<tr>
<td>S(4\text{vii}) -- S(2\text{vii}) 85.4</td>
<td>S (4\text{vii}) -- S (3\text{iii}) 91.5</td>
<td></td>
</tr>
<tr>
<td>Mean: 90°</td>
<td>S (4\text{vii}) -- S (2\text{vii}) 85.4</td>
<td></td>
</tr>
<tr>
<td>-S(4\text{vii}) 91.5</td>
<td>S (4\text{vii}) -- S (3\text{iii}) 91.5</td>
<td></td>
</tr>
<tr>
<td>-S(3\text{iii}) 94.5</td>
<td>S (4\text{vii}) -- S (3\text{iii}) 91.5</td>
<td></td>
</tr>
<tr>
<td>-S(2\text{vii}) 93.1</td>
<td>Mean: 90°</td>
<td></td>
</tr>
</tbody>
</table>

Table 4. Six-Coordination for In (2) atom
mized function was \( w |F_0| - |F_C| |^2 \), where \( w = (a + |F_0| + \mid b |F_C|^2)^{-1} \) being \( a \) and \( b \) the weight of Cruickshank (1965). A Fourier synthesis revealed in this moment the positions of the \( S \) atoms. During the first part of the refinement process, isotropic thermal parameters were used and the \( R \) index dropped to the value of 0.106. At this moment, an anisotropic refinement using the \( (1965). \) A Fourier synthesis revealed in this moment the positions of the \( S \) atoms. During the first part of the refinement process, isotropic thermal parameters were used and the \( R \) index dropped to the value of 0.106. At this moment, an anisotropic refinement using the \( F_0 \) obtained after having corrected absorption effects was carried out. The final \( R \) was 0.057.

Lists of structure factors and anisotropic thermal parameters are available upon request from the "Departamento de Cristalografía y Mineralogía de la Universidad del País Vasco".

Figure 1. The crystal structure of \( \text{PbIn}_2\text{S}_4 \). In order of decreasing size the circles indicate \( S, \text{Pb, In.} \) this (010) structure projection along the \( \sim 4 \AA \) period, empty and full circles indicate atoms at two discrete structure levels, approx. \( 2 \AA \) apart. Ruled shading: "lillianite-like octahedral layers"; stippled: bicapped trigonal coordination.

DISCUSSION OF THE STRUCTURE

Table 1 gives the final atomic parameters of \( \text{PbIn}_2\text{S}_4 \) and figure 1 shows a projection of its crystal structure on the plane (010).

The chemical composition derived from the crystal structure determination of this low-temperature form is in perfect agreement with the elemental analysis of the compound. The structure determination also allows to confirm the ordered state of this phase i.e. the metal sites are fully occupied and no partial substitution between \( \text{Pb} - \text{In} \) could be detected.

The crystal structure of this synthetic phase may be regarded as an incomplete lillianite homologue. If the \( y \) coordinate of the \( \text{In (1)} \) atom is changed by \( 1/2 \ b \), then the resultant crystal structure will correspond to the distorted one of the \( 1,1 \) lillianite (\( \text{Pb}_3\text{Bi}_2\text{S}_6 \)) homologue, where every superscript of \( L \) expresses the number of octahedra in the chain of octaëdras, running diagonally across an individual "galena-like" layer and parallel to \( (011)\text{PbS} \) (Makovicky and Karup-Møller, 1977), and, therefore, the two alternating layers of "galena-like" structure parallel to \( (131)\text{PbS} \) are related by a "pseudomirror plane" normal to the direction (see figure 1). The sites with bicapped trigonal prismatic coordination \((6 + 2)\) on this "mirror-plane" are occupied by the \( \text{Pb} \) atoms.

The \( \text{Pb-S} \) distances for this coordination are given in Table 2, the values ranging between 3.008(3) and 3.251(5)\( \AA \) (average: 3.08(3)\( \AA \)). All the \( S \) atoms in the structure are involved in the \( \text{Pb} \) coordination, each one being bonded to two \( \text{Pb} \) atoms and to three \( \text{In} \) atoms.

The \( \text{In} \) atoms are at the centers of the slightly distorted octahedra forming the lillianite-like octahedral portions (Tables 3 and 4). Unlike the lillianite homologues, these portions do not form two alternating layers of "galena-like" structure in \( \text{PbIn}_2\text{S}_4 \). The orientation of these portions is illustrated in figure 1. The \( \text{In-S} \) mean distance is 2.63(4)\( \AA \) (range: 2.528(4)-2.702(3)\( \AA \)) and the \( S-\text{In-S} \) mean angle 90(1)\( ^\circ \) (range: 82.3(1)-96.2(1)\( ^\circ \)).

Other related natural chalcogenides belonging to the lillianite homologous series are listed in Table 5.

There is no direct correlation between this crystal structure and the observed structure types of \( \text{AB}_2\text{X}_4 \) compounds given by Iglesias and Steinfink (1973).

### Table 1. Crystal data for \( \text{PbIn}_2\text{S}_4 \) and for two lillianite homologues.

<table>
<thead>
<tr>
<th>Mineral</th>
<th>Lillianite&lt;sup&gt;1)&lt;/sup&gt;</th>
<th>Outrayite&lt;sup&gt;2)&lt;/sup&gt;</th>
<th>Synth. phase&lt;sup&gt;3)&lt;/sup&gt;</th>
</tr>
</thead>
<tbody>
<tr>
<td>Formula:</td>
<td>( \text{Pb}_3\text{Bi}_2\text{S}_6 )</td>
<td>( \text{A}<em>8\text{Bi}</em>{12.5}\text{Pb}<em>15 \text{Bi}</em>{20.5}\text{S}_2 )</td>
<td>( \text{PbIn}_2\text{S}_4 )</td>
</tr>
<tr>
<td>Space group:</td>
<td>( \text{Bbmm} )</td>
<td>( \text{Bbmm} )</td>
<td>( \text{Pnma} )</td>
</tr>
<tr>
<td>Homologue:</td>
<td>( 4,4,1 )</td>
<td>( 11,11,1 )</td>
<td>( 11,1 )</td>
</tr>
<tr>
<td>a, ( \AA )</td>
<td>13.54</td>
<td>13.46</td>
<td>13.754*</td>
</tr>
<tr>
<td>b</td>
<td>20.45</td>
<td>44.04</td>
<td>11.675*</td>
</tr>
<tr>
<td>c</td>
<td>4.10</td>
<td>4.10</td>
<td>3.848*</td>
</tr>
</tbody>
</table>

1) Takagi & Takéuchi (1972)  
2) Makovicky & Karup-Møller (1977b)  
3) This work  
* for comparison with the lillianite homologues, the cell parameters are interchanged.

### Table 5. Crystal data for \( \text{PbIn}_2\text{S}_4 \).

ACKNOWLEDGEMENTS

We thank Prof. U. Thewalt and Dr. T. Debaerdemaecker of the University of Ulm for assistance with the intensity measurements on the Philips diffractometer. Thanks are also extended to the Alexander von Humboldt Foundation awarding to one of us (J.M.A.) during his stay in Ulm.
REFERENCES


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