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## Abstract

## Full Text

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*CRYSTALLOGRAPHY*

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# ON THE ISOMORPHOUS ENTRY OF THALLIUM INTO GALENA

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One of the principal carrier minerals of thallium is galena. Elevated concentrations of thallium in this mineral are, as a rule, observed in varieties that also contain bismuth or antimony ($^1$-$^4$). By contrast, in ores for which the latter elements are not typical, the thallium content in galena is lower than in other sulfides ($^5$). This is in full agreement with the concept of the entry of thallium into galena according to the compensation scheme:

$$2\mathrm{Pb}^{2+} \rightarrow \mathrm{Tl}^{+} + \mathrm{A}^{3+},$$

where $\mathrm{A} = \mathrm{Bi}, \mathrm{Sb}, \mathrm{As}$ ($^2$).

Indeed, replacement of divalent lead by monovalent thallium could be admitted either according to the scheme $\mathrm{Pb}^{2+} \rightarrow 2\mathrm{Tl}^{+}$, or $2\mathrm{Pb}^{2+} + \mathrm{S}^{2-} \rightarrow 2\mathrm{Tl}^{+}$. The first of these schemes is not feasible, since in the structure of galena there are no "free positions" for the "extra," sufficiently large thallium atom. The second scheme seems unlikely, since it requires subtraction of sulfur, i.e., the appearance of vacancies in sites occupied by sulfur atoms, which, so far as we know, has not yet been observed in sulfides with a structure of the NaCl type. Replacement of lead by trivalent thallium according to the scheme $3\mathrm{Pb}^{2+} \rightarrow 2\mathrm{Tl}^{3+}$, accompanied by the formation of vacancies at cation sites, is quite permissible. Such a phenomenon is observed, for example, when bismuth is introduced into galena or gallium into sphalerite ($^6$). However, realization of such a scheme in the hydrothermal solutions from which galena forms is also unlikely, in view of the closeness of the oxidation potentials of the reactions $\mathrm{Tl}^{+} \rightarrow \mathrm{Tl}^{3+}$ and $\mathrm{Pb}^{2+} \rightarrow \mathrm{Pb}^{4+}$.

**Fig. 1.** Phase diagram of the system

Fig. 2. Powder patterns of the compound $BiTlS_2$ (a) and of alloys containing 80 ( ), 70 ( ), and 60 ( )% 1/2 $BiTlS_2$

Figure 2: Fig. 2. Powder patterns of the compound $BiTlS_2$ (a) and of alloys containing 80 ( ), 70 ( ), and 60 ( )% 1/2 $BiTlS_2$

## PbS—$BiTlS_2$

To test the feasibility of the compensation scheme for the entry of thallium into galena, the system galena (PbS)–the double sulfide of thallium and bismuth ($BiTlS_2$) was studied. The end members and intermediate compositions of the system were prepared from chemically pure elements by fusion in evacuated quartz ampoules. After synthesis, carried out at 1050–1150°, the ampoules containing the melts were slowly cooled to 700°, annealed at this temperature for 60 hours, and then quenched by rapid removal from the furnace.

Thermal analysis of the melts made it possible to construct the phase diagram of the system (Fig. 1). As can be seen, it belongs to the first type (according to Roozeboom) of systems with a continuous series of solid solutions. The homogeneity of all annealed melts, established by examination of polished sections under the microscope, confirms the continuity of the series of solid solutions in this system. At the same time, in contrast to isotropic galena, in all sulfides; beginning with the alloy containing 5% $\frac{1}{2}BiTlS_2$, optical anisotropy is clearly observed. At the same time, the strength of the anisotropy effect gradually increases with distance from galena.

Powder X-ray diffraction patterns of the alloys were obtained in an RKD camera with a diameter of 57.3 mm (Cu anticathode) and on a URS-50I instrument (Fe anticathode). In the latter case, in addition to recording on a potentiometer, the position of some maxima was determined from the results of counting the number of pulses at fixed counter positions with an interval of 1—3′. This made it possible to calculate the lattice parameters of the alloys with a relative error of no more than 0.002—0.003 Å.

**Fig. 2.** Powder patterns of the compound $BiTlS_2$ (a) and of alloys containing 80 (b), 70 (c), and 60 (d)% $\frac{1}{2}BiTlS_2$

In all powder X-ray diffraction patterns of alloys containing more than 40 mol.% lead sulfide, only reflections characteristic of the NaCl-type structure (galena) are present. At higher $BiTlS_2$ contents, the diffraction pattern becomes more complicated owing to the splitting of most lines. Analysis of the X-ray diffraction patterns of these samples led to the conclusion, that the splitting of the lines is caused by rhombohedral deformation of the original cubic cell. Indeed, as can be seen from the powder X-ray photographs (Fig. 2), reflections of the $h00$ type do not split, those of the $hhh$ and $hk0$

types give two maxima each, and those of the *hhl* type give three maxima; this, according to the theory of homology, corresponds to a transition from cubic to trigonal symmetry (7). No other lines, apart from those derived from the cubic face-centered lattice, were found on the X-ray patterns obtained both on the diffractometer and in the RKD camera.

The indexing of the X-ray patterns was carried out taking into account the intensities of lines of the *hhh* type (repeatability factor 2) and $\bar{h}hh$ (repeatability factor 6). In doing so, the intensity ratios on the X-ray patterns of specimens with 70 and 80% $^{1}/_{2}\mathrm{BiTlS_2}$ were used, since here there are no additional distortions, as is indicated by the equal intensity of lines formed by reflections with equal repeatability factors (220 and $\bar{2}20$—see Fig. 2).

On the X-ray pattern of the end member of the series—the compound $\mathrm{BiTlS_2}$—the intensity ratio of all lines changes substantially. Probably, in addition to stretching along the axis of the third order, here there is an additional distortion of the original structure, associated not only with the ordered arrangement of cations but also with their partial displacement from the ideal positions of the original lattice. The latter evidently occurs in the plane perpendicular to the axis of the third order, as indicated by the relative increase in the intensity of the 111 and 222 lines (0003 and 0006 in hexagonal setting) in comparison with the others. These distortions do not, however, cause additional changes in the metric of the unit cell. As can be seen from the data of Table 1, the agreement of the interplanar spacings calculated from the experimental data and computed for a rhombohedral cell with parameters $a = 5.985$ Å, $\alpha = 86°40'$, is quite satisfactory.

**Table 1**

**Interplanar spacings of the compound** $\mathrm{BiTlS_2}$
$a_R = 5.985$ Å, $\alpha = 86°40'$, $a_H = 8.221$, $c_H = 10.962$ Å, $c/a = 1.333$
Recording conditions: RKD camera $D = 57.3$ mm, Cu radiation, Ni filter

| *hkl* rhomb. | *hkil* hex. | $I$ | $d_{\mathrm{exp}}$ | $d_{\mathrm{calc}}$ | *hkl* rhomb. | *hkil* hex. | $I$ | $d_{\mathrm{exp}}$ | $d_{\mathrm{calc}}$ |
|---|---|---|---|---|---|---|---|---|---|
| 111 | 0003 | 10 | 3.647 | 3.651 | 422 | $20\bar{2}8$ | 1.5 | 1.277 | 1.278 |
| $\bar{1}11$ | $20\bar{2}1$ | 3 | 3.385 | 3.387 | $4\bar{2}2$ | $42\bar{6}4$ | 1.5 | 1.206 | 1.206 |
| 200 | $20\bar{2}2$ | 9 | 2.983 | 2.986 | $\bar{4}22$ | $60\bar{6}0$ | 0.5 | 1.183 | 1.185 |
| 220 | $20\bar{2}4$ | 5 | 2.164 | 2.169 | 511 | $40\bar{4}7$ | 1 | 1.175 | 1.175 |
| $\bar{2}20$ | $22\bar{4}0$ | 3 | 2.054 | 2.056 | $\bar{5}11$ | $42\bar{6}5$ | 1.5 | 1.146 | 1.146 |
| 311 | $20\bar{2}5$ | 2 | 1.859 | 1.862 | $\bar{5}11$ | $60\bar{6}3$ | 1 | 1.126 | 1.126 |
| 222 | 0006 | 4 | 1.823 | 1.825 | 440 | $40\bar{4}8$ | 0.5 | 1.084 | 1.085 |
| $\bar{3}11$ | $22\bar{4}3$ | 1.5 | 1.787 | 1.789 | 531 | $22\bar{4}9$ | 1.5 | 1.045 | 1.047 |
| $\bar{3}11$ | $40\bar{4}1$ | 1 | 1.756 | 1.755 | $\bar{5}31$ | $42\bar{6}7$ | 1 | 1.020 | 1.020 |
| 222 | $40\bar{4}2$ | 1 | 1.689 | 1.692 | 600 | $60\bar{6}6$ | 1 | 0.994 | 0.995 |
| 400 | $40\bar{4}4$ | 1.5 | 1.491 | 1.492 | 620 | $42\bar{6}8$ | 1 | 0.959 | 0.960 |
| 331 | $20\bar{2}7$ | 1.5 | 1.431 | 1.433 | $\bar{6}20$ | $62\bar{8}4$ | 0.5 | 0.930 | 0.929 |

Fig. 3. Dependence of the magnitude of the rhombohedral angle (a) and the unit-cell edge (b) on the composition of the solid solution in the PbS—BiTlS2 system

Figure 3: Fig. 3. Dependence of the magnitude of the rhombohedral angle (a) and the unit-cell edge (b) on the composition of the solid solution in the PbS—BiTlS2 system

| *hkl* rhomb. | *hkil* hex. | *I* | $d_{\text{exp}}$ | $d_{\text{calc}}$ | *hkl* rhomb. | *hkil* hex. | *I* | $d_{\text{exp}}$ | $d_{\text{calc}}$ |
|---|---|---|---|---|---|---|---|---|---|
| 420 | $22\bar{4}6$ | 2 | 1.365 | 1.365 | 622 | $44\bar{8}6$ | 1 | 0.874 | 0.870 |
| $\bar{3}31$ | $42\bar{6}1$ | 0.7 | 1.335 | 1.335 | 711 | $62\bar{8}7$ | 0.7 | 0.834 | 0.834 |
| $\bar{4}20$ | $42\bar{6}2$ | 1 | 1.305 | 1.306 | | | | | |

Thus, in the continuous series of solid solutions under consideration, as the $BiTlS_2$ content increases there is a gradual increase in the degree of distortion of the original structure. The optical anisotropy of alloys with small contents of the double sulfide indicates that, already from the very beginning of the series, the bismuth and thallium atoms, replacing lead atoms, are arranged in a certain degree of order. X-rayographically, the first signs of lattice deformation are detect—

appear only after more than half of the lead atoms have been replaced. In an alloy with 60% $\frac{1}{2}BiTlS_2$, the angle of anorthogonality is only 10′ (splitting of maxima was observed only when constructing scattering curves from points for reflections with $2\theta > 90°$). Subsequently the angle of anorthogonality increases rapidly (Fig. 3a). The absence of superstructure lines, whose appearance would be expected as a result of cation ordering, is due to the closeness of their atomic numbers (Tl 81, Pb 82, Bi 83) and, accordingly, to practically equal scattering power.

The continuity of the series is confirmed by the smoothness of the change in the unit-cell edge as a function of the composition of the solid solutions (Fig. 3b). The difference in this parameter between the end members of the series is only 0.05 Å (5.934—5.985), which is associated with the closeness of the radii of the substituting atoms and emphasizes the identity of their positions in the structure.

Earlier, in the study of the PbS—$Bi_2S_3$ system, it was shown that up to 10 mol.% $Bi_2S_3$ can enter galena isomorphously ([6]). This gives grounds to believe that, at small concentrations of impurities, thallium can enter galena isomorphously in the case where the ratio Tl : Bi < 1. It is precisely such ratios of impurities of these components that are most often observed in natural galenas.

**Fig. 3.** Dependence of the magnitude of the rhombohedral angle (a) and the unit-cell edge (b) on the composition of the solid solution in the PbS—$BiTlS_2$

system

A preliminary study of the PbS—$Tl_2S$ system showed that already at a content of 1.5 wt.% thallium in the alloy a second phase is formed. This, of course, does not completely exclude the existence in this system of solid solutions containing tenths and hundredths of a percent of thallium. However, it is beyond doubt that the isomorphous entry of thallium into galena together with bismuth or its analogues must proceed considerably more readily than in their absence, even in the case when the impurity concentration does not exceed tenths of a percent.

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*Note: Figure translations are in progress. See original paper for figures.*