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# Materials with Layered Structures: Crystal Structure of $Zn_{1.25}In_{2.5}S_3Se_2$, a New Polytype of $Zn_2In_2S_5$ and the Isotypic Compounds $Cd_{0.5}Ga_2InS_5$ and $Hg_{0.8}Ga_{1.6}In_{1.2}S_5$

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The crystal structure of $Zn_{1.25}In_{2.5}S_3Se_2$ was determined from single crystal data. The compound crystallizes in the trigonal space group $P\bar{3}m1$-$D^3_{3d}$ (No. 164) with $Z = 2$. The lattice constants (hexagonal setting) are $a = 3.927(1)$ and $c = 31.83(1)$ Å. The structure is of a layer type and may be described as a slightly distorted hexagonal closed packing of the anions with two $In^{3+}$ in octahedral voids and all other cations in tetrahedral coordination. The isotypic compounds $Cd_{0.5}Ga_2InS_5$ and $Hg_{0.8}Ga_{1.6}In_{1.2}S_5$ have lattice parameters $a = 3.809(1)$, $c = 30.64(1)$ Å, and $a = 3.820(1)$, $c = 30.929(3)$ Å, respectively.

## Introduction

Layer-type materials have attracted much attention in recent years because of their anisotropic physical properties. One group of such compounds contains the various polytypes of $ZnIn_2S_4$ and $Zn_2In_2S_5$ (*1*). We recently found a new compound in the system $ZnIn_2S_4$–$ZnIn_2Se_4$ (*2*) which was obviously not isotypic with one of these polytypes. In this paper we therefore report the structures of this material and two isotypic compounds $Cd_{0.5}Ga_2InS_5$ and $Hg_{0.8}Ga_{1.6}In_{1.2}S_5$ which we found in the systems CdS–$Ga_2S_3$–$In_2S_3$ and HgS–$Ga_2S_3$–$In_2S_3$ (*3*), respectively.

## Experimental

Single crystals of $Zn_{1.25}In_{2.5}S_3Se_2$ were prepared by recrystallization of the microcrystalline product (*2*) at 600°C in a small silica ampoule sealed under vacuum using a small amount of iodine. Under these conditions plate-like crystals of violet color are formed. The composition of the crystals was checked by comparison of their lattice parameters with those of powdered samples (*2, 4*).

Powder samples of $Cd_{0.5}Ga_2InS_5$ and $Hg_{0.8}Ga_{1.6}In_{1.2}S_5$ were prepared from stoichiometric amounts of the corresponding binary sulfides CdS (Schuchardt, Munich), $In_2S_3$ (Fluka, Buchs, Swizerland), and $Ga_2S_3$ (prepared by reaction of the elements at 1100°C (*5*)) in closed silica ampoules at 800 and 600°C, respectively. To obtain pure samples three firing periods of 3 days were necessary. Between the heat treatments the products were ground carefully in an agate mortar and the process of the reaction was checked by X-ray investigations. Recrys-

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TABLE I

Atomic Positions, Anisotropic Thermal Parameters (pm$^2$), and Site Occupation Factors

| Atom | Position | $x$ | $y$ | $z$ | $u_{11}$ | $u_{33}$ | s.o.f. |
|---|---|---|---|---|---|---|---|
| In(1) | 2c | 0 | 0 | 0.2987(1) | 152(2) | 245(4) | 1.0 |
| In/Zn(2) | 2d | $\frac{1}{3}$ | $\frac{2}{3}$ | 0.0809(1) | 151(3) | 231(5) | 0.78/0.15 |
| In/Zn(3) | 2d | $\frac{1}{3}$ | $\frac{2}{3}$ | 0.4212(1) | 156(4) | 246(6) | 0.68/0.25 |
| Zn(1) | 2d | $\frac{1}{3}$ | $\frac{2}{3}$ | 0.8199(1) | 171(6) | 161(8) | 0.84 |
| S/Se(1) | 2d | $\frac{1}{3}$ | $\frac{2}{3}$ | 0.9519(1) | 139(5) | 208(9) | 0.63/0.37 |
| S/Se(2) | 2d | $\frac{1}{3}$ | $\frac{2}{3}$ | 0.1588(1) | 287(9) | 184(10) | 0.63/0.37 |
| S/Se(3) | 2d | $\frac{1}{3}$ | $\frac{2}{3}$ | 0.7450(1) | 125(5) | 160(8) | 0.63/0.37 |
| S/Se(4) | 2d | $\frac{1}{3}$ | $\frac{2}{3}$ | 0.3440(1) | 154(6) | 171(8) | 0.63/0.37 |
| S/Se(5) | 2d | $\frac{1}{3}$ | $\frac{2}{3}$ | 0.5483(1) | 156(6) | 195(9) | 0.63/0.37 |

*Note.* $u_{11} = u_{22} = 2u_{12}$; $u_{13} = u_{23} = 0$.

tallization experiments of the Cd and Hg compounds did not result in crystals suitable for X-ray single crystal work. The crystals obtained were very thin and bent very easily.

X-ray powder diffraction patterns were obtained at room temperature from a Huber Guinier powder camera 621 using Cr$K\alpha_1$ radiation. The photographs were calibrated internally with quartz ($a$ = 4.9136, $c$ = 5.4054 Å) and the unit cell dimensions refined by a least-squares procedure.

## Structure Determination of $Zn_{1.25}In_{2.5}S_3Se_2$

X-ray precession photographs of a single crystal of $Zn_{1.25}In_{2.5}S_3Se_2$ showed Laue symmetry $\bar{3}m1$ with no conditions for the observed reflections. This led to the possible space groups $P321$, $P3m1$, and $P\bar{3}m1$. The lattice constants obtained from the precession photographs ($a$ = 3.926, $c$ = 31.832 Å) are in good agreement with those obtained from Guinier patterns of powder samples ($a$ = 3.927(1), $c$ = 31.83(1) Å (*4*)).

Intensity data were collected at room temperature from a crystal of the dimensions 0.25 × 0.12 × 0.03 mm on an Enraf-Nonius CAD 4 diffractometer with monochromatic Mo$K\alpha$ radiation. Independent reflections (1933) were measured up to $\theta_{max}$ = 50° in an $\omega$-$2\theta$ scan and the intensities corrected for Lorentz polarization, anomalous dispersion, and absorption (empirically by $\psi$-scans).

The calculations were performed with the program SHELX 86 via Patterson function and Fourier syntheses on the basis of space group $P\bar{3}m1$. A least-squares refinement of the fractional coordinates, the anisotropic thermal parameters, and the cation distribution over the different sites converged at $R$ = 0.057 for the 1144 observed reflections with $I \geq 2\sigma_I$. Final positions, thermal parameters, and site occupation factors are listed in Table I, interatomic distances in Table II.

The X-ray diffraction patterns of $Cd_{0.5}Ga_2InS_5$ and $Hg_{0.8}Ga_{1.6}In_{1.2}S_5$ look very much like that of $Zn_{1.25}In_{2.5}S_3Se_2$ with regard to the sequence and intensities of the

TABLE II

Interatomic Distances [Å] and Angles

| | | | |
|---|---|---|---|
| In(1)–S/Se(3) | 2.660(1) | Zn(1)–S/Se(2) | 2.366(1) |
| –S/Se(4) | 2.687(1) | –S/Se(3) | 2.387(3) |
| S/Se(3)–S/Se(4) | 3.631(2) | S/Se(2)–S/Se(3) | 3.814(3) |
| S/Se(3)–In(1)–S/Se(4) | 85.52(4) | S/Se(2)–Zn(1)–S/Se(3) | 106.71(8) |
| S/Se(3)–In(1)–S/Se(3) | 95.09(6) | S/Se(2)–Zn(1)–S/Se(2) | 112.08(8) |
| S/Se(4)–In(1)–S/Se(4) | 93.87(6) | | |
| In/Zn(2)–S/Se(1) | 2.496(1) | In/Zn(3)–S/Se(4) | 2.460(3) |
| –S/Se(2) | 2.480(3) | –S/Se(5) | 2.467(1) |
| S/Se(1)–S/Se(2) | 4.191(3) | S/Se(4)–S/Se(5) | 4.114(3) |
| S/Se(1)–In/Zn(2)–S/Se(2) | 114.75(6) | S/Se(4)–In/Zn(3)–S/Se(5) | 113.25(6) |
| S/Se(1)–In/Zn(2)–S/Se(1) | 103.71(7) | S/Se(5)–In/Zn(3)–S/Se(5) | 105.43(7) |

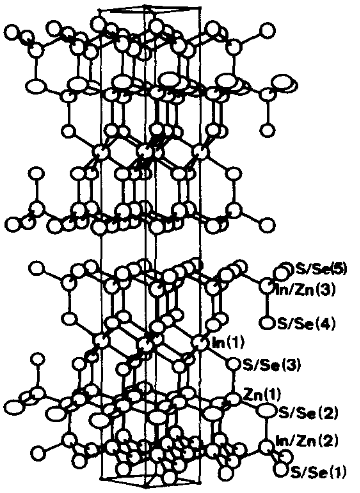

FIG. 1. Structure of $Zn_{1.25}In_{2.5}S_3Se_2$.

reflections. The patterns could be fully indexed on the basis of the hexagonal cell found for $Zn_{1.25}In_{2.5}S_3Se_2$ (see Table III). The lattice constants are $a = 3.809(1)$, $c = 30.644(12)$ Å for $Cd_{0.5}Ga_2InS_5$ and $a = 3.820(1)$, $c = 30.929(3)$ Å for $Hg_{0.8}Ga_{1.6}In_{1.2}S_5$.

## Description of the Structure

The structure of $Zn_{1.5}In_{2.5}S_3Se_2$ shown in Fig. 1 is of a layer type. It is a new polytypic form of the $Zn_2In_2S_5$ structure (*1*) which we would like to designate as the IIb type. Figure 2 shows this structure in comparison with the $Zn_2In_2S_5$(IIa) type in a (110) section through the structure.

The anion arrangement with a statistical distribution of $S^{2-}$ and $Se^{2-}$ is based on hexagonal close packing. Within this *hcp* array of anions there are six tetrahedral and two octahedral cation sites distributed in such a way that packs of five anion layers are formed which are separated from each other by a van der Waals gap. Two of these packs are stacked in the direction of the *c*-axis to build the unit cell at which the second pack is rotated 180° on the 100 direction (i.e., it is upside down with respect to the first pack) and 60° on the 001 direction thus resulting in a centrosymmetric structure. The only difference between the $Zn_2In_2S_5$ (IIa) type and the IIb type is the fact that in the IIa type the second pack is only rotated 60° on the *c*-axis and shifted for *c*/2.

The cation sites are occupied by $Zn^{2+}$ and $In^{3+}$ in the way shown in Table I by the different site occupation factors (s.o.f.).

TABLE III

POWDER DIFFRACTION DATA OF $Cd_{0.5}Ga_2InS_5$ AND $Hg_{0.8}Ga_{1.6}In_{1.2}S_5$

| | $Cd_{0.5}Ga_2InS_5$ | | | $Hg_{0.8}Ga_{1.6}In_{1.2}S_5$ | | |
|---|---|---|---|---|---|---|
| *h k l* | $D_{calc}$ | $D_{obs}$ | $I_0$ | $D_{calc}$ | $D_{obs}$ | $I_0$ |
| 0 0 1 | 20.6441 | | | 20.9289 | | |
| 0 0 2 | 15.3220 | | | 15.4644 | | |
| 0 0 3 | 10.2147 | | | 10.3096 | | |
| 0 0 4 | 7.6610 | | | 7.7322 | | |
| 0 0 5 | 6.1288 | | | 6.1858 | | |
| 0 0 6 | 5.1073 | | | 5.1548 | 5.1545 | w |
| 0 0 7 | 4.3777 | | | 4.4184 | 4.4154 | vw |
| 0 0 8 | 3.8305 | 3.8263 | m | 3.8661 | 3.8650 | m |
| 0 0 9 | 3.4049 | | | 3.4365 | | |
| 1 0 0 | 3.2991 | 3.2982 | vw | 3.3084 | 3.3083 | m |
| 1 0 1 | 3.2802 | 3.2875 | vw | 3.2896 | 3.2897 | w |
| 1 0 2 | 3.2252 | 3.2270 | m | 3.2352 | 3.2341 | st |
| 1 0 3 | 3.1394 | 3.1394 | st | 3.1502 | 3.1301 | vst |
| 0 0 10 | 3.0644 | | | 3.0929 | | |
| 1 0 4 | 3.0301 | 3.0272 | w | 3.0417 | 3.0413 | m |
| 1 0 5 | 2.9050 | 2.9019 | m | 2.9173 | 2.9165 | st |
| 0 0 11 | 2.7858 | | | 2.8117 | | |
| 1 0 6 | 2.7712 | 2.7701 | vw | 2.7843 | 2.7839 | m |
| 1 0 7 | 2.6347 | 2.6336 | w | 2.6483 | 2.6480 | w |
| 0 0 12 | 2.5537 | | | 2.5774 | 2.5777 | vw |
| 1 0 8 | 2.4998 | | | 2.5137 | | |
| 1 0 9 | 2.3693 | 2.3697 | w | 2.3834 | 2.3838 | w |
| 0 0 13 | 2.3572 | | | 2.3791 | | |
| 1 0 10 | 2.2453 | 2.2479 | vw | 2.2593 | 2.2589 | w |
| 0 0 14 | 2.1889 | | | 2.2092 | | |
| 1 0 11 | 2.1285 | | | 2.1425 | 2.1430 | vw |
| 0 0 15 | 2.0429 | | | 2.0619 | | |
| 1 0 12 | 2.0194 | 2.0197 | w | 2.0332 | 2.0334 | w |
| 1 0 13 | 1.9180 | | | 1.9316 | | |
| 0 0 16 | 1.9153 | | | 1.9331 | | |
| 1 1 0 | 1.9047 | 1.9055 | vst | 1.9101 | 1.9103 | vst |
| 1 1 1 | 1.9011 | | | 1.9065 | | |
| 1 1 2 | 1.8902 | | | 1.8957 | | |
| 1 1 3 | 1.8725 | 1.8713 | vw | 1.8781 | | |
| 1 1 4 | 1.8485 | | | 1.8544 | | |
| 1 0 14 | 1.8239 | | | 1.8372 | | |
| 1 1 5 | 1.8189 | | | 1.8251 | | |
| 0 0 17 | 1.8026 | | | 1.8193 | | |
| 1 1 6 | 1.7847 | | | 1.7911 | 1.7911 | vw |
| 1 1 7 | 1.7466 | | | 1.7533 | | |
| 1 0 15 | 1.7369 | 1.7368 | vw | 1.7499 | 1.7512 | vw |
| 1 1 8 | 1.7055 | 1.7057 | vw | 1.7125 | 1.7126 | m |
| 0 0 18 | 1.7024 | | | 1.7183 | | |

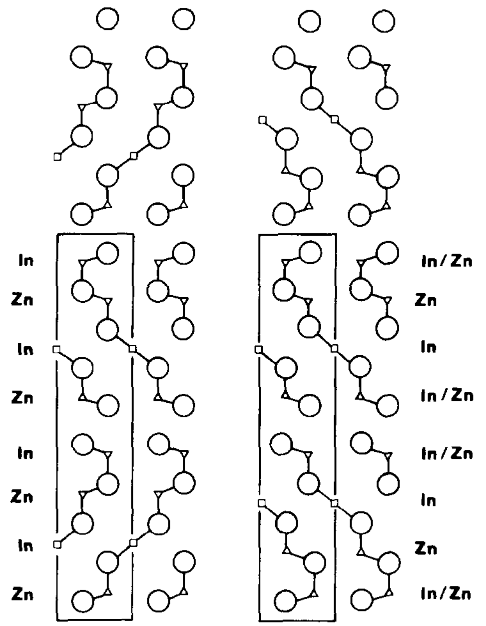

FIG. 2. A (110) section through the $Zn_2In_2S_5$(IIa)-type structure (left) and the structure of $Zn_{1.25}In_{2.5}S_3Se_2$ (right).

The slightly distorted octahedral sites (position 2c) are fully occupied by $In^{3+}$ while all tetrahedral voids contain vacancies as can be seen from the s.o.f. for the cations in position 2c (see Table I). $Zn^{2+}$ can only be found as usual in tetrahedral coordination. The two tetrahedral positions which bound the packs contain $In^{3+}$ and $Zn^{2+}$ in a statistical distribution and one nearly ideal tetrahedral site is solely occupied by $Zn^{2+}$ with s.o.f. = 0.84.

## Discussion

As can be seen from the existence of a large phase width observed for $Zn_{1.25}In_{2.5}S_3Se_2$ (*2*) and for the isotypic compounds $Cd_{0.5}Ga_2InS_5$ and $Hg_{0.8}Ga_{1.6}In_{1.2}S_5$ (*3*) the structure accepts the formation of additional vacancies in the cation lattice.

Recently Attolini *et al.* (*6*) also reported a new layered compound in the $Hg(Ga_xIn_{1-x})_2S_4$ system. The lattice parameters of this compound are given as $a = 3.82$ Å and $c = 30.88$ Å in good agreement with our results , but according to their powder diffraction data this compound is isotypic to $Zn_2In_2S_5$ (IIa type) with space group $P6_3mc$ which is shown by the fact that the 001 reflexes satisfy the condition $1 = 2n$. As can be seen from Table III this extinction condition is not displayed by the mercury compound reported in this paper.

From the view point of cation coordination, the structure of $Zn_{1.25}In_{2.5}S_3Se_2$ is, along with the $ZnIn_2S_4$ or $FeGa_2S_4$ structure, a further connecting link between the spinel structure, with a ratio of octahedral to tetrahedral sites $M_{oct}/M_{tetr} = 2:1$, and the thiogallate structure, with $M_{oct}/M_{tetr} = 0:3$. So if starting from a compound with spinel structure the preference of the cations for tetrahedral coordination is gradually increased (for instance, by substituting sulfur with selenium or by exchange of the cations a compound with the $ZnIn_2S_4$ or $FeGa_2S_4$ structure ($M_{oct}/M_{tetr} = 1:2$) may be formed). If the tetrahedral site preference is further increased the formation of compounds which crystallize in the $Zn_{1.25}In_{2.5}S_3Se_2$ structure ($M_{oct}/M_{tetr} = 1:2.75$) may be observed. This is shown in the system $CdIn_2S_4$–$Ga_2S_3$: by exchange of indium for gallium at the composition $Cd_{0.6}In_{1.2}Ga_{1.06}S_4$ a compound with $ZnIn_2S_4$(IIIa) structure (*7*) is formed and at the composition $Cd_{0.4}In_{0.8}Ga_{1.6}S_4 = Cd_{0.5}Ga_2InS_5$ the structure described in this paper is formed.

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