

radical chain process that produce isobutene. This means that the mechanism for pyrolysis of *tert*-butylarsine must involve at least two independent reactions. The isobutane producing reaction could occur either by a reductive elimination step (reaction 1) or by a radical chain process. The reaction to form isobutene in the gas phase results from a concerted, four-centered β -hydrogen elimination. The total reactor pressure influences the pyrolysis route, but the reason for this is unknown. It is possible that isobutene could be formed in both homogeneous and

heterogeneous steps, the latter of which would become increasingly important at lower pressures. Quantitative rates studies in the low-pressure regime are needed to clarify this point.

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Synthesis and Characterization of Alkaline-Earth Indium Sulfides

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In the course of studies of the Aln_2S_4 ($A = \text{Ca}, \text{Sr}, \text{Ba}$) system, a number of sulfides with metal stoichiometries near, but not necessarily equal to, 1:2 were encountered, including the new phases $\text{Ca}_{1.2}\text{In}_{1.9}\text{S}_4$ and $\text{Sr}_{0.9}\text{In}_{2.1}\text{S}_4$. Indexed X-ray powder diffraction patterns of $\text{Ca}_{3.3}\text{In}_{6.5}\text{S}_{13}$ (" $\text{Ca}_{1.0}\text{In}_{2.0}\text{S}_{4.0}$ "), $\text{Sr}_{0.9}\text{In}_{2.1}\text{S}_4$, SrIn_2S_4 , and BaIn_2S_4 are reported. All compounds have been grown as crystals from $\text{ACl}_2\text{-KCl}$ ($A = \text{Ca}, \text{Sr}, \text{Ba}$) fluxes. $\text{Ca}_{3.3}\text{In}_{6.5}\text{S}_{13}$ (" $\text{Ca}_{1.0}\text{In}_{2.0}\text{S}_{4.0}$ ") forms in the monoclinic space group $C2/m$ with unit cell parameters $a = 37.628$ (4), $b = 3.8360$ (8), $c = 13.722$ (1) Å, and $\beta = 91.66$ (1)°. X-ray powder diffraction data indicate that this compound is isostructural with the previously reported phases $\text{Ca}_{3.1}\text{In}_{6.6}\text{S}_{13}$ (" $\text{Ca}_{1.0}\text{In}_{2.0}\text{S}_{4.0}$ "), $\text{Sn}_{2.5}\text{In}_{7.5}\text{S}_{13}$ (" $\text{Sn}_{0.8}\text{In}_{2.2}\text{S}_{4.0}$ "), and $\text{Pb}_3\text{In}_{6.6}\text{S}_{13}$ (" $\text{Pb}_{0.9}\text{In}_{2.1}\text{S}_{4.0}$ "). These compounds, along with the known phases $\text{Sn}_{5.5}\text{In}_{11}\text{S}_{22}$ (" $\text{Sn}_{1.0}\text{In}_{2.0}\text{S}_{4.0}$ "), $\text{Sn}_{3.5}\text{In}_9\text{S}_{17}$ (" $\text{Sn}_{0.8}\text{In}_{2.1}\text{S}_{4.0}$ "), and $\text{Pb}_4\text{In}_9\text{S}_{17}$ (" $\text{Pb}_{0.9}\text{In}_{2.1}\text{S}_{4.0}$ "), share structural features that consist of stepped "layers" of edge-sharing InS_6 octahedra interconnected by vertex-sharing with columns comprised of other InS_6 octahedra to form a three-dimensional structure. The divalent cations reside in bicapped trigonal prismatic sites in the channels formed by the In-S framework. Observed X-ray powder diffraction data for crystals of a new compound, $\text{Ca}_{1.2}\text{In}_{1.9}\text{S}_4$, are reported. Another newly prepared phase, $\text{Sr}_{0.9}\text{In}_{2.1}\text{S}_4$, forms with a C-centered monoclinic unit cell, $a = 27.66$ (1), $b = 3.943$ (2), $c = 12.683$ (7) Å, and $\beta = 94.25$ (4)°. The poor crystallinity of these phases has precluded single-crystal X-ray structure determinations. Indexed powder diffraction data are also given for the previously reported orthorhombic forms of SrIn_2S_4 and BaIn_2S_4 . Although the empirical formulas are similar, the structures of these two latter compounds are unrelated to those of the other ternary indium sulfides mentioned above and feature tetrahedrally coordinated indium.

Introduction

Ceramic compounds that transmit in the long-wavelength infrared region are currently of interest. The variety of structures found in the literature for Aln_2S_4 -related ($A = \text{Ca}, \text{Sr}, \text{Ba}$) compounds suggests that these systems may comprise a fruitful area to search for new compounds. Our investigation of these ternary indium sulfide systems was undertaken to identify new compounds for possible applications as optical ceramics and to confirm reported structures and structural interrelationships.

Previously reported ternary alkaline-earth indium sulfides are CaIn_2S_4 (two forms), $\text{Ca}_{3.1}\text{In}_{6.6}\text{S}_{13}$, SrIn_2S_4 , and BaIn_2S_4 . Our interest in these systems was piqued by the report that CaIn_2S_4 , synthesized from CaS and In_2S_3 in an evacuated silica ampule, has the normal spinel structure ($a = 10.77$ Å).¹ This report is surprising, since the large Ca^{2+} ion would occupy a tetrahedral site in a normal spinel. It is possible that the reported X-ray powder diffraction data correspond to $\beta\text{-In}_2\text{S}_3$, which has a spinellike structure.² Another report of a compound with the stoi-

chiometry CaIn_2S_4 , synthesized from the corresponding ternary oxide under H_2S , gives a cubic unit cell ($a = 10.63$ Å) and an X-ray powder diffraction pattern different from that of spinel.³ A compound with a similar formula, $\text{Ca}_{3.1}\text{In}_{6.6}\text{S}_{13}$,⁴ has been synthesized as yellow whiskers by iodine transport of a mixture of CaS and In_2S_3 . An X-ray single-crystal structure determination⁵ found the indium octahedrally coordinated and the calcium in bicapped trigonal prismatic coordination in a monoclinic unit cell (space group $C2/m$: $a = 37.63$ (1), $b = 3.8358$ (9), $c = 13.713$ (3) Å, $\beta = 91.65$ (1)°; $Z = 4$).

SrIn_2S_4 and BaIn_2S_4 were first reported in 1974.⁶ These compounds were prepared from the elements by iodine transport and found to be isostructural to each other by X-ray powder diffraction. The powder patterns were in-

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dexed on orthorhombic subcells ($a = 10.439$, $b = 10.548$, $c = 6.510$ Å for SrIn_2S_4 ; $a = 10.885$, $b = 10.840$, $c = 6.556$ Å for BaIn_2S_4), although the possibility of a larger orthorhombic superlattice was acknowledged.⁶ A single-crystal X-ray structure determination of BaIn_2S_4 found the barium in distorted eight-coordinate square antiprismatic sites and the indium in tetrahedral sites.⁷ The structure determination confirmed an orthorhombic unit cell⁷ with each axis doubled relative to the first report⁶ (correct unit cell is $Fddd$: $a = 21.824$ (6), $b = 21.670$ (6), and $c = 13.125$ (4) Å; $Z = 32$).

Our studies were undertaken to grow crystals of these phases to confirm the structure of CaIn_2S_4 , to elucidate structural trends in alkaline-earth indium sulfide systems, and to obtain compounds for property characterization to determine suitability as optical materials.

Experimental Methods

Sample Preparation. Crystals of $\text{Ca}_{3.3}\text{In}_{6.5}\text{S}_{13}$, $\text{Ca}_{1.2}\text{In}_{1.9}\text{S}_4$, SrIn_2S_4 , $\text{Sr}_{0.9}\text{In}_{2.1}\text{S}_4$, and BaIn_2S_4 were grown in a similar manner from halide fluxes. The first four compounds were obtained as whiskers, many of which were revealed to be agglomerations of thinner parallel whiskers by optical microscopy. To prepare the fluxes, CaCl_2 (Baker, reagent), SrCl_2 (RIC 99.99%), BaCl_2 (Alfa, reagent), and KCl (Baker, reagent) were dried under vacuum at 150 °C, weighed, ground together quickly in air, and then dried again prior to use. The flux compositions were CaCl_2/KCl 74:26 mol % eutectic (mp = 640 °C⁸) for Ca-In-S systems, SrCl_2/KCl 45:55 mol % eutectic (mp = 580 °C⁹) for SrIn_2S_4 , SrCl_2/KCl 33:67 mol % (mp = 600 °C⁹) for $\text{Sr}_{0.9}\text{In}_{2.1}\text{S}_4$, and BaCl_2/KCl 42:58 mol % eutectic (mp = 644 °C⁸) for BaIn_2S_4 . Crystal growth experiments were done in graphite crucibles enclosed in silica ampules previously outgassed under vacuum at 900 °C, then cooled, and loaded with mixtures of charge and flux. The loaded ampules were held under dynamic vacuum at least 2.5 h to obtain a pressure of less than 4×10^{-4} Torr prior to sealing. The reaction mixtures were held above 1050 °C for several days to maximize the amount of charge dissolved in the flux; chemical attack on the interior ampule surfaces was minimal. Crystals were removed from the flux by soaking in distilled water.

A 1:1 mol mixture of CaS (Cerac 99.99%) and In_2S_3 (prepared from $\text{In}(\text{NO}_3)_3$ and H_2S at 750 °C) was prereacted in a graphite crucible in an evacuated silica ampule at 1100 °C for 6 days. According to X-ray powder diffraction, the yellow-brown polycrystalline product contained CaS , In_2S_3 , and a phase later identified as $\text{Ca}_{3.3}\text{In}_{6.5}\text{S}_{13}$; this powder served as the charge in the Ca-In-S flux growth experiments. The flux:charge mass ratio was 4:1 for $\text{Ca}_{3.3}\text{In}_{6.5}\text{S}_{13}$ and 7:1 for $\text{Ca}_{1.2}\text{In}_{1.9}\text{S}_4$. The crystal growth reaction mixtures were heated to 1070 °C, held for 3 days, cooled 1.5 °C/h to 500 °C, and then cooled to room temperature in 1 day.

A 1:1 mol mixture of SrS (Cerac 99.9%) and In_2S_3 was ground together quickly in air and used as the charge in the crystal growth experiment that yielded $\text{Sr}_{0.9}\text{In}_{2.1}\text{S}_4$, whereas a 1:1.15 mol ratio was used when SrIn_2S_4 crystals were obtained. The flux:charge mass ratio was 6:1 in both experiments. These reaction mixtures were heated to 1100 °C, held for 4 days, cooled 1.0–1.2 °C/h to 500 °C, and then cooled to room temperature in 24 h.

Polycrystalline BaIn_2S_4 , prepared by heating a 1:1 mol mixture of BaS (Cerac, 99.9%) and In_2S_3 in a graphite crucible in an evacuated silica ampule at 1050 °C for 6 days, was used as the charge in the BaIn_2S_4 crystal growth. The flux:charge mass ratio was 22:1. The crystal growth reaction mixture was heated to 1050 °C, held for 4 days, cooled 1.0 °C/h to 550 °C, and then cooled to room temperature over 4 days.

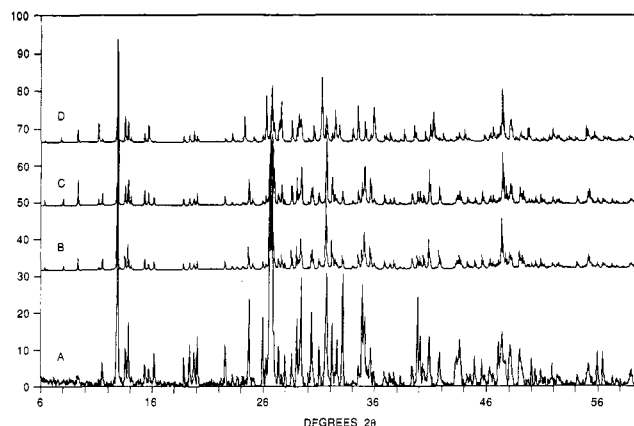


Figure 1. X-ray powder diffraction patterns: (A) observed pattern of $\text{Ca}_{3.3}\text{In}_{6.5}\text{S}_{13}$ crystals (Tables I and II), (B) calculated pattern of $\text{Ca}_{3.1}\text{In}_{6.6}\text{S}_{13}$ using corrected atomic positions (see text) and the unit cell of $\text{Ca}_{3.3}\text{In}_{6.5}\text{S}_{13}$ (Table II), (C) calculated pattern of “ $\text{Ca}_{2.5}\text{In}_7\text{S}_{13}$ ”, using atomic positions of $\text{Sn}_{2.5}\text{In}_7\text{S}_{13}$ ¹² and the unit cell of $\text{Ca}_{3.3}\text{In}_{6.5}\text{S}_{13}$ (Table II), and (D) calculated pattern of “ $\text{Ca}_3\text{In}_{6.67}\text{S}_{13}$ ” using atomic positions of $\text{Pb}_3\text{In}_{6.67}\text{S}_{13}$ ¹¹ and the unit cell of $\text{Ca}_{3.3}\text{In}_{6.5}\text{S}_{13}$.

Sample Characterization. X-ray powder diffraction data were obtained by using nickel-filtered copper $K\alpha$ radiation with a Scintag PAD V diffractometer and/or by Gandolfi/Debye-Scherrer camera methods. The PAD V is equipped with a solid-state germanium detector with the goniometer set at a radius of 220 mm; fixed slits with a divergence angle 1.4° and acceptance angle of 0.14° were used. Samples were mounted on zero-background off-axis-cut quartz substrates on thin layers of petroleum jelly to minimize preferred orientation arising from the needlelike morphology. Data were collected at intervals of 0.02° 2θ , corrected for background, and stripped of $K\alpha_2$. Powder patterns were recorded digitally with continuous scans at 0.5°/min or with step scans of 2 s/0.02° step. For single crystals, unit cells and lattice symmetries were obtained with a Nicolet R3 diffractometer using monochromated molybdenum $K\alpha$ radiation. Thirteen to seventeen reflections were computer-centered and auto-indexed. The unit cell parameters obtained from single crystals were refined from the powder diffraction data of crushed crystals by using a least-squares refinement program. Calculated X-ray powder diffraction patterns were generated by using the Scintag-version of POWD10¹⁰ with Cauchy profiles applied to calculated peak positions.

Metal ratios were determined by inductively coupled plasma (ICP) emission analysis (ICAP/OES, Perkin-Elmer 6500); complete elemental analyses were performed by Schwarzkopf Microanalytical Laboratory. From multiple determinations, the errors in the metal stoichiometries are estimated to be ± 0.06 mol. Semiquantitative elemental analyses were obtained by energy-dispersive X-ray spectroscopy (EDX) using a scanning electron microscope (Amray 1400, Tracor TN2000 analyzer). Auger electron spectroscopy was performed with a Perkin-Elmer PHI 6000 scanning Auger multiprobe; depth profiles were analyzed after sputtering with Ar^+ ions. EDX and Auger spectroscopy indicated no incorporation of K or Cl from the flux into any of the ternary sulfide crystals; Auger analyses of crystals did not detect bulk oxygen.

The oxidative stabilities of several of the compounds were determined by thermogravimetric analysis (TGA) of samples of powdered crystals under flowing oxygen (Du Pont 1090 system, heating rate 10°/min). The onset decomposition temperatures were as follows: $\text{Ca}_{3.3}\text{In}_{6.5}\text{S}_{13}$, 375 °C; $\text{Ca}_{1.2}\text{In}_{1.9}\text{S}_4$, 425 °C; SrIn_2S_4 , 425 °C; BaIn_2S_4 , 425 °C.

Results and Discussion

$\text{Ca}_{3.3}\text{In}_{6.5}\text{S}_{13}$ was obtained as mats of bright yellow whiskers up to 3 mm in length. With a single-crystal

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Table I. X-ray Powder Diffraction Data for $\text{Ca}_{3.3}\text{In}_{6.5}\text{S}_{13}$ Whiskers^a

| <i>h</i> | <i>k</i> | <i>l</i> | <i>d</i> _{obs} , Å | <i>d</i> _{calc} , Å | <i>I</i> / <i>I</i> ₀ |
|----------|----------|----------|-----------------------------|------------------------------|----------------------------------|
| 4 | 0 | 1 | 7.67 | 7.6528 | 7 |
| 0 | 0 | 2 | 6.87 | 6.8584 | 100 |
| -2 | 0 | 2 | 6.51 | 6.5044 | 12 |
| 2 | 0 | 2 | 6.39 | 6.3840 | 20 |
| -6 | 0 | 1 | 5.772 | 5.7651 | 7 |
| 6 | 0 | 1 | 5.642 | 5.6400 | 5 |
| 4 | 0 | 2 | 5.471 | 5.4661 | 10 |
| 8 | 0 | 0 | 4.701 | 4.7015 | 8 |
| 0 | 0 | 3 | 4.572 | 4.5723 | 12 |
| -2 | 0 | 3 | 4.478 | 4.4728 | 11 |
| 2 | 0 | 3 | 4.417 | 4.4136 | 14 |
| -8 | 0 | 2 | 3.933 | 3.9314 | 13 |
| 8 | 0 | 2 | 3.828 | 3.8264 | 4 |
| 10 | 0 | 0 | 3.760 | 3.7612 | 3 |
| 10 | 0 | 1 | 3.602 | 3.6008 | 27 |
| 0 | 0 | 4 | 3.430 | 3.4292 | 22 |
| -2 | 0 | 4 | 3.391 | 3.3910 | 8 |
| 2 | 0 | 4 | 3.357 | 3.3564 | 75 |
| 1 | 1 | 2 | 3.330 | 3.3306 | 70 |
| 10 | 0 | 2 | 3.259 | 3.2582 | 13 |
| 3 | 1 | 2 | 3.225 | 3.2232 | 4 |
| 4 | 0 | 4 | 3.192 | 3.1920 | 9 |
| 7 | 1 | 0 | 3.125 | 3.1220 | 10 |
| -12 | 0 | 1 | 3.076 | 3.0750 | 20 |
| 12 | 0 | 1 | 3.037 | 3.0365 | 34 |
| -10 | 0 | 3 | 2.946 | 2.9470 | 24 |
| -12 | 0 | 2 | 2.882 | 2.8825 | 13 |
| 7 | 1 | 2 | 2.825 | 2.8236 | 36 |
| -9 | 1 | 1 | 2.779 | 2.7787 | 19 |
| 0 | 0 | 5 | 2.744 | 2.7434 | 14 |
| 2 | 0 | 5 | 2.703 | 2.7035 | 36 |
| 9 | 1 | 2 | 2.596 | 2.5950 | 6 |
| -10 | 0 | 4 | 2.571 | 2.5715 | 32 |
| 7 | 1 | 3 | 2.557 | 2.5583 | 22 |
| -11 | 1 | 1 | 2.518 | 2.5192 | 13 |
| 10 | 0 | 4 | 2.498 | 2.4983 | 5 |
| -5 | 1 | 4 | 2.436 | 2.4367 | 4 |
| -11 | 1 | 2 | 2.408 | 2.4093 | 5 |
| 9 | 1 | 3 | 2.383 | 2.3831 | 4 |
| -13 | 1 | 1 | 2.287 | 2.2865 | 7 |
| 2 | 0 | 6 | 2.261 | 2.2616 | 27 |
| -10 | 0 | 5 | 2.247 | 2.2477 | 16 |
| -1 | 1 | 5 | 2.231 | 2.2306 | 7 |
| -13 | 1 | 2 | 2.205 | 2.2046 | 17 |
| 9 | 1 | 4 | 2.1589 | 2.1602 | 11 |
| 14 | 0 | 4 | 2.0852 | 2.0857 | 19 |
| -18 | 0 | 1 | 2.0748 | 2.0747 | 14 |
| 7 | 1 | 5 | 2.0443 | 2.0438 | 4 |
| 8 | 0 | 6 | 2.0326 | 2.0329 | 4 |
| -18 | 0 | 2 | 2.0147 | 2.0152 | 9 |
| -9 | 1 | 5 | 1.9880 | 1.9880 | 8 |
| -10 | 0 | 6 | 1.9796 | 1.9792 | 4 |
| 0 | 0 | 7 | 1.9598 | 1.9596 | 6 |
| -3 | 1 | 6 | 1.9470 | 1.9476 | 4 |
| 10 | 0 | 6 | 1.9288 | 1.9289 | 13 |
| 17 | 1 | 0 | 1.9172 | 1.9166 | 18 |
| 4 | 0 | 7 | 1.9073 | 1.9073 | 9 |
| -11 | 1 | 5 | 1.8896 | 1.8892 | 13 |
| -17 | 1 | 2 | 1.8573 | 1.8580 | 11 |

^a $C2/m$; $a = 37.628$ (4), $b = 3.8630$ (8), $c = 13.722$ (1) Å, $\beta = 91.66$ (1)°.

diffractometer, a C-centered monoclinic unit cell for a whisker of $\text{Ca}_{3.3}\text{In}_{6.5}\text{S}_{13}$ was obtained. A least-squares refinement of this cell, using powder data from crushed crystals (Figure 1A), gave cell parameters of $a = 37.628$ (4), $b = 3.8361$ (8), $c = 13.722$ (1), $\beta = 91.66$ (1)°, with the b axis corresponding to the needle axis (Table I). This unit cell is similar to those reported for other ternary indium sulfides with similar stoichiometries, i.e., $\text{Ca}_{3.1}\text{In}_{6.6}\text{S}_{13}$,⁵ $\text{Pb}_3\text{In}_{6.67}\text{S}_{13}$,¹¹ and $\text{Sn}_{2.5}\text{In}_7\text{S}_{13}$ ¹² (Table IIA). The X-ray

Table II. Unit Cell Parameters^a for $\text{Ca}_{3.3}\text{In}_{6.5}\text{S}_{13}$ and Related Compounds

| | $\text{Ca}_{3.3}\text{In}_{6.5}\text{S}_{13}$ | $\text{Ca}_{3.1}\text{In}_{6.6}\text{S}_{13}$ | $\text{Pb}_3\text{In}_{6.67}\text{S}_{13}$ | $\text{Sn}_{2.5}\text{In}_7\text{S}_{13}$ |
|---------------|---|---|--|---|
| ref | this work | 5 | 11 | 12 |
| <i>a</i> , Å | 37.628 (4) | 37.63 (1) | 38.13 (2) | 37.917 (4) |
| <i>b</i> , Å | 3.8360 (8) | 3.8358 (9) | 3.869 (2) | 3.8433 (6) |
| <i>c</i> , Å | 13.722 (1) | 13.713 (3) | 13.809 (5) | 13.758 (3) |
| β , deg | 91.66 (1) | 91.65 (1) | 91.25 (2) | 91.20 (1) |

^a Space group $C2/m$.

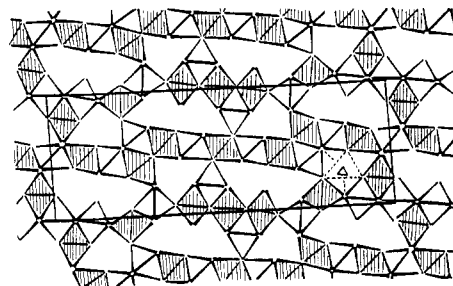


Figure 2. Projection along the b axis of the InS framework in the structure of $\text{Ca}_{3.3}\text{In}_{6.5}\text{S}_{13}$. Nonshaded octahedra have indium atoms at $y = 0$, shaded at $y = 1/2$. The infinite ribbons seven InS_6 octahedra wide extend perpendicular to the plane of the paper. Note the resultant stepped "layers" that arise from interconnection of these ribbons. One capped trigonal prismatic calcium site is denoted with a triangle.

powder diffraction pattern of the $\text{Ca}_{3.3}\text{In}_{6.5}\text{S}_{13}$ whiskers is shown in Figure 1 along with powder patterns for $\text{Ca}_{3.1}\text{In}_{6.6}\text{S}_{13}$, $\text{Sn}_{2.5}\text{In}_7\text{S}_{13}$, and $\text{Pb}_3\text{In}_{6.67}\text{S}_{13}$ that were calculated from the reported single-crystal data. In the calculations, the calcium scattering factor was substituted for lead and tin to allow intensity comparisons and all three patterns were calculated with the cell parameters from our $\text{Ca}_{3.3}\text{In}_{6.5}\text{S}_{13}$ whiskers (Table I) to overlap corresponding reflections. In an earlier report,¹³ we concluded that the $\text{Ca}_{3.3}\text{In}_{6.5}\text{S}_{13}$ whiskers, then formulated as CaIn_2S_4 , were a new compound because the experimental X-ray powder diffraction pattern did not correspond to that calculated from the single-crystal data reported for $\text{Ca}_{3.1}\text{In}_{6.6}\text{S}_{13}$.⁵ We subsequently discovered a typographical error in the atom positions reported in ref 5; the x coordinate for $\text{In}(4)$ in ref 5 is given as 0.2670 but should be 0.1670 to agree with the unit cell projection and produce reasonable interatomic distances. Recalculation of the X-ray powder diffraction pattern of $\text{Ca}_{3.1}\text{In}_{6.6}\text{S}_{13}$ gave that shown in Figure 1B. The striking similarity of the patterns shown in Figure 1A and 1B strongly suggests that $\text{Ca}_{3.1}\text{In}_{6.6}\text{S}_{13}$ and $\text{Ca}_{3.3}\text{In}_{6.5}\text{S}_{13}$ are the same compound, although slight differences in stoichiometry cannot be ruled out. The $\text{Ca}_{3.3}\text{In}_{6.5}\text{S}_{13}$ whiskers obtained in the present study were insufficiently crystalline for a full X-ray structure redetermination.

The calcium, tin, and lead compounds given in Table II share a common structure despite the small differences in stoichiometries. A projection of this structure is shown in Figure 2. Distorted edge-shared InS_6 octahedra form infinite ribbons seven octahedra in width that are interconnected by edge-sharing to form stepped "layers". These stepped "layers" are interconnected to form a three-dimensional framework by vertex-sharing with infinite columns comprised of other InS_6 octahedra (see Figure 2). The divalent cations reside in bicapped trigonal prismatic sites in the channels formed by the InS framework. In this

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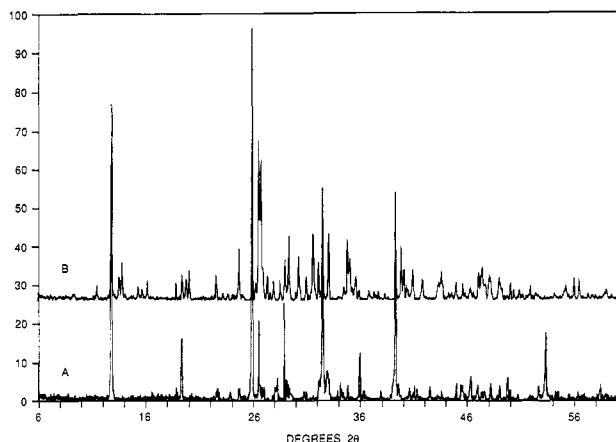


Figure 3. Observed X-ray powder diffraction patterns of (A) bronze $\text{Ca}_{1.2}\text{In}_{1.9}\text{S}_4$ (" $\text{Ca}_{3.9}\text{In}_{6.2}\text{S}_{13}$ ") whiskers (Table III) and (B) yellow $\text{Ca}_{3.3}\text{In}_{6.5}\text{S}_{13}$ whiskers (Table I).

Table III. Observed X-ray Powder Diffraction Data for Bronze $\text{Ca}_{1.2}\text{In}_{1.9}\text{S}_4$ (" $\text{Ca}_{3.9}\text{In}_{6.2}\text{S}_{13}$ ") Whiskers

| $d_{\text{obs}}, \text{\AA}$ | I/I_0 | $d_{\text{obs}}, \text{\AA}$ | I/I_0 |
|------------------------------|---------|------------------------------|---------|
| 6.90 | 81 | 2.601 | 2 |
| 4.705 | 3 | 2.572 | 4 |
| 4.592 | 17 | 2.496 | 13 |
| 3.922 | 3 | 2.469 | 3 |
| 3.730 | 2 | 2.372 | 3 |
| 3.604 | 4 | 2.293 | 58 |
| 3.441 | 100 | 2.277 | 4 |
| 3.360 | 20 | 2.222 | 3 |
| 3.322 | 3 | 2.1992 | 4 |
| 3.302 | 3 | 2.1845 | 3 |
| 3.182 | 4 | 2.1258 | 4 |
| 3.160 | 6 | 2.0757 | 2 |
| 3.087 | 22 | 2.0147 | 4 |
| 3.064 | 5 | 1.9955 | 4 |
| 3.050 | 4 | 1.9898 | 4 |
| 3.036 | 3 | 1.9592 | 7 |
| 2.905 | 2 | 1.9335 | 4 |
| 2.884 | 3 | 1.9187 | 2 |
| 2.774 | 6 | 1.9093 | 2 |
| 2.753 | 58 | 1.8867 | 4 |
| 2.718 | 9 | 1.8566 | 4 |
| 2.644 | 3 | 1.8315 | 6 |
| 2.622 | 4 | 1.8232 | 3 |

structure, the ratio of trigonal prismatic channel sites to octahedral framework sites to sulfur sites is 3:7:13. Variable cation stoichiometry can be accommodated by mixing of cations across the framework and channel sites (as in $\text{Ca}_{3.1}\text{In}_{6.6}\text{S}_{13}$ and $\text{Pb}_3\text{In}_{6.7}\text{S}_{13}$)^{5,11} and/or by formation of vacancies in the divalent metal channel sites.^{5,11,12}

Whiskers up to 4 mm in length, having a uniform bronze color and overall stoichiometry $\text{Ca}_{1.2}\text{In}_{1.9}\text{S}_4$ (" $\text{Ca}_{3.9}\text{In}_{6.2}\text{S}_{13}$ "), were the product of another crystal growth experiment with an increase in the flux:charge ratio from 4:1 for $\text{Ca}_{3.3}\text{In}_{6.5}\text{S}_{13}$ to 7:1. The observed X-ray powder diffraction data of crushed crystals of $\text{Ca}_{1.2}\text{In}_{1.9}\text{S}_4$ (" $\text{Ca}_{3.9}\text{In}_{6.2}\text{S}_{13}$ ") are given in Table III, and the pattern is shown in Figure 3 along with that of the $\text{Ca}_{3.3}\text{In}_{6.5}\text{S}_{13}$ crystals. The substantial differences in these X-ray powder diffraction patterns indicate that the structure of $\text{Ca}_{1.2}\text{In}_{1.9}\text{S}_4$ (" $\text{Ca}_{3.9}\text{In}_{6.2}\text{S}_{13}$ ") is different from that of $\text{Ca}_{3.3}\text{In}_{6.5}\text{S}_{13}$. Three different unit cells, all of questionable validity because of the poor crystal quality, were found from different whiskers using single-crystal methods. The X-ray powder diffraction pattern of the crushed whiskers could not be completely indexed on any of these unit cells; the apparently individual whiskers used for the single-crystal studies may not have been true single crystals but rather agglomerations of single crystals. Individual $\text{Ca}_{1.2}\text{In}_{1.9}\text{S}_4$ whiskers, although uniform

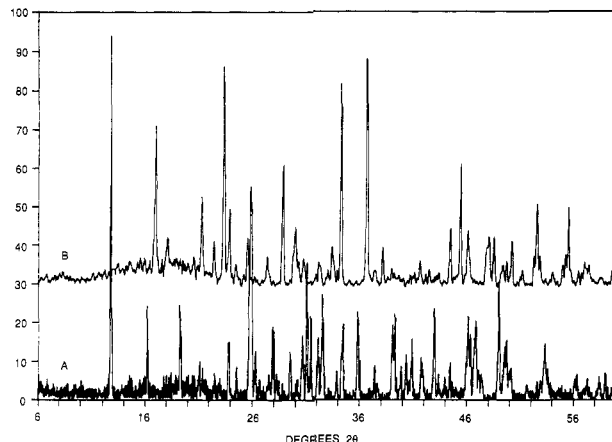


Figure 4. X-ray powder diffraction pattern of (A) monoclinic $\text{Sr}_{0.9}\text{In}_{2.1}\text{S}_4$ crystals (Table IV) and (B) X-ray powder diffraction pattern of orthorhombic SrIn_2S_4 crystals (Table V).

in appearance, may be a mixture of polytypes and/or compositions of differing stoichiometries, the elemental analyses having indicated the average composition. The elemental composition was found to be uniform between whiskers within the limits of EDX, but the overlap of calcium and indium transitions limited the accuracy of this analysis. Although the structure of the $\text{Ca}_{3.1}\text{In}_{6.6}\text{S}_{13}$ -type compounds (Figure 2, Table II) can accommodate variable stoichiometry as described above, the X-ray powder diffraction patterns in Figure 3 indicate a substantial difference in the structures of $\text{Ca}_{1.2}\text{In}_{1.9}\text{S}_4$ (" $\text{Ca}_{3.9}\text{In}_{6.2}\text{S}_{13}$ ") and $\text{Ca}_{3.3}\text{In}_{6.5}\text{S}_{13}$. The structural variety in this class of ternary indium sulfides is especially rich because the details of the interconnections of the ribbons of edge-sharing InS_6 octahedra can vary, giving rise to different three-dimensional frameworks. For example, $\text{Pb}_4\text{In}_9\text{S}_{17}$,¹¹ $\text{Sn}_{3.5}\text{In}_9\text{S}_{17}$,¹⁴ and $\text{Sn}_{5.5}\text{In}_{11}\text{S}_{22}$ ¹⁵ have stoichiometries similar to the $\text{Ca}_{3.1}\text{In}_{6.6}\text{S}_{13}$ family described above but display considerably different structures. However, these structures also display InS frameworks formed by infinite ribbons of edge-shared InS_6 octahedra, seven octahedra in width, interconnected by vertex sharing to columns of other InS_6 octahedra, with the divalent metals similarly found in bicapped trigonal prismatic channel sites. $\text{Pb}_4\text{In}_9\text{S}_{17}$ and $\text{Sn}_{3.5}\text{In}_9\text{S}_{17}$ are isostructural,^{11,14} while no analogues of $\text{Sn}_{5.5}\text{In}_{11}\text{S}_{22}$ ¹⁵ have been found. Comparison of the observed X-ray powder diffraction pattern of the $\text{Ca}_{1.2}\text{In}_{1.9}\text{S}_4$ (" $\text{Ca}_{3.9}\text{In}_{6.2}\text{S}_{13}$ ") whiskers with those calculated from reported single-crystal data of $\text{Pb}_4\text{In}_9\text{S}_{17}$,¹¹ $\text{Sn}_{3.5}\text{In}_9\text{S}_{17}$,¹⁴ and $\text{Sn}_{5.5}\text{In}_{11}\text{S}_{22}$ ¹⁵ did not indicate structural similarities. A variety of these ternary indium sulfide structures seems to be possible, distinguished only by the connectivity of the same types of building blocks.

Crystals of a new phase, $\text{Sr}_{0.9}\text{In}_{2.1}\text{S}_4$, were obtained as mats of bright yellow whiskers up to 3 mm in length. With a single-crystal diffractometer, a C-centered monoclinic cell was obtained for a whisker of $\text{Sr}_{0.9}\text{In}_{2.1}\text{S}_4$. With this cell, 42 of 43 reflections in the X-ray powder diffraction pattern (Table IV, Figure 4A) obtained from approximately 20 mg of crushed crystals were indexed; refinement of the powder data yielded $a = 27.66$ (1), $b = 3.943$ (2), $c = 12.683$ (7) \AA , and $\beta = 94.25$ (4) $^\circ$, with the b axis corresponding to the needle axis. The intensity of the unindexed reflection at $d = 5.480$ \AA varied widely among different samples in the

(14) Likforman, A.; Guittard, M.; Jaulmes, S. *Acta Crystallogr.* 1987, C43, 177.

(15) Likforman, A.; Guittard, M.; Jaulmes, S. *Acta Crystallogr.* 1988, C44, 1339.

Table IV. X-ray Powder Diffraction Data for $\text{Sr}_{0.9}\text{In}_{2.1}\text{S}_4$ Whiskers^a

| <i>h</i> | <i>k</i> | <i>l</i> | <i>d</i> _{obs} , Å | <i>d</i> _{calc} , Å | <i>I</i> / <i>I</i> ₀ |
|----------|----------|----------|-----------------------------|------------------------------|----------------------------------|
| 4 | 0 | 0 | 6.93 | 6.8949 | 100 |
| | | | 5.480 ^b | | 24 |
| 6 | 0 | 0 | 4.607 | 4.5966 | 28 |
| 0 | 0 | 3 | 4.206 | 4.2159 | 10 |
| -2 | 0 | 3 | 4.150 | 4.1180 | 8 |
| 2 | 0 | 3 | 3.940 | 3.9506 | 8 |
| -4 | 0 | 3 | 3.730 | 3.7217 | 16 |
| 3 | 1 | 0 | 3.623 | 3.6237 | 10 |
| 8 | 0 | 0 | 3.448 | 3.4474 | 64 |
| -8 | 0 | 1 | 3.387 | 3.3905 | 14 |
| -1 | 1 | 2 | 3.338 | 3.3372 | 6 |
| -6 | 0 | 3 | 3.239 | 3.2285 | 7 |
| 5 | 1 | 0 | 3.203 | 3.2077 | 22 |
| -3 | 1 | 2 | 3.186 | 3.1845 | 20 |
| 0 | 0 | 4 | 3.158 | 3.1619 | 7 |
| 2 | 0 | 4 | 3.025 | 3.0333 | 15 |
| -5 | 1 | 2 | 2.915 | 2.9118 | 18 |
| -1 | 1 | 3 | 2.877 | 2.8793 | 41 |
| 1 | 1 | 3 | 2.846 | 2.8493 | 24 |
| 7 | 1 | 0 | 2.786 | 2.7870 | 16 |
| -7 | 1 | 1 | 2.750 | 2.7522 | 30 |
| 10 | 0 | 1 | 2.643 | 2.6540 | 8 |
| -7 | 1 | 2 | 2.602 | 2.6012 | 22 |
| 7 | 1 | 2 | 2.505 | 2.5023 | 27 |
| -1 | 1 | 4 | 2.491 | 2.4696 | 11 |
| -9 | 1 | 1 | 2.402 | 2.4026 | 10 |
| -5 | 1 | 4 | 2.303 | 2.3020 | 21 |
| -12 | 0 | 1 | 2.291 | 2.2914 | 25 |
| 8 | 0 | 4 | 2.259 | 2.2486 | 10 |
| 10 | 0 | 3 | 2.234 | 2.2333 | 13 |
| 5 | 1 | 4 | 2.207 | 2.2048 | 19 |
| -10 | 0 | 4 | 2.1623 | 2.1592 | 12 |
| -3 | 1 | 5 | 2.1052 | 2.1032 | 28 |
| -12 | 0 | 3 | 2.0853 | 2.0839 | 7 |
| -4 | 0 | 6 | 2.0588 | 2.0590 | 6 |
| 7 | 1 | 4 | 2.0373 | 2.0384 | 10 |
| -14 | 0 | 1 | 1.9684 | 1.9688 | 24 |
| 12 | 0 | 3 | 1.9598 | 1.9578 | 17 |
| -11 | 1 | 3 | 1.9402 | 1.9403 | 23 |
| -14 | 0 | 2 | 1.9183 | 1.9217 | 7 |
| 2 | 2 | 2 | 1.8593 | 1.8594 | 35 |
| -14 | 0 | 3 | 1.8346 | 1.8378 | 18 |
| -13 | 1 | 2 | 1.8247 | 1.8244 | 8 |

^a Monoclinic C-centered; *a* = 27.66 (1), *b* = 3.943 (2), *c* = 12.683 (7) Å, *β* = 94.25 (4)°. ^b The line has an unacceptably large deviation from any expected line position for this unit cell for reasons suggested in the text.

same reaction. This suggests that it could arise from another phase in the Sr-In-S system which would not be unexpected given the polymorph formation observed in the Ca-In-S system and the poor crystallinity exhibited by all of these compounds. The $\text{Sr}_{0.9}\text{In}_{2.1}\text{S}_4$ whiskers were insufficiently crystalline for a single-crystal structure determination.

Crystals of SrIn_2S_4 grew as clusters of golden-yellow whiskers up to 5 mm in length. All observed X-ray powder diffraction data from a sample of crushed crystals (Figure 4B) were indexed by using an orthorhombic cell consistent with the space group *Fddd*: *a* = 20.892 (3), *b* = 21.123 (3), and *c* = 13.017 (2) Å (Table V). In this cell, all three lattice parameters are doubled relative to the previously reported orthorhombic subcell,⁶ just as is the case for BaIn_2S_4 .^{6,7} Comparison of the X-ray powder diffraction pattern of $\text{Sr}_{0.9}\text{In}_{2.1}\text{S}_4$ (Figure 4A) with that of SrIn_2S_4 (Figure 4B) indicates that their structures, despite the similar stoichiometries, are considerably different. The orthorhombic structure type is markedly different from those discussed thus far. The arrangement is derived from that of TlSe , i.e., thallous thallic selenide, which is considered to be an ionic compound, $\text{Tl}(\text{TlSe}_2)$, containing large Tl^+ ions that charge balance covalently bonded TlSe_2^-

Table V. X-ray Powder Diffraction Data for SrIn_2S_4 Whiskers^a

| <i>h</i> | <i>k</i> | <i>l</i> | <i>d</i> _{obs} , Å | <i>d</i> _{calc} , Å | <i>I</i> / <i>I</i> ₀ |
|----------|----------|----------|-----------------------------|------------------------------|----------------------------------|
| 4 | 0 | 0 | 5.225 | 5.2230 | 68 |
| 2 | 2 | 2 | 4.899 | 4.8948 | 17 |
| 1 | 1 | 3 | 4.160 | 4.1648 | 35 |
| 1 | 5 | 1 | 3.948 | 3.9459 | 17 |
| 4 | 2 | 2 | 3.802 | 3.8006 | 97 |
| 4 | 4 | 0 | 3.716 | 3.7134 | 32 |
| 3 | 1 | 3 | 3.630 | 3.6279 | 6 |
| 3 | 5 | 1 | 3.482 | 3.4804 | 18 |
| 0 | 0 | 4 | 3.253 | 3.2542 | 13 |
| 0 | 6 | 2 | 3.095 | 3.0965 | 53 |
| 1 | 5 | 3 | 2.995 | 2.9955 | 12 |
| 5 | 1 | 3 | 2.977 | 2.9796 | 21 |
| 6 | 2 | 2 | 2.950 | 2.9484 | 9 |
| 1 | 7 | 1 | 2.904 | 2.9109 | 8 |
| 3 | 5 | 3 | 2.775 | 2.7760 | 6 |
| 2 | 4 | 4 | 2.677 | 2.6778 | 13 |
| 8 | 0 | 0 | 2.612 | 2.6115 | 99 |
| 4 | 4 | 4 | 2.448 | 2.4474 | 100 |
| 4 | 8 | 0 | 2.357 | 2.3564 | 17 |
| 3 | 3 | 5 | 2.306 | 2.3042 | 6 |
| 6 | 4 | 4 | 2.1676 | 2.1679 | 9 |
| 8 | 0 | 4 | 2.0367 | 2.0367 | 23 |
| 8 | 6 | 2 | 1.9968 | 1.9963 | 54 |
| 4 | 2 | 6 | 1.9683 | 1.9684 | 22 |
| 3 | 7 | 5 | 1.8981 | 1.8966 | 13 |
| 1 | 11 | 1 | 1.8925 | 1.8919 | 17 |
| 4 | 10 | 2 | 1.8748 | 1.8752 | 21 |
| 1 | 1 | 7 | 1.8442 | 1.8451 | 6 |
| 3 | 11 | 1 | 1.8326 | 1.8327 | 9 |
| 6 | 2 | 6 | 1.8147 | 1.8139 | 15 |
| 1 | 11 | 3 | 1.7489 | 1.7498 | 11 |
| 6 | 10 | 2 | 1.7403 | 1.7402 | 33 |
| 10 | 6 | 2 | 1.7308 | 1.7319 | 10 |
| 4 | 12 | 0 | 1.6682 | 1.6680 | 7 |
| 12 | 2 | 2 | 1.6608 | 1.6609 | 11 |
| 12 | 4 | 0 | 1.6536 | 1.6535 | 37 |
| 8 | 8 | 4 | 1.6136 | 1.6127 | 7 |
| 7 | 11 | 1 | 1.6018 | 1.6026 | 6 |
| 8 | 6 | 6 | 1.5077 | 1.5079 | 10 |
| 12 | 4 | 4 | 1.4740 | 1.4741 | 10 |

^a *Fddd*; ¹ *a* = 20.892 (3), *b* = 21.123 (3), *c* = 13.017 (2) Å.

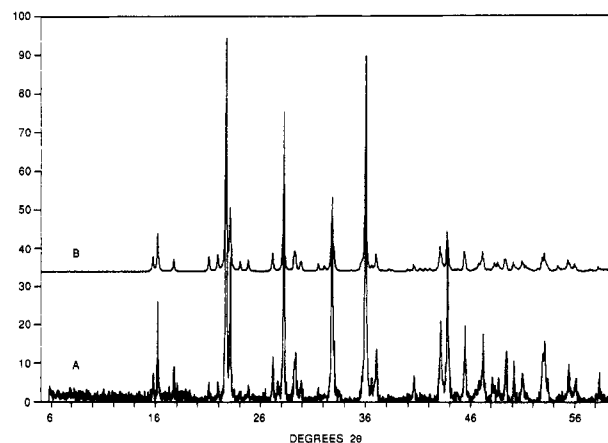


Figure 5. X-ray powder diffraction patterns: (A) observed pattern of BaIn_2S_4 platelets (Table VI) and (B) calculated pattern of BaIn_2S_4 .⁷

chains.^{7,16} In SrIn_2S_4 and BaIn_2S_4 , the large divalent metals occupy half of the eight-coordinate, distorted square antiprismatic sites, while the indium atoms are tetrahedrally coordinated.⁷ Each InS_4 tetrahedron shares one edge and two vertices with other InS_4 tetrahedra, forming a

Table VI. X-ray Powder Diffraction Data for BaIn₂S₄ Platelets^a

| <i>h</i> | <i>k</i> | <i>l</i> | <i>d</i> _{obs} , Å | <i>d</i> _{calc} , Å | <i>I</i> / <i>I</i> ₀ |
|----------|----------|----------|-----------------------------|------------------------------|----------------------------------|
| 0 | 2 | 2 | 5.608 | 5.6063 | 7 |
| 4 | 0 | 0 | 5.457 | 5.4520 | 29 |
| 2 | 2 | 2 | 4.989 | 4.9859 | 9 |
| 1 | 1 | 3 | 4.205 | 4.2023 | 5 |
| 1 | 5 | 1 | 4.041 | 4.0409 | 5 |
| 4 | 2 | 2 | 3.910 | 3.9086 | 100 |
| 4 | 4 | 0 | 3.843 | 3.8414 | 39 |
| 0 | 0 | 4 | 3.277 | 3.2766 | 12 |
| 0 | 6 | 2 | 3.162 | 3.1613 | 77 |
| 1 | 5 | 3 | 3.042 | 3.0456 | 13 |
| 1 | 7 | 1 | 2.985 | 2.9824 | 5 |
| 3 | 5 | 3 | 2.833 | 2.8326 | 4 |
| 8 | 0 | 0 | 2.726 | 2.7260 | 55 |
| 0 | 8 | 0 | 2.693 | 2.7067 | 4 |
| 4 | 4 | 4 | 2.493 | 2.4929 | 94 |
| 4 | 8 | 0 | 2.424 | 2.4244 | 14 |
| 6 | 4 | 4 | 2.220 | 2.2197 | 7 |
| 8 | 0 | 4 | 2.0960 | 2.0956 | 21 |
| 8 | 6 | 2 | 2.0646 | 2.0645 | 41 |
| 1 | 7 | 5 | 1.9927 | 1.9915 | 21 |
| 1 | 11 | 1 | 1.9390 | 1.9390 | 5 |
| 4 | 10 | 2 | 1.9236 | 1.9238 | 18 |
| 0 | 6 | 6 | 1.8683 | 1.8688 | 6 |
| 2 | 6 | 6 | 1.8426 | 1.8419 | 13 |
| 12 | 0 | 0 | 1.8172 | 1.87173 | 11 |
| 6 | 10 | 2 | 1.7898 | 1.7896 | 8 |
| 12 | 4 | 0 | 1.7232 | 1.7228 | 16 |
| 8 | 8 | 4 | 1.6565 | 1.6570 | 9 |
| 0 | 0 | 8 | 1.6376 | 1.6383 | 6 |
| 0 | 12 | 4 | 1.5803 | 1.5806 | 7 |
| 8 | 6 | 6 | 1.5407 | 1.5414 | 6 |
| 12 | 4 | 4 | 1.5242 | 1.5249 | 8 |

^a *Fddd*; *a* = 21.808 (3), *b* = 21.654 (4), *c* = 13.107 (2) Å.

covalently bonded two-dimensional net with the formula In₂S₄²⁻.

Crystals of BaIn₂S₄ formed as light yellow platelets up to 1 mm per side. The X-ray powder diffraction pattern of crushed platelets agreed well with that calculated by using the reported single-crystal structure data,⁷ as shown in Figure 5. The X-ray powder diffraction data, given in Table VI, were indexed by using an orthorhombic unit cell consistent with space group *Fddd* (*a* = 21.808 (3), *b* =

21.654 (4), and *c* = 13.107 (2) Å), in good agreement with the literature report.⁷ The stability of BaIn₂S₄ toward water, as required by the isolation of the crystals from the flux, is in contrast to an earlier report⁷ of its decomposition in moist air. Orthorhombic SrIn₂S₄ is reportedly⁶ isostructural with BaIn₂S₄, although, curiously, SrIn₂S₄ was obtained as whiskers while BaIn₂S₄ was obtained with the platelet morphology.

Conclusions

Yellow Ca_{3.3}In_{6.5}S₁₃ crystals obtained in the present study appear to be isostructural with Ca_{3.1}In_{6.6}S₁₃,⁵ Pb₃In_{6.67}S₁₃,¹¹ and Sn_{2.5}In₇S₁₃,¹² by detailed comparison of the observed and calculated X-ray powder diffraction patterns.

Bronze crystals of a new phase, Ca_{1.2}In_{1.9}S₄ ("Ca_{3.9}In_{6.2}S₁₃") were obtained. On the basis of the X-ray powder diffraction data, the structure of this phase is considerably different from that of the Ca_{3.3}In_{6.5}S₁₃-type series. A new monoclinic phase, Sr_{0.9}In_{2.1}S₄, was obtained as yellow whiskers. The X-ray powder diffraction data indicated that the structure of this compound is substantially different from that of known, orthorhombic SrIn₂S₄, which was also obtained in the form of golden-yellow whiskers.

Orthorhombic BaIn₂S₄ was obtained as light yellow platelets. This compound is isostructural with orthorhombic SrIn₂S₄, and the indexed X-ray powder diffraction data of both compounds are reported.

Further studies to assess the potential of these compounds as optical windows are in progress and will include quantitative transmission measurements on single crystals using an IR microscope.

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Registry No. Ca_{1.2}In_{1.9}S₄, 125390-58-1; Cr_{0.9}In_{2.1}S₄, 128302-16-9; Ca_{3.3}In_{6.5}S₁₃, 128302-17-0; SrIn₂S₄, 51404-22-9; BaIn₂S₄, 51403-86-2.

Synthesis of Metal Hydroxide-Layer Silicate Intercalation Compounds (Metal = Mg(II), Ca(II), Mn(II), Fe(II), Co(II), Ni(II), Zn(II), and Cd(II))

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Layer silicate intercalation compounds with metal(II) hydroxide (metal(II) = Mg, Ca, Mn, Fe, Co, Ni, Zn, and Cd) are prepared by adding a base into the metal salt solutions containing layer silicates with cation-exchange properties. The preparation procedures for the intercalates with manganese(II), iron(II), and cobalt(II) hydroxides are conducted under oxygen-free conditions. The hydroxides of these metal cations can crystallize with the cadmium iodide layer structure; the basic unit layer of these metal hydroxides is intercalated into the two-dimensional silicate interlayer region.

Introduction

We previously reported preparation of metal(II) hydroxide (metal = Fe, Co, Ni)-layer silicate (2:1 layer silicate) intercalation compounds in which a basic unit layer of the metal hydroxide alternates with a silicate layer, the

intercalated 3d transition elements forming a bidimensional lattice.¹⁻³

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