Materials with Layered Structures. III. The System $CoGa_2S_4$–$CoIn_2S_4$ and the Crystal Structure of $CoGaInS_4$

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The crystal structure of $CoGaInS_4$ has been determined from single crystal X-ray diffraction data and refined to $R = 0.03$. It crystallizes in the trigonal $FeGa_2S_4$ type (space group $P\bar{3}m1$, No. 164, $a = 3.759(1)$, $c = 12.184(2)$ Å, $Z = 1$) with the following cation distribution: $(Co_{0.61}In_{0.39}Ga)_t(Co_{0.39}In_{0.61})_oS_4$. The system $xCoGa_2S_4$–$(1 - x)CoIn_2S_4$ is quasibinary. The compound $CoGaInS_4$ has a large region of homogeneity with a marked dependence on temperature, ranging from $x = 0.2$ to $x = 0.8$ at 800°C. Compounds with high indium content show a phase transition to the $ZnIn_2S_4(IIIa)$ type at 1000°C. Electronic spectra have been recorded on samples with different composition and on samples quenched from different temperatures. © 1990 Academic Press, Inc.

Introduction

Recently Razzetti et al. (1) reported on a new layered compound $CoGaInS_4$ for which they proposed the space group $R3m$. We also obtained this compound independently (2) and found from X-ray powder diffraction data that $CoGaInS_4$ crystallizes in the $FeGa_2S_4$ type structure (space group $P\bar{3}m1$). Battistoni et al. (3, 4), who investigated $CoGaInS_4$ by X-ray photoelectron spectroscopy and magnetic measurements, reported a structure of the $ZnIn_2S_4(I)$ type (space group $P3m1$). From their XP spectra they obtained the result that Co^{2+} is distributed over the tetrahedral and octahedral sites of the lattice. Because of the contradictory findings regarding the crystal structure we started an investigation of the structure of $CoGaInS_4$ based on single-crystal X-ray data.

Since there is no information on the phase width of this compound we also in-

vestigated the whole system $CoGa_2S_4$–$CoIn_2S_4$ by X-ray phase analyses.

Experimental

For the investigation of the phase diagram, samples were prepared from the binary sulfides Ga_2S_3 (prepared by reaction of the elements at 1100°C), In_2S_3 (Fluka, Buchs, Switzerland), and prereacted "CoS," which is not single phase, in evacuated silica ampoules at 800°C. Three firing periods of 5 days each were necessary to reach equilibrium. After the last heating period the samples were quenched.

To determine the temperature dependence of the phase widths of the different compounds, the samples were also annealed at 1000°C for 3 days, at 600°C three times for 5 days, and at 500°C for 4 weeks.

The powder samples were investigated by X-ray powder methods with an Enraf–Nonius Guinier IV camera using $CuK\alpha_1$ ra-

diation. The photographs were calibrated internally with α-quartz (a = 4.9136, c = 5.4054 Å) and the unit cell dimensions refined by a least-squares procedure.

Single crystals of $CoGaInS_4$ were prepared by recrystallization of a powder sample with iodine as a mineralizer in a small evacuated silica ampoule at 800°C. After 5 days single crystals of plate-like habit with metallic luster were obtained from the reaction mixture.

For the determination of the crystal structure a small plate with dimensions $0.17 \times 0.17 \times 0.13$ mm³ was selected. X-ray precession photographs of this crystal 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 calculation of the crystal structure was performed with the structure determination package SDP via Fourier syntheses on the basis of space group $P\bar{3}m1$.

Intensity data were collected at room temperature on an Enraf-Nonius CAD4 diffractometer with graphite-monochromatized MoKα radiation in an $\omega - 2\theta$ scan. 899 independent reflections were measured up to θ_{max} = 50° and the intensities corrected for Lorentz and polarization effects. Absorption correction was done empirically by ψ-scans (absorption coefficient = 122.1 cm^{-1}).

Measurements of the diffuse reflectance were done with a Perkin–Elmer UV-VIS-NIR spectrophotometer Lambda 9 in the wavelength range 2800–280 nm (resolution of 2 nm). The spectra were evaluated according to the Kubelka-Munk function.

Results

1. Structure of CoGaInS$_4$

On the basis of space group $P\bar{3}m1$ the least-squares refinement of the fractional coordinates, the anisotropic thermal pa-

TABLE I

ATOMIC COORDINATES AND THERMAL PARAMETERS u_{ij} OF $CoGaInS_4$; SPACE GROUP $P\bar{3}m1$ (No. 164)

Atom		x	y	z	u_{11} (pm²)	u_{33} (pm²)
O	1b	0	0	0.5000	125(2)	191(3)
T	2d	$\frac{1}{3}$	$\frac{2}{3}$	0.1995(1)	130(1)	177(2)
S1	2d	$\frac{1}{3}$	$\frac{2}{3}$	0.3896(1)	151(3)	133(5)
S2	2d	$\frac{1}{3}$	$\frac{2}{3}$	0.8720(2)	194(4)	182(6)

Note. $u_{11} = u_{22} = 2u_{12}$, $u_{13} = u_{23} = 0$. O: octahedral site, 0.612 In + 0.388 Co. T: tetrahedral site, $\frac{1}{2}$ Ga + 0.388/2 In + 0.612/2 Co.

rameters, and the site occupation factors converged at R = 0.03 (R_w = 0.036) for 652 independent reflections with $I \geq 2\sigma_I$. Final positions and thermal parameters are listed in Table I. Interatomic distances and principal angles are given in Table II.

We were also able to refine the crystal structure in space group $P3m1$ with a final R = 0.051. But this led to fractional coordinates and thermal parameters suggesting a structure with a center of symmetry.

The structure of $CoGaInS_4$ (see Fig. 1) is a typical layer structure. It can be described as being built up from a hexagonal close-packed array of sulfur atoms in which the cations occupy the tetrahedral and octahedral voids. Due to the cation distribution

TABLE II

INTERATOMIC DISTANCES AND PRINCIPAL ANGLES FOR $CoGaInS_4$

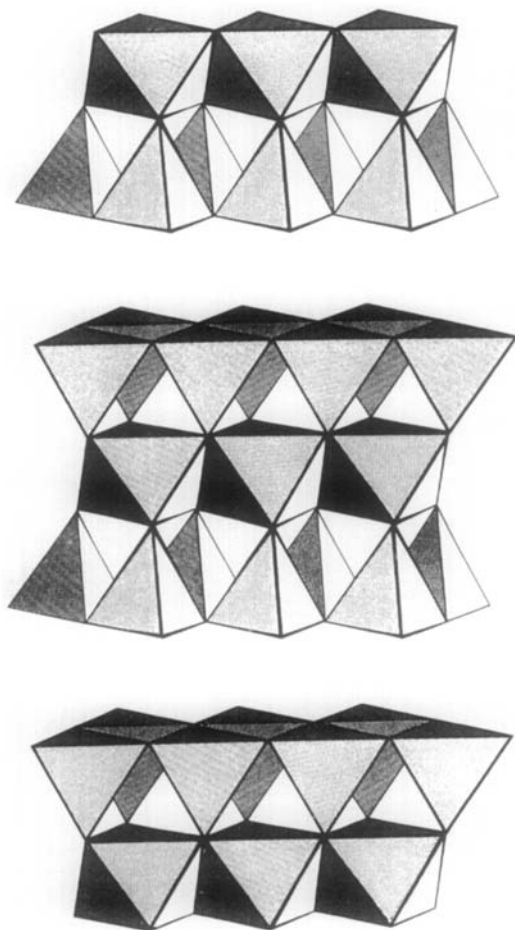| Interatomic distances (pm)		Principal angles (°)	
O–S1	255.0(1)	S1–O–S1	94.78(3)
T–S1	231.4(2)	S1–O–S1	85.22(3)
T–S2	233.6(1)	S1–T–S2	111.88(4)
S1–S1	375.1(1)	S2–T–S2	106.95(4)
S1–S1	345.3(3)		
S1–S2	385.2(3)		
S2–S2	375.4(1)		

FIG. 1. Structure of CoGaInS$_4$ symbolized by the anion polyhedron stacking.

packs of 4 anion layers each are formed, and separated from each other by a van der Waals gap. These packs are built from a sheet of edge-sharing octahedra which are connected on both sides to two sheets of corner-sharing tetrahedra by common corners. Best agreement between experimental and calculated intensities is obtained with the following cation distribution: the octahedral site is statistically occupied by 0.612 In + 0.388 Co while 1 Ga + 0.388 In + 0.612 Co are distributed over the two tetrahedral sites.

2. The System CoGa$_2$S$_4$–CoIn$_2$S$_4$

Samples in the system xCoGa$_2$S$_4$–$(1 - x)$CoIn$_2$S$_4$ were prepared in steps of 10 mole %. The lattice constants of the layered phases are listed in Table III. The cell parameters of the thiogallate CoGa$_2$S$_4$ and the spinel CoIn$_2$S$_4$ show no variation with the composition of the samples within the accuracy of measurement, leading to the conclusion that both parent compounds do not show any detectable phase width in this system.

The compound CoGaInS$_4$, on the other hand, has a relatively large region of homogeneity ranging from $x = 0.2$ to $x = 0.8$ at 800°C. As can be seen from Fig. 2 the phase width of CoGaInS$_4$ shows a marked dependence on temperature. It decreases with decreasing temperature so that at 600°C the compositions of the border phases are CoGa$_{1.5}$In$_{0.5}$S$_4$ and CoGa$_{0.9}$In$_{1.1}$S$_4$. At 1000°C again there is a slight decrease in phase width. This is due to a phase transition of the mixed crystals to a structure of the ZnIn$_2$S$_4$(IIIa) type.

The observed phase transition is reversible. The transition temperature increases

TABLE III

LATTICE CONSTANTS OF THE MIXED CRYSTALS CoGa$_{2x}$In$_{2-2x}$S$_4$ QUENCHED FROM 800 AND 1000°C

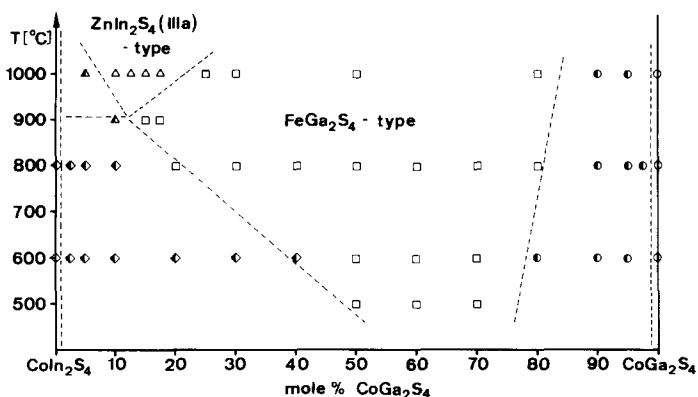|	800°C		1000°C	
x	a (Å)	c (Å)	a (Å)	c (Å)
0.8	3.700(1)	12.106(3)	3.697(1)	12.110(5)
0.7	3.720(1)	12.133(3)		
0.6	3.741(1)	12.167(3)		
0.5	3.759(1)	12.184(2)	3.749(1)	12.177(3)
0.4	3.778(1)	12.220(1)		
0.3	3.796(1)	12.247(3)	3.795(1)	12.247(9)
0.25	3.799(1)	12.251(3)	3.798(1)	36.777(16)[a]
0.2	3.814(1)	12.282(4)	3.810(1)	36.826(8)
0.15	—	—	3.817(1)	36.866(8)
0.1	—	—	3.827(1)	36.929(5)

[a] Sample quenched from 1020°C.

FIG. 2. Phase diagram of the system $CoGa_2S_4$–$CoIn_2S_4$.

with increasing gallium content of the samples. At 1000°C only samples with $x = 0.1$ to $x = 0.2$ crystallize in the $ZnIn_2S_4$(IIIa) type while $CoGa_{0.5}In_{1.5}S_4$ already shows the $FeGa_2S_4$-type structure. For this latter composition the transition temperature is near 1000°C. By raising the firing temperature by only 20°C a sample with $ZnIn_2S_4$(IIIa)-type structure is formed. At 900°C we could not obtain any pure sample with $ZnIn_2S_4$(IIIa) structure. At this temperature the compound $CoGa_{0.3}In_{1.7}S_4$ crystallizes in the $FeGa_2S_4$ type and the samples with $x \leq 0.125$ are two-phase, containing $ZnIn_2S_4$ (IIIa)-type mixed crystals alongside with a spinel phase. That is, the phase width of the $ZnIn_2S_4$(IIIa) type is only very small at 900°C.

3. Optical Properties of the Layered Compounds

Measurements of the diffuse reflectance spectra were carried out on samples with $x = 0.3$ to $x = 0.7$ prepared at 800°C and in the case of the composition $CoGaInS_4$ on samples quenched from 600, 800, and 1000°C. The spectra of the quenched samples are shown in Fig. 3. They are dominated by absorption bands arising from Co^{2+} in tetrahedral coordination. The energies of the absorption bands are in good

agreement with those found by Borghesi *et al.* (*5*) in the case of Co^{2+}-doped $ZnIn_2S_4$. Neither the ratio Ga/In nor the temperature of preparation affect the energies of the
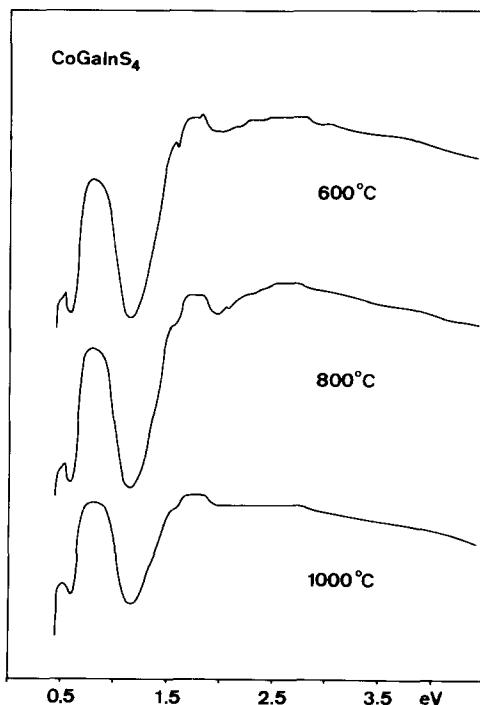

FIG. 3. Diffuse reflectance spectra (evaluated according to Kubelka-Munk) of samples of $CoGaInS_4$ quenched from 600, 800, and 1000°C.

transitions. There is only a slight decrease in intensity of the bands observed in the spectra of the samples quenched from higher temperatures.

An influence of Co^{2+} occupying octahedral sites on the spectra cannot be observed presumably because of the much lower extinction coefficient of the corresponding bands.

Information on the optical band gap of the samples cannot be drawn from the spectra since the corresponding absorption band overlaps with the band at 1.7 eV of the d-electron spectrum of Co^{2+}. So an influence of composition on the band gap cannot be observed.

Discussion

In accord with our results obtained by powder diffraction studies (2) the structure of CoGaInS₄ is of the FeGa₂S₄ type. There is no evidence that the occupation of the two tetrahedral sites is different as one would expect if the structure were of the ZnIn₂S₄(I) type as claimed by Battistoni *et al.* (3, 4).

According to the cation distribution there is a difference to our former results (2) and also to the results of Battistoni *et al.* (4) who found from XP-spectra that nearly two-thirds of Co^{2+} occupy octahedral sites. The site occupation factors given in this paper show that the octahedral site is occupied statistically by 0.39 Co^{2+} + 0.61 In^{3+}, while the remaining cobalt and indium atoms are filling the tetrahedral voids together with Ga^{3+}. While the discrepancy to the findings of our previous paper (2) certainly are due to texture effects in our powder diffraction data, we have no exact explanation for the differing results of Battistoni *et al.* (4). One reason for these findings could be a temperature dependence of the cation distribution. But since such alterations should lead to a temperature dependence of the lattice constants and the intensities in the powder patterns of samples quenched from different temperatures, that we could not observe, we do not think this to be the true reason.

To our knowledge the observed phase transition from a FeGa₂S₄-type to a ZnIn₂S₄(IIIa)-type structure has not yet been described in the literature. These two structures are known to be polytypes (6) differing only in the stacking sequence of the sulfur layers. While in the FeGa₂S₄ structure there is a hexagonal packing, the sulfur atoms show a mixed *hcp* and *ccp* arrangement in the ZnIn₂S₄(IIIa) structure.

Acknowledgments

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