Structural Studies in the Systems $CoS-Cr_2S_3-Ga_2S_3$ and $MGa_2S_4-MCr_2S_4$ (M = Zn, Cd, Hg)

H. HAEUSELER AND W. KWARTENG-ACHEAMPONG

Laboratorium für Anorganische Chemie, Universität Siegen, Postfach 101240, Siegen D-5900, Federal Republic of Germany

The quasibinary systems $MGa_2S_4-MCr_2S_4$ are studied for M = Zn, Cd, and Hg by X-ray investigations on powdered samples. The end members of these series show no detectable phase width. The formation of quaternary compounds is not observed. A new sulfide $CoGa_{1.5}Cr_{0.5}S_4$ is obtained in the system $CoGa_2S_4-CoCr_2S_4$ and characterized by X-ray and IR studies. $CoGa_{1.5}Cr_{0.5}S_4$ is isomorphous with α-$FeGa_2S_4$ and crystallizes trigonally (space group $P\bar{3}m1$) with a = 363.7(1) and c = 1200.7(1) pm. A study of the extension of the phase fields for this compound and the spinel $CoCr_2S_4$ in the system $CoGa_2S_4-CoCr_2S_4-Cr_2S_3-Ga_2S_3$ is also undertaken.   © 1988 Academic Press, Inc.

Introduction

Layer-type materials and compounds which crystallize in one of the polytypes of $ZnIn_2S_4$ have attracted interest because of their interesting physical properties such as photoluminescence (*1, 2*), photoconduction (*3*), and semiconduction (*4, 5*). Until now only relatively few examples of this structure were known, but we recently found that some quaternary compounds, CoGa InS$_4$ (*6*), MnGaInS$_4$, MnIn$_2$S$_2$Se$_2$ (*7*), and CdIn$_2$S$_2$Se$_2$ (*8*), also crystallize in the $ZnIn_2S_4$-type structures.

All of these new examples of this structure type were obtained from their quasibinary systems where one of the ternary border phases crystallizes with the spinel and the other one with the thiogallate structure.

In the search for additional compounds with lamellar-type structures isomorphous with one of the polytypes of $ZnIn_2S_4$, we followed the hypothesis that starting, for in-stance, from a thiogallate one could obtain such compounds by enhancing the octahedral site preference of the cations. We therefore made solid-state powder studies of the quaternary systems $MGa_2S_4-MCr_2S_4$ (M = Co, Zn, Cd, Hg) where the MGa_2S_4 are all thiogallates and the MCr_2S_4 spinels.

Experimental

Samples of $xMCr_2S_4-(1 - x)MGa_2S_4$ were prepared by introducing stoichiometric mixtures of their powered binary sulfides into silica ampoules. These were subsequently evacuated and tempered at 800°C in cylindrical, horizontal electric ovens for 10 days and oven cooled to room temperature. The products in the ampoules were homogenized and annealed for a second time. The ampoules were then quenched in ice water. The second heat treatment was at different temperatures depending on the type of system.

324

TABLE I

LATTICE CONSTANTS FOR THE SYSTEM
$xMCr_2S_4-(1 - x)MGa_2S_4$ (M = Zn, Cd, Hg)

| M | x | Thiogallate phase | | Spinel phase |
		a (pm)	c (pm)	a (pm)
Zn	1.00	—	—	998.6(1)
	0.75	530.6(9)	1038.4(9)	999.0(1)
	0.25	529.1(2)	1039.3(9)	999.0(1)
	0.00	529.1(2)	1038.3(8)	—
Cd	1.00	—	—	1024.3(1)
	0.75	555.4(2)	1016.4(5)	1024.7(1)
	0.25	555.2(1)	1016.3(2)	1024.9(1)
	0.00	555.1(1)	1015.7(2)	—
Hg	1.00	—	—	1023.9(1)
	0.75	551.4(1)	1023.7(7)	1023.5(1)
	0.25	551.5(1)	1024.4(1)	1023.1(1)
	0.00	551.4(2)	1024.4(7)	—

Structural studies of the powdered products were made by X-ray investigations with $CrK\alpha1$ and $CuK\alpha1$ radiation. The lattice constants were computed from Guinier radiographs using α-SiO_2 (a = 491.36, c = 540.54 pm) as internal standard and refined by the program LSUCR.

Determination of the relative intensities of the reflections were carried out with both a Huber Guinier powder goniometer with a counter tube attachment and densitometric measurements of the Guinier photographs. The relative intensities of the maxima were calculated from the product of peak height and half-width.

FIR-spectra were obtained using the Fourier spectrophotometer Bruker IFS 114V. The samples were mulled in Nujol and the spectra were recorded with a resolution of 4 cm^{-1}.

Results

1. The Systems MCr_2S_4–MGa_2S_4 (M = Zn, Cd, Hg)

In the system $xMCr_2S_4-(1 - x)MGa_2S_4$ for M = Zn, Cd, and Hg samples were prepared for x = (0.00, 0.25, 0.5, 0.75, 1.00) at 800°C. X-Ray powder diffraction patterns for the quaternary compositions showed the simultaneous existence of only two phases, the spinel and thiogallate phases.

The lattice constants for the different compositions and phases are tabulated in Table I. These were determined using the space groups $I\bar{4}$ and $Fd\bar{3}m$ for the thiogallate and spinel phases, respectively.

The cell parameters of the thiogallates remain constant within the accuracy of measurement thus showing that no chromium can be incorporated into the thiogallate structure. The variation of the lattice constants of the spinels are also not significant. One can therefore conclude that the spinels have nearly no phase width in these systems.

2. The System CoS–Cr_2S_3–Ga_2S_3

The ternary edges CoS–Ga_2S_3 and CoS–Cr_2S_3 have already been studied. In the system CoS–Cr_2S_3 there is the ternary phase $CoCr_2S_4$ crystallizing as a normal spinel with the space group $Fd\bar{3}m$ and a = 992.3 pm (9) whereas the compound $CoGa_2S_4$ in the system CoS–Ga_2S_3 is a thiogallate crystallizing in the space group $I\bar{4}$ with the lattice constants a = 524.3 and c = 1041.6 pm (10).

2.1. $xGa_2S_3-(1 - x)Cr_2S_3$. Our experiments in the border system Ga_2S_3–Cr_2S_3, with samples quenched from 600, 700, and 800°C after 15 days, show in agreement with (11, 12), in addition to the existence of the two binary edges, two ternary phases, one gallium rich phase which has a layered structure, and the spinel $Ga_{2/3}Cr_2S_4$ at x = 0.25.

But, contrary to Gastaldi et al. (12), who found homogeneous mixed crystals with $FeGa_2S_4$ structure in the range 0.625 ≤ x ≤ 0.675, we could not detect any phase width. The lattice constants for different compositions remain constant within experimental accuracy at a = 360.5(1) and c = 1194.7(1) pm. The samples always contain traces of the spinel $Ga_{2/3}Cr_2S_4$ for x < 0.66 or Ga_2S_3 for x > 0.66.
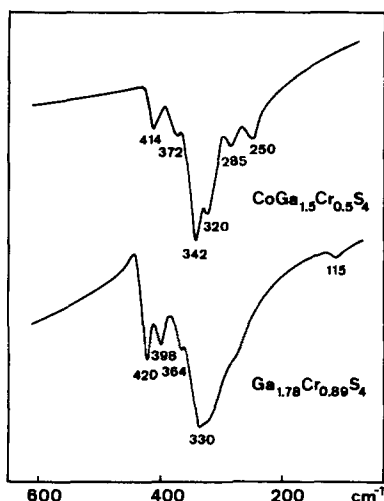
FIG. 1. FIR spectra of the $FeGa_2S_4$-type compounds $CoGa_{1.5}Cr_{0.5}S_4$ and $Ga_{1.78}Cr_{0.89}S_4$.

There is also a significant difference in the lattice constants: while the a values are in good agreement we find a much smaller c parameter than Gastaldi *et al*. This is caused according to our opinion by the different preparation conditions. The samples prepared by Gastaldi *et al*. could have lost some sulfur and consequently could contain a corresponding amount of Cr^{2+}. This should result accordingly to an expansion in the c axis, as Cr^{2+} has a larger ionic radius than Cr^{3+}.

Contrary to group theoretical calculations (*13*), which predict the existence of six infrared active vibrations for samples crystallizing in the $FeGa_2S_4$ structure, the infrared spectrum of $Ga_{1.78}Cr_{0.89}S_4$ (see Fig. 1) mainly consists of three absorption bands. This is probably due to the destruction of the local symmetry by the occurrence of vacancies on the octahedral as well as the tetrahedral sites. This effect is especially pronounced on the band at 330 cm^{-1} which is very broad and probably consists of more than one component.

2.2. The section $CoGa_2S_4$–$CoCr_2S_4$. In the system $xCoGa_2S_4$–$(1 - x)CoCr_2S_4$ there

exists in addition to mixed crystals with spinel and thiogallate structure a new phase with the composition $CoGa_{1.5}Cr_{0.5}S_4$. This new compound could be indexed trigonally with $a = 363.7(1)$ and $c = 1200.7(1)$ pm (see Table II). The lattice constants as well as the intensities of the reflections in the powder pattern show great similarity

TABLE II

GUINIER PATTERN OF $CoGa_{1.5}Cr_{0.5}S_4$

hkl	θ	d (Å) (calc)	d (Å) (obs)	I/I_0 (obs)	I/I_0 (calc)
001	3.68	12.00	12.00	13	25
002	7.38	6.00	6.00	7	13
003	11.11	4.00	4.00	44	64
100	14.17	3.148	3.150	31	24
101	14.66	3.044	3.047	100	100
004	14.88	2.999	—	—	0
102	16.04	2.787	2.789	98	77
103	18.15	2.473	2.475	19	16
005	18.73	2.399	—	—	5
104	20.78	2.171	2.173	45	50
006	22.66	1.999	—	—	0
105	23.81	1.908	1.909	36	37
110	25.08	1.817	1.818	97	78
111	25.39	1.797	—	—	1
112	26.29	1.739	1.742	—	2
007	26.71	1.714	—	—	3
016	27.16	1.688	1.686	36	50
113	27.75	1.654	1.656	42	32
200	29.30	1.574	1.575	—	3
021	29.58	1.560	1.562	18	15
114	29.71	1.554	—	—	0
022	30.40	1.522	1.535	29	13
107	30.78	1.505	—	—	0
008	30.91	1.500	—	—	1
203	31.74	1.464	1.466	—	1
115	32.12	1.449	1.450	—	4
024	33.56	1.394	1.395	19	14
108	34.68	1.354	—	—	4
116	34.95	1.345	—	—	0
009	35.30	1.333	—	—	0
025	35.83	1.316	1.317	19	13
117	38.16	1.247	—	—	4
206	38.53	1.237	1.237	23	23
109	38.87	1.227	1.225	—	1
0010	39.95	1.200	—	—	3
210	40.35	1.190	—	—	4
211	40.59	1.184	1.181	32	15
212	41.31	1.167	1.165	50	15
207	41.65	1.159	—	—	0
118	41.76	1.157	—	—	5
213	42.50	1.140	—	—	4
1010	43.40	1.121	—	—	1
214	44.15	1.105	1.104	20	20
0011	44.93	1.091	—	—	3

Note. In order to lower the effects of texture the observed intensities were measured after mixing the sample with fine glass particles.
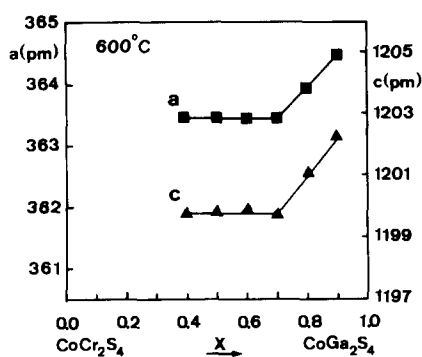
FIG. 2. A plot of variation of lattice constants a and c as a function of composition x for the system $x\text{CoGa}_2\text{S}_4$–$(1 - x)\text{CoCr}_2\text{S}_4$ from samples quenched from 600°C.

with those of CoGaInS_4 which crystallizes in the layer-type structure of FeGa_2S_4.

This is supported by calculations of the relative intensities of the powder pattern by LAZY PULVERIX (14), for which we assumed the following cation distribution: $(\text{Co}_{0.5}\text{Ga}_{1.5})_t(\text{Co}_{0.5}\text{Cr}_{0.5})_o\text{S}_4$ and the fractional coordinates obtained for FeGa_2S_4 by Dogguy-Smiri et al. (15). The differences in the two sets of obtained intensities are probably due to texture effects (see Table II).

X-ray patterns taken with a high-temperature camera showed no phase transition from 100 to 800°C. There was only a slight increase in the lattice constants as expected. Samples also quenched from 600, 800, and 1000°C did not show otherwise.

$\text{CoGa}_{1.5}\text{Cr}_{0.5}\text{S}_4$ shows a region of homogeneity in the range $0.7 \leq x < 0.9$ in which the variation of the lattice constants for the layered structure obeys Vegard's law as shown in Fig. 2. Mixed crystals with the spinel structure are obtained for $0 \leq x \leq 0.1$ whereby the lattice constant slightly decreases from $a = 992.3(1)$ to $991.8(1)$ pm. Mixed crystals with the thiogallate structure containing Cr^{3+} could not be observed. The lattice constants of the thiogallate phase remain constant within the accuracy in measurement.

The infrared spectrum of $\text{CoGa}_{1.5}\text{Cr}_{0.5}\text{S}_4$ is shown in Fig. 1. The number of observed bands is in agreement with that predicted by group theory (15).

2.3. The section CoCr_2S_4–$\text{Ga}_{2/3}\text{Cr}_2\text{S}_4$. Both end members of this section crystallize in the spinel structure. There exists therefore as expected a series of solid solutions with spinel structure with lattice constants increasing from $a = 988.7(1)$ for the $\text{Ga}_{2/3}\text{Cr}_2\text{S}_4$ to $992.3(1)$ pm for CoCr_2S_4. The lattice constants are tabulated in Table III. The dimension of the spinel phase field as obtained from our investigations is shown in Fig. 4.

2.4. The section $\text{Ga}_{5/3}\text{CrS}_4$–$\text{CoGa}_2\text{S}_4$. Samples of the general composition $\text{Co}_x\text{Ga}_{(5+x)/3}\text{Cr}_{1-x}\text{S}_4$ with $x = 0.25$ and 0.5 quenched after 35 days of tempering at 800°C showed the existence of layered mixed crystals of FeGa_2S_4 type. The observed lattice parameters are tabulated in Table IV. X-ray photographs for $x = 0.75$ showed some traces of CoGa_2S_4 apart from the layered structure. The range of homogeneity for the FeGa_2S_4-type structure in this section is estimated to be $0.25 \leq x < 0.75$.

2.5. The section $\text{CoGa}_{1.5}\text{Cr}_{0.5}\text{S}_4$–$\text{Ga}_{5/3}\text{CrS}_4$. The system $x\text{CoGa}_{1.5}\text{Cr}_{0.5}\text{S}_4$–$(1 - x)\text{Ga}_{5/3}\text{CrS}_4$ is not quasibinary. This again confirms our findings that $\text{Ga}_{5/3}\text{CrS}_4$ does not correspond to a single-phase compound

TABLE III

LATTICE CONSTANTS FOR
THE MIXED CRYSTALS
WITH SPINEL STRUCTURE
IN THE SYSTEM
$x\text{CoCr}_2\text{S}_4$–
$(1 - x)\text{Ga}_{2/3}\text{Cr}_2\text{S}_4$

x	a (pm)
1.00	992.3(1)
0.75	991.6(1)
0.50	990.1(1)
0.25	989.2(1)
0.00	988.7(1)

TABLE IV

LATTICE CONSTANTS FOR THE SYSTEM
$x\text{CoGa}_2\text{S}_4-(1-x)\text{Ga}_{5/3}\text{CrS}_4$

x	Space group	a (pm)	c (pm)
1.00	$I\bar{4}$	524.3(1)	1041.6(2)
0.75[a]	$P\bar{3}m1$	363.4(1)	1200.9(2)
0.50	$P\bar{3}m1$	362.5(1)	1199.0(3)
0.25	$P\bar{3}m1$	361.3(1)	1196.2(3)
0.00[b]	$P\bar{3}m1$	360.5(1)	1194.8(1)

Note. Samples were quenched after 35 days at 800°C.

[a] Sample contains traces of CoGa_2S_4.

[b] Lattice constants were obtained from samples tempered at 800°C for 5 days.

FIG. 4. Phase diagram of the system $\text{CoGa}_2\text{S}_4-\text{CoCr}_2\text{S}_4-\text{Cr}_2\text{S}_3-\text{Ga}_2\text{S}_3$ showing the different sections investigated in this work and the extension of the phase fields for (I)spinel- and (II)FeGa$_2$S$_4$-type mixed crystals.

with FeGa$_2$S$_4$ structure. For $0.6 \leq x \leq 1$ we obtain single-phase samples with the lamellar structure of FeGa$_2$S$_4$ type. X-ray photographs for $x < 0.6$ show the presence of traces of a second phase which crystallizes in the spinel structure. As it is shown in Fig. 3 the lattice constants of the single-phase solid solutions obey Vegard's law.

The cell parameters obtained from the two-phase samples ($0.0 \leq x < 0.6$) nearly fit
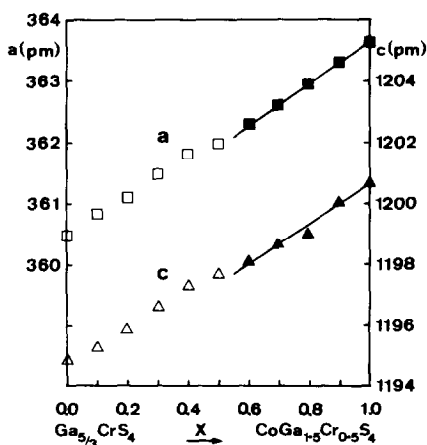

FIG. 3. A plot of variation of lattice constants a and c as a function of composition x for the trigonally layered solid solutions in the system $x\text{CoGa}_{1.5}\text{Cr}_{0.5}\text{S}_4-(1-x)\text{Ga}_{5/3}\text{CrS}_4$. ■ and ▲, single-phase samples; □ and △, two-phase samples.
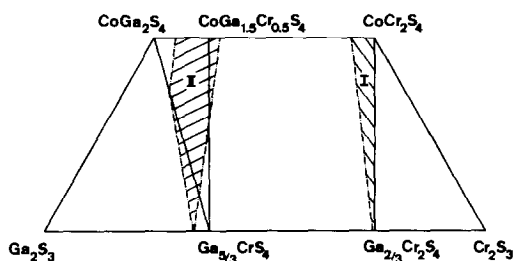
the Vegard's plot for $x = 0.6$ to 1 thus showing that the deviation from stoichiometry is not very large. The a and the c parameters increase with increasing cobalt content, i.e., they increase when more and more of the vacancies existing on the tetrahedral and octahedral sites of $\text{Ga}_{1.78}\text{Cr}_{0.89}\text{S}_4$ are filled. While for the end members of this series $(\text{Ga}_{1.78}\square_{0.22})_t(\text{Cr}_{0.89}\square_{0.11})_o\text{S}_4$ and $(\text{Co}_{0.5}\text{Ga}_{1.5})_t(\text{Co}_{0.5}\text{Cr}_{0.5})_o\text{S}_4$ the cation distribution seems to be clear, the question of whether, especially in the cobalt-poor mixed crystals, Co^{2+} prefers octahedral or tetrahedral voids, i.e., which of the vacancies are first filled, is not solved. From the results given under sections 2.1, 2.2, 2.4, and 2.5 the extension of the field where solid solutions crystallizing in the FeGa$_2$S$_4$ structure are formed can be estimated. This is shown in Fig. 4.

Discussion

Regarding the coordination numbers of the cations in different AB_2X_4 structures, the layered structures of FeGa$_2$S$_4$ or ZnIn$_2$S$_4$-type are intermediate between the spinels and thiogallates (*16*). While in the thiogallates all cations are tetrahedrally coordinated, the coordination numbers in spinels are 2×6 and 1×4 and in the layered structures 1×6 and 2×4. From this point of view one could expect the formation of

new compounds with layered structures if one could change the preference of the cations for a particular coordination. This can be done for instance by replacing the sulfur in a spinel AIn_2S_4 successively by selenium, thus intensifying the tetrahedral site preference of indium (7, 8) or by substituting a cation with a higher tetrahedral site preference for a cation with a lower one (6, 7, 17).

In this paper we tried according to this concept to prepare new compounds with the lamellar structure of $ZnIn_2S_4$ or Fe Ga_2S_4 type by replacing in the thiogallates MGa_2S_4 gallium by chromium which has a strong preference for octahedral coordination. However, while this was successful in the case of $M = Co^{2+}$ our attempts were not crowned with success for $M = Zn^{2+}$, Cd^{2+}, and Hg^{2+}. One reason for this finding may be due to the different ionic radii (18): while the radius of Co^{2+} is comparable in tetrahedral coordination to that of Ga^{3+} and in octahedral coordination to Cr^{3+} the radii of Zn^{2+}, Cd^{2+}, and Hg^{2+} are larger in both cases. But this cannot be the only reason since in the case of $M = Mn^{2+}$ (19), which has an ionic radius of 0.725 compared to 0.59 Å for Co^{2+} in tetrahedral coordination, the formation of a quaternary compound with layered structure is observed. A further condition for the formation of solid solutions of the type $MGa_{2-x}Cr_xX_4$ which crystallize in the $ZnIn_2S_4$ or $FeGa_2S_4$ structure is that the preference of the bivalent metal ion for tetrahedral coordination should not be too pronounced, so that it is able to occupy tetrahedral as well as octahedral voids. And in fact in all examples of this type known until now (19, 20) part of the bivalent metal ion must occupy octahedral sites. There is no example of a layered-type compound with the composition $MGaCrX_4$ with all the M^{2+} in tetrahedral coordination.

References

1. D. CRANDLES AND E. FORTIN, Phys. Status Solidi A 95, K47 (1986).
2. T. IRIE, S. ENDO, H. KUROGANE, H. NAKANISHI, AND T. TOYODA, Japan. J. Appl. Phys. 25, 922 (1986).
3. L. TARRICONE AND L. ZANOTTI, Mater. Chem. Phys. 11, 161 (1984).
4. A. ANAGNOSTOPOULOS, K. KAMBAS, AND J. SPYRIDELIS, Mater. Res. Bull. 21, 407 (1986).
5. K. KAMBAS, A. ANAGNOSTOPOULOS, B. FLOSS, AND J. SPYRIDELIS, Phys. Status Solidi A 95, K139 (1986).
6. H. HAEUSELER, Mater. Res. Bull. 21, 709 (1986).
7. H. HAEUSELER, Naturwissenschaften 73, 264 (1986).
8. H. HAEUSELER, J. Solid State Chem. 29, 121 (1979).
9. P. M. RACCAH, R. J. BOUCHARD, AND A. WOLD, J. Appl. Phys. 37, 1436 (1966).
10. M. P. PARDO, Mater. Res. Bull. 17, 1477 (1982).
11. D. BRASEN, J. M. VANDENBERG, M. ROBBINS, R. H. WILLENS, W. A. REED, R. C. SHERWOOD, AND X. J. PINDER, J. Solid State Chem. 13, 298 (1975).
12. L. GASTALDI, S. VITICOLI, M. GUITTARD, A. TOMAS, M. WINTENBERGER, AND J. FLAHAUT, Mater. Res. Bull. 20, 1483 (1985).
13. H. D. LUTZ, W. BUCHMEIER, AND H. SIWERT, Z. Anorg. Allg. Chem. 533, 118 (1986).
14. K. YVON, W. JEITSCHKO, AND E. PARTHÉ, J. Appl. Crystallogr. 10, 73 (1977).
15. L. DOGGUY-SMIRI, NGUYEN-HUY DUNG, AND M. P. PARDO, Mater. Res. Bull. 15, 861 (1980).
16. C. RAZZETTI, P. P. LOTTICI, AND L. ZANOTTI, Mater. Chem. Phys. 11, 65 (1984).
17. W. A. SHAND, Phys. Status Solidi A 3, K77 (1970).
18. R. D. SHANNON, in "Structure and Bonding in Crystals" (M. O'Keefe and A. Novrotsky, Eds.), Vol. 2, p. 52, Academic Press, New York (1981).
19. H. HAEUSELER AND W. KWARTENG-ACHEAMPONG, unpublished results.
20. H. SIWERT AND H. D. LUTZ, J. Solid State Chem. 69, 215 (1987).