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Phase relationships in the systems MGa_2S_4–MSc_2S_4 (M ≡ Co, Zn, Cd)

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Abstract

The systems $CoGa_{2-x}Sc_xS_4$, $ZnGa_{2-x}Sc_xS_4$ and $CdGa_{2-x}Sc_xS_4$ were investigated by X-ray powder methods on polycrystalline samples quenched at 800 and 1000 °C. Three new compounds were obtained: $CoGa_{1.8}Sc_{0.2}S_4$ ($a = 366.1$ pm, $c = 1208.4$ pm) and $ZnGaScS_4$ ($a = 373.3$ pm, $c = 1222.8$ pm), both crystallizing in an $FeGa_2S_4$-type structure, and a spinel-type $CoGa_{0.2}Sc_{1.8}S_4$ ($a = 1043.3$ pm). Formation of a quaternary compound could not be obtained in the cadmium system.

1. Introduction

In the search for new compounds with layered structures of the $ZnIn_2S_4$ or $FeGa_2S_4$ type, we have investigated, amongst others, systems of the type AGa_2S_4–AB_2S_4 with B ≡ Cr [1, 2], In [3, 4], V [5] and Ti [5]. In the case where element B is scandium, only one example is currently known [6] in which element A is manganese. According to the structure map [7] based on the St. John–Bloch parameters r_σ and r_π, which were calculated from the pseudopotential radii given by Zunger [8], we predict that new compounds with one of the polytypic structures of the $ZnIn_2S_4$ type should be formed in the systems $CoGa_2S_4$–$CoSc_2S_4$ and $CdGa_2S_4$–$CdSc_2S_4$, whereas in the corresponding zinc system the formation of a quaternary compound with a $ZnIn_2S_4$-type structure seems to be questionable. In order to check this prediction we began an investigation of these systems.

Of the end members of these systems the compounds $CoGa_2S_4$ [9, 10], $ZnGa_2S_4$ [11] and $CdGa_2S_4$ [11] crystallize in the thiogallate type while $ZnSc_2S_4$ and $CdSc_2S_4$ have been reported to be spinel-type compounds [12]. The compound $CoSc_2S_4$ is not known. From the position in the structure map one would predict a Cr_3S_4 structure if it exists at all.

2. Experimental details

For the investigation of the phase diagram, samples were prepared from the binary sulfides CoS, ZnS, CdS, Ga_2S_3 and Sc_2S_3 by sintering mixtures of

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appropriate stoichiometry in evacuated, sealed, silica ampoules at 800 and 1000 °C. After three firing periods lasting two weeks each, interrupted only to thoroughly grind the materials in an agate mortar and reseal, the samples were quenched.

The powder samples were investigated by X-ray powder methods using an Enraf–Nonius Guinier IV camera using Cu $K\alpha_1$ radiation. The photographs were calibrated internally with α-quartz ($a = 4.9136$ Å, $c = 5.4054$ Å) and the unit-cell dimensions refined by a least-squares procedure [13].

The infrared measurements were made with a Bruker Fourier spectrometer IFS 114v. The samples were mulled in nujol and recorded with a resolution of 4 cm^{-1}.

3. Results

3.1. The system $CoGa_2S_4$–$CoSc_2S_4$

In the system $CoGa_{2-x}Sc_xS_4$, the border compound $CoSc_2S_4$ is not described in the literature and we were unable to prepare a compound of this composition in the temperature interval investigated. However, substitution of a small amount of Sc^{3+} by Ga^{3+} leads to a sample which is single phase and, according to our powder diffraction measurements, crystallizes in the spinel type with $a = 1043.3$ pm for the composition $CoGa_{0.2}Sc_{1.8}S_4$. An IR-absorption spectrum of this compound which confirms the results of the X-ray analysis is shown in Fig. 1. This spinel-type compound is only metastable at ambient temperature. It could only be observed in the samples quenched at 1000

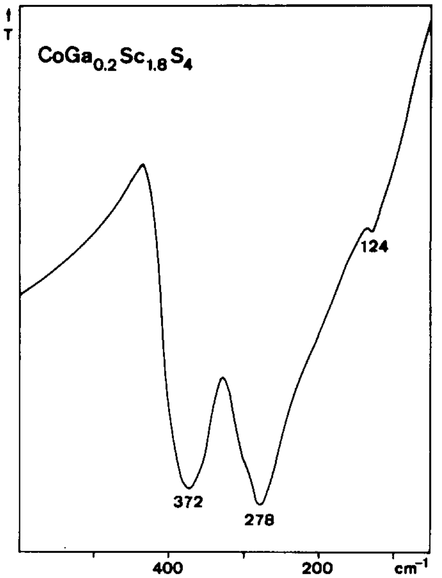

Fig. 1. IR-absorption spectrum of the spinel $CoGa_{0.2}Sc_{1.8}S_4$.

TABLE 1

Lattice constants of the $FeGa_2S_4$-type mixed crystals in the system $CoGa_{2-x}Sc_xS_4$

x	800 °C		1000 °C	
	a (pm)	c (pm)	a (pm)	c (pm)
0.2[a]	366.6(1)	1210.1(3)	366.1(1)	1208.4(1)
0.4	367.1(1)	1211.9(3)	367.4(1)	1212.4(3)
0.6	368.2(1)	1214.2(3)	369.0(1)	1215.3(2)
0.8[b]	368.9(1)	1215.6(2)	369.2(1)	1215.0(2)

[a] Not single phase at 800 °C.
[b] Not single phase at 800 and 1000 °C.

°C and decomposes at 800 °C to CoS and Sc_2S_3. At 1000 °C the spinel exhibits a small region of homogeneity: the sample with $x = 1.6$ is also single phase, with a slightly greater lattice constant ($a = 1043.8$ pm).

A second quaternary compound exists in this system: for $0.2 \leqslant x \leqslant 0.6$ (1000 °C) or $0.3 \leqslant x \leqslant 0.5$ (800 °C) the samples crystallize in the layered $FeGa_2S_4$-type structure [14]. The lattice constants of the different samples are given in Table 1.

In agreement with our knowledge on the site preference of Sc^{3+} a substitution of Ga^{3+} by Sc^{3+} in the thiogallate-type compound $CoGa_2S_4$ is not possible, as can be judged from the lattice constants of the thiogallate phases in the miscibility gap which remain constant at $a = 525.5$ pm and $c = 1042.6$ pm.

3.2. *The system $ZnGa_2S_4$–$ZnSc_2S_4$*

In the system $ZnGa_{2-x}Sc_xS_4$, we could obtain three different phases: the two border compounds $ZnGa_2S_4$ and $ZnSc_2S_4$ which according to their lattice parameters do not show any phase width, and a new compound crystallizing in the $FeGa_2S_4$-type phase as can be seen from the sequence and intensities of the scattering peaks in the X-ray powder diagrams. This $FeGa_2S_4$-type phase could not be prepared as a single phase at temperatures below 1000 °C.

In the samples quenched at 800 °C all three phases were always present, showing that the system is not quasibinary at this temperature. The composition of the new layered phase was not determined exactly, but we believe it to be a defective variant of the $FeGa_2S_4$ structure with vacancies in the tetrahedral as well as in the octahedral sites.

In the samples quenched at 1000 °C we only found two phase equilibria suggesting quasibinary behaviour of the system. The compound seems to exist only in a very small region of composition as we could only obtain monophase samples for the composition $ZnGa_{1.07}Sc_{0.93}S_4$. The sample $ZnGa_{1.1}Sc_{0.9}S_4$ already contained traces of the thiogallate, and $ZnGa_{1.05}Sc_{0.95}S_4$ already contained a small amount of the spinel. The lattice constants of the

TABLE 2

Lattice constants of the three phases obtained in the system $ZnGa_{2-x}Sc_xS_4$

Compound	System	Lattice constants	
		a (pm)	c (pm)
$ZnGa_2S_4$	Tetr.	527.5(1)	1043.7(1)
$ZnGa_{1.07}Sc_{0.93}S_4$	Trig.	373.3(1)	1222.8(1)
$ZnSc_2S_4$	Cubic	1048.6(1)	

three phases (see Table 2) in the samples of different composition are constant within the accuracy of the measurements. Quenching at 1100 °C did not result in a wider region of homogeneity.

3.3. The system $CdGa_2S_4$–$CdSc_2S_4$

The system $CdGa_2S_4$–$CdSc_2S_4$ is very simple: we could observe neither the formation of a new quaternary compound in the temperature range investigated nor the phase width of the two ternary border compounds. The lattice constants of $CdGa_2S_4$ remain constant within the accuracy of our measurements over the whole system at $a = 555.1$ pm and $c = 1015.9$ pm, which is in fairly good agreement with the values given by Hahn *et al.* [11]. The same is true for $CdSc_2S_4$, for which we obtained a lattice constant of $a = 1073.3$ pm (in agreement with ref. 12).

4. Discussion

The results of our investigation of the phase relationships in the systems $CoGa_{2-x}Sc_xS_4$, $ZnGa_{2-x}Sc_xS_4$ and $CdGa_{2-x}Sc_xS_4$ show once more the power of the structure field map [7] in predicting compositions for new materials with layered structures of the $ZnIn_2S_4$ type. The line connecting the points for $CoGa_2S_4$ and the hypothetical compound $CoSc_2S_4$ in the structure field map (see Fig. 2) crosses the field of the $ZnIn_2S_4$ type and consequently a new compound could be found in this system crystallizing in the $FeGa_2S_4$ type, one of the polytypes of the $ZnIn_2S_4$ structure.

In the case of the zinc-containing system, the connecting line between the two end members of the system only passes the edge of the $ZnIn_2S_4$-structure field; an $FeGa_2S_4$-type quaternary compound is formed nevertheless. However, according to our results, this compound tends to be deficient in zinc and scandium and therefore exhibits smaller r_π and r_σ values. By this, the point corresponding to the compound is shifted into the $ZnIn_2S_4$ structure field.

Although the connecting line crosses the $ZnIn_2S_4$ structure field, no such compound is formed in the system $CdGa_2S_4$–$CdSc_2S_4$. This shows that the structure field concept is unable to predict whether a compound is formed or not, but can only be used to predict a structure if a compound forms.

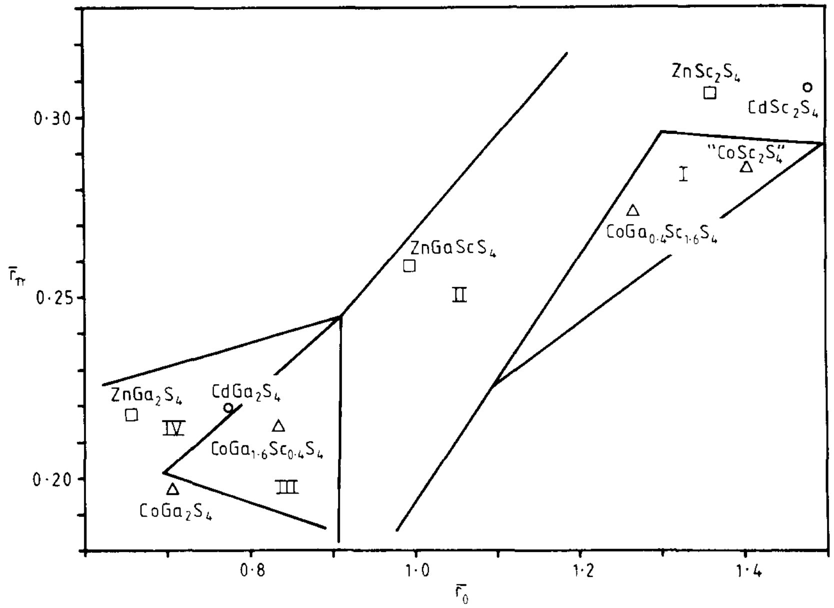

Fig. 2. Structure field map (according to ref. 7) of the compounds investigated in this paper.

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