

Phase Relationships of the Quaternary Systems $M\text{Cr}_2\text{Se}_4$ - MGa_2Se_4 ($M = \text{Mn, Fe, Co, Ni}$): New Layered ZnIn_2S_4 -III Type Selenides

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The phase relationships of the quaternary systems $M\text{Cr}_2\text{Se}_4$ - MGa_2Se_4 ($M = \text{Mn, Fe, Co, Ni}$) and $M\text{V}_2\text{S}_4$ - MGa_2S_4 ($M = \text{Fe, Ni}$) and the ternary system NiS - Ga_2S_3 were studied by X-ray phase analyses with the aim to prepare new layered structure and spinel-type chalcides. The hitherto unknown selenides $\text{MnCr}_{0.5}\text{Ga}_{1.5}\text{Se}_4$, $\text{FeCr}_{0.5}\text{Ga}_{1.5}\text{Se}_4$, $\text{CoCr}_{0.5}\text{Ga}_{1.5}\text{Se}_4$, and $(\text{Ni, Cr, Ga, } \square)_3\text{Se}_4$ (all ZnIn_2S_4 -III type) were obtained and characterized by X-ray and FIR studies. No quaternary chalcides are formed in the systems $M\text{V}_2\text{S}_4$ - MGa_2S_4 ; ternary NiGa_2Se_4 and CoGa_2Se_4 were likewise not obtained. Whereas the phase widths of the end-member phases are small (with the exception of α' - Ga_2S_3 at 1000°C) because of the strong tetrahedral and octahedral site preferences of gallium and both chromium and vanadium, respectively, the quaternary selenides form solid solutions of the type $M\text{Cr}_{2-x}\text{Ga}_x\text{Se}_4$ with $x = 0.65$ - 0.80 for $M = \text{Mn}$ and Fe . © 1987 Academic Press, Inc.

Introduction

For preparation of new ternary or multinary chalcides, it is useful to study the phase diagrams of systems with end-member phases which differ in the coordination of the metal sites in such a manner that those of possible new compounds are intermediate (1, 2). In order to obtain new layered structure or spinel-type chalcides with interesting physical properties we therefore studied the phase diagrams of the quaternary systems $M\text{Cr}_2\text{Se}_4$ - MGa_2Se_4 with $M = \text{Mn, Fe, Co, Ni}$ and $M\text{V}_2\text{S}_4$ - MGa_2S_4 with $M = \text{Fe, Ni}$, which fulfill the conditions discussed above.

The ternary chromium selenides (3-5) and vanadium sulfides (6, 7) crystallize in the NiAs defect structure Cr_3S_4 type with only octahedral sites occupied by the metal

atoms. The other end-member phases possess crystal structures with tetrahedrally coordinated metal atoms. The gallium sulfides (2, 8) crystallize in the layered structure FeGa_2S_4 type with both octahedral and tetrahedral sites occupied, and MnGa_2Se_4 and FeGa_2Se_4 (9-12) crystallize in defect sphalerite structures with only tetrahedral sites occupied; ternary CoGa_2Se_4 and NiGa_2Se_4 are not known so far (13-14). Hence, the metal coordination of AB_2X_4 layered structures as the ZnIn_2S_4 (15, 16) and the FeGa_2S_4 type (2, 8) with one octahedral and two tetrahedral sites occupied is intermediate between those of the Cr_3S_4 and the ZnS defect structures, that of spinels, i.e., one tetrahedral and two octahedral sites occupied, between those of the Cr_3S_4 and the layered structures.

Experimental

Polycrystalline samples of the quaternary chalcide systems under investigation were prepared by firing appropriate mixtures of the ternary compounds in evacuated closed silica tubes at elevated temperatures (two heating periods of 8–30 days depending on annealing temperature chosen) and quenching with ice water to ambient temperature. The ternary chalcides were synthesized from the elements by heating at 800°C for 48 hr and then at 1000°C for 12 hr. The polycrystalline samples obtained were ground and reheated at 800°C for 5 days to achieve homogeneity. Starting materials were sulfur, 5 N (Fluka), selenium, 4 N (Fluka), chromium, 4 N (Fluka), gallium, 4 N (Ventron), vanadium, 2 N (Fluka), manganese, 3 N (Ventron), iron, 6 N (Ventron), cobalt, 3 N (Ventron), and nickel, 4 N (Janssen).

The ternary and quaternary chalcides and equilibrated phase mixtures obtained were analyzed by X-ray Guinier powder technique (Huber Guinier 600 system); $\text{CrK}_{\alpha 1}$ radiation was used. The unit cell dimensions of the various chalcide phases were calculated by least-squares methods ("LSUCR," "ITO" (17)); α -quartz was used as an internal standard ($a_0 = 491.36$ and $c_0 = 540.54$ pm). The far-infrared spectra of the new layered structure compounds were recorded with a Bruker IFS 114 FT-IR spectrometer (nujol mulls).

Results

1. Layered Structure Selenides

$\text{MnCr}_{0.5}\text{Ga}_{1.5}\text{Se}_4$, $\text{FeCr}_{0.5}\text{Ga}_{1.5}\text{Se}_4$,

$\text{CoCr}_{0.5}\text{Ga}_{1.5}\text{Se}_4$, and $(\text{Ni}, \text{Cr}, \text{Ga}, \square)_3\text{Se}_4$

In the systems under investigation, the hitherto unknown quaternary selenides $\text{MnCr}_{0.5}\text{Ga}_{1.5}\text{Se}_4$, $\text{FeCr}_{0.5}\text{Ga}_{1.5}\text{Se}_4$, and $\text{CoCr}_{0.5}\text{Ga}_{1.5}\text{Se}_4$ were synthesized. Equilibrated samples of composition $\text{NiCr}_{0.5}\text{Ga}_{1.5}\text{Se}_4$ are three-phase, viz. $\text{Ni}_{1-x}\text{Cr}_x\text{Se}$, Ga_2Se_3 , and a ZnIn_2S_4 -III type quaternary selenide. No

quaternary chalcides were obtained in the systems $\text{MV}_2\text{S}_4\text{-MGa}_2\text{S}_4$ ($M = \text{Fe}, \text{Ni}$). Ternary CoGa_2Se_4 and NiGa_2Se_4 could likewise not be prepared.

The quaternary selenides, which can be best obtained by firing appropriate mixtures of the ternary selenides or the elements at 800°C for two heating periods of 8 days, crystallize in the layered structure ZnIn_2S_4 -III A type (space group $R3m$, $Z = 3$). The unit cell dimensions are given in Table I. The X-ray powder photographs of the layered structure selenides show strong texture effects. The FIR spectra (see Fig. 1) reveal only a few of the 40 group theoretical allowed (18) bands.

In the case of $\text{MnCr}_{0.5}\text{Ga}_{1.5}\text{Se}_4$, the X-ray patterns of samples quenched from temperatures $< 800^\circ\text{C}$ differ from those of samples quenched from higher temperatures, particularly there are reflections additional to those allowed in the rhombohedral system. The patterns, however, could also be indexed in the hexagonal system and the unit cell dimensions obtained are very similar to those of the ZnIn_2S_4 -type compound (see Table 1). Furthermore, the FIR spectra of both samples are very similar. From additional experiments it is shown that the low-temperature form can be converted into the ZnIn_2S_4 -type compound by heating at higher temperatures, whereas the reverse transformation at lower temperatures is not possible (within 8 weeks). Hence, low-tem-

TABLE I
UNIT CELL DIMENSIONS (pm) OF
QUATERNARY ZnIn_2S_4 -III TYPE SELENIDES

	<i>a</i>	<i>c</i>
$\text{MnCr}_{0.5}\text{Ga}_{1.5}\text{Se}_4^a$	386.6(1)	3843(1)
$\text{FeCr}_{0.5}\text{Ga}_{1.5}\text{Se}_4^a$	382.8(1)	3794(1)
$\text{CoCr}_{0.5}\text{Ga}_{1.5}\text{Se}_4^a$	380.5(2)	3770(1)
$(\text{Ni}, \text{Cr}, \text{Ga}, \square)_3\text{Se}_4^a$	379.1(1)	3763(2)
$\text{MnCr}_{0.5}\text{Ga}_{1.5}\text{Se}_4^b$	386.9(1)	3839(1)

^a Quenched from 800°C.

^b Quenched from 600°C; see text.

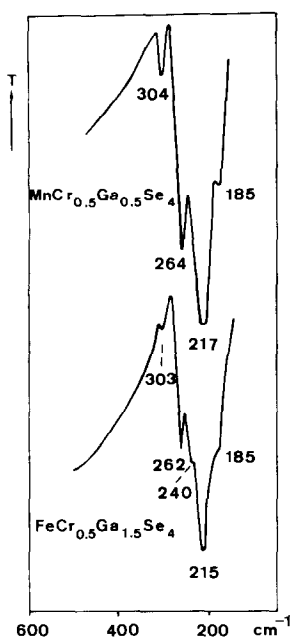


FIG. 1. Far-infrared spectra of the ZnIn_2S_4 -IIIa type $\text{MnCr}_{0.5}\text{Ga}_{1.5}\text{Se}_4$ and $\text{FeCr}_{0.5}\text{Ga}_{1.5}\text{Se}_4$.

perature $\text{MnCr}_{0.5}\text{Ga}_{1.5}\text{Se}_4$ is probably a metastable compound.

2. Phase Diagrams of the Systems

$\text{MCr}_{2-2x}\text{Ga}_{2x}\text{Se}_4$ ($M = \text{Mn}, \text{Fe}$),
 $\text{MV}_{2-2x}\text{Ga}_{2x}\text{S}_4$ ($M = \text{Fe}, \text{Ni}$), and
 $\text{NiS-Ga}_2\text{S}_3$

The phase diagrams of the manganese and iron selenide systems were studied by X-ray phase analyses of quenched samples. The phase widths of the ternary end-member phases are very small, i.e., no mutual substitution could be detected by the X-ray method. The ZnIn_2S_4 -III type quaternary selenides exist, independently of the equilibration temperatures studied (600 to 900°C), in the range from $x = 0.65$ to $x = 0.80$ in both systems. The unit cell dimensions of these solid solutions, however, alter only little depending on x (see Fig. 2). The lattice constants of the ternary selenides resemble the literature data (see Table II). The iron system is not fully quasi-binary, as shown from forming solid

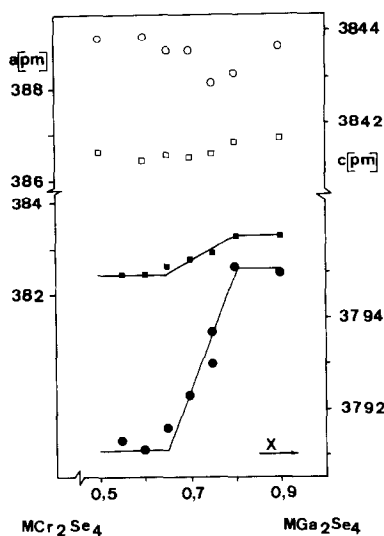


FIG. 2. Unit cell dimensions of $\text{MnCr}_{2-2x}\text{Ga}_{2x}\text{Se}_4$ (\square , \circ) and $\text{FeCr}_{2-2x}\text{Ga}_{2x}\text{Se}_4$ (\blacksquare , \bullet) solid solutions.

TABLE II
 LATTICE CONSTANTS (pm) OF THE TERNARY
 END-MEMBER PHASES IN THE MCr_2Se_4 - MGa_2Se_4
 AND MV_2S_4 - MGa_2S_4 SYSTEMS

	<i>a</i>	<i>b</i>	<i>c</i>	β ($^\circ$)	Reference
MnCr_2Se_4	629.2(2)	365.2(1)	1220.6(2)	90.63(2) ^a	(4)
	628.9(2)	364.8(1)	1217.8(2)	90.62(3) ^b	
	630.8	364.9	1221.6	90.67	
FeCr_2Se_4	625.5(1)	360.9(1)	1175.7(1)	90.81(1)	(5)
	626	361	1178	90.85	
	621.9(2)	358.8(1)	1159.2(4)	90.91(2) ^c	
Fe_3Se_4	614.0(1)	351.4(1)	1109.9(2)	91.54(1)	
FeV_2S_4	585.5(1)	329.3(1)	1127.3(1)	91.92(1)	(7)
	587.2	330.0	1129.4	92.12	
NiV_2S_4	584.8(1)	328.0(1)	1108.6(2)	92.33(1)	(6)
	584	328	1107	92.57	
MnGa_2Se_4	567.5(1)		1075.9(1)		(9)
	567.6		1076.0		
FeGa_2Se_4	550.1(1)		550.0(1)		(12)
	550.1		550.1		
FeGa_2S_4	366.8(1)		1209.3(2)		(8)
	365.4		1205.6		
NiGa_2S_4	362.49(2)		1199.56(5)		(2)

^a Quenched from 600°C .

^b Quenched from 800°C .

^c $\text{FeCr}_{2-2x}\text{Fe}_2\text{Se}_4$ mixed crystals, non-quasi-binary behavior.

solutions of type $\text{FeCr}_{2-2x}\text{Fe}_{2x}\text{Se}_4$ (see Table II).

The mutual substitutions of MV_2S_4 and MGa_2S_4 ($M = \text{Fe}, \text{Ni}$) are very small. Quaternary sulfides of spinel type or other structures were not found. The lattice constants of the ternary sulfides are in agreement with the literature data (see Table II).

In the ternary system $\text{NiS}-\text{Ga}_2\text{S}_3$, layer structure (FeGa_2S_4 type) ternary NiGa_2S_4 is formed (2). The phase widths of the ternary and both binary end-member sulfides (β - NiS and monoclinic α - Ga_2S_3) are very small. Only in the case of hexagonal α' - Ga_2S_3 (19, 20) at higher temperatures can some amounts of nickel, but less than reported in (21), i.e., about 10, not 30 mole%, be substituted into the binary gallium sulfide. The unit cell dimensions of monophase Ga_2S_3 with 10 mole% NiS , with sample quenched from 1000°C , were $a = 639.7(1)$ and $c = 1808.1(2)$ pm.

Discussion and Conclusion

The pseudoternary layered selenides presented in this paper are the first compounds of the ZnIn_2S_4 family which are not exclusively composed of d^{10} metal ions as Zn^{2+} , In^{3+} , etc. (see also (22)). The crystal structures of the new compounds were not determined, but the cation distribution is obviously such that chromium is only on octahedral sites, gallium on tetrahedral ones, and the bivalent metals (Mn, Fe) on both enabling some nonstoichiometry. However, the maximum and minimum chromium contents thus possible, viz. MCrGaSe_4 and MGa_2Se_4 , are not realized.

The relatively small alterations of the unit cell dimensions with increasing gallium content (see Fig. 2), especially in the manganese system, are probably due to the fact that simultaneously chromium is substituted by the larger manganese on octahedral sites and manganese by the smaller gallium on tetrahedral sites.

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References

1. C. RAZZETTI AND P. P. LOTTICI, *Mater. Chem. Phys.* **11**, 65 (1984).
2. H. D. LUTZ, W. BUCHMEIER, AND H. SIWERT, *Z. Anorg. Allg. Chem.* **533**, 118 (1986).
3. B. L. MORRIS, P. RUSSO, AND A. WOLD, *J. Phys. Chem. Solids* **31**, 635 (1970).
4. P. GIBART, M. ROBBINS, AND V. G. LAMBRECHT, *J. Phys. Chem. Solids* **34**, 1363 (1973).
5. E. RIEDEL, A. AL-JUANI, R. RACKWITZ, AND H. SÖCHTIG, *Z. Anorg. Allg. Chem.* **480**, 49 (1981).
6. R. J. BOUCHARD AND A. WOLD, *J. Phys. Chem. Solids* **27**, 591 (1966).
7. H. NAKAZAWA, K. TSUKIMURA, H. HIRAI, AND H. WADA, *Acta Crystallogr., Sect. B* **39**, 532 (1983).
8. L. DOGGUY-SMIRI, D. NGUYEN-HUY, AND M. P. PARDO, *Mater. Res. Bull.* **15**, 861 (1980).
9. K. J. RANGE AND H.-J. HÜBNER, *Z. Naturforsch., B: Anorg. Chem., Org. Chem.* **31**, 886 (1976).
10. M. P. PARDO AND J. FLAHAUT, *Mater. Res. Bull.* **13**, 1231 (1978).
11. M. R. ALLAZOV, P. K. BABAEVA, AND P. G. RUSTAMOV, *Izv. Akad. Nauk SSSR, Neorg. Mater.* **15**, 1177 (1979); *Inorg. Mater.* **15**, 923 (1979).
12. M. P. PARDO AND J. FLAHAUT, *Mater. Res. Bull.* **15**, 1043 (1980).
13. M. P. PARDO, *Mater. Res. Bull.* **17**, 1477 (1982).
14. P. K. BABAEVA, M. P. ALLAZOV, AND P. G. RUSTAMOV, *Issled. Obl. Neorg. Fiz. Khim.*, **73** (1980).
15. F. LAPPE, A. NIGGLI, R. NITSCHKE, AND J. G. WHITE, *Z. Kristallogr.* **117**, 146 (1962).
16. F. HULLIGER, "Structural Chemistry of Layer-Type Phases," Reidel, Dordrecht (1976).
17. J. W. VISSER, *J. Appl. Crystallogr.* **2**, 89 (1969).
18. C. RAZZETTI AND P. P. LOTTICI, *Phys. Status Solidi B* **100**, K23 (1980).
19. D. NGUYEN-HUY, M.-P. PARDO, AND L. DOGGUY-SMIRI, *Mater. Res. Bull.* **17**, 293 (1982).
20. H. HAHN AND W. KLINGLER, *Z. Anorg. Allg. Chem.* **259**, 135 (1949).
21. M. R. ALLAZOV, P. K. BABAEVA, A. N. MAMEDOV, AND P. G. RUSTAMOV, *Izv. Akad. Nauk SSSR, Neorg. Mater.* **17**, 351 (1981).
22. H. HAEUSELER, *Naturwissenschaften* **73**, 264 (1986).