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PHASE STUDIES IN THE SYSTEMS Ag_2Te–Ga_2Te_3, ZnSe–In_2Se_3, AND ZnS–Ga_2S_3

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SUMMARY

The title systems were investigated by means of differential thermal analysis (DTA) and X-ray phase analysis (XPA). From these measurements phase diagrams were constructed; crystal data of intermediate compounds and a structure model of $ZnGa_2S_4$ are added.

INTRODUCTION

Ternary semiconducting crystals with the chalcopyrite and defect-chalcopyrite structure find growing interest because of their non-linear optical properties. As a suitable basis for their crystal growth, the phase relations in the corresponding systems should be known. For this reason, the systems Ag_2Te–Ga_2Te_3, ZnSe–In_2Se_3, and ZnS–Ga_2S_3 were (re-)examined and their tentative phase diagrams as well as the results of X-ray diffraction studies on some of the intermediate compounds are dealt with.

EXPERIMENTAL

The binary components were synthesized from high purity elements. DTA experiments were performed and evaluated as described earlier [1]. X-ray phase analyses of the DTA products were done with a Guinier-de Wolff camera (CuKα radiation) using cubic As_2O_3 as internal standard and programs GUINIER [2] and LSUCRE [3] for precise determination of lattice parameters. Single-crystals were prepared by chemical vapour transport (CVT). For a structure analysis of $ZnGa_2S_4$, an intensity data set of a suitable CVT crystal was collected on an ENRAF-NONIUS CAD-4 diffractometer (graphite-monochromatized AgKα radiation). Calculations were performed with the X-RAY76 program system [4] on the basis of 857 unique observed reflections, corrected for absorption and extinction effects.

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RESULTS

1. The system Ag_2Te-Ga_2Te_3.

Palatnik and Belova [5] studied this system in the range 20-100 mole % Ga_2Te_3. A complete re-examination of the phase diagram over the whole concentration region (Fig. 1) shows no essential differences of the already published phase boundaries, but at the Ag_2Te rich side of the system, a new compound of composition Ag_7GaTe_4 was found. It melts incongruently at 705(5) °C and shows a phase transition in the temperature interval 2-30 °C. Contrary to the homologous compounds in the systems Ag_2S-Ga_2S_3 [6] and Ag_2Se-Ga_2Se_3 [7-9] which belong to a large family of isotypic compounds (the "argyrodites", space group $F\bar{4}3m$ of the aristotypes [10]) this compound crystallizes hexagonally [11]. Crystal data of both polymorphs of Ag_7GaTe_4 and of $AgGaTe_2$ (chalcopyrite structure type) are listed in Table 1. So far, the Ga rich phase $AgGa_5Te_8$ could not be obtained single-crystalline.

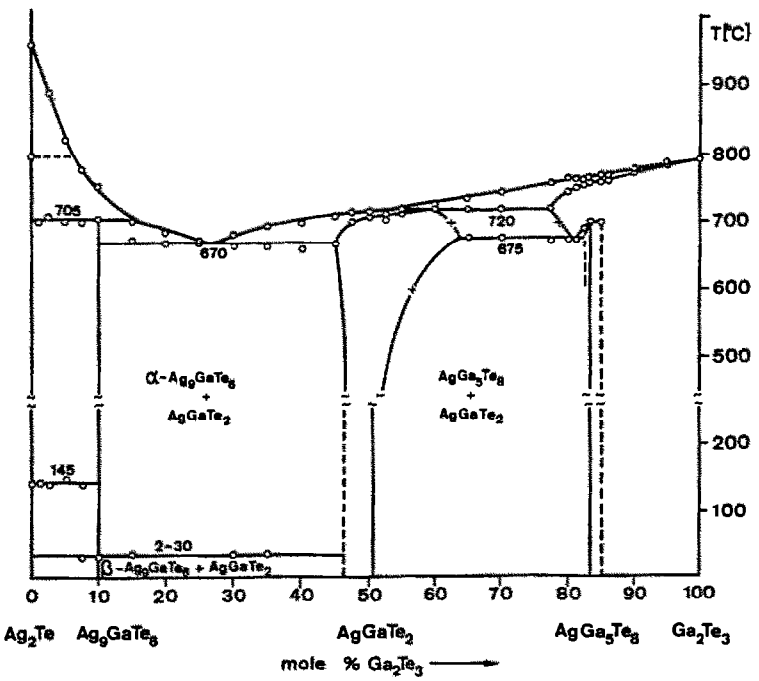

Fig. 1. Phase diagram of the system Ag_2Te-Ga_2Te_3.

2. The system $ZnSe-In_2Se_3$.

Fig. 2 shows the proposed phase diagram; the only intermediate compound found, $ZnIn_2Se_4$, melts incongruently at 960(10) °C. Small DTA effects and electrical conductivity measurements indicate a phase transition at 45(5)°C. A structure analysis [12] showed that $ZnIn_2Se_4$ crystallizes with space group $I\bar{4}2m$, i.e. a variety of the thiogallate/defect-chalcopyrite structure, caused by statistical disorder of the cations. Its crystal data are listed in Table 1.

Haeuseler et al. [13] report on a second intermediate compound of composition $Zn_{0.4}In_2Se_{3.4}$ ($\triangleq 2ZnSe.5In_2Se_3$) which cannot be confirmed unequivocally: the continuously detected α-β phase transition of In_2Se_3 suggests a two-phase region between $ZnIn_2Se_4$ and In_2Se_3, but weak additional X-ray diffraction lines point at ambiguous equilibrium conditions in the related composition/temperature region.

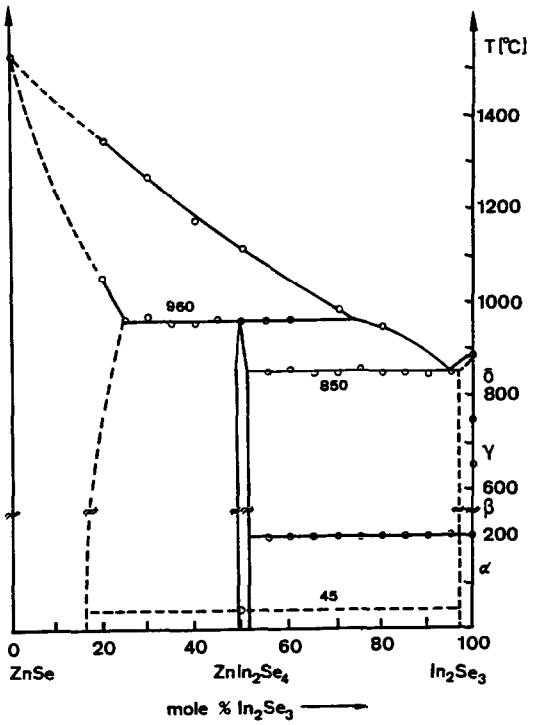

Fig. 2: Phase diagram of the system $ZnSe-In_2Se_3$.

3. The system ZnS-Ga_2S_3.

Rather preliminary and contradictious phase diagrams were published by Flahaut et al. [14] and Malevskii [15]. Fig. 3 shows the results of our treatment. At high temperatures, a complete solid solution between ZnS and Ga_2S_3 with defect-wurtzite structure exists as confirmed by quenching annealed specimens from temperatures just below the solidus. By DTA the liquidus and solidus curves could be established up to 1300 °C, but in the subsolidus region considerable kinetic barriers prevent the elucidation of the phase boundaries. Besides $ZnGa_2S_4$ (its crystal data shows Tab. 1), a second phase with a phase width from 80 to 92 mole % Ga_2S_3 was found; various attempts to prepare single-crystals failed.

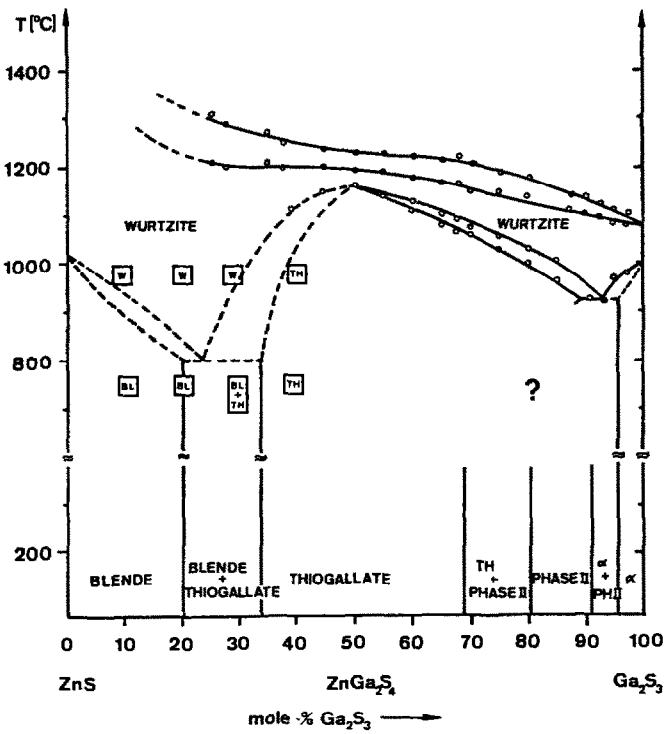

Fig. 3. Tentative phase diagram of the system ZnS-Ga_2S_3. Phases in boxes were identified after annealing and quenching (TH: thiogallate, W: wurtzite).

TABLE 1

Crystal data.

		Ag_7BaTe_4 α [11]	Ag_7BaTe_4 β [11]	$AgBaTe_2$	$ZnIn_2Se_4$ [12]	$ZnGa_2S_4$
a	(Å)	8.260(5)	16.498(4)	6.313(2)	5.7095(7)	5.290(1)
c	(Å)	13.407(8)	13.274(5)	11.981(6)	11.449(2)	10.354(5)
c/a		1.623	0.805	1.898	2.005	1.957
V	($Å^3$)	792.2	3128.9	477.5	372.2	289.8
Z		2	8	4	2	2
D_x	(gcm^{-3})	7.57	7.67	6.02	5.43	3.70
D_o	(gcm^{-3})				5.51	3.76
SG		$P6_3/mmc$	$P6_3/m$	$I\bar{4}2d$	$I\bar{4}2m$	$I\bar{4}$
Habit		< plates >		bisphenoids	columns	bisphenoids
Form		{001}, {100}, {101}		{112}	{112}, {001}	{112}
Colour		< black >		black	dark red	colourless

4. Structure of $ZnGa_2S_4$.

Zn and Ga cannot be discriminated in X-ray experiments because of their nearly identical scattering factors. However, Haeuseler [16] and Siebert [17] postulated on the basis of FIR, Raman, and spinprobe investigations that $ZnGa_2S_4$ possesses an ordered arrangement of the Zn and Ga atoms in accordance with the thiogallate structure type (prototype $CdGa_2S_4$ [18]). Therefore, the structure of $ZnGa_2S_4$ was treated in space group $I\bar{4}$ with starting parameters from [18] and substituting Cd by Zn; refinement converged at R= 4.5%. Tables 2 and 3 show the results of the structure analysis.

TABLE 2

Fractional atomic and anisotropic thermal ($Å^2 \times 10^2$) parameters, e.s.d.'s in parentheses.

Atom	x	y	z	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Me1 (Zn)	0	0	0	1.94(7)	1.94(7)	1.6(1)	-	-	-
Me2 (Ga)	0	0	0.5	0.68(4)	0.68(4)	0.8(1)	-	-	-
Me3 (Ga)	0	0.5	0.25	1.39(4)	1.39(4)	1.02(7)	-	-	-
S	0.2541(4)	0.2418(4)	0.1314(2)	1.53(7)	1.53(7)	1.12(6)	-0.14(6)	0.35(5)	0.10(5)

TABLE 3

Bond distances (A).

Me1 (Zn) - S	2.301(2) 4x
Me2 (Ga) - S	2.326(2) 4x
Me3 (Ga) - S	2.276(2) 4x

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