

PHASE RELATIONS IN THE SYSTEM Zn–Ga–S AT 900°C AND 800°C

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ABSTRACT

Phase relations in the ternary system Zn–Ga–S were investigated by dry synthesis at 900° and 800°C, and phase diagrams were obtained for both temperatures. Along the ZnS–Ga₂S₃ join, there are four solid solutions at both temperatures: (Zn,Ga)_{1-x}S, phase V, phase U, and (Ga,Zn)₂S₃. Along the Zn–Ga join, zinc liquid and gallium liquid coexist at both temperatures, and they have small fields of miscibility. (Zn,Ga)_{1-x}S forms an extensive solid-solution. At 800°C, the phase has a mixed sphalerite and wurtzite X-ray-diffraction pattern for all compositions (pure ZnS shows a sphalerite pattern), but at 900°C there is a pattern of sphalerite, wurtzite or a mixture of sphalerite and wurtzite, depending on composition. The mixture is probably metastable, in which case the inversion temperature from the sphalerite form to the wurtzite form must be lower than 800°C. Phase V (tetragonal structure) and phase U (sphalerite structure) have small fields of solid solution at both temperatures.

Keywords: system Zn–Ga–S, phase equilibrium, dry synthesis, solid solution, sphalerite, wurtzite.

SOMMAIRE

Les relations de phases dans le système ternaire Zn–Ga–S ont fait l'objet d'une étude par voie sèche à 900° et 800°C; il en résulte des coupes isothermales. Le long du joint ZnS–Ga₂S₃ se trouvent quatre solutions solides aux deux températures, soit (Zn,Ga)_{1-x}S, phase V, phase U, et (Ga,Zn)₂S₃. Le long du joint Zn–Ga, zinc liquide et gallium liquide coexistent aux deux températures, et font preuve d'une miscibilité restreinte. L'étendue du champ de la solution solide (Zn,Ga)_{1-x}S est grande. A 800°C, cette phase possède un spectre de diffraction X indiquant un mélange de sphalérite et de wurtzite dans tous les cas (spectre de sphalérite dans le cas de ZnS), mais à 900°C, nous trouvons un spectre de sphalérite, de wurtzite, ou de sphalérite + wurtzite selon la composition. Le mélange est tout probablement métastable; la température de l'inversion serait, dans ce cas, inférieure à 800°C. Les phases V (structure tétraogonale) et U (structure de la sphalérite) font preuve d'un champ de solution solide restreint à ces températures.

(Traduit par la Rédaction)

Mots-clés: système Zn–Ga–S, équilibres de phases, synthèses par voie sèche, solution solide, sphalérite, wurtzite.

INTRODUCTION

Phase relations involving the sulfides of gallium, an important industrial metal that occurs predominantly in solid solutions with sphalerite in nature (Sheka *et al.* 1966), are poorly known. Hahn *et al.* (1955) were the first to investigate phase relations along the join Ga₂S₃–ZnS at 900°C. They measured the variations of cell parameters of phases, reported the presence of ZnGa₂S₄ as a phase, and determined its crystal structure. Gates & Edwards (1978) emphasized the important practical applications of ZnS, Ga₂S₃ and ZnGa₂S₄ to high technology (*e.g.*, cathodoluminescent display devices, radiation detectors and semicon-

ductors). They studied the phase relations along the join Ga₂S₃–ZnGa₂S₄ from 960° to 1150°C, proposed a Zn_{1-x}Ga_{2x}S_{3+x} solid solution (0 < x < 0.07), and found a binary compound of stoichiometry ZnGa₈S₁₃. Ueno & Scott (1991) measured the solubility of gallium in sphalerite in the systems Zn–Ga–S and Zn–Fe–Ga–S at 900° and at 800°C, and found a maximum of 24.9 atomic % Ga at 900°C and 16.3 atomic % at 800°C in the iron-free system. Subsequently, Ueno & Scott (1994) investigated the system Ga–Fe–S and found three new ternary phases (Z, W and X). Their determination of ternary phase-relations at 900° and 800°C, together with earlier determinations on the system Zn–Fe–S (Barton & Toulmin 1966), provided

basic information with which to evaluate the controls on gallium contents in zinc-iron sulfides.

In this study, we conducted synthetic phase-equilibrium experiments in the ternary system Zn-Ga-S at 900° and 800°C. These results represent further essential progress toward our ultimate goal of understanding the quaternary system Zn-Fe-Ga-S.

EXPERIMENTS

Elemental Zn (99.98% purity, Pb+Cu+Fe+Cd = 0.02%), Ga (99.9999% purity), and S (99.999% purity), and three synthetic sulfides (ZnS, GaS and Ga₂S₃) were used as starting materials. Synthesis of the starting monosulfides and other experimental details are described in Ueno & Scott (1991).

Table 1 shows the proportions and bulk compositions of the reactants, temperature and duration of each experiment and the reaction products. Reactants were heated in an electric furnace at 900° and 800°C and were quenched in cold water after 19 to 25 days (900°C runs) or 28 to 50 days (800°C runs). Products were examined by reflected-light microscopy and by X-ray powder diffractometry (Ni-filtered CuK α radiation, 40 kV, 100 mA), with Si as an internal standard. Cell parameters were calculated for some phases by the least-squares method from precisely measured *d*-values. For mixtures of sphalerite (sp) and wurtzite (wz), we calculated, in a manner similar to Smith (1955), the mol % sphalerite from measurements of the X-ray intensity ratios for wz(100) and sp(111) + wz(002) reflections and the equation:

TABLE 1. EXPERIMENTAL RESULTS FOR THE Zn-Ga-S SYSTEM AT 900°C AND 800°C

Run no.	Temp.(°C)	Reactants	Bulk compositions (At. %)			Heating days	Products	Mol % Sp in mixture
			Zn	Ga	S			
T027	900	ZnS+2GaS	16.7	33.3	50.0	2.2	Sp+GaS+Ga	
T047	900	ZnS+GaS	25.0	25.0	50.0	1.9	Sp(Wz)+Ga	88.4
T068	900	7ZnS+3GaS	35.0	15.0	50.0	2.3	Wz+Ga	
T069	900	9ZnS+GaS	45.0	5.0	50.0	2.3	Wz(Sp)+Ga	48.1
T094	900	ZnS+5GaS+8S	5.0	25.0	70.0	2.0	U+S	
T095	900	3ZnS+3GaS+8S	15.0	15.0	70.0	2.0	Wz(Sp)+S	29.1
T096	900	5ZnS+GaS+8S	25.0	5.0	70.0	2.0	Wz+S	
T097	900	GaS+3Zn	60.0	20.0	20.0	2.0	Sp+Ga+Zn	
T122	900	ZnS+Ga ₂ S ₃	14.3	28.6	57.1	2.5	V	
T123	900	ZnS+4Ga ₂ S ₃	4.5	36.4	59.1	2.5	U	
T134	900	20ZnS+23GaS+14S	20.0	23.0	57.0	2.0	V+Sp(Wz)	57.5
T135	900	2ZnS+7GaS+2S	10.0	35.0	55.0	2.0	V+GaS	
T136	900	11ZnS+30GaS+18S	11.0	30.0	59.0	2.0	V+S	
T137	900	ZnS+6GaS+6S	5.0	30.0	65.0	2.0	U+S	
T139	900	3ZnS+6GaS+2S	15.0	30.0	55.0	2.0	V+Sp+GaS	
T140	900	17ZnS+22GaS+22S	17.0	22.0	61.0	2.0	V+Sp(Wz)+S	91.2
T141	900	13ZnS+26GaS+22S	13.0	26.0	61.0	2.0	V+S	
T142	900	4ZnS+15GaS+12S	8.0	30.0	62.0	2.0	V+U+S	
T143	900	7ZnS+36GaS+14S	7.0	36.0	57.0	2.0	U+V+GaS	
T144	900	3ZnS+40GaS+14S	3.0	40.0	57.0	2.0	U+GaS	
T147	900	ZnS+10Ga ₂ S ₃	1.9	38.5	59.6	2.0	Ga ₂ S ₃ +U+GaS	
T148	900	ZnS+20GaS+8S	2.0	40.0	58.0	2.0	U+GaS	
T186	900	2ZnS+3GaS	20.0	30.0	50.0	2.3	Sp(Wz)+Ga	70.5
T028	800	ZnS+2GaS	16.7	33.3	50.0	2.8	Sp(Wz)+GaS+Ga	63.7
T048	800	ZnS+GaS	25.0	25.0	50.0	3.1	Sp(Wz)+GaS+Ga	82.7
T070	800	7ZnS+3GaS	35.0	15.0	50.0	3.5	Sp(Wz)+Ga	80.4
T071	800	9ZnS+GaS	45.0	5.0	50.0	3.5	Sp(Wz)+Ga	59.5
T098	800	ZnS+5GaS+8S	5.0	25.0	70.0	4.0	V+U+S	
T099	800	3ZnS+3GaS+8S	15.0	15.0	70.0	4.0	V+Sp(Wz)+S	70.5
T100	800	5ZnS+GaS+8S	25.0	5.0	70.0	4.0	Sp(Wz)+S	70.5
T101	800	GaS+3Zn	60.0	20.0	20.0	4.0	Sp(Wz)+Zn+Ga	97.0
T120	800	3ZnS+32GaS+30S	3.0	32.0	65.0	4.3	U+Ga ₂ S ₃ +S	
T121	800	2ZnS+5GaS+6S	10.0	25.0	65.0	4.3	V+S	
T129	800	4ZnS+5GaS+2S	20.0	25.0	55.0	5.0	V+Wz(Sp)+GaS	20.8
T130	800	10ZnS+33GaS+14S	10.0	33.0	57.0	5.0	V+GaS	
T131	800	ZnS+20GaS+8S	2.0	40.0	58.0	4.2	U+Ga ₂ S ₃ +GaS	
T132	800	ZnS+6GaS+6S	5.0	30.0	65.0	4.2	U+S	
T133	800	ZnS+Ga ₂ S ₃	14.3	28.6	57.1	4.2	V	
T145	800	ZnS+4Ga ₂ S ₃	4.5	36.4	59.1	4.3	U	

Sp: Sphalerite, Wz: Wurtzite, U: Phase U, V: Phase V, Zn: zinc liquid, S: sulfur liquid, Ga: gallium liquid

Sp(Wz): Mixed phases in which Sphalerite predominates

Wz(Sp): Mixed phases in which Wurtzite predominates

TABLE 2. CHEMICAL COMPOSITIONS OF PHASES IN THE Zn-Ga-S SYSTEM

Run no.	Temp.(°C)	Weight %			Atomic %			
		Zn	Ga	S	Total	Zn	Ga	S
(Zn,Ga)_{1-x}S solid solution								
T027	900	27.6	36.6	36.9	101.1	20.1	24.9	55.0
T047	900	36.6	27.4	36.1	100.1	26.9	18.9	54.2
T068	900	49.1	16.5	34.3	99.9	35.5	11.5	52.0
T069	900	62.9	3.8	33.5	100.2	46.7	2.6	50.7
T096	900	54.5	10.6	34.6	99.7	40.4	7.4	52.2
T097	900	66.5	0.7	33.1	100.3	49.4	0.5	50.1
T186	900	30.9	32.3	36.0	99.2	23.0	22.5	54.5
T028	800	40.3	23.8	36.3	100.4	29.5	16.3	54.2
T070	800	50.6	14.7	34.8	100.1	37.4	10.2	52.4
T071	800	62.5	3.6	33.4	99.5	46.7	2.5	50.8
T099	800	39.8	23.9	36.8	100.5	29.0	16.3	54.7
T100	800	50.2	13.9	35.9	100.0	36.8	9.6	53.6
T101	800	66.2	0.4	32.7	99.3	49.7	0.3	50.0
(Ga,Zn)₂S₃ solid solution								
T147	900	3.0	55.8	40.4	99.2	2.2	38.0	59.8
T131	800	2.3	56.0	40.2	98.5	1.7	38.4	59.9
(Ga,Zn)₈S solid solution								
T143	900	0.9	67.6	31.9	100.4	0.7	49.0	50.3
T144	900	0.7	67.9	31.8	100.4	0.5	49.3	50.2
T148	900	0.8	67.1	31.4	99.3	0.6	49.3	50.1
T130	800	0.4	68.0	31.8	100.2	0.3	49.4	50.3
Phase V								
T122	900	18.3	42.2	39.4	99.9	13.3	28.6	58.1
T134	900	23.9	37.5	38.2	99.6	17.4	25.7	56.9
T135	900	14.8	45.4	39.3	99.5	10.7	31.0	58.3
T136	900	17.8	42.5	39.3	99.6	12.9	28.9	58.2
T139	900	23.0	38.7	38.7	100.4	16.6	26.3	57.1
T140	900	23.6	37.7	38.9	100.2	17.1	25.6	57.3
T141	900	19.3	41.3	38.9	99.5	14.0	28.2	57.8
T142	900	14.8	45.6	39.4	99.8	10.7	31.0	58.3
T098	800	12.8	47.2	39.6	99.6	9.3	32.1	58.6
T121	800	15.7	44.8	39.7	100.2	11.3	30.3	58.4
T129	800	23.2	37.9	38.2	99.3	17.0	26.0	57.0
T130	800	14.9	45.1	38.4	98.4	11.0	31.2	57.8
Phase U								
T094	900	9.2	49.7	41.1	100.0	6.6	33.4	60.0
T123	900	4.3	54.3	40.2	98.8	3.1	37.1	59.8
T137	900	9.0	50.0	41.5	100.5	6.4	33.4	60.2
T142	900	9.9	48.3	40.5	98.7	7.2	32.9	59.9
T143	900	10.0	48.3	40.3	98.6	7.3	32.9	59.8
T144	900	6.9	53.3	41.3	101.5	4.9	35.4	59.7
T148	900	4.4	54.8	40.5	99.7	3.2	37.1	59.7
T120	800	4.2	55.0	40.6	99.8	3.0	37.2	59.8
T132	800	7.4	51.3	41.4	100.1	5.3	34.4	60.3
T145	800	5.4	53.7	40.6	99.7	3.9	36.3	59.8
Ga liquid								
T068	900	1.4	97.9	0.1	99.4	1.5	98.2	0.3
T069	900	2.4	97.0	0.2	99.6	2.6	97.0	0.4
T097	900	8.2	91.4	0.0	99.6	8.7	91.3	0.0
T071	800	2.9	97.2	0.2	100.3	3.0	96.6	0.4
T101	800	5.0	94.9	0.1	100.0	5.3	94.5	0.2
Zn liquid								
T097	900	98.1	1.6	0.0	99.7	98.5	1.5	0.0
T101	800	98.0	1.0	0.0	99.0	99.1	0.9	0.0

$$\text{Mol \% Sp} = 100.00 - 303.38R + 336.5R^2 - 137.84R^3$$

where $R = I_{wz(100)}/[I_{sp(111)} + I_{wz(002)}]$. The coefficients for this equation were obtained from X-ray patterns of mixtures of pure sphalerite and wurtzite made at ten mol % intervals of composition.

The chemical compositions of the phases were determined with an ETEC electron microprobe (EDX) at the University of Toronto or a JEOL 50A electron microprobe (WDX) at Fukuoka University of Education, with metallic zinc and synthetic GaP, GaS, Ga₂S₃ and ZnS as standards. The analytical results, each an average of several grains, are shown in Table 2. All analytical errors are within ±0.1 wt.%. Chemical formulae were calculated for each phase from normalized atomic proportions.

SOLID SOLUTIONS

Along the join ZnS-Ga₂S₃, four solid solutions exist: (Zn,Ga)_{1-x}S, phase V, including the composition ZnGa₂S₄, phase U, including the composition ZnGa₈S₁₃, and (Ga,Zn)₂S₃. Along the join Zn-Ga, zinc liquid and gallium liquid have small fields of miscibility at both temperatures. These four solid-solutions and two liquids are described as follows.

(Zn,Ga)_{1-x}S solid solution

According to Ueno & Scott (1991), the maximum solubility of gallium in zinc sulfide is 24.9 atomic % at 900°C (Zn_{20.1}Ga_{24.9}S_{55.0}) and 16.3 atomic % at 800°C (Zn_{29.5}Ga_{16.3}S_{54.2}). Members of this solid solution have a bluish grey color in reflected light and no anisotropy. From X-ray-diffraction patterns, the phase produced at 800°C (except the pure ZnS composition) is a mixture of sphalerite and wurtzite structures and, at 900°C, sphalerite, wurtzite or mixed sphalerite and wurtzite structures (Table 1). Table 3 shows the X-ray data and cell size of the (Zn,Ga)_{1-x}S solid solu-

TABLE 3. X-RAY POWDER-DIFFRACTION DATA FOR SPHALERITE AND (Zn,Ga)_{1-x}S SOLID SOLUTION

1			2		3		4		5		6	
Sphalerite			(Zn,Ga) _{1-x} S solid solution									
d(Å)	I	hkl	d(Å)	I	d(Å)	I	d(Å)	I	d(Å)	I	d(Å)	I
3.123	100	111	3.121	100	3.108	100	3.085	100	3.064	100	3.055	100
2.705	10	200	2.704	6	2.687	2	2.667	4	2.653	3	2.642	4
1.912	51	220	1.9088	67	1.8983	50	1.8839	34	1.8725	65	1.8682	40
1.633	30	311	1.6274	40	1.6190	32	1.6053	15	1.5964	31	1.5934	26
a(Å)	5.4060		5.399(2)		5.370(2)		5.327(3)		5.297(2)		5.285(1)	
Ga/(Zn+Ga)	0.000		0.051		0.214		0.413		0.495		0.553	

1: JCPDS card 5-566, ZnS; 2: T071, Zn_{16.7}Ga_{2.8}S_{50.5}; 3: T070, Zn_{17.4}Ga_{10.2}S_{52.4}; 4: T047, Zn_{16.5}Ga_{18.8}S_{54.2}; 5: T186, Zn_{13.0}Ga_{22.8}S_{54.2}; 6: T027, Zn_{20.1}Ga_{24.9}S_{55.0}

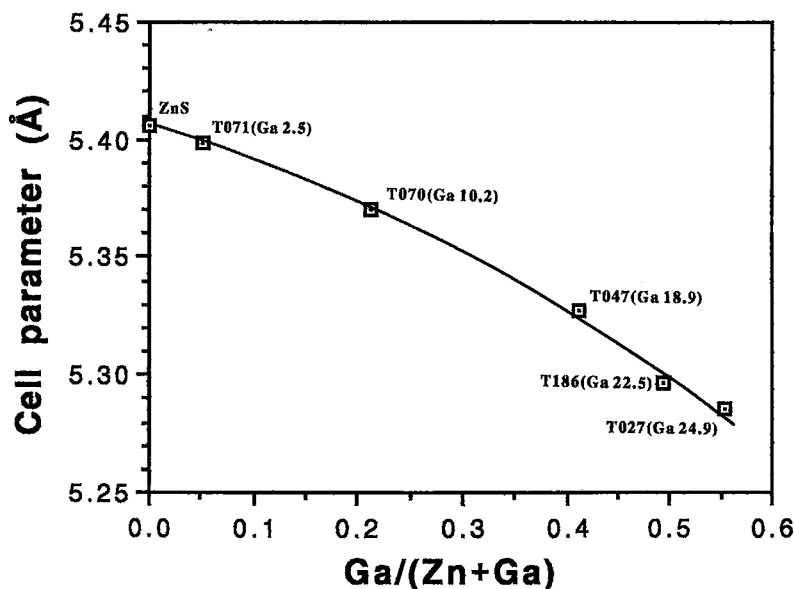


FIG. 1. Relationship between unit-cell parameter a of Ga-bearing sphalerite and composition, expressed as Ga/(Zn + Ga) ratio. Numbers in brackets express the atomic % of Ga.

tion (sphalerite type). Figure 1 is a plot of the unit-cell size of Ga-bearing sphalerite solid-solution *versus* chemical composition, given as the atomic ratio Ga/(Zn + Ga). The unit-cell parameter decreases from 5.4060 Å to 5.285 Å with increasing gallium content for reasons of ionic size and valence, as explained by Ueno & Scott (1991). The cell parameter of the resulting defect structure is described by the quadratic equation $a(\text{Å}) = 5.406 - 0.1282X - 0.1692X^2$, where X is the atomic ratio of Ga/(Zn + Ga).

Phase V solid-solution

Phase V has a pale grey color in reflected light and is yellowish white internal reflections. Its composition ranges from $\text{Zn}_{17.4}\text{Ga}_{25.7}\text{S}_{56.9}$ to $\text{Zn}_{10.7}\text{Ga}_{31.0}\text{S}_{58.3}$ at 900°C, and from $\text{Zn}_{17.0}\text{Ga}_{26.0}\text{S}_{57.0}$ to $\text{Zn}_{9.3}\text{Ga}_{32.1}\text{S}_{58.6}$ at 800°C, and includes the stoichiometric composition ZnGa_2S_4 ($\text{Zn}_{14.3}\text{Ga}_{28.6}\text{S}_{57.1}$) of Hahn *et al.* (1955) at both temperatures. Phase V solid-solution produces tetragonal-sphenoidal crystals (Fig. 2a) that give an X-ray pattern consistent with tetragonal symmetry (Table 4). The cell parameters of phase V decrease with increasing Ga-content.

(Ga,Zn)₂S₃ solid-solution

The upper stability-limit of Ga_2S_3 is 1090°C (Lieth *et al.* 1966). This phase has a restricted field of solid

solution in the system Zn–Ga–S and contains a maximum of 2.2 atomic % Zn at 900° and 1.7 atomic % Zn at 800°C. Ga_2S_3 has a dirty grey color in reflected light and whitish yellow internal reflections. The powder-diffraction data have been given by Goodyear *et al.* (1961) and Ueno & Scott (1991).

TABLE 4. X-RAY POWDER-DIFFRACTION DATA FOR ZnGa_2S_4 AND PHASE V

ZnGa_2S_4		Phase V						
1		2		3		4		
d(Å)	I	d(Å)	I	d(Å)	I	d(Å)	I	
5.196	3	0.02	5.27	2		5.27	3	
4.711	14	0.11	4.746	12	4.710	5	4.751	18
3.730	6	1.10	3.751	4	3.720	2	3.754	7
3.034	100	1.12	3.052	100	3.024	100	3.048	100
2.902	8	0.13	2.921	5	2.903	2	2.915	7
2.637	3	0.20	2.647	2	2.626	2	2.648	2
2.604	2	0.04	2.618	1			2.606	1
2.356	4	0.22	2.362	4	2.348	2	2.361	5
2.302	12	1.21	2.309	6	2.299	2	2.309	7
2.137	2	1.14	2.148	2			2.143	2
1.9538	3	1.23	1.9577	3	1.9505	1	1.9561	4
1.9382	4	0.15						
1.8655	21	2.20	1.8711	22				
1.8537	26	0.24	1.8611	42	1.8483	44	1.8574	40
1.7572	3	2.22	1.7597	1			1.7590	1
1.7351	4	0.31	1.7379	3			1.7385	2
1.6684	2	1.30	1.6722	1			1.6698	1
1.5894	22	1.32	1.5924	19	1.5861	6	1.5918	18
1.5743	9	1.16	1.5829	9	1.5767	19	1.5745	6
1.5622	1	1.25						
1.5171	2	2.24	1.5218	1			1.5190	1
tetragonal:		tetragonal:		tetragonal:		tetragonal:		
a (Å)	5.2779(2)	a (Å)	5.289(3)	a (Å)	5.262(3)	a (Å)	5.287(2)	
c (Å)	10.4179(8)	c (Å)	10.496(8)	c (Å)	10.436(9)	c (Å)	10.428(6)	

1: JCPDS Card No. 40-1462, Lowe-Ma (1990), $\text{Zn}_{14.3}\text{Ga}_{28.6}\text{S}_{57.1}$

2: T-140, $\text{Zn}_{17.0}\text{Ga}_{26.0}\text{S}_{57.0}$; 3: T-098, $\text{Zn}_{9.3}\text{Ga}_{32.1}\text{S}_{58.6}$; 4: T-122, $\text{Zn}_{9.3}\text{Ga}_{32.1}\text{S}_{58.6}$



FIG. 2. Scanning electron micrographs for (a) phase V and (b) phase U. The scale bar is 10 μm in (a) and 1 μm in (b).

Phase U solid-solution

Between phase V solid-solution and $(\text{Ga,Zn})_2\text{S}_3$ solid-solution at 900° and 800°C, there is a small field of solid solution that we have named phase U. Its compositional range is from $\text{Zn}_{7.3}\text{Ga}_{32.9}\text{S}_{59.8}$ to $\text{Zn}_{3.1}\text{Ga}_{37.1}\text{S}_{59.8}$ at 900°C and from $\text{Zn}_{5.3}\text{Ga}_{34.4}\text{S}_{60.3}$ to

$\text{Zn}_{3.0}\text{Ga}_{37.2}\text{S}_{59.8}$ at 800°C. The stoichiometric composition of $\text{ZnGa}_8\text{S}_{13}$ ($\text{Zn}_{4.5}\text{Ga}_{36.4}\text{S}_{59.1}$) of Gates & Edwards (1978) lies just outside this solid-solution area. Phase U produces tetrahedral crystals (Fig. 2b) that have a greyish white color in reflected light and yellowish internal reflections. Table 5 compares X-ray powder-diffraction data for the $\text{ZnGa}_8\text{S}_{13}$ phase of

TABLE 5. X-RAY POWDER-DIFFRACTION DATA FOR $ZnGaS_3$ AND PHASE U

1 $ZnGaS_3$			2		3	
$d(\text{\AA})$	I	hkl	$d(\text{\AA})$	I	$d(\text{\AA})$	I
3.34	20	310				
3.02	100	222	3.033	100	3.023	100
2.61	20	400	2.629	2	2.620	1
2.04	10	431			2.0474	1
1.843	90	440	1.8490	49	1.8468	55
1.739	10L	600				
1.573	80	622	1.5804	19	1.5750	25
1.506	10L	444	1.5128	1		
1.304	40	800	1.3140	2	1.3048	4
cubic:			cubic:		cubic:	
$a(\text{\AA})$	10.436(2)		10.493(8)		10.444(4)	

1: JCPDS Card No. 41-0797, Gates & Edwards (1978), $Zn_{0.5}Ga_{0.5}S_{1.5}$ 2: T-142, $Zn_{0.2}Ga_{0.2}S_{0.6}$ 3: T-120, $Zn_{0.6}Ga_{0.6}S_{1.8}$

Gates & Edwards (1978) with our phase U. The reflections (310) and (600) were not observed in our phase U.

Zinc liquid

Zinc was in the liquid state during the experiments (melting point 419.4°C , normal boiling point about 930°C). Zinc solid is a pinkish white phase in-

reflected light and has strong anisotropy, with blue, brown and yellow colors. After quenching in water, solid zinc contains 1.5 atomic % Ga at 900°C and 0.9 atomic % Ga at 800°C (Table 2). No exsolved phases were seen in reflected-light microscopy at $400\times$ magnification.

Gallium liquid

Gallium also was in the liquid state during the experiments (melting point 29.8°C , normal boiling point about 2300°C). Pure gallium solid is bright white, and zinc-containing gallium is yellowish white in reflected light. Both pure gallium and zinc-containing gallium have very strong reflection anisotropy, from blue to brown. Water-quenched solid gallium contains 8.7 atomic % Zn at 900°C , and 5.3 atomic % Zn at 800°C (Table 2). No exsolved phases were seen at $400\times$ magnification.

DISCUSSION

Phase diagrams of the ternary system Zn-Ga-S at 900°C (Fig. 3) and 800°C (Fig. 4) have been constructed from the experimental results in Table 1 and the chemical compositions of the phases in Table 2.

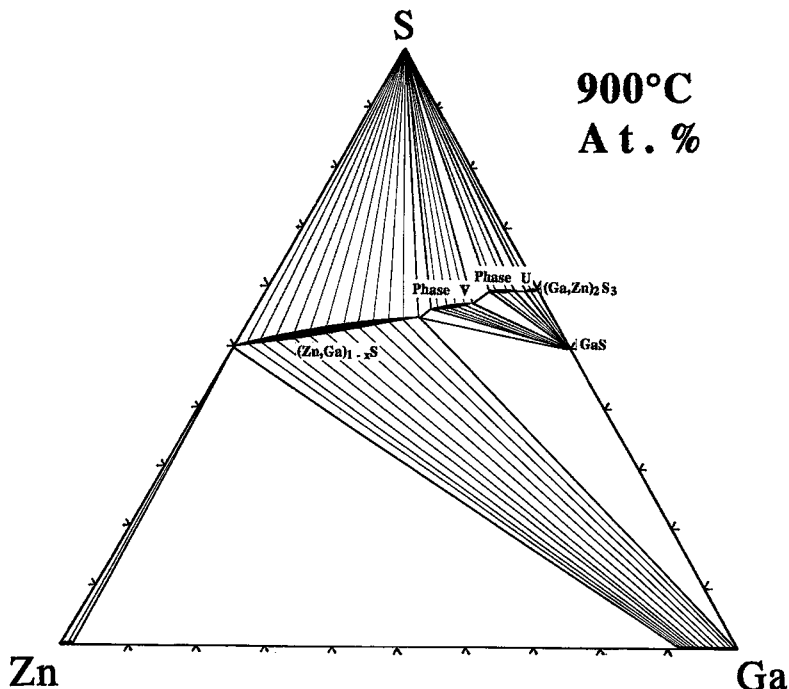


FIG. 3. Phase relations in the system Zn-Ga-S at 900°C determined by dry synthesis.

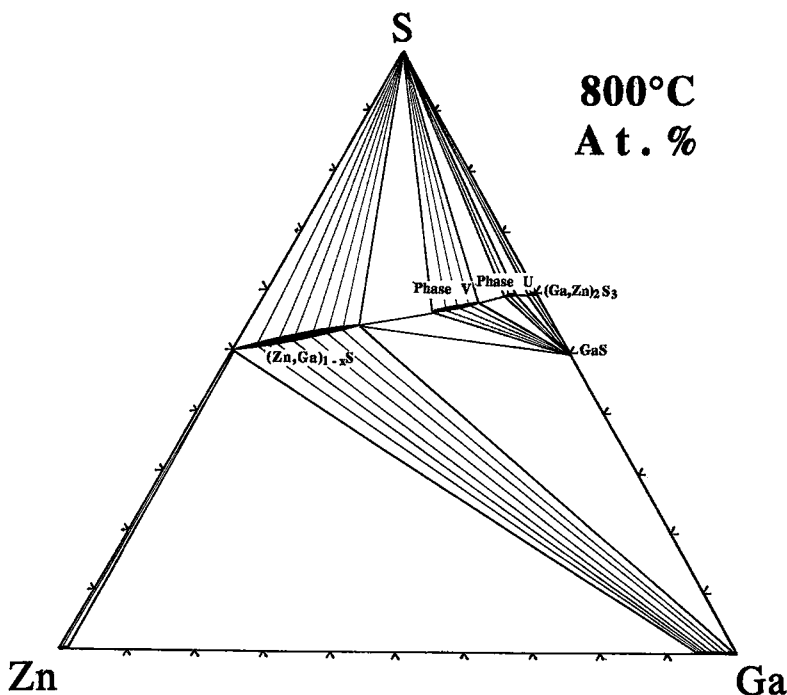


FIG. 4. Phase relations in the system Zn-Ga-S at 800°C determined by dry synthesis.

Tic-line relations are essentially the same at both temperatures. Eight phases exist in the following univariant assemblages at both temperatures: $(\text{Zn,Ga})_{1-x}\text{S} + \text{Zn} + \text{Ga}$, $(\text{Zn,Ga})_{1-x}\text{S} + \text{phase V} + \text{S}$, phase V + phase U + S, phase U + $\text{Ga}_2\text{S}_3 + \text{S}$, phase U + $\text{Ga}_2\text{S}_3 + \text{GaS}$, phase U + phase V + GaS, phase V + $(\text{Zn,Ga})_{1-x}\text{S} + \text{GaS}$, and $(\text{Zn,Ga})_{1-x}\text{S} + \text{GaS} + \text{Ga}$.

According to the pseudobinary phase-diagram for Ga_2S_3 - ZnGa_2S_4 presented by Gates & Edwards (1978), Ga_2S_3 has a solid-solution field, their $\text{ZnGa}_8\text{S}_{13}$ phase is stable at temperatures less than 1070°C, and their ZnGa_2S_4 phase exists over a wide range of temperature. According to the diagram of Hahn *et al.* (1955), there is continuous solid-solution along the Ga_2S_3 - ZnS binary join at 900°C: Ga_2S_3 contains up to about 20 mol % ZnS and has a sphalerite structure, the solid solution from $(\text{Ga}_2\text{S}_3)_{80}(\text{ZnS})_{20}$ to $(\text{Ga}_2\text{S}_3)_{35}(\text{ZnS})_{65}$ has a tetragonal structure, the solid solution from $(\text{Ga}_2\text{S}_3)_{35}(\text{ZnS})_{65}$ to $(\text{Ga}_2\text{S}_3)_{10}(\text{ZnS})_{90}$ has a wurtzite structure, and the phase containing more than 90% ZnS has a sphalerite structure. Hahn *et al.* (1955) also determined that the stoichiometric ZnGa_2S_4 phase of Gates & Edwards (1978) is a member of this extensive solid-solution, and that the cell dimensions of all phases increase with ZnS content.

Our results (Figs. 3, 4) agree reasonably well with those of Hahn *et al.* (1955) on the join ZnS - Ga_2S_3 , the

main difference being the compositional gaps that we have determined between the four solid-solution fields of $(\text{Zn,Ga})_{1-x}\text{S}$, phase V, phase U and $(\text{Ga,Zn})_2\text{S}_3$. The stoichiometric $\text{ZnGa}_8\text{S}_{13}$ and ZnGa_2S_4 phases of Gates & Edwards (1978) are included in these solid solutions. The solid-solution field determined by Hahn *et al.* (1955) to extend from Ga_2S_3 to $(\text{Ga}_2\text{S}_3)_{80}(\text{ZnS})_{20}$ corresponds to our $(\text{Ga,Zn})_2\text{S}_3$ and phase U solid-solutions. The $(\text{Ga,Zn})_2\text{S}_3$ solid solution has monoclinic symmetry, as does α - Ga_2S_3 , and phase U has the sphalerite structure. However, at both 800° and 900°C, our phase U is distinctly more sulfur-rich than compositions on the join. The solid solution of Hahn *et al.* from $(\text{Ga}_2\text{S}_3)_{80}(\text{ZnS})_{20}$ to $(\text{Ga}_2\text{S}_3)_{35}(\text{ZnS})_{65}$ corresponds to our phase V solid-solution, having a tetragonal structure, and their solid solution from $(\text{Ga}_2\text{S}_3)_{35}(\text{ZnS})_{65}$ to $(\text{Ga}_2\text{S}_3)_{10}(\text{ZnS})_{90}$ corresponds to our $(\text{Zn,Ga})_{1-x}\text{S}$ solid-solution.

At 800°C, our run products for the entire $(\text{Zn,Ga})_{1-x}\text{S}$ solid-solution were found to be a mixture of sphalerite and wurtzite structures. Lacking single-crystal X-ray data for our fine-grained experimental products, we have not determined whether these are mechanical mixtures of end-member sphalerite (3C) and wurtzite (2H) structures or are true polytypes (see Scott 1974). At 900°C, we obtained a sphalerite structure, a wurtzite structure or a mixture of sphalerite and

wurtzite structures depending on composition. Pure ZnS and the Ga-rich end of the solid solution (run T027) gave a sphalerite structure, neighboring areas to both ends (run T069, T047 and T186), a mixture of sphalerite and wurtzite structures, and the intermediate area (run T068 and T096) of this solid solution, a wurtzite structure. Although thermodynamic considerations require that sphalerite and wurtzite coexisting as separate phases must have different Ga contents, we were not able to distinguish these individual phases with the electron microprobe.

A good explanation for the structural complexity within the $(\text{Zn,Ga})_{1-x}\text{S}$ solid solutions is lacking, although metastability probably plays a role. Nonstoichiometry in the ratio of metal to sulfur, as proposed by Scott & Barnes (1972) to explain the stability of sphalerite (low metal/sulfur value) versus wurtzite (high metal/sulfur value) in the pure Zn-S system, cannot be the explanation here because the sphalerite structure was the one produced at 900°C in the most sulfur-poor composition of $(\text{Zn,Ga})_{1-x}\text{S}$ (run T097 in Tables 1 and 2). Scott & Barnes (1972) pointed out that the activation energy for the production of wurtzite from sphalerite in the pure Zn-S system is considerably greater than that required for the reverse reaction. This means that it is easier for sphalerite to exist metastably relative to wurtzite than the reverse. By analogy, in the case of mixed sphalerite and wurtzite forms in the $(\text{Zn,Ga})_{1-x}\text{S}$ solid solution, the wurtzite form may be stable, and the sphalerite form, metastable. If this is indeed the case, the inversion temperature from the sphalerite to the wurtzite form of the intermediate compositions of the $(\text{Zn,Ga})_{1-x}\text{S}$ solid solution is below 800°C, and it depends on chemical composition and perhaps sulfur fugacity.

Phase U is distinctly more sulfur-rich by 1.1 atomic % at both 800° and 900°C than expected for a composition on the Ga_2S_3 -ZnS binary join. The reason for this nonstoichiometry is not known, but a refinement of its crystal structure would probably reveal the answer.

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