

PHASE RELATIONS IN THE SYSTEM Ga-Fe-S AT 900°C AND 800°C

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ABSTRACT

Phase relations in the system Ga-Fe-S were investigated by dry synthesis at 900°C and 800°C. Three ternary phases (Z, W and X) were found in the central portion of this system. Phase Z has a sphalerite-type X-ray-diffraction pattern and a compositional range from $\text{Ga}_{37.7}\text{Fe}_{3.4}\text{S}_{58.9}$ to $\text{Ga}_{28.0}\text{Fe}_{13.7}\text{S}_{58.3}$ at 900°C and from $\text{Ga}_{35.9}\text{Fe}_{4.2}\text{S}_{59.9}$ to $\text{Ga}_{28.4}\text{Fe}_{13.9}\text{S}_{57.7}$ at 800°C. Phase W is hexagonal and has an X-ray powder pattern similar to that of the Ga_2FeS_4 phase of Pardo *et al.* (1981), but the composition is different and is close to stoichiometric $\text{Ga}_{12}\text{Fe}_9\text{S}_{29}$. Phase X is tetragonal; its composition is close to stoichiometric $\text{Ga}_{21}\text{Fe}_{22}\text{S}_{57}$. Other phases obtained in this study are GaS, Ga_2S_3 , pyrrhotite solid-solution, gallium liquid, alloy Y, α -iron, and sulfur liquid. Both GaS (maximum 0.1 at.% iron) and Ga_2S_3 (maximum 1.8 at.% iron at 900°C and 1.0 at.% iron at 800°C) have very small fields of solid solution. Pyrrhotite solid-solution contains a maximum of 0.5 at.% Ga at 900°C and 0.4 at.% Ga at 800°C. Gallium liquid contains 1.7 at.% iron at 900°C and 1.1 at.% iron at 800°C. Alloy Y has an extensive solid-solution area, from $\text{Ga}_{73.5}\text{Fe}_{26.5}\text{S}_{0.2}$ to $\text{Ga}_{22.7}\text{Fe}_{77.1}\text{S}_{0.2}$ at 900°C and from $\text{Ga}_{57.6}\text{Fe}_{42.2}\text{S}_{0.2}$ to $\text{Ga}_{24.0}\text{Fe}_{75.7}\text{S}_{0.3}$ at 800°C. Alpha-iron has a compositional range from Fe_{100} to $\text{Fe}_{82}\text{Ga}_{18}$ at 900°C and to $\text{Fe}_{89.9}\text{Ga}_{10.1}$ at 800°C.

Keywords: Ga-Fe-S system, phase equilibrium, solid solution, dry synthesis.

SOMMAIRE

Nous avons étudié les relations de phases dans le système Ga-Fe-S par synthèse en milieu sec à 900° et 800°C. Nous avons trouvé trois phases ternaires (Z, W et X) dans la partie centrale de ce système. Le cliché de diffraction de la phase Z ressemble à celui de la sphalérite; cette phase varie en composition entre $\text{Ga}_{37.7}\text{Fe}_{3.4}\text{S}_{58.9}$ et $\text{Ga}_{28.0}\text{Fe}_{13.7}\text{S}_{58.3}$ à 900°C, et entre $\text{Ga}_{35.9}\text{Fe}_{4.2}\text{S}_{59.9}$ et $\text{Ga}_{28.4}\text{Fe}_{13.9}\text{S}_{57.7}$ à 800°. La phase W est hexagonale; son cliché de diffraction ressemble à celui de la phase Ga_2FeS_4 de Pardo et al. (1981), mais la composition est différente, et plus proche de la stoechiométrie $\text{Ga}_{12}\text{Fe}_9\text{S}_{29}$. La phase X est tétraédrique, et sa composition se rapproche de la stoechiométrie $\text{Ga}_{21}\text{Fe}_{22}\text{S}_{57}$. En plus, nous avons reconnu GaS, Ga_2S_3 , solution solide de pyrrhotite, gallium liquide, alliage Y, fer sous forme α , et soufre liquide. Les phases GaS (contenant au maximum 0.1% de fer, base atomique) et Ga_2S_3 (maximum de 1.8% de fer à 900°C et 1.0% à 800°C) montrent un champ de solution solide très limité. La solution solide de pyrrhotite contient un maximum de 0.5% (base atomique) de Ga à 900°C et 0.4% à 800°C. Le gallium liquide contient 1.7% de fer (base atomique) à 900°C et 1.1% à 800°C. L'alliage Y forme une solution solide dont l'étendue va de $\text{Ga}_{73.5}\text{Fe}_{26.5}\text{S}_{0.2}$ à $\text{Ga}_{22.7}\text{Fe}_{77.1}\text{S}_{0.2}$ à 900°C et de $\text{Ga}_{57.6}\text{Fe}_{42.2}\text{S}_{0.2}$ à $\text{Ga}_{24.0}\text{Fe}_{75.7}\text{S}_{0.3}$ à 800°C. La composition de la forme α du fer varie de Fe_{100} jusqu'à $\text{Fe}_{82}\text{Ga}_{18}$ à 900°C, et jusqu'à $\text{Fe}_{89.9}$ à 800°C.

(Traduit par la Rédaction)

Mots-clés: système Ga-Fe-S, équilibre des phases, solution solide, synthèse par voie sèche.

INTRODUCTION

Sphalerite is a common host for trace amounts of gallium in sulfide ores (Sheka *et al.* 1966), and a zinc-iron sulfide from the YAMATO-74370(EH4) chondrite contains up to 5.8 wt.% Ga (Nagahara & El Goresy 1984). Ueno & Scott (1991) presented some experimental results in an attempt to explain the geochemistry and phase behavior of gallium in zinc- and

iron-containing sulfide systems. The maximum solubility of Ga in sphalerite in the system Zn-Ga-S is 24.9 at.% at 900°C and 16.3 at.% at 800°C. In the system Zn-Fe-Ga-S, gallium solubility exceeds 21.4 at.% in wurtzite (with 14.6 at.% Fe) at 900°C and 27.4 at.% in sphalerite (with 7.5 at.% Fe) at 800°C.

To fully understand the controls on gallium content in zinc sulfides from outer space and earth and to elucidate the stability relations between Ga-bearing

sphalerite and wurtzite, it is necessary to construct the quaternary phase diagram for the system Zn-Fe-Ga-S. However, in order to do this, the ternary phase relations of the bounding Zn-Fe-S, Zn-Ga-S, Ga-Fe-S and Zn-Fe-Ga systems must first be known.

The Zn-Fe-S system has been well studied from 200° to 900°C (Barton & Toulmin 1966, Scott & Barnes 1971). The Ga₂S₃-ZnS binary join in the system Zn-Ga-S was investigated at 900°C by Hahn *et al.* (1955), and the Ga₂S₃-FeS join in the system Ga-Fe-S from 400° to 1200°C by Pardo *et al.* (1981). Ternary phase relations for these two Ga-bearing systems have not been previously determined.

As a further contribution toward understanding the full quaternary system, we have examined the Ga-Fe-S ternary system by dry synthesis at 900° and 800°C. Experimental work is proceeding on the only remaining sulfide-bearing bounding ternary system, Ga-Zn-S, and on the full quaternary system.

EXPERIMENTS

Elemental Fe, Ga and S, all of 99.9% purity or better, and two synthetic monosulfides (FeS and GaS), 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 mixed by grinding in an agate mortar and sealed in evacuated silica tubes with an oxy-propane gas flame. The tubes were heated in an electric furnace at 900° and 800°C and were quenched in cold water after 20 to 24 days (900°C runs) or 33 to 62 days (800°C runs). Products were examined by reflected light microscopy and by X-ray powder diffractometry (Mn-filtered FeK α radiation and high-energy CuK α radiation), with Si as an internal standard. Cell parameters were calculated for some phases by the least-squares method from precisely measured *d*-values.

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, using metallic iron and synthetic GaP, GaS, Ga₂S₃ and troilite 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

GaS and Ga₂S₃

According to Lieth *et al.* (1966), the upper stability-limits of GaS and Ga₂S₃ are 962° and 1090°C, respec-

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

Run no.	Temp.(°C)	Reactants	Bulk compositions (At. %)			Heating days	Products
			Ga	Fe	S		
T050	900	GaS+FeS	25.0	25.0	50.0	24	X:Z+Y
T064	900	9GaS+FeS	45.0	5.0	50.0	21	GaS+Z+Y
T065	900	7GaS+3FeS	35.0	15.0	50.0	21	GaS+Z+Y
T066	900	3GaS+7FeS	15.0	35.0	50.0	21	X+Po+Y
T067	900	GaS+9FeS	5.0	45.0	50.0	21	X+Po+Y
T078	900	6GaS+FeS+6S	30.0	5.0	65.0	24	Z+S
T079	900	4GaS+3FeS+6S	20.0	15.0	65.0	24	W+S
T080	900	2GaS+5FeS+6S	10.0	25.0	65.0	24	W+Po+S
T082	900	3GaS+3FeS+8Ga	55.0	15.0	30.0	24	GaS+Y
T083	900	GaS+5FeS+8Ga	5.0	65.0	30.0	24	α +Po
T102	900	GaS+FeS+6Ga	70.0	10.0	20.0	23	GaS+Ga+Y
T103	900	GaS+FeS+6Fe	10.0	70.0	20.0	23	α +Y+Po
T104	900	5GaS+3FeS+4S	25.0	15.0	60.0	23	W+Z+S
T108	900	2GaS+3FeS+10Fe	10.0	65.0	25.0	21	Po+ α +Y
T113	900	20GaS+FeS+8S	40.0	2.0	58.0	20	Ga ₂ S ₃ +Z+GaS
T126	900	33GaS+2FeS+30S	33.0	2.0	65.0	20	Z+Ga ₂ S ₃ +S
T059	800	9GaS+FeS	45.0	5.0	50.0	33	GaS+Z+Y
T060	800	7GaS+3FeS	35.0	15.0	50.0	33	GaS+Z+Y
T061	800	3GaS+7FeS	15.0	35.0	50.0	33	X+Po+Y
T062	800	GaS+9FeS	5.0	45.0	50.0	33	X+Po+Y
T084	800	6GaS+FeS+6S	30.0	5.0	65.0	62	Z+S
T085	800	4GaS+3FeS+6S	20.0	15.0	65.0	62	W+S
T086	800	2GaS+5FeS+6S	10.0	25.0	65.0	62	W+Po+S
T087	800	3GaS+3FeS+8Ga	55.0	15.0	30.0	62	GaS+Y+Ga
T088	800	GaS+5FeS+8Fe	5.0	65.0	30.0	62	Po+ α +Y
T127	800	20GaS+FeS+8S	40.0	2.0	58.0	40	Ga ₂ S ₃ +Z+GaS
T128	800	33GaS+2FeS+30S	33.0	2.0	65.0	40	Z+Ga ₂ S ₃ +S

X:Phase X, Y:Alloy Y, Z:Phase Z, W:Phase W, Po:Pyrrhotite, α : α -iron, S:sulfur-liquid, Ga:gallium-liquid

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

Run no.	Temp.(°C)	Weight %			Total	Atomic %		
		Ga	Fe	S		Ga	Fe	S
GaS solid solution								
T064	900	68.4	0.1	31.5	100.0	49.9	0.1	50.0
T082	900	67.8	0.0	31.2	99.0	50.0	0.0	50.0
T102	900	68.6	0.0	31.6	100.2	50.0	0.0	50.0
T059	800	67.7	0.1	31.6	99.4	49.6	0.1	50.3
T087	800	68.4	0.1	31.8	100.3	49.7	0.1	50.2
Ga₂S₃ solid solution								
T113	900	57.0	2.1	40.2	99.3	38.8	1.8	59.4
T127	800	57.1	1.2	40.2	98.5	39.1	1.0	59.9
Phase Z								
T065	900	42.5	16.5	40.7	99.7	28.0	13.6	58.4
T050	900	42.7	16.7	40.9	100.3	28.0	13.7	58.3
T078	900	51.6	6.2	41.0	98.8	34.8	5.2	60.0
T113	900	55.9	4.0	40.2	100.1	37.7	3.4	58.9
T126	900	54.8	4.4	39.6	98.8	37.4	3.8	58.8
T084	800	51.8	6.4	40.9	99.1	34.8	5.4	59.8
T060	800	43.0	16.7	40.2	99.9	28.4	13.8	57.8
T051	800	43.1	16.9	40.3	100.3	28.4	13.9	57.7
T127	800	53.9	5.0	41.4	100.3	35.9	4.2	59.9
T128	800	53.1	5.2	41.1	99.4	35.6	4.4	60.0
Phase W								
T079	900	37.8	22.3	41.3	101.4	24.3	17.9	57.8
T080	900	37.7	22.4	41.4	101.5	24.2	18.0	57.8
T104	900	38.4	20.8	40.8	100.0	25.1	17.0	57.9
T085	800	36.3	22.4	40.9	99.6	23.7	18.3	58.1
T086	800	36.4	22.5	40.8	99.7	23.8	18.3	57.9
Phase X								
T050	900	32.6	27.4	40.3	100.3	21.1	22.2	56.7
T066	900	32.3	27.5	40.6	100.4	20.9	22.1	57.0
T051	800	32.7	26.9	40.3	99.9	21.3	21.8	56.9
T061	800	32.3	27.0	40.5	99.8	21.0	21.8	57.2
Pyrrhotite solid solution								
T066	900	0.8	61.7	35.9	98.4	0.5	49.4	50.1
T080	900	0.6	59.5	40.0	100.1	0.4	45.9	53.7
T083	900	0.2	64.1	36.7	101.0	0.1	50.0	49.9
T103	900	0.1	63.7	36.5	100.3	0.1	50.0	49.9
T061	800	0.7	61.8	36.2	98.7	0.4	49.3	50.3
T086	800	0.5	59.7	39.8	100.0	0.3	46.1	53.6
T088	800	0.0	63.7	36.7	100.4	0.0	49.9	50.1
Alloy Y								
T050	900	30.1	69.8	0.2	100.1	25.6	74.1	0.3
T064	900	34.6	65.0	0.1	99.7	29.8	70.0	0.2
T066	900	27.0	73.6	0.1	100.7	22.7	77.1	0.2
T082	900	69.5	29.7	0.1	99.3	65.2	34.7	0.1
T102	900	77.3	22.4	0.1	99.9	73.5	26.3	0.2
T051	800	30.2	69.6	0.1	99.9	25.7	74.1	0.2
T059	800	32.6	66.3	0.1	99.0	28.2	71.6	0.2
T062	800	28.2	71.2	0.2	99.6	24.0	75.7	0.3
T087	800	62.4	36.7	0.1	99.2	57.6	42.2	0.2
α-iron								
T103	900	17.3	81.5	0.0	98.8	14.5	85.5	0.0
T108	900	21.5	78.4	0.0	99.9	18.0	82.0	0.0
T088	800	12.2	87.3	0.0	99.5	10.1	89.9	0.0
Gallium liquid								
T102	900	98.2	1.4	0.0	99.6	98.3	1.7	0.0
T087	800	98.3	0.7	0.1	99.3	98.7	1.1	0.2

tively. As shown in Table 2, GaS has a very small field of solid solution, and contains a maximum of 0.1 atomic % iron. The phase has a yellow color and forms hexagonal crystals (Fig. 1a). Ga₂S₃ also has a small field of solid solution, and contains a maximum of 1.8 atomic % iron at 900°C and 1.0 atomic % iron at 800°C. This phase is a sugar-like transparent white material made up of polyhedral crystals (Fig. 1b). Both GaS and Ga₂S₃ form polymorphs: β-GaS, HP-GaS, ε-GaS; α-Ga₂S₃, β-Ga₂S₃, γ-Ga₂S₃ (Goodman *et al.* 1985, Hahn & Frank 1955). The X-ray-diffraction data for these two phases are given by Ueno & Scott (1991).

Phases Z, W and X

In the central portion of the system, three ternary phases were found and are named provisionally phases Z, W and X. Phase Z has a bluish gray color in reflected light, and shows no anisotropy. Scanning electron micrographs reveal tetrahedral crystals (Fig. 2a). The X-ray pattern is that of a sphalerite structure (Table 3). However, the cell parameter of Phase Z is considerably smaller than that of sphalerite and decreases with increasing gallium content, from 5.262 Å (28.0 at.% Ga) to 5.219 Å (37.7 at.% Ga). Phase Z occupies a solid-solution field that extends from Ga_{37.7}Fe_{3.4}S_{58.9} to Ga_{28.0}Fe_{13.7}S_{58.3} at 900°C, and from Ga_{35.9}Fe_{4.2}S_{59.9} to Ga_{28.4}Fe_{13.9}S_{57.7} at 800°C. The gallium-rich compositions of Phase Z (T078, T084, T113, T126, T127, and T128 in Table 2) have orange to red internal reflections.

Phase W is a dark gray phase in reflected light, has a strong reflection anisotropy from dark gray to yellowish white, and forms hexagonal crystals

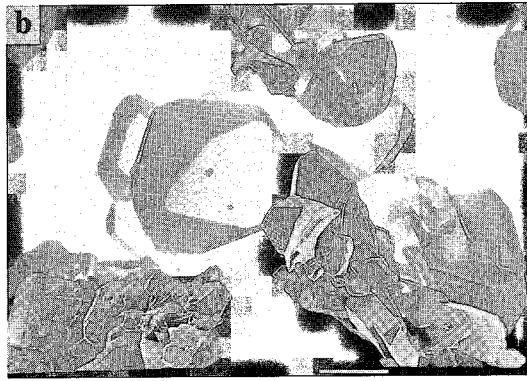


FIG. 1. Scanning electron micrographs of (a) GaS and (b) β-Ga₂S₃. Scale bars are 10 μm in (a) and 100 μm in (b).

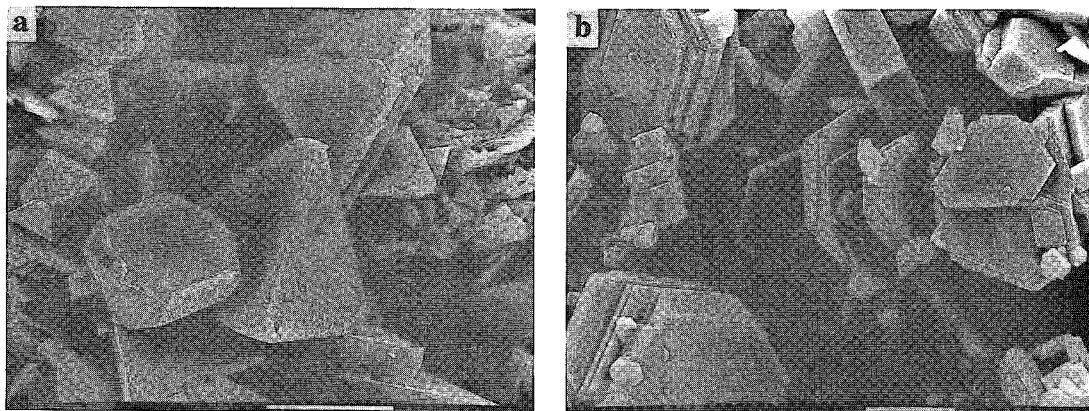


FIG. 2. Scanning electron micrographs of (a) Phase Z and (b) Phase W. Scale bars in (a) and (b) correspond to 5 μm .

(Fig. 2b). Powder X-ray diffraction reveals Phase X to be hexagonal. It has a powder X-ray-diffraction pattern similar to that of the hexagonal Ga_2FeS_4 phase of Pardo *et al.* (1981) (Table 4), but the compositions of these two phases are significantly different. Phase W has only a small field of solid solution at both temperatures, with a composition close to stoichiometric $\text{Ga}_{12}\text{Fe}_9\text{S}_{29}$.

Phase X has a brownish gray color in reflected light and strong reflection anisotropy, from dark gray to grayish white. Needle-like or sword-like crystals are common (Fig. 3a). X-ray-diffraction measurements show that this Phase X is tetragonal. It has only a small field of solid solution at both temperatures, with a composition close to stoichiometric $\text{Ga}_{21}\text{Fe}_{22}\text{S}_{57}$.

Pyrrhotite solid-solution

According to Kullerud & Yoder (1959) and Kullerud (1967), the pyrrhotite solid-solution extends from stoichiometric FeS to $\text{Fe}_{43.7}\text{S}_{56.3}$ at 900°C and to $\text{Fe}_{44.2}\text{S}_{55.8}$ at 800°C. In the system Ga–Fe–S, pyrrhotite contains a maximum of 0.5 at.% Ga at 900°C and 0.4 at.% Ga at 800°C (Table 2). Optically, Ga-bearing pyrrhotite is similar to pure pyrrhotite in the Fe–S system.

Gallium liquid, alloy Y and α -iron

Three phases exist along the Ga–Fe join at 900° and 800°C: gallium liquid, alloy Y and α -iron. The melting point of gallium is 29.8°C; it contains a maximum of 1.7 at.% Fe at 900°C and 1.1 at.% Fe at 800°C (Table 2). Gallium has two crystal structures, cubic and orthorhombic (PDF 31–539, and 5–601, respec-

tively). Pure gallium is bright white in reflected light, and iron-containing gallium obtained in this study is yellowish white. Both have strong anisotropy from bright yellow to dark green, so are probably of the orthorhombic form.

Alloy Y [(Fe,Ga) alloy] is a yellowish white phase in reflected light and has weak anisotropy from pinkish gray to greenish gray. According to Kroll (1932), gallium alloys easily with iron. Dasarathy (1964) reported an alloy $\text{Fe}_{70}\text{Ga}_{30}$ with a primitive cubic cell. Our alloy Y, on the other hand, is tetragonal according to its powder-diffraction pattern (Ueno & Scott 1991) and has an extensive field of solid solution, from $\text{Ga}_{73.5}\text{Fe}_{26.3}\text{S}_{0.2}$ to $\text{Ga}_{22.7}\text{Fe}_{77.1}\text{S}_{0.2}$ at 900°C, and from $\text{Ga}_{57.6}\text{Fe}_{42.2}\text{S}_{0.2}$ to $\text{Ga}_{24.0}\text{Fe}_{75.7}\text{S}_{0.3}$ at 800°C.

TABLE 3. X-RAY POWDER-DIFFRACTION DATA FOR SPHALERITE AND PHASE Z

1 Sphalerite			2 Phase Z			3 Phase Z		
d(Å)	I	hkl	d _{obs} (Å)	d _{calc} (Å)	I	d _{obs} (Å)	d _{calc} (Å)	I
3.123	100	111	3.039	3.038	100	3.020	3.014	100
2.705	10	200	2.629	2.631	1	2.612	2.610	2
1.912	51	220	1.8586	1.8601	26	1.8460	1.8454	46
1.633	30	311	1.5870	1.5863	9	1.5730	1.5737	16
a=5.4060 Å			a=5.262(2) Å			a=5.219(2) Å		

1: JCPDS card 5-566, ZnS
 2: T050: Fe_{13.7}Ga_{28.3}S_{58.3}
 3: T113: Fe_{42.7}Ga_{7.7}S_{59.9}

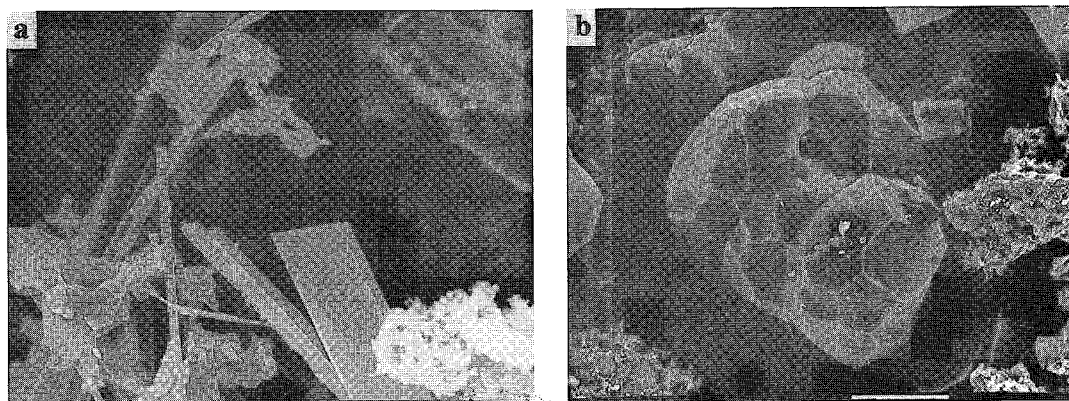
TABLE 4. X-RAY POWDER-DIFFRACTION DATA FOR PHASE X, PHASE W AND FeGa₂S₄

1 Phase X				2 Phase W				3 FeGa ₂ S ₄		
d _{obs} (Å)	d _{calc} (Å)	I	hkl	d _{obs} (Å)	d _{calc} (Å)	I	hkl	d(Å)	I	hkl
14.9	15.0	22	001	12.2	12.2	4	001			
7.49	7.50	8	002	6.10	6.08	12	002	6.05	38	002
5.00	5.00	38	003	4.080	4.052	100	003	4.021	13	003
3.753	3.751	100	004							
3.144	3.150	5	200	3.200	3.188	6	100	3.179	25	100
2.997	3.001	3	005	3.090	3.084	24	101	3.075	100	101
2.766	2.769	6	211	2.830	2.823	20	102			
2.501	2.501	10	006	2.510	2.506	5	103	2.493	25	103
2.263		4		2.438	2.431	9	005	2.416	25	005
2.250	2.253	2	214	2.204	2.200	22	104	2.186	63	104
2.142	2.143	2	007	1.9356	1.9331	16	105	1.9230	63	105
1.8337	1.8324	7	304	1.8420	1.8407	23	110	1.8340	63	110
				1.7636	1.7617	1	112			
1.7211	1.7206	4	305	1.7368	1.7364	5	007	1.7270	25	007
				1.7098	1.7098	29	106	1.7010	100	106
1.6667	1.6670	6	009	1.6762	1.6758	10	113	1.6690	63	113
				1.5806	1.5805	3	201	1.5750	25	201
				1.5413	1.5419	2	202	1.5370	25	202
1.5007	1.5003	5	0010	1.5180	1.5193	1	008	1.5090	25	008
				1.4826	1.4834	1	203	1.4780	25	203
				1.4662	1.4675	2	115			
				1.4109	1.4116	3	204			
tetragonal: a = 6.300(2)Å c = 15.003(3)Å				hexagonal: a = 3.681(1)Å c = 12.155(5)Å				hexagonal: a = 3.669Å c = 12.079Å		

1: This study, T051 Ga_{21.3}Fe_{21.8}S_{56.9}2: This study, T104 Ga_{25.1}Fe_{17.0}S_{57.9}3: Pardo *et al.* (1981), JCPDS card 35-1290, Ga_{28.6}Fe_{14.3}S_{57.1}

Alpha-iron developed well-formed crystals in our experiments (Fig. 3b). This phase has cubic symmetry, on the basis of powder-diffraction data. Compositional

ranges are from Fe₁₀₀ to Fe₈₂Ga₁₈ at 900°C, and from Fe₁₀₀ to Fe_{89.9}Ga_{10.1} at 800°C.

FIG. 3. Scanning electron micrographs of (a) Phase X and (b) α -iron. Scale bars are 5 μ m in (a) and 10 μ m in (b).

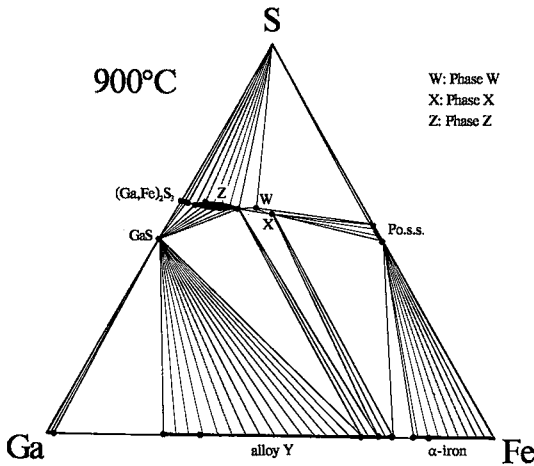


FIG. 4. Phase diagram for the system Ga-Fe-S at 900°C, as determined by dry synthesis. Dots are experimentally determined compositions.

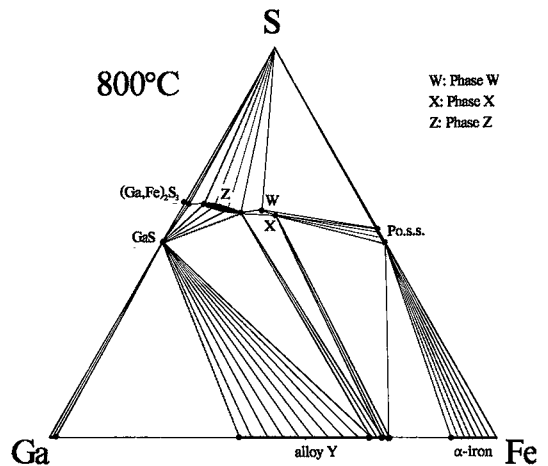


FIG. 6. Phase diagram for the system Ga-Fe-S at 800°C, as determined by dry synthesis. Dots are experimentally determined compositions.

DISCUSSION

Phase diagrams of the ternary system Ga-Fe-S at 900° and 800°C have been constructed (Figs. 4, 5, 6, and 7) from the experimental results (Table 1) and the chemical compositions of the phases (Table 2). Tie-line relations are essentially the same at both 900° and

800°C. The only significant difference lies in the size of the solid-solution fields of Phase Z, alloy Y, α-iron and pyrrhotite. There are eleven univariant assemblages: Ga + GaS + alloy Y, GaS + alloy Y + Phase Z, Phase Z + alloy Y + Phase X, Phase X + alloy Y + Po_{ss}, Po_{ss} + alloy Y + α-iron, Po_{ss} + Phase X + Phase W, Phase W + Po_{ss} + S, S + Phase Z + Phase W, S +

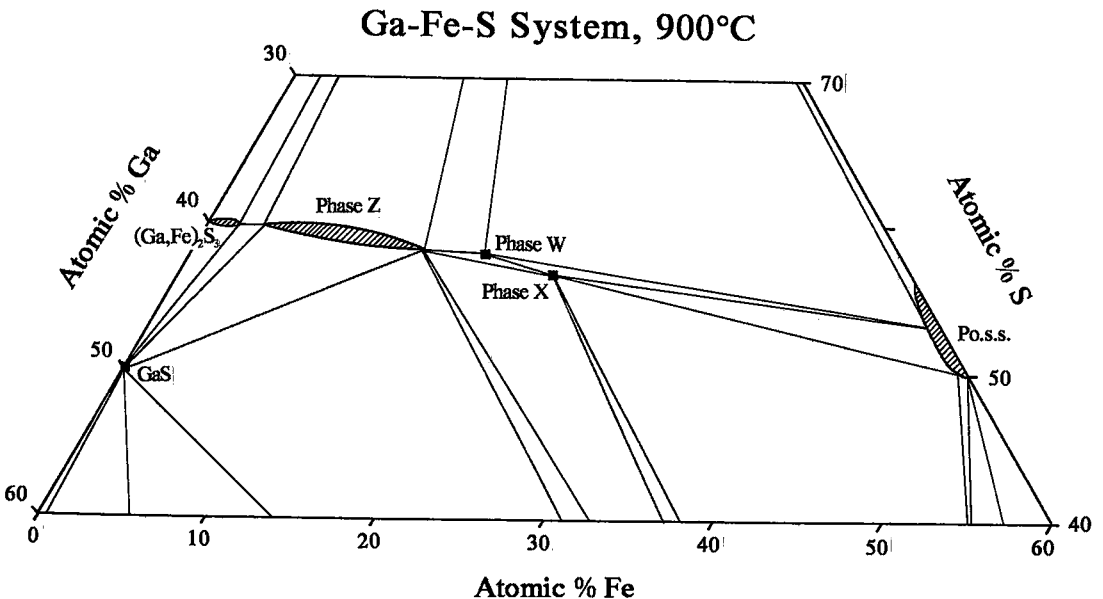


FIG. 5. Details of phase relations in the central portion of the system Ga-Fe-S at 900°C.

Ga-Fe-S System, 800°C

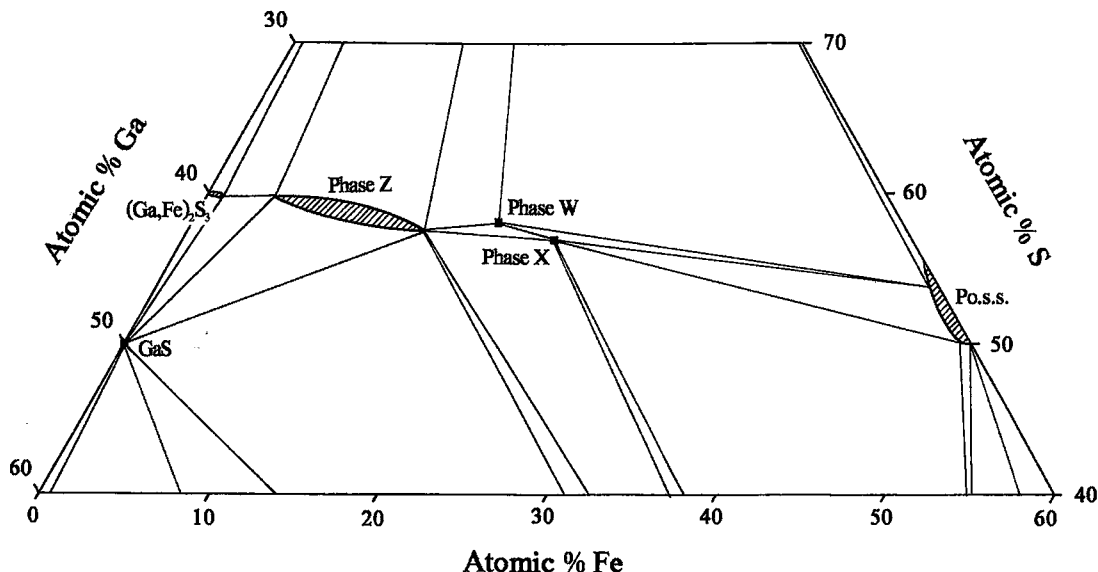


FIG. 7. Details of phase relations in the central portion of the system Ga-Fe-S at 800°C.

Phase Z + Ga_2S_3 , Ga_2S_3 + GaS + Phase Z and Phase Z + Phase X + Phase W. Phase Z has a moderate solid-solution field and a sphalerite structure. Ueno & Scott (1991) explained the structure of Ga-bearing sphalerite and wurtzite by means of a solid-solution model of $(\text{Zn},\text{Fe},\text{Ga},\square)\text{S}$, where \square represents a vacancy, or $(\text{Zn},\text{Fe},\text{Ga})_{1-x}\text{S}$. Assuming Phase Z to be a zinc-free sphalerite analogue, its formula may be written as $(\text{Ga},\text{Fe},\square)\text{S}$ or $(\text{Ga},\text{Fe})_{1-x}\text{S}$. Phase W and Phase X are stoichiometric $\text{Ga}_{12}\text{Fe}_9\text{S}_{29}$ and $\text{Ga}_{21}\text{Fe}_{22}\text{S}_{57}$, respectively. However, in order to maintain charge balance, vacancies must exist in the sulfur site; $2(\text{GaS}) \cdot 5(\text{Ga}_2\text{S}_3) \cdot 9(\text{FeS}) \cdot 3(\square\text{S})$ for Phase W and $(\text{GaS}) \cdot 10(\text{Ga}_2\text{S}_3) \cdot 22(\text{FeS}) \cdot 4(\square\text{S})$ for Phase X.

Pardo *et al.* (1981) presented X-ray-diffraction data for FeGa_2S_4 phases (hexagonal and orthorhombic forms), $\text{Fe}_2\text{Ga}_2\text{S}_5$ phases (hexagonal and rhombohedral forms), a $(\text{Fe}_x\text{Ga}_{8-2x})_3\text{S}_4$ phase (hexagonal form) and a $\text{Fe}_{0.73}\text{Ga}_{2.18}\text{S}_4$ phase (tetragonal form). Compositionally, their $\text{Fe}_{0.73}\text{Ga}_{2.18}\text{S}_4$ phase ($\text{Fe}_{10.6}\text{Ga}_{31.5}\text{S}_{57.9}$) is nearly included within the solid-solution field of our Phase Z, but the X-ray-diffraction data are different. Conversely, the X-ray data for our Phase W are similar to those for the FeGa_2S_4 phase (hexagonal form) of Pardo *et al.* (1981), but the chemical composition is different. Pardo *et al.* conducted synthesis experiments along the Ga_2S_3 -FeS join at different Fe/(Fe + Ga) ratios and identified phases by X-ray diffraction. However, they did not chemically

analyze their products, which probably explains the differences between the two sets of results.

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