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PHASE EQUILIBRIA IN THE SYSTEM Cu–Ga–S AT 500° AND 400°C

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ABSTRACT

Phase equilibria in the system Cu–Ga–S were investigated by dry synthesis at 500° and 400°C using the three elements (Cu, Ga and S) and four synthetic sulfides (CuS, Cu_2S, GaS and Ga_2S_3) as starting materials; we established the phase diagrams for this ternary system at both temperatures. Gallite, the only reported mineral in the system, is located in the central position in these diagrams, and many tie lines extend from it to other phases; covellite, digenite, phases α, ζ, γ, GaS, X and and sulfur. Gallite shows essentially no solid solution with the other phases, appearing as stoichiometric $CuGaS_2$. On the join between gallite and Ga_2S_3, a new phase, named X, was found. It is whitish gray with yellow internal reflections in reflected light. It is optically very similar to Ga_2S_3, but its X-ray powder-diffraction data show a tetragonal symmetry. The cell parameters are *a* 2.250, *c* 10.474 Å. It has a limited solid-solution field ranging from $Cu_{10.0}Ga_{31.7}S_{58.3}$ to $Cu_{10.5}Ga_{32.5}S_{57.0}$ at 500°C and from $Cu_{9.7}Ga_{32.2}S_{58.1}$ to $Cu_{10.4}Ga_{32.2}S_{57.3}$ at 400°C. Digenite contains between 0.2 and 0.4 at.% Ga, GaS contains from 1.1 to 1.4 at.% Cu, and Ga_2S_3 contains from 0.9 to 1.0 at.% Cu at both temperatures. Along the Cu–Ga join, five phases, labeled α, ζ, γ, ω and gallium liquid, exist at both temperatures. The phases α, ζ, and γ are connected to gallite with tie lines, and the phases γ, ω, and gallium liquid are connected to GaS with tie lines at both temperatures.

Keywords: system Cu–Ga–S, phase equilibria, dry synthesis, gallite, phase X.

SOMMAIRE

Nous avons étudié les équilibres de phases dans le système Cu–Ga–S par synthèses à sec à 500° et 400°C en utilisant comme matériaux de départ les trois éléments (Cu, Ga et S) et quatre sulfures synthétiques (CuS, Cu_2S, GaS et Ga_2S_3); nous avons établi les diagrammes de phases pour ce système ternaire aux deux températures. La gallite, le seul minéral connu dans ce système, est situé à une position centrale dans ces diagrammes, et plusieurs lignes de coexistence vont de ce point vers les autres phases: covellite, digénite, α, ζ, γ, GaS, X et soufre. La gallite ne montre quasiment aucun écart à la composition idéale, $CuGaS_2$. Nous avons établi l'existence d'une nouvelle phase, X, sur le joint entre gallite et Ga_2S_3. Cette phase est blanchâtre avec des réflexions internes jaunes en lumière réfléchie; elle est optiquement très semblable au Ga_2S_3, mais son spectre de diffraction montre qu'il s'agit d'une phase tétragonale. Ses paramètres réticulaires sont *a* 2.250, *c* 10.474 Å. Elle fait preuve d'une solution solide limitée allant de $Cu_{10.0}Ga_{31.7}S_{58.3}$ à $Cu_{10.5}Ga_{32.5}S_{57.0}$ à 500°C et de $Cu_{9.7}Ga_{32.2}S_{58.1}$ à $Cu_{10.4}Ga_{32.2}S_{57.3}$ à 400°C. La digénite contient de 0.2 à 0.4% Ga (proportion atomique), GaS contient entre 1.1 à 1.4% Cu, et Ga_2S_3 contient entre 0.9 et 1.0% Cu aux deux températures. Sur la lignée Cu–Ga, cinq phases, désignées α, ζ, γ, ω et gallium liquide, existent aux deux températures. Les phases α, ζ, et γ sont connectées à la gallite par des lignes de coexistence, et les phases γ, ω, et gallium liquide sont connectées à GaS par des lignes de coexistence aux deux températures.

(Traduit par la Rédaction)

Mots-clés: système Cu–Ga–S, équilibre des phases, synthèse à sec, gallite, phase X.

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INTRODUCTION

Copper, one of the principal metallic elements, has been widely used since prehistory; on the other hand, gallium only recently has been found useful in high technology (*e.g.,* semiconductors, radiation detectors and cathodoluminescent display devices). In nature, only one phase of the ternary system Cu–Ga–S has been described until now, by Strunz *et al.* (1958). They found the $CuGaS_2$ phase in the ores from Tsumeb mine in Namibia, and Kipushi mine (Prince Leopold mine) in the Democratic Republic of Congo. Both Tsumeb and Kipushi mines are hydrothermal vein-type ore deposits and produce Cu–Fe–Zn–Pb–S ores containing rare metals (Ge and Ga). According to Strunz *et al.* (1958), gallite occurs in association with germanite, renierite, sphalerite, galena, chalcopyrite, pyrite, bornite, and chalcocite.

PREVIOUS EXPERIMENTAL STUDIES

Phase equilibria of the Cu–S system have received much attention from mineralogists and economic geologists, so that this binary system is now well understood (*e.g.,* Roseboom 1966). Lieth *et al.* (1966, 1967) studied the phase relations in the system Ga–S using the sublimation method, and presented the P–T–X phase diagram of this binary system. Weibke (1934), Hume-Rothery & Raynor (1937) and Betterton & Hume-Rothery (1951–1952) investigated phase relations in the system Cu–Ga and showed this binary diagram from 0° to 1,100°C from the metallurgical point of view. Hahn *et al.* (1953) first synthesized $CuGaS_2$ phase using the evacuated silica-tube method (900°–1000°C, 12 hours heating) from a mixture of Cu_2S and Ga_2S_3, and found that it has a chalcopyrite structure.

Here, we present the first phase-equilibrium study of the ternary system Cu–Ga–S at 500° and at 400°C in order to elucidate the field of stability of $CuGaS_2$, gallite, and the phase relations in this ternary system, including the discovery of a new phase. These temperatures are important for understanding the genesis of ore deposits and also are suitable for the attainment of the equilibrium state in synthetic experiments.

EXPERIMENTAL

We performed dry-synthesis equilibrium experiments in the system Cu–Ga–S in evacuated pyrex tubes. Elemental Cu (99.999% purity), Ga (99.9999% purity) and crystalline S (99.999% purity), and four synthetic sulfides (CuS, Cu_2S, GaS and Ga_2S_3) were used as starting materials. Syntheses of GaS and Ga_2S_3, and other experimental details, are described in Ueno & Scott (1991).

Reactants were mixed by grinding in an agate mortar and sealed in evacuated pyrex tubes with an oxy-propane gas flame. The tubes were heated in an electric furnace at 500° and 400°C, and quenched in cold water after heating for 60 to 70 days at 500°C and 90 to 100 days at 400°C. These experiment durations are considered adequate to attain the equilibium state, because we examined the phase assemblages of products from the point of view of the phase rule. Products were examined by reflected light microscopy and by X-ray powder diffractometry (Mac Science high-energy X-ray diffractometer, Ni-filtered Cu$K\alpha$ 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. The chemical compositions of the phases synthesized were determined using a JEOL 50A electron microprobe. Operating conditions were 25 kV accelerating voltage and 20 nA probe current (measured on a MgO crystal). Synthetic CuS, Cu_2S, GaS, and Ga_2S_3 and metallic Cu were used as standards.

RESULTS

In Tables 1 and 2, we show the experimental results for the joins CuS–GaS, Cu_2S–GaS and CuS–Ga_2S_3 at 500° and at 400°C, respectively. In Tables 3 and 4, we show the experimental results for the Cu_2S–Ga_2S_3, CuS–Ga, Cu–GaS and Cu–Ga joins at 500° and at 400°C, respectively. These tables show the assemblages

TABLE 1. EXPERIMENTAL RESULTS FOR THE CuS–GaS, Cu_2S–GaS AND CuS–Ga_2S_3 JOINS AT 500°C

Run no.	Reactants	Bulk compositions			Duration (days)	Products
		Cu	Ga	S		
NA007	9CuS + GaS	45.0	5.0	50.0	60	cv + gal
NA008	8CuS + 2GaS	40.0	10.0	50.0	60	cv + gal
NA009	7CuS + 3GaS	35.0	15.0	50.0	60	cv + gal
NA010	6CuS + 4GaS	30.0	20.0	50.0	60	cv + gal
NA011	5CuS + 5GaS	25.0	25.0	50.0	60	gal
NA012	4CuS + 6GaS	20.0	30.0	50.0	60	gal + GaS
NA013	3CuS + 7GaS	15.0	35.0	50.0	60	gal + GaS
NA014	2CuS + 8GaS	10.0	40.0	50.0	60	gal + GaS
NA015	CuS + 9GaS	5.0	45.0	50.0	60	gal + GaS
NA025	$9Cu_2S$ + GaS	62.1	3.4	34.5	70	α + dg + gal
NA026	$8Cu_2S$ + 2GaS	57.7	7.1	35.7	70	α + dg + gal
NA027	$7Cu_2S$ + 3GaS	51.9	11.1	37.0	70	α + dg + gal
NA028	$6Cu_2S$ + 4GaS	46.2	15.4	38.5	70	α + dg + gal
NA029	$5Cu_2S$ + 5GaS	40.0	20.0	40.0	70	α + dg + gal
NA030	$4Cu_2S$ + 6GaS	33.3	25.0	41.7	70	gal + ζ
NA031	$3Cu_2S$ + 7GaS	26.1	30.4	43.5	70	gal + GaS + γ
NA032	$2Cu_2S$ + 8GaS	18.2	36.4	45.4	70	gal + GaS + γ
NA033	Cu_2S + 9GaS	9.5	42.9	47.6	70	gal + GaS + γ
NA040	9CuS + Ga_2S_3	39.1	8.7	52.2	65	cv + gal + S
NA041	8CuS + $2Ga_2S_3$	30.8	15.4	53.8	65	cv + gal + S
NA042	7CuS + $3Ga_2S_3$	24.1	20.7	55.2	65	cv + gal + S
NA043	6CuS + $4Ga_2S_3$	18.8	25.0	56.2	65	gal + X + S
NA044	5CuS + $5Ga_2S_3$	14.3	28.6	57.1	65	gal + X + S
NA045	4CuS + $6Ga_2S_3$	10.5	31.6	57.9	65	gal + X + S
NA046	3CuS + $7Ga_2S_3$	7.3	34.2	58.5	65	Ga_2S_3 + X + S
NA047	2CuS + $8Ga_2S_3$	4.5	36.4	59.1	65	Ga_2S_3 + X + S
NA048	CuS + $9Ga_2S_3$	2.1	38.3	59.6	65	Ga_2S_3 + X + S

Symbols: cv: covellite, gal: gallite, GaS: GaS phase, α: phase α, dg: digenite, ζ: phase ζ, γ: phase γ, S: sulfur, Ga_2S_3: phase Ga_2S_3, X: phase X. The bulk compositions are quoted in atom %.

of reactants, bulk compositions (atom %), duration of the experiments and the reacted products.

In the join CuS–GaS, covellite, gallite and GaS were produced at both temperatures. In the runs having the bulk composition of $Cu_{25}Ga_{25}S_{50}$, (single phase) gallite was synthesized. Along the join Cu_2S–GaS, the phases α, digenite, gallite, GaS, γ and Ω were produced at both temperatures. Along the join CuS–Ga_2S_3, covellite, gallite, sulfur, phase X and Ga_2S_3 were produced at both temperatures. Phase X had not been encountered before (see below). Along the join Cu_2S–Ga_2S_3, gallite, digenite, phase X, GaS and Ga_2S_3 were produced at both temperatures. Along the join CuS–Ga, gallite, digenite, covellite, phases α, Ω, γ, GaS, ω and Ga liquid were produced at both temperatures. Along the last join, Cu–Ga, the phases α, Ω, γ, ω and Ga liquid were produced at both temperatures. The results of the electron-microprobe analyses, each an average of measurements on several grains, are shown in Tables 5 and 6. All analytical errors are within 0.1 weight %.

Descriptions of synthesized phases

Gallite forms small irregularly shaped grains (less than 20 μm) in polished thin section and coexists with covellite, digenite, GaS, phase X, sulfur, phases α, Ω and γ. Gallite is brownish gray in reflected light and

TABLE 2. EXPERIMENTAL RESULTS FOR THE CuS–GaS, Cu_2S–GaS AND CuS–Ga_2S_3 JOINS AT 400°C

Run no.	Reactants	Bulk compositions Cu	Ga	S	Duration (days)	Products
MU-009	9CuS + GaS	45.0	5.0	50.0	90	cv + gal
MU-010	8CuS + 2GaS	40.0	10.0	50.0	90	cv + gal
MU-011	7CuS + 3GaS	35.0	15.0	50.0	90	cv + gal
MU-012	6CuS + 4GaS	30.0	20.0	50.0	90	cv + gal
MU-013	5CuS + 5GaS	25.0	25.0	50.0	90	gal
MU-029	4CuS + 6GaS	20.0	30.0	50.0	90	gal + GaS
MU-028	3CuS + 7GaS	15.0	35.0	50.0	90	gal + GaS
MU-014	2CuS + 8GaS	10.0	40.0	50.0	90	gal + GaS
MU-015	CuS + 9GaS	5.0	45.0	50.0	90	gal + GaS
HO-005	$9Cu_2S$ + GaS	62.1	3.4	34.5	95	α + dg + gal
HO-006	$8Cu_2S$ + 2GaS	57.7	7.1	35.7	95	α + dg + gal
HO-007	$7Cu_2S$ + 3GaS	51.9	11.1	37.0	95	α + dg + gal
HO-008	$6Cu_2S$ + 4GaS	46.2	15.4	38.5	95	α + dg + gal
HO-009	$5Cu_2S$ + 5GaS	40.0	20.0	40.0	95	α + dg + gal
HO-010	$4Cu_2S$ + 6GaS	33.3	25.0	41.7	95	gal + ζ + γ
HO-011	$3Cu_2S$ + 7GaS	26.1	30.4	43.5	95	gal + GaS + γ
HO-012	$2Cu_2S$ + 8GaS	18.2	36.4	45.4	95	gal + GaS + γ
HO-013	Cu_2S + 9GaS	9.5	42.9	47.6	95	gal + GaS + γ
HO-017	3CuS + $7Ga_2S_3$	7.3	34.2	58.5	95	Ga_2S_3 + X + S
MU-019	9CuS + Ga_2S_3	39.1	8.7	52.2	90	cv + gal + S
MU-020	8CuS + $2Ga_2S_3$	30.8	15.4	53.8	90	cv + gal + S
MU-022	7CuS + $3Ga_2S_3$	24.1	20.7	55.2	90	cv + gal + S
MU-021	6CuS + $4Ga_2S_3$	18.8	25.0	56.2	90	gal + X + S
MU-023	5CuS + $5Ga_2S_3$	14.3	28.6	57.1	90	gal + X + S
MU-024	4CuS + $6Ga_2S_3$	10.5	31.6	57.9	90	gal + X + S
MU-025	3CuS + $7Ga_2S_3$	7.3	34.2	58.5	90	Ga_2S_3 + X + S
MU-026	2CuS + $8Ga_2S_3$	4.5	36.4	59.1	90	Ga_2S_3 + X + S
MU-027	CuS + $9Ga_2S_3$	2.1	38.3	59.6	90	Ga_2S_3 + X + S

Symbols: cv: covellite, gal: gallite, GaS: GaS phase, α: phase α, dg: digenite, ζ: phase ζ, γ: phase γ, S: sulfur, Ga_2S_3: phase Ga_2S_3, X: phase X. The bulk compositions are quoted in atom %.

TABLE 3. EXPERIMENTAL RESULTS FOR THE Cu_2S–Ga_2S_3, CuS–Ga, Cu–GaS AND Cu–Ga JOINS AT 500°C

Run no.	Reactants	Bulk compositions Cu	Ga	S	Duration (days)	Products
CGS-009	$7Cu_2S$ + 3 Ga_2S_3	38.9	16.7	44.4	60	gal + dg
CGS-010	Cu_2S + Ga_2S_3	25.0	25.0	50.0	60	gal
CGS-011	$3Cu_2S$ + 7 Ga_2S_3	13.6	31.8	54.6	60	X + gal + GaS
CGS-012	Cu_2S + 4 Ga_2S_3	8.7	34.8	56.5	60	X + gal + GaS
CGS-013	Cu_2S + 9 Ga_2S_3	4.2	37.5	58.3	60	X + Ga_2S_3 + GaS
CGS-001	4CuS + Ga	44.5	11.0	44.5	60	gal + dg + cv
CGS-002	7CuS + 3Ga	41.2	17.6	41.2	60	gal + dg + α
CGS-003	3CuS + 2Ga	37.5	25.0	37.5	60	gal + γ + ζ
CGS-004	CuS + Ga	33.3	33.3	33.3	60	gal + GaS + γ
CGS-005	2CuS + 3Ga	28.5	43.0	28.5	60	γ +GaS + gal
CGS-006	3CuS + 7Ga	23.1	53.8	23.1	60	γ +GaS + ω
CGS-007	4Cu + GaS	66.7	16.6	16.6	60	gal + α + dg
CGS-008	Cu + GaS	33.3	33.3	33.3	60	gal + GaS + γ
CGS-014	CuS + 4Ga	16.6	66.7	16.6	60	GaS + ω + Ga
CGS-015	CuS + 9Ga	9.1	81.8	9.1	60	GaS + ω + Ga
CG-001	4Cu + Ga	80.0	20.0	0.0	70	α
CG-002	7Cu + 3Ga	70.0	30.0	0.0	70	γ
CG-003	3Cu + 2Ga	60.0	40.0	0.0	70	γ + ω
CG-004	Cu + Ga	50.0	50.0	0.0	70	γ + ω
CG-006	2Cu + 3Ga	40.0	60.0	0.0	70	γ + ω
CG-007	3Cu + 7Ga	30.0	70.0	0.0	70	ω + Ga
CG-008	3Cu + Ga	75.0	25.0	0.0	70	ζ + γ
CG-009	Cu + 4Ga	20.0	80.0	0.0	70	ω + Ga
CG-010	Cu + 9Ga	10.0	90.0	0.0	70	ω + Ga
CG-011	9Cu + Ga	90.0	10.0	0.0	70	α

Symbols: gal: gallite, dg: digenite, X: phase X, GaS: phase GaS, Ga_2S_3: phase Ga_2S_3, cv: covellite, α: phase α, γ: phase γ, ζ: phase ζ, ω: phase ω, Ga: gallium. The bulk compositions are quoted in atom %.

TABLE 4. EXPERIMENTAL RESULTS FOR THE Cu_2S–Ga_2S_3, CuS–Ga, Cu–GaS AND Cu–Ga JOINS AT 400°C

Run no.	Reactants	Bulk compositions Cu	Ga	S	Duration (days)	Products
KKM-023	$7Cu_2S$ + 3 Ga_2S_3	38.9	16.7	44.4	100	gal + dg
KKM-024	Cu_2S + Ga_2S_3	25.0	25.0	50.0	100	gal
KKM-025	$3Cu_2S$ + 7 Ga_2S_3	13.6	31.8	54.6	100	X + gal + GaS
KKM-026	Cu_2S + 4 Ga_2S_3	8.7	34.8	56.5	100	X + gal + GaS
KKM-027	Cu_2S + 9 Ga_2S_3	4.2	37.5	58.3	100	X+ Ga_2S_3 + GaS
KKM-003	4CuS + Ga	44.5	11.0	44.5	90	gal + dg + cv
KKM-004	7CuS + 3Ga	41.2	17.6	41.2	90	gal + dg + α
KKM-005	3CuS + 2Ga	37.5	25.0	37.5	90	gal + g + ζ
KKM-006	CuS + Ga	33.3	33.3	33.3	90	gal + GaS + γ
KKM-007	2CuS + 3Ga	28.5	43.0	28.5	90	gal + GaS + γ
KKM-008	3CuS + 7Ga	23.1	53.8	23.1	90	γ +GaS + ω
KKM-009	4Cu + GaS	66.7	16.6	16.6	100	gal + α + dg
CGS-016	Cu + GaS	33.3	33.3	33.3	100	gal + GaS + γ
KKM-010	4Cu + Ga	80.0	20.0	0.0	100	α
KKM-011	7Cu + 3Ga	70.0	30.0	0.0	100	ζ + γ
KKM-012	3Cu + 2Ga	60.0	40.0	0.0	100	γ + ω
KKM-013	Cu + Ga	50.0	50.0	0.0	100	γ + ω
KKM-019	2Cu + 3Ga	40.0	60.0	0.0	100	γ + ω
KKM-020	3Cu + 7Ga	30.0	70.0	0.0	100	ω
KKM-021	Cu + 4Ga	25.0	75.0	0.0	100	ω + Ga
KKM-022	Cu + 9Ga	20.0	80.0	0.0	100	ω + Ga
KKM-028	3Cu + Ga	75.0	25.0	0.0	100	ζ + γ
KKM-029	9Cu + Ga	90.0	10.0	0.0	100	α
KKM-030	CuS + 4Ga	16.6	66.7	16.6	100	GaS + ω + Ga
KKM-031	CuS + 9Ga	9.1	81.8	9.1	100	GaS + ω + Ga

Symbols: gal: gallite, dg: digenite, X: phase X, GaS: phase GaS, Ga_2S_3: phase Ga_2S_3, cv: covellite, α: phase α, γ: phase γ, ζ: phase ζ, ω: phase ω, Ga: gallium. The bulk compositions are quoted in atom %.

has weak anisotropy, from dark brownish gray to dark bluish gray. It is located in the central position of the Cu–Ga–S system, and its chemical composition is considered to be $CuGaS_2$ (Strunz *et al.* 1958). In our experiment, the reactants having the bulk composition of $CuGaS_2$ produce only gallite (Tables 1, 2), and the electron-probe micro-analyses show a nearly stoichiometric composition (Tables 5, 6). Gallite thus shows very limited solid-solution toward other phases at 500° and 400°C.

In Table 7, we present the X-ray-diffraction data on our sample of synthetic gallite so as to compare with the first data presented for this mineral, by Hahn *et al.* (1953). This mineral shows tetragonal symmetry similar to chalcopyrite. Except for the absence of a (008) reflection, our data are very similar to those of Hahn *et al.* (1953), and the cell parameters *a* and *c* are nearly the same. At the two localities of this mineral, Tsumeb and Prince Leopold mine, Strunz *et al.* (1958) found gallite to be a light gray mineral with a metallic luster, and located in germanite, $Cu_3(Ge,Fe)S_4$, and renierite, $Cu_3(Fe,Ge)S_4$, and as exsolution lamellae along (100) and (111) in sphalerite, and itself contains exsolution lamellae of sphalerite oriented on (001).

TABLE 5. CHEMICAL COMPOSITION OF PHASES IN THE SYSTEM Cu–Ga–S AT 500°C

Run no.	Cu	Ga	S	Total	Cu	Ga	S
		weight %				atom %	
			gallite				
CGS-002	32.7	35.1	32.7	100.5	25.2	24.7	50.1
CGS-003	32.3	35.6	32.6	100.5	25.0	25.1	49.9
CGS-004	32.3	35.1	32.2	99.6	25.2	25.0	49.8
CGS-010	32.5	35.6	32.8	100.9	25.0	25.0	50.0
			digenite				
CGS-002	79.2	0.4	20.1	99.7	66.3	0.3	33.4
			phase X				
CGS-011	14.0	47.6	38.4	100.0	10.5	32.5	57.0
CGS-013	13.5	46.9	39.6	100.0	10.0	31.7	58.3
			phase GaS				
CGS-005	1.7	67.3	31.5	100.5	1.3	48.9	49.8
CGS-006	1.8	66.0	31.5	99.3	1.4	48.4	50.2
CGS-015	1.8	67.2	31.7	100.7	1.4	48.7	49.9
			phase Ga_2S_3				
CGS-013	1.3	57.1	41.2	99.6	1.0	38.5	60.5
			phase α				
CG-001	78.5	21.4	0.0	99.9	80.1	19.9	0.0
CG-011	89.8	11.1	0.0	100.9	89.9	10.1	0.0
			phase ζ				
CG-008	75.1	24.7	0.0	99.8	76.9	23.1	0.0
			phase γ				
CG-003	62.6	37.3	0.0	99.9	64.8	35.2	0.0
CG-008	67.7	31.8	0.0	99.5	70.0	30.0	0.0
			phase ω				
CG-006	34.0	66.2	0.0	100.2	36.0	64.0	0.0
CG-010	30.9	68.7	0.0	99.6	33.0	67.0	0.0
			Ga liquid				
CG-010	2.4	97.1	0.0	99.5	2.6	97.4	0.0

Digenite occurs as small granular grains (less than 30 μm) or rectangularly shaped long grains (500 μm × 10 μm) in polished thin sections, and coexists with covellite, gallite and phase α. This phase is light gray-blue in reflected light and isotropic. According to Roseboom (1966), chalcocite, the orthorhombic low-temperature form of Cu_2S, is stable from below room temperature to 103.5°C, and according to Skinner (1966), it inverts upon heating to a hexagonal polymorph that remains stable to 420°C, at which point it inverts to a cubic polymorph. This cubic polymorph is considered to be continuous with the digenite solid-solution. Thus from the chemical composition point of view, digenite is a high-temperature form of chalcocite containing other elements (*e.g.*, iron) (Morimoto & Koto 1970). In the

TABLE 6. CHEMICAL COMPOSITION OF PHASES IN THE SYSTEM Cu–Ga–S AT 400°C

Run no.	Cu	Ga	S	Total	Cu	Ga	S
		weight %				atom %	
			gallite				
KKM-008	32.7	35.2	32.6	100.5	25.3	24.8	49.9
KKM-023	31.9	36.0	32.6	100.5	24.7	25.4	49.9
KKM-024	32.0	34.8	32.2	99.0	25.1	24.9	50.0
KKM-025	31.8	36.1	32.4	100.3	24.7	25.5	49.8
			digenite				
KKM-008	79.8	0.3	20.5	100.6	66.1	0.2	33.7
KKM-023	79.3	0.5	19.8	99.6	66.6	0.4	33.0
			phase X				
KKM-025	13.0	47.8	38.6	99.4	9.8	32.7	57.5
KKM-026	13.9	47.1	38.5	99.5	10.4	32.2	57.3
KKM-027	12.9	47.1	39.0	99.0	9.7	32.2	58.1
			phase Ga_2S_3				
KKM-026	1.2	57.6	39.8	98.6	0.9	39.6	59.5
KKM-027	1.0	58.1	40.1	99.2	0.7	39.7	59.6
			phase γ				
CGS-016	65.8	34.0	0.0	99.8	67.9	32.1	0.0
KKM-019	61.0	38.8	0.0	99.8	63.3	36.7	0.0
			phase ω				
KKM-019	33.4	66.5	0.0	99.9	35.5	64.5	0.0
KKM-020	28.1	71.4	0.0	99.5	30.2	69.8	0.0
			Ga liquid				
KKM-021	2.0	97.7	0.0	99.7	2.2	97.8	0.0

case of our experiments, it is stabilized by gallium, from 0.2 to 0.4 atom % (Tables 5, 6).

Phase X is a new phase produced in this experiment. It appears as very small grains (less than 10 μm) in polished thin sections and coexists with gallite, GaS, Ga_2S_3 and sulfur. It is whitish gray with yellow internal reflections in reflected light and is optically very similar to Ga_2S_3. The phase Ga_2S_3 is also whitish gray, but its internal reflections are bluish yellow. Phase X has a limited solid-solution field, ranging from $Cu_{10.0}Ga_{31.7}S_{58.3}$ to $Cu_{10.5}Ga_{32.5}S_{57.0}$ at 500°C (Table 5) and from $Cu_{9.7}Ga_{32.2}S_{58.1}$ to $Cu_{10.4}Ga_{32.2}S_{57.3}$ at 400°C (Table 6). Table 8 shows the X-ray powder-diffraction data for α-Ga_2S_3 and phase X. The latter is tetragonal, *a* 2.250, *c* 10.474 Å.

The phases GaS and Ga_2S_3 were described completely by Ueno & Scott (1991). In the present experiments, phase GaS contains up to 1.4 atom % Cu at 500°C (Table 5) and 1.1 atom % Cu at 400°C (Table 6). Phase Ga_2S_3 contains up to 1.0 atom % Cu at 500°C (Table 5) and 0.9 atom % Cu at 400°C (Table 6). The Cu-doped GaS and Ga_2S_3 phases are very similar to the pure phases optically.

The phase α forms small granular grains (less than 20 μm) or long rectangular grains (80 × 5 μm) and coexists with gallite, digenite and phase ζ. This phase has a solid-solution field ranging from Cu_{100} to $Cu_{80}Ga_{20}$ at both temperatures (Tables 5, 6). The color of this phase changes from copper brown (Cu_{100}) to reddish yellow ($Cu_{80}Ga_{20}$). Table 9 shows the X-ray powder-diffraction data for phase α. This phase has a face-centered cubic structure, and the cell parameter *a* increases with increasing Ga content, owing to the difference of atomic radii of copper and gallium.

The phase ζ appears as irregularly shaped grains (less than 70 μm) and coexists with gallite, phases α and γ. This phase is light yellow with strong anisotropy from reddish brown to pale green in reflected light. It has a hexagonal close-packed structure. Its cell parameters (composition of $Cu_{79}Ga_{21}$) are *a* 2.593, *c* 4.229 Å (Zintl & Treusch 1936). In the present study, we synthesized the ζ phase with the composition $Cu_{77}Ga_{23}$ (Tables 5, 6), and the cell parameters are *a* 2.6039, *c* 4.249 Å (Table 10), values that are a little larger than those of Zintl & Treusch (1936).

TABLE 7. X-RAY POWDER-DIFFRACTION DATA FOR GALLITE

	1			2	
d (Å)	I	*hkl*	d_{obs} (Å)	d_{calc} (Å)	I
3.070	100	112	3.072	3.076	100
2.680	2	200	2.680	2.679	4
2.630	2	004	2.632	2.633	2
1.8940	60	220	1.8975	1.8944	21
1.8760	90	204	1.8776	1.8780	41
1.6100	90	312	1.6143	1.6130	24
1.5820	40	215	1.5898	1.5822	9
1.5360	2	224	1.5373	1.5378	2
1.3380	20	400	1.3386	1.3395	3
1.3110	6	008			
1.2270	20	332	1.2285	1.2281	3
1.2150	60	316	1.2169	1.2192	6
	Tetragonal *a* 5.360 Å *c* 10.49 Å			Tetragonal *a* 5.358(5) Å *c* 10.53(2) Å	

1. JCPDS Card No. 6–0358 (Hahn *et al.* 1953); 2. This study (sample no. NA–011).

TABLE 8. X-RAY POWDER-DIFFRACTION DATA FOR α-Ga_2S_3 AND PHASE X

	1			2		
d (Å)	I	*hkl*	d_{obs} (Å)	d_{calc} (Å)	I	*hkl*
5.34	20	110	5.235	5.237	1	002
4.775	16	200				
4.732	7	111	4.696	4.694	8	101
3.519	5	311	3.715	3.713	4	110
3.496	9	202				
3.215	64	020				
3.014	100	402	3.027	3.029	100	112
2.848	15	310	2.903	2.907	4	103
2.830	25	112				
2.746	5	021				
2.663	4	220				
2.656	3	002	2.626	2.625	2	200
2.384	1	400				
2.363	1	222	2.346	2.343	6	104
2.209	13	511	2.292	2.291	5	211
2.197	7	203				
2.190	7	313	2.137	2.140	2	114
2.103	3	602				
2.089	6	513				
2.046	3		1.9442	1.9456	3	105
1.8868	2		1.8518	1.8539	55	204
1.8533	29		1.7263	1.7262	1	301
			1.5809	1.5826	26	312
			1.5172	1.5143	1	224
			1.4552	1.4550	1	304
			1.4419	1.4423	5	321
	monoclinic *a* 12.652(4) Å *b* 6.421(3) Å *c* 7.048(2) Å β 131.07(3)°			tetragonal *a* 2.250(2) Å *c* 10.474(8) Å		

1. α-Ga_2S_3 (Ueno & Scott 1991); 2. this study (sample no. HO–017).

TABLE 9. X-RAY POWDER-DIFFRACTION DATA FOR THE α PHASE

	1			2			3	
d (Å)	I	*hkl*	d_{obs} (Å)	d_{calc} (Å)	I	d_{obs} (Å)	d_{calc} (Å)	I
2.088	100	111	2.096	2.091	100	2.128	2.125	100
1.808	46	200	1.8138	1.8112	40	1.8419	1.8401	37
1.278	20	220	1.2799	1.2807	17	1.3005	1.3011	22
Cubic *a* 3.6150 Å			Cubic *a* 3.622(3) Å			Cubic *a* 3.680(2) Å		

1. Cu_{100}, JCPDS Card no. 4–836; 2. $Cu_{90}Ga_{10}$, this study (sample no.CG–011); 3. $Cu_{80}Ga_{20}$, this study (sample no. CG–001).

The phase γ occurs as irregularly shaped grains (less than 100 μm) and coexists with gallite, GaS, phases ζ and ω. This phase is yellowish white and isotropic in reflected light. According to Weibke (1934) and Zintl & Treusch (1936), this phase has a γ-brass structure. Betterton & Hume-Rothery (1951–1952) published values of the cell parameter *a* 8.758, 8.7387, 8.7209 and 8.6352 Å for Cu–Ga alloys with the contents of 29.68, 33.90, 35.89 and 42.64 atom % gallium, respectively. In this study, we synthesized the γ-phase solid solution ranging from $Cu_{70.0}Ga_{30.0}$ to $Cu_{64.8}Ga_{35.2}$ at 500°C (Table 5) and from $Cu_{67.9}Ga_{32.1}$ to $Cu_{63.3}Ga_{36.7}$ at 400°C (Table 6). Table 11 shows the X-ray powder-diffraction data for the phase γ. The cell parameter *a* of our γ phase ($Cu_{70.0}Ga_{30.0}$) is 8.726 Å.

TABLE 10. X-RAY POWDER-DIFFRACTION DATA FOR THE ζ PHASE

1 d (Å)	1 I	hkl	2 d_{obs} (Å)	2 d_{calc} (Å)	2 I
2.256	6	100	2.258	2.255	21
2.115	100	002	2.125	2.125	52
1.9881	22	101	1.9927	1.9919	100
1.5473	3	102	1.5462	1.5464	18
1.2960	26	110	1.3017	1.3019	9
hexagonal *a* 2.593 Å *c* 4.229 Å			hexagonal *a* 2.6039(7) Å *c* 4.249(2) Å		

1. $Cu_{79}Ga_{21}$ phase, Zintl & Treusch (1936); 2. $Cu_{76.9}Ga_{23.1}$, phase ζ, this study (sample no. CG–008).

TABLE 11. X-RAY POWDER-DIFFRACTION DATA FOR THE γ PHASE

1 d (Å)	1 I	hkl	2 d_{obs} (Å)	2 d_{calc} (Å)	2 I
3.91	60	210			
3.57	70	211			
2.92	20	300			
2.53	50	222	2.520	2.519	9
2.35	60	321	2.333	2.332	5
2.12	40	410			
2.05	100	330	2.057	2.057	100
2.00	10	331			
1.95	40	420	1.9513	1.9513	2
1.91	20	421			
1.86	60	332	1.8610	1.8605	6
1.79	70	422	1.7814	1.7813	3
1.71	50	510	1.7119	1.7114	4
1.68	40	511			
1.62	20	520			
1.52	20	441			
1.50	10	530			
1.47	10	531			
1.45	80	600	1.4544	1.4544	11
1.43	10	610			
1.42	40	611	1.4158	1.4156	1
1.36	10	540			
1.35	20	541			
1.31	10	630			
1.30	10				
1.29	50	631	1.2865	1.2866	3
1.26	60	444	1.2593	1.2596	4
cubic *a* 8.746 Å			cubic *a* 8.7264(5) Å		

1. JCPDS Card no. 21253 (Weibke 1934); 2. $Cu_{70}Ga_{30}$ phase, this study (sample no. CG–002).

The phase ω forms irregularly shaped grains (less than 150 μm) and coexists with GaS, the phase γ and gallium liquid. This phase is bluish creamy white with strong anisotropy of dark brown to dark green in reflected light. Zintl & Treusch (1936) showed the presence of a $CuGa_2$ phase and demonstrated that it has tetragonal symmetry, *a* 2.836, *c* 5.843 Å. El-Boragy & Schubert (1972) presented the X-ray-diffraction data of this phase (Table 12). In this study, we obtained a similar phase, with solid solution ranging from $Cu_{36}Ga_{64}$ to $Cu_{33}Ga_{67}$ at 500°C (Table 5) and from $Cu_{35.5}Ga_{64.5}$ to $Cu_{30.2}Ga_{69.8}$ at 400°C (Table 6). Table 12 shows the X-ray powder-diffraction data for the $CuGa_2$ phase of El-Boragy & Schubert (1972) and for our phase ω.

Gallium was in the liquid state during the experiments; it melts at 29.8°C, and boils at about 2300°C. Gallium liquid coexists with GaS and the phase ω at 500° and 400°C. Pure gallium solid is bright white, and Cu-bearing gallium is bluish white in reflected light. Both pure gallium and Cu-bearing gallium have very strong reflection from blue to brown. Solid gallium produced by quenching the liquid in water from 500° and 400°C contains 2.6 and 2.2 atom % Cu, respectively (Tables 5, 6).

TABLE 12. X-RAY POWDER-DIFFRACTION DATA FOR THE ω PHASE ($CuGa_2$ PHASE)

1 d (Å)	1 I	hkl	2 d_{obs} (Å)	2 d_{calc} (Å)	2 I	3 d_{obs} (Å)	3 d_{calc} (Å)	3 I
5.84	12	001	5.862	5.834	28	5.800	5.818	30
2.92	7	002	2.921	2.917	27	2.899	2.909	63
2.829	35	100	2.834	2.832	62			
2.545	80	101	2.549	2.547	19	2.536	2.542	17
2.031	100	102	2.033	2.032	74	2.027	2.027	53
2.000	80	110	2.002	2.002	100	1.9952	1.9983	13
1.946	16	003	1.9458	1.9447	48	1.9380	1.9393	100
1.893	3	111						
1.650	6	112						
1.603	1	103						
1.460	6	004	1.4585	1.4585	15	1.4548	1.4545	43
1.415	30	200	1.4162	1.4158	45	1.4135	1.4130	5
1.395	30	113	1.3941	1.3950	4	1.3923	1.3917	8
1.375	1	201						
1.297	1	104						
1.273	2	202						
1.265	5	210						
1.237	14	211	1.2374	1.2375	4			
tetragonal *a* 2.830 Å *c* 5.839 Å			tetragonal *a* 2.8316(5) Å *c* 5.834(2) Å			tetragonal *a* 2.826(1) Å *c* 5.818(3) Å		

1. $CuGa_2$ phase, JCPDS Card no. 25–275 (El-Boragy & Schubert 1972);
2. $Cu_{36.0}Ga_{64.0}$, this study (sample no. CG–006); 3. $Cu_{33.0}Ga_{67.0}$, this study (sample no. CG–010).

Phase relations at 500° and 400°C

Phase diagrams of the ternary system Cu–Ga–S at 500° (Fig. 1) and 400°C (Fig. 2) have been constructed from the experimental results in Tables 1, 2, 3 and 4, and the chemical compositions of the phases in Tables 5 and 6. The tie-line relations are essentially the same at both temperatures.

Along the Cu–S join, there are four phases, sulfur, covellite, digenite and copper; along the Ga–S join, therer are four phases, sulfur, Ga_2S_3, GaS and gallium liquid, and along the Cu–Ga join, there are five phases, α, ζ, γ, ω and gallium liquid at both temperatures. The α, ζ and γ phases are connected to gallite with tie lines, and the phases γ and ω and gallium liquid are connected to GaS with tie lines at both temperatures. The principal ternary phases are gallite and phase X. Gallite appears in the central position of this ternary system, and it has tie lines to many other phases. Phase X appears between gallite and Ga_2S_3, and it has a limited solid-solution area.

DISCUSSION

Gallium is found in nature in oxide, silicate and sulfide minerals. According to Johan *et al.* (1983), sphalerite from zinc deposits in the Ordovician and Devonian of the French central Pyrénées contains several Ge- and Ga-rich mineral phases. They are argutite (GeO_2), Ga-rich magnetite (containing 3.5 weight % Ga_2O_3), carboirite [$FeAl_2GeO_5(OH)_2$], and Ga-rich chlorite (containing 22.33 weight % Ga_2O_3), among others. Bernstein (1986) reported Ga-rich jarosite (containing 0.7 wt.% Ga) and Ga-rich "limonite" (containing 2 wt.% Ga) from the Apex Ge–Ga mine, Washington County, Utah. Recently, Roberts *et al.* (2004) reported the new mineral eyselite [$Fe^{3+}Ge^{4+}{}_3O_7(OH)$] from the Tsumeb mine, Namibia. This mineral contains 1.01 wt.% Ga_2O_3. The main Ga-containing sulfide minerals are renierite, germanite, gallite and sphalerite. According to Sheka *et al.* (1966), the dominant host of Ga in sulfide ores is sphalerite; the concentration of Ga varies between tens and hundreds of ppm. Some high values of gallium (up to 5.8 wt.%) have been reported in a zinc sulfide phase in meteorites (Nagahara & El Goresy 1984). Experimentally, Ueno & Scott (1991) showed the maximum solubility of Ga in sphalerite in the system Zn–Ga–S to be 24.9 at.% at 900°C and 16.3 at.% at 800°C. In the first account on gallite, Strunz *et al.* (1958) found that in sulfide ore, it occurs in sphalerite as exsolution lamellae with a brownish gray color in reflected light. They concluded that gallite may be the gray lamellar ore of Schneiderhöhn (1920) and Moritz (1933), and that it is surely the same mineral as that mentioned by Ramdohr (1944, 1956). In our phase-equilibrium experiments of the ternary system Cu–Ga–S, we obtained

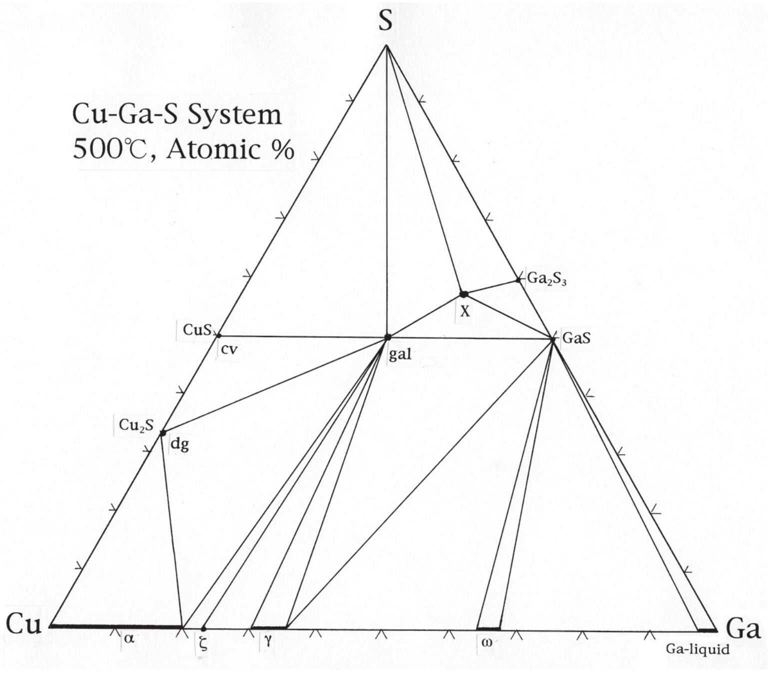

FIG. 1. Phase diagrams of the system Cu–Ga–S at 500°C, determined by dry synthesis.

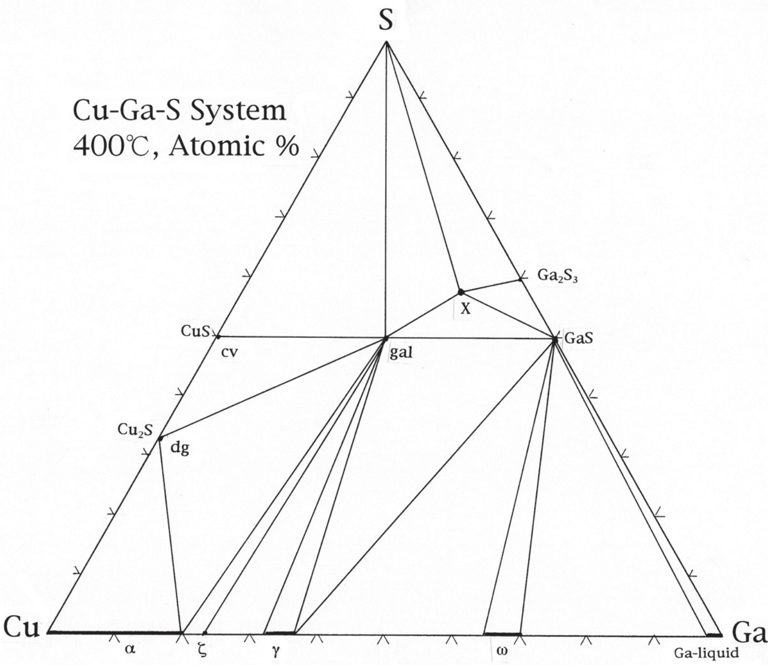

FIG. 2. Phase diagrams of the system Cu–Ga–S at 400°C, determined by dry synthesis.

gallite in the central position and a new phase, phase X, between gallite and Ga_2S_3. Gallite coexists with covellite, digenite, phase X, GaS, the phases α, ζ, γ and sulfur. In natural copper ore, gallite may occur in association with covellite and digenite. There is a possibility of finding phase X in natural ore containing gallite. As gallite occurs in association with sphalerite in nature, it would be informative to investigate the phase equilibria in the quaternary system Cu–Ga–Zn–S. That study would elucidate the stability relations between gallite and sphalerite and the phase relations with other phases, like covellite, phase X, Ga_2S_3, GaS and Cu–Ga phases.

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