

# New data on Phase Relations in the System Cu-Fe-Sn-S

## 4성분계 Cu-Fe-Sn-S의 상관계에 대한 새로운 데이터

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**ABSTRACT:** Two solid solution-type phases has been experimentally found in the quaternary system Cu-Fe-Sn-S:  $(\text{Fe, Cu, Sn})_{1+x}\text{S}$  and  $\text{Cu}_{2-y}\text{Fe}_{1+y}\text{SnS}_4$ . These solid solutions are stable around the CuS-FeS-SnS reference plane in the composition tetrahedron. One is the sphalerite-type monosulfide solid solution which has a extensive stability range with varying degrees of sulfur/metal ratio 9.7-1.0/1.0. The other is tetrahedrite-type phase  $\text{Cu}_{2-y}\text{Fe}_{1+y}\text{SnS}_4$  ( $y_{\text{max}}=0.4$ ) which is stable along the  $\text{Cu}_2\text{FeSnS}_4$ -FeS tie line, but shows no phase transformation in the subsolidus range and decomposes incongruently at the range of 835-862°C, depending on the compositional variation. Particularly, the latter phase shows the characteristic superstructure reflections, indicating that it is a derivative of sphalerite structure. The stability field of these two sphalerite-type phases are defined on the basis of diffraction pattern and optical homogeneity of the synthetic materials at the temperature range of 700-400°C.

**요약:** 四成分系 Cu-Fe-Sn-S 시스템의 相關係에 대한 합성실험에서 두 개의 固溶體 타입의 合成相  $(\text{Fe, Cu, Sn})_{1+x}\text{S}$ 와  $\text{Cu}_{2-y}\text{Fe}_{1+y}\text{SnS}_4$ 가 발견되었으며 이들은 成分四面體 내에서 CuS-FeS-SnS로 표시될 수 있는 reference面의 주위에서 안정한 것으로 밝혀졌다. 前者는 섬아연석 結晶構造를 갖고 있는 단순황화물 고용체로서 온도함수인 금속과 유황의 비율(9.7-1.0/1.0)에 따라 광범위한 화학적 안정영역을 차지하고 있다. 또한 섬아연석 超格子중에 하나인 테트라헤드라이트 結晶構造를 갖고 있는 後者는  $\text{Cu}_2\text{FeSnS}_4$ -FeS conode를 따라 렌즈형의 안정범위를 갖으나 subsolidus 범위(350°C 까지) 내에서 相轉移 현상이 없고 835-862°C에서 不調和熔融을 한다. 위 두 개의 고용체는 온도변화에 따라 相互溶解度 그리고 관련된 각각의 합성상의 화학조성이 변화하는 소위 Incorporation-type Solid Solution이다.

특히 後者の 경우 섬아연석 subcell을 기본골격으로 하는 超格子의 특징적인 양상을 X-ray 연구에서 찾을 수 있으며 이 패턴은 超格子의 안전성이 높다는 것을 암시해 주고 물리, 화학적 특성이 stoichiometric phase  $\text{Cu}_2\text{FeSnS}_4$ 와 相異하다.

## INTRODUCTION

After the report of Borchert (1934), many discussions have been continued, centering on the presence of "chalcopryrhotite", although it is used as a valid mineral name in the literature. The chalcopryrhotite(after Ramdohr, 1969), characterized by optical isotropism with the composition of  $\text{CuFe}_6\text{S}_7$  by Bromstand (1870) and  $\text{Cu}_3\text{Fe}_5\text{S}_7$  by Scholz(1936), was not found in the pure Cu-Fe-S system (Merwin & Lombard, 1937; Yund &

Kullerud, 1966; Cabri, 1973). It is widely accepted that chalcopryrhotite is identical with the high temperature cubic cubanite, which is isostructural to high temperature cubic chalcopyrite, and the so called "intermediate solid solution" (hereafter iss). In the Cu-Fe-S system the iss is a nonquenchable in most part of the ss range, metal-rich sphalerite type phase, but unstable at room temperature.

On the other hand, since the discovery of stannite,  $\text{Cu}_2(\text{Fe, Zn})\text{SnS}_4$  by klapproth (1797), it

was regarded to be the only tin sulfide mineral for a long time. After the study of the "Stannite problem" (Ramdohr, 1944), the identity of stannite and the related minerals have been a topic of hot discussions and that results in findings of many of stannite-related species like stannoidite ( $\text{Cu}_3\text{Fe}_3\text{Sn}_2\text{S}_{12}$ ), mawsonite ( $\text{Cu}_6\text{Fe}_2\text{SnS}_8$ ), cernyite ( $\text{Cu}_2\text{CdSnS}_4$ ), Hocartite ( $\text{Ag}_2\text{FeSnS}_4$ ) (omitting intermediate solid solutions) etc.. All stannite-related phases show a superstructure diffraction pattern of sphalerite, with the exception that rhodostannite ( $\text{Cu}_2\text{FeSnS}_4$ ) being the sulfur-rich phase with a inversed spinel structure. From such reasons, it is very difficult to distinguish one species from the other. However, microscopic intergrowth texture in natural ores, including that of chalcopyrite-stannite, may propose the possibility of existence of extensive solid solutions at high temperatures.

Recent publications regarding both natural and synthetic materials in the Cu-Fe(Zn)-Sn-S system are numerous and the data available cover an extensive composition range (Springer 1969, 1972; Oen 1970; Franz 1971; Harris & Owens 1972; Lee et al. 1975; Moh 1975; Kissin & Owens, 1979; Wang, 1982; Jang, 1986; Osadchii, 1990). The present work is part of an experimental approach to determine, within the Cu-Sn-M (Zn, Fe, Cd, Hg, Mn)-S system, the stability ranges of the various phases under the experimentally permissible temperature conditions. Of special interest are the phases which are stable around the CuS-FeS-SnS reference plane.

### METHODS OF INVESTIGATION

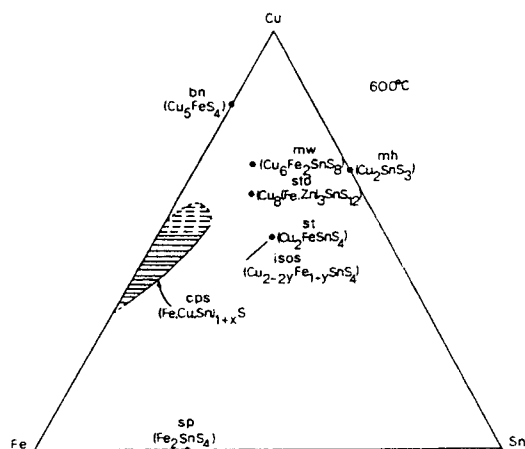
Experiments were performed by means of conventional evacuated silica tube technique as described elsewhere (Kullerud 1971; Moh & Taylor, 1971). The starting materials used are elements of 99.99% purity as specified by suppliers' analysis. Synthesis and annealing experiments were conducted in 'kantel' wound resistance furnaces in which the temperature was regulated to the accuracy of  $\pm 2^\circ\text{C}$ , and temperatures were measured by means of calibrated chromel-alumel thermocouples.

Experimental products were analyzed by means of x-ray diffraction, reflected light micros-

copy and differential thermal analysis. As internal standard, Si-powder from NBS were used for measuring the d-values and the indexed diffraction data were refined by the least squares method (Appleman & Evance, 1973). DTA runs were made in sealed silica tubes without supporting pressure. Temperature calibration was achieved by using the solidification points of NaCl, KCl, Sb and Sn. The material loss per regrinding for polished section and for X-ray work was in most case less than 5mg (about 1wt %). At the end of annealing procedure, the samples were quenched in ice water. To check equilibrium the sequence of temperature was changed in selected runs.

### EXPERIMENTAL RESULTS

In the Cu-Fe-Sn-S composition tetrahedron two solid solutions are found on the CuS-FeS-SnS reference plane in the present study. These solid solutions are designated as cps (chalcopyrite solid solution) and isos (isostannite solid solution) hereafter tentatively.



**Fig. 1.** Phase relation diagram for phases existing around the CuS-FeS-SnS reference plane in the system Cu-Fe-Sn-S at 600°C. It shows only the variation of metal components. The ratio of metal/sulfur is omitted. Abb: bn =  $\text{Cu}_3\text{FeS}_4$ , mw =  $\text{Cu}_6\text{Fe}_2\text{SnS}_8$ , std =  $\text{Cu}_8\text{Fe}_3\text{Sn}_2\text{S}_{12}$ , st =  $\text{Cu}_2\text{FeSnS}_4$ , isos =  $\text{Cu}_{2-2y}\text{Fe}_{1+y}\text{SnS}_4$ , cps =  $(\text{Fe}, \text{Cu}, \text{Sn})_{1+x}\text{S}$ , mh =  $\text{Cu}_2\text{SnS}_3$  (mohite), sp =  $\text{Fe}_2\text{SnS}_4$ .

The stability phase boundary of the solid solution fields are determined at 600-400°C by the interpretation of the phases observed at room temperature (Table 1). Fig. 1 illustrates the variable metal contents and stable phase assemblage determined in this study. The diagram, however, does not show the metal:sulfur ratios; the phases would not lie in the same plane if a sulfur apex were added. The dotted lines drawn in the phase diagram are only approximate as there were insufficient experiment data available in establishing them.

### Monosulfide Solid Solution(Fe, Cu, Sn)<sub>1+x</sub>S

The stability field of the monosulfide solid solution(Fe, Cu, Sn)<sub>1+x</sub>S extends from, in approximation, CuFe<sub>2</sub>S<sub>3</sub> composition point over the that of CuFeS<sub>2</sub> into the Cu-Sn rich zone, approaching to the stannoidite ss field. The cps is quenchable only about on the SnS saturation curve of the field, but on the middle field of the ss range the phases are so hardly quenchable that the all reflex of the x-ray powder reflection are blurred, reflecting the instability of the cubic cell under the normal condition. Between 400 and 600°C this ss has no noticeable variation in sulfur/metal ratio from the CuFe<sub>2</sub>S<sub>3</sub> composition point to the that of CuFeS<sub>2</sub> and isos tie line(which is discussed in later section of this paper). But over the tie line into the metal- rich zone, the ss field dips steeply toward the high stannoidite- and bornite ss field.

The sulfur/metal ratio approach 9.7/10 at the metal- rich flank of the field, similar to the tendency of high stannoidite- and lower series on the CuS-FeS-SnS reference plane which Wang(1982) has found in this system. The stability range of cps in Cu-Fe-Sn-S system corresponds, therefore, to the extended(from Cu-Fe-S into tetrahedron) iss stability field of Merwin and Lombard(1937) or that of chalcopyrite ss range of Yund and Kullerud(1966). The value of Cu/Fe varies from 0.5 to about 1.1 and that of Sn/Cu+Fe, 0-0.25 for S=4.

On the sulfur-deficient portion of the field cps is in equilibrium with bornite ss, high-stannoidite ss and isos, and on Fe-rich portion, pyrite, Fe<sub>2</sub>SnS<sub>4</sub> and pyrrotite according to the

ratio of metal/sulfur and metal/metal.

All reflections on the x-ray diffraction diagram could be indexed on sphalerite-type cubic cell. The cell parameters depend largely on Cu/Fe ratio; a<sub>0</sub>=5.314 Å for the Fe rich composition (with 3% SnS-content), a<sub>0</sub>=5.340 Å for Cu\Fe=1 composition(with 10% SnS-content and Cu-rich composition (with 20% Sn-S content) a<sub>0</sub>=5.329 Å at 600°C(Table 2).

Down to 400°C the feature of the ss field remains unchanged but the solubilities of the phase diminish, as well expected, with the decrease of the temperature. In the annealing experiments the composition of chalcopyrite within the ss contains 12% at 500°C and 8% SnS at 400°C and oversaturated Sn was expelled as homogeneous exsolution body of isos under the control of crystallographic direction.

This process was well reproducible. In the reheating experiments at higher temperature (600 or 700°C) exsolution bodies of cps with various composition have been produced in the exsolved stannite and/or first-phase stannite in an irregular way, comparing to the lamellar intergrowth of the phases in the annealing experiments. This subsolidus reactions suggest that SnS content in ores prefers to be dissolved in cps rather than in stannite at higher temperature range and vice versa. Such a resolution-dissolution reaction indicates that cps and isos compose the so-called incorporation-type solid solution of Osadccii(1990), as they have variable compositions with a function of temperature.

Under the microscope cps is brighter than iss; it is light yellow with slightly grayish tint. The color change with varying Sn- contents was not easily discernible.

### The Phase Cu<sub>2-2y</sub>Fe<sub>1+y</sub>SnS<sub>4</sub>

The phase Cu<sub>2-2y</sub>Fe<sub>1+y</sub>SnS<sub>4</sub> (isos) is practically a linear extension of isostannite (Franz, 1971) stability field toward the Fe<sub>1-x</sub>S corner in the Cu-Fe-Sn-S tetrahedron. The lens-shaped isos is stable approximately from stoichiometric composition Cu<sub>2.03</sub>Fe<sub>1.01</sub>SnS<sub>4.0</sub> to Cu<sub>1.2</sub>Fe<sub>1.4</sub>SnS<sub>4.0</sub> at 400°C, and at the lower temperature

**Table 1.** Results of quenching experiments in the system Cu-Fe-Sn-S at 750–350°C. Annealing time is given in days.

Run No.	Starting materials	T (°C)	Heating period	Products
85009	68.5po+27.4cv+4.0hz	470	8	cps+isos+po
84334	65.6po+32.8cv+2.0hz	600	110	cps
		500	52	cps+isos
85015	65.4po+32.7cv+2.0hz	600	24	cps+(po?)
84312	63.5po+31.7cv+5.0hz	500	107	cps+(po)
84310	62.0po+37.0cv+2.0hz	500	2	cps
84314	59.0po+39.0cv+2.0hz	400	174	cps
84307	58.0po+39.0cv+3.0hz	600	56	cps
		400	91	cps+(isos)
84301	57.0po+38.0cv+5.0hz	500	3	cps+isos
		400	24	cps+isos
		350	175	cps+isos
		600	1	cps+(isos)
84309	56.6po+28.3cv+15.0hz	600	12	isos+hz+po
84321	56.0po+42.0cv+2.0hz	500	12	cps+isos
84309a	55.7po+41.8cv+2.5hz	600	2	cps+isos
84300b	55.5po+37.0cv+7.5hz	600	28	cps+isos
		700	3	cps
84356	53.0po+35.5cv+11.5hz	600	12	cps+isos
		500	47	isos+po(hz)
84338	50.0po+45.0cv+5.0hz	600	11	cps
84319	50.0po+40.0cv+10.0hz	500	11	cps+isos
84323	50.0po+33.3cv+17.0hz	600	15	isos+po+hz
		500	48	isos+po+hz
84322	48.8po+48.8cv+2.4hz	600	24	cps
84330	48.0po+49.0cv+3.0hz	600	17	isos+cps+(s)
84327	47.6po+47.6cv+4.8hz	450	60	cps+isos
		400	135	cps+isos
		440	84	cps+isos
		550	6	cps
84320a	47.4po+49.8cv+2.8hz	600	10	isos
84332	47.1po+47.1cv+5.7hz	500	18	cps
		450	13	cps+isos
		400	175	cps+isos
		600	1	cps
84326a	46.5po+46.5cv+7.0hz	600	1	cps+isos
84318	45.5po+45.5cv+9.0hz	500	16	cps+isos
		600	122	cps+isos
		400	114	cps+isos
		350	60	cps+isos
84319a	43.5po+34.8cv+21.7hz	500	25	isos+hz+po
84330b	43.0po+48.8cv+3.2hz	600	110	cps+?
84328	42.2po+50.6cv+6.3hz	600	12	cps+isos+(s)
84339	40.0po+55.0cv+5.0hz	600	53	cps+s
84341	40.0po+52.5cv+7.5hz	600	47	cps+s
		500	121	cps+?
84343	40.0po+50.0cv+10.0hz	600	13	cps+?
84320	40.0po+40.0cv+20.0hz	600	16	isos+po+hz
84328a	38.0po+53.3cv+8.7hz	600	5	cps+(isos)
		500	10	cps+std
84340	35.0po+55.0cv+10.0hz	600	23	cps+s+(py?)
		500	54	cps+std
84338	35.0po+50.0cv+15.0hz	600	32	cps+iso+(s)
85005	33.3po+33.3cv+33.3hz	400	87	isos+po+hz
		500	31	isos+po+hz
84320b	32.2po+32.2cv+35.5hz	600	12	isos+hz+po
		700	13	Schm.
		750	5	Schm.
84340a	30.0po+60.0cv+10.0hz	600	124	cps+bn+?
84342	30.0po+55.0cv+15.0hz	600	29	cps+?
85036	1.0st+1.0cb	500	21	isos+cps
85055	1.0st+1.0cp	600	12	cps+isos
85056	1.0st+0.5cp	500	6	isos+cps
85052	1.0st+0.2po+1.0s	500	8	isos+s
85053	1.0st+0.4po+0.8s	600	38	isos+s
85054	1.0st+0.5po+0.7s	500	11	isos+po
85059	1.0st+0.7po+0.8s	500	16	isos+py
85067	1.0st+0.7po+0.5s	400	47	isos+po
85068	1.0st+0.4po+0.7s	400	29	isos

Abb. isos :  $\text{Cu}_{2-2y}\text{Fe}_{1+y}\text{SnS}_4$ , cps :  $(\text{Fe}, \text{Cu}, \text{Sn})_{1+x}\text{S}$ , s : sulfur, po : pyrrhotite, FeS or  $\text{Fe}_{1-x}\text{S}$ , hz : herzenbergite, SnS, bn : bornite ss, cp :  $\text{CuFeS}_{2-x}$ , cv : CuS or  $\text{Cu}_{1-x}\text{S}$ , std : stannoidie ss., cb : cubanite, schm : melt

range composition of the phase approaches to the hypothetical composition  $\text{CuFe}_2\text{Sn}_4\text{S}_8$  which lies slightly over the  $\text{Cu}_2\text{FeSn}_4$ -FeS tie line (the experiment at lower temperatures now in progress).

Isos, same as the pure phase  $\text{Cu}_2\text{FeSn}_4$  (Jang, 1984), decomposes incongruently into SnS,  $\text{Fe}_2\text{SnS}_4$  and  $\text{Cu}_9\text{S}_5$ . The thermal stability of isos ranges  $835 \pm 5^\circ\text{C}$ , according to the metal/metal ratio and it shows no phase transformation in DTA and annealing experiments in the temperature range of  $400$ – $800^\circ\text{C}$ , contrasting to that of stoichiometric composition. Isos is in equilibrium with cps, high stannoidite ss,  $\text{SnS}_2$ ,  $\text{Fe}_{1-x}\text{S}$ , and/or  $\text{Fe}_2\text{SnS}_4$  on the  $\text{CuS}$ - $\text{SnS}$ - $\text{FeS}$  reference plane and also with  $\text{FeS}_2$ , SnS over or below the reference plane at  $400$ – $700^\circ\text{C}$ . The phase rhodostannite ( $\text{Cu}_2\text{FeSn}_4\text{S}_8$ ; Springer, 1972), which is stable only on the conode  $\text{Cu}_2\text{FeSn}_4$ - $\text{SnS}_2$ , was not observed during the quenching experiments. This may indicate that the starting point of isos exists slightly apart from the stoichiometric composition.

Isos, like stoichiometric isostannite (Claringsbull & Hey, 1955; Franz, 1971), shows structurally a close relationship with tetrahedrite ( $\text{Cu}_{12}\text{Sb}_4\text{S}_{13}$ ). The comparatively intense superstructure peaks indicate a highly-ordered structure and a unit cell parameters twice as large as the sphalerite-type subcell. Refined crystallographical data of isos shows that the unit cell parameter of the phase

decreases with increasing metal/sulfur (m/s) ratio;  $a_0 = 10.817 \text{ \AA}$  for  $m/s = 1/1$  and  $a_0 = 10.837 \text{ \AA}$  for  $m/s = 0.9/1$  (Table 3).

Isos is isotropic under reflecting microscope and shows gray color with greenish tone in oil immersion, contrasting to the "brown-toning isostannite" of stoichiometric composition.

## DISCUSSION

Cps and isos are incorporation-type solid solutions over the experimental range of conditions. Detailed study on the behavior of the coexisting solid solutions indicates that their continuity is of a complex nature as a result of the structural features of the phases involved. At different temperatures, the phase boundaries are commonly defined using different methods. These include, for example, the most efficient and conventional x-ray analysis coupled with the phase appearance technique, and the DTA method which is proved to be sufficient for the case of the coexisting isos and cps.

The reciprocal solubility of phases of variable composition experiences small changes with decreasing temperature from  $600$ – $400^\circ\text{C}$  as discussed above. Isos is different from stoichiometric  $\text{Cu}_2\text{FeSn}_4$  in the structural and thermal characteristics.  $\text{Cu}_2\text{FeSn}_4$  shows tetragonal symmetry

**Table 2.** Crystallographic data of  $(\text{Fe}, \text{Cu}, \text{Sn})_{1+x}\text{S}$  in the system Cu-Fe-Sn-S. Powder data of the isostructural "cubic cubanite" ( $\text{CuFeS}_3$ ) and "cubic chalcopyrite" ( $\text{CuFeS}_{2-x}$ ) are given for comparison.  $\text{CuK}\alpha$  radiation. Internal standard, Si.

h	k	l	I/I <sub>0</sub>	CuFeS <sub>2-x</sub> * d <sub>obs</sub>	≅CuFeS <sub>2</sub> **		≅CuFe <sub>1.5</sub> S <sub>2.5</sub> **		≅CuFeS <sub>2</sub> **		*** CuFe <sub>2</sub> S <sub>3</sub> d <sub>obs</sub>
					d <sub>obs</sub>	d <sub>cal</sub>	d <sub>obs</sub>	d <sub>cal</sub>	d <sub>obs</sub>	d <sub>cal</sub>	
1	1	1	10	3.160	3.079	3.082	3.073	3.073	3.067	3.069	3.066
2	0	0	4	2.680	2.666	2.670	2.662	2.662	2.659	2.657	2.655
2	2	0	9	1.890	1.883	1.888	1.882	1.872	1.879	1.879	1.877
3	1	1	7	1.613	1.614	1.610	1.605	1.605	1.602	1.602	1.601
2	2	2	1	—	1.540	1.541	1.536	1.537	1.534	1.534	1.533
4	0	0	4	1.340	1.335	1.335	1.330	1.331	1.326	1.328	1.327
3	3	1	5	1.230	1.225	1.225	1.221	1.221	1.218	1.219	1.218
4	2	0	1	—	1.194	1.194	1.188	1.190	1.186	1.188	1.187
a <sub>0</sub> (Å)				5.36	5.340		5.323		5.314		5.310
V				153.99	152.253		150.842		150.026		149.721

\* natural  $\text{CuFeS}_{2-x}$ , x-rayed at  $573^\circ\text{C}$  (Cabri, 1967).

\*\* synthesized at  $600^\circ\text{C}$  and quenched (this study).

\*\*\* synthesized at  $400^\circ\text{C}$  and quenched, refined (this study).

above 706°C, and it transforms reversibly in the temperature range 580–600°C to an intermediate modification of unknown symmetry. The cubic pattern of the  $\text{Cu}_2\text{FeSnS}_4$ , which corresponds to isostannite of Franz(1971), is stable at 500°C (Wang, 1982). But isos shows no such a structural transition from melting point to 400°C, and the stability range of isos decreases gradually to the direction of Fe-rich part, as the solubility of isos in cps decreases. This suggests the possibility of natural occurrence of cubic stannite. It seems that the phases could become practically pure binary solution above the temperature at which the transition of stannite takes place. The fact that stannite transition occurs well below 350°C from high temperature cubic to tetragonal phase is recently documented experimentally and is dealt with elsewhere.

Iss has a high capability to resolve various kinds of metals in the structure. Craig and Kullerud (1969) have found in the Cu-Fe-Ni-S system that  $\text{CuFeS}_2$  takes up to 15% Ni in solid solution at 600°C and the transition temperature of chalcopyrite lowered to less than 400°C with the Ni-content. Comparing with the present study, the effect of Ni content in iss is the same as those of Sn-content. In view of this, 3 Ni-containing metal-rich phases of iss, mooihoekite, haycockite and talnakhite, which are not discernable microscopically from one another and from chalcopyrite, must be classified in the Cu-Ni-Fe-S system. Cps, better to say, relating to cubic chalcopyrite and-cubanite, Sn-containing iss is stabilized with tin content alone to at least 350°C in a extensive ss range.

**Table 3.** Crystallographic data of  $\text{Cu}_{2-3}\text{Fe}_{1+y}\text{SnS}_4$ . Powder diffraction data of  $\text{Cu}_2\text{FeSnS}_4$  and  $\text{Cu}_2\text{FeSnS}_{3.95}$ , all indexed on the tetrahedrite-type cell, are given for comparison.  $\text{CuK}\alpha$  radiation, Internal standard, Si.

h k l	I/I <sub>0</sub>	$\text{Cu}_{2-3}\text{Fe}_{1+y}\text{Sn}_4^*$		$\text{Cu}_{2-3}\text{Fe}_{1+y}\text{SnS}_4^{**}$		$\text{Cu}_2\text{FeSnS}_{3.95}^{***}$
		d <sub>obs</sub>	d <sub>cal</sub>	d <sub>obs</sub>	d <sub>cal</sub>	d <sub>obs</sub>
0 0 2	10	5.388	5.413	5.385	5.408	5.42
0 2 2	10	3.822	3.828	3.819	3.824	3.82
2 2 2	100	3.121	3.125	3.117	3.122	3.12
0 0 4	30	2.370	2.707	2.701	2.704	2.70
0 2 4	20	2.420	2.421	2.418	2.419	2.42
2 2 4	10	2.212	2.210	2.208	2.208	2.21
0 4 4	80	1.914	1.914	1.911	1.912	1.917
2 4 4	10	1.804	1.804	1.803	1.803	1.802
0 2 6	5	1.714	1.712	1.712	1.710	1.715
2 2 6	50	1.632	1.632	1.631	1.631	1.633
4 4 4	10	1.563	1.563	1.562	1.561	1.562
6 4 0	3	1.502	1.501	1.500	1.500	1.052
6 4 2	5	1.449	1.447	1.446	1.445	1.448
8 0 0	20	1.375	1.375	1.374	1.374	1.354
8 2 0	5	1.314	1.313	1.313	1.312	1.314
8 2 2	5	1.277	1.276	1.276	1.275	1.277
6 6 2	30	1.242	1.242	1.241	1.241	1.243
8 4 0	10	1.211	1.210	1.209	1.209	1.211
8 4 2	5	1.182	1.181	1.180	1.180	1.182
6 6 4	3	1.155	1.154	1.153	1.153	1.155
8 4 4	40	1.106	1.105	1.105	1.104	1.106
a <sub>c</sub> (Å)		10.827		10.817		10.837
V		1269.077		1265.527		1272.703

\* at 500°C, quenched, y=0 (this study).

\*\* at 500°C, quenched, y=0.4 (this study).

\*\*\* synthesized at 420°C (Franz, 1975).

These sphalerite type ss, cps and isos can be further stabilized to much lower temperature alone or with other impurities, mutual solubilities of the coexisting phases, pressure etc. in natural condition. Or it differentiates presumably in a number of phases which have not been detected to present time.

## CONCLUSION

It is experimentally found that the phases  $(\text{Fe, Cu, Sn})_{1+x}\text{S}$  (cps) and  $\text{Cu}_{2-y}\text{Fe}_{1+y}\text{SnS}_4$  (isos) form the incorporation type solid solution, which result from reciprocal solubility of phases of variable composition.

Cps has a wide compositional range of stability; the value of  $\text{Cu/Fe}=0.5-1.1$ ,  $\text{Sn/Cu+Fe}=0-0.25$ . It equilibrates with bornite ss, high stannoidite ss and isos,  $\text{Fe}_{1-x}\text{S}$ ,  $\text{Fe}_2\text{SnS}_4$  and  $\text{FeS}_2$  according to the ratio of metal/sulfur and metal/metal. The cell dimension of this sphalerite-type (fcc) phase varies from  $a=5.340 \text{ \AA}$  to  $a=5.329 \text{ \AA}$  at  $600^\circ\text{C}$ .

The compositional stability range of isos is lineal from  $\text{Cu}_{2.0}\text{Fe}_{1.0}\text{SnS}_4$  to  $\text{Cu}_{1.2}\text{Fe}_{1.8}\text{SnS}_{4.0}$  and the phase melts in a range of  $835-862^\circ\text{C}$ , contrasting to that of stoichiometric composition. This phase is in equilibrium with cps,  $\text{FeS}_2$ , high stannoidite ss,  $\text{SnS}$ ,  $\text{SnS}_2$ ,  $\text{Fe}_{1-x}\text{S}$  and  $\text{Fe}_2\text{SnS}_4$  at  $600^\circ\text{C}$  in the composition tetrahedron Cu-Fe-Sn-S. The unit cell parameter of the phase varies with metal/sulfur ratio:  $a=10.817 \text{ \AA}$  for  $m/s=1/1$  and  $a=10.837 \text{ \AA}$  for  $m/s=0.9/1$ .

With the temperature decrease, the solubility range of the cps decreases and the excess Sn-content is expelled in a form of exsolution body of isos and reversed reaction is observed for the higher temperatures.

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