SHORT COMMUNICATIONS

Copper–tin sulphides in the system Cu–Sn–S

I T is well known that copper and tin form complex sulphides. In two preliminary studies, Moh (1960, 1963) identified four phases in the system Cu–Sn–S. Both Cu_2SnS_3 and $Cu_2Sn_2S_5$ are on the join $Cu_2S–SnS_2$. Cu_2SnS_3 is characterized by a tetragonal–cubic transition at 780 °C, whereas $Cu_2Sn_2S_5$ exhibits an extensive range of solid solution between Cu_2SnS_3 and SnS_2. The other two phases, Cu_5SnS_4 and Cu_5SnS_6, are stable below 600 °C. Subsequent studies suggested that $Cu_2Sn_2S_5$ and Cu_5SnS_4 be discarded (Wang, 1974), and seven new copper–tin sulphides were proposed: $Cu_2Sn_3S_7$ (Wang, 1974; Sobott and Teh, 1977), Cu_4SnS_4 (Wang, 1974; Jaulmes et al., 1977), $Cu_{9.67}Sn_{2.33}S_{13}$ (Wang, 1976), $Cu_5Sn_2S_7$, $Cu_7Sn_3S_{10}$ (Wang, 1977), Cu_4SnS_6 (Wang, 1981) and Cu_3SnS_4 (Moh, 1982). This study examines their relations in the system Cu–Sn–S.

Experimental procedure. Experiments were performed by means of the conventional evacuated glass capsule technique using elements of 99.99 % purity as specified by suppliers' analyses. Heat treatment was conducted in muffle furnaces controlled to ±3 °C. Quenched products were examined by X-ray powder diffraction, reflected light microscopy, and electron microprobe analysis. Cell dimensions ±0.005 Å were computed by using a least-squares refinement program.

Results and discussion. Phase relations in the system Cu–Sn–S were studied in the temperature range between 400 and 650 °C. Five copper–tin sulphides are stable in the system, $Cu_2Sn_3S_7$, Cu_2SnS_3, Cu_4SnS_4, $Cu_5Sn_2S_7$, and $Cu_{10}Sn_2S_{13}$. The latter is structurally an equivalent to $Cu_{9.67}Sn_{2.33}S_{13}$, but with a slightly different composition. X-ray powder diffraction data of $Cu_2Sn_3S_7$, Cu_2SnS_3, Cu_4SnS_4, and $Cu_{10}Sn_2S_{13}$ are listed in Table I.

Phase relations in a 500 °C isothermal section are illustrated in fig. 1. Metallic liquid develops only in the Sn-rich portion of the system, and is isolated from sulphide assemblages, except SnS, by the join $SnS–Cu_3Sn$. In the S-rich portion, sulphur in the form of liquid exists in equilibrium with sulphides.

$Cu_2Sn_3S_7$ is monoclinic with cell dimensions $a = 12.68$, $b = 7.351$, $c = 12.76$ Å, and $\beta = 109.60°$. The X-ray powder diffraction pattern is very similar to that of rhodostannite, as Wang (1974) pointed

out, except for several weak reflection lines. Electron probe analysis give a formula $Cu_{2.1}Sn_{3.4}S_{7.5}$ comparable with Wang's $Cu_2Sn_{3.34}S_{7.68}$. Cu_2SnS_3 (Wang, 1974; Moh, 1976) has a triclinic superstructure of sphalerite, pseudomonoclinic in symmetry with cell dimensions of $a = 6.640$, $b = 11.53$, $c = 19.91$ Å, $\alpha = 90°$, $\beta = 109.45°$, and $\gamma = 90°$ which are in good agreement with published data. Both phases are stable in the temperature range of this study and have no detectable range of solid solution. The composition of $Cu_2Sn_2S_5$ produced an assemblage of $Cu_2Sn_3S_7$ and Cu_2SnS_3.

Cu_4SnS_4 was successfully synthesized, but with much difficulty from the required initial charge. A prolonged period of heat treatment of 120 days, compared to 60 days for the other phases, with intermediate grinding was necessary. It is orthorhombic with $a = 13.50$, $b = 7.66$, and $c = 6.395$ Å, and the formula derived from probe data is $Cu_{3.9}Sn_{1.1}S_4$. This phase forms binary assemblages with Cu_2S, SnS, Cu_2SnS_3, and $Cu_5Sn_2S_7$.

The other two copper–tin sulphides in the system at 500 °C have compositions of $Cu_{10}Sn_2S_{13}$ and $Cu_5Sn_2S_7$ assigned on the basis of probe compositions of $Cu_{9.7}Sn_{2.2}S_{13}$ and $Cu_{4.9}Sn_2S_7$. The former is comparable to $Cu_{9.67}Sn_{2.33}S_{13}$ (Wang, 1976), and the latter is identical with Wang's $Cu_5Sn_2S_7$ (1977). $Cu_{10}Sn_2S_{13}$ is tetragonal with $a = 9.540$ and $c = 10.93$ Å which match well with $a = 9.53$ and $c = 10.93$ Å of $Cu_{9.67}Sn_{2.33}S_{13}$. According to Wang (1976), $Cu_{9.67}Sn_{2.33}S_{13}$ coexists with CuS in samples of compositions with Cu/Sn ratio higher than 4.15, and coexists with Cu_2SnS_3 when the ratio is lower than 4.15 at 500 °C. As shown in fig. 1, $Cu_{10}Sn_2S_{13}$ does not coexist with Cu_2SnS_3 in any compositional region. $Cu_{10}Sn_2S_{13}$ is stable up to 641 ± 3 °C. With the melting of CuS at 507 °C (Kullerud, 1965), the equilibrium assemblages of $Cu_{2-x}S + Cu_{10}Sn_2S_{13} + CuS$, $CuS + Cu_{10}Sn_2S_{13} + S(L)$, and $Cu_{10}Sn_2S_{13} + Cu_5Sn_2S_7 + S(L)$ at 500 °C are replaced by the assemblage $Cu_{2-x}S + Cu_5Sn_2S_3 + S(L)$ at 650 °C, the upper temperature limit reached in this study.

Attempts to index the X-ray powder diffraction pattern of $Cu_5Sn_2S_7$ were not successful. Its d-values and relative intensities are $(d$ Å, $(I/I_0))$ 5.251(5), 4.911(5), 4.887(5), 4.724(5), 4.202(5), 3.292(5), 3.109(100), 3.034(5), 2.949(5), 2.882(5),

Table I. X-ray Powder Diffraction Data of Cu-Sn Sulfides.

Cu₄SnS₄				Cu₂SnS₃				Cu₂Sn₃S₇				Cu₁₀Sn₂S₁₃			
d(meas), Å	I/I₀	d(calc), Å	(hkl)	d(meas), Å	I/I₀	d(calc), Å	(hkl)	d(meas), Å	I/I₀	d(calc), Å	(hkl)	d(meas), Å	I/I₀	d(calc), Å	(hkl)
4.670	5	4.642	201	5.468	10	5.489	110	5.985	40	5.972	200	5.495	15	5.465	002
3.850	10	3.831	020	4.230	10	4.234	023	4.762	5	4.775	$11\bar{2}$	3.663	60	3.643	003
3.381	90	3.375	400	3.641	5	3.633	024	3.673	10	3.676, 3.666	020, 202	3.224	10	3.205	113
3.326	85	3.331, 3.317	220, 311	3.138	100	3.137, 3.121	$20\bar{4}$, 200					3.016	100	3.017	130
3.196	40	3.193	121					3.134	100	3.141, 3.130	$20\bar{4}$, 220	2.909	15	2.908, 2.895	131, 023
3.110	70	3.111	102	2.840	10	2.847, 2.831	$22\bar{3}$, 124	3.004	15	3.005	004				
2.965	10	2.954	221	2.714	50	2.718	$20\bar{6}$	2.600	90	2.599	$40\bar{4}$	2.748	60	2.749, 2.732	032, 004
2.884	60	2.883	112	2.611	5	2.617	043	2.385	20	2.387, 2.383, 2.375	224, $20\bar{4}$, 402	2.312	25	2.314, 2.301	140, 124
2.702	5	2.704	212	2.439	5	2.454, 2.419	044, 213	2.326	5	2.319	313	1.999	40	1.995	043
2.657	50	2.654	321	2.289	10	2.299, 2.273	143, 223	2.124	5	2.113	$60\bar{2}$	1.898	40	1.908, 1.901	340, 234
2.605	15	2.606	302	2.166	10	2.163, 2.161	$31\bar{4}$, 150	2.003	50	2.003, 1.991	006, 600	1.872	60	1.879, 1.871	341, 150
2.495	10	2.487	501	2.121	10	2.122, 2.117	$24\bar{4}$, 240								
2.372	40	2.372, 2.366	031, 511	2.059	10	2.066, 2.055	$32\bar{3}$, $32\bar{4}$	1.840	100	1.841, 1.838, 1.832	$22\bar{6}$, 040, $40\bar{4}$	1.833	15	1.840	243
2.311	15	2.307	222									1.741	25	1.736	334
2.159	15	2.159	610	1.967	10	1.969, 2.966	242, $32\bar{6}$	1.760	20	1.756, 1.751	240, 620	1.666	40	1.675, 1.664	126, 153
2.103	10	2.098	331	1.920	100	1.922	060	1.590	15	1.578	$80\bar{2}$				
2.069	15	2.063	502	1.890	10	1.898, 1.885	302, 321	1.570	10	1.570, 1.565	$40\bar{8}$, 440	1.592	20	1.603, 1.590	226, 060
2.048	10	2.045	411	1.835	5	1.837	$33\bar{6}$					1.574	20	1.573, 1.567	061, 335
2.038	15	2.036, 2.030	430, 113	1.696	10	1.698, 1.693	304, $34\bar{6}$					1.549	10	1.544	154
1.996	25	1.992	512	1.638	80	1.643, 1.636, 1.636	$41\bar{4}$, 260, $201\bar{2}$								
1.967	5	1.974, 1.965	132, 213	1.570	20	1.575, 1.560	$42\bar{6}$, 400								
1.948	90	1.940	620												
1.918	20	1.915, 1.913	040, 232												
1.873	20	1.868, 1.863	313, 023												
1.821	5	1.824	332												
1.802	100	1.802, 1.795	403, 223												
1.726	5	1.721	323												
1.695	25	1.699, 1.687	341, 800												
1.679	5	1.673	503												
1.664	30	1.666, 1.663	440, 721												
1.656	15	1.659	622												
1.636	10	1.632, 1.631	632, 142												
1.621	35	1.614	712												
1.610	10	1.605, 1.599	532, 004												
1.549	10	1.559, 1.447, 1.543	204, 603, 342												

2.694(5), 2.484(5), 2.452(5), 2.401(5), 2.328(5), 2.274(5), 2.241(5), 2.179(5), 2.043(5), 1.997(5), 1.906(90), 1.858(5), 1.685(5), 1.627(7), and 1.559(15). Judged from major reflection lines (3.109, 2.694, 1.906, 1.627, and 1.559), this phase may also have a superstructure derived from sphalerite.

Among the copper–tin sulphides, Cu_2SnS_3 and Cu_3SnS_4 have been identified in natural assemblages. Mohite (Cu_2SnS_3) (Kovalenker et al., 1982) has cell dimensions of $a = 6.64$, $b = 11.51$, $c = 19.93$ Å, $\alpha = 90°$, $\beta = 109.75°$, and $\gamma = 90°$, which are in good agreement with results of synthetic Cu_2SnS_3 obtained in this study. Kuramite (Kovalenker et al., 1979) has a reported composition ranging from $Cu_{2.6}(Fe,Zn)_{0.4}SnS_4$ to $Cu_{2.8}(Fe,Zn)_{0.2}SnS_4$. Its (Fe,Zn)-free equivalent in the system Cu–Sn–S was produced by sulphidization of Cu_4SnS_4 at 90 °C and has a Cu/Sn ratio of 3.278 (Moh, 1982). According to Moh, this phase breaks down at temperatures above 330 °C.
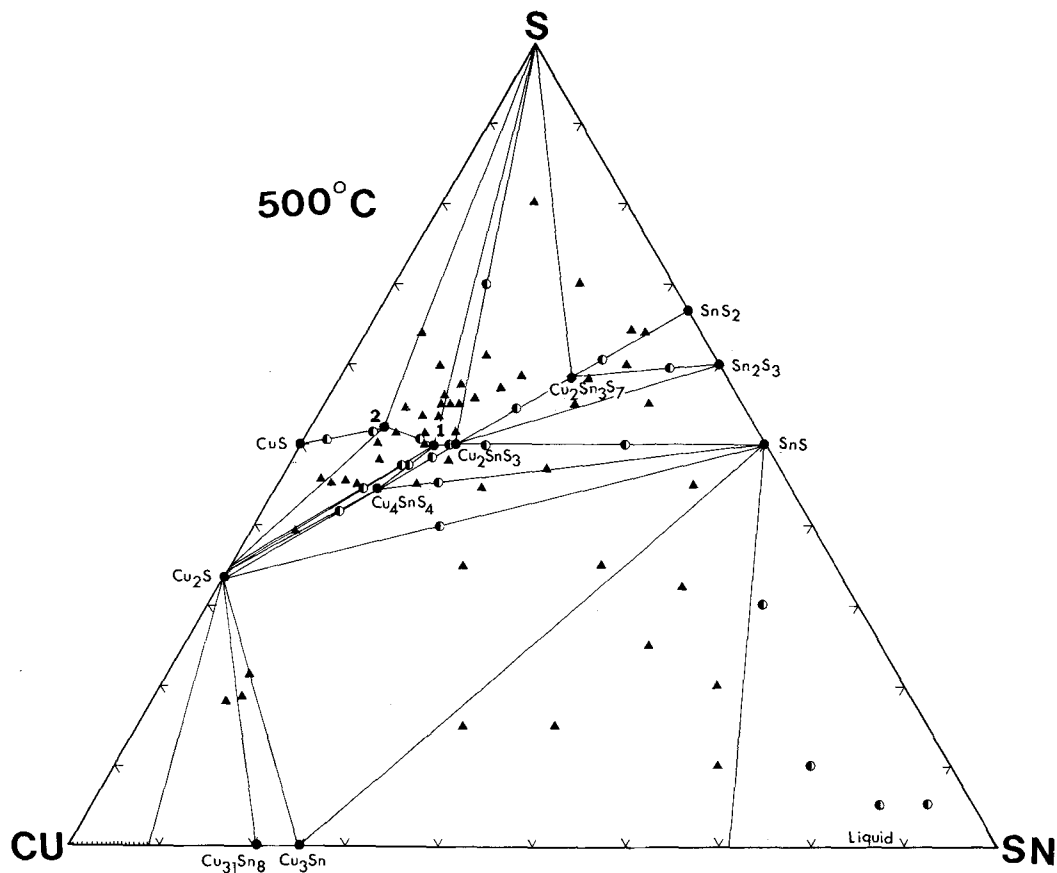
FIG. 1. Phase relations in the system Cu–Sn–S at 500 °C. In the figure, solid circles, half-filled circles, and solid triangles represent one-, two-, and three-phase assemblages, respectively. '1' and '2' denote $Cu_5Sn_2S_7$ and $Cu_{10}Sn_2S_{13}$.

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