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Compounds in the System $Cu_2Se–As_2Se_3$

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The phase diagram $Cu_2Se–As_2Se_3$ was investigated by thermal and X-ray methods. Cu_2Se has a limited solubility for As_2Se_3 (5 mole% at 769 K). The stoichiometric compound Cu_3AsSe_3 exists between 696 and 769 K. $Cu_4As_2Se_5$, a phase at 66.6 mole% Cu_2Se, decomposes peritectically at 746 K. The narrow homogeneity range (4 mole% at 683 K) extends far into the ternary space. $CuAsSe_2$ also decomposes peritectically at 683 K. A degenerated eutectic between $CuAsSe_2$ and As_2Se_3 was found at 641 K. Single crystals of $Cu_4As_2Se_5$ were grown in a salt melt. A metastable modification of the high-temperature phase Cu_3AsSe_3 can be obtained by quenching. $Cu_4As_2Se_5$ (space group $R3$, lattice constants a = 1404.0(1) pm, c = 960.2(1) pm), $Cu_6As_4Se_9$, obtained by Cambi and Elli, and $Cu_7As_6Se_{13}$ of Takeuchi and Horiuchi are different versions of a sphalerite-type compound with a broad homogeneity range in the system Cu–As–Se. $CuAsSe_2$ is possibly monoclinic with lattice parameters of a = 946.5(1) pm, b = 1229.3(1) pm, c = 511.7(1) pm, and β = 98.546(4)°. The enthalpy of mixing of Cu_2Se and As_2Se_3 in the liquid state is endothermic.

Introduction

Several papers on the glass-forming ability of the system Cu–As–Se have been published (*1–3*), in which the necessity of a reliable phase diagram for a complete understanding of the glasses in this system was stressed. However, the phase relations and the number of compounds in the ternary system Cu–As–Se are at present not well established. Cambi and Elli (*4*) prepared compounds in the system $Cu_2Se–As_2Se_3$ by hydrothermal synthesis. In the region from 60 to 100 mole% Cu_2Se they obtained the phase $Cu_6As_4Se_9$ with pseudocubic symmetry and a lattice constant of a = 1099 pm. Wernick and Benson (*5*) synthesized $CuAsSe_2$ (T_m = 688 K) and assumed the structure was probably related to the sphalerite type. According to Krestovnikov (*6*) this phase transforms into a hexagonal lattice of wurtzite type at temperatures > 570 K. Similarly Imamov and Petrov (*7*) reported two modifications of $CuAsSe_2$; one with the cubic sphalerite structure with a = 575 pm and another hexagonal phase with the space group $R3m$ and lattice parameters of a = 405 pm and c = 1972 pm.

Khvorostenko *et al.* (*8*) made the first investigation of the phase diagram $Cu_2Se–As_2Se_3$ by thermal and X-ray methods (Fig. 1). They reported two phases: Cu_3AsSe_3, formed by a peritectic reaction at 773 K,

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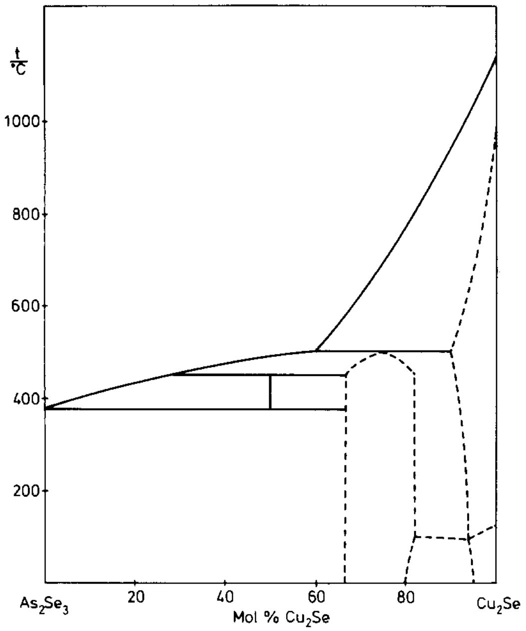

FIG. 1. The phase diagram $Cu_2Se-As_2Se_3$, according to Khvorostenko *et al.* (*8*).

with a region of homogeneity from 66.7 to 82 mole% Cu_2Se, and $CuAsSe_2$—formed by a peritectic reaction at 723 K—which decomposes eutectoidally into As_2Se_3 and Cu_3AsSe_3 below 608 K. We have investigated the section $Cu_2Se-As_2Se_3$ in order to clarify some of these discrepancies.

The high-temperature modification of Cu_2Se has the space group $F\bar{4}3\,m$, with Cu distributed on the octahedral, tetrahedral, and trigonal holes of the cubic face-centered Se sublattice (*9*). The low-temperature modification shows tetragonal symmetry (*10*). As_2Se_3 crystallizes in the monoclinic space group $P2_1/c$ and is built from sheets of As–Se nets (*11*). Another purpose of this work was thus to establish in which steps the polymeric As–Se network is destroyed by the addition of increasing amounts of Cu^+ ions.

Experimental

The alloys were prepared from the proper amounts of high-purity elemental solids (Cu 99.9998% Preussag; As 99.9995% Preussag; Se 99.999% Retorte; As was further purified by heating at 673 K in a hydrogen-gas stream) by encapsulating them under vacuum in quartz ampoules, melting in a flame, and annealing for 2 months at 570 K. In the more complicated regions of the system samples were annealed at different temperatures and quenched to ambient temperature. All samples were subjected to systematic thermal and X-Ray analysis. The difference thermal analysis was carried out with a DTA apparatus constructed in this laboratory (*12*), as well as with a Du Pont 990 DSC instrument, at a standard heating/cooling rate of 10 K/min. X-Ray analyses were performed with a Guinier-4-camera ($CuK\alpha_1$ radiation) resp. a Huber-600-camera ($CrK\alpha_1$ radiation, SiO_2 as internal standard) or a Simon–Guinier heating camera (heating rates 5 K/hr). Single-crystal data were collected by a precession camera. Some liquid–liquid enthalpies of mixing were measured in a high-temperature calorimeter (Calvet-type, Setaram) at 847 K.

Results

The phase diagram $Cu_2Se-As_2Se_3$ is given in Fig. 2. β-Cu_2Se shows a limited solubility for As_2Se_3, which increases from ambient temperature to a value of 5 mole% As_2Se_3 at 769 K. The higher solubility found by Khvorostenko (10 mole% at 770 K) could not be verified. Samples of this composition, annealed at 770 K, consist, according to the X-ray pattern, of two phases (Cu_2Se + Cu_3AsSe_3). In DSC-runs the peritectic temperature of Cu_3AsSe_3 was also observed. Our X-ray results indicate the existence of super structures in the Cu_2Se-based solid solution. The ability of Cu_2Se to form different ordered phases within its homogeneity range at low temperatures is well known (*13–15*). The presence of As^{3+}

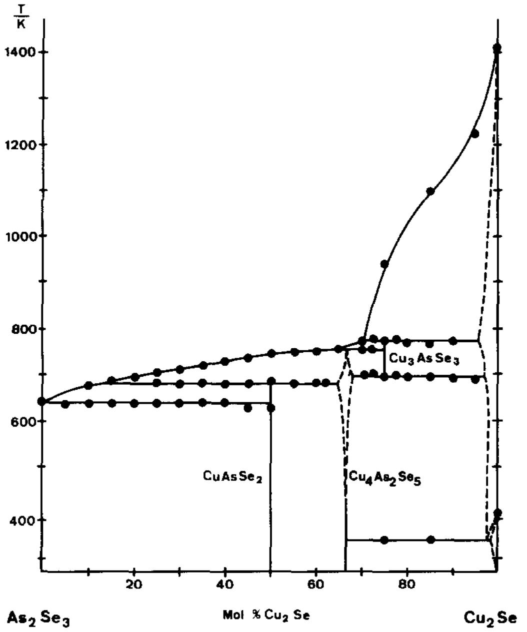

FIG. 2. The phase diagram Cu_2Se–As_2Se_3.

TABLE I

X-RAY POWDER DATA OF Cu_3AsSe_3 QUENCHED FROM 750 K (λ = 228.962 pm)

No.	d [pm]	I	No.	d [pm]	I
1	392.47	m	20	253.52	vw
2	370.43	m	21	244.76	w
3	367.58	st	22	240.88	vw
4	337.28	m	23	216.81	w
5	329.34	m	24	209.72	m
6	316.38	w	25	208.74	w
7	309.38	w	26	205.27	vw
8	302.39	m	27	185.52	m
9	292.10	m	28	184.48	st
10	290.20	st	29	183.80	m
11	285.58	st	30	181.91	m
12	283.38	st	31	181.17	m
13	270.28	st	32	178.98	w
14	263.72	w	33	176.88	w
15	263.06	w	34	175.01	vw
16	261.22	m	35	174.66	vw
17	260.53	m	36	174.13	m
18	257.64	m	37	172.25	w
19	254.70	vw			

Note. Estimated intensities: vw = very weak, w = weak, m = medium, st = strong.

ions in the solid solutions is responsible for the assumed new super structures. The introduction of As^{3+} in the β-Cu_2Se lattice lowers the transformation temperature $\beta \rightarrow \alpha$ from 401 K in stoichiometric Cu_2Se to 345 K at 5 mole% As_2Se_3.

The broad homogeneity range of Cu_3AsSe_3, reported by Khvorostenko, was not observed. According to our results a stoichiometric compound Cu_3AsSe_3 exists in the temperature interval between 696 and 769 K. The eutectoid decomposition reaction of Cu_3AsSe_3 at 696 K, is sluggish. After short annealing above this temperature in a second run in the Differential Scanning Calorimeter the DSC signal, which indicates the formation of Cu_3AsSe_3, has vanished. The Guinier X-ray photographs, taken of these samples after slow cooling to room temperature, reveal a new pattern. This pattern can also be obtained by quenching Cu_3AsSe_3 samples from temperatures between 696 and 769 K in an ice/water mixture. The *d*-values of this metastable Cu_3AsSe_3 modification are given in Table I.

A continuous high-temperature X-ray photograph (Fig. 3) of this phase shows that it transforms into the high-temperature modification of the phase Cu_3AsSe_3 at approximately 350 K. At about 510 K this high-temperature modification, which is still metastable, decomposes into the phase Cu_2Se and $Cu_4As_2Se_5$. Both phases form by a eutectoid reaction at 696 K the high-temperature phase, which is now stable. This

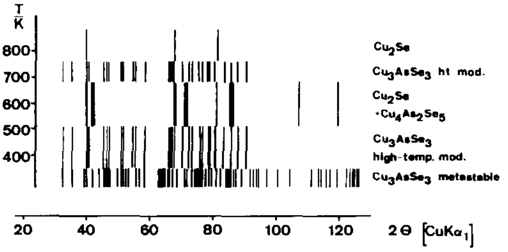

FIG. 3. High-temperature X-ray photograph of quenched Cu_3AsSe_3.

reaction occurs immediately as well with the slow heating rates of 10 K/hr in the high-temperature X-ray experiments as with the high heating rates of 10 K/min in the DSC experiments. The formation of Cu_3AsSe_3, however, can be suppressed by mechanical treatment of the samples. In finely ground powders the DSC signal, indicating the formation of Cu_3AsSe_3, was not observed (Fig. 4).

In agreement with the results of Khvorostenko the phase $Cu_6As_4Se_9$, first prepared by Cambi and Elli by hydrothermal synthesis, was not observed in the equilibrium diagram. Samples of this composition, annealed at 650 K, consist of $CuAsSe_2$ and $Cu_4As_2Se_5$. This phase at 66.6 mole% Cu_2Se decomposes in a peritectic reaction at 746 K which seems to be a borderline case between peritectic decomposition and congruent melting. The experimental techniques used in this investigation were not able to distinguish between the two possibilities. The phase has a narrow homogeneity region which exhibits a maximum range from 64 to 69 mole% Cu_2Se at a temperature of 683 K. The investigation of samples in the ternary system Cu–As–Se revealed that the homogeneity range of this phase extends rather far into the ternary space. The phase $Cu_6As_4Se_9$ of Cambi and Elli has a similar X-ray pattern (Table II). A characteristic difference is the separation of the strong reflections observed by Cambi and Elli into two or three lines in our Huber–Guinier photographs.

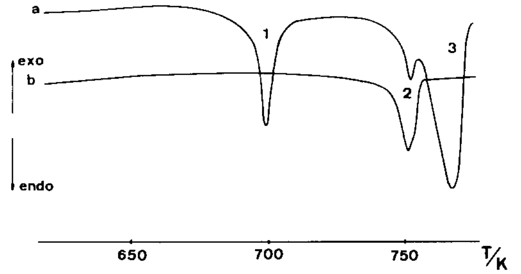

FIG. 4. Traces of differential scanning calorimetric runs of Cu_3AsSe_3. (a) Crystalline sample: (1) formation of Cu_3AsSe_3, (2) peritectic decomposition of $Cu_4As_2Se_5$ (unreacted parts), (3) peritectic decomposition of Cu_3AsSe_3. (b) Finely ground sample (2) peritectic decomposition of $Cu_4As_2Se_5$.

This observation was only made after long annealing periods (60 days; 570 K). A diffuse pattern with unseparated lines was observed after short annealing times. If one neglects this line separation and some weak lines, the reflections of the phase could be indexed on the basis of a cubic lattice with a lattice constant of $a = 552$ pm; this is approximately half the lattice constant observed by Cambi and Elli for $Cu_6As_4Se_9$ ($a = 1099$ pm). The relation to the cubic high-temperature phase of Cu_2Se ($a = 584$ pm) is evident. The phase "$Cu_6As_4Se_9$" lies probably within the broad homogeneity range of $Cu_4As_2Se_5$ in the ternary space, but not on the section Cu_2Se–As_2Se_3.

Single crystals of the compound were grown in form of trigonal prisms from a eutectic CuI/KI melt. The symmetry and the lattice constants were obtained from Buerger-precession photographs. The lattice constants were refined by a least-square method from the powder diffraction pattern. $Cu_4As_2Se_5$ has the rhombohedral space group $R3$ or $R\bar{3}$. The phase, treated on the basis of hexagonal axes, has lattice constants of $a = 1404.0(1)$ pm and $c = 960.2(1)$ pm. The c-axis is running parallel to the axes of the needles.

First results of a structure determination show that $Cu_4As_2Se_5$ has a defect structure derived from the sphalerite structure by vacancies in the Se sublattice. These vacancies cause the broad homogeneity range of the phase. The results indicate too that the composition is probably more complex than $Cu_4As_2Se_5$.[1] The compound shows similarities to the mineral Nowackiit (*16*),

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[1] *Note added in proof.* According to the structure determination the composition of the compound at low temperatures is $Cu_{18}As_8Se_{21}$, derived from Nowackiit by the substitution of $3Zn^{2+}$ by $6Cu^+$ and removal of 1.5 Se^{2-}.

TABLE II

X-RAY POWDER DATA OF "$Cu_4As_2Se_5$"

	$Cu_4As_2Se_5$ (this work)				$Cu_6As_4Se_9$ (4)		$Cu_4As_2Se_5$	
No.	d_{obs} [pm]	d_{calc} [pm]	*hkl*	*I*	*d* [pm]	*I*	*d* [pm]	*hkl*
							Pseudocubic indices	
1	414.66	414.53	211	vw			(λ = 154.051 pm)	
2	405.26	405.29	300	vw				
3	320.07	320.07	003	vst	316	100	318.71	111
4	318.16	318.17	131	vst				
5	275.94	275.95	312	m	279.3	1		
6	241.15	241.19	232	m				
7	236.51	236.50	223	m				
8	235.56	235.51	104	m				
9	234.01	234.00	330	w				
10	223.49	223.47	241	w				
11	216.99	216.94	502	w				
12	207.30	207.26	422	vw				
13	204.29	204.27	413	m				
14	202.65	202.65	600	w				
15	195.55	195.56	134	vst				
16	194.71	194.70	520	vst	194.5	49	195.17	220
17	177.19	177.19	125	vw				
18	175.52	175.50	440	vw				
19	172.94	172.97	612	vw				
20	171.21	171.22	603	vw				
21	170.90	170.92	701	w				
22	166.87	166.88	315	vst				
23	166.33	166.34	523	vst	166.1	30	166.44	311
24	166.05	166.07	621	st				
25	163.32	163.34	532	vw				
26	162.34	162.35	045	vw				
27	161.51	161.54	514	vw				
28	160.05	160.03	006	vw				
29	159.11	159.09	262	vw			138.01	400
30	158.18	158.18	235	vw			126.64	331
		(λ = 228.962 pm)				(*a* = 552 pm)		

Note. Estimated intensities: vw = very weak, w = weak, m = medium, st = strong, vst = very strong.

($Cu_6Zn_3As_4S_{12}$), which has a defect structure, and crystallizes in the space group *R*3 with similar lattice constants (a = 1344 pm, c = 917 pm). As the cation sublattice of the sphalerite-type cell is fully occupied in Nowackiit, the removal of Zn^{2+} by Cu^+ must generate additional Se vacancies. The presence of Cu^{2+} in our phase was excluded by qualitative magnetic measurements. It was shown that the substance is diamagnetic. The compound $CuAsSe_2$ decomposes peritectically at 683 K in liquid and $Cu_4As_2Se_5$. Takeuchi and Horiuchi (*17*) reported the structure determination of a sphalerite-like compound $Cu_7As_6Se_{13}$, which lies in the ternary system close to the $CuAsSe_2$ phase. This compound has lattice constants of a = 1402.5 pm and c = 961 pm and the space group *R*3, which does not correspond to the results of Imamov and Petrov. Our X-ray powder pattern could neither be indexed with the lattice constants of Takeuchi and Horiuchi nor with those of Imamov and Petrov.

An acceptable indexing of the observed reflections was obtained with aid of the ITO-method (*18*) by a monoclinic lattice with lattice constants of a = 946.4(1) pm, b = 1229.3(1) pm, c = 511.7(1) pm, and β = 98.546(4)°.

A list of *d*-values is given in Table III. Takeuchi and Horiuchi gave no reflection list in their paper though it would be interesting to compare it with the pattern of the $Cu_4As_2Se_5$ phase. $Cu_7As_6Se_{13}$ is a derivative ZnS type with all anion sites occupied while $Cu_4As_2Se_5$ shows vacant anion sites. The powder pattern of $Cu_7As_6Se_{13}$ was calculated by us with the aid of the programm LAZY PULVER IX (*19*). It resembles closely the $Cu_4As_2Se_5$ pattern with variations in the intensities of the reflections, i.e., this phase may lie also in the homogeneity range of $Cu_4As_2Se_5$ in the ternary space.

A degenerated eutectic between $CuAsSe_2$ and As_2Se_3 was found at 641 K. The experiments in this region were difficult due to the tendency of the samples to solidify as glasses. The flat liquidus of this part of the system is caused by a tendency for immiscibility in the liquid state. This was confirmed by preliminary measurements of the enthalpies of mixing of Cu_2Se and As_2Se_3 in the liquid state at 847 K between 0 and 60 mole% Cu_2Se. Endothermic values were observed, which reach a maximum value of 3000 J mole^{-1} at 25 mole% Cu_2Se.

TABLE III

X-RAY POWDER DATA OF $CuAsSe_2$
(λ = 228.962 pm)

No.	d_{obs} [pm]	d_{calc} [pm]	*hkl*	*I*
1	468.27	467.93	011	w
2	397.61	397.27	111	st
3	344.08	346.66	121	w
4	317.98	318.41	$22\bar{1}$	st
5	310.35	310.25	211	w
6	307.71	307.33	040	vw
7	302.77	302.39	310	st
8	291.65	291.99	140	vw
9	284.45	284.28	221	vw
10	279.66	278.19	320	vw
11	252.84	253.01	002	w
12	248.83	248.69	$11\bar{2}$	w
13	244.68	244.52	311	st
14	237.43	237.84	$20\bar{2}$	vw
15	233.95	233.97	022	vw
16	229.40	229.85	410	m
17	221.46	221.82	$41\bar{1}$	vw
18	198.69	198.64	411	vw
19	197.95	197.58	$43\bar{1}$	w
20	187.51	187.69	260	w
21	186.27	186.21	$35\bar{1}$	w
22	174.94	174.83	$34\bar{2}$	m

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