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The Polythermal $CuGaSe_2$–Cu_8GeSe_6 Section of the Quasiternary Cu_2Se-Ga_2Se_3–$GeSe_2$ System

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The polythermal $CuGaSe_2$–Cu_8GeSe_6 section has been constructed using differential thermal, X-ray and microstructural analyses. It has been established that this section is a quasibinary one only in the subsolidus part. The ranges of the solid solutions have been determined.

Key words: DTA, polythermal section, ternary phase, peritectic reaction

The $CuGaSe_2$–Cu_8GeSe_6 section belongs to the Cu_2Se–Ga_2Se_3–$GeSe_2$ system, which has not been studied so far. It is interesting, because it is formed by compounds with valuable semiconducting properties. The interactions in the Cu_2Se–Ga_2Se_3 system have been reported in [1–3] but the diagrams differ from each other. As a result of these investigations the existence of the ternary $CuGaSe_2$ compound has been confirmed. This compound is formed by the peritectic reaction $L + \gamma \Leftrightarrow CuGaSe_2$ at 1323 K [1,2] or 1313 K [3]. $CuGaSe_2$ crystallizes in the chalcopyrite structure [4,5], space group $I\bar{4}2d$ with lattice parameters $a = 0.5614$ nm, $c = 1.1022$ nm [4] or $a = 0.5596$ nm, $c = 1.1004$ nm [5].

The investigations of the phase equilibria in the Cu_2Se–$GeSe_2$ system have been carried out in [6–9]. They differ from each other in the character of the Cu_2GeSe_3 formation and in the composition of the other phase (Cu_8GeSe_6 or Cu_6GeSe_5). The Cu_2Se–$GeSe_2$ phase diagram in 15–60 mol.% $GeSe_2$ concentration interval has been constructed in [9]. The existence of two ternary phases: Cu_2GeSe_3 and Cu_8GeSe_6 has been confirmed. Cu_2GeSe_3 melts congruently at 1053 K. The formation of Cu_8GeSe_6 corresponds to the peritectic process $L + Cu_2Se \Leftrightarrow Cu_8GeSe_6$ at 1083 K. The polymorphic transformations of this phase have been observed at 983 and 333 K.

The crystal structure of both polymorphic modifications can be found in [6, 10–12]. Both the low-temperature (α-Cu_8GeSe_6) and the high-temperature (β-Cu_8GeSe_6) modifications are hexagonal, space group $P6_3cm$ and $P6_3mc$ respectively. The lattice parameters are summarized in Table 1.

Table 1. Lattice parameters for Cu_8GeSe_6.

Compound	Lattice parameters		References
	a, nm	*c*, nm	
α-Cu_8GeSe_6	1.249	1.167	[6]
	1.2632	1.1758	[10]
	1.2648(5)	1.176(4)	[11]
	1.26438(2)	1.17570(1)	[12]
β-Cu_8GeSe_6	0.728	1.167	[6]
	0.7632	1.1782	[10]
	0.73164(4)	1.17679(7)	[12]

EXPERIMENTAL

23 samples in the field 0–100 mol. % Cu_8GeSe_6 were synthesized to construct the polythermal $CuGaSe_2$–Cu_8GeSe_6 section (Table 2). Samples were prepared from pure elements (Se 99.999 wt.%, Ga 99.9997 wt.%, Ge 99.9994 wt.%, Cu 99.99 wt.%) using the method of direct high temperature synthesis in evacuated to 1.3×10^{-4} hPa quartz ampoules. The highest temperature was 1420 K. Annealing took place at 820 K during 250 hours. Samples obtained in this way were investigated using differential thermal, microstructural and X-ray analyses.

Table 2. DTA results of $CuGaSe_2$–Cu_8GeSe_6 system samples.

№	Phase composition (mol.%)		Thermal effects (K)			
	$CuGaSe_2$	Cu_8GeSe_6	liquidus	subliquidus	solidus	subsolidus
1.	100	0	1373	–	1333	–
2.	99	1	1348	–	1293	1023
3.	97	3	1343	1328 1293	–	1023
4.	96	4	1340	1310	1043	–
5.	95	5	1330	1293	–	1028
6.	92.5	7.5	1310	1303	1038	–
7.	80	20	1268	1058	1043	973
8.	73	23	1258	1073	1043	–
9.	70	30	1213	–	1043	983
10.	65	35	1203	1073	1048	983
11.	60	40	1183	1068	–	–
12.	55.5	44.5	1173	–	1048	983
13.	45	55	1148	1053	–	983
14.	40	60	1138	1053	–	973
15.	35	65	1103	–	1043	983
16.	30	70	–	1073	1048	983
17.	25	75	1083	1068	–	983
18.	20	80	1073	1068	–	985
19.	15	85	1073	1068	–	983
20.	10	90	1078	1068	–	983
21.	5	95	1098	1073	–	958
22.	0	100	1108	–	1078	973

RESULTS AND DISCUSSION

As far as $CuGaSe_2$ and Cu_8GeSe_6 form by peritectic reactions [1–3, 6–9], the $CuGaSe_2$–Cu_8GeSe_6 section is not a quasibinary one in the full concentration and temperature ranges (Fig. 1). Due to the situation in the quasiternary Cu_2Se–Ga_2Se_3–$GeSe_2$ system, it crosses three surfaces of primary phase crystallization: solid solutions on the basis of γ-phase (the curve *ab*); the curve *bc* corresponding to the δ-solid solutions on the basis of $CuGaSe_2$ and the curve *cd* corresponding to the primary crystallization of Cu_2Se. Subliquidus consists of three fields of secondary phase crystallization: L+γ+δ (*ebf*), L+Cu_2Se+δ (*gch*), L+Cu_2Se+ε (*jhi*). The peritectic process L+γ⇔ $CuGaSe_2$ corresponds to the beginning of the secondary falling of $CuGaSe_2$ (the line *eb*). As far as the $CuGaSe_2$–Cu_8GeSe_6 section is connecting one in the quasiternary Cu_2Se–Ga_2Se_3–$GeSe_2$ system, so one- and three-phase fields coexist on the lines *ef* and *ij*. Solidus is presented by the lines: *ef* and *ij*, which correspond to the finishing of the secondary crystallizations of L + γ + $CuGaSe_2$ and L + Cu_2Se + ε respectively; *fg*, which corresponds to the limited δ-solid solutions; and by the horizontal *gi* of the nonvariant peritectic process L + Cu_2Se ⇔ δ + ε at 1043 K. The peritectoid transformation δ + ε ⇔ β takes place at 983 K.

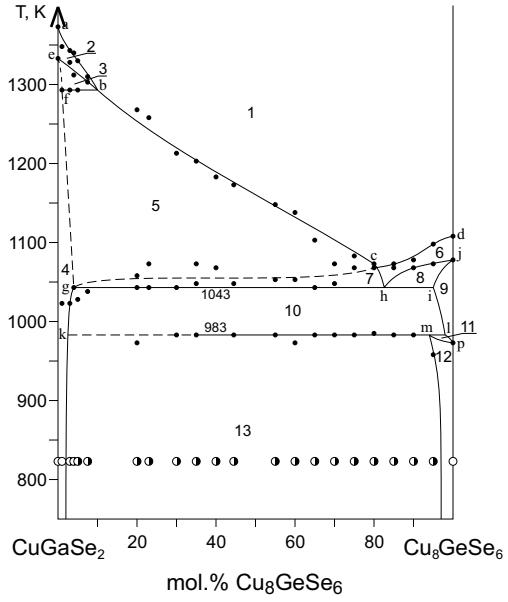

Figure 1. The polythermal $CuGaSe_2$–Cu_8GeSe_6 section of the quasiternary Cu_2Se–Ga_2Se_3–$GeSe_2$ system: 1 – L, 2 – L + γ, 3 – L + γ + δ, 4 – δ, 5 – L + δ, 6 – L + Cu_2Se, 7 – L + Cu_2Se + δ, 8 – L + Cu_2Se + ε, 9 – ε, 10 – δ + ε, 11 – ε + β, 12 – β, 13 – δ + β; ○ – one-phase samples, ◑ – two-phase samples.

Using X-ray and microstructural analyses the solubility on the basis of the components has been determined. δ-Solid solutions on the basis of $CuGaSe_2$ reach ~5 mol.% Cu_8GeSe_6 at the temperature of nonvariant transformation (1043 K) and de-

crease with decreasing temperature to 2.5 mol.% Cu_8GeSe_6 at the annealing temperature. Within the range of δ-solid solutions, the lattice parameters change from a = 0.5588(1) nm, c = 1.0981(6) nm for $CuGaSe_2$ to a = 0.5604(1) nm, c = 1.1005(4) nm for an extreme composition (Fig. 2). The diffractogram of the Cu_8GeSe_6 compound has been indexed in the space group $P6_3cm$ with the lattice parameters a = 1.2579(5) nm, c =1.1692(6) nm, what agrees well with the literature data corresponding to the low-temperature modification. The solubility on the basis of Cu_8GeSe_6 reaches up to 5 mol.% $CuGaSe_2$ at the peritectoid temperature. The change of the lattice parameters varies from a = 1.2579(5) nm and c = 1.1692(6) nm for Cu_8GeSe_6 to a = 1.2644(5) nm, c = 1.1744(6) nm for 5 mol.% $CuGaSe_2$ (Fig. 2). All samples between 3–96 mol.% Cu_8GeSe_6 form two-phases at the annealing temperature.

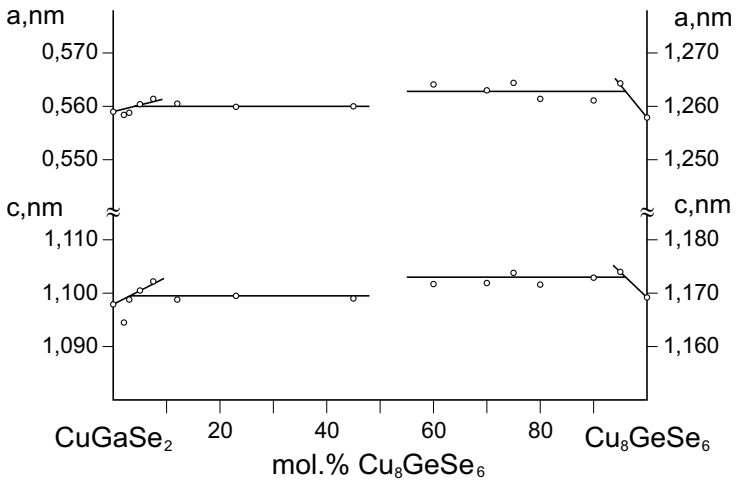

Figure 2. Plots of the lattice parameters of the solid solutions in the $CuGaSe_2$–Cu_8GeSe_6 section at 820 K.

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