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Preparation and analysis of the $CuAl_xIn_{1-x}Se_2$ solid solutions

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$CuAl_xIn_{1-x}Se_2$ solid solutions as well as $CuInSe_2$ and $CuAlSe_2$ ternary compounds are promising materials for optoelectronics and non-linear optics. The properties of these compounds have been given detailed coverage [1–4]. However, investigations of solid solutions based on these compounds are scarce in the literature [5, 6].

The present letter reports on the results of an investigation of the physicochemical properties of these solutions and the phase diagram of the $CuInSe_2$–$CuAlSe_2$ system.

$CuInSe_2$, $CuAlSe_2$ ternary compounds and their solid solutions were obtained by one-temperature synthesis from elementary compounds. The starting components in ratios corresponding to definite solid-solution composition were loaded into boron nitride crucibles which were placed into quartz ampoules. The ampoules were evacuated (up to $\cong 10^{-3}$ Pa), sealed off from the vacuum system and placed in a vertical one-zone furnace. The temperature of the furnace was raised at a rate of $\cong 50\ K\,h^{-1}$ to a value exceeding by 20–30 K the melting temperature for the higher melting compound ($CuAlSe_2$) and the vibrational mixing of the melt was switched on, exposure and vibration of the melt being from 2 to 3 h. Then the temperature was lowered at a rate of $\simeq 100\ K\,h^{-1}$ (without switching off the vibration) down to room temperature. To achieve homogeneity the synthesized ingots were annealed for 800 h at 1070 K. The chemical and X-ray analyses of the as-annealed samples revealed uniformly homogeneous ingots.

The composition of the $CuAl_xIn_{1-x}Se_2$ solid solutions was tested by chemical analysis. The copper, aluminium, indium and selenium concentrations were identified by methods described elsewhere [7–9]. The chemical analysis data are listed in the Table I. It is seen that the experimental agree well with the calculated data.

The equilibrium of the $CuInSe_2$, $CuAlSe_2$ compounds and homogeneity of the $CuAl_xIn_{1-x}Se_2$ solid solutions were determined by X-ray analysis. The angular positions of the diffraction spectra lines were measured on a DRON-2 apparatus by an X-ray method using CuK_α radiation with a nickel filter. The X-ray diffraction patterns of both ternary compounds and their solid solutions show a system of lines corresponding to a chalcopyrite structure. The equilibrium of the as-obtained $CuAl_xIn_{1-x}Se_2$ solid solutions was judged from the resolution of high angular lines on the X-ray diffraction patterns. The unit cell parameters a and c calculated from the well resolved doublets of the lines (332), (316), (424), (228), (512), (336), and (532) by the least-squares method are: $a = 56.05 \pm 0.01$ nm, $c = 109.64 \pm 0.05$ nm, for $CuAlSe_2$ and $a = 57.82 \pm 0.01$ nm, $c = 11.620 \pm 0.05$ nm, for $CuInSe_2$. The concentration dependences of the parameters a and c are given in Fig. 1a. It is seen that they change linearly in accordance with the Vegard law, and are described by the following relations:

$$\left.\begin{aligned} a &= 5.782 - 0.177x \\ c &= 11.620 - 0.656x \end{aligned}\right\} \quad (1)$$

The sample density was determined for the $CuInSe_2$, $CuAlSe_2$ ternary compounds and their solid solutions by the picknometer method described in [10]. The experimental data obtained by the present authors are presented in Fig. 1b along with X-ray density values calculated using the formula

$$d = 1.65 \cdot 10^{-24} \frac{nM}{V} \quad (2)$$

where n is the number of formula units in a unit cell, M is the molar mass of the compound or solid solution, and V is the unit cell volume.

As seen from Fig. 1b the density of the above materials (as well as the a and c parameters) varies linearly with composition x.

TABLE I Chemical analysis of the $CuAl_xIn_{1-x}Se_2$ solid solutions

Composition (x) (mol)	Cu (w %)		Al (w %)		In (w %)		Se (w %)	
	Theoretical	Experimental	Theoretical	Experimental	Theoretical	Experimental	Theoretical	Experimental
1.0	25.57	25.60	10.86	11.04	–	–	63.56	63.55
0.7	23.12	24.80	6.87	6.29	12.53	14.14	57.46	54.13
0.5	21.73	21.94	4.61	4.38	19.63	20.67	54.01	53.28
0.3	20.30	21.05	2.61	3.05	25.93	25.59	50.95	49.11
0.1	19.40	22.00	0.82	0.82	31.56	30.06	48.22	46.85

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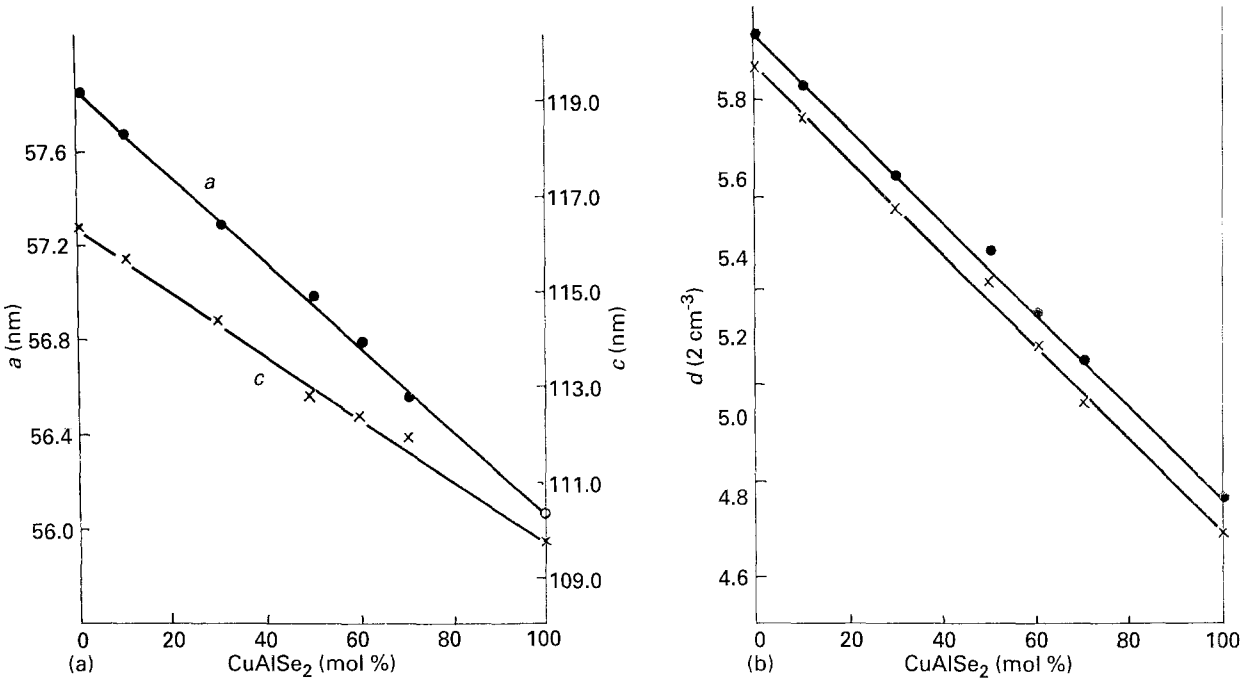

Figure 1 (a) Composition dependence of the a and c parameters for the $CuAl_xIn_{1-x}Se_2$ solid solutions. (b) Composition dependence of $CuAl_xIn_{1-x}Se_2$ solid solutions with x variation.

The phase equilibria in the $CuInSe_2$–$CuGaSe_2$ system were examined by differential thermal (DT) and X-ray phase analyses. The DT analysis was made on an apparatus recording the ratio $\Delta T = f(T)$. The linear heating and cooling of the furnace at a rate of $\simeq 5\ K\ min^{-1}$ was carried out on an RIF-101 apparatus. More details of the DT analysis technique are given in [11, 12].

Our investigations revealed two thermal effects on thermograms for the $CuInSe_2$ ternary compound at 1083 and 1259 K. The first corresponds to the cation–cation disordering (the transformation from the chalcopyrite structure to the sphalerite), the second to the melting temperature [12].

The analogous thermal effects are also representative of solid solutions on the $CuInSe_2$ side which points to the similar nature of these defects in the ternary compound and solid solutions.

The thermogram of the $CuAlSe_2$ ternary compound shows one thermal effect at 1336 K, corresponding to the melting temperature of this compound [13].

The phase transformation diagram for the $CuInSe_2$–$CuAlSe_2$ system was plotted from the DT analysis data (Fig. 2). As seen it is characterized by a small temperature interval of crystallization and can be referred to as the first type in accordance with the Rosebom classification. The liquidus and solidus curves are concave downward which is peculiar to the majority of phase diagrams based on the $A^IB^{III}C_2^{VI}$ ternary compounds [11–14].

From the experimental findings obtained by DT analysis the thermodynamic analysis of phase equilibria in the $CuInSe_2$–$CuAlSe_2$ system was performed, permitting calculation of the interaction parameters for liquid (k^l) and solid (k^s) phases to be made.

Using the as-obtained interaction parameters the liquidus and solidus lines in the approximation of the

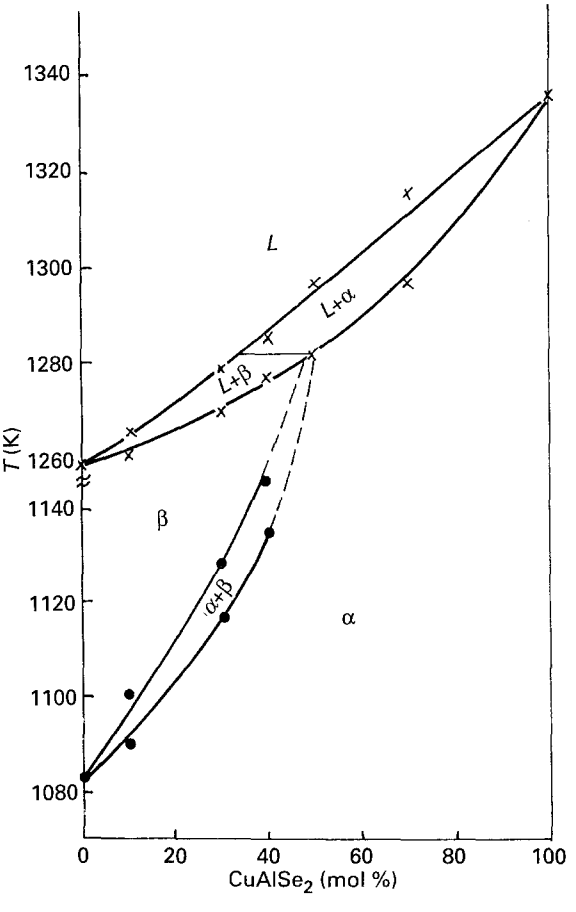

Figure 2 Phase diagram of the $CuInSe_2$–$CuAlSe_2$ system (●, experimental data; — calculation in approximation of the regular solution theory).

theory of regular solutions were computed using the known formulas

$$\left.\begin{aligned}\ln\frac{1-x^s}{1-x^l} &= (x^l)^2\frac{k^l}{RT} + (x^s)^2\frac{k^s}{RT} \\ &\quad - \frac{\Delta S_1}{R}\left(1-\frac{T_1}{T}\right) \\ \ln\frac{x^s}{x^l} &= (1-x^l)^2\frac{k^l}{RT} + (1-x^s)^2\frac{k^s}{RT} \\ &\quad - \frac{\Delta s_2}{R}\left(1-\frac{T_2}{T}\right)\end{aligned}\right\} \quad (3)$$

where x^l and x^s are the $CuAlSe_2$ concentration in liquid and solid phases; ΔS_1 and ΔS_2 are the entropy of melting for $CuInSe_2$ and $CuAlSe_2$; and T_1 and T_2 are the melting temperatures for $CuInSe_2$ and $CuAlSe_2$.

The solidus and liquidus lines calculated in the approximation of regular solutions theory agree well with the experimental results (Fig. 2).

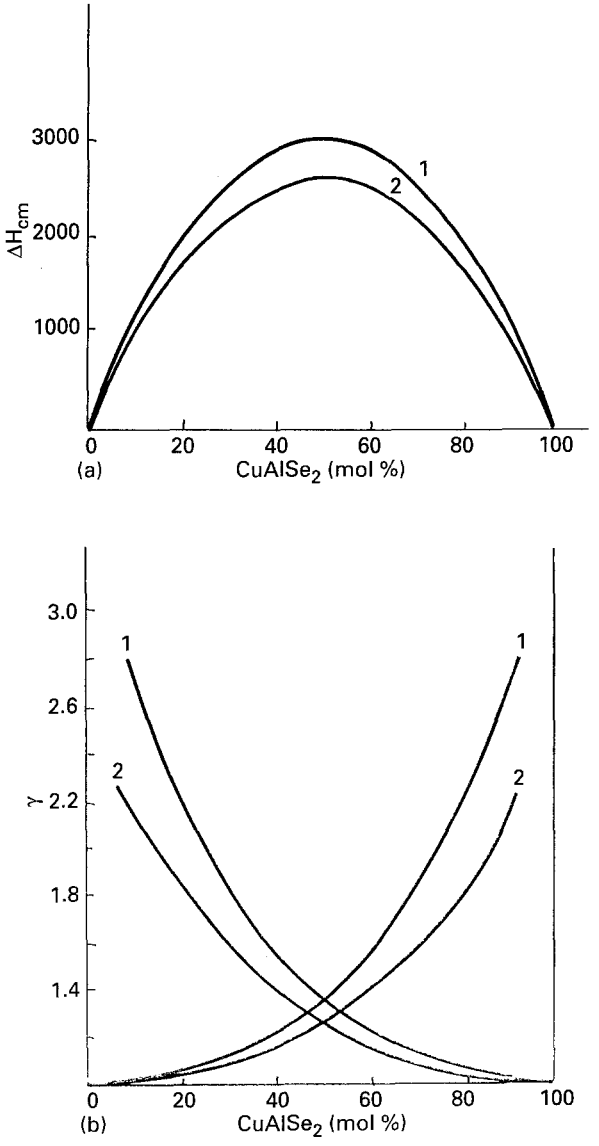

Figure 3 (a) The heat mixture change in liquid (1) and solid (2) phases in the $CuInSe_2$–$CuAlSe_2$ system. (b) The composition dependence of the activity coefficients in liquid (1) and solid (2) phases in the $CuInSe_2$–$CuAlSe_2$ system.

From the known values of interaction parameters k^l and k^s the heats of mixture are calculated for the liquid and solid phases using the relations

$$\left.\begin{aligned}\Delta H^l_{sm} &= k^l x(1-x) \\ \Delta H^s_{sm} &= k^s x(1-x)\end{aligned}\right\} \quad (4)$$

The curves of change of heats of mixture in liquid (1) and solid (2) phases are illustrated in Fig. 3a.

Using the formulas

$$\ln\gamma^l_1 = \frac{k^l}{kT}(1-x)^2;\ \ln\gamma^s_1 = \frac{k^s}{kT}(1-x)^2 \quad (5)$$

$$\ln\gamma^l_2 = \frac{k^l}{kT}x^2; \qquad \ln\gamma^s_2 = \frac{k^s}{kT}x^2 \quad (6)$$

the concentration dependencies of activity coefficients in liquid (1) and solid (2) states are calculated (Fig. 3b).

The $CuInSe_2$ and $CuAlSe_2$ ternary compounds and $CuAl_xIn_{1-x}Se_2$ solid solutions have been synthesized by the one-temperature method. The existence of a continuous series of solid solutions in the $CuInSe_2$–$CuAlSe_2$ system has been established by X-ray phase analysis, DT analysis, and density measurements. The phase diagram of transformations in the $CuInSe_2$–$CuAlSe_2$ system has been plotted and its thermodynamic analysis has been carried out.

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