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Crystallographic, magnetic and luminescence characteristics of $CuIn_2Se_4$ with a cadmium thioaluminate structure and $Cu(In_{1-x}Ga_x)_2Se_4$ solid solutions ($0 < x \leqslant 0.3$)

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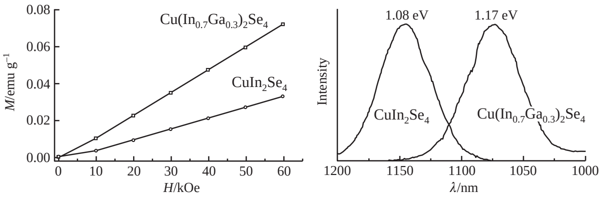
The crystallographic parameters of $CuIn_2Se_4$ possessing a $CdAl_2S_4$-type crystal structure and $Cu(In_{1-x}Ga_x)_2Se_4$ solid solutions based on it were determined. The evaluated magnetic properties confirmed the presence of copper(II) in the crystal lattices of $CuIn_2Se_4$ and $Cu(In_{0.7}Ga_{0.3})_2Se_4$ solid solutions, which are semiconductors with band gaps of $\geqslant$1.08 and $\geqslant$1.17 eV (at 298 K), respectively, found from their cathodoluminescence spectra.



magnetic properties cathodoluminescence

Solid solutions $Cu_{1-x}In_{1-y}Ga_ySe_2$ (CIGS) possessing the chalcopyrite structure are applied in a new generation of thin-filmed solar cells.[1–3] Compound $CuIn_2Se_4$ can be used in the synthesis of copper-deficient CIGS materials possessing a chalcopyrite structure, in particular, $Cu_{1-x}(In_{0.7}Ga_{0.3})_2Se_2$ ($0 < x \leqslant 0.32$) solid solutions are employed as materials for the absorption layers of solar panels.[4]

The compound $CuIn_2Se_4$ was not detected in the Cu–In–Se ternary system,[5] while the stannite structure of $CuIn_2Se_4$ was reported.[6] The magnetic and luminescent properties of $CuIn_2Se_4$ and solid solutions based on it have not been studied in the $CuIn_2Se_4$–$CuGa_2Se_4$ system.

The aim of this work was to synthesize the compound $CuIn_2Se_4$ and $Cu(In_{1-x}Ga_x)_2Se_4$ ($0 < x \leqslant 0.3$) solid solutions based on it and to determine their crystallographic parameters and luminescent and magnetic properties.[†]

The obtained $CuIn_2Se_4$ is a black crystalline substance. Its XRD pattern (Figure 1) does not contain any lines of impurity phases; all of the lines were indexed (21 reflexes, Table 1) in a tetragonal syngony, and the structural type was that of cadmium thioaluminate $CdAl_2S_4$. The unit cell parameters of $CuIn_2Se_4$ were a = 5.754(2) and c = 11.513(4) Å, c/a = 2.0008, and V = 382.12(6) Å^3. Its pycnometer density was 5.319±0.007 g cm^{-3}. The X-ray density of 5.328 g cm^{-3} and the number of $CuIn_2Se_4$ formula units in the unit cell ($Z = 1.9995 \approx 2$) were calculated from the acquired data.

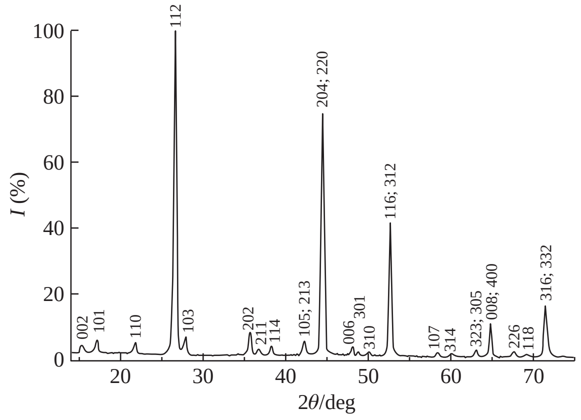


Figure 1 XRD pattern of $CuIn_2Se_4$.

Taking into account reflections in the XRD pattern of $CuIn_2Se_4$, the space group was established as $I\bar{4}2m$, which is the same as that of its prototype, $CdAl_2S_4$.[8] The XRD pattern of $CuIn_2Se_4$ (see Figure 1 and Table 1) contains lines $00l$, wherein l is the even number not a multiple of four: l = 2, l = 6; in the case of a space group $I\bar{4}2d$, these lines are prohibited, while only lines $00(4l)$ are allowed. Moreover, among hhl lines in the XRD pattern in the case of space group $I\bar{4}2d$, only those possessing the sum $(2h + l)$ being the multiple of four are allowed, while in the case of space group $I\bar{4}2m$, lines possessing the sum $(2h + l)$ being an

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[†] The samples were synthesized from high-purity indium, gallium, copper, and selenium of grades 6N, 5N, 4N, and B-4, respectively (the purity was at least 99.99 wt%), in sealed evacuated quartz glass ampoules according to a known procedure.[4] The final annealing was carried out at 750 °C for 100 h in the ampoules. The phase composition of obtained samples was investigated by X-ray diffraction analysis using a DRON-4 diffractometer (CuKα radiation) and the WinX^{POW} software package. The density was measured picnometrically in twice-distilled bromoform of ultra-pure grade. Cathodoluminescence (CL) spectra were recorded at 298 K. The samples were excited by a pulsed 40-keV electron beam. The CL spectra were recorded on a DFS-13 monochromator.[7] The error in the wavelength determination was ±4 nm for the spectrum, while the error in the calculation of photon energy E_g was estimated at ±0.01 eV. Magnetic measurements were performed on a Cryogenic S700 SQUID (Superconducting Quantum Interference Device) magnetometer designed for measurements in magnetic fields of 60 kOe at 290 K. The measurement precision for the magnetic moment was 1%, and that for the applied magnetic field was ±10 Oe. Error in the determination of magnetic susceptibility was 1%.

Table 1 Indexing of XRD pattern of $CuIn_2Se_4$.

I (%)	d_{exp}/Å	$h\,k\,l$	$10^4 d_{exp}^{-2}$ (Q_{exp})	$10^4 d_{calc}^{-2}$ (Q_{calc})	$\Delta = Q_{exp} - Q_{calc}$
2.5	5.755	0 0 2	301.93	302.04	–0.11
5	5.148	1 0 1	377.33	377.48	–0.15
3.5	4.068	1 1 0	604.28	604.08	+0.20
100	3.3219	1 1 2	906.10	905.84	+0.26
6.0	3.1930	1 0 3	980.95	981.02	–0.07
7.0	2.5740	2 0 2	1509.0	1509.1	–0.1
2.0	2.5034	2 1 1	1586.1	1585.6	+0.5
2.5	2.3495	1 1 4	1811.5	1811.1	+0.4
4.5	2.1374	1 0 5 2 1 3	2188.6	2188.0 2189.2	+0.6 –0.6
72	2.0344	2 0 4 2 2 0	2416.1	2415.4 2416.6	+0.7 –0.6
2.5	1.9192	0 0 6	2715.9	2715.8	+0.1
1.5	1.8953	3 0 1	2794.2	2793.8	+0.4
1.0	1.8197	3 1 0	3019.7	3020.4	–0.7
40	1.7353	1 1 6 3 1 2	3321.0	3319.9 3322.2	+1.1 –1.2
1.5	1.5826	1 0 7	3992.8	3991.6	+1.2
1.5	1.5385	3 1 4	4225.3	4226.6	–1.3
2.0	1.4733	3 2 3 3 0 5	4607.0	4605.7 4606.0	+1.3 +1.0
10	1.4382	0 0 8 4 0 0	4831.2	4829.3 4833.1	+1.9 –1.9
2.0	1.3957	2 2 6	5132.9	5132.5	+0.4
1.0	1.3569	1 1 8	5432.6	5432.2	+0.4
15	1.3202	3 1 6 3 3 2	5737.6	5736.2 5739.1	+1.4 –1.5

even number and not multiple of four are additionally allowed among the *hhl* ones. Thus, the XRD pattern of $CuIn_2Se_4$ contains the 002, 006, 114, 118 and 226 lines (Table 1), which has clearly indicated the space group $I\bar{4}2m$.

Note that $CuIn_2Se_4$ and $CuInSe_2$ (chalcopyrite structure) compounds are characterized by different space groups, $I\bar{4}2m$ and $I\bar{4}2d$, respectively.

The closest analogue of $CuIn_2Se_4$ is $ZnIn_2Se_4$, which possesses the structure of $CdAl_2S_4$ with the unit cell parameters a = 5.7095 and c = 11.449 Å, c/a = 2.0053, Z = 2, and space group $I\bar{4}2m$.[9] A comparison of the XRD patterns of $CuIn_2Se_4$ and $ZnIn_2Se_4$ revealed their good correspondence. A disorder in the crystal structure of $ZnIn_2Se_4$ was observed:[9] some of the zinc atoms belong to an indium sublattice, and some of the indium atoms were in a zinc sublattice, while a statistical distribution occurred. We compared the relative intensities of lines in the XRD patterns of $CuIn_2Se_4$ and $ZnIn_2Se_4$ (Table 2) to reveal that the relative intensities of the majority of weak lines that correspond to a thioaluminate structure are almost equal in the compounds $CuIn_2Se_4$ and $ZnIn_2Se_4$. This fact indicates that the disorder in the distribution of copper and indium was also observed in the structure of $CuIn_2Se_4$: a part of copper atoms entered into the indium sublattice from its sublattice, and some indium atoms entered into the copper sublattice.

Table 2 Comparison of relative intensities of weak lines in XRD patterns of $CuIn_2Se_4$ and $ZnIn_2Se_4$.

$h\,k\,l$	Line intensities, I (%)		$h\,k\,l$	Line intensities, I (%)	
	$CuIn_2Se_4$ (this work)	$ZnIn_2Se_4$[9]		$CuIn_2Se_4$ (this work)	$ZnIn_2Se_4$[9]
0 0 2	3.5	3	2 1 1	2.0	11
1 0 1	5.0	9	1 1 4	2.5	3
1 1 0	3.5	3	1 0 5 2 1 3	4.5	5
1 0 3	6.0	6			
2 0 2	7.0	7	0 0 6	2.5	3

Thus, $CuIn_2Se_4$ was crystallized in the lattice possessing the structure of $CdAl_2S_4$. The assignment of the $CuIn_2Se_4$ structure reported previously[5] as a stannite-like type was not correct since the stannite is characterized by a cation : anion ratio of 4 : 4, while this ratio in $CuIn_2Se_4$ (and $CdAl_2S_4$) is 3 : 4.

It is interesting to note an unusual ternary compound containing the 11th Group element copper (Cu^{2+}) crystallized in the structure of cadmium thioaluminate. $CuIn_2Se_4$ is paramagnetic. It is well known that only 12th Group compounds can be crystallized in the structure of cadmium thioaluminate, *e.g.*, $ZnGa_2S_4$, ZnM_2Se_4 (M = Al, Ga, or In), $CdAl_2X_4$, $CdGa_2X_4$, and $HgGa_2X_4$ (X = S, Se, or Te), and all these compounds are diamagnetic.

We found that a noticeable region of $Cu(In_{1-x}Ga_x)_2Se_4$ solid solutions with a thioaluminate structure is formed in a range of $0 < x \leqslant 0.3$ in the $CuIn_2Se_4$–$CuGa_2Se_4$ system based on $CuIn_2Se_4$. No lines of impurity phases were detected in the XRD pattern of $Cu(In_{0.7}Ga_{0.3})_2Se_4$; all the lines were indexed in a tetragonal syngony confirming the structural type of cadmium thioaluminate $CdAl_2S_4$. The unit cell parameters were determined upon indexing the XRD pattern with x = 0.3 [$Cu(In_{0.7}Ga_{0.3})_2Se_4$]: a = 5.685(3), c = 11.372(6) Å, c/a = 2.0005, and the space group $I\bar{4}2m$. The change in the unit cell parameters, as compared to those of $CuIn_2Se_4$, indicates the formation of solid solutions based on $CuIn_2Se_4$. The decrease in the unit cell parameters is due to the size of Ga^{3+} smaller than that of In^{3+}.

The magnetic susceptibility values were determined by magnetometry using the field dependences of magnetization. $CuIn_2Se_4$ is a paramagnetic compound (Figure 2, curve *1*) with a susceptibility of $+0.55\times10^{-7}$ emu g^{-1}. Paramagnetism indicates the existence of copper in the oxidation state +2 in the crystal lattice of $CuIn_2Se_4$. The solid solution based on $CuIn_2Se_4$ was also paramagnetic (Figure 2, curve *2*). In the $Cu(In_{0.7}Ga_{0.3})_2Se_4$ solid solution, the susceptibility was $+1.2\times10^{-7}$ emu g^{-1}. The acquired data are consistent with the oxidation state +2 of copper in the above compound and solid solution.

The cathodoluminescence spectrum (CL) of compound $CuIn_2Se_4$ at 298 K (Figure 3, spectrum *1*) exhibited a peak at 1148 nm (1.08 eV). This peak can be due to an interband transition (E_g), but it more likely corresponds to an energy level inside

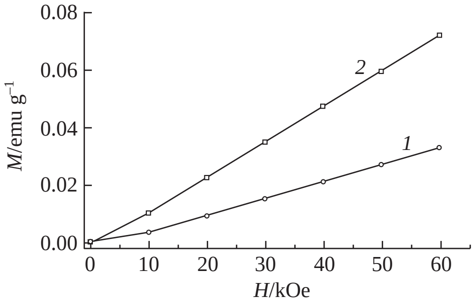

Figure 2 Dependence of magnetization M on the magnetic field strength H for (*1*) $CuIn_2Se_4$ and (*2*) $Cu(In_{0.7}Ga_{0.3})_2Se_4$ solid solution.

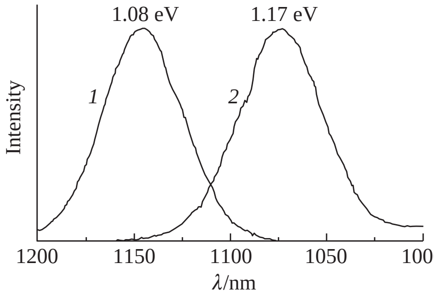

Figure 3 CL spectra (298 K) of (*1*) $CuIn_2Se_4$ and (*2*) $Cu(In_{0.7}Ga_{0.3})_2Se_4$ solid solution.

Table 3 Energy gap values at 298 K of solid solutions $Cu_{1-x}(In_{0.7}Ga_{0.3})Se_2$ and $Cu(In_{0.7}Ga_{0.3})_2Se_4$.

x in $Cu_{1-x}(In_{0.7}Ga_{0.3})Se_2$	Cu^{2+} content (%) of copper sublattice	E_g at 298 K	Reference
0	0	1.17; 1.20	4, 10
0.1	10	1.16	4
0.2	20	1.15	4
0.3	30	1.14	4
$Cu(In_{0.7}Ga_{0.3})_2Se_4$	100	$\geqslant$1.17	this work

the band gap, in this case, $E_g > 1.08$ eV. Thus, $CuIn_2Se_4$ is a semiconductor with $E_g \geqslant 1.08$ eV. In the CL spectrum (298 K) of $Cu(In_{0.7}Ga_{0.3})_2Se_4$ solid solution (Figure 3, spectrum *2*), a peak at 1052 nm (1.17 eV) was observed. Analogously, this band likely indicates that there is an inside energy level of 1.17 eV in band gap; hence, $E_g \geqslant 1.17$ eV. It was interesting to compare the energy gap values for a series of CIGS solid solutions with different copper(II) contents. In the $Cu_{1-x}(In_{0.7}Ga_{0.3})Se_2$ solutions possessing a chalcopyrite structure, the band gap slightly decreased with x (the Cu^{2+} content) (Table 3). In the case of 100% Cu^{2+} content, the E_g value is $\geqslant$1.17 eV, which is of interest for practical applications of these $Cu(In_{1-x}Ga_x)_2Se_4$ solid solutions as an absorbing layer in solar cells.

Therefore, the existence of $CuIn_2Se_4$ has been confirmed, but there was no evidence for the stannite structure of this compound. It was found that $CuIn_2Se_4$ and $Cu(In_{1-x}Ga_x)_2Se_4$ ($0 < x \leqslant 0.3$) solid solutions based on it are crystallized in the structure of cadmium thioaluminate, and the tetragonal unit cell parameters were determined. These data are of interest for the comparative analysis of compounds possessing the structure of cadmium thioaluminate.

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