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Magnetic and luminescent properties of copper-deficient $Cu_{1-x}(In_{0.7}Ga_{0.3})Se_2$ ($0 < x \leqslant 0.32$) solid solutions with chalcopyrite structure

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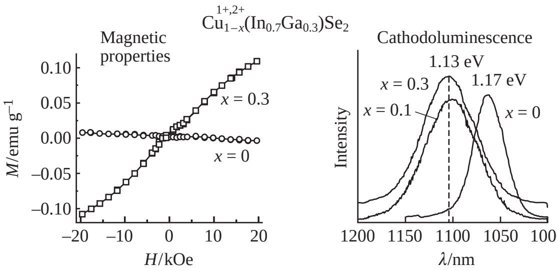
For synthesized copper-deficient $Cu_{1-x}(In_{0.7}Ga_{0.3})Se_2$ solid solutions with chalcopyrite structure, a monophase region within $0 < x \leqslant 0.32$ interval was found for the first time and dependences of the unit cell parameters on x were determined. The magnetometry method revealed that the crystal lattice of $Cu_{1-x}(In_{0.7}Ga_{0.3})Se_2$ contains copper in both 2+ and 1+ oxidation states. The band with a maximum at 1.13 eV in the cathode luminescence spectra of the above solid solutions with x of 0.1–0.3 is apparently due to Cu^{2+} V_{Cu} defect associates.



In recent years, solar cells based on inorganic chalcogenide thin films have been actively developed.[1,2] Solid $Cu_{1-x}In_{1-y}Ga_ySe_2$ solutions with chalcopyrite structure (CIGS) are used in the design of next-generation thin-film solar cells.[1,3] The best characteristics were obtained for solar cell compositions with y within 0.25–0.30 and x within 0.1–0.3 values.[1] The efficiency of solar energy conversion is about 20% for the best laboratory-made devices.[4] However, such a value is considerably smaller than the theoretically possible one of 30%,[5] which indicates insufficient studies of the CIGS materials. In particular, the data on the composition effect are incomplete for the defective structure of the chalcopyrite phase.

Only scarce data are available for chalcopyrite solid solutions with deficiency in copper sublattice. The copper-deficient $Cu_{1-z}(In_{0.5}Ga_{0.5})_{1+z/3}Se_2$ solid solutions with the compositions from the Cu_2Se to $(In_{0.5}Ga_{0.5})_2Se_3$ range were reported.[6] In all the phases belonging to the above range, the copper oxidation state was 1+. On the other hand, $Cu_{1-x}In_{1-v}Ga_vSe_2$ solid solutions can simultaneously contain copper in both 1+ and 2+ oxidation states. Their compositions are arranged, *e.g.*, along the $Cu(In_{0.7}Ga_{0.3})Se_2$ to $Cu(In_{0.7}Ga_{0.3})_2Se_4$ interval: the first formula (a well known chalcopyrite solid solution) contains copper in the 1+ oxidation state, while the second formula corresponds to copper in the 2+ oxidation state. Practical applications of copper-deficient chalcopyrite solid solutions are hindered by the lack of data on the one-phase $Cu_{1-x}(In_{0.7}Ga_{0.3})Se_2$ region and structural data. The lack of knowledge about magnetic and luminescent characteristics prevents the comprehensive data acquisition on the defectiveness in the chalcopyrite phase structure.

Taking into account the above mentioned facts, this work was aimed at the synthesis of $Cu_{1-x}(In_{0.7}Ga_{0.3})Se_2$ solid solutions ($0 < x \leqslant 0.32$),[†] determination of their boundaries, investigation of structural features as a function of x, and their luminescent and magnetic properties determination in the context of structure defectiveness studies.

All the lines in the X-ray patterns of $Cu_{1-x}(In_{0.7}Ga_{0.3})Se_2$ samples with x of 0.1, 0.2 and 0.3 were indexed in the tetragonal lattice of chalcopyrite, while no superstructure lines were found. Lines of impurity phases were also absent. The parameters of the tetragonal unit cell (a, c) of $Cu_{1-x}(In_{0.7}Ga_{0.3})Se_2$ decreased with an increase in x (Figure 1).[‡] The character of their changes indicated that $Cu_{1-x}(In_{0.7}Ga_{0.3})Se_2$ solid solutions were actually formed in the $0 < x \leqslant 0.32$ region of x values. A sample with $x = 0.35$ was not the monophase one. The unit cell volume V decreased with an increase in x (see Figure 1). In $Cu_{1-x}(In_{0.7}Ga_{0.3})Se_2$ solid solutions, V_{Cu} vacancies appeared in the copper sublattice. To keep the crystal electroneutrality, x copper atoms per x vacancies in the copper sublattice have to possess the

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[†] Polycrystalline samples of $Cu_{1-x}(In_{0.7}Ga_{0.3})Se_2$ ($0 < x \leq 0.35$) were synthesized in two steps. The required amounts of special purity copper, indium, gallium and selenium were annealed in graphitized quartz tubes at 1120 °C *in vacuo* ($p_{res} = 0.02$ Torr) for 10 h. Once the tubes were opened, their contents were grounded in an agate mortar; in addition, mixtures in evacuated tubes were subjected to homogenizing annealing at 750 °C for 100 h.

[‡] The phase composition of the obtained samples was studied by powder X-ray diffraction using a DRON-4 diffractometer (CuKα radiation).

Magnetic measurements were performed in a ‘Faraday balance’ magnetometer (Institute of Solid State Chemistry, Ural Branch of the Russian Academy of Sciences) at magnetic field strengths up to 20 kOe and temperature of 295 K. The error in applied magnetic field strength determination was ±100 Oe. The instrument was calibrated using standard samples of yttrium iron garnet (NIST SRM-2853) and Mohr’s salt.

Cathodoluminescence (CL) spectra were recorded at 78 and 298 K. The samples were excited by a pulsed electron beam with 40 keV energy. CL spectra were recorded using a DFS-13 monochromator according to the known procedure.[7]

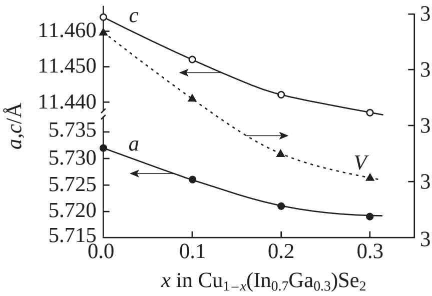

Figure 1 Unit cell parameters of $Cu_{1-x}(In_{0.7}Ga_{0.3})Se_2$ solid solutions *vs.* the *x* values.

Table 1 Percentage of selenium Se in $Cu_{1-x}(In_{0.7}Ga_{0.3})Se_2$ solid solutions and the content of Cu^{2+} and V_{Cu}.

x	Se (%)	Cu^{2+}	V_{Cu}
0.1	51.28	0.1	0.1
0.2	52.63	0.2	0.2
0.3	54.05	0.3	0.3

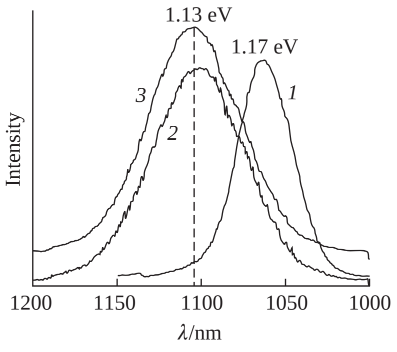

Figure 4 CL spectra of $Cu_{1-x}(In_{0.7}Ga_{0.3})Se_2$ samples at $T = 78$ K; (*1*) $x = 0$, (*2*) $x = 0.1$ and (*3*) $x = 0.3$.

2+ oxidation state. Note that the selenium percentage increases in the samples of $Cu_{1-x}(In_{0.7}Ga_{0.3})Se_2$ solid solutions with an increase in *x* (Table 1).

The magnetometry method was used to plot magnetization *vs.* field strength (Figure 2).‡ A sample with $x = 0$ ($CuIn_{0.7}Ga_{0.3}Se_2$) was the diamagnetic one (Figure 2, curve *1*) with a magnetic susceptibility of -2.84×10^{-7} emu g^{-1}, while a sample with $x = 0.3$ ($Cu_{0.7}In_{0.7}Ga_{0.3}Se_2$) was the paramagnetic one (Figure 2, curve *2*) with a magnetic susceptibility of $+5.95\times10^{-6}$ emu g^{-1}. The paramagnetism of samples indicated the presence of copper in the 2+ oxidation state in the crystal lattice of $Cu_{1-x}(In_{0.7}Ga_{0.3})Se_2$ solid solutions.

The cathodoluminescence (CL)‡ spectrum (at 298 K) of the $Cu(In_{0.7}Ga_{0.3})Se_2$ sample (Figure 3, spectrum *1*) contains a band with a maximum at 1.17 eV. This energy value corresponds to the E_g energy gap: valence–conductivity bands transition, which agrees with the reported data.[8] The CL spectra (at 298 K) of $Cu_{1-x}(In_{0.7}Ga_{0.3})Se_2$ solid solutions (see Figure 3) contain a broad bands with a maxima at 1.16 eV for $x = 0.1$ (spectrum *2*) and 1.14 eV for $x = 0.3$ eV (spectrum *3*). These maxima appeared due to a band-to-band transition. An increase of *x* up to 0.3 decreased the luminescence intensity.

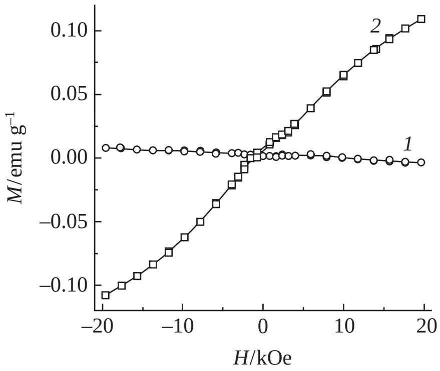

Figure 2 Magnetization *M* of $Cu_{1-x}(In_{0.7}Ga_{0.3})Se_2$ solid solutions *vs.* magnetic field strength *H*; (*1*) $x = 0$ and (*2*) $x = 0.3$.

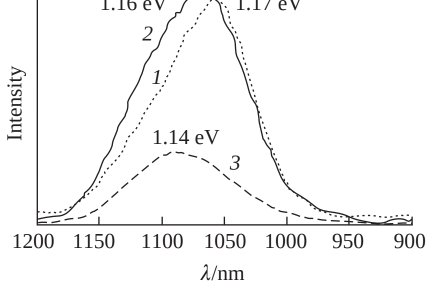

Figure 3 CL spectra of $Cu_{1-x}(In_{0.7}Ga_{0.3})Se_2$ at 298 K; (*1*) $x = 0$, (*2*) $x = 0.1$, and (*3*) $x = 0.3$.

The CL spectrum (at 78 K) of $Cu(In_{0.7}Ga_{0.3})Se_2$ ($x = 0$) contains a band with a maximum at 1.17 eV (Figure 4, spectrum *1*), while no exciton lines that would unambiguously indicate the exact E_g band gap were identified. The E_g value of 1.20 eV for the sample with $x = 0$ was determined from optical absorption spectra. The peak at 1.17 eV corresponds to the formation of a shallow donor level in the band gap due to V_{Cu} copper vacancies.[9,10]

The CL spectra for each sample of $Cu_{1-x}(In_{0.7}Ga_{0.3})Se_2$ solid solutions (at 78 K) with $x = 0.1–0.3$ contain a broad band with a maximum at 1.13 eV (see Figure 4, spectra *2* and *3*). This band appeared certainly due to the presence of copper in the 2+ oxidation state, which exists in the copper sublattice in the positions that were previously occupied by Cu^{1+} at $x = 0$. It forms associates of Cu^{2+} V_{Cu} defects. The concentration of vacancies in the copper sublattice is equal to the concentration of Cu^{2+} (see Table 1).

It is interesting that the position of the band maximum at all *x* values within the 0.1–0.3 range remained the same (1.13 eV), though the composition was varied in a broad range. This can be explained by both the same structure of $Cu_{1-x}(In_{0.7}Ga_{0.3})Se_2$ solid solutions within the entire range of compositions and the existance of above mentioned defect associates in all cases.

In conclusion, the copper-deficient $Cu_{1-x}(In_{0.7}Ga_{0.3})Se_2$ chalcopyrite solid solutions have been for the first time characterized within the $0 < x \leqslant 0.32$ range. The obtained results can be used for an estimation of the maximum acceptable copper deficiency in $Cu_{1-x}(In_{0.7}Ga_{0.3})Se_2$ layers, which are applied in the solar cells. The dependences of unit cell parameters of $Cu_{1-x}(In_{0.7}Ga_{0.3})Se_2$ solid solutions on the *x* value have been determined. Studies of the magnetic properties of $Cu_{1-x}(In_{0.7}Ga_{0.3})Se_2$ solid solutions ($0 < x \leqslant 0.32$) revealed that the crystal lattice contained copper in both 2+ and 1+ oxidation states, which indicates a possible Cu^{2+} presence in the crystal lattice defects of the reported solid solutions. The band with a maximum at 1.17 eV in the CL spectrum (at 78 K) of $Cu(In_{0.7}Ga_{0.3})Se_2$ ($x = 0$) corresponds to the formation of a shallow donor level in the band gap due to copper vacancies, V_{Cu}. The broad band with a maximum at 1.13 eV in the CL spectrum of $Cu_{1-x}(In_{0.7}Ga_{0.3})Se_2$ solid solutions with $x = 0.1–0.3$ appears most likely due to Cu^{+2} V_{Cu} defect associates. The formation of such associates should be taken into account in the analysis of electrophysical and optical properties of CIGS samples containing a high selenium amount.

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