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Structural and luminescence characteristics of $CuAl_xIn_{1-x}Se_2$ ($0 < x \leqslant 0.30$) chalcopyrite solid solutions

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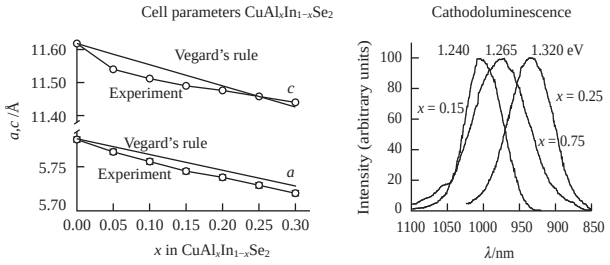
$CuAl_xIn_{1-x}Se_2$ solid solutions with a chalcopyrite crystal structure were synthesized from elemental Cu, In, Al and Se. The dependence of their unit cell parameters on x in a range of $0 < x \leqslant 0.30$ was determined. The band with a maximum at 1.320 eV in the cathodoluminescence spectra of $CuAl_xIn_{1-x}Se_2$ solid solutions at 78 K was most likely due to defects formed upon mutual substitution of atoms between the copper and aluminum–indium sublattices in the chalcopyrite structure.



Keywords: CIASe, chalcopyrite, solid solutions, structural data, unit cell parameters, Vegard's rule, cathodoluminescence, band gap levels.

Alternative energetics, in particular, the manufacture of solar panels, has been rapidly developing in recent years.[1,2] Solid solutions based on $CuGa_xIn_{1-x}Se_2$ (CIGS) are promising inorganic materials for devices of this kind.[1,3] The efficiency of solar energy conversion by the best laboratory solar cells based on CIGS is about 20%,[4] which is much lower than a theoretical value (30%).[5] The replacement of gallium with aluminum to produce $CuAl_xIn_{1-x}Se_2$ (CIASe) can be used to produce more efficient solar cells.[6] A component of these solid solutions, $CuAlSe_2$, crystallizes in a chalcopyrite structure[7] with the tetragonal lattice parameters a = 5.6035 and c = 10.977 Å, space group $I\bar{4}2d$. This compound is characterized by a band gap of 2.68 eV, which is larger than that in $CuGaSe_2$.[8] Thus, the replacement of gallium with aluminum leads to a larger band gap at the same value of x in $CuAl_xIn_{1-x}Se_2$ and $CuGa_xIn_{1-x}Se_2$, which is of great interest. It is promising to replace gallium with aluminum that is inexpensive and nontoxic.

The efficiency of the best laboratory samples of CIASe-based solar cells is about 16.9%.[6] This can be due to both the formation of impurity phases in the synthesis of CIASe films and the presence of deep levels in the band gap that act as traps for photogenerated current carriers. Moreover, the synthesis of high-quality films is complicated by the fact that the $CuInSe_2$–$CuAlSe_2$ system, in which CIASe is formed, has been studied insufficiently. There is almost no information on the nature of defects in CIASe. Data on the crystal structure of CIASe are scanty.[9–11] The formation of CIASe films with a chalcopyrite structure was observed,[9] and the unit cell parameters were determined with a low accuracy.[10] Only two $CuAl_xIn_{1-x}Se_2$ samples with x = 0.10 and x = 0.30 were studied in the region of CIASe compositions important for practical applications.[11] They were solid solutions with a chalcopyrite structure.

Thus, the practical application of CIASe is hindered by the lack of information on phase equilibria in the $CuInSe_2$–$CuAlSe_2$ system, in particular, data on the range of solid solutions, their structural characteristics, and the nature of defects in chalcopyrite crystals.

The aim of this work was to synthesize $CuAl_xIn_{1-x}Se_2$ solid solutions with x from 0 to 0.30 and determine their phase composition, crystal structure, and luminescent properties.[†]

The lines in the X-ray diffraction patterns of $CuAl_xIn_{1-x}Se_2$ samples with x = 0.05, 0.10, 0.15, 0.20, 0.25, and 0.30 were indexed (using data for 25 reflections in each X-ray pattern) in the chalcopyrite tetragonal lattice, space group $I\bar{4}2d$. Figure 1 shows the diffractogram of a $CuAl_xIn_{1-x}Se_2$ sample with x = 0.15. Superstructural lines and lines due to impurity phases were not found

[†] The polycrystalline $CuAl_xIn_{1-x}Se_2$ ($0 < x \leqslant 0.30$) samples were synthesized in two stages. At the first stage, the required amounts of copper, indium, aluminum and selenium (high purity 5N grade) were annealed for 10 h at 1100 °C and $p_{res} = 2 \times 10^{-2}$ Torr in graphitized quartz tubes. To prevent explosion, heating was carried out at a rate of 1 K min^{-1}. After opening the tubes, their contents were ground in an agate mortar, and homogenizing annealing was performed at 650 °C for 600 h. The grain size in the resulting ingots was a few micrometers.

The phase composition of the samples was studied by powder X-ray diffraction analysis on a DRON-4 diffractometer (Cu–Kα_1 radiation). The diffraction patterns were processed using the WinXPOW software package.

The cathodoluminescence (CL) spectra were recorded at 78 K with a DFS-13 monochromator. Luminescence was excited by a 40 keV pulsed electron beam. The wavelengths were determined to within ±1 nm, and error in the calculated photon energies (line maximum positions) was ±(0.005–0.01) eV.

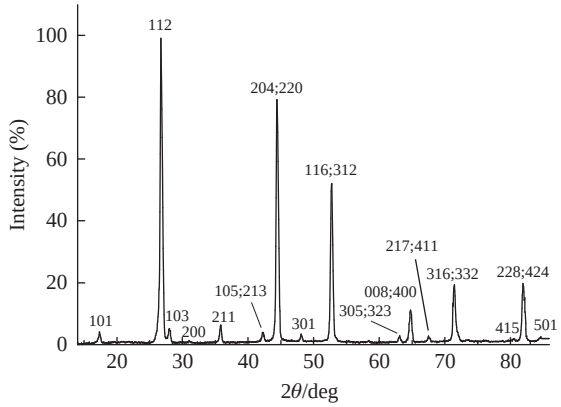


Figure 1 X-ray diffraction pattern of a $CuAl_xIn_{1-x}Se_2$ solid solution with $x = 0.15$.

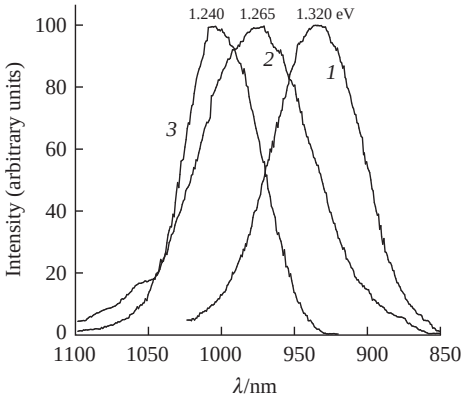


Figure 3 CL spectra of $CuAl_xIn_{1-x}Se_2$ solid solutions with x of (*1*) 0.25, (*2*) 0.175 and (*3*) 0.15 at 78 K.

in the X-ray diffraction patterns of $CuAl_xIn_{1-x}Se_2$. The tetragonal unit cell parameters of the solid solutions were determined with an accuracy of ±0.003 or ±0.005 Å (for *a* and *c*, respectively) (Figure 2). The decrease in the unit cell parameters was explained by the fact that Al^{3+} ions are smaller than In^{3+} ions. The variations in the unit cell parameters indicated that $CuAl_xIn_{1-x}Se_2$ solid solutions were formed in the region of $0 < x \leqslant 0.3$. The crystal lattice parameters are presented in Online Supplementary Materials.

The unit cell parameters (*a*, *c*) vary with a negative deviation from Vegard's rule for $x < 0.25$ (Figure 2). Negative deviations from Vegard's rule indicate an increase in the interaction between opposite ions and in the structure ordering in solid solutions. On the other hand, significant positive deviations from Vegard's rule are due to a structural disordering in solid solutions.

The CL spectra (78 K) of $CuAl_xIn_{1-x}Se_2$ ($0 < x \leqslant 0.30$) solid solutions do not contain exciton lines that unambiguously reveal the exact band gap value of E_g. the CL spectra of the samples with x = 0.25–0.30 contain a band at 1.320 eV (Figure 3, spectrum *1*). Note that, in each case, the band at 1.27 eV is rather intense.

To clarify the nature of CL bands, we consider a disordering in the crystal lattice of the $CuGa_xIn_{1-x}Se_2$ system: a fraction of copper atoms passed from the copper sublattice to the indium–gallium sublattice (in general form, M) to form a Cu_M defect (copper atoms in place of M as acceptors), while a fraction of M atoms from the indium–gallium sublattice passed to the copper sublattice as donor M_{Cu} defects (M atoms in place of copper atoms).[12,13] At x = 0.35–0.50 in $CuGa_xIn_{1-x}Se_2$, the CL method revealed the existence of a 1.235 eV level within the band gap [Figure 4(*a*)]; the Cu_M and M_{Cu} defects create similar energy levels in the band gap.

We assumed that a disordering also occurred in the $CuAl_xIn_{1-x}Se_2$ crystal lattice ($0 < x < 0.30$), namely, a fraction of Cu atoms from the copper sublattice passed to the indium–aluminum sublattice to form Cu_M defects, whereas a fraction of M atoms from the indium–aluminum sublattice passed to the copper sublattice

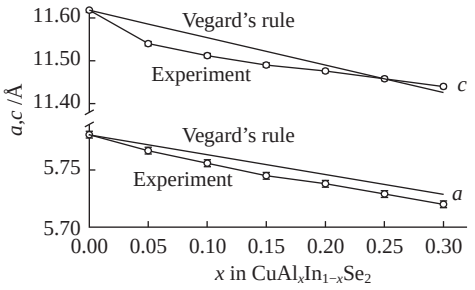


Figure 2 Unit cell parameters of $CuAl_xIn_{1-x}Se_2$ solid solutions as a function of *x*.

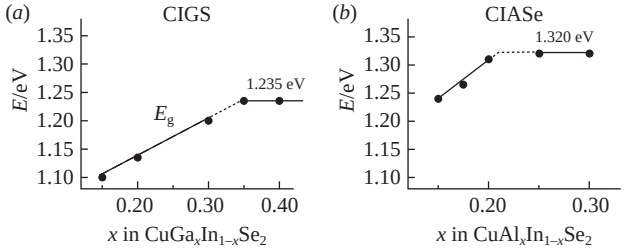


Figure 4 Arrangement of energy levels (78 K) in the band gap of the crystals of (*a*) $CuGa_xIn_{1-x}Se_2$ and (*b*) $CuAl_xIn_{1-x}Se_2$ solid solutions.

(M_{Cu} defects). The Cu_M and M_{Cu} defects create closely spaced levels in the band gap. The spectral lines due to the levels in the band gap overlap each other to result in a spectral band broadening at 1.320 eV (see Figure 3, spectrum 1).

With a decrease in the aluminum content, the energy position of a level in the band gap decreased (Figure 3, spectra *2* and *3*). A comparison with luminescence data for similar gallium materials, CIGS, is also important. The band gaps E_g were determined for CIGS [Figure 4(*a*)].[14,15] The absence of exciton lines from the CL spectra indicates that the bands at x = 0.15–0.20 [Figure 4(*b*), Figure 3, spectra *2*, *3*] are due to the energy levels in the band gap. Moreover, according to published data,[9] the values of E_g are 1.25–1.40 eV for CIASe compositions with x = 0.19–0.31. This opens up prospects for the application of $CuAl_xIn_{1-x}Se_2$ solid solutions to the creation of solar cells.

Note that the promising samples of $CuAl_xIn_{1-x}Se_2$ were found in a range of $0.15 \leqslant x \leqslant 0.20$ with high structural ordering of the solid solutions, as compared to CIGS materials in which a noticeable disordering is observed at the gallium content x = 0.25–0.30.

Thus, the dependence of the unit cell parameters on x in $CuAl_xIn_{1-x}Se_2$ chalcopyrite solid solutions ($0 < x \leqslant 0.30$) was determined for the first time. These data can be used in the syntheses and studies of CIASe materials. The band observed at 1.320 eV in the CL spectra of $CuAl_xIn_{1-x}Se_2$ solid solutions ($0.20 < x \leqslant 0.30$) at 78 K was most likely due to defects formed upon mutual substitution of atoms between the copper and aluminum–indium sublattices in the chalcopyrite structure (Cu_M and M_{Cu} defects). These data are important for analyzing the electrophysical and optical properties of $CuAl_xIn_{1-x}Se_2$ samples.

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Online Supplementary Materials

Supplementary data associated with this article can be found in the online version at doi: 10.1016/j.mencom.2020.09.038.

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