Structure and Luminescence Properties of $Cu_{1-x}Al_{0.25}In_{0.75}Se_2$ ($0 < x \leq 0.20$) Copper-Deficient Chalcopyrite Solid Solutions

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Abstract—$Cu_{1-x}Al_{0.25}In_{0.75}Se_2$ copper-deficient solid solutions with the chalcopyrite structure have been prepared by elemental synthesis from Cu, In, Al, and Se, and their unit-cell parameters have been determined for the first time as functions of x in the range $0 < x \leq 0.20$. It has been shown that the band peaking at 1.320 eV in the 78-K cathodoluminescence spectra of the $Cu_{1-x}Al_{0.25}In_{0.75}Se_2$ solid solutions is most likely due to Cu_M and M_{Cu} (M = Al, In) antisite defects resulting from exchange of atoms between the copper and indium−aluminum sublattices in the chalcopyrite structure and that the band peaking at 1.245 eV arises from $Cu^{2+} \cdot V_{Cu}$ associates, which are predominant defects.

INTRODUCTION

In recent years, intensive research effort has been concentrated on alternative power generation technologies, in particular on the fabrication of solar cells [1]. Promising inorganic materials for such devices include $Cu_{1-x}Ga_yIn_{1-y}(S,Se)_2$ (CIGS) solid solutions [1]. Chalcopyrite CIGS materials are used in the fabrication of a new generation of thin-film solar cells [1]. In the best laboratory prototypes of CIGS-based solar cells, solar energy conversion efficiency has reached 21.7% [2]. This value is substantially lower than the theoretically possible 30% [3]. Replacing gallium by aluminum to give a CIASe material has recently been viewed as a way to produce more efficient solar cell materials [4]. The $CuAlSe_2$ compound crystallizes in the chalcopyrite structure [5] and has a broad band gap, $E_g = 2.68$ eV, whereas $CuGaSe_2$ has $E_g = 1.70$ eV [1]. Therefore, aluminum substitution for gallium should lead to a broader band gap of CIASe materials, which is of considerable interest. Also important is that expensive gallium is replaced by cheap and readily available aluminum, which is, in addition, nontoxic.

Even the best CIASe-based laboratory prototypes of solar cells still have a comparatively low efficiency, near 16.9% [4]. This is attributable to the presence of deep levels in their band gap, which act as traps for photogenerated current carriers. Note that high-quality films are difficult to grow because the $CuInSe_2$−$CuAlSe_2$ system, containing CIASe, has been little

studied: there are no phase diagram data in the literature and essentially no data on the nature of defects in CIASe. Paulson et al. [7] obtained films of CIASe solid solutions, but they did not determine their unit-cell parameters. Sugiyama et al. [8] determined the unit-cell parameters of films of CIASe solid solutions with a relatively low accuracy, to the second decimal place, which makes any comparison impossible. Gebicki et al. [9] studied only two samples in the range of CIASe compositions important for practical application. Their results showed that the samples consisted of solid solutions with the chalcopyrite structure. The materials were prepared by means of chemical vapor transport. Note that the composition of the solid solution crystals thus grown was assumed by Gebicki et al. [9] to be identical to the composition of the precursor mixture used in synthesis, which might be not so. Odin et al. [10] synthesized $CuInSe_2$-based solid solutions in the $CuAlSe_2$−$CuInSe_2$ system with the chalcopyrite crystal structure, determined their unit-cell parameters as functions of composition, and studied their cathodoluminescence (CL) spectra.

The efficiency of CIASe can be improved by using copper-deficient materials. It is known that the best solar cell performance so far has been offered by $Cu_{1-x}Ga_yIn_{1-y}Se_2$ copper-deficient materials with $y = 0.25$−0.30 and $x = 0.1$−0.3 [11]. Odin et al. [12] determined the unit-cell parameters of the $Cu_{1-x}(Ga_{0.3}In_{0.7})Se_2$ ($0 < x \leq 0.32$) copper-defi-

Table 1. Fractions of Cu^+ and Cu^{2+} ions and V_{Cu} vacancies in the crystal lattice of the $Cu_{1-x}Al_{0.25}In_{0.75}Se_2$ solid solutions

x	Fraction		
	Cu^+	Cu^{2+}	V_{Cu}
0	1	0	0
0.05	0.90	0.05	0.05
0.10	0.80	0.10	0.10
0.20	0.60	0.20	0.20

cient solid solutions and demonstrated the presence of copper in the oxidation states Cu^{2+} and Cu^+ in their crystal lattice. In addition, copper deficiency was shown to have a significant effect on the lifetime of photogenerated current carriers in $Cu_{1-x}(Ga_{0.3}In_{0.7})Se_2$ [13].

The reduced copper content in the copper-deficient solid solutions can ensure required p-type conductivity and increase the electrical conductivity of the material. Reports on studies of copper-deficient CIASe solid solutions, including $Cu_{1-x}Al_{0.25}In_{0.75}Se_2$, are still missing in the literature. Clearly, potential practical applications of the CIASe materials are limited by the absence of data on structural characteristics of the $Cu_{1-x}Al_{0.25}In_{0.75}Se_2$ copper-deficient solid solutions and the effect of their composition on the defect structure of the chalcopyrite phase.

The objectives of this work were to synthesize $Cu_{1-x}Al_{0.25}In_{0.75}Se_2$ ($0 < x \le 0.20$) solid solutions, determine their phase composition, and investigate their structural and luminescence properties.

EXPERIMENTAL

Polycrystalline $Cu_{1-x}Al_{0.25}In_{0.75}Se_2$ ($0 < x \le 0.20$) samples were synthesized in two steps. In the first step, appropriate amounts of high-purity copper, indium, aluminum, and selenium (5N grade) were fired at a temperature of 1100°C for 10 h in graphitized quartz ampules sealed off under vacuum (residual pressure $p_{res} = 2 \times 10^{-3}$ mm Hg). To eliminate the risk of explosion during the synthesis process, the samples were heated to this temperature at a rate of 1°C/min. After the ampules were opened, the resultant materials were ground in an agate mortar. Next, the mixtures were again sealed in ampules under vacuum and homogenized by annealing 650°C for 600 h.

The phase composition of the samples thus prepared was determined by X-ray diffraction. Intensity data were collected on a DRON-4 diffractometer (CuK_{α_1}) radiation). X-ray diffraction patterns were analyzed using WinX^{POW} software.

CL spectra were measured at 78 K. The luminescence was excited by a pulsed electron beam with an energy of 40 keV. The CL spectra were recorded using a DFS-13 monochromator. The procedure used to measure CL spectra was described in greater detail previously [14].

RESULTS AND DISCUSSION
Structural Data

The unit-cell parameters and volume V of the $CuInSe_2$-based chalcopyrite solid solutions in the $CuAlSe_2$–$CuInSe_2$ system were measured as functions of composition (Fig. 1). The observed decrease in these characteristics is due to the fact that the ionic radius of Al^{3+} is smaller than that of In^{3+}. These data were considered in detail previously [10].

$Cu_{1-x}Al_{0.25}In_{0.75}Se_2$ **copper-deficient solid solutions.** $Cu_{1-x}Al_{0.25}In_{0.75}Se_2$ solid solutions were found to exist in the composition range $0 < x \le 0.20$. All of the lines observed in the X-ray diffraction patterns of the $Cu_{1-x}Al_{0.25}In_{0.75}Se_2$ samples could be indexed in a tetragonal chalcopyrite lattice (using data for 27 lines in each X-ray diffraction pattern), with space group $I\bar{4}2d$. No lines of any impurity phases were detected. As an example, Fig. 2 shows the X-ray diffraction pattern of the $Cu_{1-x}Al_{0.25}In_{0.75}Se_2$ sample with $x = 0.20$. No superstructure reflections were detected in the X-ray diffraction patterns. The tetragonal unit-cell parameters of the $Cu_{1-x}Al_{0.25}In_{0.75}Se_2$ solid solutions were determined with an accuracy of ± 0.003 Å for the a cell parameter and ± 0.005 Å for the c cell parameter and were shown to decrease with increasing x (Fig. 3). The unit-cell volume V (determined with an accuracy of ± 0.06 Å^3) was also found to decrease with increasing x (Fig. 3).

The observed behavior of the unit-cell parameters clearly indicates the formation of $Cu_{1-x}Al_{0.25}In_{0.75}Se_2$ solid solutions in the composition range $0 < x \le 0.20$. The copper sublattice in the crystal lattice of the $Cu_{1-x}Al_{0.25}In_{0.75}Se_2$ solid solutions contains V_{Cu} vacancies ($\square$). To maintain electroneutrality of the materials, one copper atom per vacancy in the copper sublattice passes to the oxidation state 2+ (Table 1). Therefore, the general formula of the $Cu_{1-x}Al_{0.25}In_{0.75}Se_2$ solid solutions should be represented in the form $Cu^+_{1-x}Cu^{2+}_{x/2}\square_{x/2}Al_{0.25}In_{0.75}Se_2$ ($0 < x \le 0.20$).

The above-mentioned decrease in unit-cell parameters can be accounted for by the fact that the ionic radius of Cu^{2+} is smaller than that of Cu^+.

Defects in the copper and aluminum–indium sublattices of CIASe. The crystal lattice of $CuGa_yIn_{1-y}Se_2$ solid solutions is known to be disordered [15, 16]: some of the copper atoms reside in the indium–gallium sublattice (in the general form M) instead of the copper sublattice, to form Cu_M defects (copper atoms on the M site), and some of the M atoms reside in the copper sublattice instead of the indium–gallium sublattice, to form M_{Cu} defects (M atoms on the copper
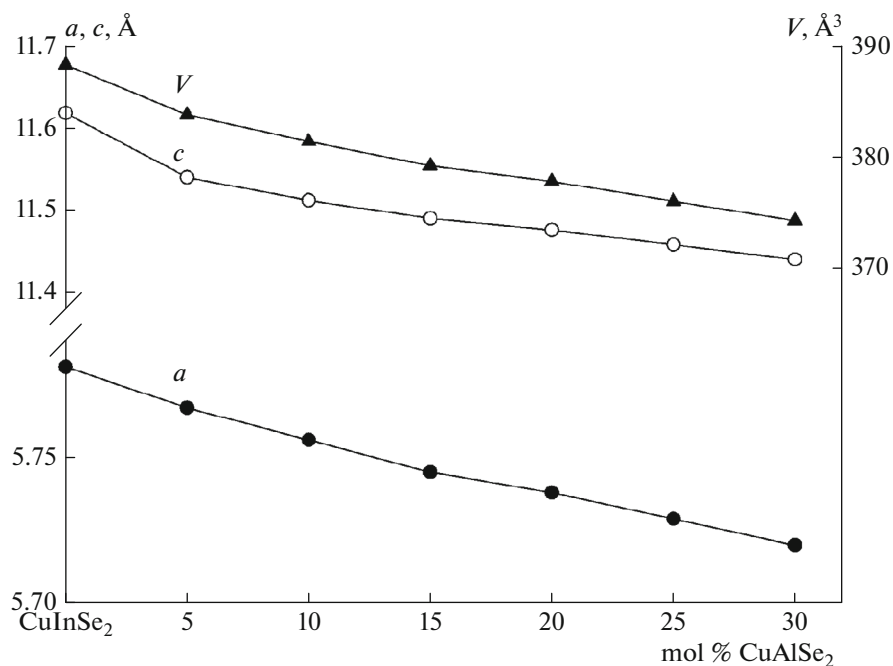
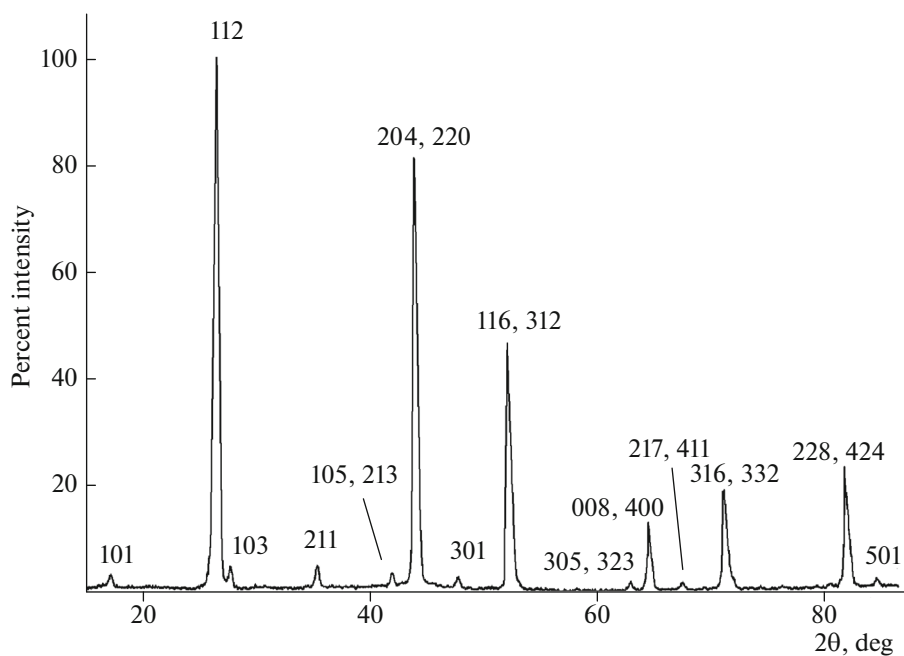**Fig. 1.** Unit-cell parameters of the $CuInSe_2$-based solid solutions in the $CuAlSe_2$–$CuInSe_2$ system.

Fig. 2. X-ray diffraction pattern of the $Cu_{1-x}Al_{0.25}In_{0.75}Se_2$ solid solution with $x = 0.20$.

site). Figure 4a shows the crystal structure of the $CuGa_yIn_{1-y}Se_2$ chalcopyrite solid solutions free of antisite defects [11] (random gallium/indium distribution on the M site), and Fig. 4b shows a possible structure of $CuAl_yIn_{1-y}Se_2$ containing Cu_M and M_{Cu} (M = In, Al) antisite defects. We compared intensity of reflections in the X-ray diffraction patterns of the $CuGa_yIn_{1-y}Se_2$ and $CuAl_yIn_{1-y}Se_2$ solid solutions with $y = 0.25$. The intensities of the weak lines characterizing the chalcopyrite structure were found to be

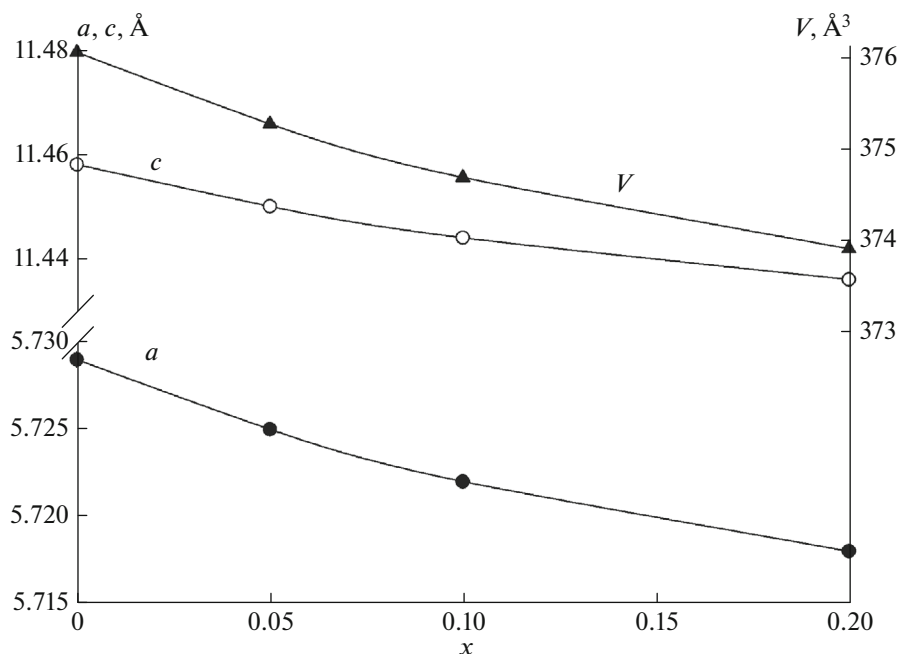**Fig. 3.** Unit-cell parameters as functions of x for the $Cu_{1-x}Al_{0.25}In_{0.75}Se_2$ copper-deficient solid solutions.

roughly equal for these two phases (Table 2). A very similar situation was observed in the case of the $Cu_{1-x}Ga_{0.25}In_{0.75}Se_2$ and $Cu_{1-x}Al_{0.25}In_{0.75}Se_2$ solid solutions with $x = 0.1$ (Table 2). Most likely, the crystal lattices of $CuAl_xIn_{1-x}Se_2$ ($0 < x < 0.30$) and $Cu_{1-x}Al_{0.25}In_{0.75}Se_2$ are also disordered: some of the Cu atoms reside in the indium–aluminum sublattice to form Cu_M defects (acceptors) and some of the aluminum and indium atoms reside in the copper sublattice to form M_{Cu} defects (donors).

Cathodoluminescence Spectra

The 78-K CL spectra of the $Cu_{1-x}Al_{0.25}In_{0.75}Se_2$ solid solutions were found to contain no excitonic lines suitable for accurately determining the band gap

E_g of the samples. The spectrum of the $x = 0$ sample contained a band peaking at 1.320 eV (Fig. 5a). To find out the origin of this band, we turned to $CuGa_yIn_{1-y}Se_2$, a better studied solid solution system. At gallium contents in the range $y = 0.35–0.50$, CL data indicate the presence of a level at 1.235 eV in the band gap. Cu_M and M_{Cu} defects produce similar energy levels in the band gap. As mentioned above, the crystal lattices of $CuAl_yIn_{1-y}Se_2$ ($0 < y \leq 0.30$) and $Cu_{1-x}Al_{0.25}In_{0.75}Se_2$ ($0 < x \leq 0.20$) contain Cu_M and M_{Cu} defects, which produce similar levels in the band gap.

The 78-K CL spectrum of the $Cu_{1-x}Al_{0.25}In_{0.75}Se_2$ sample with $x = 0.10$ contains a strong, broad band peaking at 1.245 eV (Fig. 5b), in addition to the 1.320-eV band considered above. Clearly, the 1.245-eV band is

Table 2. Relative intensities of the weak lines in the X-ray diffraction patterns of the solid solutions

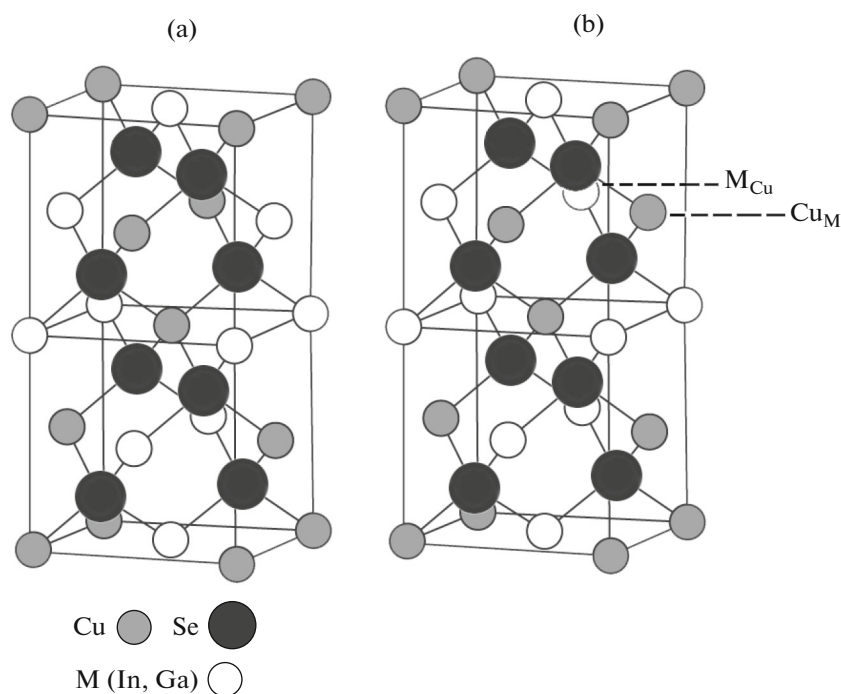| $h\,k\,l$	Intensity, arb. units			
	$Cu_{0.9}Al_{0.25}In_{0.75}Se_2$	$Cu_{0.9}Ga_{0.25}In_{0.75}Se_2$	$CuAl_{0.25}In_{0.75}Se_2$	$CuGa_{0.25}In_{0.75}Se_2$
1 0 1	1.5	2	1.5	2
1 0 3	2.5	1	2	1
2 1 1	2.5	2	3	2
2 1 3; 1 0 5	1	1	1	1
3 0 1	1	1.5	1.5	1
3 2 3; 3 0 5	1	1	1	1
2 1 7; 4 1 1	1	0.5	1	0.5
5 0 1	1	0.5	0.5	0.5

Cu ◯ Se ⬤

M (In, Ga) ◯

Fig. 4. (a) Crystal structure of $CuGa_yIn_{1-y}Se_2$ solid solutions [11] and (b) possible structure of $CuAl_yIn_{1-y}Se_2$ solid solutions containing Cu_M and M_{Cu} antisite defects.
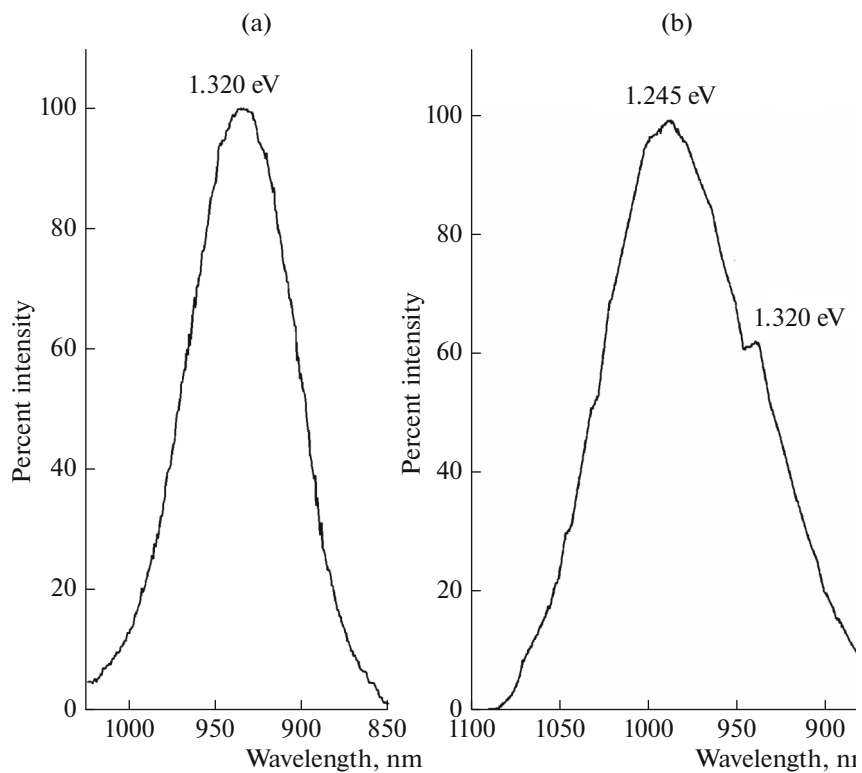

Fig. 5. 78-K CL spectra of the $Cu_{1-x}Al_{0.25}In_{0.75}Se_2$ solid solutions with $x =$ (a) 0 and (b) 0.10.

due to copper in the oxidation state 2+: the presence of Cu^{2+} instead of Cu^+ gives a positively charged defect, which combines with a negatively charged copper vacancy (V_{Cu}) to form a $Cu^{2+} \cdot V_{Cu}$ defect associate. The V_{Cu} vacancy concentration in the copper sublattice is equal to the Cu^{2+} concentration (Table 1). These concentrations are high and, hence, the $Cu^{2+} \cdot V_{Cu}$ associates are predominant defects. It is of interest to note that, throughout the composition range $x = 0.05-0.20$, the peak position of the band remains unchanged (at 1.245 eV), even though the composition of the solid solutions varies in a wide range. The reason for this is that, throughout the composition range $0 < x \le 0.20$, the structure of the $Cu_{1-x}Al_{0.25}In_{0.75}Se_2$ solid solutions remains unchanged and contains such defect associates.

CONCLUSIONS

$Cu_{1-x}Al_{0.25}In_{0.75}Se_2$ ($0 < x \le 0.20$) copper-deficient solid solutions with the chalcopyrite structure have been identified for the first time and their unit-cell parameters have been measured as functions of x. In the crystal lattice of $Cu_{1-x}Al_{0.25}In_{0.75}Se_2$, some of the copper atoms reside in the indium−aluminum sublattice and some of the indium and aluminum atoms reside in the copper sublattice.

It has been shown for the first time that the band peaking at 1.320 eV in the 78-K CL spectra of the $Cu_{1-x}Al_{0.25}In_{0.75}Se_2$ solid solutions is most likely due to Cu_M and M_{Cu} antisite defects resulting from exchange of atoms between the copper and indium−aluminum sublattices in the chalcopyrite structure and that the band peaking at 1.245 eV arises from $Cu^{2+} \cdot V_{Cu}$ associates, which are predominant defects. The formation of these defects should be taken into account in analyzing the electrical transport and optical properties of selenium-enriched CIASe materials.

FUNDING

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