

## Preparation and Phase Relations in the CuSbSe<sub>2</sub> – CuInSe<sub>2</sub> System

Barys V. Korzun<sup>1</sup>, Valery R. Sobol<sup>1</sup>, Marin Rusu<sup>2</sup>, Ruben M. Savizky<sup>3</sup>, Alena A. Fadzeyeva<sup>4</sup>, Ivan I. Maroz<sup>4</sup>, Andrei N. Gavrilenko<sup>5</sup>, Vadim L. Matukhin<sup>5</sup>, and Martha Ch. Lux-Steiner<sup>2</sup>

<sup>1</sup>Belarusian State Pedagogical University, 18 Sovetskaya, Minsk, 220030, Belarus

<sup>2</sup>Helmholtz-Zentrum Berlin für Materialien und Energie, 1 Hahn-Meitner Platz, Berlin, 14109, Germany

<sup>3</sup>The Cooper Union for the Advancement of Science and Art, 30 Cooper Square, New York, NY 10003, U.S.A.

<sup>4</sup>Scientific-Practical Materials Research Centre of the National Academy of Sciences of Belarus, 19 P. Brovki, Minsk, 220072, Belarus

<sup>5</sup>Kazan State Power Engineering University, 51 Krasnoselskaya, Kazan, 420066, Russia

### ABSTRACT

The CuInSe<sub>2</sub> and CuSbSe<sub>2</sub> ternary compounds and alloys of the (CuSbSe<sub>2</sub>)<sub>1-x</sub>·(CuInSe<sub>2</sub>)<sub>x</sub> system with the mole fraction of CuInSe<sub>2</sub> (x) equal to 0.05, 0.15, 0.25, 0.375, 0.50, 0.625, 0.75, 0.85, and 0.95 were prepared and the phase relations in this system were investigated by X-ray powder diffraction, optical microscopy, and scanning electron microscopy. It was shown that the alloys of the CuSbSe<sub>2</sub>-CuInSe<sub>2</sub> system are biphasic at room temperature in the whole range of compositions, and the limits of solubility for CuSbSe<sub>2</sub> in CuInSe<sub>2</sub> and for CuInSe<sub>2</sub> in CuSbSe<sub>2</sub> do not exceed 0.001 mole fraction.

### INTRODUCTION

Copper indium diselenide (CuInSe<sub>2</sub>) belongs to the I-III-VI<sub>2</sub> group compounds and is extensively studied and used as an absorbing material in solar cells, especially with the combination of CuGaSe<sub>2</sub> compound with which it forms promising CIGS compounds. CIGS-based solar cells have the third largest market, following Si- and CdTe-based solar cells [1]. One of the methods to optimize physical properties of these compounds is to improve the procedure of doping. Chemical elements of the group 15 (As, Sb, Bi) can be used as doping elements; moreover, CuSbS<sub>2</sub>, CuSbSe<sub>2</sub>, CuBiS<sub>2</sub>, and CuBiSe<sub>2</sub> themselves are studied as potential photovoltaic materials [2, 3]. Previously, the (CuBiSe<sub>2</sub>)<sub>1-x</sub>·(CuInSe<sub>2</sub>)<sub>x</sub> [4] and (CuSbS<sub>2</sub>)<sub>1-x</sub>·(CuInSe<sub>2</sub>)<sub>x</sub> [5] alloys were prepared and the phase relations in these systems above 600 K were investigated by X-ray powder diffraction, microstructure studies, and differential thermal analysis. It was established that the T-x phase diagram of the CuInSe<sub>2</sub>-CuBiSe<sub>2</sub> system has a peritectic character with a peritectic temperature of 837 K [4]. The limits of solubility from both sides of the system do not exceed 0.05 mole fraction of the corresponding ternary compounds. By contrast, the T-x phase diagram of the CuInS<sub>2</sub>-CuSbS<sub>2</sub> system has a eutectic character with a eutectic temperature of 807 K [5]. The alloys of the CuSbS<sub>2</sub>-CuInS<sub>2</sub> system where the mole fraction of CuInS<sub>2</sub> ranged from 0.038 to 0.941 are biphasic at room temperature, and the limits of solubility are 0.059 mole fraction for CuSbS<sub>2</sub> in CuInS<sub>2</sub> and 0.038 mole fraction for CuInS<sub>2</sub> in CuSbS<sub>2</sub>.

To perform successful doping of CuInSe<sub>2</sub> by antimony, the phase relations in the Cu-Sb-Se system have to be known. To date, the knowledge of the Cu-Sb-Se system is rather scarce and contradictory. In the previous studies this system was experimentally studied only across the Cu<sub>2</sub>Se-Sb<sub>2</sub>Se<sub>3</sub> [6] and Cu<sub>0.75</sub>Sb<sub>0.25</sub>-Se [7] intersections. The phase diagram of the Cu<sub>2</sub>Se-Sb<sub>2</sub>Se<sub>3</sub>

system in the whole series of compositions was constructed and the formation of only one ternary compound with the chemical composition  $\text{CuSbSe}_2$  was found [6]. Its melting has a congruent character with a melting point of 763 K. This is in contradiction with previous findings [8], in which the second ternary compound in the  $\text{Cu}_2\text{Se}-\text{Sb}_2\text{Se}_3$  system with the composition of  $\text{Cu}_3\text{SbSe}_3$  was prepared. One more compound of the Cu-Sb-Se system— $\text{Cu}_3\text{SbSe}_4$ —was first synthesized separately [9] and its phase diagram indicates that this material forms via a peritectic reaction at about 663 K [7]. Its crystal structure was also established [10, 11]. Recently, in addition to  $\text{CuSbSe}_2$ ,  $\text{Cu}_3\text{SbSe}_3$ , and  $\text{Cu}_3\text{SbSe}_4$  compounds, prediction of the new stable, previously unknown in the Cu-Sb-Se system, compounds  $\text{Cu}_4\text{SbSe}_5$  and  $\text{Cu}_{12}\text{Sb}_4\text{Se}_{13}$ , was made [12].

To determine the homogeneity region of  $\text{CuSbSe}_2$ , the alloys  $(\text{Cu}_2\text{Se})_{1-x}(\text{Sb}_2\text{Se}_3)_x$  in the range of  $x$  from 0.485 to 0.515 were studied [13]. It was found that at the eutectic temperatures (750 and 744 K) the range of homogeneity of  $\text{CuSbSe}_2$  is 0.0088 mole fraction, and the solubility of  $\text{Cu}_2\text{Se}$  in  $\text{CuSbSe}_2$  is 0.0068 mole fraction and the solubility of  $\text{Sb}_2\text{Se}_3$  in  $\text{CuSbSe}_2$  is 0.0020 mole fraction. The homogeneity range of  $\text{CuSbSe}_2$  at 298 K does not exceed 0.0060 mole fraction. A maximal melting point (764 K) is shifted to  $\text{Cu}_2\text{Se}$  and corresponds to the composition  $(\text{Cu}_2\text{Se})_{0.496}(\text{Sb}_2\text{Se}_3)_{0.504}$ . An alloy with the stoichiometric composition  $\text{CuSbSe}_2$  melts at 754 K.

The crystal structure of  $\text{CuSbSe}_2$  was studied on thin films and was found to be an orthorhombic structure with the space group  $\text{Pnma}$  and the lattice constants 6.400, 3.950, and 15.33 Å for  $a$ ,  $b$ , and  $c$ , respectively [14]. It was determined that the lattice constants for  $\text{CuSbSe}_2$  prepared by solid state reaction from elements are 6.303, 3.976, and 15.008 Å for  $a$ ,  $b$ , and  $c$ , respectively [15]. A low temperature solvothermal method was used for the preparation of  $\text{CuSbSe}_2$  and the crystal structure was determined using single crystal X-ray diffraction analysis to be an orthorhombic structure with the space group  $\text{Pnma}$  and the lattice constants 6.299, 3.9734, and 15.005 Å for  $a$ ,  $b$ , and  $c$ , respectively [16].

The absence of the complete formation of solid solutions was found when the  $(\text{CuSbSe}_2)_{1-x}(\text{CuInSe}_2)_x$  alloys were prepared for the first time [15]. Then the doping of  $\text{CuInSe}_2$  by Sb in the  $\text{CuIn}_{1-x}\text{Sb}_x\text{Se}_2$  for  $x=0.0025$ , 0.005, and 0.010 was developed [17]. By introduction of  $\text{CuSbSe}_2$  doping into  $\text{CuInSe}_2$ , the well-crystallized ceramic samples can be perfectly sintered at 773 K.

Considering that the best way of determination of solubility of antimony in  $\text{CuInSe}_2$  and indium in  $\text{CuSbSe}_2$  is to study phase equilibria in the  $\text{CuInSe}_2$ - $\text{CuSbSe}_2$  system, the goal of the present paper was to prepare and study the microstructure of alloys and phase relations in the  $\text{CuSbSe}_2$ - $\text{CuInSe}_2$  system and to determine the limits of solubility.

## EXPERIMENT

Nine alloys of the  $(\text{CuSbSe}_2)_{1-x}(\text{CuInSe}_2)_x$  system with the mole fraction of  $\text{CuInSe}_2$  ( $x$ ) equaling 0.05, 0.15, 0.25, 0.375, 0.50, 0.625, 0.75, 0.85, and 0.95 and pure  $\text{CuSbSe}_2$  and  $\text{CuInSe}_2$  compounds were prepared. The initial elements for the preparation of the alloys and  $\text{CuInSe}_2$  ( $x=1$  in the  $(\text{CuSbSe}_2)_{1-x}(\text{CuInSe}_2)_x$  system) and  $\text{CuSbSe}_2$  ( $x=0$ ) ternary compounds were 99.9998% copper, 99.9997% indium, 99.999% antimony, and 99.9999% selenium. The required amounts of the corresponding chemical elements were weighted and sealed in evacuated quartz ampules. Samples of the alloys and ternary compounds were prepared by melting. The quartz ampules with their content were heated up to 1280 K, which exceeds by 20 K the melting point of the compound with the highest melting point in this system ( $\text{CuInSe}_2$ ), and were maintained at

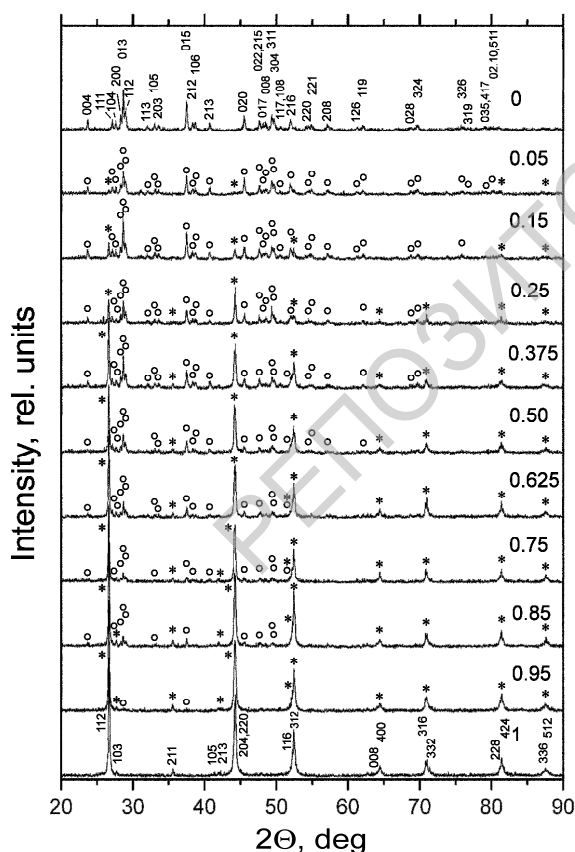
this temperature for 2 hours. The cooling was carried out with a velocity of 3-5 K/min. The isothermal annealing was at 683 K during 550 hours.

The phase relations in the  $\text{CuSbSe}_2$ - $\text{CuInSe}_2$  system were investigated by means of X-ray powder diffraction (DRON 3 diffractometer, monochromatic Cu  $K_\alpha$ -radiation, 1.5406 Å, step size 0.01° or 0.04°, counting time 10 s), optical microscopy (MIM 7 microscope), and scanning electron microscopy (Jeol electron microscope, equipped with an energy-dispersive X-ray detector, EDX). Microstructure was studied on the freshly-polished samples without additional etching.

## RESULTS AND DISCUSSION

### X-ray powder diffraction studies

The XRPD pattern of  $\text{CuInSe}_2$  has in the range from 20 to 90 degrees the characteristic peaks (112), (103), (211), (105), (213), (204)/(220), (116), (312), (008), (400), (316), (332), (228), (424), (336), and (512), which correspond to the chalcopyrite-like tetragonal structure (SG: I42d) with the lattice constants 5.782 and 11.62 Å for  $a$  and  $c$ , respectively (figure 1).

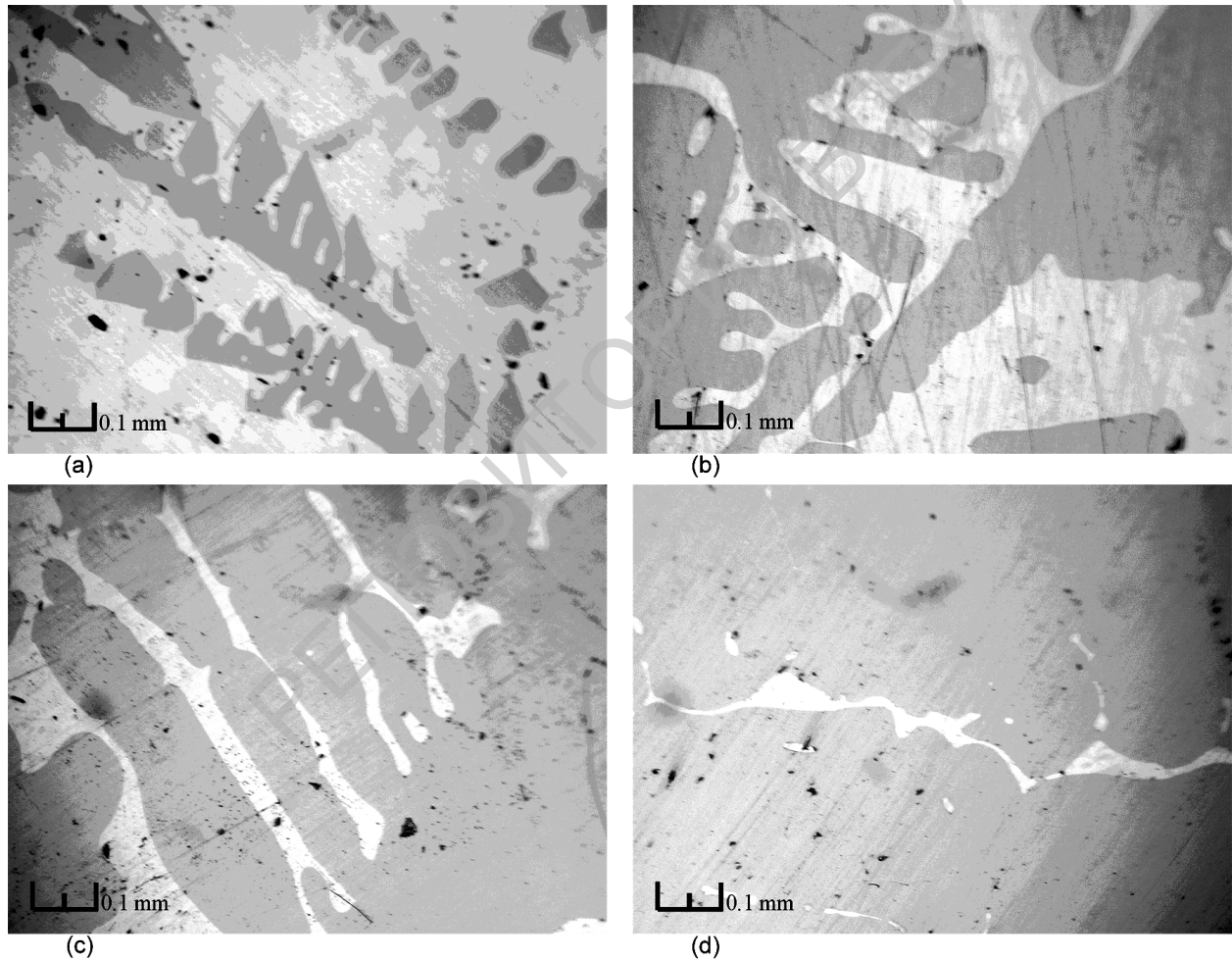


**Figure 1.** XRPD patterns at room temperature for  $\text{CuInSe}_2$  (1),  $\text{CuSbSe}_2$  (0), and alloys of the  $(\text{CuSbSe}_2)_{1-x} \cdot (\text{CuInSe}_2)_x$  system. The denotations of XRPD patterns for alloys correspond to their initial composition, expressed in mole fraction of  $\text{CuInSe}_2$ . The Bragg peaks of the phase with the chalcopyrite-like structure are denoted by a \* and the Bragg peaks of the phase with the orthorhombic structure are denoted by a ○

$\text{CuSbSe}_2$  crystallizes in the orthorhombic structure (SG:  $\text{Pnma}$ ) with the lattice constants 6.303, 3.976, and 15.008 Å for  $a$ ,  $b$ , and  $c$ , respectively. The difference of the lattice constants with the values given in [14] may be explained by the difference in chemical compositions of the samples, which can vary inside the region of homogeneity of  $\text{CuSbSe}_2$ . The XRPD data show that all prepared alloys of the  $\text{CuSbSe}_2$ - $\text{CuInSe}_2$  system consist of two phases. From the XRPD results it can be concluded that the solubility of  $\text{CuInSe}_2$  in  $\text{CuSbSe}_2$  and  $\text{CuSbSe}_2$  in  $\text{CuInSe}_2$  does not exceed 0.05 mole fraction of the ternary compound.

### **Microstructure studies**

The microstructure studies using optical microscopy and scanning electron microscopy confirmed the absence of the formation of complete solid solutions in the  $\text{CuSbSe}_2$ - $\text{CuInSe}_2$  system as they showed that all of the prepared alloys were biphasic (figure 2).



**Figure 2.** Microstructure of alloys of the  $(\text{CuSbSe}_2)_{1-x} \cdot (\text{CuInSe}_2)_x$  system with  $x = 0.15$  (a), 0.50 (b), 0.75 (c), and 0.95 (d) mole fraction of  $\text{CuInSe}_2$

The primary crystals with the chalcopyrite-like structure, based on the compound with a higher melting point ( $\text{CuInSe}_2$ ), crystallize in regular form. The regularity of crystallographic forms is detected as dendrites in figure 2a, b (grains of black color). When the content of  $\text{CuInSe}_2$

increases these primary crystals are completely growing together and a phase based on  $\text{CuSbSe}_2$  is detected as irregular inclusions (figure 2c, white color) or thin veinlets (figure 2d, white color). Thus, two prevailing colors on the photographs of the microsection—black and white—indicate the presence of two phases with different chemical compositions and crystal structures. Each of these phases has an area of homogeneity, within the limits of which its chemical composition can vary. Because of such variation of chemical composition in addition to the black and white colors one can also observe on the photographs their shades—several levels of dark to light grey.

The results of the determination of the chemical composition of these two phases are presented in table I. The chemical composition for copper antimony diselenide  $\text{CuSbSe}_2$  is  $\text{CuSb}_{0.94}\text{Se}_{1.99}$ , which indicates a slight deficiency of antimony. This result is in accordance with the previous results which establish that the homogeneity region of  $\text{CuSbSe}_2$  is shifted toward the  $\text{Cu}_2\text{Se}$  binary compound on the  $\text{Cu}_2\text{Se}$ - $\text{Sb}_2\text{Se}_3$  intersection and the solubility of  $\text{Cu}_2\text{Se}$  in  $\text{CuSbSe}_2$  is higher than the solubility of  $\text{Sb}_2\text{Se}_3$  in  $\text{CuSbSe}_2$  (0.0068 mole fraction versus 0.0020 mole fraction) [13]. The EDX results also confirmed a full interaction of all constituent elements, as theoretical (initial) compositions of alloys agree well with the experimental total compositions of alloys. For the alloy with the initial composition  $\text{CuIn}_{0.50}\text{Sb}_{0.50}\text{Se}_2$  (an atomic ratio  $\text{In/Sb} = 1$ ) the atomic ratio  $\text{In/Sb}$  for experimental total composition of alloy is  $0.60/0.59 = 1.02$ , and for the alloy with the initial composition  $\text{CuIn}_{0.75}\text{Sb}_{0.25}\text{Se}_2$  (an atomic ratio  $\text{In/Sb} = 3$ ) the atomic ratio  $\text{In/Sb}$  for experimental total composition of alloy is  $0.70/0.21 = 3.33$ .

**Table I.** Chemical composition of discovered phases for the  $(\text{CuSbSe}_2)_{1-x}(\text{CuInSe}_2)_x$  alloys, determined from Energy Dispersive X-ray analysis.

Theoretical composition of alloy	Experimental total composition of alloy	Phase with the tetragonal structure	Phase with the orthorhombic structure
$\text{CuSbSe}_2$	$\text{CuSb}_{0.94}\text{Se}_{1.99}$		
$\text{CuIn}_{0.15}\text{Sb}_{0.85}\text{Se}_2$			$\text{CuSb}_{0.85}\text{Se}_{1.69}$
$\text{CuIn}_{0.50}\text{Sb}_{0.50}\text{Se}_2$	$\text{CuIn}_{0.60}\text{Sb}_{0.59}\text{Se}_{1.87}$	$\text{CuIn}_{0.96}\text{Se}_{2.07}$	$\text{CuSb}_{0.93}\text{Se}_{2.32}$
$\text{CuIn}_{0.75}\text{Sb}_{0.25}\text{Se}_2$	$\text{CuIn}_{0.70}\text{Sb}_{0.21}\text{Se}_{2.34}$		
$\text{CuIn}_{0.95}\text{Sb}_{0.05}\text{Se}_2$		$\text{CuIn}_{0.78}\text{Se}_{1.90}$	$\text{CuSb}_{0.84}\text{Se}_{1.69}$

Chemical compositions of the two phases detected on the polished sections correspond to the chemical compositions of the phase with the tetragonal structure (average composition  $\text{CuIn}_{0.87}\text{Se}_{1.99}$ ) and the phase with the orthorhombic structure (average composition  $\text{CuSb}_{0.87}\text{Se}_{1.90}$ ). These phases contain only three chemical elements which indicate that the solubility of antimony in  $\text{CuInSe}_2$  and the solubility of indium in  $\text{CuSbSe}_2$  do not exceed the limits of determination of these elements by energy-dispersive X-ray analysis. It can be concluded that the limits of solubility for  $\text{CuSbSe}_2$  in  $\text{CuInSe}_2$  and for  $\text{CuInSe}_2$  in  $\text{CuSbSe}_2$  do not exceed 0.001 mole fraction. This result is in contrast to the limits of solubility in the  $\text{CuInS}_2$ - $\text{CuSbS}_2$  system where the limits of solubility are 0.059 mole fraction for  $\text{CuSbS}_2$  in  $\text{CuInS}_2$  and 0.038 mole fraction for  $\text{CuInS}_2$  in  $\text{CuSbS}_2$ .

## CONCLUSIONS

The  $\text{CuInSe}_2$  and  $\text{CuSbSe}_2$  ternary compounds and alloys of the  $(\text{CuSbSe}_2)_{1-x}(\text{CuInSe}_2)_x$  system with the mole fraction of  $\text{CuInSe}_2$  ( $x$ ) equal to 0.05, 0.15, 0.25, 0.375, 0.50, 0.625, 0.75,

0.85, and 0.95 were prepared and the phase relations in this system were investigated by X-ray powder diffraction, optical microscopy, and scanning electron microscopy. XRPD found that CuInSe<sub>2</sub> crystallizes in the chalcopyrite-like tetragonal structure (space group: I4<sub>2</sub>d) with the lattice constants 5.782 and 11.62 Å for *a* and *c*, respectively, and CuSbSe<sub>2</sub> crystallizes in the orthorhombic structure (space group: Pnma) with the lattice constants 6.303, 3.976, and 15.008 Å *a*, *b*, and *c*, respectively. Chemical composition of copper antimony diselenide has a slight deficiency of antimony and corresponds to CuSb<sub>0.94</sub>Se<sub>1.99</sub>. This result can be explained by the shift of composition inside the homogeneity region of CuSbSe<sub>2</sub> toward Cu<sub>2</sub>Se binary compound on the Cu<sub>2</sub>Se-Sb<sub>2</sub>Se<sub>3</sub> intersection. It was shown that the alloys of the CuSbSe<sub>2</sub>-CuInSe<sub>2</sub> at room temperature are biphasic in the whole range of compositions, and the limits of solubility for CuSbSe<sub>2</sub> in CuInSe<sub>2</sub> and for CuInSe<sub>2</sub> in CuSbSe<sub>2</sub> do not exceed 0.001 mole fraction.

## ACKNOWLEDGMENTS

It is a pleasure to thank Ms. C. Kelch (Helmholtz-Zentrum Berlin für Materialien und Energie, Berlin, Germany) for fruitful help with the SEM studies. The partial financial support from the Belarusian Republican Foundation for Fundamental Research (grant No. Φ06-166) is greatly appreciated by A.A. Fadzeyeva, I.I. Maroz, and B.V. Korzun, the latter of whom is also thankful for the financial support from the DAAD (A/12/00618).

## REFERENCES

1. C.A. Wolden, J. Kurtin, J.B. Baxter, I. Repins, S.E. Shaheen, J.T. Torvik, A.A. Rockett, V.M. Fthenakis, and E.S. Aydil, *J. Vac. Sci. Technol. A* **29**, 030801, 62 p. (2011)
2. M. Kumar, C. Persson, *Energy Procedia* **44**, 176 (2014)
3. J.T.R. Dufton, A. Walsh, P.M. Panchmatia, L.M. Peter, D. Colombara, M.S. Islam, *Phys. Chem. Chem. Phys.* **14**, 7229 (2012)
4. B.V. Korzun, A.A. Fadzeyeva, and I.I. Maroz, *Phys. Status Solidi C* **6**, 1047 (2009)
5. B.V. Korzun, A.N. Gavrilenko, A.A. Fadzeyeva, O.V. Ignatenko, I.I. Maroz, V.R. Sobol, M. Rusu, R. Klenk, C. Merschjann, Th. Schedel-Niedrig, M. Ch. Lux-Steiner, *Cryst. Res. Technol.* **48**, 641 (2013)
6. R.A. Kuliev, A.N. Krestovnikov, V.M. Glazov, *Zhurnal fizicheskoi khimii* **XLIII**, 3063 (1969) (in Russian)
7. W. Scott, J.R. Kench, *Mat. Res. Bull.* **8**, 1257 (1973)
8. A. Pfitzner, *Z. anorg. Allg. Chem.* **621**, 685 (1995) (in German)
9. J.H. Wernick, K.E. Benson, *J. Phys. Chem. Solids* **3**, 157 (1957)
10. J. Garin, E. Parthé, *Acta Crystallogr. B* **28**, 3672 (1972)
11. A. Pfitzner, *Z. Kristallogr.* **209**, 685 (1994)
12. Y. Zhang, V. Ozoliņš, D. Morelli, C. Wolverton, *Chem. Mater.* **26**, 3427 (2014)
13. M.I. Golovei, V.I. Tkachenko, M.Y. Rigan, N.P. Stasyuk, *Izvestiia Akademii nauk SSSR. Neorganicheskie materialy* **26**, 933 (1990) (in Russian)
14. R.M. Imamov, Z.G. Pinsker, A.I. Ivchenko, *Kristallografiya* **19**, 853 (1964) (in Russian)
15. B.V. Korzun, A.A. Fadzeyeva, in *Proceedings of the International Conference "Actual Problems of Physics of Solids,"* edited by N.M. Olekhovich (Minsk, Belarus, 2007), Minsk, 2007, Vol. 2, pp. 274-275
16. J. Zhou, G.-Q. Bian, Q.-Y. Zhu, Y. Zhang, C.-Y. Li, J. Dai, *J. Solid State Chem.* **182**, 259 (2009)
17. C. Yang, Y. Wang, S. Li, D. Wan, F. Huang, *J. Mater. Sci.* **47**, 7085 (2012)