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Luminescence and magnetic properties of copper-deficient $Cu^{+}_{2-x}Cu^{2+}_{x/2}\square_{x/2}ZnSnS_4$ ($0 < x \leqslant 0.30$) solid solutions with a kesterite structure

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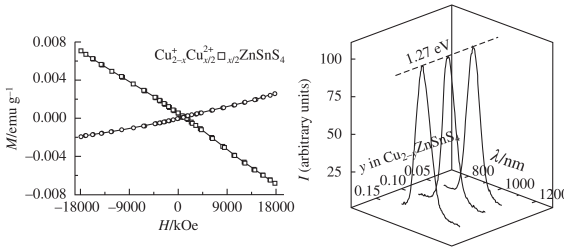
The copper-deficient solid solutions $Cu_{2-y}ZnSnS_4$ ($0 < y \leqslant 0.45$) with a kesterite crystal structure were synthesized and their unit cell parameters at different values of *y* were determined. Based on magnetometry it was found that the crystal lattice of $Cu^{+}_{2-x}Cu^{2+}_{x/2}\square_{x/2}ZnSnS_4$ ($0 < x \leqslant 0.30$) contains copper in the oxidation states 2+ and 1+. A band at 1.27 eV in the cathodoluminescence spectra of the $Cu^{+}_{2-x}Cu^{2+}_{x/2}\square_{x/2}ZnSnS_4$ solid solutions at 78 K is due to the $Cu^{2+}{\cdot}V_{Cu}$ associates of defects.



Magnetic properties — Cathodoluminescence

Keywords: kesterite, CZTS, structural data, cathodoluminescence, magnetic properties, associates of defects.

Alternative energetics, in particular, the development of solar panels, is of considerable current importance.[1,2] Solid solutions based on compound Cu_2ZnSnS_4 (CZTS) with a kesterite structure is among the most promising inorganic materials for devices of this kind.[2–4] The CZTS materials are formed from readily available nontoxic elements, and Cu_2ZnSnS_4 has an optimal band gap E_g (~1.5 eV) for solar cells and a high optical absorption coefficient (>104 cm^{-1}).[2] However, the efficiency of devices based on CZTS barely reaches 12% *vs.* a theoretically possible value of 30%.[5] New methods for CZTS synthesis, namely, an electrochemical method[6] and synthesis in iodide melts,[7] are under development. Kesterite solid solutions with a deficiency in the copper sublattice are promising materials for the preparation of monograin kesterite powders $Cu_{1.8}Zn_{1.05}Sn_{0.95}S_4$ for solar cells.[7]

The aim of this work was to synthesize $Cu_{2-y}ZnSnS_4$† samples ($0 < y \leqslant 0.45$) and to study their structure as well as luminescent and magnetic properties in the context of structure defectiveness.

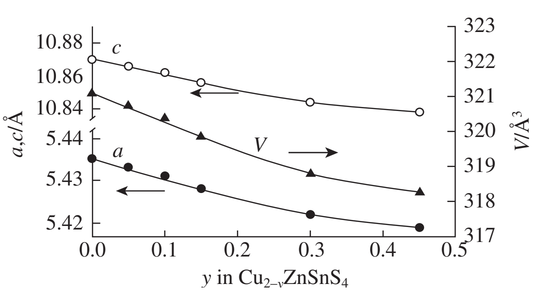


Figure 1 Unit cell parameters of $Cu_{2-y}ZnSnS_4$ solid solutions as functions of *y*.

All the lines in the X-ray diffraction patterns‡ of Cu_2ZnSnS_4 samples (0.05; 0.10; 0.15; 0.30; and 0.45) were indexed (using data for 23 reflexes for each X-ray pattern) in a tetragonal kesterite lattice, space group $I\bar{4}2m$. No superstructure lines and lines due to impurity phases were found. The tetragonal unit cell parameters of $Cu_{2-y}ZnSnS_4$ determined with an accuracy of ±0.003 Å (for *a*) or ±0.005 Å (for *c*) decreased with *y* (Figure 1). Variations in the unit cell parameters indicated that $Cu_{2-y}ZnSnS_4$ solid solutions were actually formed in the region $0 < y \leqslant 0.45$. The unit cell volume *V* (determined to within ±0.06 Å^3) decreased with *y* (see Figure 1). V_{Cu} vacancies (or □) appear in the copper sublattice in $Cu_{2-y}ZnSnS_4$ solid solutions. To keep crystal electroneutrality, copper atoms in the copper sublattice acquired the oxidation state 2+. From $Cu_{2-y}ZnSnS_4$ with $y = x$ and adding $x/2$ for Cu^{2+} and copper vacancy, we obtained the formula $Cu^{+}_{2-x}Cu^{2+}_{x/2}\square_{x/2}ZnSnS_4$. The decrease in unit cell parameters (see Figure 1) was explained by the fact that Cu^{2+} ions are smaller than Cu^{+} ions.[9]

† Polycrystalline samples of $Cu_{2-y}ZnSnS_4$ ($0 < y \leqslant 0.45$) were synthesized from $Cu_{2-x}S$, ZnS, and SnS_2 using high-purity zinc sulfide single crystals and elementary copper, tin and sulfur of 4N grade. At the first stage, the amounts required for the synthesis were annealed at 1120 °C in evacuated ($p_{res} = 2\times10^{-2}$ Torr) graphitized quartz tubes for 10 h. Once the tubes were opened, their contents were ground in an agate mortar. After that, homogenizing annealing was performed in evacuated tubes at 750 °C for 100 h and then for 300 h at 550 °C.

‡ The phase composition of the samples was studied by powder X-ray diffraction analysis using a DRON-4 diffractometer (CuKα radiation) and the WinXPOW software package.

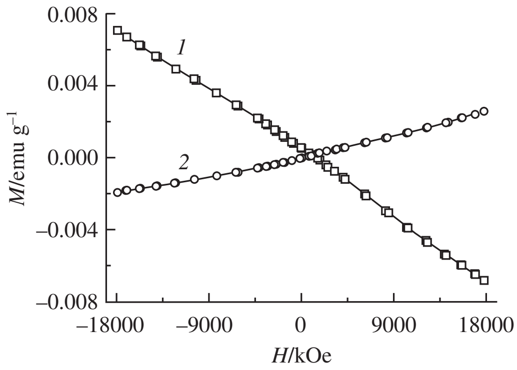


Figure 2 Dependence of magnetization M on magnetic field strength H for (*1*) Cu_2ZnSnS_4 and (*2*) $Cu^+_{2-x}Cu^{2+}_{x/2}\square_{x/2}ZnSnS_4$ solid solution with $x = 0.3$.

Magnetometry[§] was used to obtain the plots of magnetization *vs.* field strength for $Cu^+_{2-x}Cu^{2+}_{x/2}\square_{x/2}ZnSnS_4$ (see Figure 2). The sample of Cu_2ZnSnS_4 was diamagnetic (see Figure 2, curve *1*) with a magnetic susceptibility of -3.8×10^{-7} emu g^{-1}, whereas the solid solution $Cu^+_{1.40}Cu^{2+}_{0.30}\square_{0.30}ZnSnS_4$ was paramagnetic (curve 2) with a magnetic susceptibility of $+1.4\times10^{-7}$ emu g^{-1}. The paramagnetism of the samples indicated that copper with the oxidation state 2+ occurred in the crystal lattice of $Cu^+_{2-x}Cu^{2+}_{x/2}\square_{x/2}ZnSnS_4$ solid solutions.

In the CL spectra[¶] of $Cu^+_{2-x}Cu^{2+}_{x/2}\square_{x/2}ZnSnS_4$ solid solutions, no exciton lines that would unambiguously indicate the exact value of the band gap E_g were found. The CL spectra of samples with $x = 0.05$–0.30 contained an intense band at 1.27 eV (Figure 3) due to the presence of copper in the oxidation state 2+: a Cu^{2+} ion in a Cu^+ site creates a positively charged defect that is bound with a negatively charged copper vacancy V'_{Cu} into a $Cu^{2+}\cdot V_{Cu}$ associate of defects. An electron beam decomposes this associate into Cu^{2+} and, and V'_{Cu} radiation with an energy of 1.27 eV is released upon their subsequent interaction to give the associate. It was found using a cathodoluminescent method[10] that $Cu^{2+}\cdot V_{Cu}$ associates of defects exist in $Cu_{1-x}(In_{0.7}Ga_{0.3})Se_2$ solid solutions with a chalcopyrite structure at 78 K. Thus, in $Cu^+_{2-x}Cu^{2+}_{x/2}\square_{x/2}ZnSnS_4$ solid solutions ($0 < x \leqslant 0.30$), copper in the oxidation state 2+ is located in the copper sublattice in the positions that were occupied by Cu^+ at $x = 0$, and it forms $Cu^{2+}\cdot V_{Cu}$ associates of defects. The concentration of vacancies in the copper sublattice is equal to the concentration of Cu^{2+} (Table 1); therefore, the $Cu^{2+}\cdot V_{Cu}$ associates of defects are the predominant defects at 78 K.

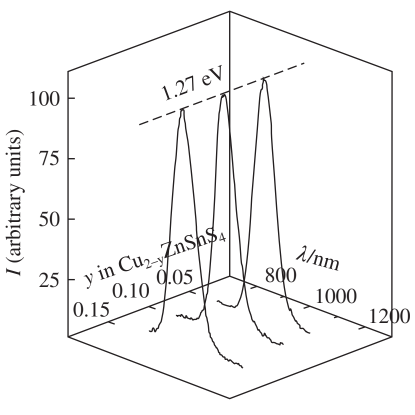


Figure 3 CL spectra of $Cu_{2-y}ZnSnS_4$ samples at $T = 78$ K: 1–$y = 0.05$; 2–$y = 0.10$; 3–$y = 0.15$; or x in $Cu^+_{2-x}Cu^{2+}_{x/2}\square_{x/2}ZnSnS_4$ ($x = y/1.5$): 1–$x = 0.033$; 2–$x = 0.067$; 3–$x = 0.10$.

Table 1 Fractions of Cu^+, Cu^{2+} and V_{Cu} (or □) in the copper sublattice of $Cu^+_{2-x}Cu^{2+}_{x/2}\square_{x/2}ZnSnS_4$ solid solutions.

x in $Cu^+_{2-x}Cu^{2+}_{x/2}\square_{x/2}ZnSnS_4$	Fractions		
	Cu^+	Cu^{2+}	□ (or V_{Cu})
0.05	1.90	0.05	0.05
0.10	1.80	0.10	0.10
0.15	1.70	0.15	0.15
0.30	1.40	0.30	0.30

Thus, we found that the copper-deficient $Cu^+_{2-x}Cu^{2+}_{x/2}\square_{x/2}ZnSnS_4$ kesterite solid solutions are formed in the range $0 < x \leqslant 0.30$. This result can be used to estimate the copper deficiency in $Cu^+_{2-x}Cu^{2+}_{x/2}\square_{x/2}ZnSnS_4$ layers applied to create solar cells. We determined the dependence of the unit cell parameters of $Cu_{2-y}ZnSnS_4$ ($0 < y \leqslant 0.45$) solid solutions on y. The magnetic properties of $Cu^+_{2-x}Cu^{2+}_{x/2}\square_{x/2}ZnSnS_4$ ($0 < x \leqslant 0.30$) indicated that the crystal lattice contains copper in the 2+ oxidation state (along with 1+). A band at 1.27 eV in the CL spectrum (78 K) of its solid solutions with $x = 0.05$–0.30 is most likely due to $Cu^{2+}\cdot V_{Cu}$ associates of defects. The formation of such defect associates should be taken into account in the analysis of the electrophysical and optical properties of CZTS samples with copper deficiency in the crystal lattice.

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

¶ The cathodoluminescence (CL) spectra were recorded at 78 K using a DFS-13 monochromator. Luminescence was excited by a 40 keV pulsed electron beam.[8] The accuracy of determining the wavelengths was ±4 nm, and the photon energy was calculated to within ±0.01 eV.

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