X-ray diffraction and differential scanning calorimetry analysis of $CuInZnSe_3$

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The compound $CuInZnSe_3$ was synthesized, the crystal structure was investigated by X-ray diffraction and thermal properties was investigated by differential scanning calorimetry analysis. It was found that, under normal conditions, the crystal structure of this compound corresponds to cubic symmetry with the space group $F\text{-}43m$ (216). The temperature dependence is obtained at a constant rate of heat treatment of the heat flow in the temperature range $T = 30-900^\circ C$. The observed endothermic effects at $T = 43$, 600 and 756°C are explained by the resonance of thermal vibrations of atoms in the crystal structure of the $CuInZnSe_3$ compound and the release of relatively weakly bound atoms.

Keywords: X-ray diffraction, semiconductors, chalcogenides.

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1. Introduction

Recently, the focus is on the study of a crystal structure, optical and thermal properties of the semiconductor compounds with various physical properties [1–5]. Among semiconductor compounds, the A^2B^2 and $A^1B_2^2$ chalcogenides occupy a very special place [6–10]. The A_2Se (A = Cu, In, Zn) are the most studied chalcogenides due to their optical and electrical properties [11–13]. The X-ray diffraction structural studies show that the crystal structure of these compounds may have an orthorhombic, tetragonal, hexagonal or cubic symmetry [10].

The structural studies of the chalcogenide semiconductors reveal many interesting structures. The AgCuSe compound was investigated to have established different phases: a tetragonal, rhombic, cubic one and the Ag_2Se-Cu_2Se solid solution [10]. The studies showed that with partial replacement of Cu atoms with Zn and Cd atoms the binary chalcogenides have evident changes of the crystal structure, which is explained by the difference of ionic radii of the atoms. This phenomenon has been also observed in perovskites during the previous studies and shown generation of a chemical pressure in the compounds due to the difference of the ionic radii [14].

The previous structural studies show that the binary and ternary chalcogenide compounds have various structural phases. This work was the first one to synthesize the $CuInZnSe_3$ compound and investigate its structure (by means of the X-ray diffraction) and thermal properties (by the differential scanning calorimetry (DSC)) of polycrystalline samples.

2. Experiment description

2.1. Sample synthesis

The samples for the study have been produced by melting initial elements (cleanliness of Cu, Zn, In, Se was at least 99.9998%), taken by stoichiometry (weight 5 g). The initial elements filled a quartz ampoule, which was then evacuated to a residual pressure of 10^{-4} mm Hg, soldered and placed in a single-zone heating thermostat, whose temperature was preset at 327°C. After holding at this temperature for 1 hour, the thermostat temperature was raised at the rate of 50°C per hour to 1000°C. Holding the synthesis process at this temperature for 1 hour, the thermostat temperature was reduced to 477°C, at which the alloy had been annealed for 15 days for homogenization. Visual microscope examination of the synthesized sample showed that it was in a compact state and the alloy was reddish.

2.2. X-ray diffraction

The structural analysis of the study subject was performed by the X-ray diffraction method. The X-ray diffraction of the samples was performed on the D8 Advance (Bruker) powder diffractometer with the following parameters: 40 kV, 40 mA, radiation CuK_α ($\lambda = 1.5406$ Å).

2.3. Differential scanning calorimetry

The thermal properties of the subject were investigated by the X-ray diffraction calorimetry method. The XDC was

performed in the „Jupiter“ STA 449F3 instrument (Netzsch, Germany). The analysis was performed in a dynamic mode in the inert atmosphere (helium) in a thermoanalyzer at the heating rate of 5 degrees/minute by using the Pt−Pt/Rh thermocouple. The instrument was controlled by means of the „Proteus“ software. The experiments were performed within the temperature range $T = 30-900°C$ [15].

3. Results and discussion thereof

3.1. Structural analysis

Fig. 1 shows the X-ray diffraction spectrum of the $CuInZnSe_3$ compound, which is produced at the room temperature and in the normal conditions.This spectrum has been analyzed by the Rietveld method. It has been found that the crystal structure of this compound corresponds to the cubic symmetry of the space group F-43m (216). The values of the lattice cell parameters are equal to $a = b = c = 5.7877$ Å.

It has been established that the crystal structure has the atoms of the metals Cu, In and Zn in the same position: $x = 0, y = 0, z = 0$. The Se chalcogen atoms form covalent bonds with the metal atoms in the position $x = 0.25$, $y = 0.25$, $z = 0.25$. Fig 2 shows the crystal structure of the $CuInZnSe_3$ compound, which is obtained by means of the Diamond 3.2 software. As it is clear from the crystal structure, the atoms Cu, In and Zn are in the same position in points and faces of the crystal lattice. The Se atoms form tetrahedron around the metal atoms. The distances between the atoms of the metal (Cu, In and Zn) and the chalcogen (Se): $d_{M-H} = 2.4998$ Å.

3.2. Thermal analysis

It is known that the physical characteristics of the thermal flux can reflect important structural processes in the compound, like structural phase transitions, a decomposition mechanism, types of chemical reactions and oxidation. On the other hand, it is possible to transition from the thermal flux function to thermal conductivity, thermal diffusion, heat capacity and thermodynamic parameters. The transition from the thermal flux functions to the thermal conductivity and the temperature dependence of the heat capacity allow explaining the mechanism of the change of the thermodynamic functions [16]. Fig. 3 shows the DSC curves and the DSC first derivative within the temperature range $30 \le T \le 900°C$ of the $CuInZnSe_3$ compound.

The values of the thermal flux $\Delta\Phi$ and the DSC derivative were investigated at the constant rate of thermal processing (5°/min). Fig. 3 shows the temperature dependence of the thermal flux function, which is characterized by five main effects. The central peaks of the thermal transitions (effects) due to an amount of heat transferred to the crystal corresponded to the following temperatures: $T_1 = 221°C$, $T_2 = 421°C$, $T_3 = 492°C$, $T_4 = 596°C$ and $T_5 = 753°C$. Fig. 4 shows the DSC spectrum with

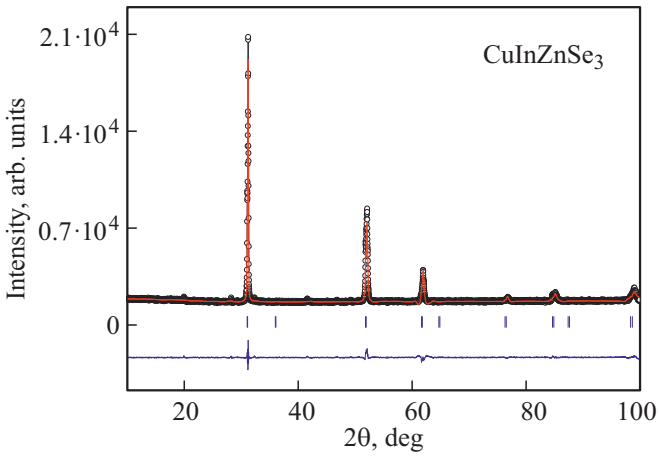

Figure 1. X-ray diffraction spectrum of the $CuInZnSe_3$ compound at the room temperature in the normal conditions.

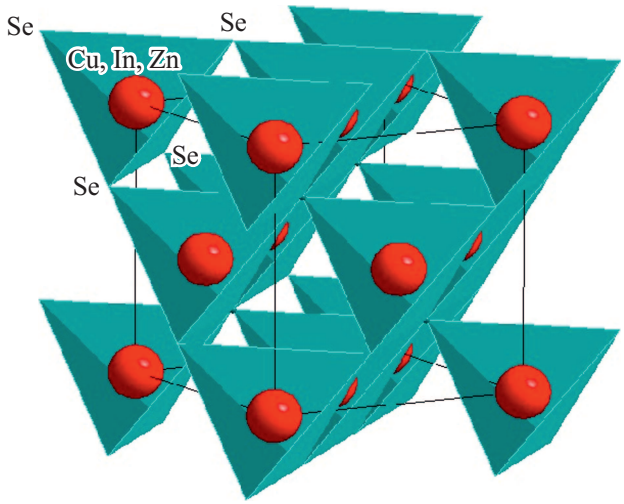

Figure 2. Crystal structure of the $CuInZnSe_3$ compound.

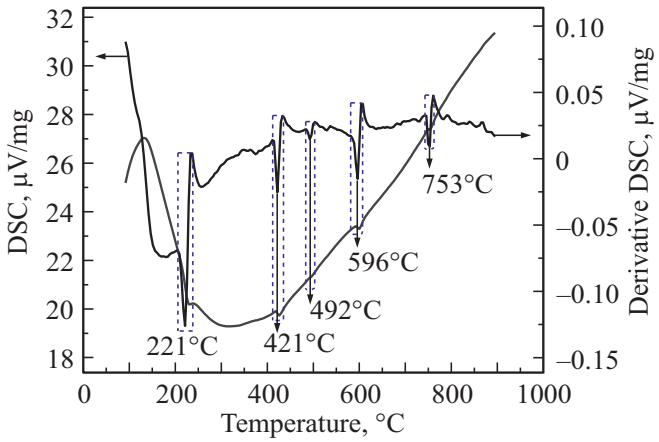

Figure 3. DSC curves and the DSC first derivative within the temperature range $30 \le T \le 900°C$ of the $CuInZnSe_3$ compound.

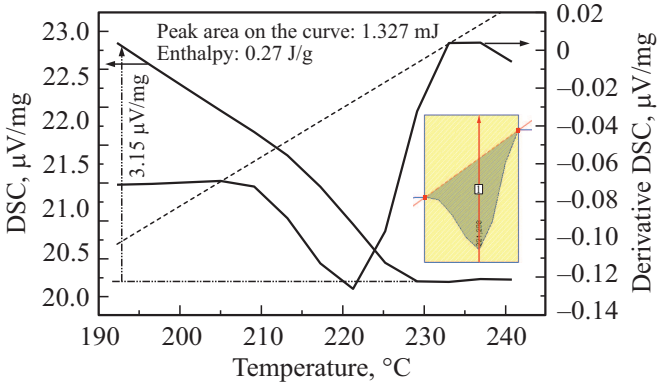

Figure 4. DSC curves and the DSC first derivative within the temperature range $192 \leq T \leq 242$°C of the $CuInZnSe_3$ compound.

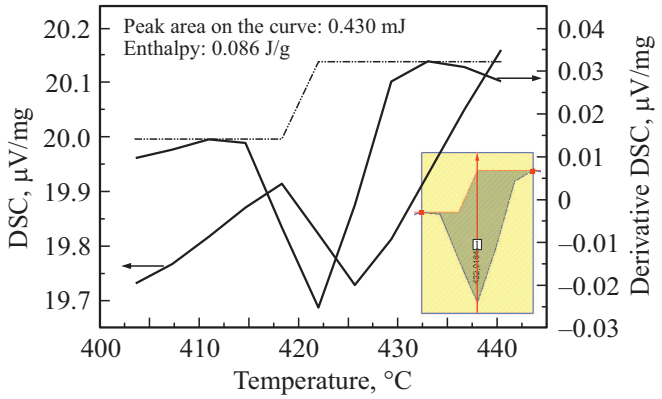

Figure 5. DSC curves and the DSC first derivative within the temperature range $403 \leq T \leq 441$°C of the $CuInZnSe_3$ compound.

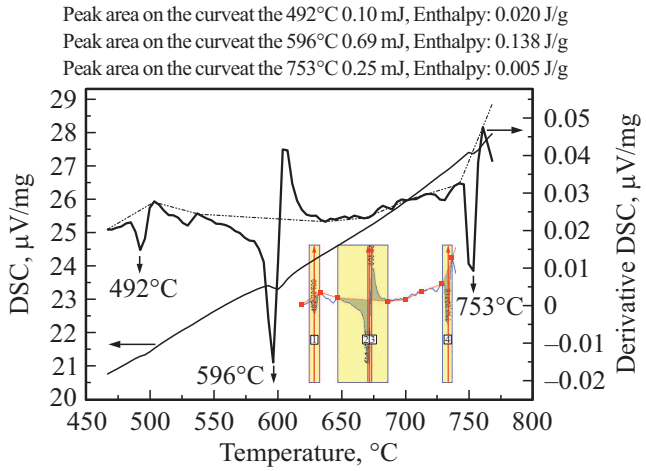

Figure 6. DSC curves and the DSC first derivative within the temperature range $460 \leq T \leq 770$°C of the $CuInZnSe_3$ compound.

the central peak $T = 221$°C within the temperature range $195 \leq T \leq 240$°C. The completed effect was characterized within the $CuInZnSe_3$ DSC spectrum in the given temperature range. It is determined for the effect with the 221°C central peak that a value of the thermal flux function decreases to 3.15 μW/mg and goes into a stable area at the temperature of 229°C. The energy of the field generated by the heat function is determined to be 1.327 mJ, while the enthalpy value was determined to be 0.27 J/g.

Fig. 5 shows the thermal flux spectra with the central peak of 422°C for $CuInZnSe_3$ within the temperature range $400 \leq T \leq 440$°C. For the effect with the central peak in the DSC spectrum at 422°C the field energy is 0.430 mJ, while the value of the thermal flux function increases from 19.75 to 20.15 μW/mg.

Fig. 6 shows the DSC spectrum for the $CuInZnSe_3$ compound with the central peaks 492, 596 and 753°C within the temperature range $450 \leq T \leq 770$°C. The effects of the linear increase in the thermal flux of the $CuInZnSe_3$ compound in the said temperature range and of a small change of the central peaks are characterized by the resonance of thermal vibrations of atoms in the crystal structure and release of relatively weakly bound atoms. In the DSC spectrum within the temperature range $450 \leq T \leq 770$°C for the effect with the central peak 422°C the field energy is 0.10 mJ, the enthalpy is 0.02 J/g; while for the effect with the central peak 596°C the field energy is 0.69 mJ, the enthalpy is 0.138 J/g; for the effect with the central peak 753°C the field energy is 0.25 mJ, and the enthalpy is 0.005 J/g. Besides, the value of the thermal flux function was linearly increasing from 20.5 to 28.5 μW/mg. The temperature range of the first endo-effect is determined: the initial temperature of 484°C and the final temperature of 503°C; so is the temperature range of the second endo-effect: the initial temperature of 580°C and the final temperature of 627°C; so is the temperature range of the third endo-effect: the initial temperature of 745°C and the final temperature of 760°C.

4. Conclusion

The structural studied of the $CuInZnSe_3$ compound at the room temperature have shown that this compound has the cubic symmetrical crystal structure with the space group F-43m (216). As a result of the thermal analysis within the high-temperature region it has been determined that within the temperature range $T = 30-900$°C this compound had no structural phase transition, but still had the cubic symmetry. There is no structural phase transition at the higher temperatures, but at the same time there are phenomena such as decomposition and melting. The effects of the linear increase in the thermal flux of the $CuInZnSe_3$ compound in the said temperature range and of a small change of the central peaks at the temperatures 492, 596 and 753°C are characterized by the resonance of thermal vibrations of atoms in the crystal structure and release of relatively weakly bound atoms.

Conflict of interest

The authors declare that they have no conflict of interest.

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