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PHYSICAL PROPERTIES OF CRYSTALS

Synthesis and X-Ray Diffraction Study of $Cu_2ZnSn(S_xSe_{1-x})_4$ Solid Solutions

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Abstract—Quaternary compounds Cu_2ZnSnS_4 and $Cu_2ZnSnSe_4$ and solid solutions on their basis have been fabricated by one-temperature synthesis from elementary components: Cu, Zn, Sn, S, and Se. Single crystals of these compounds have been grown by the method of chemical gas-transport reactions from polycrystalline samples. The compositional dependence of the unit-cell parameters of $Cu_2ZnSn(S_xSe_{1-x})_4$ has been investigated by X-ray diffraction. It is found that parameters *a* and *c* linearly decrease with an increase in sulfur concentration in accordance with Vegard's law. The temperature dependences of parameters *a* and thermal-expansion coefficients α_a of Cu_2ZnSnS_4 and $Cu_2ZnSnSe_4$ single crystals in the range of 100–300 K are determined.

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INTRODUCTION

Silicon, which is widely used in solar light converters, is an indirect-gap semiconductor. This circumstance reduces its conversion efficiency. Currently, silicon is being actively replaced with new materials. $Cu(In,Ga)Se_2$, CuIn(S,Se), and CuGa(S,Se) solid solutions are promising materials for basic layers of light converters. They are direct-gap semiconductors, which, in contrast to silicon, have a large absorption coefficient in the visible and near-IR spectral regions. Currently, the efficiency of solar light converters based on $Cu(In,Ga)Se_2$ solid solutions reaches 19.0–20.8% [1–4].

However, in view of the high cost of indium and gallium and their sparse resources, these metals have begun to be replaced with more inexpensive and available elements. Much attention is paid to quaternary compounds Cu_2ZnSnS_4 and $Cu_2ZnSnSe_4$. These are direct-gap semiconductors, in which In and Ga are replaced, respectively, with Sn and Zn (the closest elements in the Mendeleev periodic table). Recently, there have been many studies on the synthesis, analysis of physical properties, and practical application of materials based on Cu_2ZnSnS_4 and $Cu_2ZnSnSe_4$ compounds and $Cu_2ZnSn(S_xSe_{1-x})_4$ solid solutions [5–18]. Nevertheless, despite the great efforts and rapid progress in this field in the last few years, the highest photoelectric conversion efficiency of solar cells based on $Cu_2ZnSnSe_4$ is only 11.1–12.6% [10, 16]. The reason is that modern technologies do not make it possible to fabricate these materials in the form of thin films with high structural quality and electrical properties appropriate for solar cells.

The synthesis of Cu_2ZnSnS_4 and $Cu_2ZnSnSe_4$ quaternary compounds meets a number of problems, the solution of which may increase the photoelectric conversion efficiency of these materials. One of the main problems is their significant deviation from stoichiometry, which leads to a high concentration of intrinsic structural defects of different nature and the formation of undesirable binary- or ternary-phase impurities. It should be taken into account that, depending on technological conditions, these compounds can be crystallized into both kesterite and stannite structures. The crystalline quality is also significantly affected by the Cu/Zn ratio.

In addition to Cu_2ZnSnS_4 and $Cu_2ZnSnSe_4$ quaternary compounds, $Cu_2ZnSn(S_xSe_{1-x})_4$ solid solutions are also of great interest for solar power engineering. Changing their composition, one can obtain

Crystallographic parameters of $Cu_2ZnSn(S_xSe_{1-x})_4$ solid solutions

x	*a*, Å	*c*, Å	*H*
0	5.685	11.408	1.0033
0.3	5.613	11.228	1.0018
0.5	5.575	11.134	0.9986
0.7	5.542	11.020	0.9942
1	5.431	10.851	0.9990

materials with continuously changing physical properties, which makes it possible to choose compositions with characteristics most appropriate for practical applications.

The purpose of our study was to synthesize polycrystals of Cu_2ZnSnS_4 and $Cu_2ZnSnSe_4$ quaternary compounds and $Cu_2ZnSn(S_xSe_{1-x})_4$ solid solutions on their basis, grow single crystals of these compounds, and determine their crystallographic characteristics as functions of composition and temperature.

SAMPLE PREPARATION TECHNIQUE

Synthesis

Cu_2ZnSnS_4 and $Cu_2ZnSnSe_4$ quaternary compounds and $Cu_2ZnSn(S_xSe_{1-x})_4$ solid solutions were synthesized by the one-temperature method, which provides a sufficiently high purity of synthesized material and excludes component loss. The initial agents were elementary components: copper, zinc, and tin with a purity of 99.999% and sulfur and selenium of special purity grade. Synthesis was performed in double quartz ampoules. The initial components were loaded (in ratios corresponding to the formula composition; total weight ~15 g) into an ampoule, after which the ampoule was evacuated and placed in another evacuated ampoule; the latter was installed in a vertical single-zone furnace.

The temperature in the furnace was raised in stages (with a 2-h exposure) either to values exceeding the melting temperature of the compounds by 20–30°C or to the liquidus temperature of a solid solution of the corresponding composition. When the desired temperature was reached, vibrational stirring was switched on, and the temperature was kept for 4 h. Then vibration was switched off, and the temperature was reduced a rate of 5°C/h to complete solidification of the solution. The thus obtained ingots of solid solutions were homogenized by isothermal annealing in vacuum at 750°C for 300 h.

Single Crystal Growth

Cu_2ZnSnS_4 and $Cu_2ZnSnSe_4$ single crystals were grown by chemical gas-transport reactions from previously synthesized polycrystalline ingots. The carrier gas was elementary iodine of V5 grade.

The polycrystals synthesized were triturated and used as the initial material for gas transport. An ampoule with the initial material and iodine was placed in a horizontal furnace with two independently controlled zones, which provided a desired temperature gradient along the ampoule axis. The temperature in the furnace was controlled so as to provide ~700°C in the crystallization zone and ~780°C in the reaction zone. Single crystals were grown under these conditions for about 192 h.

EXPERIMENTAL TECHNIQUE

The unit-cell parameters of powder samples of the Cu_2ZnSnS_4 and $Cu_2ZnSnSe_4$ compounds and solid solutions on their basis were measured on a DRON-3 X-ray diffractometer in monochromatic CuK_α radiation (graphite monochromator). Diffraction spectra were recorded automatically with a step of 0.03° (over 2θ). The unit-cell parameters were determined from the recorded diffraction spectra based on full-profile analysis by the Rietveld method using the Fullprof software [19].

Low-temperature X-ray diffraction study was carried out on TUR-M62 diffractometer (CuK_α radiation) in the temperature range of 100–300 K using a low-temperature Rigaku–Denki X-ray chamber. This chamber allows one to gradually control the sample temperature using a heater installed on a massive sample holder. The holder is connected with the bottom of a Dewar flask containing liquid nitrogen.

$Cu_2ZnSnSe_4$ single-crystal samples were elongated (~6 mm) triangular prisms faceted by (100) and (112) crystallographic planes. Cu_2ZnSnS_4 samples were single-crystal plates ~3 × 4 × 0.3 mm in size with surface oriented in the (112) plane.

Diffraction spectra were collected in the continuous-scan mode; the profiles of chosen reflections were recorded at a rate of 0.25 deg/min. Diffraction angles were determined from the positions of peak centroids with an error of ~6'. Profiles were recorded with a step of 2–4 K. The sample temperature was measured by a copper–constantan thermocouple and set by a control unit based on VRT-3.

RESULTS AND DISCUSSION

Figure 1 shows diffraction patterns of $Cu_2ZnSn(S_xSe_{1-x})_4$ solid solutions of different compositions with $x = 0$, 0.3, 0.5, 0.7, and 1. These diffraction patterns contain reflections characteristic of only the tetragonal structure of these compounds, which is indicative of the single-phase character of the samples. It follows from Fig. 1 that the replacement of selenium atoms (having a large atomic radius) with sulfur atoms (characterized by a smaller radius) leads to the compression of the $Cu_2ZnSn(S_xSe_{1-x})_4$ lattice, because all reflections are shifted to larger angles.

Based on the diffraction spectra, we determined the unit-cell parameters of the samples under study. Figure 2 shows the compositional dependences of parameters a and c of polycrystalline samples of $Cu_2ZnSn(S_xSe_{1-x})_4$ solid solutions. It can be seen that these parameters decrease linearly with an increase in x; this behavior corresponds to Vegard's law and indicates the formation of a continuous series of solid solutions in the $Cu_2ZnSn(S_xSe_{1-x})_4$ system in the range $0 \leqslant x \leqslant 1$. In Fig. 2, the unit-cell parameters of $Cu_2ZnSn(S_xSe_{1-x})_4$ films, which were obtained previ-

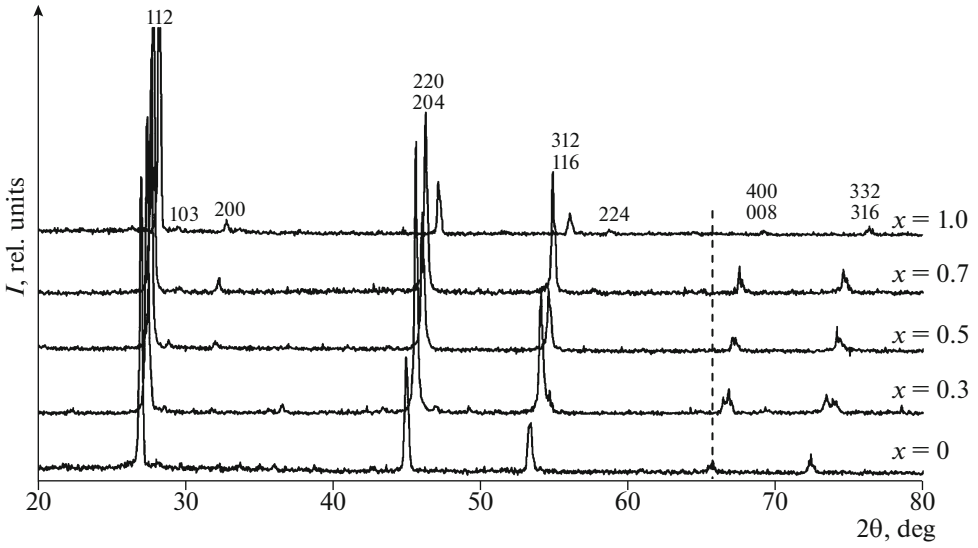

Fig. 1. Diffraction patterns of $Cu_2ZnSn(S_xSe_{1-x})_4$ solid solutions of different compositions with $x = 0$, 0.3, 0.5, 0.7, and 1.

ously in [17], are presented as circles for comparison. In addition, the Cu_2ZnSnS_4 and $Cu_2ZnSnSe_4$ unit-cell parameters taken from [20] are shown by crosses. One can see that the results of our study are in good agreement with the data in the literature.

An important structural characteristic of the compounds under study, which is directly related to the electronic structure and, therefore, photoconversion efficiency, is the parameter of tetragonal lattice distortion, which is determined as a deviation of the ratio $\eta = c/2a$ (a and c are unit-cell parameters) from unity [21]. The table contains the a, c, and η values for the $Cu_2ZnSn(S_xSe_{1-x})_4$ solid solutions under consideration. One can see that η is close to unity for almost all compositions, which is indicative of small lattice distortions in the samples synthesized by the one-temperature method.

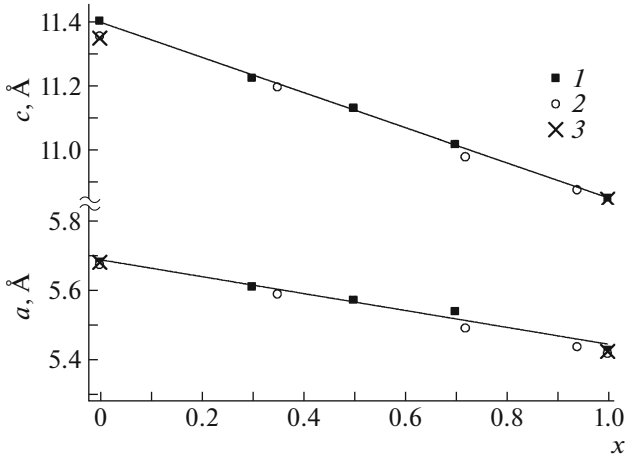

Fig. 2. Compositional dependences of unit-cell parameters a and c for $Cu_2ZnSn(S_xSe_{1-x})_4$ solid solutions: (*1*) polycrystalline samples, (*2*) films, and (*3*) data in the literature.

Note that there are studies devoted to the physical properties of $Cu_2ZnSn(S_xSe_{1-x})_4$ solid solutions [9, 22, 23]. The results of investigating the structural and optical properties of powder samples of $Cu_2ZnSn(S_xSe_{1-x})_4$ solid solutions synthesized from binary compounds $Cu_2S(Se)$, ZnS(Se), and ZnS_2 and from S, Se, and Sn were reported by He et al. [22]. They determined unit-cell parameters a and c as functions of the composition and found that a continuous series of solid solutions having a tetragonal structure is formed in the range $0 \leqslant x \leqslant 1$ in this system. The structural and optical characteristics of $Cu_2ZnSn(S_xSe_{1-x})_4$ nanocrystals were investigated in [9, 23]. It was shown that in this case a continuous series of solid solutions in the range $0 \leqslant x \leqslant 1$ is also formed in the $Cu_2ZnSn(S_xSe_{1-x})_4$ system; however, these solutions are based on the wurtzite structure.

In addition to polycrystalline Cu_2ZnSnS_4 and $Cu_2ZnSnSe_4$ samples, we grew single crystals of these compounds and performed their low-temperature X-ray diffraction study. Figure 3 shows diffraction patterns of Cu_2ZnSnS_4 and $Cu_2ZnSnSe_4$ single crystals; they contain (112) and (100) reflections, respectively. It can be seen that these single crystals are single-phase.

Parameter a for the Cu_2ZnSnS_4 compound was determined from the interplanar spacing d_{336}. The interplanar spacing in a tetragonal lattice is determined by the expression $1/d^2 = (h^2 + k^2)/a^2 + l^2/c^2$, where a and c are unit-cell parameters and h, k, and l are the Miller indices of the corresponding planes. With allowance for the fact that the relation $c \approx 2a$ is

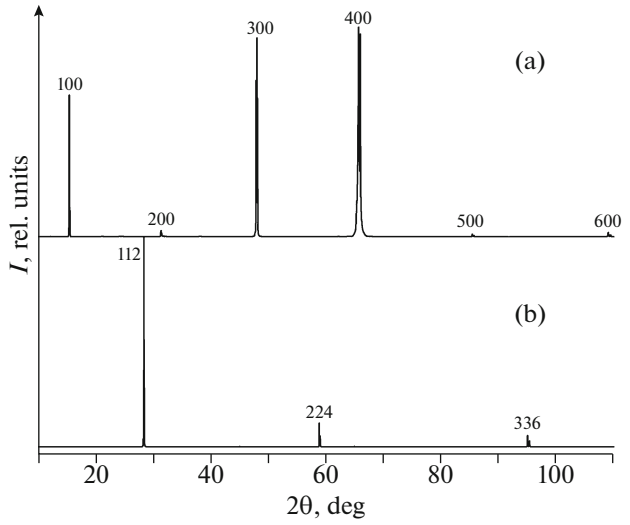

Fig. 3. Diffraction patterns of (a) $Cu_2ZnSnSe_4$ and (b) Cu_2ZnSnS_4 single crystals.

satisfied for this compound, we find that $a = d_{336}\sqrt{3}$. The (400) reflection was used to obtain the temperature dependence for unit-cell parameter a of $Cu_2ZnSnSe_4$.

To determine the temperature dependence of the thermal-expansion coefficient, the experimental values of unit-cell parameter a were smoothed by approximation curves, divided into segments 0.5 K long. The thermal-expansion coefficient was calculated on individual segments from the formula $\alpha_a = \Delta a/(a\Delta T)$, where Δa and ΔT are, respectively, the changes in the unit-cell parameter and temperature and a is the mean value of parameter a within a segment.

Figure 4 shows temperature dependences of unit-cell parameter a and thermal-expansion coefficient α_a of Cu_2ZnSnS_4 and $Cu_2ZnSnSe_4$ single crystals in the temperature range 100–300 K. It can be seen that parameters a of both compounds increase almost linearly with an increase in temperature. Thermal-expansion coefficients α_a increase to 5.4×10^{-6} K^{-1} for $Cu_2ZnSnSe_4$ and 6.6×10^{-6} K^{-1} for Cu_2ZnSnS_4 in the range ~100–140 K and change only slightly with a further increase in temperature.

CONCLUSIONS

Cu_2ZnSnS_4, $Cu_2ZnSnSe_4$, and $Cu_2ZnSn(S_xSe_{1-x})_4$ quaternary semiconductor compounds were synthesized by the one-temperature method from elementary components Cu, Zn, Sn, S, and Se. Cu_2ZnSnS_4 and $Cu_2ZnSnSe_4$ single crystals were grown.

The crystallographic parameters of the grown crystals were determined by X-ray diffraction. A continuous series of solid solutions was shown to be formed in the range $0 \leqslant x \leqslant 1$ in the $Cu_2ZnSn(S_xSe_{1-x})_4$ system.

A compositional dependence was obtained for the unit-cell parameters of $Cu_2ZnSn(S_xSe_{1-x})_4$ crystals. The a and c values were shown to decrease with an increase in sulfur concentration.

The temperature dependences of parameter a and thermal-expansion coefficient α_a of Cu_2ZnSnS_4 and $Cu_2ZnSnSe_4$ single crystals were determined in the temperature range of 100–300 K. It was established that the thermal-expansion coefficients of both compounds somewhat increase with an increase in temperature in the range of ~100–140 K, reaching 6.6×10^{-6} K^{-1} and 5.4×10^{-6} K^{-1} for Cu_2ZnSnS_4 and $Cu_2ZnSnSe_4$, respectively, and then change only slightly.

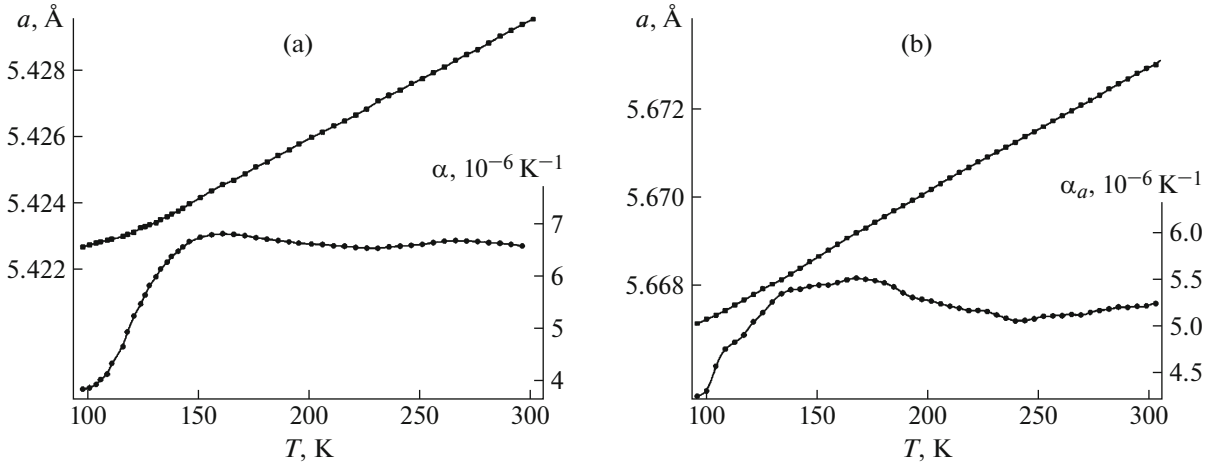

Fig. 4. Temperature dependences of unit-cell parameter a and thermal-expansion coefficient α_a of (a) Cu_2ZnSnS_4 and (b) $Cu_2ZnSnSe_4$ single crystals.

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