

STRUCTURE OF INORGANIC COMPOUNDS

Synthesis and X-ray Diffraction Analysis of $\text{Cu}_2\text{CdGe}_x\text{Sn}_{1-x}\text{Se}_4$ Solid Solutions

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Abstract—The high-temperature orthorhombic phase of $\text{Cu}_2\text{CdGeSe}_4$ quaternary compound, tetragonal phase of $\text{Cu}_2\text{CdSnSe}_4$ compound, and $\text{Cu}_2\text{CdGe}_x\text{Sn}_{1-x}\text{Se}_4$ solid solutions have been grown from elementary components Cu, Cd, Ge, Sn, and Se by one-temperature synthesis. The unit-cell parameters of the grown compounds and solid solutions have been determined by X-ray diffraction analysis at room temperature. It is shown that a continuous series of solid solutions, based on $\text{Cu}_2\text{CdSnSe}_4$ compound, is formed in the $\text{Cu}_2\text{CdGe}_x\text{Sn}_{1-x}\text{Se}_4$ system in the range of $0 \leq x \leq 0.8$, and the $\text{Cu}_2\text{CdGe}_x\text{Sn}_{1-x}\text{Se}_4$ system at $x \geq 0.9$ is an orthorhombic crystalline phase.

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INTRODUCTION

Quaternary compounds $\text{Cu}_2\text{CdGeSe}_4$ and $\text{Cu}_2\text{CdSnSe}_4$ belong to a wide family of Cu-based chalcogenide semiconductors with the general formula $\text{Cu}_2B^{\text{II}}C^{\text{IV}}X_4$ ($B = \text{Zn, Cd, Hg}$; $C = \text{Si, Ge, Sn}$; $X = \text{S, Se}$). The compounds of this family are promising not only from the scientific point of view but also for practical applications. They have unique optical and electrical properties and are of great interest for experts in optoelectronics, nonlinear optics, and photovoltaics (as converters of solar energy to electricity) [1–8]. Note that most of compounds of this family belong to the tetragonal (sp. gr. $I\bar{4}2m$) and orthorhombic (sp. gr. $Pmn2_1$) systems.

The $\text{Cu}_2\text{CdGeSe}_4$ compound is a typical p -type semiconductor with a band gap of 1.20–1.29 eV [9, 10], which is optimal for its efficient use in solar power elements (1.2–1.5 eV) [10]. The $\text{Cu}_2\text{CdSnSe}_4$ compound is also a p -type semiconductor with a band gap of 0.96 eV [10]. It has been recently shown in several studies that $\text{Cu}_2\text{CdGeSe}_4$ and $\text{Cu}_2\text{CdSnSe}_4$ compounds are promising for thermoelectric elements [7, 11–13]. It was found in [14] for the first time that $\text{Cu}_2\text{CdGeSe}_4$ compound belongs to the tetragonal system (sp. gr. $I\bar{4}2m$, unit-cell parameters $a = 5.657 \text{ \AA}$ and $c = 10.988 \text{ \AA}$). Orthorhombic $\text{Cu}_2\text{CdGeSe}_4$ compound with the parameters $a = 8.088 \text{ \AA}$, $b = 6.875 \text{ \AA}$, and $c = 6.564 \text{ \AA}$ was obtained in [10]. It was shown in [15] that $\text{Cu}_2\text{CdGeSe}_4$ compound is polymorphic and has low-temperature (LT) and high-temperature (HT)

modifications. The LT modification of $\text{Cu}_2\text{CdGeSe}_4$ has a tetragonal lattice with parameters $a = 5.748 \text{ \AA}$ and $c = 11.053 \text{ \AA}$ and sp. gr. $I\bar{4}2m$. The HT modification has an orthorhombic lattice with parameters $a = 8.097 \text{ \AA}$, $b = 6.893 \text{ \AA}$, and $c = 6.626 \text{ \AA}$ and sp. gr. $Pmn2_1$.

The HT modification of $\text{Cu}_2\text{CdGeSe}_4$ was grown in [15] and [10] by quenching alloy in cold water at 673 K and horizontal gradient cooling, respectively. The LT modification was grown in [15] by slow cooling of alloy with subsequent long-term annealing. $\text{Cu}_2\text{CdSnSe}_4$ belongs to the tetragonal system with unit-cell parameters $a = 5.832 \text{ \AA}$ and $c = 11.389 \text{ \AA}$ and sp. gr. $I\bar{4}2m$ [10].

Since $\text{Cu}_2\text{CdGeSe}_4$ and $\text{Cu}_2\text{CdSnSe}_4$ crystals have interesting physical properties and different structures, there is much interest in the solid solutions on their basis (one can obtain new materials with continuously changing physical properties by varying their composition). Therefore, the purpose of this study was to synthesize $\text{Cu}_2\text{CdGeSe}_4$ and $\text{Cu}_2\text{CdSnSe}_4$ compounds and $\text{Cu}_2\text{CdGe}_x\text{Sn}_{1-x}\text{Se}_4$ solid solutions and determine their crystallographic characteristics in dependence of composition.

SAMPLE PREPARATION TECHNIQUE

$\text{Cu}_2\text{CdGeSe}_4$ and $\text{Cu}_2\text{CdSnSe}_4$ quaternary compounds and $\text{Cu}_2\text{CdGe}_x\text{Sn}_{1-x}\text{Se}_4$ solid solutions were synthesized by the one-temperature method, which provides purity of grown material and excludes component loss. The initial materials were elementary

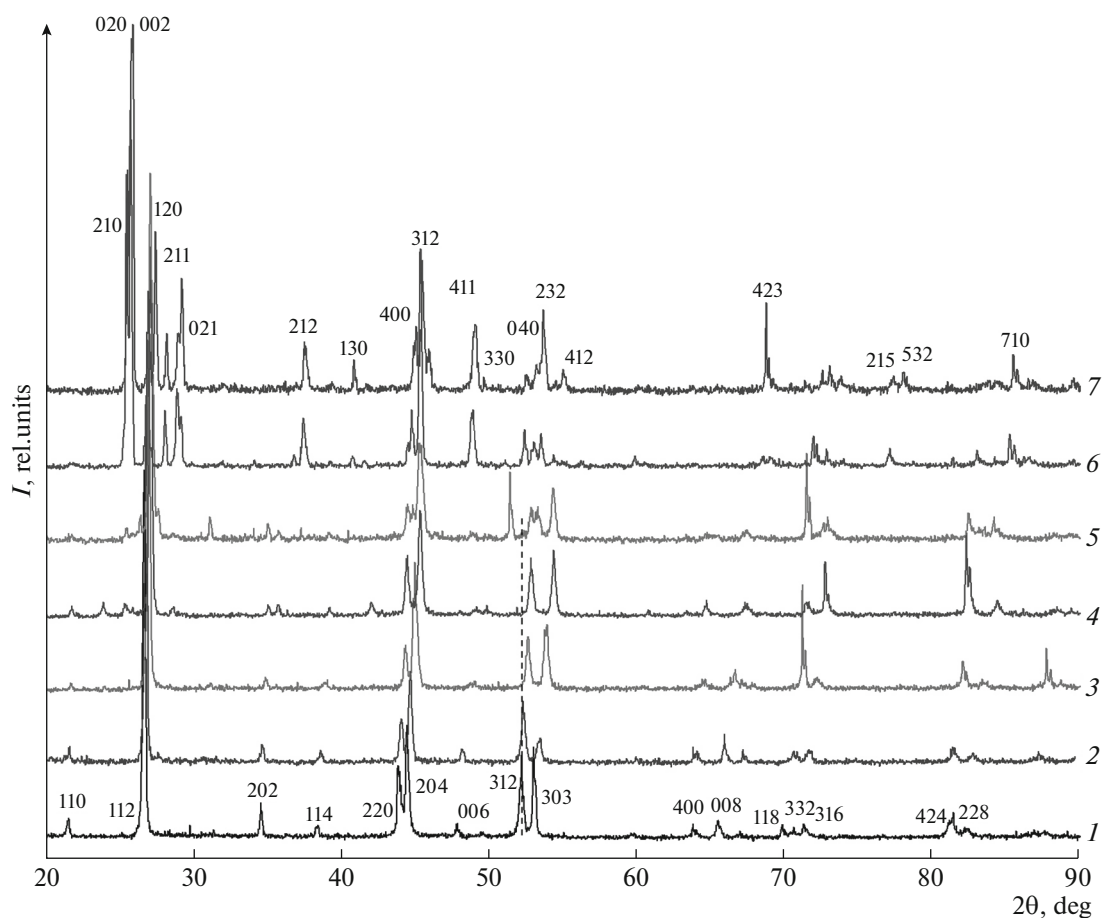


Fig. 1. Diffraction patterns of the $\text{Cu}_2\text{CdGe}_x\text{Sn}_{1-x}\text{Se}_4$ solid solutions with $x = (1) 0, (2) 0.25, (3) 0.5, (4) 0.75, (5) 0.8, (6) 0.9,$ and $(7) 1$.

components: copper, cadmium, tin, and germanium of 99.999% purity and selenium of special purity grade. Synthesis has been carried out in double quartz ampoules, which were subjected to preliminary chemical thermal treatment (ampoules were etched in nitrohydrochloric acid, carefully washed in distilled water, and dried in a heat chamber at $T \sim 120^\circ\text{C}$). Double ampoules were used to prevent synthesized compound from oxidation in air in the case of internal ampoule cracking during crystallization. The initial components in amount of $\sim 10\text{--}12$ g and ratios corresponding to a certain formula composition were loaded in the ampoule, evacuated to a residual pressure of $\sim 10^{-3}$ Pa, and unsoldered from the vacuum system. Then this ampoule was placed in another ampoule with a previously soldered quartz rod, evacuated, unsoldered, and placed in a vertical single-zone furnace.

In the initial stage, the furnace temperature was increased at a rate of $\sim 200^\circ\text{C}/\text{h}$ to 600°C and maintained at this level for 2 h. Then the temperature was increased at a rate of $\sim 100^\circ\text{C}/\text{h}$ to 860°C and maintained at this level for 2 h. Then the temperature was increased to $880\text{--}890^\circ\text{C}$. When this value was reached, vibrational mixing was turned on, and the

system was kept in this state for 12 h. Then the vibration was turned off and the temperature was reduced at a rate of $\sim 5^\circ\text{C}/\text{h}$ to $\sim 550^\circ\text{C}$, after which the furnace was turned off. To homogenize the grown ingots of compounds and solid solutions, they were annealed isothermally in vacuum at $\sim 710^\circ\text{C}$ for 500 h.

EXPERIMENTAL

X-ray diffraction analysis of the grown compounds and solid solutions was carried out on a DRON-3 X-ray diffractometer ($\text{CuK}\alpha$ radiation). A single-crystal graphite plate was used as a monochromator. The diffraction patterns of powder samples of the compounds under study were recorded automatically using 2θ scanning with a step of 0.03° . The samples were powders of the grown compounds and solid solutions, pressed into plastic cells. The unit-cell parameters of the samples were determined based on the recorded diffraction patterns using the Fullprof software package [16].

RESULTS AND DISCUSSION

Figure 1 shows the room-temperature diffraction patterns of $\text{Cu}_2\text{CdGe}_x\text{Sn}_{1-x}\text{Se}_4$ solid solutions of dif-

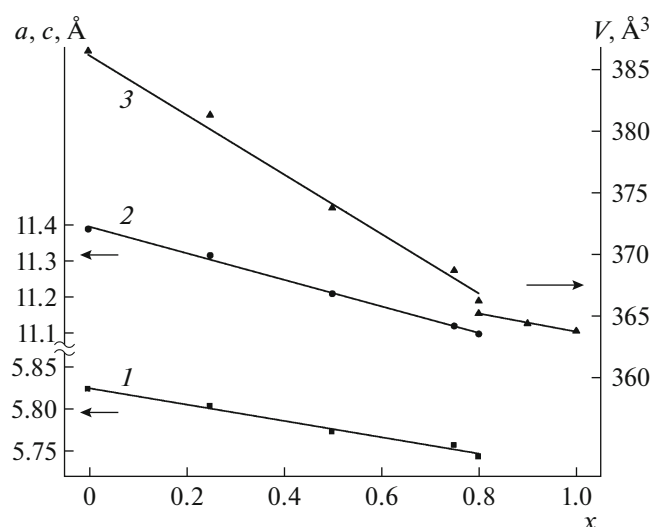


Fig. 2. Unit-cell parameters and volume of the $\text{Cu}_2\text{CdGe}_x\text{Sn}_{1-x}\text{Se}_4$ system: (1) a , (2) c , and (3) V .

ferent compositions with $x = 0, 0.25, 0.5, 0.75, 0.8, 0.9$, and 1 . It can be seen in Fig. 1 that the reflections characteristic of only the tetragonal phase are observed in the diffraction patterns at $x = 0-0.75$. The diffraction patterns of the $\text{Cu}_2\text{CdGe}_x\text{Sn}_{1-x}\text{Se}_4$ system with $x \geq 0.9$ completely correspond to the orthorhombic phase. It is noteworthy that the reflections characteristic of both tetragonal and orthorhombic phases are observed in the diffraction pattern of $\text{Cu}_2\text{CdGe}_x\text{Sn}_{1-x}\text{Se}_4$ with $x = 0.8$ (i.e., two phases coexist in the alloy). Thus, a continuous series of solid solutions with a wide range of compositions, based on the tetragonal $\text{Cu}_2\text{CdSnSe}_4$ compound, is observed in the $\text{Cu}_2\text{CdGe}_x\text{Sn}_{1-x}\text{Se}_4$ system, and the $\text{Cu}_2\text{CdGe}_x\text{Sn}_{1-x}\text{Se}_4$ system is orthorhombic in the range of compositions $x \geq 0.8$. Note that traces of binary compounds (CdSe ,

SnSe) were observed in the diffraction patterns of some samples of this system.

It can be seen in Fig. 1 that the substitution of Ge atoms with a smaller atomic radius for Sn atoms in the $\text{Cu}_2\text{CdGe}_x\text{Sn}_{1-x}\text{Se}_4$ system shifts all reflections in the diffraction patterns to larger angles with an increase in x (i.e., the lattice undergoes compression). The unit-cell parameters of the $\text{Cu}_2\text{CdGe}_x\text{Sn}_{1-x}\text{Se}_4$ system under investigation were determined based on the obtained diffraction spectra.

Figure 2 shows the dependences of the unit-cell volume and parameters a and c of the $\text{Cu}_2\text{CdGe}_x\text{Sn}_{1-x}\text{Se}_4$ system on the composition. It can be seen that the parameters a and c gradually decrease with an increase in x according to a linear law, which corresponds to Vegard's rule and indicates formation of a continuous series of solid solutions in the range of $0 \leq x \leq 0.8$ in the $\text{Cu}_2\text{CdGe}_x\text{Sn}_{1-x}\text{Se}_4$ system. However, the reflections of both LT tetragonal and HT orthorhombic modifications are observed in the $\text{Cu}_2\text{CdGe}_x\text{Sn}_{1-x}\text{Se}_4$ system at $x = 0.8$. It can also be seen in Fig. 2 that the unit-cell volume of both $\text{Cu}_2\text{CdGe}_x\text{Sn}_{1-x}\text{Se}_4$ phases gradually decreases with an increase in x .

The unit-cell parameters of the $\text{Cu}_2\text{CdGe}_x\text{Sn}_{1-x}\text{Se}_4$ system for the tetragonal and orthorhombic solid solutions in the ranges of compositions of $0 \leq x \leq 0.8$ and $x \geq 0.8$, respectively, are listed in Table 1. It is noteworthy that the parameters a , b , and c of the orthorhombic phase barely change with a change in the composition.

The found room-temperature values of the unit-cell parameters for the $\text{Cu}_2\text{CdGeSe}_4$ ($a = 8.051 \text{ \AA}$, $b = 6.862 \text{ \AA}$, $c = 6.586 \text{ \AA}$) and $\text{Cu}_2\text{CdSnSe}_4$ ($a = 5.825 \text{ \AA}$, $c = 11.389 \text{ \AA}$) crystals are in good agreement with the data of [10].

Table 1. Unit-cell parameters of the $\text{Cu}_2\text{CdGe}_x\text{Sn}_{1-x}\text{Se}_4$ system

x	$a, \text{ \AA}$	$b, \text{ \AA}$	$c, \text{ \AA}$	$V, \text{ \AA}^3$
Tetragonal				
0	5.825	5.825	11.389	386.502
0.25	5.804	5.804	11.316	381.327
0.5	5.774	5.774	11.209	373.815
0.75	5.758	5.758	11.120	368.752
0.8	5.745	5.745	11.098	366.289
Orthorhombic				
0.8	8.062	6.868	6.597	365.274
0.9	8.057	6.863	6.591	364.450
1	8.051	6.862	6.586	363.849

CONCLUSIONS

The four-component orthorhombic $\text{Cu}_2\text{CdGeSe}_4$ and tetragonal $\text{Cu}_2\text{CdSnSe}_4$ compounds and $\text{Cu}_2\text{CdGe}_x\text{Sn}_{1-x}\text{Se}_4$ system were synthesized. The unit-cell parameters of the $\text{Cu}_2\text{CdGe}_x\text{Sn}_{1-x}\text{Se}_4$ system were measured in dependence of composition. It was shown that the unit-cell parameters a , b , and c of the $\text{Cu}_2\text{CdGe}_x\text{Sn}_{1-x}\text{Se}_4$ system gradually decrease with an increase in concentration x . It was established that solid solutions based on the $\text{Cu}_2\text{CdSnSe}_4$ compound are formed in the $\text{Cu}_2\text{CdGe}_x\text{Sn}_{1-x}\text{Se}_4$ system in the range of $0 \leq x \leq 0.8$. At $x = 0.8$, a further change in the composition leads to the formation of an orthorhombic phase in the system (along with the tetragonal phase), and then the $\text{Cu}_2\text{CdGe}_x\text{Sn}_{1-x}\text{Se}_4$ system becomes completely orthorhombic.

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