

NONELECTRONIC PROPERTIES OF SEMICONDUCTORS
(ATOMIC STRUCTURE, DIFFUSION)

Polymorphic Transformations and Thermal Expansion in $\text{AgCuSe}_{0.5}(\text{S}, \text{Te})_{0.5}$ Crystals

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Abstract—The high-temperature X-ray diffraction technique is used to study $\text{AgCuSe}_{0.5}(\text{S}, \text{Te})_{0.5}$ crystals. It is shown that, at room temperature, the $\text{AgCuSe}_{0.5}\text{S}_{0.5}$ crystal is composed of $\text{Cu}_{1.96}\text{S}$ and AgCuSe phases. At a temperature of 695 K, these phases transform into a single face-centered cubic (fcc) phase. The transformation is reversible. The $\text{AgCuSe}_{0.5}\text{Te}_{0.5}$ composition consists of three phases, specifically, Cu_2Te , AgCuSe , and a cubic phase. At 444 K, both orthorhombic phases simultaneously transform into a diamond-like cubic phase. In this transformation, the cubic phase plays the role of a seed. From the temperature dependence of the lattice parameters, the thermal-expansion coefficients of the phases involved in both compositions are calculated for the main crystallographic directions.

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1. INTRODUCTION

The AgCuSe compound is formed by a peritectic reaction at a relation between components of $\text{Ag}_2\text{Se}:\text{Cu}_2\text{Se} = 1:1$, at a temperature of 1033 K [1]. The structure of the low-temperature AgCuSe phase is determined as being tetragonal, with the lattice parameters $a = 4.083 \text{ \AA}$ and $c = 6.30 \text{ \AA}$, $Z = 2$, the space group $P4/nmm$, and the density $\rho = 7.91 \text{ g cm}^{-3}$ [2, 3]. Later [4, 5], the crystal structure of AgCuSe was determined to be orthorhombic, with the lattice parameters $a = 4.105 \text{ \AA}$, $b = 20.350 \text{ \AA}$ and $c = 6.310 \text{ \AA}$, $Z = 10$, and $\rho = 7.885 \text{ g cm}^{-3}$. Such a structure is a superstructure of the tetragonal lattice. The parameter b of the orthorhombic lattice is a multiple of five parameters b of the tetragonal lattice. According to the data of [4], in the orthorhombic structure of AgCuSe , silver atoms are arranged in the planes orthogonal to the c axis. Around each of the Ag atoms, there are four Ag atoms at a distance of 2.96 \AA and six Se atoms at the distances 2.67 \AA (four Se atoms), 3.59 \AA (one Se atom) and 3.64 \AA (one Se atom). The Se atoms form elongated tetrahedra, in which there are Cu atoms at the centers. The Se–Se spacings are 3.03 \AA , the Cu–Se spacings are $2.06\text{--}2.50 \text{ \AA}$, and the smallest Cu–Ag spacing is 2.98 \AA .

In [6, 7], it is shown that, at 504 K, the orthorhombic modification transforms into a high-temperature face-centered cubic (fcc) modification with the unit-cell parameter $a = 6.0694 \text{ \AA}$. The transformations in AgCuSe are reversible.

In this study, we consider polymorphic transformations in $\text{AgCuSe}_{0.5}\text{S}_{0.5}$ and $\text{AgCuSe}_{0.5}\text{Te}_{0.5}$.

2. EXPERIMENTAL

To form the above-indicated compositions, we chose the direct synthesis method. For the reactor, we used double-wall cells with an internal diameter of 1 cm and a length of 10 cm. The cells were made of high-quality quartz possessing high thermal stability and providing high-quality sealing, which excludes the contamination and oxidation of the materials to be synthesized in the case of the cracking of one of the two cells. The cells were filled with the initial substances (Ag, Cu, S, Se or Te) in the amounts required to synthesize each of the compositions, evacuated to a pressure of 10^{-3} Pa , and then sealed. The initial components involved in the compositions were electrolytically pure (Cu), 99.999%-pure (Ag), and corresponding to the purity of brand V5 (S, Se, Te). The cells with the components of the $\text{AgCuSe}_{0.5}\text{S}_{0.5}$ and $\text{AgCuSe}_{0.5}\text{Te}_{0.5}$ compositions were placed into a furnace. To prevent explosion and to ensure the complete diffusion of molten sulfur, selenium, and tellurium into silver and copper, the furnace temperature was slowly elevated first to the melting temperature of sulfur ($T_m = 391 \text{ K}$) and then to the melting temperature of selenium ($T_m = 493 \text{ K}$) and tellurium ($T_m = 725 \text{ K}$); the cells were kept at the latter temperature for 4 h. Thereafter, with a rate of 50 K h^{-1} , the furnace temperature was elevated to temperatures higher than the

melting point of AgCuSe ($T_m = 1039$ K). After 3 h exposure at a temperature of 1039 K with simultaneous cyclic vibration, the cells with the samples were slowly cooled to 400 K and, with the purpose of homogenization, annealed at this temperature for 200 h. To establish the structure of the samples synthesized, we carried out microstructural and X-ray phase analysis.

The X-ray diffraction pattern recorded for the AgCuSe_{0.5}S_{0.5} powders at room temperature can be interpreted on the basis of the parameters of the Cu_{1.96}S monoclinic lattice and AgCuSe orthorhombic lattice. This means that, at room temperature, the AgCuSe_{0.5}S_{0.5} compound is a two-phase composition (Table 1).

Analysis of the diffraction pattern obtained for the AgCuSe_{0.5}Te_{0.5} powder at room temperature shows that this composition consists of three phases. As can be seen from Table 2, phase I corresponds to the orthorhombic Cu₂Te phase in unit-cell dimensions, phase II can be interpreted on the basis of the parameters of the AgCuSe orthorhombic lattice, and phase III at room temperature is identified as a metastable diamond-structured cubic phase.

To produce AgCuSe_{0.5}S_{0.5} and AgCuSe_{0.5}Te_{0.5} single crystals, we used the Bridgman method [8], with the addition of a third temperature zone. The synthesized polycrystalline materials in the ground form were loaded into cells (specially fabricated to produce crystals by the Bridgman method). The length and diameter of the cells were 10 and 1 cm, respectively. The cells evacuated to a pressure of 10^{-3} Pa were placed in the upper zone of the furnace; the temperature of this zone was varied with a heat controller. In the first zone, the furnace temperature was elevated to temperatures above the melting point of AgCuSe. After exposure at this temperature for 3 h, we turned on the electromotor which lowered the cell at a rate of 0.2 cm h^{-1} .

As the material in the cell passes through the melting point, crystals of the high-temperature modification start to grow; as the temperature is lowered, crystals of the low-temperature modification are formed and grow inside the single crystal of the high-temperature modification. The single-crystal structure of this modification depends mainly on the difference between the densities of the matrix crystal (ρ_1) and growing crystals (ρ_2): at $\rho_1 \approx \rho_2$, (single crystal)–(single crystal) transformations occur, whereas at $\rho_1 \gg \rho_2$ and $\rho_1 \leq \rho_2$, (single crystal)–(polycrystalline material) transformations occur. It is impossible to produce single crystals from such polycrystalline material by means of polymorphic transformations.

Therefore, the single-crystal character of the low-temperature modification does not depend on the

method chosen. Because of the ordering process which occurs as the temperature is lowered, several phases different in composition and structure separate out from the single crystal of the high-temperature modification.

High-temperature studies were conducted with a DRON-3M diffractometer (CuK α radiation, the wavelength 1.5418 Å, a Ni filter) equipped with a URVT-2000 high-temperature attachment. The measurements were performed in vacuum, at a residual pressure in the chamber of 10^{-2} Pa. In recording the diffraction patterns, the angular resolution was $\sim 0.1^\circ$. We used the continuous mode of scanning. In the experiments, the error in determining the diffraction θ did not exceed $\Delta\theta = \pm 0.02^\circ$.

3. DISCUSSION

AgCuSe_{0.5}S_{0.5}. To study polymorphic transformations in AgCuSe_{0.5}S_{0.5} at room temperature, we fabricated a sample $4 \times 4 \times 2$ mm in dimensions. In the angle range $10^\circ \leq 2\theta \leq 100^\circ$, we detected 16 diffraction reflections (Table 1). Analysis of these reflections supports the fact that, in the sample, there exist two phases. One of these two phases is identical in terms of unit-cell dimensions to the low-temperature monoclinic Cu_{1.96}S phase with the lattice parameters $a = 26.897$ Å, $b = 15.745$ Å, $c = 13.565$ Å, $\beta = 90.13^\circ$, and $Z = 128$ and the space group $P21/n$ [6], whereas the other phase possesses the unit cell of the low-temperature orthorhombic AgCuSe phase with the parameters $a = 4.086$ Å, $b = 20.533$ Å, $c = 6.275$ Å, and $Z = 10$ and the space group $P4/nmm$ [4].

After recording the diffraction patterns at room temperature, we turned on the furnace (without distortion of the crystal orientation) and carried out test recordings every 100 K. It should be noted that, as the temperature was increased, the number of reflections and their intensities observed at room temperature remained unchanged. Only at 773 K did we observe nine new reflections in the same angle region. These reflections belong to the high-temperature fcc modification with the unit-cell parameter $a = 6.356$ Å, $Z = 4$, the space group $Fm\bar{3}m$, and the density $\rho = 6.376 \text{ g cm}^{-3}$ (Table 1). It is established that the temperature corresponding to equilibrium between the low- and high-temperature modifications is $T_0 = 695$ K.

We calculated the lattice parameters of modifications involved in AgCuSe_{0.5}S_{0.5} in the temperature range 293–973 K. The parameters are listed in Table 1 and plotted in Fig. 1. As can be seen from Fig. 1, the parameter a_1 of the orthorhombic phase and the parameters a_2 and b_2 of the monoclinic phase increase linearly in the temperature range 293–673 K, and the parameter b_1 decreases in the range from 473 to 573 K and increases at higher temperatures. The parameter

Table 1. Experimentally observed and calculated parameters of the diffraction pattern of $\text{AgCuSe}_{0.5}\text{S}_{0.5}$ at different temperatures

T, K (exp)	θ	I/I ₀	d, Å (exp)	Cu _{1.96} Se		AgCuSe		Crystal-lattice parameters
				d, Å (calcd.)	hkl	d, Å (calcd.)	hkl	
1	2	3	4	5	6	7	8	9
293	18°00'	30	2.897	2.898	243	2.890	150	Cu _{1.96} S
	19°30'	80	2.682	2.690	10.0.0	2.681	0.42	Monoclinic
	20°24'	100	2.568	2.569	044	—	—	a = 26.897 Å
	21°36'	50	2.432	2.437	162	—	—	b = 15.745 Å
	23°30'	70	2.245	2.245	942	—	—	c = 13.565 Å
	25°06'	40	2.111	2.111	326	—	—	β = 90.13°, Z = 128
	25°36'	50	2.072	2.073	11.2.3	—	—	space group P21/n
	26°36'	60	1.999	1.998	645	2.012	220	ρ = 5.870 g/cm ³
	28°24'	90	1.882	1.882	027	1.890	191	AgCuSe
	31°24'	40	1.718	1.717	275, 390	1.710	0.10.2	Orthorhombic
	33°42'	50	1.613	1.614	038	—	—	a = 4.086 Å
	37°24'	10	1.474	1.473	908, 286	—	—	b = 20.533 Å
	39°06'	30	1.419	1.419	938	1.411	243	c = 6.275 Å
	41°24'	10	1.354	1.354	078, 1.0.10	—	—	Z = 10
45°54'	10	1.247	1.246	0.5.10	1.247	0.10.4	space group P4/nmm	
48°00'	20	1.205	1.205	0.6.10	1.204	115	ρ = 7.883 g/cm ³	
373	17°55'	30	2.909	2.910	243	2.909	150	Cu _{1.96} S
	19°28'	80	2.686	2.686	10.0.0	2.684	042	Monoclinic
	20°19'	100	2.578	2.579	044	—	—	a = 26.856 Å
	21°27'	45	2.448	2.447	162	—	—	B = 15.811 Å
	23°28'	70	2.248	2.248	942	—	—	c = 13.608 Å
	25°00'	40	2.118	2.118	326	—	—	β = 90.13°, Z = 128
	25°33'	50	2.075	2.074	11.2.3	—	—	space group P21/n
	26°32'	60	2.004	2.004	645	2.014	220	ρ = 5.759 g/cm ³
	28°18'	90	1.888	1.888	027	1.906	191	CuAgSe
	31°17'	35	1.724	1.724	275, 390	1.724	0.10.2	Orthorhombic
	33°34'	45	1.619	1.619	038	—	—	a = 4.107 Å
	37°17'	10	1.478	1.478	908	—	—	b = 20.664 Å
	38°59'	25	1.423	1.423	938	1.411	243	c = 6.374 Å
	41°12'	10	1.359	1.359	1.0.10	—	—	Z = 10
45°44'	10	1.250	1.250	0.5.10	1.250	0.10.4	space group P4/nmm	
47°46'	20	1.209	1.209	0.6.10	1.201	115	ρ = 7.672 g/cm ³	
473	17°49'	30	2.925	2.926	243	2.925	150	Cu _{1.96} S
	19°26'	75	2.691	2.691	10.0.0	2.712	042	Monoclinic
	20°10'	100	2.596	2.597	044	—	—	a = 26.905 Å
	21°22'	50	2.456	2.456	162	—	—	b = 15.852 Å
	23°24'	70	2.254	2.255	942	—	—	c = 13.753 Å
	24°45'	40	2.138	2.138	326	—	—	β = 90.13°
	25°27'	50	2.083	2.082	11.2.3	—	—	Z = 128
	26°30'	60	2.006	2.006	645	2.030	220	ρ = 5.759 g/cm ³
	28°00'	90	1.907	1.908	027	1.915	191	AgCuSe
	31°05'	40	1.734	1.734	275, 390	1.734	0.10.2	Orthorhombic
	33°12'	50	1.635	1.635	038	—	—	a = 4.142 Å
	37°17'	10	1.490	1.490	908, 286	—	—	b = 20.664 Å
	38°59'	30	1.434	1.434	938	1.425	243	c = 6.374 Å
	41°12'	10	1.374	1.374	078, 1.0.10	—	—	Z = 10
45°44'	10	1.262	1.262	0.5.10	1.262	0.10.4	space group P4/nmm	
47°46'	20	1.220	1.221	0.6.10	1.216	115	ρ = 7.607 g/cm ³	

Table 1. (Contd.)

T, K (exp)	θ	I/I_0	$d, \text{\AA}$ (exp)	$\text{Cu}_{1.96}\text{Se}$		AgCuSe		Crystal-lattice parameters
				$d, \text{\AA}$ (calcd.)	hkl	$d, \text{\AA}$ (calcd.)	hkl	
1	2	3	4	5	6	7	8	9
573	17°47'	30	2.931	2.931	243	2.931	150	$\text{Cu}_{1.96}\text{S}$ $a = 26.936 \text{\AA}$ $b = 15.893 \text{\AA}$ $c = 13.775 \text{\AA}$ $\beta = 90.13^\circ$ $Z = 128$ space group $P21/n$ $\rho = 5.643 \text{ g/cm}^3$
	19°24'	80	2.694	2.694	10.0.0	2.716	042	
	20°07'	100	2.602	2.602	044	—	—	
	21°20'	45	2.460	2.460	162	—	—	
	23°22'	70	2.257	2.258	942	—	—	
	24°42'	40	2.142	2.142	326	—	—	
	25°25'	50	2.086	2.850	11.2.3	—	—	
	26°17'	60	2.022	2.021	645	2.039	220	
	27°56'	90	1.911	1.910	027	1.923	191	
	31°02'	35	1.736	1.737	275	1.741	0.10.2	
	33°08'	45	1.638	1.638	038	—	—	
	36°51'	10	1.493	1.493	908	—	—	
	38°32'	25	1.437	1.437	938	1.430	243	
	40°35'	10	1.376	1.376	1.0.10	—	—	
45°06'	10	1.264	1.264	0.0.10	1.266	0.10.4		
47°06'	20	1.222	1.222	0.6.10	1.218	115		
673	17°44'	30	2.937	2.937	243	2.939	150	$\text{Cu}_{1.96}\text{S}$ $a = 26.963 \text{\AA}$ $b = 15.921 \text{\AA}$ $c = 13.793 \text{\AA}$ $\beta = 90.13^\circ$ $Z = 128$ space group $P21/n$ $\rho = 5.620 \text{ g/cm}^3$
	19°23'	80	2.696	2.696	10.0.0	2.720	042	
	20°05'	100	2.606	2.606	044	—	—	
	21°15'	50	2.466	2.467	162	—	—	
	23°20'	70	2.260	2.260	942	—	—	
	24°40'	40	2.145	2.145	326	—	—	
	25°24'	50	2.087	2.087	11.2.3	—	—	
	26°15'	60	2.024	2.024	645	2.039	220	
	27°54'	90	1.913	1.913	027	1.923	191	
	30°57'	40	1.740	1.740	275	1.741	0.10.2	
	33°05'	50	1.640	1.640	038	—	—	
	36°48'	10	1.494	1.494	908	—	—	
	38°29'	30	1.438	1.438	938	1.430	243	
	40°32'	10	1.377	1.377	1.0.10	—	—	
45°01'	10	1.266	1.266	0.5.10	1.266	0.10.4		
47°00'	20	1.224	1.224	0.6.10	1.220	115		
773	16°19'	40	3.176	3.185	200			fcc $\text{AgCuSe}_{0.5}\text{S}_{0.5}$ $a = 6.356 \text{\AA}$ space group $Fm3m$ $Z = 4$ $\rho = 6.376 \text{ g/cm}^3$
	23°30'	65	2.246	2.245	220			
	27°52'	100	1.915	1.915	311			
	29°12'	70	1.834	1.835	222			
	34°19'	30	1.588	1.588	400			
	37°54'	80	1.457	1.458	331			
	39°04'	30	1.420	1.420	420			
	43°39'	50	1.297	1.297	422			
47°04'	90	1.222	1.223	333, 511				
873	16°16'	40	3.196	3.182	200			fcc $\text{AgCuSe}_{0.5}\text{S}_{0.5}$ $a = 6.363 \text{\AA}$ space group $Fm3m$ $Z = 4$ $\rho = 6.355 \text{ g/cm}^3$
	23°27'	65	2.250	2.250	220			
	27°49'	100	1.918	1.919	311			
	29°10'	70	1.837	1.837	222			
	34°16'	30	1.590	1.591	400			
	37°51'	80	1.459	1.460	311			
	39°02'	30	1.422	1.423	420			
	43°36'	50	1.298	1.299	422			
47°01'	90	1.225	1.225	333				

Table 1. (Contd.)

T, K (exp)	θ	I/I_0	$d, \text{\AA}$ (exp)	$\text{Cu}_{1.96}\text{S}$		AgCuSe		Crystal-lattice parameters
				$d, \text{\AA}$ (calcd.)	hkl	$d, \text{\AA}$ (calcd.)	hkl	
1	2	3	4	5	6	7	8	9
973	16°13'	40	3.205	3.186	200			fcc $\text{AgCuSe}_{0.5}\text{S}_{0.5}$ $a = 6.372 \text{\AA}$ space group $Fm\bar{3}m$ $Z = 4$ $\rho = 6.328 \text{ g/cm}^3$
	23°24'	65	2.254	2.253	220			
	27°46'	100	1.921	1.921	311			
	29°07'	70	1.840	1.840	222			
	34°13'	30	1.592	1.593	400			
	37°49'	80	1.460	1.462	331			
	39°00'	30	1.422	1.425	420			
	43°33'	50	1.299	1.301	422			
46°58'	90	1.225	1.226	333				

The experimental conditions: $\text{CuK}\alpha$ radiation (the wavelength 1.5418 \AA), Ni filter, 35 kV, 10 mA. I/I_0 is the relative intensity. Abbreviations exp and calc refer to the experimental data and the results of calculations.

c_1 of the orthorhombic phase and the parameter c_2 of the monoclinic phase deviate from linearity at 473 K and linearly increase at higher temperatures. Despite such behavior of the lattice parameters of both modifications with temperature, there are no substantial changes in the numbers of diffraction reflections and their intensities.

The thermal expansion coefficients α calculated from the temperature dependences of the lattice parameters of modifications involved in the $\text{AgCuSe}_{0.5}\text{S}_{0.5}$ composition are given in Table 3. As can be seen from Table 2, in the modification corresponding to the $\text{Cu}_{1.96}\text{S}$ structure, thermal expansion along the [010] direction noticeably differs from that along the [100] and [001] directions: $\alpha_{[100]} < \alpha_{[010]} > \alpha_{[001]}$.

As can be seen from the anisotropy of thermal expansion, the $\text{AgCuSe}_{0.5}\text{S}_{0.5}$ crystals consisting of two phases at room temperature deform each other, as the temperature is elevated. At the interface between these phases, a nucleus of the fcc modification is formed and then grows from these phases. Upon cooling, two phases are formed from the single fcc phase; i.e., the crystal returns to its initial state.

$\text{AgCuSe}_{0.5}\text{Te}_{0.5}$. For the arbitrarily oriented $\text{AgCuSe}_{0.5}\text{Te}_{0.5}$ sample at room temperature, we detected 22 diffraction reflections in the angle range $10^\circ \leq 2\theta \leq 90^\circ$. These reflections coincided with the reflections observed in the diffraction patterns of the powder of the synthesized sample (Table 2). From Table 2, it can be seen that, at room temperature, the $\text{AgCuSe}_{0.5}\text{Te}_{0.5}$ compound consists of three phases. Phase I is identical in terms of unit-cell dimensions to the low-temperature orthorhombic Cu_2Te phase with the crystal-lattice parameters $a = 7.319 \text{\AA}$, $b = 22.236 \text{\AA}$, and $c = 36.458 \text{\AA}$; phase II possesses a unit cell corresponding to the low-temperature orthorhombic AgCuSe modification; and phase III is a

structurally diamond-like cubic phase with the lattice parameter $a = 7.319 \text{\AA}$.

In the diffraction pattern, most reflections of the three phases observed are superimposed. The multi-phase character of the $\text{AgCuSe}_{0.5}\text{Te}_{0.5}$ composition is basically caused by the redistribution of anions (Se, Te) and cations (Ag, Cu). After recording the diffraction pattern at room temperature, we turned on the furnace

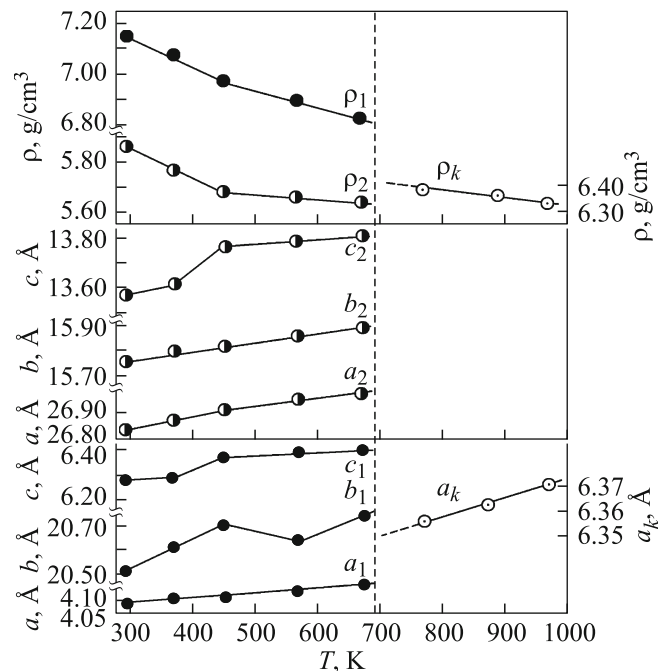


Fig. 1. Temperature dependences of the crystal-lattice parameters (a, b, c) and densities (ρ) of phases entering into the $\text{AgCuSe}_{0.5}\text{S}_{0.5}$ composition: a_1, b_1, c_1 , and ρ_1 refer to the orthorhombic AgCuSe phase; a_2, b_2, c_2 , and ρ_2 to the monoclinic $\text{Cu}_{1.96}\text{S}$ phase; and a_k and ρ_k to the cubic phase.

Table 2. Experimentally observed and calculated parameters of the diffraction pattern of AgCuSe_{0.5}S_{0.5} at different temperatures

<i>T</i> , K (exp)	θ	<i>I</i> / <i>I</i> ₀	<i>d</i> , Å (exp)	Cu _{1.96} Se		AgCuSe		Cubic		Crystal-lattice parameters		
				<i>d</i> , Å (calcd.)	<i>hkl</i>	<i>d</i> , Å (calcd.)	<i>hkl</i>	<i>d</i> , Å (calcd.)	<i>hkl</i>			
293	14°06'	30	3.165	3.1646	071, 066	3.1550	022	1.7276	220	Cu ₂ Te		
	15°03'	50	2.970	2.9675	217							Orthorhombic
	15°41'	100	2.852	2.8534	208							<i>a</i> = 7.319 Å
	16°23'	40	2.734	2.7344	069							<i>b</i> = 22.236 Å
	16°42'	20	2.682	—	—	2.6813	042					<i>c</i> = 36.458 Å
	17°36'	10	2.549	2.5498	239	2.5437	080					<i>Z</i> = 104
	18°56'	20	2.376	2.3736	088	2.3725	170					space group <i>P6/nmm</i>
	19°33'	70	2.304	2.3055	324	2.3101	062					ρ = 7.41 g/cm ³
	20°12'	60	2.233	2.2322	097	—	—			2.2271	222	
	20°48'	30	2.171	2.1720	098	—	—					AgCuSe
	21°09'	40	2.137	2.1360	345	2.1312	152					Orthorhombic
	21°59'	10	2.059	—	—	2.0598	023			2.0619	321	<i>a</i> = 4.107 Å
	22°42'	30	1.998	1.9979	294	—	—					<i>b</i> = 20.412 Å
	23°41'	5	1.920	1.9108	373	1.9169	221			1.9287	400	<i>c</i> = 6.299 Å
	26°22'	10	1.736	1.7358	441	—	—					<i>Z</i> = 10
	26°50'	10	1.708	1.7073	444	1.7101	0.10.2					space group <i>P4/nmm</i>
	27°09'	10	1.690	1.6889	395	1.6917	261					ρ = 8.00 g/cm ³
	29°03'	5	1.588	1.5865	3.10.6	—	—					Cubic
32°18'	10	1.443	1.4423	514	1.4419	193			<i>a</i> = 7.715 Å			
34°22'	20	1.366	1.3658	555	1.3653	310	1.3638	440	<i>Z</i> = 8, space group <i>Fd3m</i>			
38°22'	10	1.242	1.2410	595	1.2414	224			ρ = 7.94 g/cm ³			
41°00'	10	1.175	1.1758	651	1.1735	264						
373	15°40'	30	2.855	2.853	208	—	—	2.7325	220	Cu ₂ Te		
	16°21'	5	2.739	2.7385	069	—	—					Orthorhombic
	16°38'	20	2.693	2.6958	219	2.6880	042					<i>a</i> = 7.313 Å
	17°34'	20	2.554	2.5528	177	2.5549	080					<i>b</i> = 22.361 Å
	18°15'	20	2.462	2.4641	178	—	—					<i>c</i> = 36.515 Å
	18°36'	20	2.417	2.4161	302	—	—					<i>Z</i> = 104
	19°30'	60	2.310	2.3051	324	2.3168	062					ρ = 7.36 g/cm ³
	20°10'	100	2.236	2.2308	341	2.2277	171			2.2310	222	
	21°28'	30	2.106	2.1077	353	—	—					
	21°54'	40	2.067	2.0695	279	—	—			2.0656	321	AgCuSe
	23°39'	10	1.922	—	—	1.9195	221			1.9322	400	Orthorhombic
	25°58'	10	1.760	1.7568	433	1.7604	260					<i>a</i> = 4.1100 Å
	27°07'	10	1.691	1.6925	395	1.6829	192					<i>b</i> = 20.4419 Å
	29°00'	10	1.590	1.5905	3.10.6	1.5805	004					<i>c</i> = 6.3224 Å
	31°26'	10	1.478	1.4838	486	1.4782	144					<i>Z</i> = 10
	31°48'	5	1.463	1.4594	510	1.4671	0.10.3					space group <i>P4/nmm</i>
	32°16'	5	1.444	1.4411	514	1.4493	2.10.0					ρ = 7.82 g/cm ³
	33°36'	20	1.393	1.3901	545	1.3877	154					Cubic
34°20'	5	1.367	1.3662	555	1.3669	310	1.3662	440	<i>a</i> = 7.729 Å			
37°12'	10	1.275	1.2831	584	1.2751	283			<i>Z</i> = 8, space group <i>Fd3m</i>			
39°03'	10	1.224	1.2213	5.8.10	1.2275	045			ρ = 7.90 g/cm ³			

Table 2. (Contd.)

<i>T</i> , K (exp)	θ	<i>I</i> / <i>I</i> ₀	<i>d</i> , Å (exp)	Cu _{1.96} Se		AgCuSe		Cubic		Crystal-lattice parameters
				<i>d</i> , Å (calcd.)	<i>hkl</i>	<i>d</i> , Å (calcd.)	<i>hkl</i>	<i>d</i> , Å (calcd.)	<i>hkl</i>	
473	16°19'	40	2.743	2.7431	220					Cubic <i>a</i> = 7.759 Å <i>Z</i> = 8 space group <i>Fd3m</i> ρ = 7.81 g/cm ³
	20°08'	100	2.240	2.2397	222					
	21°49'	75	2.074	2.0716	321					
	23°25'	30	1.940	1.9396	400					
	31°05'	30	1.493	1.4931	333					
	34°12'	40	1.371	1.3715	440					
573	16°17'	40	2.749	2.7493	220					Cubic <i>a</i> = 7.774 Å <i>Z</i> = 8 space group <i>Fd3m</i> ρ = 7.763 g/cm ³
	20°04'	100	2.246	2.2462	222					
	21°46'	75	2.078	2.0785	321					
	23°22'	30	1.944	1.9438	400					
	31°02'	30	1.495	1.4954	333					
	34°10'	40	1.373	1.3727	440					

The experimental conditions: CuK α radiation (the wavelength 1.5418 Å), Ni filter, 35 kV, 10 mA. *I*/*I*₀ is the relative intensity. Abbreviations exp and calc refer to the experimental data and the results of calculations.

Table 3. Thermal expansion of the AgCuSe_{0.5}S_{0.5} crystal

Composition	<i>T</i> , K	$\alpha_{[100]}$	$\alpha_{[010]}$	$\alpha_{[001]}$	$\bar{\alpha} = \frac{\alpha_{[100]} + \alpha_{[010]} + \alpha_{[001]}}{3}$	$\beta = \alpha_{[100]} + \alpha_{[010]} + \alpha_{[001]}$
AgCuSe	293–373	52.007	55.423	17.917	41.782	125.347
	293–473	66.623	47.370	83.170	65.721	197.163
	293–573	45.451	27.320	61.998	44.923	134.769
	293–673	49.592	28.080	47.778	41.817	125.450
Cu _{1.96} S	293–373	18.638	38.901	42.388	33.309	99.927
	293–473	17.810	23.288	81.091	40.730	122.189
	293–573	16.109	23.137	57.132	32.126	96.378
	293–673	14.126	23.232	46.365	27.908	83.723
AgCuSe _{0.5} S _{0.5}	773–873	11.013	11.013			33.039
	773–973	12.587			12.587	37.761

$\alpha_{[100]}$, $\alpha_{[010]}$, and $\alpha_{[001]}$ are the thermal-expansion coefficients corresponding to the [100], [010], and [001] directions (in 10⁻⁶ K⁻¹ units)

Table 4. Thermal-expansion coefficients of the AgCuSe_{0.5}Te_{0.5} crystal (in 10⁶ K⁻¹)

Composition	<i>T</i> , K	$\alpha_{[100]}$	$\alpha_{[010]}$	$\alpha_{[001]}$	$\bar{\alpha} = \frac{\alpha_{[100]} + \alpha_{[010]} + \alpha_{[001]}}{3}$	$\beta = \alpha_{[100]} + \alpha_{[010]} + \alpha_{[001]}$
Cu ₂ Te	293–373	17.079	70.268	24.605	37.317	111.951
AgCuSe	293–373	9.310	12.854	45.642	22.542	67.627
AgCuSe _{0.5} S _{0.5} , cubic	293–373	22.683			22.683	68.049
	293–473	31.684			31.684	95.052
	293–573	27.312			27.312	81.936

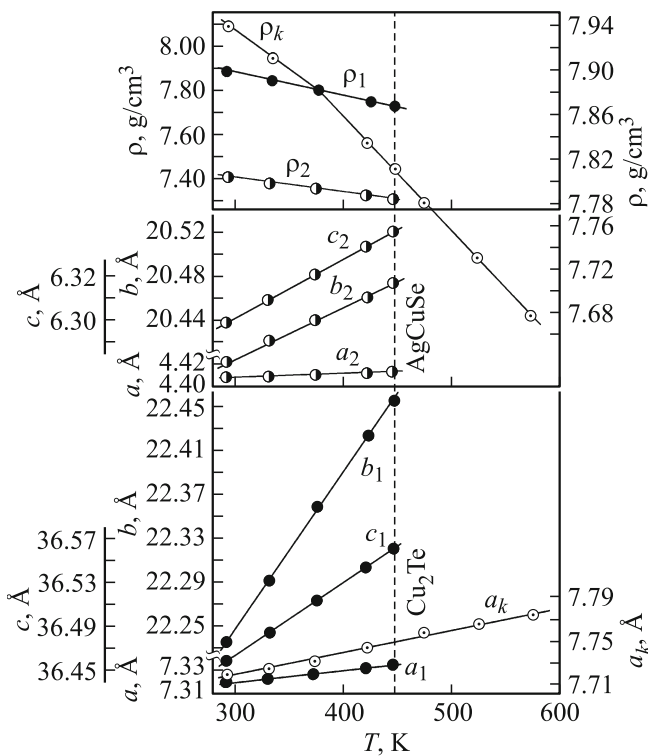


Fig. 2. Temperature dependence of the crystal-lattice parameters (a , b , c) and densities (ρ) of phases entering into the $\text{AgCuSe}_{0.5}\text{Te}_{0.5}$ composition: a_1 , b_1 , c_1 , and ρ_1 refer to the orthorhombic Cu_2Te phase; a_2 , b_2 , c_2 , and ρ_2 to the monoclinic AgCuSe phase, and a_k and ρ_k to the cubic modification.

and conducted test recordings every 50 K. Before the beginning of each recording, we kept the sample temperatures constant for 40 min. Under these conditions, the three-phase composition of the $\text{AgCuSe}_{0.5}\text{Te}_{0.5}$ sample is retained, and at 444 K, both of the orthorhombic phases transform into the cubic phase (see Table 2). This transformation is reversible; i.e., upon cooling, the sample returns to its initial state.

Figure 2 shows the temperature dependences of the lattice parameters of phases entering into the $\text{AgCuSe}_{0.5}\text{Te}_{0.5}$ compound in the temperature range 293–573 K. From Fig. 2, it can be seen that the lattice parameters of both of the orthorhombic phases and the cubic phase increase linearly with temperature. In the case of the transformation of both of the orthor-

hombic phases into the cubic phase, the temperature dependence of the parameter $a = f(T)$ does not deviate from linearity. Hence it follows that, in the transformation of both of the orthorhombic phases, the cubic phase plays the role of a ready seed.

From the temperature dependences of the lattice parameters, we calculated the thermal-expansion coefficients for both of the orthorhombic phases and the cubic phase. The results are given in Table 4.

As can be seen from Table 4, the thermal-expansion coefficients corresponding to the basic crystallographic directions in both of the orthorhombic phases are highly anisotropic. This is one of the main causes of the structural instability of both of the orthorhombic phases.

4. CONCLUSIONS

At room temperature, the AgCuSe crystals are orthorhombic in structure. Replacement of half the content of Se anions with S atoms brings about the appearance of the $\text{Cu}_{1.96}\text{S}$ and AgCuSe phases. If half the content of Se anions is replaced with Te atoms, the compound becomes a three-phase crystal consisting of AgCuSe , Cu_2Te , and a cubic phase. At the temperature 695 K, the $\text{Cu}_{1.96}\text{S}$ and AgCuSe phases transform into a single fcc phase, and at 444 K, the Cu_2Te and AgCuSe phases transform into a diamond-like cubic phase. In both cases, the transformations are reversible.

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