

## STRUCTURAL PHASE TRANSITIONS IN THE COMPOUND $\text{Ag}_{1.55}\text{Cu}_{0.45}\text{S}$ AT HIGH TEMPERATURES

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**Abstract** Compound  $\text{Ag}_{1.55}\text{Cu}_{0.45}\text{S}$  was synthesized by partial replacement of Ag atoms with Cu atoms. The crystal structure of the obtained compound was investigated by X-ray diffraction. It was found that the crystal structure of this compound corresponds to the tetragonal symmetry of the space group  $I4/mmc$  and at the temperature of  $T = 425$  K a structural phase transition occurs and a highly symmetric crystal structure is formed. The structure of the new phase corresponded to the cubic symmetry of the  $Im-3m$  space group. With an increase in temperature, another phase transition occurred at a temperature of  $T = 673$  K. The crystal structure of the new phase corresponds to the cubic symmetry of the space group  $Fm-3m$ .

**Keywords:** crystal structure, X-ray diffraction, phase transition.

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### 1. Introduction

The study of phase transitions in various systems contributes to the development of the theory of phase transitions. It is known that there is no unified theory of phase transitions for all systems. Numerous experiments are needed to develop this theory. It is known that in ferroelectric, ferromagnet and other systems, fundamental changes in physical properties occur during phase transitions (Temir *et al.*, 2021; Ishii *et al.*, 2021; Tasnádi *et al.*, 2021). Many interesting physical processes can also be observed in semiconductor materials. In these compounds, phase transitions can be observed semiconductor-dielectric, semiconductor-metal, semiconductor-semimetal. Therefore, phase transitions in semiconductors are important physical processes (Aliyev *et al.*, 2019; Jabarov *et al.*, 2021; Ismayilova & Jabarov, 2017; Hashimov *et al.*, 2018).

Structural studies at high temperatures have shown that significant changes in the crystal structure and phase transitions are observed in semiconductor compounds of copper and silver chalcogenides during anion-anion substitution. The difference in the ionic radii of chalcogen atoms affects not only the interatomic bonds and lattice parameters, but also the symmetry of the crystal structure and the change in the space group. The difference in the ionic radii of chalcogen atoms affects not only the interatomic bonds and lattice parameters, but also the symmetry of the crystal structure and the change in the space group (Aliyev *et al.*, 2018; Alekperov *et al.*, 2019; Aliyev *et al.*, 2017; Zhao *et al.*, 2020)

Although the electrical properties, optical properties, and electronic structure of copper and silver chalcogenides have been widely studied, many of the physical processes

occurring in them have not been sufficiently studied (Prathiba *et al.*, 2015; Salmón-Gamboa *et al.*, 2018). It is necessary to study changes in the crystal structure and phase formation processes during cation-cation and anion-anion substitution in these compounds because this information plays the role of basic information for studying their other physical properties in the future. In this work, the compound  $\text{Ag}_{1.55}\text{Cu}_{0.45}\text{S}$  was synthesized, and its crystal structure was investigated by X-ray diffraction. X-ray diffraction spectra were obtained in the temperature range  $T = 293\text{-}873\text{ K}$ , and structural phase transitions were investigated.

## 2. Experimental

Compound  $\text{Ag}_{1.55}\text{Cu}_{0.45}\text{S}$  was obtained by a standard method. The synthesis process was carried out in several stages. At the initial stage, the elements Ag, Cu and S were selected and mixed in the corresponding stoichiometric amounts. A high vacuum ( $P = 10^{-3}\text{ Pa}$ ) was created in the quartz ampoule, the mixture was filled into this ampoule and sealed. The finished ampoule is placed in a constant temperature furnace. The sample temperature was raised to the melting point of sulfur ( $T_{\text{S}} = 393\text{ K}$ ), kept at this temperature for 3 hours, and then increased to the melting point of copper ( $T_{\text{Cu}} = 1357\text{ K}$ ). At the end of these stages, the furnace temperature was slowly increased to the melting point of the  $\text{AgCuS}$  compound ( $T_{\text{AgCuS}} = 1357\text{ K}$ ) at a rate of 50 K/h. The ampoule was stored at this temperature in a furnace for two hours. At the next stage, the temperature of the ampoule was slowly lowered to  $T = 473\text{ K}$  and kept at this temperature for 48 hours to homogenize the sample. After the completion of the synthesis process, research samples were prepared from the obtained material.

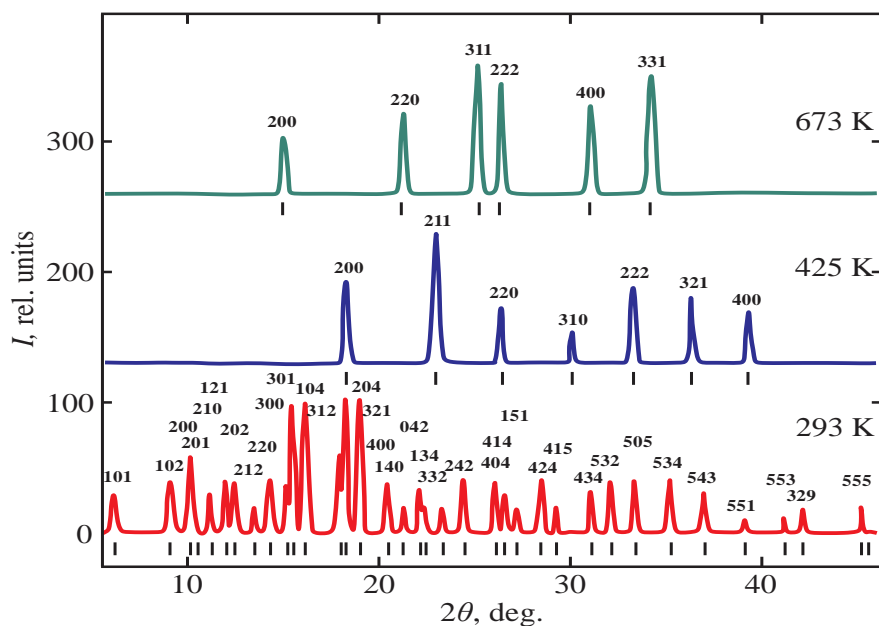
Structural studies of the  $\text{Ag}_{1.55}\text{Cu}_{0.45}\text{S}$  compound at high temperatures were performed by X-ray diffraction. The experiments were carried out on a DRON-3M X-ray diffractometer with  $\text{CuK}\alpha$ -radiation,  $\lambda = 1.5418\text{ \AA}$ , a Ni-filter parameter and an URVT-2000 system in a vacuum of  $10^{-2}\text{ Pa}$ . By analyzing the spectra, the atomic planes and unit cell parameters were determined in accordance with the distances between the atomic planes.

## 3. Results and discussions

X-ray diffraction patterns obtained for different phases of the  $\text{Ag}_{1.55}\text{Cu}_{0.45}\text{S}$  compound at room temperature and high temperatures are given in Fig. 1. Analysis of the diffraction pattern obtained at room temperature showed that the crystal structure of the  $\text{Ag}_{1.55}\text{Cu}_{0.45}\text{S}$  compound consists of one phase, and this phase corresponds to the tetragonal crystal structure of the space group  $I4/mmc$ . As can be seen from the spectrum, 35 maximum were observed in the range  $0 \leq 2\theta \leq 50^\circ$  at room temperature. These maxima correspond to the planes: (1 0 1), (1 0 2), (2 0 0), (2 0 1), (2 1 0), (1 2 1), (2 0 2), (2 1 2), (2 2 0), (3 0 0), (3 0 1), (1 0 4), (3 1 2), (2 0 4), (3 2 1), (4 0 0), (1 4 0), (0 4 2), (1 3 4), (3 3 2), (2 4 2), (4 0 4), (4 1 4), (1 5 1), (4 2 4), (4 1 5), (4 3 4), (5 3 2), (5 0 5), (5 3 4), (5 4 3), (5 5 1), (5 5 3), (3 2 9), and (5 5 5).

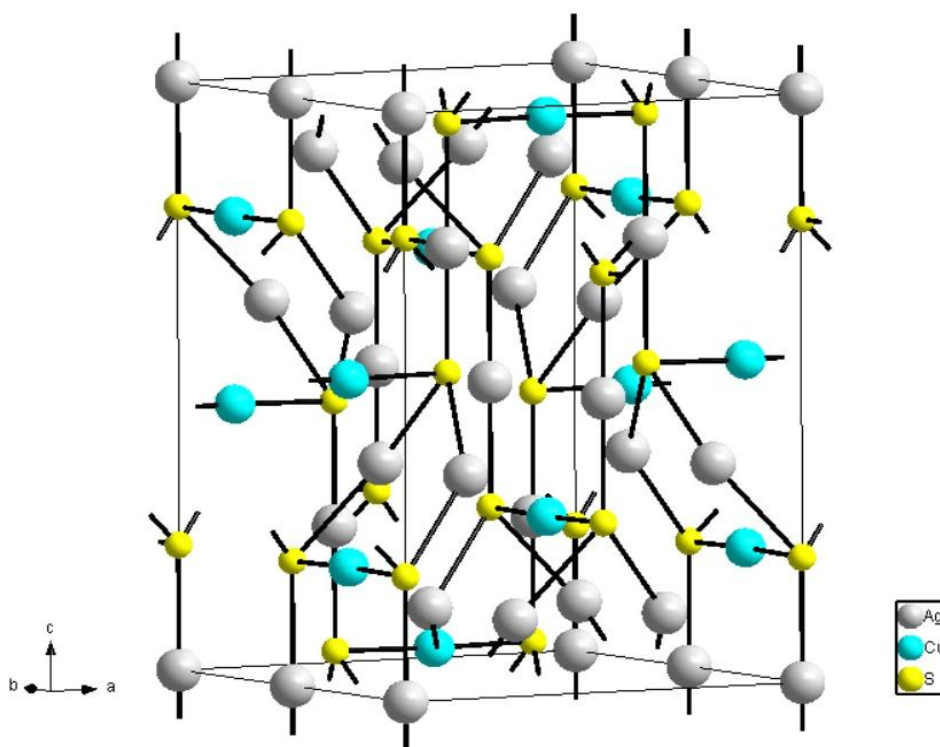
The values of the unit cell parameters are calculated using the following formula for the distances  $d_{hkl}$  between atomic planes:

$$\frac{1}{d^2} = \frac{h^2+k^2}{a^2} + \left(\frac{l}{c}\right)^2 \quad (1)$$



**Fig. 1.** X-ray diffraction spectra of the compound  $\text{Ag}_{1.55}\text{Cu}_{0.45}\text{S}$  at room temperature and high temperatures

By formula (1), the values of the parameters of the elementary nucleus are determined:  $a = b = 8.647 \text{ \AA}$ , and  $c = 11.576 \text{ \AA}$ . The crystal structure obtained in the Diamond 3.2 program in accordance with the parameters obtained by the X-ray method of the  $\text{Ag}_{1.55}\text{Cu}_{0.45}\text{S}$  compound is shown in Fig. 2.



**Fig. 2.** Crystal structure of the  $\text{Ag}_{1.55}\text{Cu}_{0.45}\text{S}$  compound at room temperature

As can be seen in the figure, Ag atoms are deposited at the sites of the crystal lattice. Cu atoms, on the other hand, occupy different positions in the volume of the crystal structure. S - chalcogen atoms form covalent bonds with Ag and Cu atoms. Chalcogen atoms are in the same position in the crystal structure. Metal atoms are in three different positions. Ag atoms are in two of these positions, and Cu atoms are in one position. Since the atoms that make up the  $\text{Ag}_{1.55}\text{Cu}_{0.45}\text{S}$  compound form different bonds, the distances between the atoms also change. The distance between the chalcogen and metal atoms is  $d_{\text{H-M}} \approx 2.5 \text{ \AA}$ . The distances between the metal atoms are:  $d_{\text{M-M}} \approx 3 \text{ \AA}$ , and the distance between the halogen atoms:  $d_{\text{H-H}} \approx 4 \text{ \AA}$ .

The X-ray spectra obtained in the high-temperature of the  $\text{Ag}_{1.55}\text{Cu}_{0.45}\text{S}$  crystal differ sharply from the X-ray spectra obtained at room temperature. If you look at the diffraction patterns shown in Fig. 1, it can be seen that fewer diffraction maxima were found in the diffraction spectra obtained at  $T = 425 \text{ K}$ . Under normal conditions, only 7 maxima can be observed at  $T = 425 \text{ K}$  out of 35 maxima observed in the range  $0^\circ \leq 2\theta \leq 50^\circ$  of the diffraction angle. These reflexes correspond to the planes: (2 0 0), (2 1 1), (2 2 0), (3 1 0), (2 2 2), (3 2 1), and (4 0 0). It was found that the crystal structure of the new phase formed has a high symmetry and corresponds to the cubic system of the  $\text{Im-3m}$  (229) space group. Based on the distances  $d_{hkl}$  between the planes of atoms  $hkl$ , the values of the unit cell parameters:  $a = b = c = 4.833 \text{ \AA}$  were calculated according to formula (2):

$$\frac{1}{d^2} = \frac{h^2+k^2+l^2}{a^2} . \quad (2)$$

The reflections observed in the spectrum obtained at  $T = 675 \text{ K}$  were more different (Fig. 1). This is due to the fact that a new structure has arisen in the high-temperature interval. New reflections observed in the X-ray diffraction pattern correspond to atomic planes: (2 0 0), (2 2 0), (3 1 1), (2 2 2), (4 0 0), and (3 3 1). As a result of the analysis of the spectra, it was found that the crystal structure of this new phase also corresponds to the highly symmetric cubic system. The high-temperature cubic symmetry of the  $\text{Ag}_{1.55}\text{Cu}_{0.45}\text{S}$  compound corresponds to the  $\text{Fm-3m}$  space group (225). The values of the unit cell parameters:  $a = b = c = 5.951 \text{ \AA}$  were calculated by formula (2) with respect to atomic planes forming a cubic crystal structure.

Crystallographic parameters of  $\text{Ag}_{1.55}\text{Cu}_{0.45}\text{S}$ , determined on the basis of X-ray diffraction patterns obtained at room temperature and at high temperatures: symmetry, space group, unit cell parameters, volume,  $Z$  and density in different phases are given in Table 1.

As you can see from the Table 1 values of crystallographic parameters, the symmetry of the compound  $\text{Ag}_{1.55}\text{Cu}_{0.45}\text{S}$  increases under the influence of high temperatures. This is due to the fact that the energy of the crystal lattice increases under the influence of temperature. Therefore, due to this energy, the crystal symmetry increases. Due to the increase in temperature, the energy of the covalent bonds formed by the atoms of the chalcogen and the metal also increases, and at the same time, the lengths of the interatomic bonds increase. As a result, the crystal structure expands. It is known from the course of solid state physics that the expansion of interatomic bonds increases the density of crystals. As can be seen from the values given in Table 1, the density  $\rho = 6.981 \text{ g/cm}^3$  in the tetragonal phase  $\text{I4/mmc}$ ,  $\rho = 6.704 \text{ g/cm}^3$  in the cubic phase  $\text{Im-3m}$  and  $\rho = 7.179 \text{ g/cm}^3$  in the cubic phase  $\text{Fm-3m}$ .

**Table 1.** Crystallographic parameters of Ag<sub>1.55</sub>Cu<sub>0.45</sub>S at high temperatures

Temperature, K	Phasa	Cell parameters			z	Density, g/cm <sup>3</sup>
		a, Å	c, Å	V, Å <sup>3</sup>		
293	Tetraqonal, I4/mmc	8.647	11.576	865.5	16	6.981
385	Tetraqonal, I4/mmc	8.667	11.778	884.7	16	6.981
425	Cubic, Im-3m	4.833	-	112.9	2	6.704
573	Cubic, Im-3m	4.876	-	115.8	2	6.520
673	Cubic, Fm-3m	5.951	-	210.7	4	7.179
873	Cubic, Fm-3m	5.982	-	214.1	4	7.179

The values of the coefficients of thermal expansion for different phases are calculated. It was found that the coefficients of thermal expansion in different planes for the tetragonal phase:  $\alpha_{[100]} = 27.19 \times 10^6 \text{ K}^{-1}$  and  $\alpha_{[001]} = 3.69 \times 10^6 \text{ K}^{-1}$ , for the cubic phase Im-3m:  $\alpha_{[100]} = 60.12 \times 10^6 \text{ K}^{-1}$ , for the cubic phase Fm-3m:  $\alpha_{[100]} = 52.09 \times 10^6 \text{ K}^{-1}$ .

#### 4. Conclusion

The crystal structure and phase transitions of the Ag<sub>1.55</sub>Cu<sub>0.45</sub>S compound have been investigated. The studies were carried out by X-ray diffraction in the temperature range  $T = 293\text{-}873 \text{ K}$ . It was found that the crystal structure of this compound at room temperature corresponds to tetragonal symmetry. It was determined that the phase transition of the tetragonal-cubic structure occurs at a temperature of  $T = 425 \text{ K}$ . At higher temperatures ( $T = 673 \text{ K}$ ), a structural transformation was observed in the cubic phase. The coefficients of thermal expansion are calculated for the tetragonal and cubic phases.

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