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STUDY OF THERMAL PROPERTIES OF $Cu_4Se_{1.5}Te_{0.5}$ AND $Cu_4Te_{1.5}Se_{0.5}$ COMPOUNDS BY DIFFERENTIAL THERMAL ANALYSIS

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Abstract. The thermal properties of $Cu_4Se_{1.5}Te_{0.5}$ and $Cu_4Te_{1.5}Se_{0.5}$ compounds at high temperatures are studied by Differential Thermal Analysis (DTA). The studies are carried out in the temperature range $300 \leq T \leq 875$ K. In a $Cu_4Se_{1.5}Te_{0.5}$ crystal, endoeffects are observed at temperatures T_1 = 413 K and T_2 = 800 K, and exoeffects are observed at T = 725 K. In a $Cu_4Te_{1.5}Se_{0.5}$ crystal, endoeffects are observed at temperatures T_1 = 410 K, T_2 = 465 K, and T_3 = 800 K. The structural properties of the phases are determined from the effects observed at high temperatures. It is established that a highly symmetrical cubic phase is formed in these compounds at T = 800 K.

Keywords: *Synthesis, crystal, X-ray diffraction analysis, modification, phase, phase transformation, structure.*

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1. Introduction

It is known that copper-chalcogen (Se, S, Te) systems are studied as interesting objects for research. Interest in these materials is primarily due to the important physicochemical properties that manifest themselves in them (Perro & Cleande, 1971; Balapanov *et al*., 2003). One of the very interesting aspects of copper chalcogenides is the process of structural-phase transformations and phase transformations occurring in them under the influence of external factors. In the course of these processes, complex structural transformations can occur in terms of a change in the valence of Cu atoms (Gasimova *et al.*, 2011; Alıyeva *et al.*, 2016; Kashida *et al.*, 2003). It has been established that many copper chalcogenides do not form a single-phase system at room temperature. At high temperatures, a single-phase ideal system with cubic symmetry can form. Therefore, copper chalcogenides are widely used to study the processes of phase transitions in chalcogenide semiconductors (Vouroutzis & Manolikas, 1989).

When studying the mechanism of polymorphic transformation, it is important, in addition to structural information, to obtain information on the thermodynamic parameters for each modification. From the point of view of studying the mechanism of polymorphic transformation in opaque crystals, since copper and silver chalcogenides are rich in polymorphic transformations, the study of these systems is of greater interest. To establish the nature of polymorphic transformations, it is important to accurately determine the parameters of the crystal lattice, volume and atomic density, as well as the temperature dependence of the thermal expansion of the existing modifications. The exact determination of these parameters has always been one of the topical problems of solid

state physics. Because all physical and mechanical properties are highly dependent on the stability of the crystal structure. Research in this direction makes it possible to obtain extensive information about the mechanism of polymorphic transformations and the dynamics of the crystal lattice. X-ray diffraction studies carried out under special conditions make it possible to obtain fundamental information about a substance in the field of external forces. It is known that in order to plan in advance the working area of any transducer of the test substance, it is necessary to study this substance under external influences. In studies conducted for this purpose, the most reliable data are the results obtained in structural studies. Because structural information obtained at the atomic level is the basis for explaining any physical property (Asadov *et al.*, 2008; Azimova *et al.*, 2020; Gasimova *et al.*, 2011).

Semiconductor compounds are widely used materials in many areas of modern electronics. Chalcogenides occupy a special place among materials with semiconductor properties. Recently, the discovery of topological insulators in these materials has further increased interest in them. Therefore, both structural studies and the study of various physical properties of these compounds have entered a new stage. Structural studies of new compounds obtained as a result of cation-cation substitutions of known chalcogenide semiconductors of silver and copper are being carried out. Phase interactions and structural-phase transformations in chalcogenide systems based on Ag and Cu have been studied. It has been established that it is possible to obtain various compositions with a new crystal structure with partial substitution of not only metal atoms, but also chalcogen atoms. The results of studying new modifications obtained by anion-anion and cation-cation substitutions are very important for obtaining new functional materials using these substances in the future.

It is known that the rate of many physical and chemical processes increases at high temperatures. The processes of decomposition and oxidation occurring in materials proceed faster. To study these processes, the method of differential thermal analysis is considered the most unique method. In the course of research, it was found that thermodynamic potentials can also be calculated by analyzing DTA spectra. In the DTA analysis of copper chalcogenides, it was found that in these compounds one can observe processes going up to the melting point. It is known that the oxidation process proceeds on the surface of unoxidized materials. This process is accelerated by temperature. At this time it becomes difficult to explain the phase transitions. Therefore, when studying phase transitions in chalcogenides, DTA studies are carried out under vacuum conditions (Madatov *et al.*, 2020; Alekperov *et al.*, 2020; Aliyev *et al.*, 2020).

In this work, compounds $Cu_4Se_{2-x}Te_x$ (x = 0.5) were synthesized. X-ray phase analysis and Differential Thermal Analysis of the obtained compounds were carried out. The temperature-dependent structural changes in crystals are studied in the temperature range 300 K < T < 875 K.

2. Experimental methods

2.1. Synthesis of compounds $Cu_4Se_{1.5}Te_{0.5}$ and $Cu_4Te_{1.5}Se_{0.5}$

The synthesis of the studied samples was carried out according to the standard procedure in a single-zone furnace. According to the stoichiometric composition, the elements (Cu, Se, Te) were collected in a quartz ampoule, the air was sucked off into 10^{-4} column of mercury, the neck of the ampoule was closed. The finished ampoule was placed in an oven stabilized at a temperature of 500 K. After keeping the process in the

initial mode for 1 hour, the temperature of the oven was gradually increased. In the range T = 700-1050 K, it was stopped for half an hour at the points 800, 900, and 1000 K, and the synthesis ampoule was shaken together with the furnace. After that, the temperature was raised to 50 K and held for 1.5 hours. Then the temperature was gradually reduced to 600 K. After holding at this temperature for 3 days, the process was stopped for homogenization.

2.2. X-ray phase analysis

X-ray phase analysis was carried out to determine the structure of the synthesized compounds $Cu_4Se_{1.5}Te_{0.5}$ and $Cu_4Te_{1.5}Se_{0.5}$. The studies were carried out at room temperature on an ADVANCE D8 diffractometer (Bruker, Germany). X-ray diffraction spectra were obtained and analyzed. To determine the lattice parameters of both synthesized samples, the TOPAS program was used. As a result of the analysis, it was found that the crystallographic parameters of the studied samples are as follows:

1. The crystal structure of the $Cu_4Se_{1.5}Te_{0.5}$ compound corresponds to the space group R-3m with rhombohedral symmetry at room temperature. For lattice parameters: a = 4.162 Å, c = 20.662 Å, V = 309.9 Å^3, ρ_x = 7.0543 g/cm^3, Z = 3 values.

2. The crystal structure of the $Cu_4Te_{1.5}Se_{0.5}$ compound corresponds to the space group P3m1 with trigonal symmetry at room temperature. For lattice parameters: a = 8.2319 Å, c = 21.4145 Å, V = 1089.8 Å^3, ρ_x = 7.3324 g/cm^3, Z = 22 values.

2.3. Differential thermal analysis

The thermal properties of $Cu_4Se_{1.5}Te_{0.5}$ and $Cu_4Te_{1.5}Se_{0.5}$ compounds were determined by differential thermal analysis in the temperature range T = 300 - 875 K on a Perkin Elmer STA 6000 calorimeter. This method makes it possible to study physicochemical processes such as oxidation, melting, evaporation, phase transitions in condensed media (Jabarov *et al.*, 2021; Fokin *et al.*, 2010). The studies were carried out at a speed of 5 deg/min. The DTA spectra obtained in the high-temperature region were analyzed using the Origin 9 program.

3. Results and Discussion

When determining the crystal structures of $Cu_4Se_{1.5}Te_{0.5}$ and $Cu_4Te_{1.5}Se_{0.5}$ compounds, it was found that these compounds are compounds with high symmetry at room temperature. Calorimetric experiments were performed to determine temperature-dependent structural changes in these compounds. The thermal properties of both studied samples were studied by differential thermal analysis in the temperature range T = 300-870 K. Figure 1 shows the DTA spectra obtained for compounds $Cu_4Se_{1.5}Te_{0.5}$ (blue line) and $Cu_4Te_{1.5}Se_{0.5}$ (red line) in the high temperature region.

It is known that, depending on the thermodynamic conditions, various physicochemical processes occur in all types of materials. When these processes are implemented, either stability is preserved or an unstable transition to new phases is observed. Depending on the thermodynamic conditions, various changes can occur in the structure of a substance. As is known, temperature, pressure, radiation, atmosphere of inert gases, vacuum, atmosphere of nitrogen vapors and atmosphere are factors influencing the change in the structure of matter. Therefore, these factors must be taken into account when conducting experimental studies. The studies of differential thermal

analysis were carried out in an inert argon gas medium. The obtained spectra were analyzed and phase transitions in the compounds $Cu_4Se_{1.5}Te_{0.5}$ and $Cu_4Te_{1.5}Se_{0.5}$ were studied.

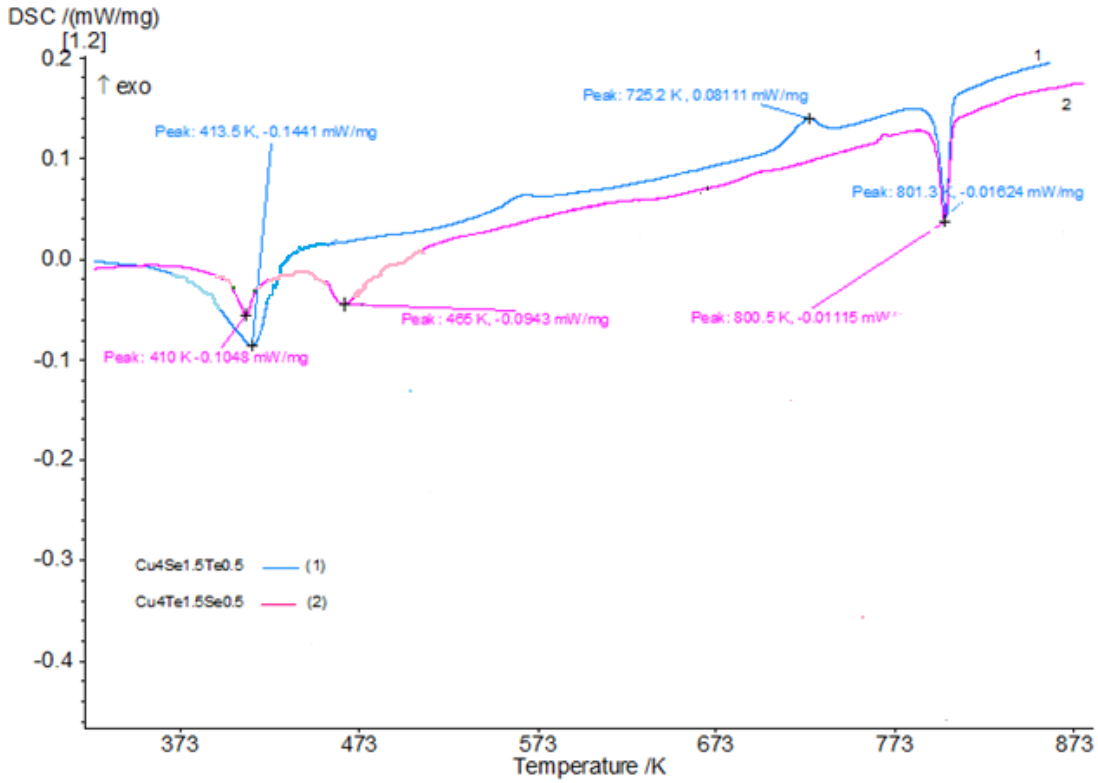

Fig. 1. Differential Thermal Analysis spectra of $Cu_4Se_{1.5}Te_{0.5}$ and $Cu_4Te_{1.5}Se_{0.5}$ compounds at high temperatures

Fig. 1 shows that endothermic and exothermic effects are observed in accordance with the structural changes in the DTA spectra obtained for the $Cu_4Se_{1.5}Te_{0.5}$ and $Cu_4Te_{1.5}Se_{0.5}$ compounds. In the $Cu_4Se_{1.5}Te_{0.5}$ compound, endoeffects were observed at temperatures T_1 = 413 K and T_2 = 800 K, while exoeffects were observed at T = 725 K. In the $Cu_4Te_{1.5}Se_{0.5}$ compound, endoeffects were observed at temperatures T_1 = 410 K, T_2 = 465 K and T_3 = 800 K. It is known that the processes occurring at temperatures $T \approx$ 400 K are associated with the evaporation of water inside the crystal. Because every real crystal contains a small amount of water molecules. Evaporation occurs at values close to the boiling point of water. Therefore, endoeffects are observed in the spectrum of the thermal function. In some cases, water molecules combine with atoms of various elements, forming complex compounds. As the temperature rises, these molecules are first destroyed. Then this malecules leave the substance. Therefore, endoeffects can be observed at slightly higher temperatures. In the $Cu_4Se_{1.5}Te_{0.5}$ compound, the endothermic effect arose at a temperature T_1 = 413 K, which corresponds to the evaporation of water. In the $Cu_4Te_{1.5}Se_{0.5}$ compound, the endoeffect at T_1 = 410 K corresponds to the evaporation of water, and the endoeffect at T_2 = 465 K corresponds to the decomposition of compounds formed by water molecules. From the spectra shown in Fig. 1, it can be seen that the same endothermic effect was observed in each of the $Cu_4Se_{1.5}Te_{0.5}$ and $Cu_4Te_{1.5}Se_{0.5}$ compounds at a temperature T = 800 K. This effect, observed upon energy absorption, corresponds to a structural phase transition. It is known from previous studies

that a highly symmetrical phase is formed in copper and silver chalcogenides under the action of high temperature. The crystal structure of this phase corresponds to the cubic syngony with the space group Fm-3m. This effect observed on the DTA curve can be explained by the fact that it corresponds to the formation of a cubic phase. The exoeffect that occurs at the temperature T = 725 K in the $Cu_4Se_{1.5}Te_{0.5}$ compound can be explained by the recombination of defects in the crystal structure.

4. Conclusions

$Cu_4Se_{1.5}Te_{0.5}$ and $Cu_4Te_{1.5}Se_{0.5}$ compounds were synthesized and their structural properties were studied. Researches were carried out by X-ray diffraction analysis and differential thermal analysis methods. Temperature dependences of the heat flux function are obtained in the region of high temperatures. It has been determined that different effects are observed with increasing temperature. These effects were explained by the evaporation of water molecules suspended in the crystals and the appearance of structural phase transitions. A structural phase transition at T = 800 K was observed in $Cu_4Se_{1.5}Te_{0.5}$ and $Cu_4Te_{1.5}Se_{0.5}$ compounds. In these compounds, a highly symmetric cubic phase with a highly symmetric space group Fm-3m was obtained.

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