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Phase transitions in copper tellurides

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This paper presents the results of model calculations of the structure of the Cu-Te system at low temperatures, as well as the results of a study of the structure and phase transitions of synthesized non-stoichiometric compounds of copper tellurides. For the first time, using the USPEX evolutionary algorithm, model computer calculations of the search for stable phases of copper tellurides Cu_nTe_m ($n, m = 1 \div 10$) were carried out. At temperature $T = 0$ K and pressure $p = 1$ atm. As stable structures, the compositions Cu_5Te_4 , Cu_3Te_2 , and Cu_7Te_4 were identified, which are indicated in the triclinic and monoclinic syngonies. Based on the study of the phase diagram, calorimetric measurements and X-ray diffraction studies of experimentally synthesized samples of copper telluride, it was found that the non-stoichiometric compositions $\text{Cu}_{1.96}\text{Te}$, $\text{Cu}_{1.85}\text{Te}$, $\text{Cu}_{1.80}\text{Te}$ and $\text{Cu}_{1.75}\text{Te}$ at room temperature are single-phase. The $\text{Cu}_{1.85}\text{Te}$, $\text{Cu}_{1.80}\text{Te}$, and $\text{Cu}_{1.75}\text{Te}$ compounds are described by hexagonal crystalline superstructures obtained on the basis of the Novotny phase for Cu_2Te with different degrees of unit cell parameter multiplicity. $\text{Cu}_{1.96}\text{Te}$ at room temperature is indicated in an orthorhombic phase with lattice parameters that are also multiples of the unit cell parameters of the Novotny phase. At high temperatures, all compositions of Cu_{2-x}Te ($x = 0.04, 0.15, 0.20, 0.25$) transform into high-temperature disordered FCC structures that exist up to their melting point. It is shown that in these compounds the transition of a low-temperature hexagonal and orthorhombic structure to a high-temperature FCC phase occurs through a series of polymorphic phase transformations.

Keywords: copper tellurides; phase transitions; crystal structure; differential scanning calorimetry; polymorphic transformations

Introduction

Copper tellurides belong to the family of copper chalcogenides and have a wide variety of electrical properties due to the presence of mixed ionic-electronic conductivity and the existence of compounds of variable composition. Copper

chalcogenides have been addressed to be functional materials for thermoelectric [1], batteries [2], photovoltaic [3] and bioapplications [4]. The Cu-Te system has a complex phase diagram of states. This is due to the existence of different phases of copper tellurides of non-stoichiometric composition, the structures and properties of which have been little studied. Studies of phase transitions depending on the stoichiometric composition are necessary, since the operation of devices based on copper tellurides occurs in different temperature ranges. In this regard, this paper presents the results of a study of phase transitions in copper tellurides of non-stoichiometric composition Cu_{2-x}Te ($0 \leq x \leq 0.25$).

Materials and Methods

Using the USPEX algorithm [5] based on the density functional theory (DFT), model computer calculations of stable Cu_nTe_m ($n, m = 1 \div 10$) phases in the Cu-Te system at ultralow temperatures were carried out. The USPEX algorithm is based on an approach in which a small number of structures are randomly generated and their energy is calculated. The calculation continues until a stable model of the structure with the lowest total energy is determined. Compounds of copper tellurides of non-stoichiometric composition Cu_{2-x}Te ($0 \leq x \leq 0,25$) were chosen as objects of experimental study. The starting materials for the production of copper tellurides were tellurium (chemically pure grade) and copper with a purity of 99.999%.

Synthesis was carried out by direct sintering of the corresponding amounts of elements at a temperature of 873–923 K in quartz ampoules evacuated to a residual pressure of $p = 1$ atm. The thermal process of synthesis was carried out at a temperature rise rate of 1 K per minute with an intermediate exposure in the temperature range of 473–523 K for 48 hours. The total time of heating and holding the mixture was 150–200 hours. Then the mixture obtained was ground in an agate mortar and annealed for homogenization at a temperature of 773 K in a vacuum at a pressure of 10^{-3} Pa for 100–150 hours. The single-phase nature of the obtained samples was controlled by X-ray phase analysis, their composition was determined by chemical analysis and coulometric titration.

X-ray diffraction studies of the studied powder samples were carried out using $\text{Cu}_{K\alpha}$ radiation on a Bruker D8 Advance X-ray diffractometer with a step of 20–25 K up to a temperature of about 660 K (up to 773 K for some samples). Refinement of the crystal structure of the synthesized compounds was carried out using the Fullprof Suite software package. Calorimetric measurements were carried out on an automated instrument NETZSCH STA 449 F1 Jupiter. Argon was used as an inert medium.

Results and discussion

Model computer calculations [6] of the search for stable phases Cu_nTe_m ($n, m = 1 \div 10$) based on the USPEX evolutionary algorithm at a temperature $T = 0$ K and pressure $p = 1$ atm. revealed the following model compounds of copper

tellurides: Cu_5Te_4 , Cu_3Te_2 and Cu_7Te_4 (in calculated per 1 tellurium atom, the chemical formula is $\text{Cu}_{1.25}\text{Te}$, $\text{Cu}_{1.5}\text{Te}$, and $\text{Cu}_{1.75}\text{Te}$, respectively). On Figure 1 shows the model crystal structures of these compounds. According to the calculations, the $\text{Cu}_{1.5}\text{Te}$ and $\text{Cu}_{1.75}\text{Te}$ compounds are indexed in the triclinic phase, except for the composition $\text{Cu}_{1.25}\text{Te}$, which is a special case of the triclinic syngony – a monoclinic structure.

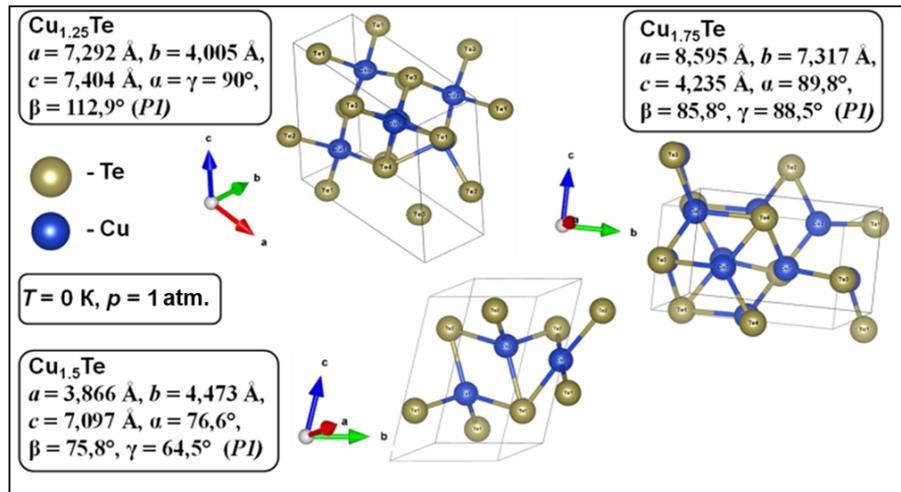


Figure 1. Models of the crystal structure of copper tellurides with the composition $\text{Cu}_{1.25}\text{Te}$, $\text{Cu}_{1.5}\text{Te}$, and $\text{Cu}_{1.75}\text{Te}$.

To study phase transitions and structural transformations with temperature changes, copper tellurides of the composition $\text{Cu}_{1.96}\text{Te}$, $\text{Cu}_{1.85}\text{Te}$, $\text{Cu}_{1.80}\text{Te}$, and $\text{Cu}_{1.75}\text{Te}$ were synthesized. Since copper telluride $\text{Cu}_{1.75}\text{Te}$ is a stable structure at ultralow temperatures according to the results of a model computer calculation, special attention is paid to the study of the evolution of the structure and phase transformations in the region of room and high temperatures. The experimental X-ray diffraction pattern of the $\text{Cu}_{1.75}\text{Te}$ compound at room temperature is shown in Figure 2. The R -factor of divergence in the calculation of the structure of the studied compounds did not exceed 8%, and the statistical index $\chi^2 < 3$. lattices that are multiples of the unit cell parameters of the Novotny phase [7] for Cu_2Te ($a_0 = 4.18 \text{ \AA}$, $c_0 = 7.2 \text{ \AA}$, $P6/mmm$). Copper telluride $\text{Cu}_{1.96}\text{Te}$ at room temperature crystallizes in the orthorhombic phase.

The evolution of changes in the structure and lattice parameters during phase transformations was studied on the basis of temperature X-ray diffraction studies of $\text{Cu}_{1.75}\text{Te}$ samples Figure 3, $\text{Cu}_{1.80}\text{Te}$, $\text{Cu}_{1.85}\text{Te}$, $\text{Cu}_{1.96}\text{Te}$ in the temperature range of 298–658 K. To increase the reliability of the results obtained, we jointly calorimetry was used with high-temperature X-ray diffraction analysis. Phase transitions accompanied by release or absorption of heat are well defined by differential scanning calorimetry. Synchronous TG-DSC curves were obtained for nonstoichiometric compositions of copper telluride $\text{Cu}_{1.96}\text{Te}$, $\text{Cu}_{1.85}\text{Te}$, $\text{Cu}_{1.80}\text{Te}$, and $\text{Cu}_{1.75}\text{Te}$. The measurements were carried out in the dynamic mode with a programmed change in the shell (heater) temperature at a rate of 10 K/min by heating and cooling in the temperature range of 303–875 K. The results of calorimetric measurements are shown in Figures 4–6. DSC and TG analysis showed that the phase transitions in these compositions are reversible in the

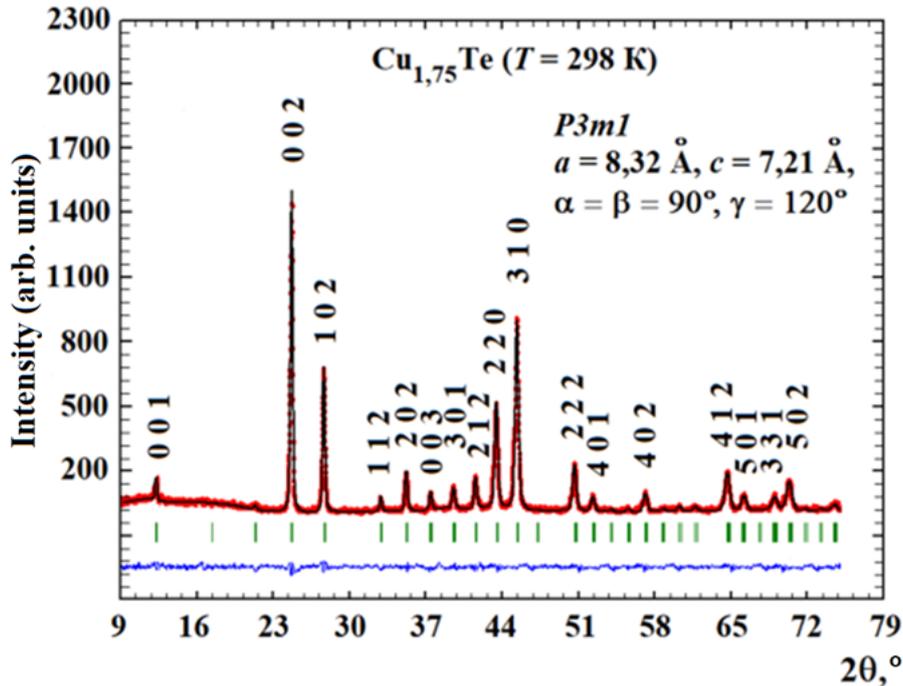


Figure 2. Experimental (red), theoretical (black) X-ray diffraction patterns and difference curve (blue) of the composition $\text{Cu}_{1.75}\text{Te}$ ($R_p = 7.73\%$, $\chi^2 = 1.97$) at $T = 298$ K.

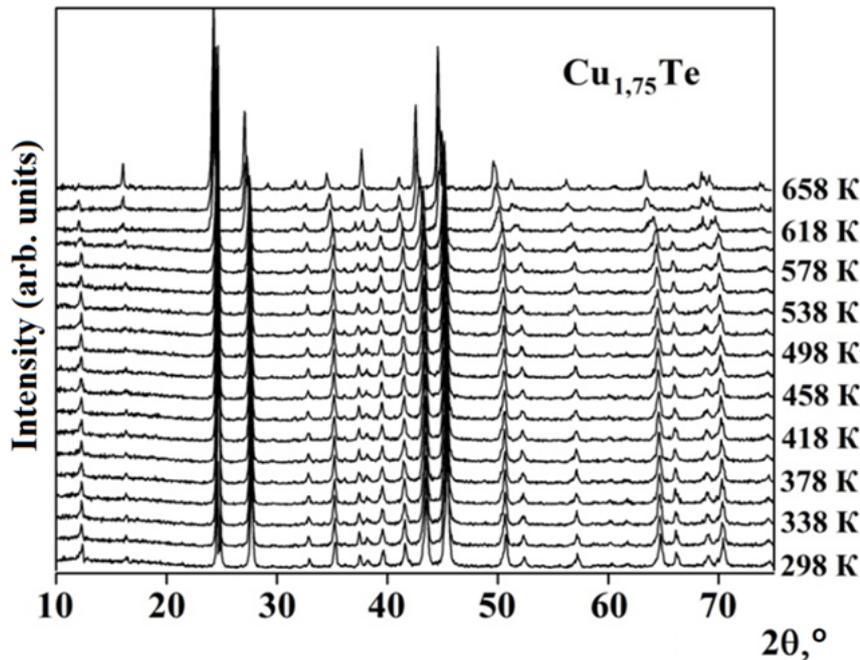


Figure 3. Experimental X-ray diffraction patterns of the composition $\text{Cu}_{1.75}\text{Te}$ in the temperature range 298–658 K.

temperature range of 303–875 K. According to the TG dependences, one can see that there is practically no mass loss of the samples upon heating and cooling. This result allows us to state that the samples under study are stable and the phase transitions are reversible in this temperature range. From the DSC curves of the studied compounds, the temperatures of the onset of phase transitions and the specific heats of phase transitions ΔH were determined.

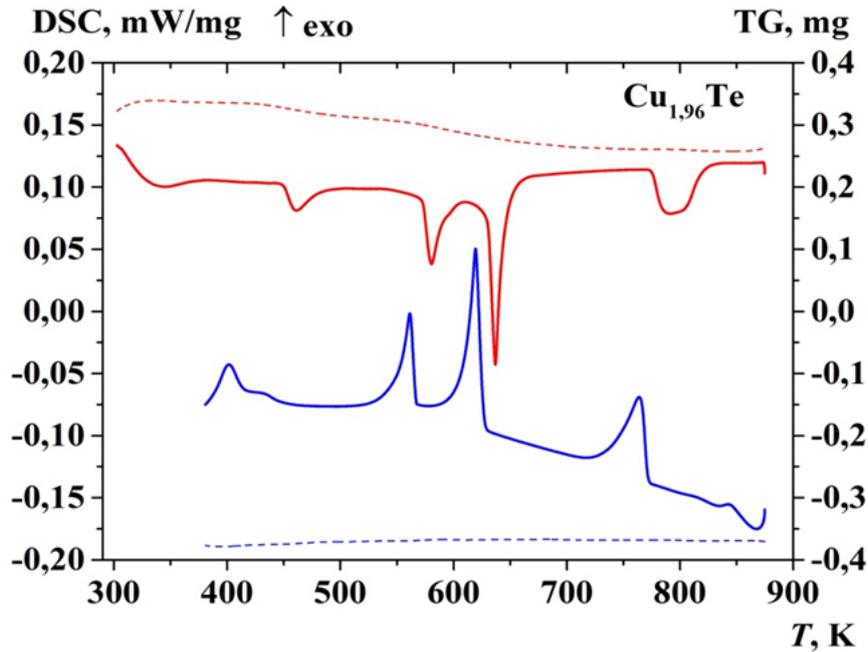


Figure 4. TG (dashed lines) and DSC (solid lines) curves obtained with heating (red) and cooling (blue) for $\text{Cu}_{1.96}\text{Te}$.

Copper telluride $\text{Cu}_{1.96}\text{Te}$ at 298 K is single-phase and is indicated in the orthorhombic system (sp. group $Pmmm$, $a = 7.31 \text{ \AA}$, $b = 22.21 \text{ \AA}$, $c = 36.47 \text{ \AA}$, $\alpha = \beta = \gamma = 90^\circ$) representing the superstructure of Novotny's hexagonal phase with lattice parameters $a \approx \sqrt{3}a_0$, $b \approx 3c_0$, $c \approx 5c_0$. According to X-ray diffraction studies, phase transitions in the $\text{Cu}_{1.96}\text{Te}$ compound are observed at temperatures of 395, 450, 538, 578 and 633 K, which are confirmed both by the results of DSC measurements (Figure 4) and by the phase diagram for the Cu-Te system. According to the DSC curves for copper telluride $\text{Cu}_{1.96}\text{Te}$, phase transitions are revealed at temperatures of 450, 572, 631 and 776 K. In the phase diagram, refined in the temperature range 593–673 K on the basis of coulometric measurements, a phase transition occurs at a temperature of 633 K. Phase transitions observed in $\text{Cu}_{1.96}\text{Te}$ are in good agreement with the results obtained for Cu_2Te [8].

It should be noted that the phase transitions in copper telluride $\text{Cu}_{1.96}\text{Te}$ in the temperature range 298–658 K represent polymorphic transformations of one structural modification into another, accompanied by the formation of a number of single-phase and two-phase regions.

Copper telluride $\text{Cu}_{1.85}\text{Te}$ at room temperature [9] is single-phase and crystallizes in the hexagonal syngony with space group $P3m1$ and lattice parameters $a = 8.38 \text{ \AA}$, $c = 21.73 \text{ \AA}$, $\alpha = \beta = 90^\circ$, $\gamma = 120^\circ$. The unit cell parameters of copper telluride $\text{Cu}_{1.85}\text{Te}$ monotonically increase with increasing temperature, showing a linear dependence up to a temperature of $\sim 613 \text{ K}$. At a temperature of 613 K, the low-temperature hexagonal phase (sp. group $P3m1$) transforms into a high-temperature hexagonal phase (sp. group $P6/mmm$, $a \approx a_0$, $c \approx 3c_0$). In the temperature range 615–658 K, the $\text{Cu}_{1.85}\text{Te}$ compound is also single-phase. At a temperature of 707 K, the high-temperature hexagonal phase transforms into the FCC phase. These results are in good agreement with the literature data

[8].

The hexagonal structure of copper telluride of non-stoichiometric composition $\text{Cu}_{1.80}\text{Te}$ with the space group $P3m1$ is similar to the compound $\text{Cu}_{1.85}\text{Te}$. The low-temperature hexagonal modification $\text{Cu}_{1.80}\text{Te}$ exists up to a temperature of $\sim 533\text{ K}$, above which, according to the results of DSC measurements and X-ray diffraction analysis, a phase transition to the second hexagonal phase begins with cell parameters $a = 8.462\text{ \AA}$, $c = 21.746\text{ \AA}$, $\alpha = \beta = 90^\circ$, $\gamma = 120^\circ$ (sp. group $P3m1$). At 615 K , a phase transition occurs to the high-temperature hexagonal modification ($a = 12.70\text{ \AA}$, $c = 21.65\text{ \AA}$, $\alpha = \beta = 90^\circ$, $\gamma = 120^\circ$, sp. group $P6/mmm$), which exists in a narrow temperature range $615\text{--}648\text{ K}$. Above a temperature of 648 K , there is a two-phase region consisting of high-temperature hexagonal and orthorhombic ($a = 15.400\text{ \AA}$, $b = 7.567\text{ \AA}$, $c = 6.423\text{ \AA}$, $\alpha = \beta = \gamma = 90^\circ$, sp. group $Pmmm$) phases, which is the nucleus upon transition to the high-temperature FCC lattice. At 713 K , the hexagonal modification of the structure transforms into the FCC phase with the lattice parameter $a = 6.097\text{ \AA}$. The phase transitions in $\text{Cu}_{1.80}\text{Te}$ observed at temperatures of 528 , 618 and 660 K on the DSC curves (Figure 5) are a good confirmation of the results obtained.

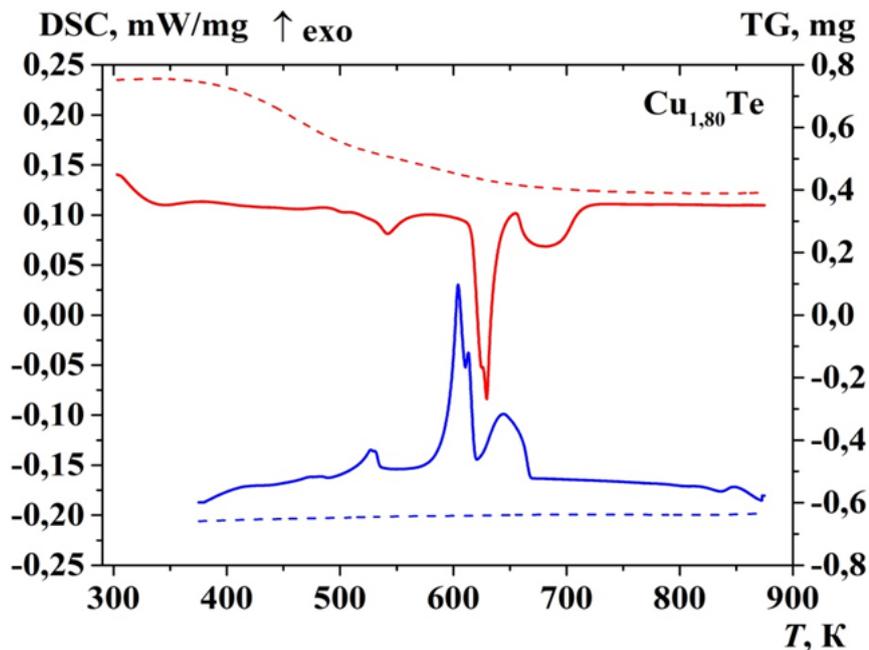


Figure 5. TG (dashed lines) and DSC (solid lines) curves obtained with heating (red) and cooling (blue) for $\text{Cu}_{1.80}\text{Te}$.

Copper telluride of non-stoichiometric composition $\text{Cu}_{1.75}\text{Te}$ at room temperature is also single-phase and is indexed in the hexagonal syngony [10] with space group $P3m1$ and lattice parameters $a = 8.31\text{ \AA}$, $c = 7.21\text{ \AA}$, $\alpha = \beta = 90^\circ$, $\gamma = 120^\circ$, which is a layered superstructure of the Novotny phase with parameters $a \approx 2a_0$ and $c \approx c_0$. In the temperature range of $298\text{--}538\text{ K}$, the parameters of the hexagonal (I) phase grow monotonically, and $\text{Cu}_{1.75}\text{Te}$ is single-phase in the indicated temperature range (Figure 6).

In the temperature range of $540\text{--}658\text{ K}$, this compound is two-phase, consisting of a set of two-phase regions in rather narrow temperature ranges: $540\text{--}618$

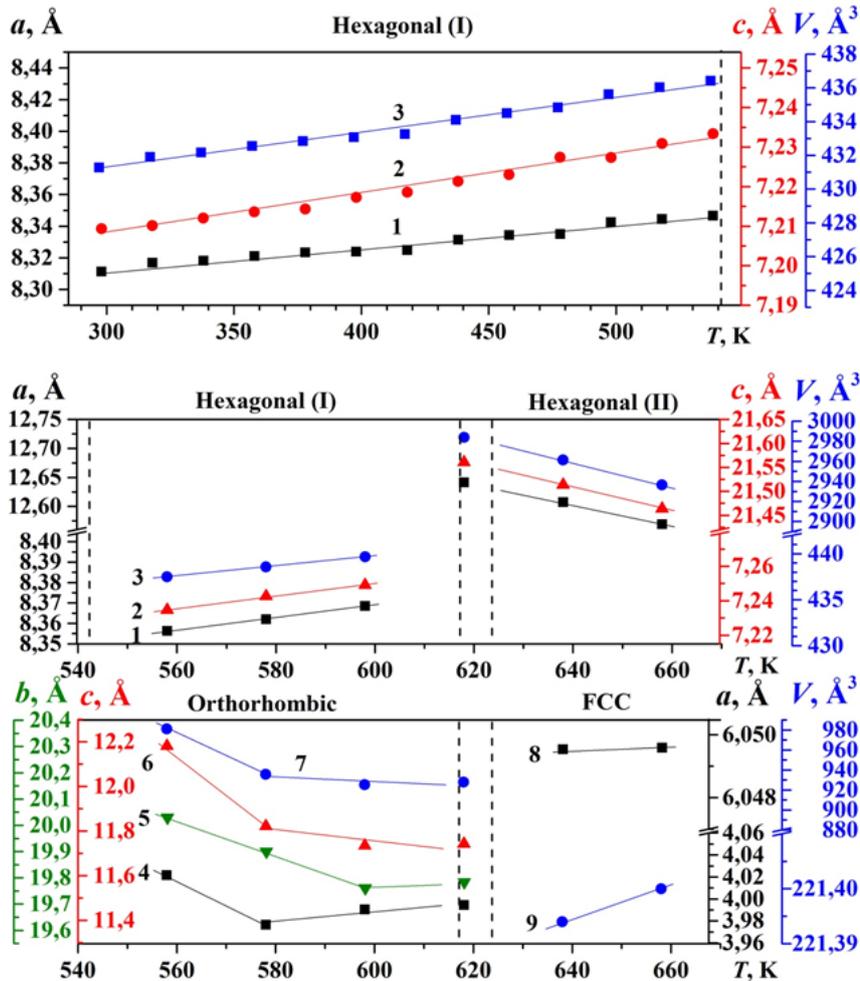


Figure 6. Dependence of unit cell parameters and volume of copper telluride of composition $\text{Cu}_{1.75}\text{Te}$ in the temperature range 298–658 K: 1,2,3 – parameters a , c and V of hexagonal (I) and hexagonal (II), 4,5,6,7 – parameters a , c , b and V of the orthorhombic phase, 8,9 – parameters a and V of the FCC phase, respectively.

K is the first two-phase region, consisting of hexagonal (I) and orthorhombic ($a = 3.99 \text{ \AA}$, $b = 19.74 \text{ \AA}$, $c = 11.96 \text{ \AA}$, $\alpha = \beta = \gamma = 90^\circ$, sp. group $Pmmm$) phases; 618–623 K – second narrow two-phase region consisting of hexagonal (II) (sp. group $P6/mmm$, $a = 12.67 \text{ \AA}$, $c = 21.59 \text{ \AA}$, $\alpha = \beta = 90^\circ$, $\gamma = 120^\circ$) and orthorhombic phase; 623–658 K is the third two-phase region, consisting of hexagonal (II) and FCC (sp. group $Fm\bar{3}m$, $a = 6.04 \text{ \AA}$, $\alpha = \beta = \gamma = 90^\circ$) phases.

According to the DSC curves (Figure 7), copper telluride $\text{Cu}_{1.75}\text{Te}$ undergoes phase transitions at temperatures of 504, 543, 621 and 630 K, which are clearly manifested in the temperature dependence of the unit cell parameters, confirming the results of calorimetric measurements. The specific heats of phase transitions ΔH for the $\text{Cu}_{1.75}\text{Te}$ compound at temperatures of 504 and 543 K are $(0.13 \pm 0.02) \text{ kJ/mol}$ and $(1.45 \pm 0.15) \text{ kJ/mol}$, respectively (for $\text{Cu}_{1.75}\text{Te} - 1 \text{ J/g} \approx 0,2388 \text{ kJ/mol}$). Due to the strong superposition of the peak areas for the phase transitions at 621 and 630 K, the total heat of the phase transition was determined to be $(6.62 \pm 0.67) \text{ kJ/mol}$.

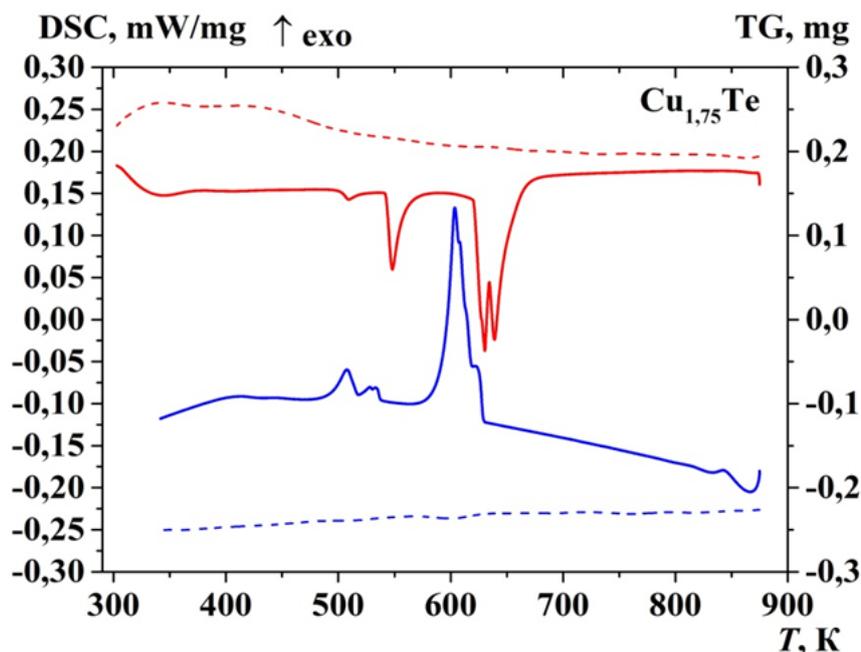


Figure 7. TG (dashed lines) and DSC (solid lines) curves obtained with heating (red) and cooling (blue) for $\text{Cu}_{1.75}\text{Te}$.

Conclusions

The model computer calculations performed at a temperature $T = 0$ K and a pressure $p = 1$ atm. using the USPEX evolutionary algorithm revealed the Cu_5Te_4 , Cu_3Te_2 and Cu_7Te_4 compositions, which are indicated in the triclinic and monoclinic syngonies. In the $\text{Cu}_{1.75}\text{Te}$ compound, the transition of the low-temperature hexagonal modification to the high-temperature FCC phase, similarly to copper tellurides $\text{Cu}_{1.96}\text{Te}$, $\text{Cu}_{1.85}\text{Te}$, $\text{Cu}_{1.80}\text{Te}$, occurs through a series of polymorphic phase transformations associated with the redistribution of lattice atoms to energetically favorable positions. At 698 K, copper telluride of non-stoichiometric composition $\text{Cu}_{1.75}\text{Te}$ completely transforms into the FCC phase and becomes single-phase [11, 12].

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