POLYMORPHİC TRANSFORMATİONS İN
$Cu_{2-x}A_xTe$ (A = Ag, Zn; x = 0.5) CRYSTALS

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ABSTRAC
In this work it have been considered polymorphic transformations in Cu_2Te crystals and an influence of partial isomorphic substitution copper atoms with silver and zinc atoms on the structure, phase formation and temperature of the polymorphic transformations.

Keywords: transformations, polymorphic, temperature, zinc atoms, isomorphic.

I. INTRODUCTION
For this purpose $Cu_{2-x}A_xTe$ (A = Ag, Zn; x = 0.5) crystals were synthesized and grown up by the Bridgman's method. High-temperature diffractometric investigations have been carried out with the DRON-3M diffractometer [CuK_α ($\lambda_\alpha = 1.5418$Å), Ni filter] with URVT – 2000 high-temperature device at vacuum 10^{-1} Pa. Taking survey was 0.1^0. The continuous scanner procedure was used. During experiments the error of reflection angle determination did not exceed the value of $\Delta\theta=0.02^0$.

II. EXPERIMENTS
1. Cu_2Te
In [1], it was shown that Cu_2Te crystallize into hexagonal modification with lattice parameters $a_0=4.237$Å, $c_0=7.274$Å, spatial group of symmetry of $D_{6h}^1 - P6/mmm$. The elementary cell consisted z=2, and density was $\rho=7.33g/cm^3$. According to [2,3] for Cu_2Te crystals at room temperature is characteristic for the orthorhombic modification with lattice parameters $a=a_0\sqrt{3}=7.319$Å, $b=3a_0\sqrt{3}=22.236$Å, $c=5c_0=36.458$Å, which is the superstructure of hexagonal modification. In [4-10] by using DTA method, electroconductivity measurements and X-ray graph method it was shown that in the interval of 290 to 900K in Cu_2Te crystals it is observed five structured transformations at 433, 531, 590, 633 and 835K. In [11] it was established that Cu_2Te crystals in the interval of 290 to 453K are two-phased, one of which is crystallized in orthorhombic modification with lattice parameters corresponding the lattice parameters given in [2,3], and hexagonal one is crystallized with parameters a=4.1481Å, c=7.1833Å. In

the interval of 290 to 418K the crystal retains its two-phased property. At 448K the second hexagonal phase is extracted from a two-phased sample with parameters a=8.4191Å, c=21.8733Å.
As seen in fig.1, the formed second hexagonal modification does not affect the first hexagonal modification parameters.
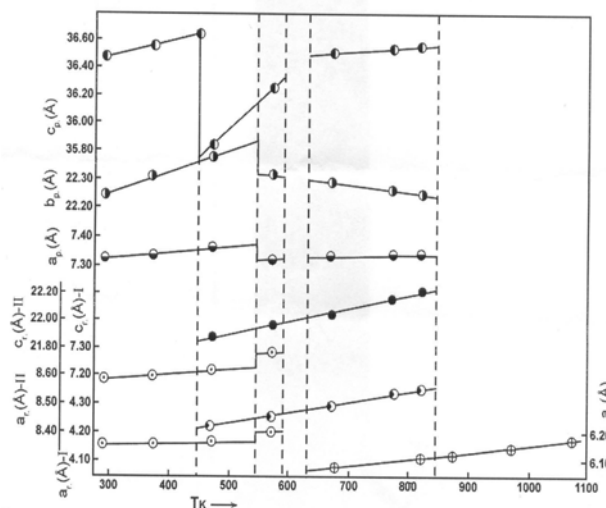

Fig.1 Temperature dependence of parameters of the crystalline lattice with existing modifications of Cu_2Te

However, with formation of this second hexagonal modification, the c parameter value of the orthorhombic modification sharply reduces, $\Delta c=0.72$Å. This fact makes it possible to conclude that this second hexagonal phase is formed for count of orthorhombic modification. At 504K a and c parameters of the first hexagonal modification jump-wise increase while a and b parameters of the orthorhombic modification jump-wise decrease. In this case probably cation displacements occur. At 590K both orthorhombic and first hexagonal modifications turn to the second hexagonal phase and the Cu_2Te crystal becomes one-phased. As in this case the

parameters of the second hexagonal modification don't change the second hexagonal modification plays role of epitaxy. Thus in the interval of 590 to 638K Cu$_2$Te crystal becomes one-phased. At 638K with appearance of reflection from (111) plane of high-temperature FCC phase, the orthorhombic modification is anew restored. At 848K the orthorhombic modification and second hexagonal phase both transform into FCC modification with the lattice parameter of a=6.1140Å. On the fig.1 it have been displayed the temperature dependence of parameters of elementary cells of all existing modifications of Cu$_2$Te in the range of 290 to 900K. All

mentioned transitions are reversible and at cooling down at room temperature the crystal gradually turns to it's the original state. From the temperature dependence of lattice parameters of all modifications the heat expansion in main crystallographic directions, shown in table 1, is calculated. The coefficient of the thermal expansion at 290K of Cu$_2$Te first hexagonal modification has some anisotropies in interval of 290 to 590K, while for the second hexagonal modification, formatted at 448K the anisotropy of the thermal expansion is absent ($\alpha_{[100]} = \alpha_{[001]}$).Sharply pronounced anisotropies have the orthorhombic modification.

Table 1. Thermal expansion of Cu$_2$Te crystal modifications

Cu$_2$Te	Temperature, K	$\alpha_{[100]}10^{-6}K^{-1}$	$\alpha_{[010]}10^{-6}K^{-1}$	$\alpha_{[001]}10^{-6}K^{-1}$	$\bar{\alpha} = \dfrac{\sum \alpha_i}{3} \cdot 10^{-6}K^{-1}$
I Hexagonal	290-373	34.62		17.78	16.77
	290-473	34.73		29.59	29.56
	290-573	50.34		45.59	45.18
II Hexagonal	473-573	37.89		37.99	37.92
	473-673	39.52		39.52	39.50
	473-773	45.57		43.87	45.01
	473-821	45.80		45.76	45.77
Orthorhombic	290-373	17.12	37.39	30.73	28.41
	290-473	32.18	32.02	-94.32	-30.12
	290-573	-0.10	11.74	-20.18	-8.54
	290-773	6.54	2.36	4.77	4.56
	290-821	4.45	1.16	5.45	3.69
FCC	673-773	32.883			
	673-821	35.216			
	673-873	32.883			
	673-973	35.898			
	673-1073	37.405			

2. Cu$_{1.50}$Ag$_{0.50}$Te

The thin plate in size 2x4x4 mm was cut from crystalline bar Cu$_{1.50}$Ag$_{0.50}$Te and obtained diffractograms at room temperature was induced on the base of lattice parameters a=7.3193Å, b=22.2435Å, c=36.3636Å of the orthorhombic phase of Cu$_2$Te and a=3.1216Å, b=4.0423Å, c=6.8708Å of the orthorhombic phase of CuAgTe. From thence it follows that Cu$_{1.50}$Ag$_{0.50}$Te crystals are two-phased at room temperature, i.e. they are crystallized in orthorhombic structure of Cu$_2$Te and CuAgTe, and therewith the relative quantity of Cu$_2$Te is larger than that of CuAgTe. In fixed diffraction reflections at room temperature until 423K it is no change. Only at 469K low-temperature two-phased Cu$_{1.50}$Ag$_{0.50}$Te crystal transforms into two primitive cubic phases with lattice parameters of a$_1$ = 7.009Å and a$_2$ = 6.878Å, which differ in the elementary cell parameters and intensities of diffraction reflection where $I^1_{220} > I^2_{220}, I^1_{222} > I^2_{222}, I^1_{320} > I^2_{320}, I^1_{400} > I^2_{400}$.

On further heating both primitive cubic phases keep their own individuality, but on reverse below 469K, they transform into two ordered phases, one of these with lattice parameters is identical to Cu$_2$Te low-temperature phase, and the other is identical to CuAgTe. As it is pointed out, low-temperature orthorhombic phase of Cu$_2$Te at 848K via four intermediate phase transformations is transformed to high-temperature FCC modification with a=6.114Å. In respect of the second phase, i.e. CuAgTe, it is known that at room temperature it is crystallized in structural type of orthorhombic phase of CuTe with parameters a=3.12Å, b=4.05Å, c=6.875Å, d=8.20Å.

In fig.2, it is presented the temperature dependence of Cu$_{1.50}$Ag$_{0.50}$Te lattice parameters. a(T), b(T), c(T) parameters of both orthorhombic phases and a(T) ones of both primitive cubic lattice, increase linearly.

Coefficients of the linear expansion, calculated from lattice parameters of existing phase, are listed in table 2.
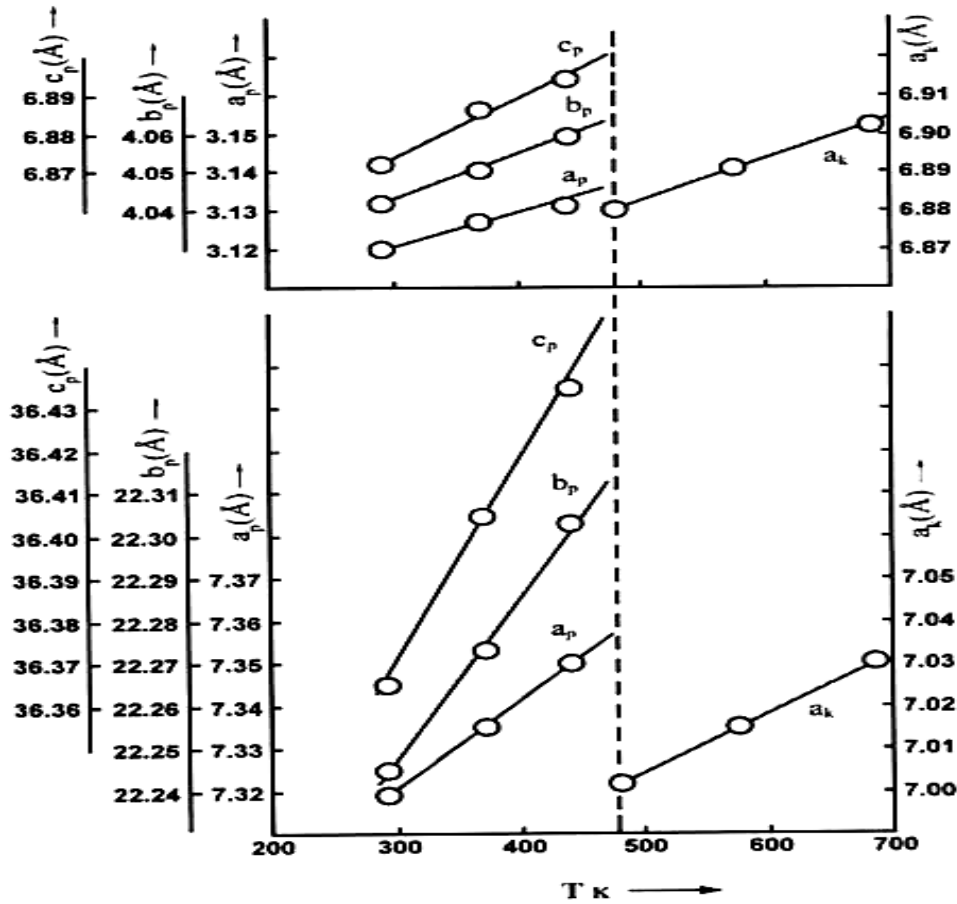
Fig.2 Temperature dependence of the lattice parameters of both orthorhombic and cubic phases of Cu$_{1.50}$Ag$_{0.50}$Te crystal

Table 2. The coefficients of thermal expansion of Cu$_{1.50}$Ag$_{0.50}$Te crystals

Modification	Temperature K	a$_{[100]}$ 10^{-6}K^{-1}	a$_{[010]}$ 10^{-6}K^{-1}	a$_{[001]}$ 10^{-6}K^{-1}	$\overline{\alpha} = \dfrac{\sum \alpha_i}{3}$
Cu$_2$Te	293-373	29.7	16.7	16.0	20.8
	293-423	29.8	22.7	13.6	20.0
CuAgTe	293-373	25.6	30.6	27.7	28.0
	293-423	23.7	37.9	26.0	29.2
P$_1$	473-573	0.80			
P$_2$	473-573	17.3			

As seen from table 2, the second orthorhombic phase is crystallized with the Cu$_2$Te structural type and deformed in direction [100], i.e. $\alpha_{[100]} > \alpha_{[010]} \approx \alpha_{[001]}$, and the orthorhombic phase, that crystallized with the CuAgTe structural type, is deformed in the direction [010], i.e. $\alpha_{[100]} < \alpha_{[010]} > \alpha_{[001]}$. It is one of reason of instability of both orthorhombic phases, at 469K each of which is transformed to own high-temperature primitive cubic phase.

It is should be emphasized that Cu$_{1.50}$Ag$_{0.50}$Te crystals at room temperature are two-phased and crystallized in the Cu$_2$Te and CuAgTe structural type, but neither temperature transformation nor structures of high-temperature modifications correspond their high-temperature modification.

3. Cu$_{1.50}$Zn$_{0.50}$Te

Fixed at room temperature (290K) diffraction reflections from Cu$_{1.50}$Zn$_{0.50}$Te crystal induce on the base of

parameters of the orthorhombic superstructure modification of Cu_2Te, with a=7.3192Å, b=22.2362Å, c=36.4581Å and some from fixed reflections are also induced on the base of parameters of the hexagonal modification with a=4.2478Å, c=7.2335Å. After determining the two-phased property of $Cu_{1.50}Zn_{0.50}Te$ a furnace was switched and at 50K intervals it was carried out diffraction records. Sample temperature before the

every record beginning is held constant for 30 minutes. Under these conditions down to 773K the number of diffractions and their intensities, fixes at room temperature, does not change. At 811±2K the orthorhombic modification in full transformed into the hexagonal modification. When passing from the orthorhombic modification into the hexagonal one, the latter is as priming. For this reason on the temperature dependence of parameters of an elementary cell of the hexagonal modification a jump is not observed (fig.3).
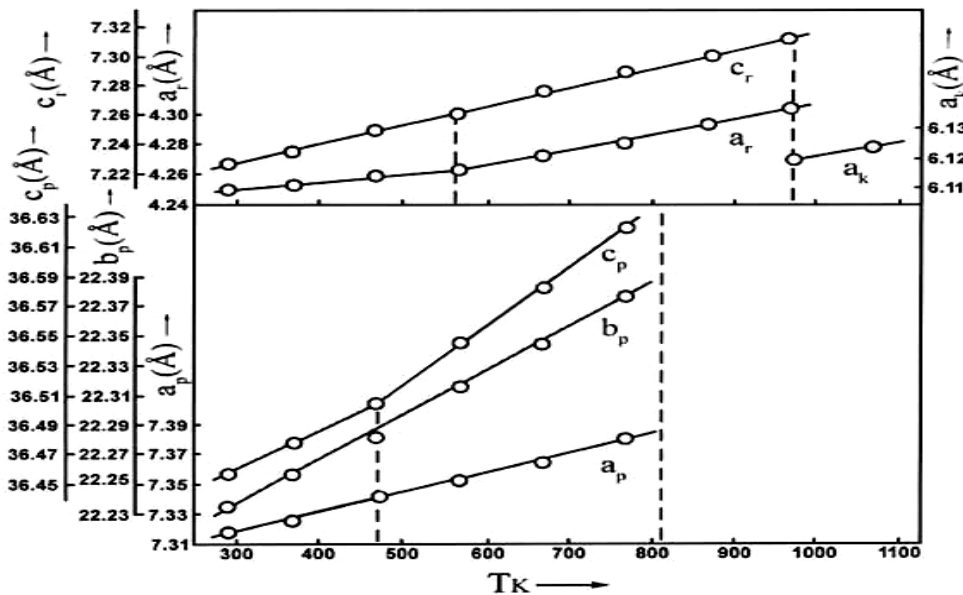

Fig.3 Temperature dependence of lattice parameters of $Cu_{1.50}Zn_{0.50}Te$ orthorhombic, hexagonal and cubic modifications

At 970K the hexagonal modification transformed into a high-temperature FCC phase with parameter a=6.1187Å. On cooling a sample up to room temperature the diffraction picture in full restored into reverse continuity. In fig.3, it have been displayed the temperature dependence of parameters of an elementary cell of all existing phases $Cu_{1.50}Zn_{0.50}Te$ crystal in the interval of 290-1000K. It is seen that a_O , c_H and a_{FCC} parameters in dependence on temperature linearly increase and in in curves of the temperature dependence of b_0, c_0 at 470K and a_H at 570K it was observed small excesses. It is probably associated with the cation re-distribution.

At 290K the coefficients of the thermal expansion have next values: for orthorhombic phase $\alpha_{[100]} = 11.9; \alpha_{[010]} = 11.9; \alpha_{[001]} = 7.0$, for hexagonal phase : $\alpha_{[100]} = 14.4; \alpha_{[001]} = 1.2$ and for FCC phase $\alpha = 13.2$. It should be emphasized that in interval 290-972K the marked anisotropy of thermal expansion was observed.

III. CONCLUSION

In structural transformations of Cu_2Te, $Cu_{1.50}Ag_{0.50}Te$ and $Cu_{1.50}Zn_{0.50}Te$ crystals isomorphic replacement of a part

of copper atoms by Ag and Zn atoms in Cu_2Te brings out to cut down of number of complex phase transitions, i.e. in $Cu_{1.50}Ag_{0.50}Te$ crystal, which at room temperature consist of two orthorhombic phases, each of them at 469K transformed in own primitive cubic phase, and in $Cu_{1.50}Zn_{0.50}Te$ which at room temperature consists of orthorhombic and hexagonal phases, the orthorhombic phase at 811K is transformed into hexagonal, and the hexagonal phase at 970K transformed into high-temperature FCC phase. Transformations in considered crystals are reversible and occur by the monocrystal-monocrystal type.

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