INFLUENCE OF COPPER AND SELENIUM ATOMS ON THE CRYSTAL STRUCTURE OF $Ga_{0.5}In_{1.5}S_3$ WITH PARTIAL REPLACEMENT OF GALLIUM AND SULFUR ATOMS BY COPPER AND SELENIUM ATOMS

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It has been established that the structure of $Ga_{0,5}In_{1,5}S_3$ crystals, characterized by TOTE and TOTEOOE structural types, with the replacement of 1/3 of the gallium atoms by copper atoms, the $Cu_{0,5}Ga_{0,33}In_{1,5}S_3$ structure becomes the TOTTE type (a = 3.861 Å, c = 30.915 Å, sp. gr. $P6_3mc$), and with the subsequent replacement of 1/6 of the sulfur atoms by selenium, the $Cu_{0,5}Ga_{0,33}In_{1,5}S_{2,5}Se_{0,5}$ structure becomes the TTOTTE type (a = 3.866 Å, c = 18.695 Å, sp. gr. P3m1).

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INTRODUCTION

The $Ga_{0,5}In_{1,5}S_3$ crystals crystallize in a structure with the lattice parameters: a = 3.819 Å, c = 21.12 Å, sp. gr. $P\bar{3}m1$[1] and a = 3.82 Å, c = 63.41 Å, sp. gr. R3m with the structural type… ${}_hT_cO_cT_hE_cO_cO_cE$…[2, 3], where O, T and E are the designations of octahedral, tetrahedral and empty layers, respectively, h and c denote the hexagonal and cubic, respectively, types of packing of S atoms in the anion layers.

The aim of this work is to establish the influence of partial replacement of gallium and sulfur atoms with copper and selenium atoms on the structures of polytypic modifications of $Ga_{0,5}In_{1,5}S_3$.

EXPERIMENTAL PART AND RESULT DISCUSSION

The $Cu_{0,5}Ga_{0,33}In_{1,5}S_3$ and $Cu_{0,5}Ga_{0,33}In_{1,5}S_{2.,5}Se_{0,5}$ compositions were synthesized. Samples for electron diffraction studies were prepared by depositing microcrystals from an aqueous suspension onto a metal grid covered with a celluloid film. Electron diffraction patterns from textures were recorded using an EG-400 high-voltage electronograph.

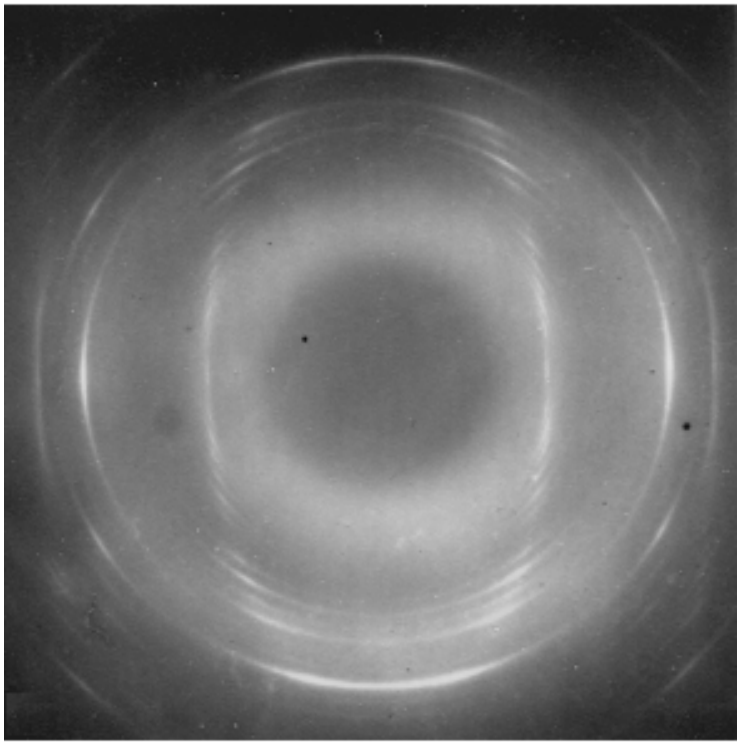

Fig. 1. Electron diffraction pattern of $Cu_{0,5}Ga_{0,33}In_{1,5}S_3$ textures.

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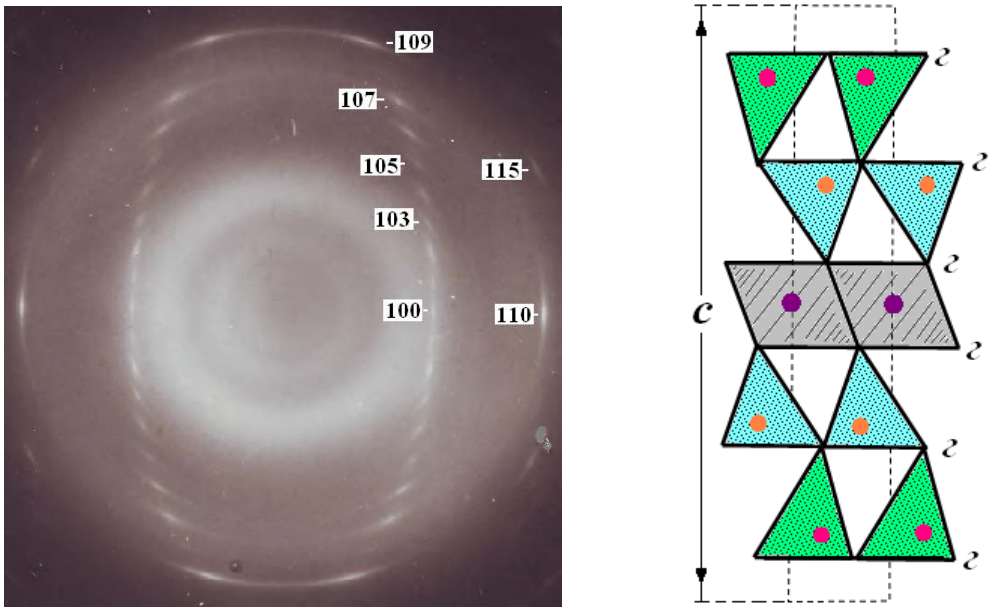

Fig.2. a) Electron diffraction pattern of $Cu_{0,5}Ga_{0,33}In_{1,5}S_{2.,5}Se_{0,5}$ textures.
b) Projection of the structure of $Cu_{0,5}Ga_{0,33}In_{1,5}S_{2.,5}Se_{0,5}$ on the plane $(11\bar{2}0)$.

The decoding of electron diffraction patterns was carried out using the following formulas for oblique textures [4]:

$$d_{100} = \sqrt{3}\,a/2 = 2L\lambda h/2R_{h00}, \quad (1)$$

$$D_{hkl} = (R^2_{hkl} - R^2_{hk0})^{1/2}, \quad (2)$$

$$\Delta D = c^*L\lambda = (D_{hkl} - D_{hk(l-1)}), \quad (3)$$

$$d_{001} = c = 1/c^* = L\lambda/\Delta D. \quad (4)$$

Fig. 1 shows the electron diffraction pattern of $Cu_{0,5}Ga_{0,33}In_{1,5}S_3$ textures. The lattice parameters were determined from this electron diffraction pattern: a=3.861Å, c=30.915Å. There are no reflections with the value l≠2n in the series $hh2\bar{h}l$ on the electron diffraction pattern. This indicates that the crystal structure is built from two identical packets. It was established that the structure has the space group $P6_3mc$. The second strong reflection in the series $11\bar{2}l$ is the reflection $11\bar{2}8$. The value l = 8 indicates that the unit cell consists of two TTO$\bar{T}$E types of packets [5] and, therefore, the structure of $Cu_{0,5}Ga_{0,33}In_{1,5}S_3$ is an isostructural analogue of the structure of the 2H polytype $Zn_2In_2S_5$[6].

Fig. 2a shows the electron diffraction pattern from the $Cu_{0,5}Ga_{0,33}In_{1,5}S_{2.,5}Se_{0,5}$ textures, where there are no systematic extinctions of reflections. The second strong reflection $11\bar{2}5$ is clearly distinguished on the second ellipse (the strongest in the series $11\bar{2}l$ is the reflection $11\bar{2}0$). The lattice parameters were determined: a = 3.866 Å, c = 18.695 Å, sp. gr. P3m1 and the structural type …TTOTTE…. By comparing the experimental and calculated values of the reflection intensities, the type of packing of the anion layers was established …hhhhhh…. The structure of $Cu_{0,5}Ga_{0,33}In_{1,5}S_{2.,5}Se_{0,5}$ is identical to the structure of $Zn_3In_2S_6$ [7] and $GaInS_3$ [8]. Fig. 2b shows the projection of the structure $Cu_{0,5}Ga_{0,33}In_{1,5}S_{2.,5}Se_{0,5}$ (i.e. $CuGa_{0,67}In_3S_5Se$) on the plane $(11\bar{2}0)$.

CONCLUSION

It has been established that the structure of $Ga_{0,5}In_{1,5}S_3$ crystals, characterized by TOTEOOE structural types, becomes TOTTE type when 1/3 of gallium atoms are replaced by copper atoms, and becomes TTOTTE type when sulfur (S) atoms are subsequently replaced by selenium (Se). The latter is probably due to an increase in the size of one of the tetrahedral voids in the unit cell, on which cations with a large ionic radius (i.e. indium atoms) can freely be located.

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