

## A NEW THREE-PACKET RHOMBOHEDRAL POLYTYPE IN $\text{Cu}_{0,5}\text{Ga}_{0,33}\text{In}_{1,5}\text{S}_{2,5}\text{Se}_{0,5}$ CRYSTALS

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A new 3R polytype with lattice parameters  $a = 3.866 \text{ \AA}$ ,  $c = 56.085 \text{ \AA}$ , and space group R3m was identified using rotational electron diffraction patterns of a thin single-crystal film of  $\text{Cu}_{0,5}\text{Ga}_{0,33}\text{In}_{1,5}\text{S}_{2,5}\text{Se}_{0,5}$  crystals.

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### INTRODUCTION

The crystal structures of the ternary and quaternary layered crystals in the Cu-Ga-In-S-Se system have the TTOTTE, TOTTE, TOTE, TOTE<sub>1</sub>OOE<sub>1</sub>, and TOTE<sub>1</sub>OOE<sub>1</sub>TOTE<sub>2</sub> structural types. Where T and O denote the tetrahedral and octahedral layers, respectively, E-denotes empty layers, and E<sub>1</sub> and E<sub>2</sub> denote partially filled (less than 1/3) polyhedral layers [1].

The work [2] publishes the crystal structure of the single-packet trigonal (1T) polytype of  $\text{Cu}_{0,5}\text{Ga}_{0,33}\text{In}_{1,5}\text{S}_{2,5}\text{Se}_{0,5}$  crystals. The crystal lattice parameters are  $a=3.866\text{\AA}$ ,  $c=18.695\text{\AA}$ . The space group is P3m1 and the structural type is TTOTTE. This type of structure was observed for the first time in the among of layered crystals included in the Cu-Ga-In-S-Se system.

### EXPERIMENTAL PART AND RESULT DISCUSSION

Thin single-crystal films of  $\text{Cu}_{0,5}\text{Ga}_{0,33}\text{In}_{1,5}\text{S}_{2,5}\text{Se}_{0,5}$  crystals were obtained by peeling them off a thick crystal using adhesive tape, which was then glued flat to a washer. The washers were positioned on the surface of the crystal holder, with the inlet opening approximately 0.8–1 mm in diameter and the outlet opening approximately 1.5–2 mm in diameter.

Electron diffraction patterns were recorded using a high-voltage electronograph EG-400 ( $V \approx 250\text{kV}$ ,  $2L\lambda = 39,4 \text{ mm}\cdot\text{\AA}$ ).

Figure 1 shows an electron diffraction pattern from a thin single-crystal film (SCF) of  $\text{Cu}_{0,5}\text{Ga}_{0,33}\text{In}_{1,5}\text{S}_{2,5}\text{Se}_{0,5}$ , where the SCF is tilted at an angle of  $\varphi = 60^\circ$  (the  $hk0$  plane of the reciprocal lattice is located in the SCF plane) from a position perpendicular to the incident electron beam and rotated at an angle of  $\omega = 60^\circ$  around an axis perpendicular to the film plane.

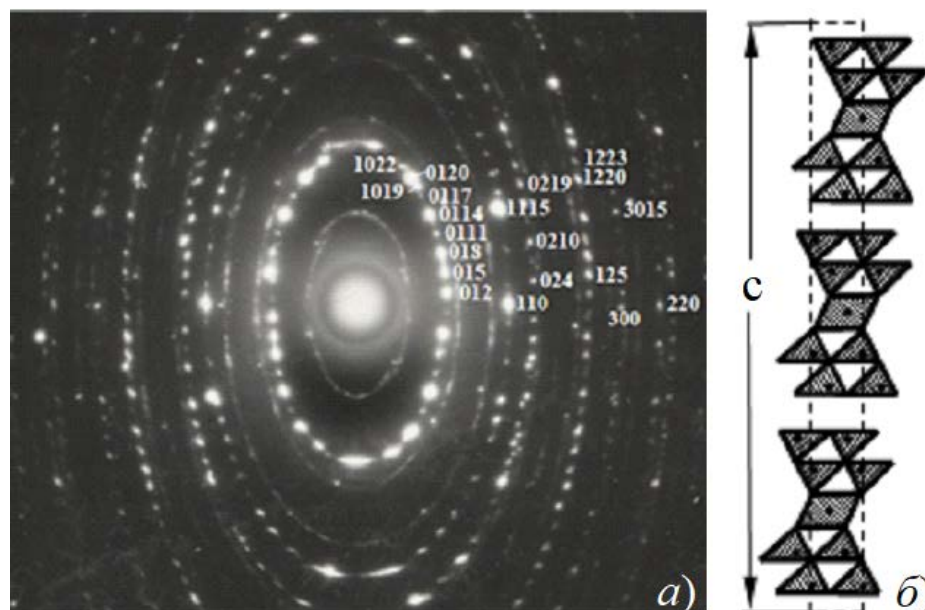


Fig. 1. a) Rotation electron diffraction pattern of a thin single-crystal film of  $\text{Cu}_{0,5}\text{Ga}_{0,33}\text{In}_{1,5}\text{S}_{2,5}\text{Se}_{0,5}$ , b) projection of the crystal structure onto the  $(21\bar{1}0)$  plane.

The decoding of electron diffraction patterns was carried out using the following formulas for oblique textures [3]:

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

$$D_{hk} \mathbf{I} = (R_{hkl}^2 - R_{hk0}^2)^{1/2}, \quad (2)$$

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

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

The presence of extinctions of the type  $-h + k + l \neq 3n$  indicates the rhombohedral structure of the sample. This indicates that the crystal structure is built from three identical packets. The second strong reflection in the series  $11\bar{2}l$  is the  $11\bar{2}15$  reflection. The value  $l = 15$  indicates that the unit cell consists of three  $T\bar{T}O\bar{T}E$  types of packets [4]. The structure of  $Cu_{0.5}Ga_{0.33}In_{1.5}S_{2.5}Se_{0.5}$  (i. e.  $CuGa_{0.67}In_3S_5Se$ ) is identical to the structure of  $ZnIn_2Se_4$  [5], and in  $Zn_3In_2S_6$  [6] and  $GaInS_3$  [7] crystals, 1T polytypes were established, in which there is only one such packet.

A new 3R-polytype of the  $Cu_{0.5}Ga_{0.33}In_{1.5}S_{2.5}Se_{0.5}$  crystal was established with the lattice parameters  $a = 3.866 \text{ \AA}$ ,  $c = 56.085 \text{ \AA}$ , space group R3m and with the structural module  ${}_hT_cT_hO_hT_cT_hE$ , where T and O are two-dimensional tetrahedral and octahedral layers, E is an empty interlayer, h and c are hexagonal and cubic packings of the S and Se atomic planes. Weak series of reflections correspond to superlattices with the parameter:  $A = 3^{1/2}a$ . The arrangement of metals

(positions a, b, c) in the closest packing of selenium (positions A, B, C) is as follows:

...A b B c C a B b C c A E C a A b B c A a B b C E B c C a A b C c A a B E...

Figure 2b shows projections of the  $Cu_{0.5}Ga_{0.33}In_{1.5}S_{2.5}Se_{0.5}$  crystal structure onto the  $(21\bar{1}0)$  plane.

Unlike the electron diffraction patterns of oblique textures, where fine structural effects are not revealed and different series of reflections are superimposed, the electron diffraction patterns obtained using new rotational methods reveal fine structural effects and separate different series, i.e., there is no superposition.

## CONCLUSION

Rotational electron diffraction patterns were obtained for a thin single-crystal film of  $Cu_{0.5}Ga_{0.33}In_{1.5}S_{2.5}Se_{0.5}$  crystals.

The  $Cu_{0.5}Ga_{0.33}In_{1.5}S_3$  crystal structure is characterized by the TOTTE structural type. When selenium replaces 1/6 of the sulfur atoms, the  $Cu_{0.5}Ga_{0.33}In_{1.5}S_{2.5}Se_{0.5}$  structure becomes the TTOTTE type. This is likely due to an increase in the size of one of the tetrahedral voids in the unit cell, which can freely accommodate cations with a large ionic radius (i.e., indium atoms).

The rhombohedral 3R polytype of the  $Cu_{0.5}Ga_{0.33}In_{1.5}S_{2.5}Se_{0.5}$  crystal was detected only in a single-crystal sample. This indicates that thick single-crystal samples may contain small amounts of other polytypes [7] that are undetectable by other diffraction methods. This is of great importance in the new era of nanotechnology.

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