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Results of Investigations on the Determination of the Lattice Parameters of the $TlInS_2$ - $TlInSe_2$ System

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Abstract: The article summarizes the results of a systematic study of the influence of the structure and composition of single crystals of the $TlInS_2$ - $TlInSe_2$ system. The equilibrium states of the pseudo binary system $TlInS_2$ - $TlInSe_2$ have been studied by differential-thermal, microstructural and X-ray phase analyses, and the limits of mutual solubility of the initial compounds have been established. It is shown that the grown crystals within ($0,3 \le x \le 1$) on the side of $TlInS_2$ crystallize in the monoclinic system, and on the side of $TlInSe_2$ ($0,3 \le x \le 1$) - in the tetragonal syngony.

Methods: We know that $TlInS_2xSe_{2(1-x)}$ ($0 \le x \le 1$) solid solutions are currently one of the most interesting semiconductor materials. A change in their composition makes it possible to widely vary the electro physical, photoelectric, optical, tensometric, and other properties.

In this regard, we have synthesized and grown single crystals of solid solutions $TlInS_2xSe_{2(1-x)}$ ($0 \le x \le 1$) by the improved Bridgman-Stockbarger method. Highly pure elements of thallium (Tl - 000), indium (In - 000), selenium (Se - OSCh - 17 - 4) and sulfur (S - OSCh - 16 - 5) were used as the initial component. The composition was placed in quartz ampoules, which, after pumping out to 10^{-4} mm Hg. soldered off.

Results: For a comprehensive study of the physical properties, the grown crystals were easily chipped along the basal plane and had a mirror-smooth surface.

The results of X - ray phase analysis of single crystals of the $TlInS_2xSe_{2(1-x)}$ system show that from a comparison of the angles and intensity of reflections, it was proved that at $0 \le x \le 1$ solid solutions are formed based on the $TlInS_2$ compound, and at $0 \le x \le 0,2$ based on $TlInSe_2$.

All X-ray diffraction patterns of $TlInS_{2x}Se_{2(1-x)}$ samples were processed under the same conditions. From the obtained X - ray patterns, inter planar distances (d, Å) were calculated. The intensity of the diffraction Debye lines was estimated on the basis of a ten-point scale. As a result of a thorough X - ray phase analysis, it was shown that the synthesized $TlInS_{2x}Se_{2(1-x)}$ samples are single - phase and the inter planar distances calculated from X-ray patterns can be unambiguously indicated on the basis of a monoclinic lattice with parameters: a~b = 10.95 Å, c = 15, 14Å, $\beta = 100^0$, sp. gr. C_S^4 or C^6_{2h}.

Conclusion: Thus, during the crystallization process, there is a slight deviation from stoichiometry. However, the noted deviations are within the range of homogeneity of the compositions. The limits of mutual solubility of the initial compounds were established: it was shown that the crystal structure of solid solutions $TlInS_{2x}Se_{2(1-x)}$ with a value of $0,3 \le x \le 1$ corresponds to the structure of $TlInS_2$, and at $0 \le x \le 0,2$ - to the structure of $TlInSe_2$.

Keywords: mono crystals, differential-thermic, micro structural, X-ray phase, pseudo binary, monoclinic.

Introduction: In recent years, there has been a sharp increase in interest in the identification of many semiconductor materials, including ternary and more complex compounds. Interest in such semiconductors,

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both from a scientific and practical point of view, is growing every year. Therefore, the expansion of the class of precisely layered semiconductors of the A^{III} B^{III} C_2^{VI} type and solid solutions based on them is one of the cardinal general problems of modern solid state physics and leads to the discovery of many semiconductor materials, including ternary and more complex compounds. The discovery of new materials, the study of the relationship between the composition, structure, and properties of multicomponent semiconductor compounds, in addition to deepening fundamental scientific ideas about semiconductors, also opens up new prospects: new compounds, as a rule, exhibit new qualities and, thereby, contribute to the solution of necessary technical problems.

Solid solutions are currently one of the most interesting semiconductor materials. A change in their composition makes it possible to widely vary the electro-physical, photoelectric, optical, tensometric, and other properties. Solid solutions of layered semiconductors, including $TlInS_{2x}Se_{2(1-x)}$ ($0 \le x \le 1$), are extremely poorly studied, although they have very interesting properties [1–9]. The study of the complex of their physical properties seems to be an urgent task in the field of modern electronic technology.

Results Of The Study And Their Discussion: In this regard, we synthesized single crystals of solid solutions $TlInS_{2x}Se_{2(1-x)}$ ($0 \le x \le 1$). Highly pure elements of thallium (Tl - 000), indium (In - 000), selenium (Se - OSCh - 17 - 4) and sulfur (S - OSCh - 16 - 5) were used as the initial component. The composition was placed in quartz ampoules, which, after pumping out to 10^{-4} mm Hg. soldered off. Then, the ampoules prepared in this way were placed for 2/3 of their length into an inclined synthesis furnace, the temperature of which gradually increased at a rate of 10 deg / h to a value of 1100° C. A total of 11 alloys of the $TlInS_{2x}Se_{2(1-x)}$ system were synthesized at x = 0; 0.1; 0.2; 0.3; 0.4; 0.5; 0.6; 0.7; 0.8; 0.9; 1.0. The single-phase nature of polycrystalline samples was verified using X-ray phase and microstructural analyses.

For a comprehensive study of the physical properties, single crystals were grown by the improved Bridgman - Stockbarger method using electronic temperature controllers to maintain the optimal thermal regime during crystallization. The directional crystallization rate was about 0.9 mm/h. $TlInS_{2x}Se_{2(1-x)}$ single crystals had **p** - type conductivity.

The grown crystals were easily chipped along the basal plane and had a mirror-smooth surface; identification of the results of X-ray diffraction patterns in Fig. 1. The studied $TlInS_{2x}Se_{2(1-x)}$ crystals show that the lattice parameters for the initial components correspond to the literature data.

All reflections on X-ray diffraction patterns are indexed based on the unit cell periods of these compounds, known from the literature [10–14], which confirms that stoichiometric compositions were obtained in each specific case. The color of crystals of $TlInS_{2x}Se_{2(1-x)}$ solid solutions, depending on the composition, changed from light orange to brownish black with a metallic sheen (see Table 1).

Table 1. Characteristic colors of single crystals $TlInS_{2x}Se_{2(1-x)}$ ($0 \le x \le 1$)

Compound	Colour
x=0,8	Gray with a metallic sheen and a yellow tint
x=0,6	Gray with a metallic sheen
x=0,4	Brown with a metallic sheen
x=0,2	Black

X-ray phase analysis of single crystals is the most acceptable and accurate method for studying multicomponent systems. On the other hand, X-ray phase analysis is absolutely indispensable in the study of mixtures of various modifications.

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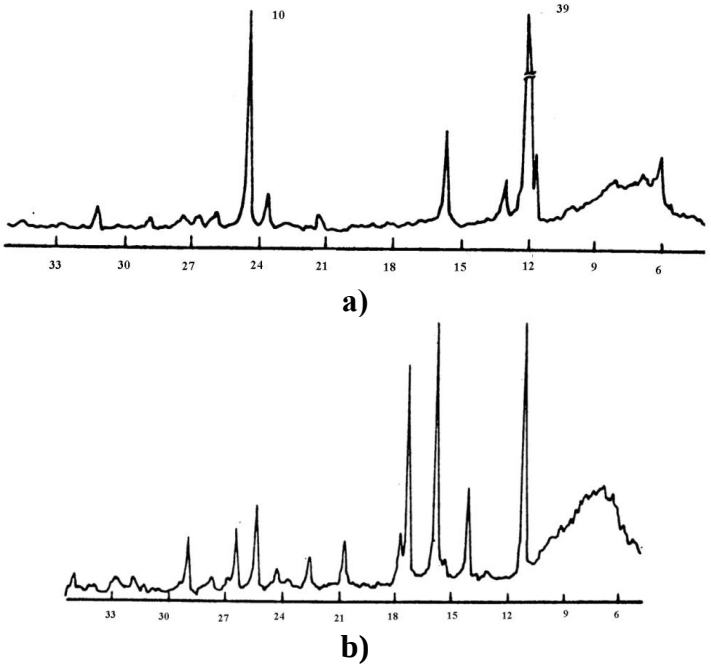

Fig.1. X-ray diffraction pattern of the compounds: (a) $TlInS_2$, (b) $TlInSe_2$.

The results of X - ray phase analysis of single crystals of the $TlInS_{2x}Se_{2(1-x)}$ system are shown in the dash diagram (Fig. 2). From a comparison of the angles and intensity of the reflections, it follows that at 0,3 ≤ x ≤ 1, solid solutions are formed based on the $TlInS_2$ compound, and at 0 ≤ x ≤ 0,2, based on $TlInSe_2$.

In this case, the X-ray analysis is facilitated by the fact that the structure of $TlInS_2$ and $TlInSe_2$, and hence their inter planar distances, are known. To carry out phase analysis of $TlInS_{2x}Se_{2(1-x)}$ samples synthesized under identical thermodynamic conditions, a powder was prepared from each composition, which is squeezed out through a capillary with an internal diameter of approximately 0.8 mm to take powder patterns using the Debye-Scherrer method. Powder patterns were taken from such samples in the RDK-57.3 chamber under the same conditions with an exposure of 18 hours using CuK_α radiation.

All X-ray diffraction patterns of $TlInS_{2x}Se_{2(1-x)}$ samples were processed under the same conditions (Fig. 2). From the obtained X - ray patterns, the inter planar distances (d, Å) were calculated. The intensity of the diffraction Debye lines was estimated on the basis of a ten - point scale. As a result of a thorough X-ray phase analysis, it was shown that the synthesized $TlInS_{2x}Se_{2(1-x)}$ samples are single-phase and the inter planar distances calculated from X-ray patterns can be unambiguously indicated on the basis of a monoclinic lattice with parameters: $a \sim b$ = 10,95 Å, c = 15,14Å, β = 100^0, sp. gr. C_S^4 or C^6_{2h} given in [14].

The lattice parameters of solid solutions as a function of composition x, calculated from the most intense diffraction lines, are in good agreement with the data of [14] and the intense diffraction lines of the powder patterns, respectively, coincide.

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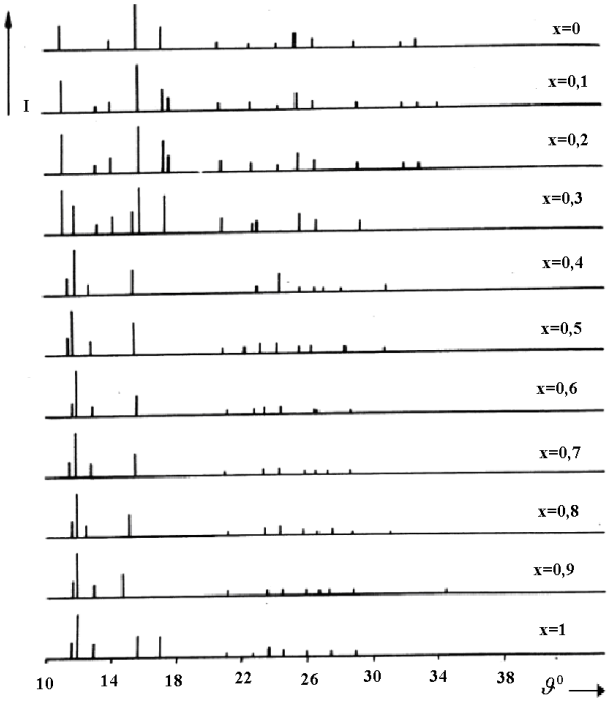

Fig.2. Bar diagrams of $TlInS_{2x}Se_{2(1-x)}$ crystals.

X-ray phase analysis was carried out on a D2 Phaser diffractometer manufactured by the German company Bruker using CuK_α radiation (λ=1.5406Å) in the angle range $2\theta = 05° - 80°$. The crystallographic parameters were calculated using the EVA and TOPAZ programs.

It should be noted that the powder patterns were taken from preparations taken from both ends and from the middle of the ingot, and then compared. Reflections 200 were used to determine the lattice parameters; 002; 400; 004; 600 and 008. In order to eliminate experimental errors, each sample was measured three times, and the average result of all measurements was taken as the grating period, the result shown in Fig. 3.

In the $TlInSe_2$ compound, the replacement of Se by S in an amount of 10% to 30% retains the tetragonal symmetry of the crystal lattice and, due to the small ionic radius of sulfur, the parameters **a** and **b** decrease in magnitude. When Se is replaced

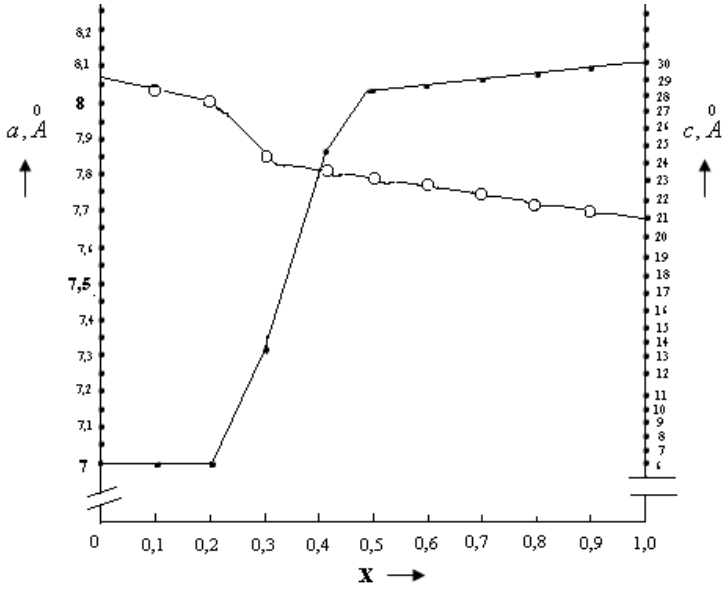

Fig.3. Crystal lattice parameters of single crystals $TlInS_{2x}Se_{2(1-x)}$ ($0 \le x \le 1$) on composition x.

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by S in an amount of about 40%, a phase transition occurs: the tetragonal phase changes to a hexagonal one (space group $P6_3/mmc$).

With a further increase in the percentage of sulfur in this solid solution, a decrease in the parameter c of the crystal lattice is observed. In the compound with the composition $TlInS_{1.6}Se_{0.4}$, an increase in the parameter c is observed, while in $TlInS_2$ it again decreases. Thus, a linear dependence is not observed in the decrease in the parameter c of the crystal lattice, i.e., Vegard's law is not fulfilled. It is possible that errors in the chemical composition were made when obtaining these crystals.

The parameters **a** and **b** of the hexagonal crystal lattice could not be calculated due to the measurement of single crystal samples and not polycrystalline powder.

It can be assumed that this is due to the difference in the ionic radii of the components of the $TlInS_{2x}Se_{2(1-x)}$ crystal: r (Tl^{+3}) = 0,67Å, r (In^{+3}) = 0,92Å, r (Se^{-2}) =1,93Å, r (S^{-2}) = 1,82Å.

In order to unambiguously decide what type the solid solution under study belongs to, we determined the number of atoms (molecules) n in the unit cell (which is one of the direct methods for determining the type of solid solutions) of $TlInS_{2x}Se_{2(1-x)}$ crystals according to the formula:

$$n = v\rho/\mu d, \qquad (1)$$

where ρ is the density, g/cm^3, v is the unit cell volume, $Å^3$, μ is the molecular weight, d is the weight of the hydrogen atom.

Since the value of n for all samples remains unchanged, that is, n = 16, we can confidently say that the studied $TlInS_{2x}Se_{2(1-x)}$ crystals belong to the substitutional solid solution type.

X-ray studies of the synthesized compositions were carried out. At the first stage, the quality of the grown single crystals was determined. Laue patterns were used to determine the symmetry and orientation of the main zones of the crystal, as well as the suitability of crystals for X-ray diffraction studies.

An analysis of the obtained Laue patterns shows that the synthesized single crystals are sufficiently perfect and suitable for X-ray diffraction studies.

To determine the parameters of the crystal structure of single crystals in the X-ray chamber for determining the identity period "RKOP-A", X-ray patterns of rocking in three non-coplanar directions (rocking interval 15^0) were obtained on copper radiation. As a result of X - ray diffraction studies, as in the case of powder patterns, it was found that the studied $TlInS_{2x}Se_{2(1-x)}$ crystals, at $0,3 \le x \le 1$, crystallize in the monoclinic system ($\beta = 100^0$), the crystal lattice periods of the studied compositions are given in Table 2[1].

It has been found that partial replacement of sulfur atoms by selenium atoms results in the formation of substitutional solid solutions that retain the primary monoclinic structure of the $TlInS_2$ crystal.

To reveal the microstructure and establish the single-phase nature of the obtained compositions, samples were prepared from each synthesized composition $TlInS_{2x}Se_{2(1-x)}$ ($0 \le x \le 1$). The surfaces of all samples after grinding and polishing were thoroughly washed, degreased with ethyl alcohol, and dried. The composition of the etchant, selected experimentally, was 3 % H_2SO_4 + 97 % $K_2Cr_2O_7$. The surface of the crystals was preliminarily etched for 1 min. Fixed microstructures of samples of each composition, shown in Figs.3, taken with a vertical metallographic microscope "MIM - 8" at the same magnification, that is, 340^X, in reflected light.

In crystals with x = 1; 0.9; and 0.3, particles of the second phase are observed, as well as an accumulation of micro twins lying on the cleavage plane. In the region of $0,3 \le x \le 1$, the crystals easily break off into plane-parallel plates, and at $0 \le x \le 0,2$, an acicular structure is observed, which is characteristic of $TlInSe_2$. As follows from Fig. 4, at x = 0.2; 0.1; 0, inclusions of the second phase are also observed, which are located at the boundaries of the needles.

Crystals of compositions with x = 0.4 and 0.8 are distinguished by high perfection of the microstructure. However, even in crystals with x = 0.4, precipitates of the second phase with a spherically symmetric deformation field are observed. Without excluding other explanations, it can be assumed that the inclusion of the second phase is a consequence of the violation of stoichiometry during the synthesis.

The properties of semiconductor crystals, as well as the possibility of effective practical use, are largely determined by both the uniformity of the composition, that is, the uniformity of the distribution of the main components, alloying additives, and contaminants, and the presence of structural defects and micro cracks.

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Various microprobe methods of control are widely used in the study of the heterogeneity of the composition that occurs in the processes of crystallization and the preparation of crystals. The most widespread among them is the method of X-ray spectral microanalysis (XSMA).

Electron-probe microanalysis is one of the most effective methods for studying the heterogeneity of the composition [15]. This method provides the possibility of

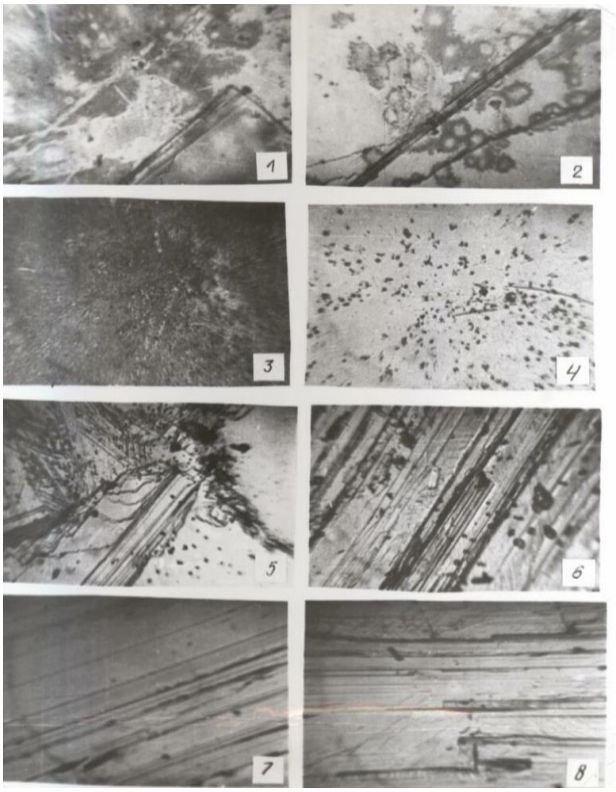

Fig.4. Microstructure of the surface of $TlInS_{2x}Se_{2(1-x)}$ crystals for compositions with x: 1-1; 2-0.9; 3-0.8; 4-0.4; 5-0.3; 6-0.2; 7-0.1;8-0

local determination of the chemical composition, based on the fact that the electron beam can be focused into a narrow probe.

Basic information about the principles, apparatus, measurement technique and processing of results in electron-probe microanalysis is contained in [16,17]. The chemical composition of $TlInS_{2x}Se_{2(1-x)}$ crystals was studied by us by X-ray diffraction analysis on a Kamebaks micro analyzer. Samples of stoichiometric $TlInS_2$ compounds, as well as pure selenium, were used as a reference in determining the composition of the considered crystals.

As mentioned above, the Bridgman - Stockbarger method was used to grow $TlInS_{2x}Se_{2(1-x)}$ crystals in a quartz ampoule moving at an ampoule lowering rate of 0.9 mm/h. The growth and subsequent annealing of the ampoule proceeded at a temperature of 900–1030 K for 12 days. When growing $TlInS_{2x}Se_{2(1-x)}$ single crystals, silicon atoms diffuse from the walls of the quartz ampoule into the crystal, which was proved in [1]. This conclusion follows from the results obtained by means of transmission electron microscopy and electron probe microanalysis.

In [1], a method was proposed for graphitization of the inner walls of the ampoule prior to crystal growth, which excludes the diffusion of silicon atoms. When growing $TlInS_{2x}Se_{2(1-x)}$ ($0 \le x \le 1$) crystals, we used the recommendations of [1]. The results of the microanalysis showed that in the solid solutions obtained by us, the amount of silicon was less than 10^{-3} %.

As is known, in addition to impurity defects, intrinsic defects also play a significant role in semiconductors. The latter are mainly associated with deviations of the crystal composition from stoichiometric. The data obtained from the microprobe analysis after mathematical processing was entered into the computer, and the concentration of individual components was calculated using the universal program [18].

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Comparison of the stoichiometric concentration with the actual results of electron microanalysis shows that in $TlInS_{2x}Se_{2(1-x)}$ (x=0; 0.8; 0.6; 0.4; 0.2) crystals there is a slight violation of stoichiometry. When determining the stoichiometry of the composition, the limit of determination is about 0.1%.

Conclusion: Thus, during the crystallization process, there is a slight deviation from stoichiometry. However, the noted deviations are within the range of homogeneity of the compositions. The limits of mutual solubility of the initial compounds were established: it was shown that the crystal structure of solid solutions $TlInS_{2x}Se_{2(1-x)}$ with a value of $0,3 \le x \le 1$ corresponds to the structure of $TlInS_2$, and at $0 \le x \le 0,2$ - to the structure of $TlInSe_2$.

Through X-ray diffraction studies, it was revealed that the grown crystals of variable composition $TlInS_{2x}Se_{2(1-x)}$ within the limits of solubility crystallize on the side of $TlInS_2$ in the monoclinic system, and on the side of $TlInSe_2$ - in the tetragonal system. It is shown that the dependences of the crystal lattice parameters on the composition on both sides are linear, but inverse to each other, in accordance with the ionic sizes of the interchangeable atoms. It has been established that the grown crystals are, in fact, substitutional solid solutions.

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