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INVESTIGATION OF THE INTERACTION OF $TlInSe_2$ WITH $TlYbSe_2$ AND THE ELECTRICAL PROPERTIES OF $Tl_2InYbSe_4$ CRYSTALS

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Abstract*: The study of the $TlInSe_2$ - $TlYbSe_2$ system state diagram showed that, with a 1:1 ratio, a $Tl_2InYbSe_4$ compound is formed with congruent melting. At room temperature, $TlInSe_2$ dissolves to 12 mol% $TlYbSe_2$. By X-ray diffraction analysis, it was established that the compound $Tl_2InYbSe_4$ crystallizes in the tetragonal syngony. Measurements of the temperature dependence of the electrical conductivity and the Hall coefficient of $Tl_2InYbSe_4$ crystals have revealed that this compound is a p-type semiconductor with a band gap of 1.45 eV. The study of charge carrier transport in the $Tl_2InYbSe_4$ compound showed that their scattering occurs on longitudinal acoustic phonons.*

Keywords*: chalcogenides, semiconductors, crystal growth, X-ray diffraction, electrical properties.*

Introduction:

Currently, in order to meet the requirements of semiconductor electronics, radio engineering and automation, intensive searching for new complex semiconductors is conducted. Such materials include compounds like $TlA^{III}X^{VI}_2$ and $TlLnX^{VI}_2$ (where A^{III} is In, Ga; Ln are lanthanides; X is S, Se, Te) obtained on the basis of TlSe type lattices, as well as solid solutions based on them [1-4]. These materials are promising for use in laser technology and nonlinear optics. They have high thermoelectric efficiency [5], high strain-sensitivity coefficients [6], switching properties with memory [7], acoustovoltaic effects [8]. The study of the photoelectric properties of the $TlInSe_2$ compound showed the promise of its use as a photoelectric converter [9].

The systems $TlA^{III}X^{VI}_2$ - $TlLnX^{VI}_2$ were studied in [10–14]. The analysis of the results of these works showed that the systems of this type are interesting both from a scientific and practical points of view.

The ternary compounds $TlInSe_2$ [15] and $TlYbSe_2$ [16] crystallize in tetragonal syngony. The $TlYbSe_2$ compound melts incongruently and has a semiconducting conductivity [16].

In this paper, the phase equilibria in the $TlInSe_2$ - $TlYbSe_2$ system, as well as the electrical properties of the $Tl_2InYbSe_4$ compound, are investigated.

Experimental part:

To study the phase equilibria in the $TlInSe_2$ - $TlYbSe_2$ system, the samples were prepared by melting $TlInSe_2$ and $TlYbSe_2$ compounds taken in different ratios in silica tubes sealed off under a vacuum of 1.3×10^{-2} Pa. The mixtures were heated at a rate of 5 K/min to 1450 K, held there for 8–10 hours, and then slowly cooled to an annealing temperature. The alloys containing up to 50 mol % $TlYbSe_2$ were annealed at 820 K for 450 h, and those containing 50–100 mol % $TlYbSe_2$ were annealed at 1070 K for 510 h.

The low-temperature part of the $TlInSe_2$ - $TlYbSe_2$ system state diagram was studied using an NTR-64 instrument; at high temperatures, we used a VDTA-8 thermal analyzer, which operates at temperatures of up to 2470 K under a spectroscopically pure helium overpressure.

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X-ray diffraction (XRD) patterns of $Tl_2InYbSe_4$ powder samples were obtained using a URS-55 X-ray generator and 57.3-mm Debye–Scherrer powder camera (Cu*K*α radiation). The error in the calculation of unit cell parameters was 0.003 Å.

In electrical measurements, we used $Tl_2InYbSe_4$ crystals grown by a modified Bridgman–Stockbarger process in purpose-designed fused silica ampules. The inner walls of the ampules were graphitized. The ampules were mounted in a vertical two-zone tube furnace. The temperature of the upper, higher temperature zone was stabilized at 25–30 K above the melting point (T_m) of the material to be prepared, and that of the lower temperature zone was 30–40 K below T_m. The temperature gradient in the transition zone was ≈20 K/cm. First, the ampule was lifted by a purpose-designed drive along the furnace axis to the upper, higher temperature zone. After stabilization for 15–20 h, it was lowered at a rate of 0.8 mm/h. The time taken for the ampule to traverse the transition (solidification) zone and reach the lower temperature zone was seven to eight days. Next, the temperatures of both zones were slowly (two to three days) lowered to room temperature. The resultant $Tl_2InYbSe_4$ ingots consisted of long (≈10 cm), very thin fibers aligned along the ampule axis, which formed a monolithic crystal.

The electrical conductivity and Hall coefficient of the $Tl_2InYbSe_4$ crystals were measured by a bridge technique using samples in the form of rectangular parallelepipeds 3×5×11 mm in dimensions. Reliable electrical contacts were made by capacitor discharge welding of tungsten lead wires to the lateral faces of the sample.

The measurement error of electrical conductivity (σ) was 2 %, and the Hall coefficient (R) – 5 %.

Results and discussion:

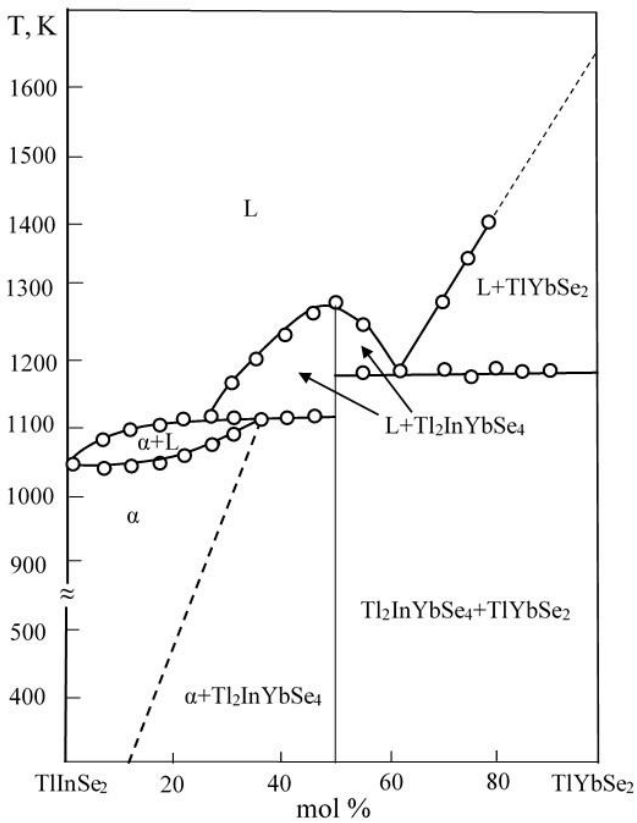

Fig. 1. $TlInSe_2$ - $TlYbSe_2$ system state diagram.

The $TlInSe_2$ - $TlYbSe_2$ phase diagram based on the presented differential thermal analysis (DTA) data is shown in Fig. 1. It follows from this phase diagram that in the $TlInSe_2$ - $TlYbSe_2$ system with 1:1 ratio $Tl_2InYbSe_4$ compound is formed that melts congruently at 1265 K and has no

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homogeneity range. At room temperature, $TlInSe_2$ dissolves 12 mol % $TlYbSe_2$. To determine the solubility region based on $TlInSe_2$, the samples were annealed at temperatures of 400, 500, 600, and 700 K for 230 hours, and then quenched in ice water. As a result, it was found that at a eutectic temperature, the solubility on the basis of $TlInSe_2$ reaches 35 mol% $TlYbSe_2$, and as the temperature drops to 300 K, it decreases to 12 mol% $TlYbSe_2$.

The non-invariant peritectic point is located at a composition $(TlInSe_2)_{0.75}(TlYbSe_2)_{0.25}$ and a temperature of 1115 K. $Tl_2InYbSe_4$ and $TlYbSe_2$ form a simple eutectic at $(TlInSe_2)_{0.37}(TlYbSe_2)_{0.63}$ with a melting point of 1175 K.

According to XRD results, the compound $Tl_2InYbSe_4$ crystallizes in tetragonal symmetry with unit cell parameters a = 8.14 Å and c = 6.72 Å. The indexing scheme for a $Tl_2InYbSe_4$ crystal is presented in the table 1. X-ray patterns of the new four-compound $Tl_2InYbSe_4$ differ from the X-ray patterns of the original $TlInSe_2$ and $TlYbSe_2$ compounds, which also have a tetragonal symmetry: $TlInSe_2$ - a = 8.002 Å; c = 7.015 Å [15]; $TlYbSe_2$ - a = 7.89 Å; c = 6.90 Å [16].

Table 1. X-ray diffraction analysis of $Tl_2InYbSe_4$ crystal.

№	*I*, %	d_{obs} (Å)	*hkl*	d_{calc} (Å)
1	8	4,070	200	4,068
2	100	3,646	210	3,645
3	16	3,364	002	3,365
4	30	2,905	112	2,906
5	9	2,718	300	2,717
6	7	2,408	311	2,409
7	10	2,036	400	2,034
8	12	1,918	330	1,917
9	32	1,875	322	1,874
10	7	1,770	223	1,769
11	4	1,728	303	1,728
12	5	1,679	004	1,678
13	2	1,595	510	1,595
14	2	1,480	413	1,480

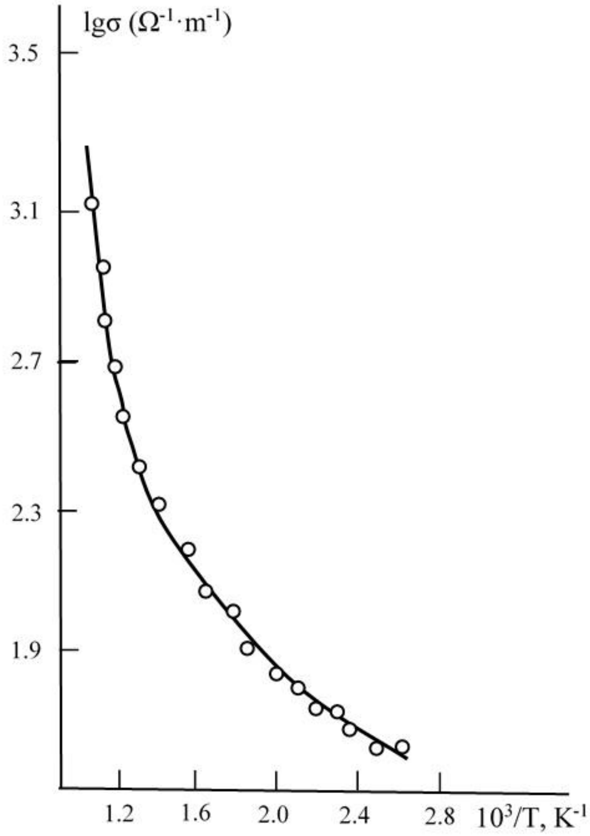

Fig. 2. Temperature dependence of the electrical conductivity of a $Tl_2InYbSe_4$ crystal.

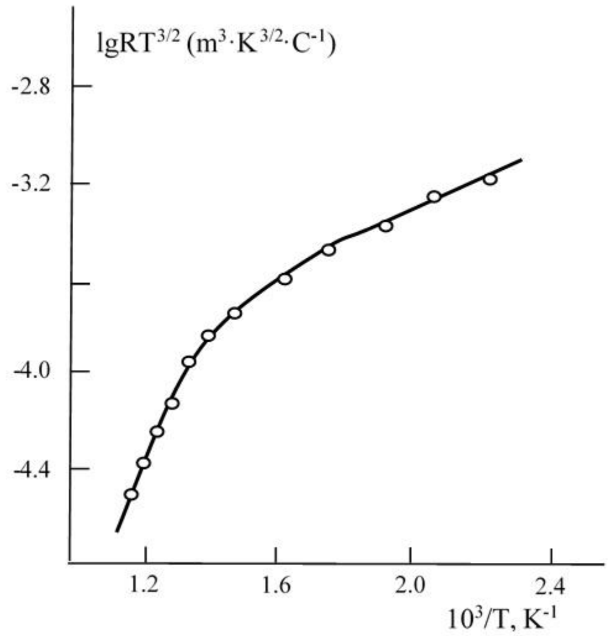

Fig. 3. Temperature dependence of the Hall coefficient of the $Tl_2InYbSe_4$ crystal.

Figures 2 and 3 present temperature dependences of the electrical conductivity and Hall data for the $Tl_2InYbSe_4$ crystals. The electrical conductivity, σ, increases with temperature, that is, σ(*T*) exhibits semiconducting behavior for $Tl_2InYbSe_4$. This compound has a p – type conductivity. The exponential growth of the electrical conductivity with temperature at high temperatures is due to the development of intrinsic conductivity. The band gap, E_g, of $Tl_2InYbSe_4$ crystals was evaluated from the high-temperature $\log RT^{3/2}$ versus $f(10^3/T)$ and logσ versus $f(10^3/T)$, data. From the slope of the curves, E_g was determined to be 1.45 eV.

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We examined the temperature dependences of carrier Hall mobility for the $Tl_2InYbSe_4$ crystals. The carrier mobility, μ, was shown to vary as $f(T^{-3/2})$ (Fig. 4), which corresponds to carrier scattering by longitudinal acoustic phonons.

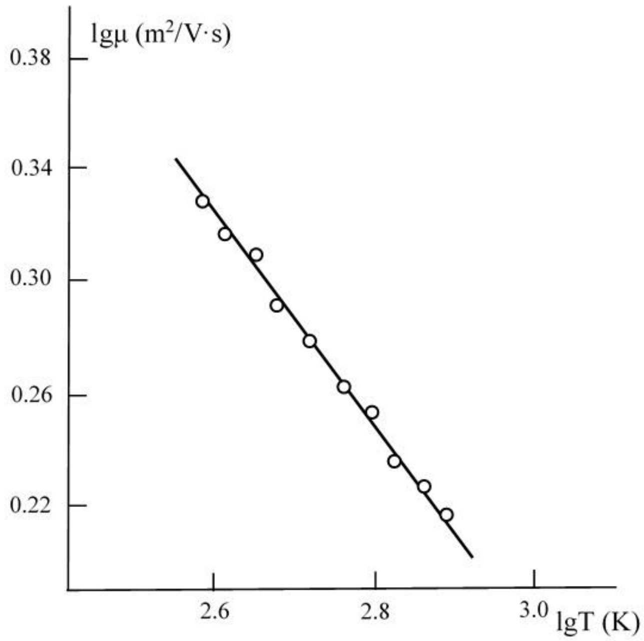

Fig. 4. Temperature dependence of the Hall mobility of $Tl_2InYbSe_4$ crystal current carriers.

Conclusion:

DTA data demonstrates that in the $TlInSe_2$-$TlYbSe_2$ system with 1:1 ratio a congruently melting compound of $Tl_2InYbSe_4$ is formed. At room temperature, $TlInSe_2$ dissolves 12 mol% $TlYbSe_2$. According to XRD results, the compound $Tl_2InYbSe_4$ crystallizes in tetragonal symmetry. $Tl_2InYbSe_4$ crystals are shown to be *p*-type. Its band gap and the mechanisms of carrier scattering in them was determined.

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