

Effect of electric field and temperature on anisotropy of conductivity in TlInTe₂ crystals

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Abstract

The specific electrical conductivity in TlInTe₂ and TlInTe₂-Te (4at.%) crystals were investigated in the range of 100-300 K and 10-10² V/cm in the parallel and perpendicular directions of the chain plane. It was determined that the presence of more than stoichiometry of Te-atom in the octahedral cavities between thallium atoms enhances the ion-covalent bond under the cation lattice and reduces the conductivity in the direction of the *c* crystal axis in the TlInTe₂ – Te system. This leads to a partial decrease in the anisotropy of the conduction at $E_k < 40$ V/cm values of electric field intensity, and the sharp increase at high field intensities. The activation energies of energy levels in parallel and perpendicular directions to InTe₄ chains were determined from $\sigma \sim f(T)$ dependencies as 0,12; 0,35 eV and 0,10 eV; 0,32 eV, respectively.

Keywords: singel crystals; anisotropy of electrical conductivity; electrical conductivity; ionic conductivity;

1. Introduction

The wide application perspectives of superion conductors increases the interest in the synthesis and research of new feature materials [1,2,3]. During the

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synthesis of such materials, metal-type dopants are added in order to purposefully control their electrophysical properties, including the superior phase transition temperature [4,5]. It was shown that the doping of $\text{Li}_2\text{Ge}_7\text{O}_{15}$ superior materials with Cr atom increases superionic phase transition [6]. Moreover, the changes in transition temperature to superionic phase with addition of Li^+ ions to AgJ crystals was observed in [7]. This property depends on the structure of the crystal, the type of chemical bond between the components and the degree of irregularity (durability of ions) of the crystal lattice [7,8].

One of the materials that combines the above properties is TlInTe_2 , which belongs to the group of $\text{A}^3\text{B}^3\text{C}_2^6$ (A-Tl; B-Ga, In; C-S, Se, Te). TlInTe_2 crystals crystallize in the TlSe structure type ($I4/mcm$) and have the following parameters: $a=8,494 \text{ \AA}$; $c=7,181 \text{ \AA}$; $c/a=0,845$; $Z=4$; $d=7,36 \text{ q/sm}^3$. The chemical bond in TlInTe_2 crystals is ion-covalent [9]. $\text{A}^3\text{B}^3\text{C}_2^6$ type crystals are defective materials and crystallize in the TlSe structure type. The density of defects in these materials are in the range of $\sim 10^{18}\text{-}10^{20} \text{ cm}^{-3}$ [10].

Electrical conductivity of $\text{A}^3\text{B}^3\text{C}_2^6$ type crystals are sensitive to the presence of dopant atoms and vacancies. Detection of ionic conductivity in TlGaTe_2 and TlInTe_2 crystals at temperatures above 300 K makes it relevant to study the effect of various additives on the electrophysical properties of these crystals [11,12,13,14].

Physicochemical studies have shown that $\text{A}^3\text{B}^3\text{C}_2^6$ type compounds and their binary analogues (TIS, TlSe) dissolve more chalcogenide in stoichiometry [15,16]. Moreover, it was found that excessive amounts of chalcogenides caused the structural phase transition in these compounds [15,16,17]. Tellurium atoms have been found to be soluble in TlGaTe_2 , TlInTe_2 compounds and shown that the solved tellurium atoms are located in the octahedral cavities of thallium columns in the unit cell of these compounds and to form solid solutions with the host matrix [18].

In the literature, numerous investigations are devoted to the study of the electrical properties of TlInTe_2 [10,11,12,13,14]. According to the results of this investigations, the specific resistance of TlInTe_2 crystals have anisotropic properties in different crystalline directions, and the mechanism of current transfer is determined by sharp transitions. The information on the tetragonal lattice structure, symmetry group, lattice parameters and superior conductivity of TlInTe_2 compound are given in [10,11,12,13,14]. It has been shown that the superionic conductivity observed in these types of crystals at temperatures $T > 400 \text{ K}$ is due to the diffusion of Tl^+ ion between the nanochains by vacancies in the thallium lattice.

The solubility of the chalcogenide atom (Te) in the TlInTe_2 crystal was determined in order to purposefully control the temperature and conductivity corresponding to the superior phase transition, and its effect on the conductivity

of TlInTe₂ crystals at T > 300 K was investigated at f = 100 kHz [18]. It is shown that the value of the observed superionic conductivity depends on the dopant concentration and the crystallographic direction. Since the main purpose of the above studies is to synthesize new superionic conductivity materials based on A³B³C₂⁶ compounds and to study their physical and chemical properties, the final model on the mechanism of superionic conductivity hasn't been given. Considering these facts and the anisotropic properties of the crystal at temperatures T > 100 K and high electric field, the study of the conductivity mechanism in the TlInTe₂-Te system can help to complete the preliminary results. For this reason, the results of the study of the effect of electric field and temperature on the anisotropic properties of conductivity in the TlInTe₂-Te system doped with chalcogenide atom (4 at%) are given in the present work.

2. Experiments

1,0 – 10,0 at% Te doped TlInTe₂-Te alloys were synthesized. The alloys were prepared from components with 99,999% purity by the direct synthesis method in quartz ampoules at vacuum condition (10² Pa). Polycrystalline TlInTe₂ and Te with 99,999% purity were obtained by melting in the furnace and then annealed at 200±5 °C for three weeks. Both TlInTe₂ and 4.0 at% Te-doped TlInTe₂-Te solid solution had p-type conductivity and the following specific resistance along the crystallographic axes, respectively. ρ_{||}=795 Ohm; ρ_⊥=77350 Ohm and ρ_{||}=1,6 Ohm; ρ_⊥=1645 Ohm. The formation of phase equilibrium in the alloys was determined by X-ray and microstructure analysis. TlInTe₂-Te alloys were studied by differential thermal (DTA), X-ray (RFA) and microstructure (MQA) analyzes, and the state diagram of the system was constructed.

Based on the TlInTe₂ compound, the solubility of tellurium at 700°C temperature in the amount of ~ 8.0 at%, and at room temperature in the amount of 5.0 at% was determined. Microstructure analysis was performed on the polished samples and according to the obtained results, alloys with 1.0 - 5.0 at% Te content are homogeneous and belong to the solid solution region on the basis of TlInTe₂ compounds.

As a result of X-ray diffraction analysis of TlInTe₂-T alloys, it was determined that there is a slight change (a = 8,494 Å, c = 7,181 Å) in the lattice parameters of samples from the solid solution region compared to TlInTe₂ crystals (Fig. 1.). The lattice parameters of 4,0 at% Te doped polycrystalline solid solution was determined as follow:

$$a = 8,4850 \text{ \AA}, c = 7,1924 \text{ \AA}.$$

As can be seen, the parameter a of the unit cell is reduced, and the parameter c is slightly increased.

The single crystals of TlInTe_2 were grown and parallelepiped shapes were cut from single crystals with $4,1 \times 1 \times 0,6$ mm (for measurements parallel to the c -axis), and $3,5 \times 1,7 \times 0,8$ mm (for measurements perpendicular to the c -axis) dimensions. Simultaneously, the parallelepiped shapes were prepared from 4,0 at% Te doped TlInTe_2 single crystals with $2,9 \times 0,8 \times 0,6$ mm (for measurements parallel to the c -axis) and $3,7 \times 1,5 \times 1,1$ mm (for measurements perpendicular to the c -axis). The contacts on the samples are made by silver paste. The volt-ampere characteristics and electrical conductivity of the samples were studied in the temperature range of 100-300 K and voltage range of 0-5 V on the basis of the methodology shown in the [19].

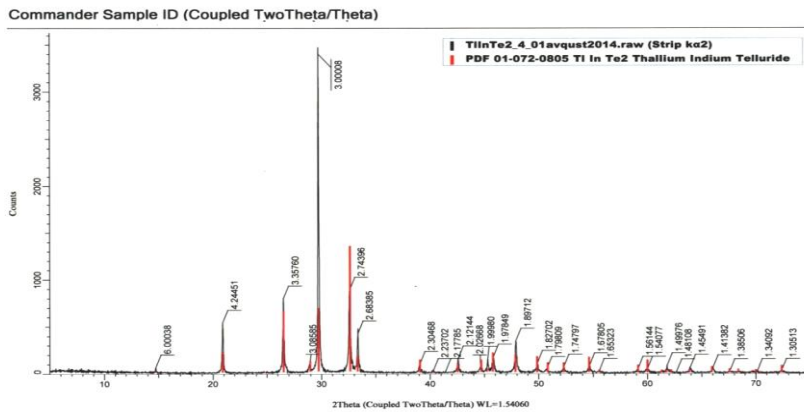


Fig. 1. X-ray diffraction spectra of powdered Te doped (4,0 at%) TlInTe_2 -Te sample.

3. Results and discussion

The effect of the distribution of defect (dopant) levels in the direction of the crystal axes on the TlInTe_2 -Te systems was studied in the temperature range of 100-300 K and $E < 10^2$ V/cm values of electric field.

The volt-ampere characteristics of TlInTe_2 and TlInTe_2 -Te compounds in different crystalline direction (001 – parallel to chain plane and 110 – perpendicular to chain plane) are given in Fig. 2(a,b). As can be seen from Fig. 2, the $I(U)$ dependence is linear in the direction of the TlInTe_2 chain and is related to the thermal ionization of the defect level. In the direction perpendicular to the chain plane this dependence is exponential, with a jump in the voltage range of 0.5-0.8 V and in the subsequent increase, the quadratic region is again observed (Fig.2 a,

curve 2). Such a transition was observed in [20] and was explained by the transition of free carriers between local areas. In the alloyed $\text{TlInTe}_2\text{-Te}$ crystals, the corresponding linear dependence was observed in the ohmic region in both crystallographic directions (Fig. 2 b).

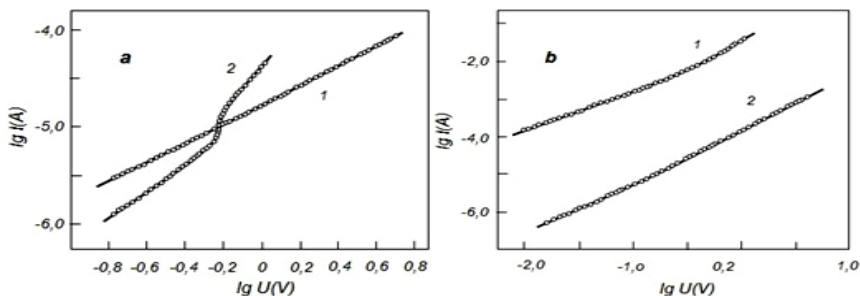


Fig. 2. (a) TlInTe_2 crystals in different crystallographic directions at 300 K. 1 – in parallel to chain plane; 2 – in perpendicular to chain plane; (b) Volt-ampere characteristics of $\text{TlInTe}_2\text{-Te}$ crystals in different crystallographic directions at 300 K. 1 – in parallel to chain plane; 2 – in perpendicular to chain plane.

A comparison of the $I(U)$ curves shown in Figure 2 shows that the density of local levels in the direction parallel to the chain plane predominates over intergenerational transition zones at certain values of the higher field in the TlInTe_2 (Fig. 2a, curve 2) crystals and as a result, hopping conductivity is observed. Such transitions have also been observed in layered InSe and chain TlInSe_2 crystals with anisotropic properties [21].

Temperature dependence of conductivity for TlInTe_2 and $\text{TlInTe}_2\text{-Te}$ systems in direction parallel (1) and perpendicular (2) to the chain plane is shown in Fig. 3(a,b). As can be seen from Fig. 3 (a), at temperatures of $100 < T < 220$ K in the parallel direction (at small values of the electric field) there is a partial decrease in specific electrical conductivity in the perpendicular direction, a very weak increase in the low temperature range and an exponential increase in the 230-300 K temperature range.

According to the inclination of the straight part of the curve, the activation energy of the dopant level calculated in the low temperature range is $e_1 = 0.12$ eV, the activation energy of the local level calculated from the high temperature region is $e_2 = 0.35$ eV, and in the perpendicular direction $e_1 = 0.12$ eV and $e_2 = 0,32$ eV, respectively. Specific electrical conductivity of Te added $\text{TlInTe}_2\text{-Te}$ system practically does not change on $(\lg[\sigma] \sim \frac{10^3}{T})$ dependence in the temperature range of

100-200 K. However, an increase in current is observed at $T > 200$ K. Fig. 3b shows that the increase in current in the parallel direction (curve 1) begins at a higher temperature ($T \approx 210$ K) than in the perpendicular direction (curve 2), which indicates that the concentration of the excited levels is different. The activation energies calculated for both curves from Fig. 3b are 0.10 and 0.30 eV, respectively (curve 1); 0.10 and 0.32 eV (curve 2), respectively. A comparison of the $\lg[\sigma] \sim \frac{10^3}{T}$ dependencies shows that the sharp increase in current ($T \sim 170$ K) may be due to the addition of the Te atom to the TlInTe_2 compound due to the increase in carrier mobility in the perpendicular direction to the chain plane. For this purpose, the dependence of conductivity on the intensity of the applied electric field was studied.

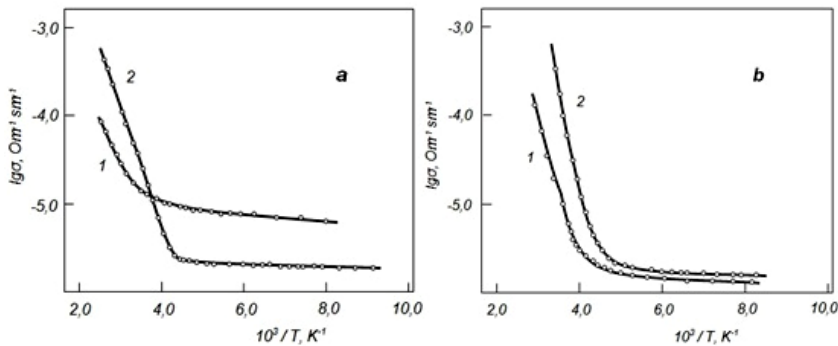


Fig. 3. (a) Temperature dependence of TlInTe_2 crystals in different crystallographic directions. 1 – in parallel to chain plane; 2 – in perpendicular to chain plane; (b) Temperature dependence of $\text{TlInTe}_2\text{-Te}$ crystals in different crystallographic directions. 1 – in parallel to chain plane; 2 – in perpendicular to chain plane;

As can be seen from Fig. 4a, the value of the specific electrical conductivity does not change at small values of the electric field ($E < 40$ V/cm) applied in the TlInTe_2 crystal in the parallel direction (curve 1) and obeys Ohm's law in this range of field intensities. At low values of the electric field in the perpendicular direction to the chain plane (curve 2), the specific electrical conductivity does not change, and during the subsequent increase, a sharp increase in the specific conductivity is observed. The observed conduction anomaly is due to the irregular distribution of defects relative to the tetragonal crystalline c -axis. According to Lampert's theory [22], the value of the specific electrical conductivity in the perpendicular direction is much smaller than in the parallel direction ($\sim 10^2$ times) at low values of field intensity, and this indicates the existence of the potential barrier for carriers moving

in the perpendicular direction. Therefore, anisotropy of conductivity is observed in the TlInTe₂ crystal, as in [10,11,12,13,14,23].

The dependence of the specific electrical conductivity on the field intensity for TlInTe₂-Te crystal is given in Fig. 4b.

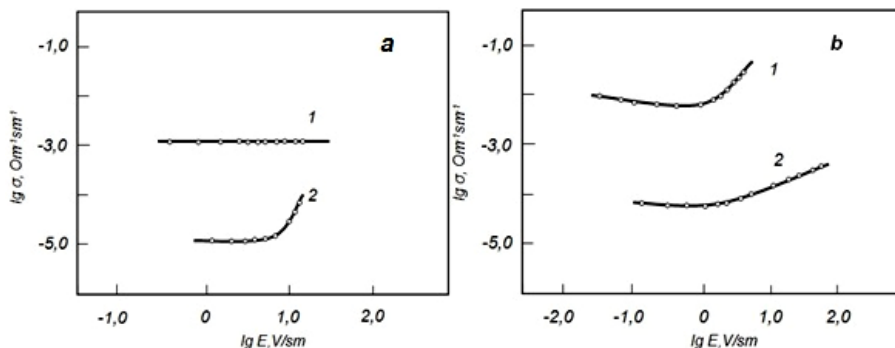


Fig. 4. (a) The dependence of specific electrical conductivity on the electric field intensity for TlInTe₂ crystals in different crystallographic directions. 1 – in parallel to chain plane; 2 – in perpendicular to chain plane; (b) The dependence of specific electrical conductivity on the electric field intensity for TlInTe₂-Te crystals in different crystallographic directions. 1 – in parallel to chain plane; 2 – in perpendicular to chain plane.

Fig. 4b shows that the addition of Te atom in the TlInTe₂-Te system in excess of the stoichiometric amount increases the conductivity in both crystalline directions and satisfies the Frenkel condition in the $\sigma \sim f(E)$ dependence. Conductivity in weak electric fields is determined by the thermo-electron emission of local levels. A comparison of curves 1 and 2 in Figs. 4a and 4b shows that the addition of the Te atom regulates the distribution of defects in both directions in the TlInTe₂-Te crystal, resulting in an increase in the conductivity of the crystal. This fact shows that by changing the amount of Te atom added to the TlInTe₂ compound, it is possible to control the value and direction of the specific electrical conductivity in parallel, as well as perpendicular direction to the tetragonal axis.

The dependence of the anisotropy of the conductivity on the electric field intensity at $T = 300$ K for TlInTe₂ and TlInTe₂-Te crystals are shown in Fig. 5a and 5b. Based on the comparison of the curves given in Fig. 5, it can be concluded that deviations from the theoretical regularity [24] are observed when the conductivity at room temperature depends on the intensity of the electric field.

Fig. 5a shows that the anisotropy of the specific electrical conductivity decreases as the intensity of the electric field increases in the $(\lg[\sigma_{||}/\sigma_{\perp}]) \sim f(E)$

dependence on the undoped TlInTe₂ crystal. The value of the critical field intensity corresponding to the reduction of anisotropy was $E_k \sim 40$ V/cm. This is due to the exponential increase in conductivity in the perpendicular direction to the chain plane with increasing the intensity of the electric field. According to Lampert's theory [22], it can be said that the increase in conductivity in the σ_{\perp} direction occurs with the increase in the concentration of free carriers in the conduction zone due to the contact-injected carriers. Anisotropy of conductivity is increased when Te atom is added to the TlInTe₂ crystal, ie the conductivity of the crystal decreases in the perpendicular direction to the chain plane (in the direction of the c -axis). From the curve (Fig. 5b), the calculated value of the critical field intensity corresponding to the increase in anisotropy of the conductivity is determined $E_k \sim 50$ V/cm. Based on the results obtained in [25,26], this allows us to say that the energy level generated by the dopant atoms acts as a capture center in weak fields, and undergoes thermoelectron ionization at critical fields due to the Frenkel effect. This leads to a sharp increase in conductivity at high field intensities. From the comparison of Figures 5a and 5b, it can be said that the addition of the Te atom into the TlInTe₂ crystal in excess than stoichiometry in the octahedral cavity surrounding the Tl⁺ ion enhances the ion-covalent bond in the cation lattice. This leads to a decrease in the conductivity of the TlInTe₂-Te crystal in the direction of the c -axis and an increase in the anisotropy of the conductivity depending on the electric field in $(\lg[\sigma_{\parallel}/\sigma_{\perp}] \sim f(E))$ dependence.

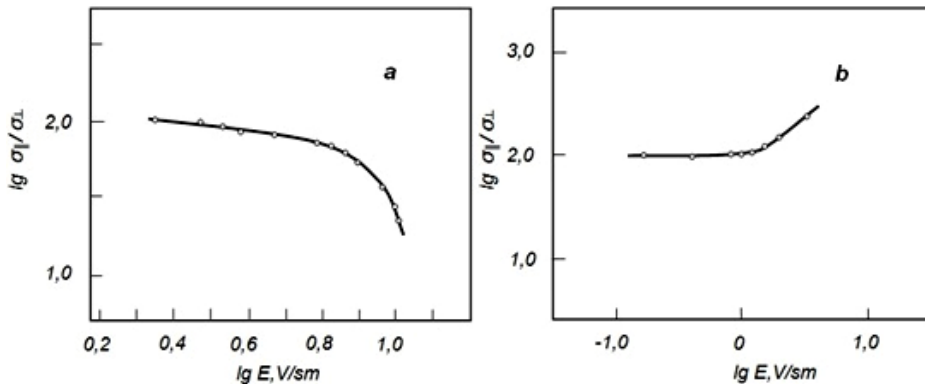


Fig.5. (a) The dependence of specific electrical conductivity anisotropy on electric field intensity in TlInTe₂ crystals; (b) The dependence of specific electrical conductivity anisotropy on electric field intensity in TlInTe₂-Te crystals.

Temperature dependence of specific electrical conductivity for TlInTe₂ and TlInTe₂-Te crystals are shown in Fig. 6. A comparison of the $(\lg[\sigma_{\parallel}/\sigma_{\perp}] \sim f(1/T))$ dependencies in Fig. 6 shows that the anisotropy of the conductivity in the TlInTe₂

crystal is weak with increasing temperature in the range of 100-250 K, and sharply increases in the temperature range of 250-300K. In the TlInTe₂-Te crystal, the anisotropy of the conduction does not change with increasing temperature in the range of 100-220 K, but increases sharply in the range of 220-300 K.

Based on the comparison of the obtained experimental results with the works [10,11,12,13,14,15,16,17,18,23], it can be note that the conductivity in the crystallographic directions *001* and *110* varies sharply depending on the position of the dopant atom in the crystal lattice. The partial filling of the octahedral cavity as a result of the adding Te atom into the TlInTe₂ crystal with excess of stoichiometry creates an additional potential barrier to the free movement of Tl⁺ ions in the *110* direction. This causes the current to decrease in the direction of the crystal axis. Since the height of the potential barrier is compensated at the values of $E_k < E$ when potential field is applied to a crystal, the anisotropy of the current does not depend on the intensity of the field (Fig. 5), and increases at high values of the critical field due to the Frenkel effect [24]. The study was stopped due to the heating effect of the carriers at high field values during the experiments [21]. On the other hand, the dependence of $\sigma \sim f(1/T)$ shows that the anisotropy of the current also depends on the temperature (Fig. 6). The anisotropy of the current in the TlInTe₂-Te crystal increases partially at temperatures $T < 250$ K (Fig.e 6, curve 2) relative to the undoped crystal, and sharply increases at $T > 250$ K as a result of ionization of the dopant levels [25, 26].

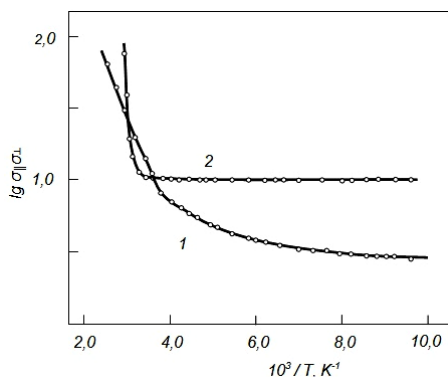


Fig. 6. Temperature dependence of anisotropy of specific electrical conductivity in TlInTe₂ (1) and TlInTe₂-Te (2) crystals.

The activation energies of the energy levels in parallel and perpendicular directions to the *c*-axis were determined for TlInTe₂-Te crystal as 0.12; 0.35 eV and 0.10 eV; 0.32 eV, respectively.

The analysis of the obtained results shows that the excess of the dopant atom in the crystals with chain structure allows to purposefully control the anisotropic properties of the materials, and this method can be used in the development of fast conversion systems.

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