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Electrical properties of the layered single crystals $TlGaSe_2$ and $TlInS_2$

Abstract. *In the doped crystals $TlGaSe_2$ and $TlInS_2$, using method of temperature dependencies of DC resistance in the temperature range of 100 – 300 K, the phase transitions at the temperatures of 240 – 245 K and 105 – 120 K were observed. The AC conductance measurements at room temperature indicated the hopping mechanism of carrier transport in the studied samples.*

Streszczenie. *W domieszkowanych kryształach $TlGaSe_2$ i $TlInS_2$ dla temperaturowych zależnościach rezystancji z przedziału 100 – 300 K zmierzonej przy użyciu prądu stałego zaobserwowano przejścia fazowe w przedziałach temperatur 240 – 245 K i 105 – 120 K. Pomiary konduktywności przy użyciu prądu przemiennego w temperaturze pokojowej wskazały skokowy mechanizm przenoszenia ładunków w badanych próbkach. (**Właściwości elektryczne monokryształów $TlGaSe_2$ and $TlInS_2$**).*

Keywords: layered crystals, phase transition, DC resistance, AC conductance.
Słowa kluczowe: kryształy warstwowe, przejście fazowe, rezystancja stałoprądowa, zmiennoprądowa przewodność.

Introduction

The ternary compounds $TlGaSe_2$ and $TlInS_2$ belong to the group of chalcogenide semiconductor-ferroelectric crystals with layered structure which are crystallized in monoclinic structure. These crystals have received a great deal of attention due to their optical and electrical properties in view of the possible optoelectronic device application. In recent years there is a growing interest to their study due to the coexistence of ferroelectric and semiconductor properties, as well as the presence of structural phase transformations in some of these compounds. In particular, it has been established that, on cooling, some of undoped $TlGaSe_2$ and $TlInS_2$ crystals exhibit a sequence of structural phase transitions which accompanied by peculiarities on temperature dependencies of different properties – dielectric, elastic, acoustic, thermal, optical, etc., at temperatures ranges of ~ 90 - 140 K and ~ 242 - 253 K for $TlGaSe_2$ and ~ 190 - 195 K and ~ 201 - 216 K in $TlInS_2$ [1-6]. In spite of all these experimental results a complete conception about the reasons of these phase transitions has not been formed yet. Moreover it was interested to check the influence of doping on electrical properties and phase transitions in these crystals.

The present paper is devoted to the study of the surface structure and some electrical properties, including carrier transport mechanisms, at different temperatures in $TlGaSe_2$ and $TlInS_2$ crystals doped with different electrically active impurities.

Experimental

The single crystals were grown and doped with Fe, Ag, B, Tb, Er and Al impurities in evacuated quartz tubes by using the modified Bridgman method. The studied samples, which were in rectangular form, were oriented along the polar axis which lies in the cleavage plane (the morphology of crystals permits cleavage to plane parallel plates).

SEM investigations of the grown single crystals were done using LEO1455-VP scanning electron microscope with energy-dispersive Si:Li detector Rontec allowing to perform X-Ray microanalysis for checking the samples` stoichiometry.

DC resistance $R(T)$ was measured in cooling regime in the temperature range 10 - 300 K using a closed-cycle cryogen-free cryostat system CFM (Cryogenic Ltd., London) and Lakeshore Temperature Controller Model 331, which allowed to scan the temperature with a rate of about 0.1 - 1 K/min and to stabilize the temperature with accuracy 0.005 K. The measurements of real part of AC conductance $G(f)$ were performed at 300 K for the frequencies f between 100 Hz and 30 MHz using Agilent LCR Meters 4980A and 42841A. All electric measurements were carried out with full computer control. For electrical measurements the wide face of plates were gently polished, cleaned and covered with two indium probes, which were applied by ultrasound soldering, so that the measuring current carried along the plane of the best split (normally to C axis).

Results and Discussion

To determine the needed bias voltage applied and the cooling rate for guaranteeing of equilibrium $R(T)$ measurement, we made firstly testing of the studied samples on the presence of ferroelectric relaxation. In this case we measured dark I-V characteristics and also the change of dark current I with time t at a constant bias voltage V applied.

Fig.1 shows examples of I-V curves at 300 K which are characterized by hysteresis that depends for the most samples on number of their sweepings. The latter means that some of samples are characterized by memorization of previous measurements (see, Figs.1a and 1b). As is seen, for the most samples *I-V*s have a linear regions, coinciding for different sweepings, only for initial parts at low *V* values (for example, for $TlGaSe_2$<Fe> sample they lie at voltages less than 0.1 V, Fig.1a). The same results were observed for the most studied samples (independently on their doping) except for $TlGaS_2$ doped with erbium (Fig.1c) which suppress the relaxation processes.

Note that at lower temperatures hysteretic behavior was enhanced and observed at higher bias voltages.

As is seen from Fig.2, at 300 K for $TlGaSe_2$<Fe> sample dark $I(t)$ curve at V=const approaches maximal value and then is lowered going to saturation. Note that beyond the maximum sign of current relaxation in the temperature range 100-300 K is changed following the law $I(t) \sim \lg(t_0/t)$ (see, insert in Fig.2).

For T <100 K the $I(t)$ curves did not have a maximum and followed by a power-like law $I(t) \sim t^n$ (see, insert in Fig.3) since the beginning the relaxation process.

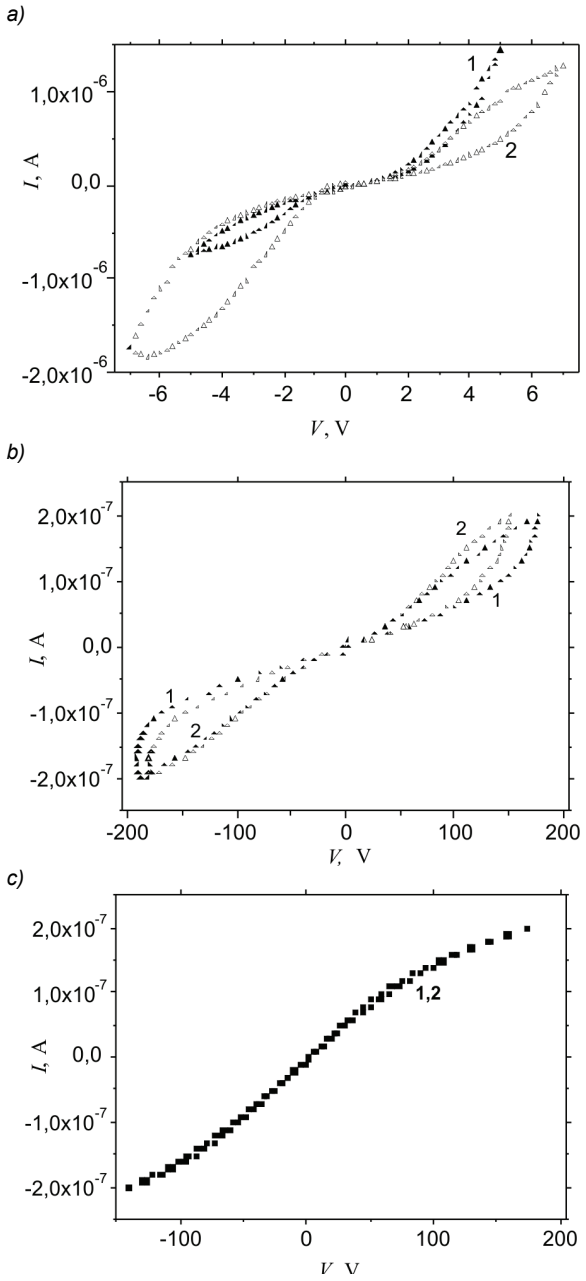

Fig.1. Dark *I-V* characteristics for $TlGaSe_2$<Fe> (*a*), $TlGaS_2$<B> (*b*) and $TlGaS_2$<Er> (*c*) samples at 300 K for the 1st (curves 1) and 2nd (curves 2) sweeping of bias voltage

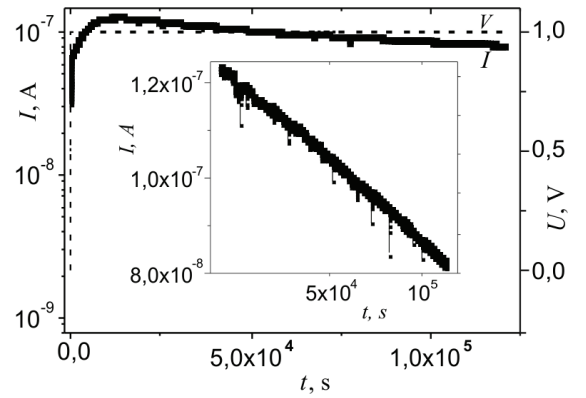

Fig. 2. Relaxation of current I (at step-like supply of bias voltage V, dotted line) with time t for $TlGaSe_2$<Fe> sample at 300 K (curve I). In insert $I(t)$ curve is given in semi-logarithmic scale

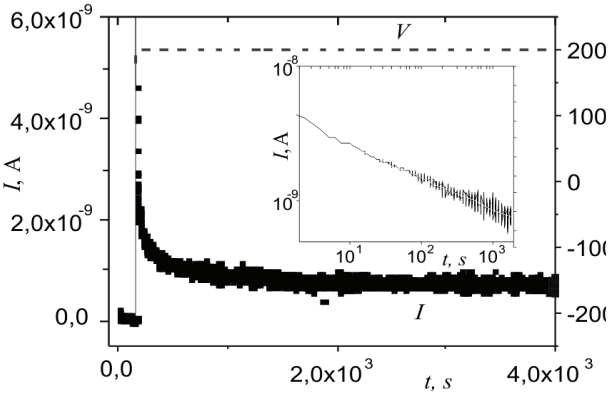

Fig.3. Relaxation of current I (at step-like supply of bias voltage V, curve I) with time t for $TlGaSe_2$<Fe> sample at 2 K (curve I). In insert $I(t)$ curve is given in double logarithmic scale

Hysteretic shape of *I-Vs* and time dependence of dark current indicate the presence of ferroelectric relaxation in the studied samples. In this context, the observed initial slow growth of *I(t)* observed at high temperatures after application of bias voltage can be attributed to slow polarization processes in the material. The subsequent relaxation of dark current (after maximum approach) at $T > 100$ K can be ascribed to the presence of deep traps which are filled by electrons at bias voltage application and than emptied gradually with time. So the following logarithmic law of relaxation of these electrically excited electrons can be attributed to scattering of traps activation energies [12] which results in time dependence of concentration of electrons exited by electric field. The power law of *I(t)*, observed at low temperatures $T < 100$ K, is usually assigned by dispersion-like carrier transport that is characteristic for highly inhomogeneous and/or disordered media [13] where mobility of carriers is randomly scattered by values and strongly depends on electric field.

The examples of temperature dependencies of resistance *R(T)* measured in cooling regimes for the samples of doped $TlGaSe_2$<Fe> and $TlInS_2$<B> crystals are presented in Fig.3. As is seen from Fig.3a, for $TlGaSe_2$<Fe> sample a low-temperature peculiarities in shape of resistance oscillations was displayed between 105 and 120 K. Note, that similar phase transitions were observed in [5, 6] by permittivity and thermal expansion coefficient temperature scanning in undoped $TlGaSe_2$ crystals.

Re-scaling of *R(T)* curves as Arrhenius plots for $T > 250$ K and for $T < 105$ K is shown in Inserts (*a*) and (*b*) in Fig. 3a appropriately. This allowed to separate high- and low-temperature linear parts of $\ln R(1/T)$ dependencies with activation energies of about 0.25 eV and 0.04 eV correspondingly for $TlGaSe_2$<Fe> and 0.21 eV for $TlInS_2$<B> near the room temperature. For $TlInS_2$<Tb> and $TlInS_2$<Er> crystals linear parts in $\ln R$-$(1/T)$ curves near room temperature have given energies of conductance activation of about 0.17 and 0.14 eV appropriately.

In order to additionally clarify carrier transport mechanisms in the studied crystals under doping we have studied the frequency dependencies of real part of AC conductance *G(f)* at room temperature. It was observed that the conductance increases with increasing frequency which is a normal trend for ferroelectric materials [7].

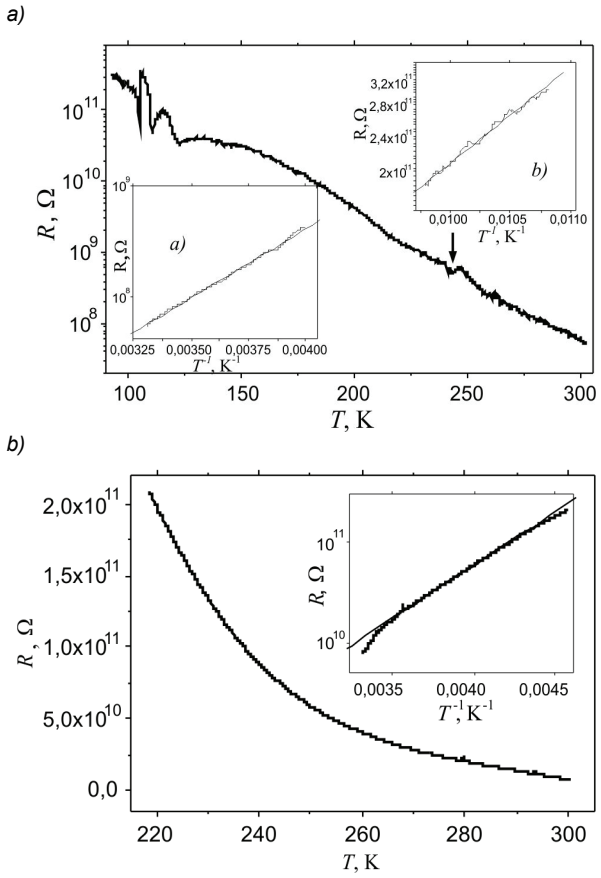

Fig.4. Temperature dependencies of DC resistance $R(T)$ for $TlGaSe_2$<Fe> (*a*) and $TlInS_2$<B> (*b*) crystals. Inserts in (*a*) present $R(T)$ in Arrhenius scale for $T > 250$ K (*a*) and for $T < 105$ K (*b*)

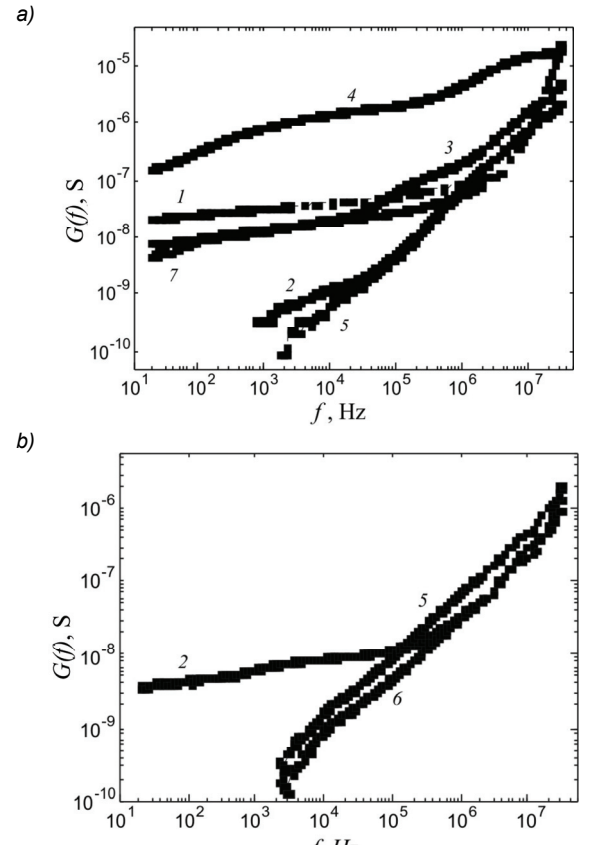

Fig.5. Frequency dependencies of real part of AC conductance $G(f)$ at 300 K for $TlGaSe_2$ (*a*) and $TlInS_2$ (*b*) crystals doped with Fe (*1*), B (*2*), Al (*3*), Ag (*4*), Tb (*5*), Er (*6*) and Nd (*7*)

Presentation of $G(f)$ dependencies in double logarithmic scale in Fig.2 shows that for the most samples in the lowest and highest frequencies $G(f)$ curves revealed power-like laws

$$G(f) = f^{\alpha} \tag{1}$$

with linear parts of $\ln G$ vs $\ln f$ that is characteristic for AC hopping mechanism of carrier transport [8]. Note that in $TlGaSe_2$ crystals doped with Al and Ag $G(f)$ curves in the whole frequency ranges display sigmoid-like shape (see, curves 3 and 4 in Fig.4a) that fully corresponds to AC hopping model described in [9-11].

The exponent α values (estimated as derivatives by frequency of $G(f)$ curves) in Eq. (*1*) are strongly dependent on the frequency range and type of doping impurities. As is seen from Table 1, α values are changing from 0.11 to 1.04. In accordance with the proposed model [9, 10], this is characteristic for hopping of electrons localized in the potential wells which representing the defects (impurities) in our case. After a jump of the electron from one neutral well to another one, the electrical dipole appears, so that the electron remains in the second well during the time τ and only then either jumps to the next (third) well (along the direction of the external electric field E) with the probability p, or returns to the first well (against E) with the probability $(1 - p)$.

Table 1. The α values in equation (*1*) for doped crystals $TlGaSe_2$ and $TlInS_2$ at low and high frequencies

Doping element	Fe	B	Al	Ag	Tb	Er	Nd
$TlGaSe_2$							
α $10^2<\omega<10^4$ Hz	0.11	0.85	0.14	0.42	0.13	-	0.14
α $10^5<\omega<10^7$ Hz	-	0.97	0.13	0.30	0.13	-	1.30
$TlInS_2$							
α $10^2<\omega<10^4$ Hz	-	0.12	-	-	0.70	0.82	-
α $10^5<\omega<10^7$ Hz	-	0.92	-	-	0.87	1.04	-

Interaction of electrons in two neighboring potential wells leads to the certain distribution $F(\tau)$ of the probability p for the time τ. The model developed in [9-11] allows to estimate the values of p and τ using the experimental $G(f)$ curves, introduced in [10] relation

$$p = \frac{G(f \to 0)}{2 \cdot G(f \to \infty)} \tag{2}$$

and also a model dependence of $\alpha(f)$, involved in the relation (*1*). In accordance with this model, $\alpha(f)$ dependence, which determines hopping probability p, has the shape of the curve with maximum at $f = f_{max}$ (see, Fig.1 in [10]). As was shown in [9], f_{max} is connected with τ by the relation $\tau = 1/2\pi f_{max}$.

The analysis carried out in accordance with the model [9, 10] have shown that the hopping carrier transport in the most studied crystals is provided by, at least, two types of potential wells (defects). This is manifested, in particular, in two different slopes (α values) in $G(f)$ curves shown in Fig.4 (see, also Table 1) for $TlGaSe_2$ (curves 3, 4, 7) and $TlInS_2$ (curve 2) samples.

Resume

In the doped crystals $TlGaSe_2$ and $TlInS_2$, using method of temperature dependencies of DC resistivity in the temperature range of 77 - 300 K, the phase transitions at the temperatures of about 105 - 120 K were observed. The AC conductance measurements at room temperature indicate the hopping mechanism of carrier transport which is described by the model developed in our earlier works [9-11].

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