POLARIZED EFFECTS IN La DOPED $TlInS_2$ LAYERED SEMICONDUCTOR-I: DEEP LEVEL DEFECTS AND PYROCURRENTS CHARACTERIZATION

M.Yu. SEYIDOV[1, 2 *], F.A. MIKAILZADE[1, 2], A.P. ODRINSKY[3], T.G. MAMMADOV[2], V.B. ALIYEVA[2], S.S. BABAYEV[2], A.I. NAJAFOV[2]

[1]Department of Physics, Gebze Technical University, 41400, Gebze, Kocaeli, Turkey
[2] Institute of Physics of NAS of Azerbaijan, H.Javid av., 33, AZ-1143, Baku, Azerbaijan
[3] Institute of Technical Acoustics, National Academy of Sciences of Belarus, Lyudnikov av. 13, Vitebsk 210717, Belarus

Lanthanum - doped high quality $TlInS_2$ ferroelectric - semiconductors were characterized by photo - induced current transient spectroscopy (PICTS). Different impurity centers are resolved and identified. Analyses of the experimental date were performed in order to determine the characteristic parameters of the extrinsic and intrinsic defects. The energies and capturing cross section of deep traps were obtained by using the heating rate method. The observed changes of the pyroelectric response of $TlInS_2$:La crystal near the phase transition points are interpreted as a result of self - polarization of the crystal due to internal electric field of charged defects. The influence of deep level defects in pyroelectric response of $TlInS_2$:La has been revealed for the first time.

Keywords: ferroelectric phase transitions; incommensurate phase; dielectric hysteresis loops; double dielectric loops.
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*Corresponding author. Address: Department of Physics, Gebze Technical University, Gebze, 41400, Kocaeli, Turkey.
Tel.: +90 262 605 1329; fax: +90 262 653 8490 , E-mail address: ***smirhasan@gyte.edu.tr*** (MH.Yu.Seyidov).

1. INTRODUCTION

Defects in semiconductor crystals significantly modify almost all physical properties of these materials. It is also well known that impurities and defects strongly influence on the ferroelectric phase transitions in crystals. The influence of defects on phase transitions is one of the hot topics in the context of modern studies of ferroelectrics. Special attention was attracted to ferroelectric - semiconductor materials, especially due to their suitability for many device applications. In ferroelectric - semiconductors, the influence of defects on material properties clearly manifests itself during external perturbation. External fields can create the own dipole moment in centrosymmetric defects or readily orientate chaotically arranged of the locally frozen dipole moment of defects in ferroelectric – semiconductors [1].

The ternary ferroelectric - semiconductor $TlInS_2$ belongs to the well - known class of $A^{III}B^{III}C_2^{VI}$ chalcogenides with layered crystal structures. At room temperature the crystal structure of $TlInS_2$ belongs to monoclinic syngony and has space symmetry group of C_{2h}^6 [2]. On cooling $TlInS_2$ undergoes successive phase transitions to incommensurate (IC) and commensurate (C) ferroelectric phases at the temperatures T_i~ 216 K and T_c~200 K, respectively [3, 4]. The phase transition from the paraelectric phase at T_i~ 216 K is a second order one and the appeared IC phase exists in the temperature range between ~ 200 and ~ 216 K, which is characterized by an incommensurately modulated displacement wave in the crystal structure of $TlInS_2$ [5 - 7].

The incommensurately modulated displacement wave in $TlInS_2$ crystal is formed due to atom displacements in the (110) symmetry plane and is directed along [001] axis. Displaced atoms don't exactly repeat themselves in neighboring elementary cells, so the three dimensional translational invariance of $TlInS_2$ crystal is broken. The IC - modulation period is near 4 unit cells of the initial crystal structure of $TlInS_2$ [2, 8].

On decreasing the temperature the IC - modulation wave vector varies continuously and locks into the commensurate value of $\frac{1}{4}\boldsymbol{c}$ at T_c [2, 8]. This corresponds to quadrupling of the unit cell volume along the direction perpendicular to the layers. The phase transition from IC to the ferroelectric phase is of the first order. At T_c, or Curie point, there is a structural change to a low temperature polar ferroelectric phase.

In the vicinity of the Curie point the IC - phase consists of a periodic arrangement of commensurate domains with constant phase and amplitudes of the modulation wave, which are separated by narrow domain walls, the so called discommensurations (DC or soliton like domains) [9 - 11]. Inside the DC's the phase of the incommensurately modulated displacement wave changes rapidly and local mechanical strains underlying crystal lattice are accompanied. Thus, DC's or soliton like domains can be considered as topological defects of the crystal lattice.

The most remarkable feature associated with DC's is that DC's can be pinned by impurities and other defects of the crystal structure. Native defects of the crystal or dopant could be strongly destroys the processes of nucleation and growth, annihilation, forward and sidewise motion of DC's [10]. Besides, topological defects can extremely affect homogeneous charge trap distribution in crystals creating an on - equilibrium internal electrical field distribution as a consequence. In this frame the synthesis and investigation of the crystals with the IC phase doped by electrically active impurities is of great importance.

This paper presents the results of investigations of the polarized effects in lanthanum - doped $TlInS_2$ ferroelectric – semiconductors caused by electrically

131 H.Javid ave, AZ-1143, Baku
ANAS, G.M.Abdullayev Institute of Physics
E-mail: jophphysics@gmail.com

active La - defects. Pyroelectric properties of $TlInS_2$:La were investigated by measuring a short circuit current through the sample on varying the temperature. Prior to the pyroelectric current measurements, $TlInS_2$:La was poled by applied electric field. It was revealed that the polarization field in $TlInS_2$:La can be concentrated among charged defects localized on the surface of the sample and its volume as well, creating surface or bulk internal electric fields originating from this intrinsic dipoles.

This fact motivated photo - induced current transient spectroscopy (PICTS) investigations of $TlInS_2$:La for the detection and identification of charged traps responsible for polarized effects in material under investigations. A clear correlation between pyroelectric properties of $TlInS_2$:La and PICTS analyses is evident from the results.

2. EXPERIMENTAL METHODS

$TlInS_2$ polycrystals were synthesized from high purity elements (at least 99.999%) taken in stoichiometric proportions. Single crystals of $TlInS_2$ were grown using Bridgman – Stockbarger method from a melt of the starting materials sealed in evacuated (10^{-5} Torr) silica tubes with a tip at the bottom, without any intentional doping. The inner wall of the ampoule was coated with a thin layer of carbon to rule out any reaction with the container. To prevent the ampoule from exploding, it was heated in a temperature gradient furnace. The doping was performed by adding the corresponding weighted portion of lanthanum to a cell with the preliminarily synthesized $TlInS_2$ compound. The resulting undoped and La - doped ingots were yellow in color showed good optical quality and were easily split along the cleavage planes with mirror like surface. No further polishing and cleaning treatments were required.

The chemical composition of the studied crystals was determined by the energy dispersive spectroscopic analysis using a scanning electron microscope. The energy dispersive X - ray analysis performed at room temperature confirmed the formula composition of the undoped and La - doped samples. This analysis also demonstrated that the doped $TlInS_2$ sample is enriched in the lanthanum impurity with a content of ∼ 0.37 at %. Moreover, it was revealed that $TlInS_2$:La sample involved an insignificant percentage of background impurities, such as carbon, oxygen and silicon.

The investigated $TlInS_2$:La sample had the form of the plates with ~ 2 mm thick and ~ 20 mm^2 surface.

The sample was mounted on a cold finger placed inside Janis closed - cycle helium cryostat equipped with glass windows for optical measurements. A control sensor (diode DT - 470) and a resistive control heater were mounted under the base and used to control the temperature with an accuracy of less than ~ 0.1K by using a Lake Shore - 340 auto tuning temperature controller. All of the measurements were made in a running vacuum of the order of 10^{-3} mbar.

The dark current measurement was carried out in the temperature interval 80 – 300K during heating at a constant rate of ~1 K/min in darkness under a voltage of ~10 V. The measurements were performed using a high precision digital Keithley - 485 pico - ammeter.

The pyroelectric properties were studied by direct method in short - circuited regime under a linear temperature variation. The temperature was changed with the different hearting rates, typically between 15 and 20 K/min. High precision digital Keithley - 617 programmable electrometer was used to measure the pyrocurrent and the data were collected by a PC. The surfaces of La doped $TlInS_2$ sample were covered by silver paste to form electrodes oriented perpendicularly to the polar axis. Two thin wire terminals were used as external leads to make the sample free and to avoid any stress on it. Prior to the measurements, sample was subjected to electrical poling by cooling in darkness in the presence of the polarizing electric field ~ 5 kV/cm using high voltage power supply. The poling field was applied to sample within a certain temperature range.

PICTS measurements were carried out in the temperature range of 77 – 300K. Under the PICTS investigation the photo - excitation of the samples was carried out by monochromatic light with photon energy less than the width of forbidden gap ($h\nu < E_g$) at homogeneity excitation of crystal surface. We used the photon energies in range of $h\nu$ = 2.30 - 2.43 eV that corresponds to the maximum of the electrical response. The illumination light was perpendicular to the layers plane of the crystal. The photon flux density was $10^{14}\ cm^{-2}s^{-1}$ at the sample surface. The frequency of the illumination pulse was 20 Hz with light to dark duration in the ratio of $1/5$. The duration of excitation pulse was 30 ms.

The sample was mounted inside the nitrogenium cryostat with grade quartz optical window. The sample was placed on massive aluminum holder close to temperature sensor Hell - 700.

The photoresponse measurements were performed along the layers plane of the crystal. The ohmic indium contacts were soldered to the lateral sides of the samples. The measuring circuit was typical for photocurrent investigation. A bias voltage up to 50 V was applied to the sample. The experimental setup was described in detail elsewhere [12].

The registration of the photoresponse decays was performed over the temperature range of 78 – 330K in a temperature step of 1K upon slow heating of the previously cooled sample. The heating rate of the sample was 2 K / min.

The home - made data acquisition system with preliminary processing and registration of transient data on a personal computer was used [12].

Pointwise accumulation and averaging were carried out across 64 realizations of photoresponse decay containing 2000 samplings located at a fixed time interval Δt = 62 μs. Taking into account the ferroelectric nature of the crystal the photo response transient was monitored and recorded also.

A conventional DLTS technique was applied for the photoresponse transient analysis using a rectangular lock - in weighting function. The data registration allowed the characterization of relaxation times in the range from 0.2 to 20 ms with regard to the selected conditions.

3. EXPERIMENTAL RESULTS

3.1 - Photoinduced Current Transient Spectroscopy Measurements

PICTS is a suitable technique for studying the trapping levels (activation energy, capture cross section or emission coefficient) in high - resistive or semi - insulating semiconductor materials which cannot be measured with capacitance based deep level transient spectroscopy [13]. The principle of PICTS technique is based on measurements of time dependent photocurrent due to carrier emission from deep levels [14, 15]. The light excitation is used to creation of defects filling by non equilibrium charge carriers. An intrinsic light creates electron – hole pairs in a small region underneath the ohmic contacts. If a bias field is applied, electrons or holes are transported through a small distance into the bulk and trapped by empty centers. When the illumination is switched off, thermal detrapping from the deep levels occurs with a characteristic time constant that is determined by the thermal emission rate.

On investigating the semiconductors with ferroelectric properties it is important that light impulse with suitable photon energies can change the defect's charge state without significant perturbation of crystal domain structure. The last case take place under applying the conventional DLTS technique, where the defects are filled by using electrical field or current pulses that is not applicable for our study.

The temperature dependence of the thermal emission rate can be used for recognizing of a defects recharging according to:

$$e_t(T) = \sigma_t T^2 B exp\left(-{}^{E_t}/_{kT}\right), \qquad (1)$$

where σ_t is the effective capture cross - section; B is a constant for the studied material, E_t is the activation energy of the recharging defect, k is Boltzmann constant, T is the absolute temperature.

From equation (1) the activation energy E_t and capture cross-section σ_t can be extracted with applying a conventional procedures of DLTS analyze [13] to the set of registered data.

3.2. Characterization of Traps.

Fig. 1 shows typical PICTS spectra of $TlInS_2$:La crystals. The well structured part of the spectra with clearly distinguishable maxima is observed in the temperature region below the temperatures of phase transition in $TlInS_2$ crystals [16].

The shift of the temperature position of the maximum in the set of spectra corresponding to various characteristic relaxation times is good compared to the thermal activation of emission from the defects that filled under photo excitation. It should be noted that the PICTS technique gives no way of determine the sign of the carriers trapped by centers (electrons or holes). We proposed that the detected traps are of acceptor type since traps of majority carriers are mostly observed in high - resistively semiconductors with wide band gap [17].

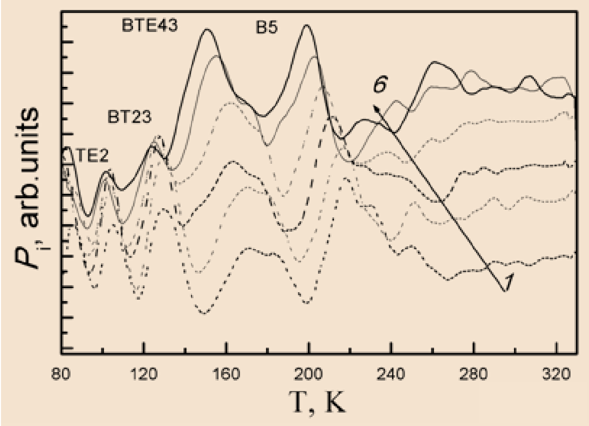


Fig. 1. - PICTS spectra of $TlInS_2$:La corresponding to the thermal emission rate: 1) 2200 s^{-1}; 2) 1350 s^{-1}; 3) 770 s^{-1}; 4) 408 s^{-1}; 5) 213 s^{-1}; 6) 108 s^{-1}; 7) 54 s^{-1}. The spectra are normalized to the height of the maximal peak and shifted along Y –axis/

The temperature dependence of the thermal emission rate for the detected traps is shown in Fig. 2.

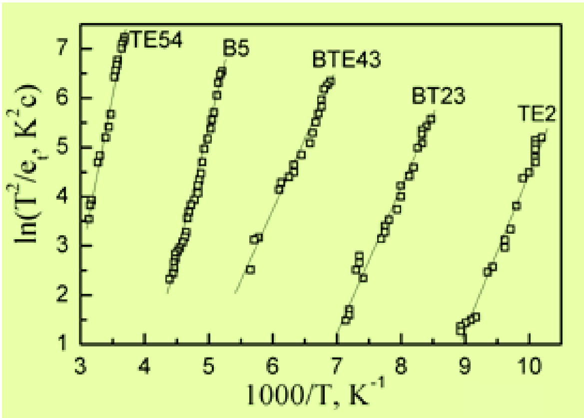


Fig. 2. - Rate of charge carrier emission from deep level traps in $TlInS_2$:La as function of temperature by taking into account T^2 correction. Solid lines represent the fitting to experimental data.

Trapping parameters of $TlInS_2$:La crystal.

Table 1.

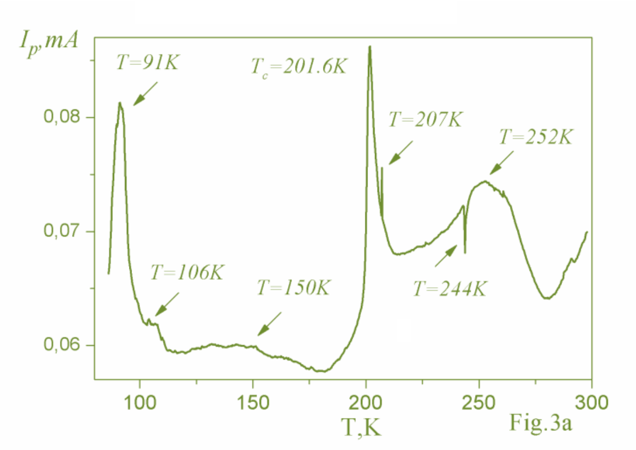
Defect	$\Delta_0 T$	E_t	σ_t
	K	eV	cm^2
TE2	98 - 115	0.2	2.2 x 10^{-14}
BT23	115 - 135	0.25	5.7 x 10^{-13}
BTE43	145 - 181	0.3	5.0 x 10^{-15}
B5	190 - 229	0.29	4.9 x 10^{-16}
TE54	270 - 320	0.57	1.0 x 10^{-13}

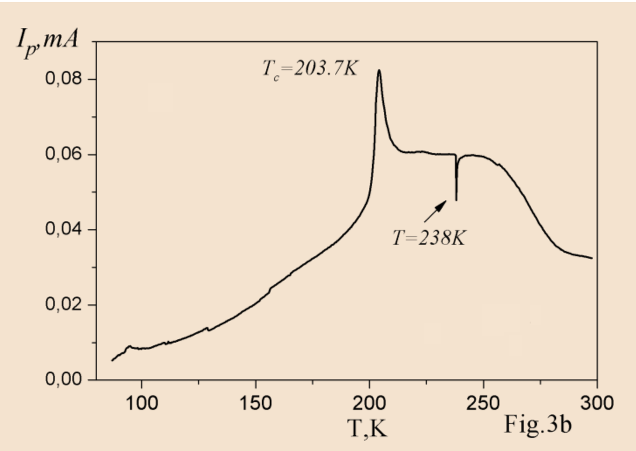
From the best fitting of plot of $ln({}^{e_t}/_{T^2})$ versus $10^3/T$, the thermal activation energies and capture cross - sections of defects were calculated. Under the σ_t evaluation the effective masses of hole was set to 0.14 m_0 according to the work [18.]. The obtained values of the thermal activation energy of the traps E_t and effective capture cross section σ_t are listed in Table 1. The temperature ranges $\Delta_0 T$ for detected signals from traps are presented in the first column of the Table 1 also.

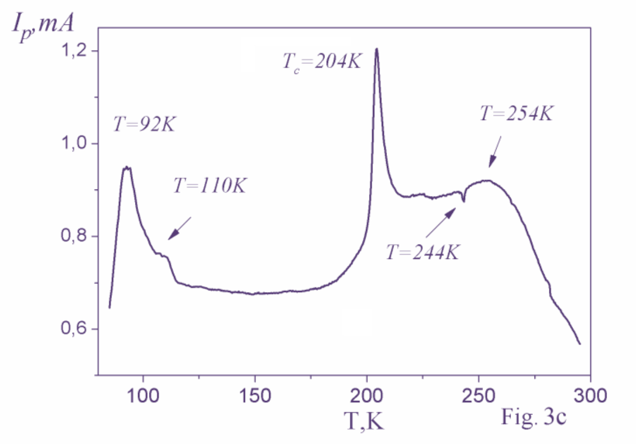
This observed defects recharging is well comparable with the results of preliminary studies of differently doped $TlInS_2$ crystals [19]. Thus, the same labels are used for defect notification in this investigation.

3.3. Polarization Effects in $TlInS_2$:La.

Fig. 3 (a – d) exhibits the temperature variation of pyroelectric current (I_p) in lanthanum doped $TlInS_2$ single crystal registered after sample poling under different electric fields in cooling. The pyroelectric current generated in $TlInS_2$:La was measured at various heating rates.







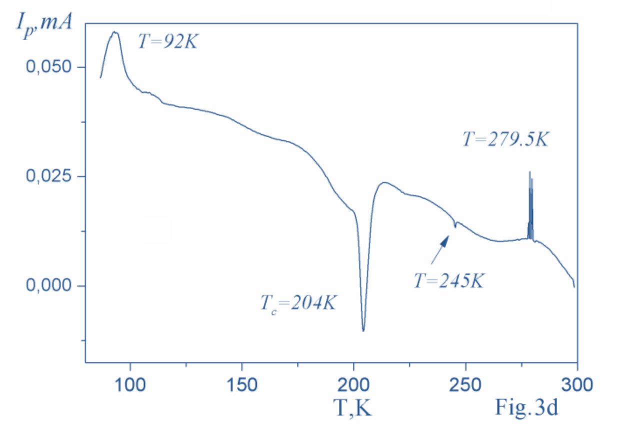


Fig. 3. - Temperature dependence of the pyroelectric current generated in $TlInS_2$:La after sample poling under different conditions.

a – The sample was polled by external electric bias field 300 V/cm in cooling from room temperature to ~ 77K. Pyroelectric current generated in $TlInS_2$:La was measured at constant heating rate 15 K / min.

b - The sample was polled by external electric bias field 300 V/cm in cooling from room temperature to ~ 77K. Pyroelectric current generated in $TlInS_2$:La was measured at constant heating rate 20 K / min.

c - The sample was polled by external electric bias field 5 kV/cm in cooling from room temperature to ~ 77K. Pyroelectric current generated in $TlInS_2$:La was measured at constant heating rate 20 K / min.

d – Same as in Fig. 3 (c), but the pyrocurrent response was measured after the short - circuit of electrodes at ~ 77K.

Fig. 1 (a) shows a shape of the pyrocurrent response of $TlInS_2$:La after poling the sample by applied dc field of about 300 V/cm. The sample was cooled from room temperature to 77K under the poling field. A constant heating rate was 15 K / min. The pyrocurrent response in Fig. 3 (a) can be divided in two parts. The low temperature part contains three peaks: one is sharp and is located around ~ 91 K; and smeared peaks in the vicinity of ~ 106 and 150K. In the high temperature part several peaks were observed at temperatures between T_c and ~250K. The sharp peak in the pyroelectric current response at T_c is connected to increase of the spontaneous polarization at Curie point of the C - phase transition. Additionally, there is remarkable peak at in the pyroelectric current response of La doped $TlInS_2$ inside the IC – phase at ~ 207 K.

According to [5, 19], the phase transition around 207K is due to intrinsic defects interacting with the IC – modulation, because defects can introduce some perturbations leading to new topological arrangement of DC's. The peaks occurring above T_i are not considered as corresponding to phase transitions. They may be due to some thermally depolarization phenomena associated with some charged defects. Note that pyroelectric current signal changes the sign at ~ 244K.

A measurement of the pyroelectric current plotted in Figs. 3 (b) and (c) was performed under the similar initial conditions but some differences were observed. The temperature dependence of I_p measured after sample poling under applied bias field ~ 300 V/cm is shown in

Fig. 3 (b). A constant heating rate was 20 K / min. It can be seen from Fig. 3 (b), that no peaks formed in the curve $I_p(T)$ in the low temperature region. The pyroelectric current maximum near Curie point is observed at T_c ~ 207.3K and sharp peak with negative sign is recorded at ~ 240K. Broad peak at ~ 250K in Fig. 3 (a) become more smeared as heating rate is increased.

Fig. 3 (c) shows the temperature dependence of pyroelectric current response of $TlInS_2$:La after sample poling under bias field ~ 5 kV/cm. The rate of temperature change was 20 K / min. It is clear that the sample previously poled under external field ~ 5 kV/cm shows significantly higher pyroelectric signal. It was revealed that the pyroelectric current values obtained from $TlInS_2$:La sample poled under ***dc*** field ~ 5 kV/cm increase by about ~ 20 times and remains qualitatively similar to that in Fig. 3 (a). One can see from the Fig. 3 (c) that the pyroelectric signal is strongly dependent on the degree of polarization state of previously poled sample.

It is known that, the pyroelectric signal in ferroelectric - semiconductors may be caused by temporary residual space charges accumulated in the trap levels in the regions directly adjacent to the electrodes (surface electric field) as well as in bulk of the crystal after initial polarization of $TlInS_2$:La in bias field [20 - 22]. An internal electric field formed in the bulk of crystal has the direction opposite to the direction of applied polarity. Using the short - circuited technique, we can separate the pyroelectric response from internal electric fields built in the bulk of $TlInS_2$:La crystal. After poling of the sample under ***dc*** electric field of ~ 5 kV/cm upon cooling from room temperature to 77K two electrodes were then short - circuited for ~ 10 min in order to eliminate the internal electric field frozen at the crystal surface. The pyroelectric current was measured on heating of crystal from 77 to 300K with the same heating rate 20 K/min. The results are plotted in Fig. 3 (d). From this figure, it can be seen that the pyroelectric signal has a maximum at about 92 K and decreases in magnitude with temperature increasing. On the approaching to the Curie point, the pyroelectric signal rapidly decreases and becomes negative forming peak at about T_c ~ 204K. Fig. 3 (d) shows reversed peak at ~ 245 K and pronounced normal peak at ~ 280K.

Fig. 4 shows the temperature dependence of the pyroelectric current for the $TlInS_2$:La specimen after poling for 10 minutes by dc electric field ~ 5 kV/cm at 78K. It is seen from Figs. 3,*a* and 4 that there is no principal difference in the temperature behavior of the pyrocurrent signal for $TlInS_2$:La sample subjected to different polarization conditions. The only difference is two normal peaks at ~ 157 and ~ 194 K. It is remarkable that similar picks on $I_p(T)$ curve was observed after crystal poling under bias electric field applied to sample in different temperature ranges. Possibly, the appearance of these additional picks is conditioned by the additional polarization induced by the crystal poling processing.

Fig. 5 demonstrates the evolution of the pyroelectric current of $TlInS_2$:La as a function of the temperature for sample poled in the temperature region ~ 210 – 300K using a ***dc*** electric field of ~ 5kV/cm. The temperatures of some peaks are indicated in this Figure. Rather unexpectedly we do not see any peaks at $T < T_c$. It can be observed that the temperature of the maximum of the pyroelectric current corresponding to T_c is a little lower in comparison with previous data.

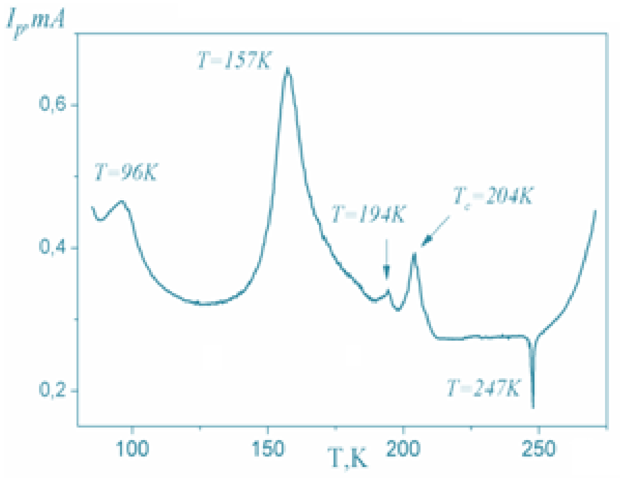


Fig. 4. - Temperature dependence of the pyroelectric current generated in $TlInS_2$:La after sample poling at ~ 77 K by dc electric field ~ 5 kV/cm. The heating rate was 20 K / min.

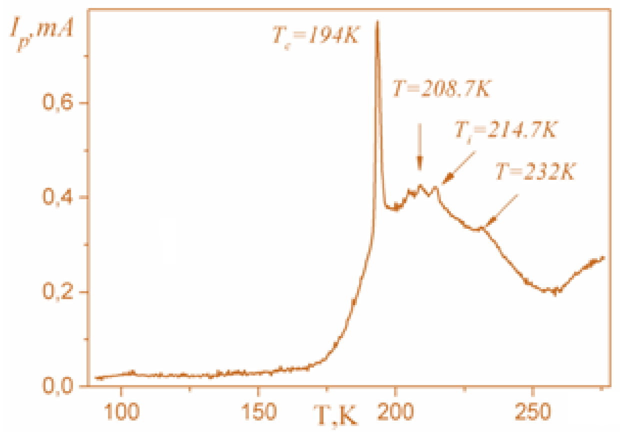
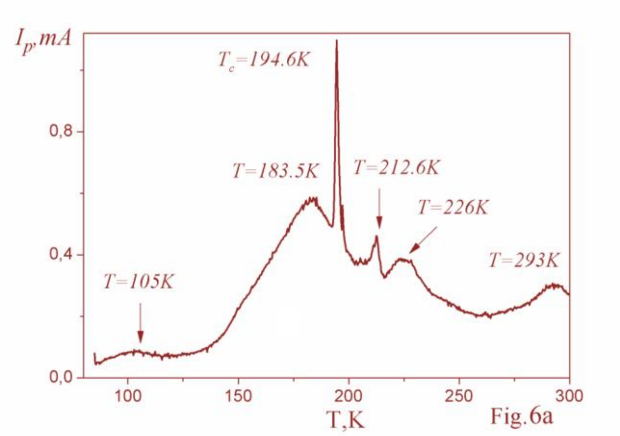
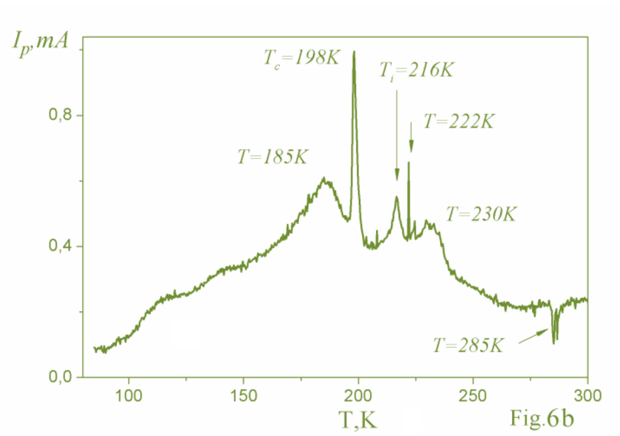


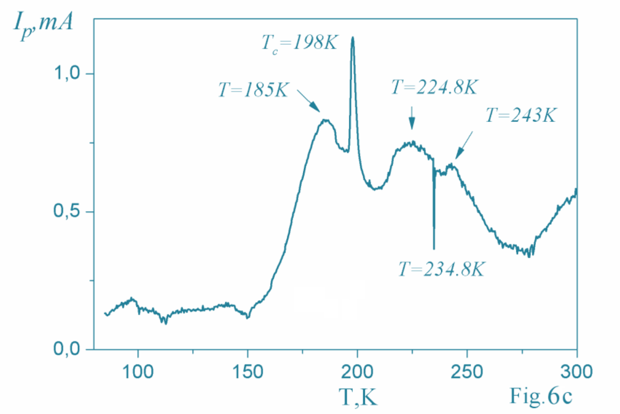
Fig. 5. - Temperature dependence of the pyrocurrent generated in $TlInS_2$:La after sample poling by dc electric field ~ 5 kV/cm in the temperature region ~ 210 – 300K in cooling . The heating rate was 20 K / min.

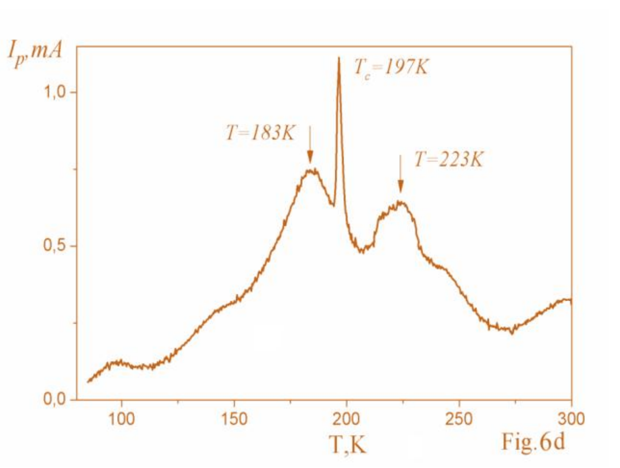
As indicated by the arrows in Fig. 5, small peaks are well defined at ~ 208 and ~ 215K corresponding to anomalies at T_i and inside the IC – phase [23]. However, it needs to be pointed out that average polarization inside IC – phase must be zero because the IC - phase possesses the center of inversion symmetry [10, 11]. This means that during poling process the external electric field does not induce aligned polarization inside IC – phase.

These results support the existence of coupling between a bias electric field the aligned polarization inside IC – phase. We assume that defects make major contributions in retained polarization of the IC – phase. These results will be discussed later together with other experimental results.









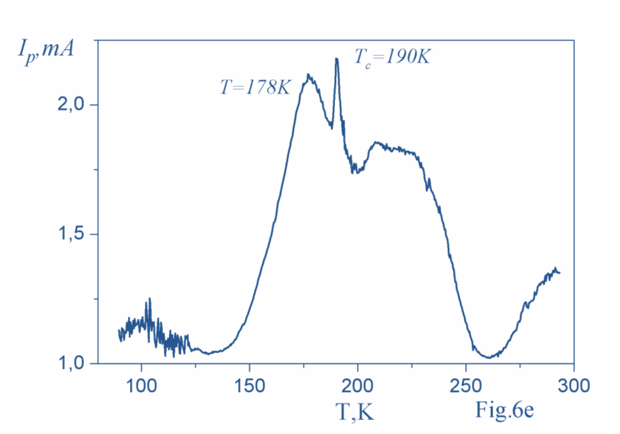


Fig. 6. - Same as Fig. 5, but the sample was polled in the temperature region: (a) –~ 180 – 300 K; (b) –~ 180 – 290 K; (c) - ~ 180 – 260 K; (d) - ~ 180 – 240 K; (e) - ~ 180 – 220 K.

Fig. 6a – Fig. 6e shows a set of typical curves of the pyroelectric current as a function of the temperature for $TlInS_2$:La recorded after sample poling in different temperature regions. The poling temperature regions were chosen in accordance with temperature intervals of traps activation TE54 and B5 (Table 1). As in previous measurements the sample was polarized by ~ 5 kV/cm electric field. The temperature was raised from liquid nitrogen to room temperature at a constant rate of ~ 20 K/min.

All curves in Fig. 6 show different features with respect to poling regimes. An anomalous maximum of $I_p(T)$ at the Curie transition point is well seen in all curves. The temperature of maxima of $I_p(T)$ at T_c is observed in the region between 190 and 198 K. The shape of $I_p(T)$ curve in Fig. 6 is significantly different. As a rule, two main peaks, a weak peak at low temperature ~ 100K and a strong one at ~ 180 K are observed in all curves. Besides, additional anomalies of $I_p(T)$ with modified shape and temperature positions are recorded in all curves in the 220 – 240K range.

Fig. 7 (a and b) demonstrates the pyroelectric current versus temperature for $TlInS_2$:La sample previously poled in the presence of dc electric field at ~ 5 kV/cm on cooling in the temperature region ~ 220 - 80K and ~ 190 - 80K, respectively. The pyroelectric current across the sample was measured at the same heating rate ~ 20 K/min. These temperature regions correlate with the range of thermal activation of deep level defects B2, BTE43, BT23 and TE2 (see Table 1).

One can see that the temperature range of the thermal activation of deep level defect B2 involves the temperature region of a sequence of structural phase transitions in $TlInS_2$:La. Therefore one must keep this in mind in dealing with influence of defects on structural phase transitions in $TlInS_2$:La. The point here is that defect B2 must get a dipole moment after poling by electric field. This brings to appearance of quasi - static internal electric field originated from charged B2 defect and existing into crystals in the temperature interval 190 – 220 K. This field, which is parallel to the poling external electric field is responsible for the polarization properties of $TlInS_2$:La inside the IC – phase during the pyrocurrent measurement. In the presence of a strong internal electric field due to B2 defect, the pyroelectric response in Fig. 7 (a) exhibits unusual behavior at ~ 185K. A sharp peak with opposite direction was also observed at T_i. This result can be interpreted on the base of assumption that space charge accumulated by B2 defect gives rise to a strong imprint internal electric field where two opposite polarization orientations is favored regardless of the sign of the external field.

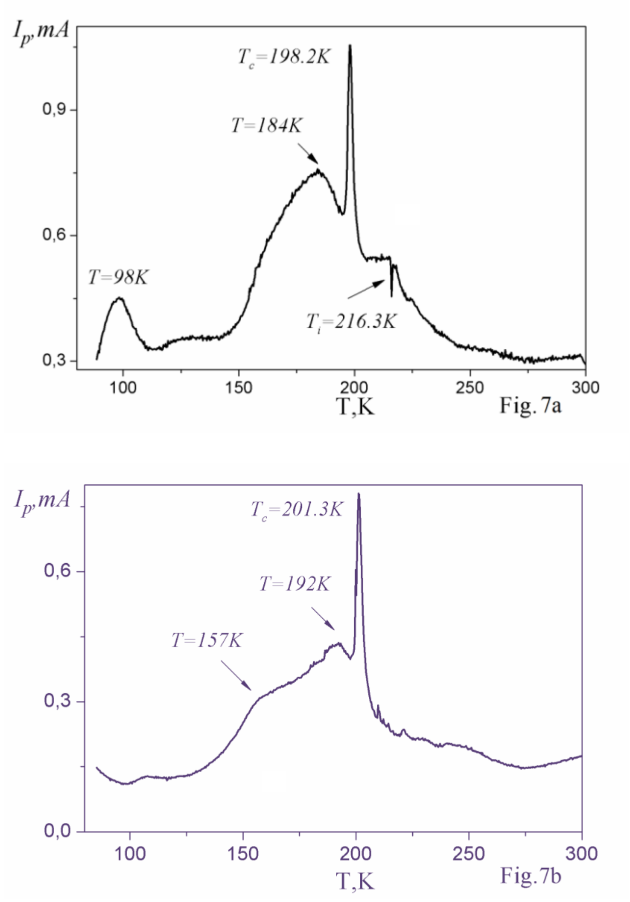


Fig. 7. - Same as Fig. 5, but the sample was polled in the temperature region: (a) – ~ 80 – 220 K; (b) – ~ 80 – 190 K.

Additionally, it is evident that, various electrically activated defects in $TlInS_2$:La lead to different internal electric fields in crystal. Such situations are illustrated in Fig. 7 (a and b). If charge carriers are captured by other trap levels, for example, BTE43, BT23 and TE2 by the crystal poling the internal electric field originated from this ionizated does not contribute to the pyrocurrent signal recorded inside the IC – phase.

The electric activation of BTE43, BT23 and TE2 defects in $TlInS_2$:La and the formation of the imprint internal electric field from charge carriers trapped by this defects should be tested by pyroelectric current measurements after sample poling in the presence of dc electric field ~ 5 kV/cm on cooling in the different temperature renges inside the commensurate ferroelectric phase ~ 170 – 80 K, ~ 140 – 80 and ~ 120 – 80 K, respectively (see Fig. 8 and Table 1). The pyroelectric current measurement in Figs.8 was performed at the same heating rate ~ 20 K/min.

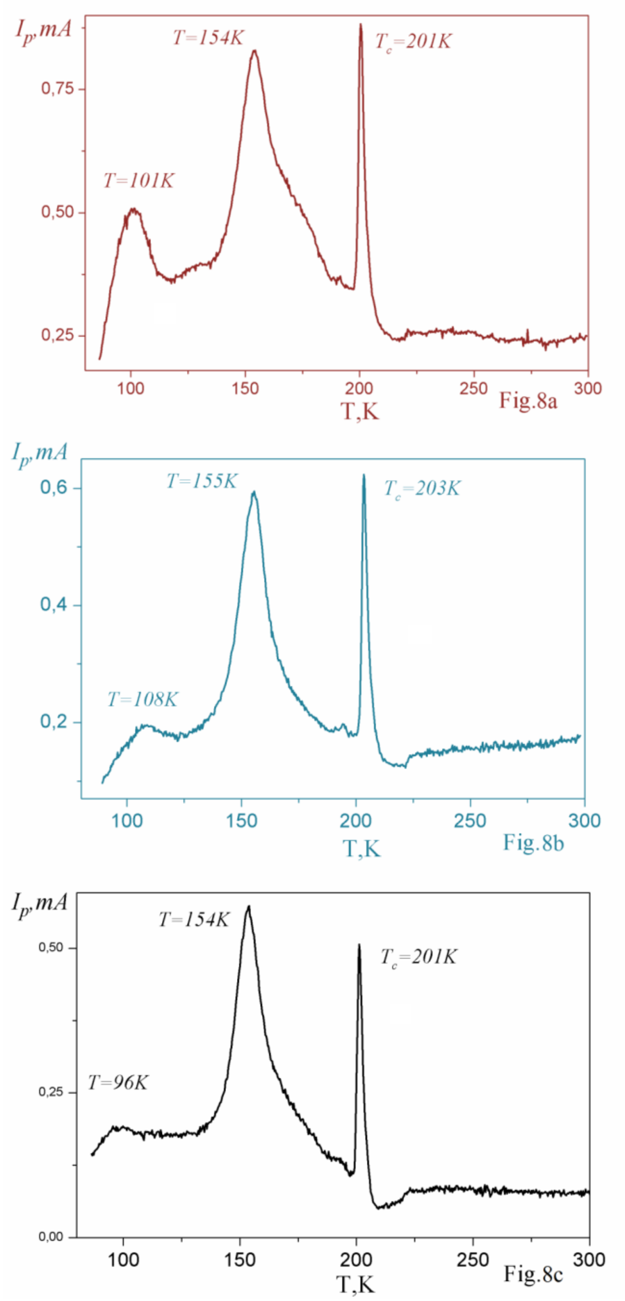


Fig. 8. - Same as Fig. 5, but the sample was polled in the temperature region: (a) – ~ 80 – 170 K; (b) – ~ 80 – 140 K; (c) - ~ 80 – 120 K.

As it can be seen from Fig. 8 similar changes of the pyroelectric current have been found. A broad maximum at ~ 155 K in $I_p(T)$ after electric polarization of $TlInS_2$:La in different temperature intervals is appeared. The magnitude of a broad peak at ~ 155 K is comparable with a sharp peak of $I_p(T)$ at the Curie temperature. Pyroelectric current around a broad anomalous at ~ 155K and near T_c has the same direction, while external field at the Curie point during the poling process has not been applied to the sample. The latter may be due to the presence of strong internal field into the sample. The origin of this internal field and a broad anomalous at ~

155K can be originated from BTE43 defects. Defects labeled as BTE43 can be activated by poling La dipoles because this type of defect is not discerned with PICTS in undoped $TlInS_2$ single crystal [16].

Experimental results in Fig. 8 demonstrate that no observable change in the pyroelectric current signal is observed at the temperatures 115 – 135K, which correspond to thermal activation of BT23 deep level defect. However, the anomalous in the pyroelectric current signal at ~ 100 K have been found in all curves of Fig. 8 and in the most curves of Figs. 3 - 7. The TE2 deep level center with a high ionization cross section (see Table 1) activated by external electric field is believed to be the source of the pyrocurrent signal observed in this material.

3.4 - Dark current measurement of $TlInS_2$:La.

From the results discussed so far one may conclude that there is a correlation between temperature ranges of the thermal activation of deep level defects revealed by using PICTS technique and polarization properties of the La doped $TlInS_2$ single crystal. These deep level traps must induce electronic states in the band gap of $TlInS_2$:La which have to alter significantly the dark current properties of $TlInS_2$:La crystal.

The results of dark current measurement in the temperature range of 77 – 300 K obtained by standard two - probe method are shown in Fig. 9. The same contacts were used to study the temperature behavior of the resistance. The measurements were performed with a heating rate of ~ 2 K/min. The dark conductivity of the $TlInS_2$:La crystal exhibits activation type temperature dependence.

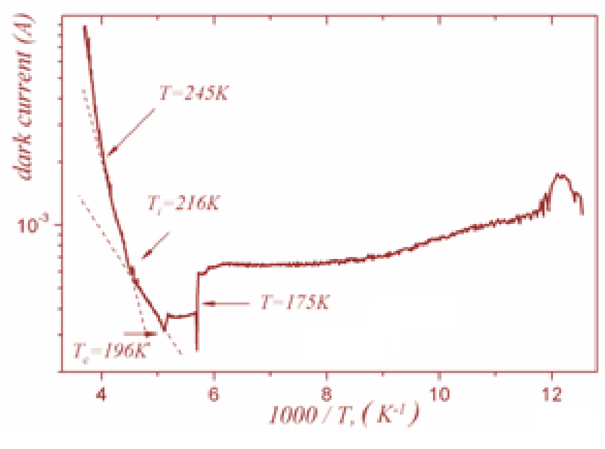


Fig. 9. - Dark current versus temperature for $TlInS_2$:La shown in the Arrhenius plot. The measurement was carried out in the direction parallel to the layer at the bias of ~ 10V. The heating rate is 2 K min^{-1}.

A large step – like thermal anomaly in the temperature dependence of dark current was observed at ~ 175K. On the other side, a small thermal anomaly was registered at Curie temperature of the phase transition at about 196 K. A characteristic feature of anomaly at ~ 175K and at Curie point is that the dark current to resemble, in general, the behaviour of the pyrocurrent observed under the action of crystal poling.

Additionally, changes of the dark current curve slope were observed at T_i and near ~ 245K. It can be interpreted by the change of the carrier activation energy at the phase transition. Three distinct temperature regions 196 – 216K, 216 – 245K and 245 – 300K with different activation energies 0.25, 0.58 and 0.72 eV, respectively, were found. The activation energies of impurities in these temperature regions were calculated from Arrhenius relationship, which are in good agreement with PICTS dates. Therefore, it can be concluded that the dark current throughout the $TlInS_2$:La sample inside the IC – phase and above the IC – phase transition point T_i is considerably controlled by B5 and TE54 intrinsic defect centers. From these results, it can safely be assumed that B5 deep level center clearly reflects the structural changes in the temperature region of the existence of an intermediate IC – phase in $TlInS_2$:La. The dark current at low temperatures is not due to excitations of carriers from TE2 and BT23 native deep levels as well as BTE43 defect center belonging to La – impurity because this process requires much larger energy of activation.

4. DISCUSSION OF EXPERIMENTAL RESULTS

Thus, trap levels labeled TE2, BT23, BTE43, B5 and TE54 have been detected in PICTS measurements in $TlInS_2$:La. Arrhenius plots of $ln\left({}^{e_t}/_{T^2}\right)$ versus $1000/T$ allowed the determination of the activation energies of defects, Fig. 2. The trap parameters extracted from the Arrhenius plot are summarized in Table 1.

The dominant deep level trap is B5 has the activation energy of 0.3 eV from the top of the valence band. It is a native defect since it has also been observed in PICTS measurements of trapping levels in undoped $TlInS_2$ [16]. The thermal activation region of B5 - localized level (variation of charge density on this trapping level) is correlated with phase transitions region in $TlInS_2$. In the presence of an external poled electric field, random electrical fields produced by ionized deep B5 impurities are aligned in the direction opposite to the direction of the applied electric field, and very strong internal electric field is appeared in the bulk of $TlInS_2$:La. It is a reversed electrets field according to the terminology used in [24, 25]. The pyroelectric signal of $TlInS_2$:La due to polarization of crystal in the presence of reversed bulk internal electric field is shown in Fig. 3 (d). An important attribute of macroscopic polarization of $TlInS_2$:La originated from charged B5 defects localized in the bulk of crystal is the presence of negative values of the pyroelectric current appeared during heating run near the Curie point for short - circuited sample.

The origin and nature of B5 deep trapping center is not known. However, we would like briefly to discuss the microscopic properties of the B5 defect. It can be concluded from the pyroelectric studies that B5 trapping centers are deep charged defects with frozen opposite bulk polarizations. It is well known that the defect with frozen dipole polarization may be realized as an interstitial defect in a site of sufficiently low symmetry [1]. Experimental facts indicate that the electronic properties of the B5 defects are also affected by lattice distortions observed at the phase transition points in

$TlInS_2$:La. This result can be interpreted on the base of the presence of electron - lattice interaction around the crystalline environments of B5 defect locations, whose symmetry allows to linear coupling to the soft mode of structural symmetry distortion. So, it can be expected that substantial lattice distortions in $TlInS_2$:La at phase transition points will occur in trigonal prismatic voids where Tl atoms are located [26].

The presence of the structural distortion together with the giant static dielectric constant ($\varepsilon \sim 1500$) inside the IC – phase of $TlInS_2$:La [3 – 5, 19 -23] transforms the B5 defects to the charged trap. It is well known that the ionization energy of the traps is inversely proportional to the dielectric constant of the medium. Thus, in the region of intermediate IC – phase there is collective accumulation of charged B5 deep defect centers. The internal electric field induced by electrically active B5 centers in the temperature region of 190 – 230 K is the electrets field. This built – in internal electrets field is far from being completely disappear even after a long time because discharged processes have a low speed at low temperatures. Self - polarization of $TlInS_2$:La due to B5 trapping centers produce the pyrocurrent current signal that exhibit all anomalies inherent in the $TlInS_2$:La sample in the region of phase transitions as it is shown in Figs. 5, 6 and 7 (a). Note that the poling procedure for normal ferroelectrics always requires application of a strong external electric field inside the ferroelectric phase. Self - polarization of $TlInS_2$:La occurs outside the ferroelectric phase and pretreatment of crystal under high external electric fields within the ferroelectric phase can be avoided. An internal electric field appeared in $TlInS_2$:La sample above T_c due to charged B5 deep level defects is higher than the coercive field at Curie temperature.

The defect labeled BTE43 was observed only in $TlInS_2$:La. This deep level is related to La dopant. The results allowed to suppose that the peak observed on the temperature dependence of pyroelectric current near 155 K is induced by charged BTE43 deep trapping center (see Fig. 8). It was found that the direction of internal electric field due to charged BTE43 defects is collinear to the direction of the applied poling electric field. The temperature of the pyroelectric current anomaly near 155 K induced by frozen – in internal field from BTE43 charged defects is significantly lower than the Curie point. The poling electric field can be applied to $TlInS_2$:La at temperatures below ~ 170K in order to detect the pyrocurrent anomaly due to BTE43 charged defects in the vicinity of 155K. If the sample is maintained under the external field up to the temperatures above 170K, the pyroelectric current peak at ~ 150 K is disappeared. Then, one may conclude that the frozen internal field from B5 charged defects screens (or discharges) the space charge polarization from charged BTE43 deep trapping centers. The reason of this phenomenon is not clear yet.

The peak on the temperature dependence of the pyroelectric current at temperatures ~ 90 – 100K is originated from charged TE2 deep level trap. It is a native defect with unknown origin with energy 0.2 eV and activation temperature interval of 98 – 115K. In our studies we found this level in almost all pyrocurrent measurement.

Two other defects BT23 and TE54 are native defects too. They have been clearly observed by PICTS in undoped $TlInS_2$ [16]. Due to their trap parameters, particularly the high cross sections $\sim 10^{-13} cm^2$, these levels correspond an extended defects.

A deep trapping level BT23 is very similar to TE2. Therefore it is very difficult to identify it contribution in crystal polarization from pyroelectric current measurements. Perhaps, BT23 and TE2 are native strongly compensated deep levels controlling the electronic properties of $TlInS_2$ at low temperatures, providing semi – insulating properties of this material in the low temperature range. Obviously, more clear evidence of the compensation nature of these defects and their microstructure must be obtained.

The contribution of native TE54 deep level in resistivity of $TlInS_2$:La can be easily identified at room temperatures from dark current measurements. $TlInS_2$ is identified as ***p*** – type semiconductor material. Therefore, TE54 is deep level acceptor. The experimental data do not allow any conclusion to be drawn about the nature of this center because of the lack of information about the crystal defects in $TlInS_2$ material.

5. CONCLUSIONS

Thus, the polarization phenomena in La – doped $TlInS_2$ ferroelectric – semiconductor due to internal electric fields originated from charged deep level trapping centers are investigated. The $TlInS_2$:La was also characterized and studied by PITCS measurements at different temperatures. Using PITCS measurements, five deep levels in $TlInS_2$:La were observed. Four of them were identified as native defects because they have been observed in undoped $TlInS_2$ also. The trap BTE43 corresponds to the La dopant. The activation energy of all deep centers and their cross sections were determined. The contribution of each charged defect in polarized properties of $TlInS_2$:La was identified from the pyroelectric current studies. It was shown that the anomaly of the pyroelectric current detected above the Curie point is attributed to the self – polarization of $TlInS_2$:La under internal electric field formed from charged B5 native deep level. The IC – phase as a medium with giant and stable dielectric constant can be responsible for the ionization of B5 deep defect because the thermal activation region of B5 defect coincides with the temperature region of existence of the intermediate IC – phase in $TlInS_2$.

It is assumed that the anomaly of pyroelectric signal near 155K is related to BTE43 deep level. Pyroelectric signals of previously poled at $T < 170$K $TlInS_2$:La crystal could not be observed near 155K since this temperature is below enough than the Curie temperature.

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