RELAXOR PROPERTIES OF $TlInS_2$ CRYSTALS DOPED BY Fe

R.M. SARDARLI, O.A. SAMEDOV, I.Sh. SADIGOV, I.I. ASLANOV, A.P. ABDULLAEV
Institute of Radiation Problems of Azerbaijan National Academy of Sciences
H.Javid ave., 31a, Baku, 370143

J.H. JABBAROV
Baku State University
Z.Khalilov St., 23, Baku, 370143

It is shown that $TlInS_2$ crystals doped by Fe show all peculiarities that are typical to the relaxor ferroelectrics. The temperature region of the microdomain (relaxor) state as well as the temperature of the transition to the macrodomain state have been determined.

The analysis of temperature dependences of the dielectric constant *ε(T)* in the phase transitions region of $TlInS_2$ crystal showed that it has a different form for the samples that were taken from various technological batches. Authors of [1] determined that the different form of *ε(T)* curves is connected with the fact that $TlInS_2$ crystal belongs to the class of compounds (berthollides) in which the rearrangement of composition occurs during the growth process. However this peculiarity does not lead to the smearing of the phase transitions and the dependence $\varepsilon^{-1}(T)$ obeys Curie-Weise law with the constant approximately equal to 10^{-3} beginning from the submillimetric spectral regions up to the measurements of *ε(T)* in the kilohertz region [2, 3]. It was established by the neutron-diffraction research that $TlInS_2$ compound is an improper ferroelectric with an incommensurate phase [4].

The temperature region, in which instability of $TlInS_2$ crystal lattice is observed is a very sensitive to the trivalent cationic impurities that have different ionic radii and the coordination numbers. Moreover, the increase of phase transition temperatures is observed for some impurities while the decrease of phase transition temperatures is observed for others impurities (the results of this research are in preparation for publication). There is an interest to investigate the nature of these processes in $TlInS_2$ crystals. The transition metals of iron group being the multicharged impure ions can form the deep centers of strong localization that capable to the strong interaction with high-polarizable $TlInS_2$ crystal lattice.

The investigation results of dielectric, polarization and pyroelectric properties of $TlInS_2$<Fe> crystals are given in this paper.

EXPERIMENTAL TECHNIQUE.

$TlInS_2$ crystals have been grown by Bridgman-Stockbarger modified method. The anisotropy of dielectric properties in the plane of layer is not observed. The measurements have been carried out from the crystal faces cut out perpendicular to the polar axis. The crystal faces have been planished, polished and then covered by a silver paste. The dielectric constant ε and the dielectric loss tangent tgδ have been measured by the alternating current bridge E7-8 at the frequency 1 kHz and E7-12 at the frequency 1 MHz in the temperature region 150 - 250K. The velocity of temperature scanning was equal to 0.1 K/min. The dielectric-hysteresis loops were studied at the frequency 50 Hz by Soyer-Tauer modified scheme. The pyroeffect has been investigated by the quasistatic method using universal voltmeter V7-30.

RESULTS AND DISCUSSION.

The temperature dependence of the dielectric constant ε*(T)* of both $TlInS_2$ (curves 1, 2) and $TlInS_2$<Fe> crystals (curves 3, 4, 5) in the cooling (curves 1, 3, 5) and heating regimes (curves 2, 4) are shown in figure 1. The measurement frequency to the curves 1, 2, 3 and 4 is equal to 1 kHz. The curve number 5 presents the results of measurement of ε(T) to $TlInS_2$<Fe> crystal at the frequency 1 MHz. As it is seen from figure 1, the known sequence of the phase transitions [3] is observed to $TlInS_2$ crystals (curves 1, 2). It is observed also the transitions from the paraelectric to the commensurate phase at 216K, as well as two transitions at 204 and 200K. The nature of these transitions was widely discussed in [5] and most likely it is connected with rearrangement of the modulated structure. The final transition to the polar phase occurs at 196K.

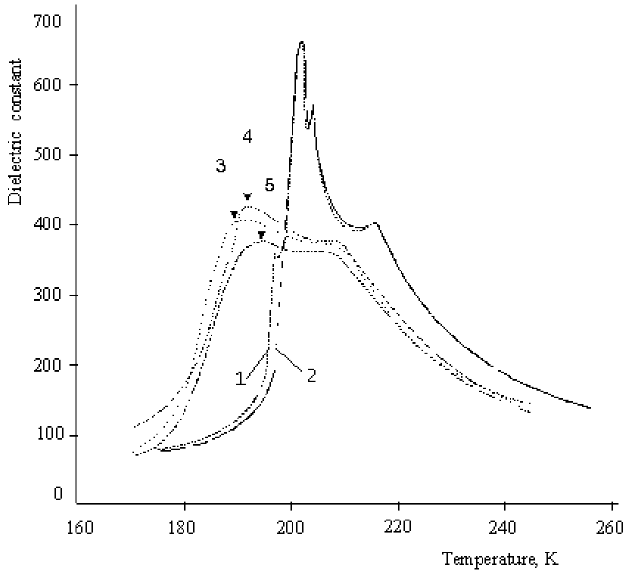

Fig.1. The temperature dependences of the dielectric constant ε*(T)*. Curves 1, 2 - the dependences ε*(T)* of $TlInS_2$crystal (1 - cooling; 2 - heating); Curves 3, 4, 5 - the dependences ε*(T)* of $TlInS_2$<Fe> crystal (3, 5 - cooling; 4 - heating). The measurement frequencies are 1 kHz (to the curves 1, 2, 3 and 4) and 1MHz (to the curve 5).

The dependence ε*(T)* is described by Curie-Weis law with Curie constant $C^+=5.3\cdot10^3$K in the temperature region $T-T_1(216)\leq50^0$. The anomaly at 196K appears during the crystal cooling and all peaks are strongly pronounced without the signatures of the smearing. As it is obvious from figure, the dielectric hysteresis for $TlInS_2$ crystals is observed only at the temperature about 196K, while the hysteresis to the doped samples at the temperature T_m (it is a maximum temperature of ε*(T)* curve) is about 2K (curves 3 and 4 in fig.1).

The nature of the dielectric constant in the same temperature region for $(TlInS_2)_{1-x}(Fe)_x$ crystals, where x = 0.001, is essentially distinctive namely the dependence ε*(T)* is strongly blurred. The displacement of phase transitions to the low temperature region in 10K and the widening of region of existence of the incommensurate phase with conservation of two anomalies at 190K and 290K have been observed. In this case the natural question arises regarding the reason of such radical rearrangement of the dependence ε*(T)* at doping 0.1-mol % of Fe.

As it is known, the composition fluctuation is a main reason of the smearing of phase transition temperatures [6, 7]. However, not any increasing in the defect concentration can be a reason to the smearing. According to [8] the defects having dipole moments are the reasons for such smearing and these defects create the electric fields in adjoining crystal regions. Besides as $TlInS_2$ is a semiconductor, the doping of impurities creates the corresponding centers of charge carrier localization, which can create the local electric fields that stimulate the initiation of the induced polarization near the phase transitions [9-11]. Important peculiarity of the ferroelectrics with smearing phase transitions is the fact that the dielectric polarization higher than T_m changes not by Curie-Weis law $(\varepsilon')^{-1}= C^{-1}(T-T_0)$ and by the law $(\varepsilon')^{-1}=A+B(T- T_0)^2$.

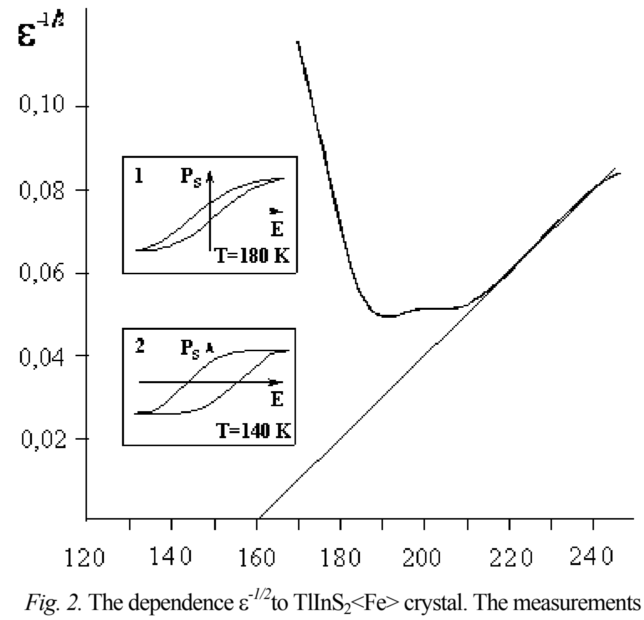

Fig. 2. The dependence $\varepsilon^{-1/2}$ to $TlInS_2$<Fe> crystal. The measurements are carried out at the frequency 1MHz.The dielectric-hysteresis loops to $TlInS_2$<Fe> crystal are given in the insertions to the figure: 1 - the measurements are carried out at 180K; 2 - the measurements are carried out at 140K.

The dependence $\varepsilon^{-1/2}(T)$ for $TlInS_2$<Fe> is shown in fig. 2. This dependence line crosses the temperature axis at 164K from the side of high-temperature phase. It corresponds to the maximum value of low-temperature pyrocoefficient (fig. 3). The investigations of polarization properties of $TlInS_2$<Fe> showed that the dielectric-hysteresis loops are observed below 164K and the maximum value of spontaneous polarization *(P_s)* for such loops reaches up to $7.5\cdot10^{-8}$ Coulomb/sm^2. The value of P_s to the undoped $TlInS_2$ crystals is equal to $1.8\cdot10^{-7}$ Coulomb/sm^2. The value of P_s in the temperature region from 164 to 190K is $1.5\cdot10^{-8}$ Coulomb/sm^2. The dielectric-hysteresis loops for $TlInS_2$<Fe> crystals are given in the insertions to the fig.2. The first insertion to the figure reflects the observed loop in the temperature region 164 - 190K. As it is obvious from figure the loop is narrow and elongated that is a typical to the relaxor ferroelectrics. The form of dielectric-hysteresis loop below 164K has been given in the second insertion of the figure. It is obvious that the loop becomes saturated and it is a typical for the ferroelectric.

The investigations of frequency dispersion have been carried out at measurement frequencies *f* - 1 KHz and 1 MHz. The displacement of T_m maximums of ε*(T)* curve with increasing frequency *f* in $TlInS_2$ crystals is not observed while the displacement of the smearing maximum of ε*(T)* to $TlInS_2$<Fe> crystals is equal to 3K (figure 1, curves 3 and 5).

The temperature dependences of the pyroelectric coefficient *γ(T)* for the pure $TlInS_2$ crystal (curve 1) and for the doped by Fe (curve 2) are given in the fig.3. The measurements were carried out in the quasistatic regime and the pyroelectric coefficient was calculated using the following equation: $\gamma=J/A_0\cdot dT/dt$, where *J* is a pyroelectric current, A_0 is an area of electrodes, *dT/dt* is a heating rate. The measurements were carried out using the samples, which were preliminary polarized in the external electric field. As it is obvious from figure, one peak with maximum value of the pyroelectric coefficient $1.4\cdot10^{-7}$ Coulomb/Ksm^2 in the curve *γ(T)* is observed to the pure $TlInS_2$ crystal at 196K. Two anomalies at T_m=190K and T_0+164K in the curve *γ(T)* are observed to $TlInS_2$<Fe> crystal. Besides, the weak current is observed in the temperature region higher than 190K, i.e. in the region of existence of the incommensurate phase.

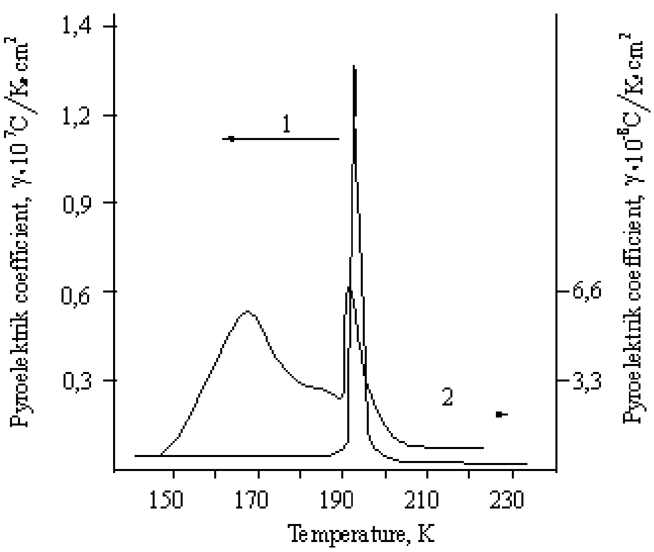

Fig.3. The temperature dependence of the pyroelectric coefficient *γ(T).* Curve 1- $TlInS_2$ crystal. Curve 2- $TlInS_2$<Fe> crystal.

The analysis of the curves are given in the figures 1-3 allows to state that $TlInS_2$<Fe> crystals show all peculiarities that are typical to the relaxation ferroelectrics namely the doping of $TlInS_2$ crystal by Fe^{3+} cations leads to the smearing of phase transitions as well as the frequency dispersion of the dielectric constant is observed. Moreover, the elongated dielectric-hysteresis loop is detected in the region of the smearing of phase transition and the temperature dependence of the dielectric constant from the side of high-temperature phase is described not by Curie-Weis law and according to the law $(\varepsilon')^{-1} = A + B(T - T_0)^2$.

The smearing of phase transitions and the peculiarities of ferroelectric properties in $TlInS_2$<Fe> crystal are unconditionally connected with the structure disorder that leads to the appearance of local distortions of both the symmetry and internal electric field in the wide temperature region. Despite the fact that the investigations of phase transitions in $TlInS_2$ crystals carried out during long period yet there are no the satisfactory understanding physical mechanisms of the processes taking place in the crystals and also the unambiguous interpretation of the observed phenomena. In our opinion it can be connected with the fact that during the investigations of phase transitions in $TlInS_2$ crystals not enough attention was given to the semiconductor properties of these crystals. Especially it concerns the crystals which are doped by the cationic impurities. These impurities can form the capture levels (traps) at the bottom of the conduction band. Here it is necessary to take into consideration both the processes of charge carrier localization on the local centers and their influence on the phase transitions. This issue has been considered in detail by Mamin in [9-11], where it was shown that the thermal filling of traps could lead to the intricate sequence of phase transitions as well as the appearance of unstable boundary state between the (incommensurate-commensurate) phases.

As it is seen in the curve $\gamma(T)$ at 164K the peak, which is not shown in the dependence $\varepsilon(T)$ (please compare fig.1and 3) is observed. According to [11] this peculiarity is a typical for the relaxors. It is connected with the fact that the oscillation frequency of the induced polarization will be determined by the characteristic relaxation time not only for the lattice subsystem as it has a place in usual ferroelectrics but also and the relaxation time of the electronic subsystem. Naturally, the characteristic time of change of parameter order γ and the characteristic time of electron concentration m in the traps strongly differ (τ_η/τ_m<<1). It allowed an author of [11] to investigate this problem by the separation method of fast and slow processes. As a result it has been established that effective temperature of the phase transition T_{cm} will be displaced below in the temperature scale due to thermal filling of the capture levels. The phase transition to the state with spontaneous polarization will occur at the temperature T_{cm}. This temperature corresponds 164K to the crystals $TlInS_2$<Fe> (fig.2). As it is seen from figure, below 164K the loop becomes saturated. As the localized charges create the local electric fields then the spontaneous polarization in the weak external fields in the separate microfields will be directed to the different directions in compliance with space distribution of the localized charges. Therefore, the hysteresis loop in the temperature region 164-190K is observed as narrow and elongated. Besides, according to the same reason, we did not observe the peculiarities in the dependence $\varepsilon(T)$ connecting with phase transition at the temperature T_{cm}.

Thus, the doping of $TlInS_2$ crystals by Fe leads to the appearance of the temperature region in which the crystals show all peculiarities that are typical for the relaxors. The phase transition from the relaxor (microdomain) to the macrodomain (ferroelectric) state occurs at the temperature 164K. The jump in the temperature dependence $\gamma(T)$ corresponds to this transition.

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R.M. Sərdarlı, O.Ə. Səmədov, İ.Ş. Sadıqov, İ.İ. Aslanov, A.P. Abdullayev, C.H. Cabbarov

Fe AŞQARLANMIŞ $TlInS_2$ BİRLƏŞMƏNİN RELAKSOR XASSƏLƏRİ

Müəyyən edilmişdir ki, $TlInI_2$ Fe-la aşqarlandıqda, kristall relaksor seqnetoelektriklər üçün xarakterik olan xassələr göstərir. Kristalın mikrodomen (relaksor) halının varlıq temperatur intervalı və makrodomen halına keçid temperaturu tə'yin olunmuşdur.

Р.М. Сардарлы, О.А. Самедов, И.Ш. Садыхов, И.И. Асланов, А.П. Абдуллаев, Д.Г. Джаббаров

РЕЛАКСОРНЫЕ СВОЙСТВА $TlInS_2$ ЛЕГИРОВАННОГО Fe

Показано, что $TlInS_2$, легированный Fe, проявляет все особенности, характерные для релаксорных сегнетоэлектриков. Установлены температурная область существования микродоменного (релаксорного) состояния и температура перехода в макродоменное состояние.

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