ELECTRIC-FIELD-INDUCED PHASE TRANSITION IN THE RELAXOR $TlInS_2$<Fe>

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ABSTRACT

Doping of $TlInS_2$ with Fe results in appearance of stable relaxor state temperature region. Nanodomain relaxor - to - macrodomain ferroelectric state phase transition takes place at $T_f \approx 174K$. Burns Temperature $T_d \approx 210K$ was determined by polarization measurements. It was shown that in the T_d - T_f temperature interval, a jumping conductivity exists and becomes non-activated below T_f. Influence of constant electric fields provokes jump of pyrocoefficient and dielectric loss tangent inducing the phase transition, which corresponds to Vogel-Fulcher temperature.

Keywords: dielectric properties, ferroelectrics, relaxor, polarization, pyroelectric properties.

I. INTRODUCTION

Ferroelectrics with smeared phase transitions, also called relaxors, belong to the most studied ferroelectric materials. The greater part of studies of relaxor ferroelectrics deal with complex compounds of perovskit structure expressed by the common formula AB'B''O, where equivalent B positions in a lattice are occupied by randomly distributed ions of different valences (compositional disorder). The most known in these materials' family are $Pb(Mg_{1/3}Nb_{2/3})O_3$ (PHN), $Pb(Fe_{1/2}Nb_{1/2})O_3$ (PFN), $Pb(Sc_{1/2}Nb_{1/2})O_3$, $Pb(Sc_{1/2}Fe_{1/2})O_3$ [1-9].

We have recently discovered a new $TlInS_2$-based layered relaxor ferroelectric [10-12]. Study of dielectric, polarization and pyroelectric properties of the crystals $TlInS_2$ doped with 0,1 at. % Fe, Ge, Cr, Mn displays that the mentioned materials can be classified as relaxor ferroelectrics. We determined the temperature region of existence of stable relaxor (nanodomain) state and the temperature of transition to ferroelectric (macrodomain) state accompanied by anomaly in temperature dependence of pyro-current.

The constant interest in studying relaxors is conditioned by the perspective of their use for fabrication of light-induced information accumulating systems. In addition, the nano sizes of the domains ingrained allow to rank the relaxors among model objects for use in the intensively developing nanotechnology.

Properties of the structural phase transitions in ferroelectrics-semiconductors are known to be manly conditioned by mutual effects of electron and lattice subsystems [13]. In this aspect, it seems interesting to study mutual effects of electron and lattice subsystems in the doped semiconductor relaxor ferroelectric $TlInS_2$.

This work represents the results of study of dielectric dispersion, polarization, pyroelectric and electric properties, as well as the effect of electric field upon dielectric properties of the crystals $TlInS_2$<Fe>, where Fe is 1 at. %.

II. METHOD

The $TlInS_2$<Fe> single crystals were grown by the modified method of Bridgman-Stockberger. The measurements were carried out on the facets cut out perpendicular to polar axis. The facets had been grinded and coated with silver paste. The permittivity ε and dielectric loss tangent were measured with AC bridge E7-8 (1 kHz), P 5058 (10 kHz), E7-12 (1 MHz) and Q-factor gauge BM 560 (100 kHz) in the temperature interval 150-250K. Temperature scanning velocity was 0,1 K/min. Dielectric-hysteresis loops were studied at the frequency of 50 Hz by modified Sawyer-Tower scheme. The pyro-effect was studied by quazi-static method using universal voltmeter B7-30, and conductivity - by AC method.

III. RESULTS AND DISCUSSION

Until now, we have studied relaxor properties of $TlInS_2$ doped with 0,1 at. % Fe. We observed two maximums on the temperature dependence of permittivity T_{m1}=190K and T_{m2}=212K [10], while 1 atm % Fe-doped $TlInS_2$ reveals only one maximum T_m=192K on the temperature dependence ε(T). This difference can be explained by different extent of disordering of In and Fe ions in the crystal $TlInS_2$.

The fig. 1 represents temperature dependences of permittivity ε(T) of $TlInS_2$<Fe> (curve 1 – 1 kHz; 2 – 10 kHz; 3 – 100 kHz; 4 – 1 MHz). Dielectric measurements showed the curves had broad maximums, which are shifted towards higher temperatures with increasing frequency, exhibiting, thus, one of the major features of relaxor ferroelectrics.

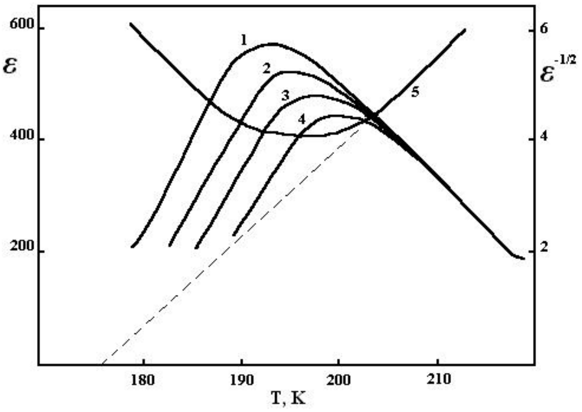

Figure 1. Temperature dependencies of permittivity in $TlInS_2$<Fe> measured at: 1 kHz (curve 1); 10 kHz (curve 2); 100 kHz (curve 3); 1 MHz (curve 4). Curve 5 – temperature dependence of $\varepsilon^{-1/2}$(T).

One more important property of the relaxor ferroelectrics is that at the temperature above T_m, the permittivity changes not according to the Curie-Weis law $\varepsilon = \dfrac{C}{T - T_0}$ but $(\varepsilon)^{-1/2} = A + B(T - T_0)^2$. The dependence $\varepsilon^{-1/2}$(T) for the crystal $TlInS_2$<Fe> (curve 5) is also shown on the fig 1: it cuts the temperature axis at T_f=174K

It is well known that in case of strong frequency dispersion, frequency dependence of temperature T_m cannot be described by the Arrenius equation for Debye relaxation processes [9, 10, 14]. Investigations of $TlInS_2$<Fe>, $TlInS_2$<Ge>, $TlInS_2$<Mn>, $TlInS_2$<Cr> [10-12] and other relaxors showed that this dependence agrees – like in spin and structural glasses – with the empiric Vogel-Fulcher law:

$$f = f_0 \exp\left[\frac{-E_a}{k(T_m - T_f)}\right], \qquad (1)$$

where f is measuring frequency, f_0 is Debye frequency, T_f is static freezing temperature (Vogel-Fulcher temperature), E_a is activation energy. The Vogel-Fulcher expression can be interpreted as correction of Debye relaxation for temperature dependence of the activation energy.

Dependence of $(\ln f_0 - \ln f)^{-1}$ on temperature T_m for the crystals $TlInS_2$<Fe> illustrating correspondence with Vogel-Fulcher law is exhibited on the fig 2 (curve 2). According to the Vogel-Fulcher equation, $f_0=2{,}5\cdot10^{13}$ Hz and static freezing temperature T_f=174K. The activation energy for fluctuation polarization of isolated cluster (dipole glasses) is E_a=0,0382 eV.

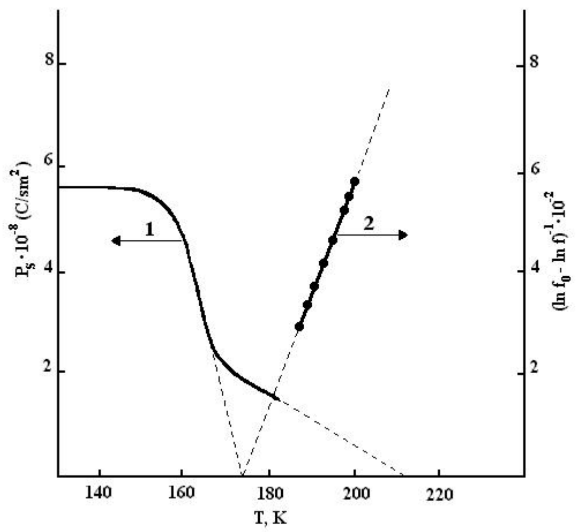

Figure 2. Temperature dependencies of spontaneous polarization P_S(T) in $TlInS_2$<Fe> (curve 1.) Dependencies of $(\ln f_0 - \ln f)^{-1}$ vice T_m in $TlInS_2$<Fe> (curve 2).

As is known, the composition fluctuations caused by defects having dipole moments generating electric fields in the bordering regions [14] is a major reason that the phase transition temperature is diffused [6]. These ferroelectric clusters of $TlInS_2$<Fe> are interacting through dipoles. It is also possible that the existing clusters can interact partially through a local tetrahedral disorder assuming that they can freeze in orientation glass state, which is close – according to the frequency dependence of T_m – to Vogel-Fulcher relation T_f=174K.

In the crystal $TlInS_2$ 1 at. % Fe, there are random fields generated by disorder in internodes, In vacancies and Fe impurities, in other words, the ferroelectric dipole order in the crystal is disordered by random fields induced by Fe ions. This disorder occurs at T_d=210K, where T_d is Burns temperature generating mixed ferroelectric glass or dipole glass state (curve 1).

As can be seen on the fig.2 (curve 1), at the temperatures below T_f, the saturated dielectric hysteresis loops are observed, and the value of spontaneous polarization $P^{\max}=5{,}6\cdot10^{-8}$ C/cm^2. At the temperature interval (T_f – T_d), the dielectric hysteresis loops converge down to Burns's temperature: this is exactly the temperature interval of existence of ferroelectric glass.

The analysis of the results of polarization measurements for the whole temperature interval can be divided into three parts (fig.2, curve 1). At $T>T_d$ the crystal behaves as a paraelectric; at T_d, some polarized clusters with local polarization P_d appear, whose value increases with decreasing temperature. With the temperature approaching T_m, the value of the local polarization P_d increases ($T_d \div T_m$ interval). Simultaneously, polarization continues to increase in the interval $T_m \div T_f$. At the temperature below T_f, saturation of the local polarization value takes place.

Study of polarization properties of the crystal $TlInS_2$<Fe> (fig. 2, curve 1) showed the existence of three phase regions: paraelectric, ferroelectric nanodomain and ferroelectric macrodomain phases.

As the $TlInS_2$<Fe> is a semiconductor, Fe doping creates a capture level whose thermal filling may have considerable effect on ferroelectric state of the crystal. In other words, the dopant creates relevant centers of localization of charges, which generate local electric fields stimulating induced polarization in the vicinity of the phase transition.

Temperature dependencies of the $TlInS_2$<Fe> conductivity σ are shown on fig. 3. The dependence of σ(T) has three temperature intervals characterized by different mechanisms of conductivity. With temperature decreasing down to T_d, the dependence σ(T) is linear that is typical of zone conductivity. At the temperature interval T_d–T_f, the dependence σ(T) satisfactorily agrees with Mott's law [15] and displays hopping mechanism of conductivity. This temperature interval exactly corresponds to glassy i.e. amorphous state of the crystal $TlInS_2$<Fe>. At temperatures below T_f, the conductivity practically does not depend on temperature – the temperature-independent conductivity is nothing but the inactivated hopping conductivity that is typical for layer crystals [16; 17].

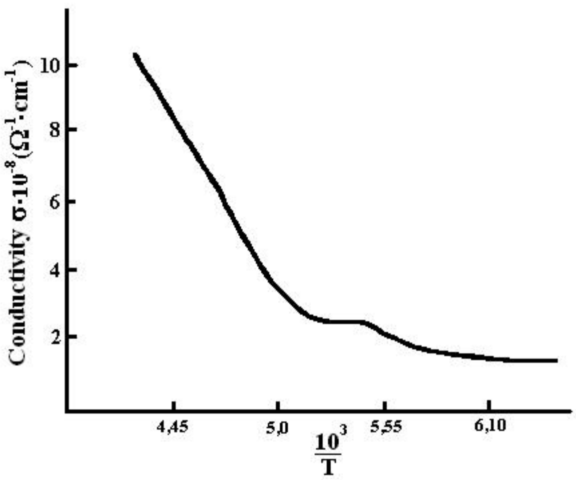

Figure 3. Temperature dependence of conductivity σ(T) in $TlInS_2$<Fe>.

In a fig. 4 the results of researches frequency dependencies of electroconductivity in an alternating field of a $TlInS_2$<Fe> crystal are given at temperature T=200K. How it is seen from figure, in the frequencies region 10^3-10^6 Hz electrocurrent changes under the law $f^{0,8}$. It testifies about hopping mechanism of carry of a charge on condition located in a vicinity of a Fermi level.

Conductivity according to works [15] is defined by the formula:

$$\sigma(f) = \frac{\pi^3}{96} e^2 KT\left[N(E_F)\right]^2 \alpha^{-5} f\left[\ln\left(\frac{\nu_{fon}}{f}\right)\right]^4 \quad (2)$$

Where e - electron charge, K - Boltsman constant, N_f - density of the located condition near to a Fermi level, $a = \frac{1}{\alpha}$ - radius of localization, α - constant recession of wave function of the located carrier of a charge $\Psi \sim e^{\alpha r}$, ν - phonon frequency.

The formula (1) allows to define density of condition at a Fermi level $N(E_f)$ of a $TlInS_2$<Fe> crystal.

$$N^2(E_F) = \frac{96\sigma(f)\alpha^5}{\pi^3 e^2 KTf\left[\ln\left(\frac{\nu_{fon}}{f}\right)\right]^4} \quad (3)$$

If T=200K, $\nu_{fon}=10^{12}$ Hz, $f=10^3$ Hz, we obtain:

$$N_F^2 =\sim \sigma(f)a^{-5} \quad (4)$$

Magnitude density of condition N_f at temperature T=200K crystal $TlInS_2$<Fe> makes ~$1{,}2\cdot10^{19}$ eV^{-1} sm^{-3}. Radius of localization (a) is taken on similarly with a GaS single crystal [16].

The theory of a hopping conductivity in alternating electrical fields allows determine average time of a jump τ The carrier of a charge from one located condition in another:

$$\tau^{-1} = \nu_{fon}\exp(-2R\alpha), \text{ where } \tau =\sim \mu s$$

Average length of a jump is calculated on the formula:

$$R = (1/2\alpha)\ln(\nu_{fon}/f) \quad (5)$$

For $TlInS_2$<Fe> average length of a jump makes R~100Å, that approximately in 7 times exceeds average distance center localization's of carriers of a charge (R_{mean}/a=7).

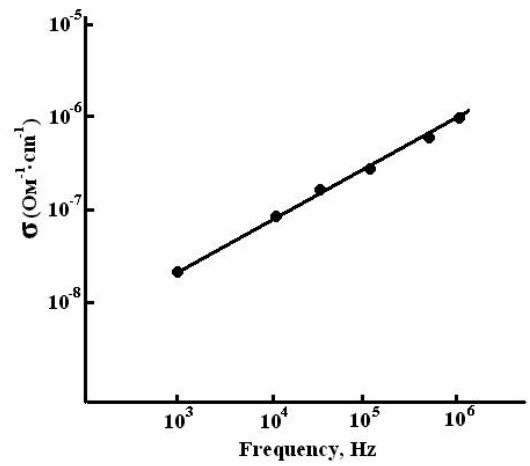

Figure 4. Dependence of σ(f) for the compound $TlInS_2$<Fe>.

If the defective zone is formed of a uniquely kind of dot defects, the bottom limit of its width can be estimated as follows. Using the theory of conductivity on impurity, width of a zone J is approximately defined from conditions:

$$\left(\frac{4\pi}{3}\right)R^3 N(E_F)\frac{J}{2} = 1 \quad (6)$$

$$J = 0{,}04eV$$

Measurements of dielectric, polarization and electric properties as well as those of pyroelectric coefficient provide important information on the process of rise and destruction of clusters of the forming phase while passing the phase transition. The fig.4 illustrates temperature dependences of dielectric loss tangent in the $TlInS_2$<Fe>. When there is no electric field (fig.5 curve 1) applied, no additional anomalies except (T_m) are revealed. The additional anomaly is clearly seen (curve 2) at the temperature T_f under heating without electric field and after cooling under the field applied. The curve 3 on the fig.5 exhibits the results of measurements of pyro-coefficient in heating mode without field and after cooling under the field. The two anomalies appear at T_f=174K and T_m=192K.

We suppose that, phenomena occurring at low-temperature phase of $TlInS_2$<Fe> relaxors are conditioned by the fact that the main features of relaxors depend on the dynamics of charges localization. It should be mentioned that applying electric field to $TlInS_2$<Fe> relaxors leads to drastic change in the picture of the phenomena observed. While cooling under the electric field above certain threshold value (E_r ~1,5 kV/cm), the temperature dependence of dielectric loss drastically change its shape (fig.5).

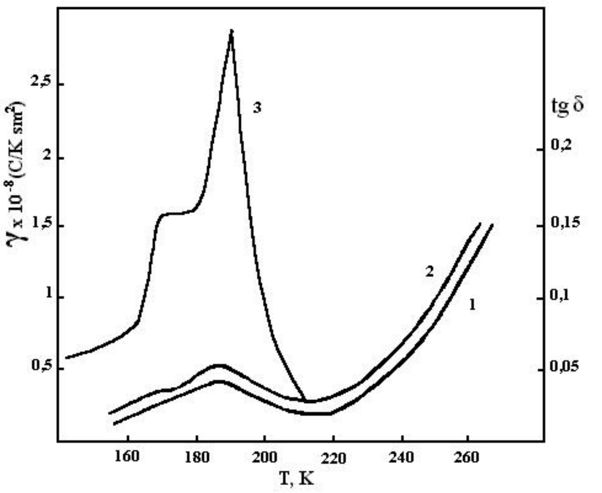

Figure 5. Temperature dependencies of dielectric loss tangent tgδ(T) in $TlInS_2$<Fe> without (curve 1) and under electric field applied (curve 2). Temperature dependence of pyro-coefficient in heating mode without electric field following the cooling under the field applied (curve 3).

Practically all charges are known to be localized at low-temperature phase [4, 5, 10]. At these temperatures, activation thermal processes are not efficient, and the charge centers can be ionized only under the strong external electric field. Under weak fields, the localized charges cannot be delocalized and, therefore, hold heterogeneous distribution of polarization. In rather strong fields, the chargers are delocalized and polarization re-orientates along the field.

Therefore, the phase transition to homogenious polarization state after applying electric field is defined by ionization of local centers and following redistribution of direction of polarization in local nano-regions. In this case, local polarization around newly captured charges is already redirected predominantly along the field. When the greater part of the centers are passed through the ionization process, the local polarization will be predominantly directed along the external electric field.

Single direction of spontaneous polarization along the whole sample becomes favorable for phase transition to ferroelectric state that is displayed as a jump of dielectric and pyro-electric properties (fig.4).

IV. CONCLUSION

The results of our experiments prove the crystals $TlInS_2$<Fe> to be attributed to the class of relaxor ferroelectrics with all corresponding properties as follows: narrow dielectric hysteresis loop in certain temperature interval (up to the Burns temperature T_d); above T_m – the dependence ε^{-1}(T) does not agree with Curie-Wais law but $(\varepsilon)^{-1/2} = A + B(T - T_0)^2$; frequency dispersion of T_m is described by Vogel-Fulcher relation. It was also discovered that constant electric fields induce phase transition corresponding with Vogel-Fulcher temperature, that reveals itself as a jump in pyro-coefficient and dielectric loss tangent.

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