$TlInS_2$ <Mn> - NEW RELAXOR FERROELECTRIC

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It was shown $TlInS_2$ doped 0,1at.% Mn displays all idiosyncrasies of relaxor ferroelectric. The temperature range of a steady relaxor (nanodomain) state and temperature of phase transition in a ferroelectric (makrodomain) state attended by anomalies of polarization and pyroelectric properties was defined.

1. Introduction

The analysis of the dielectric constant temperature dependence $\varepsilon(T)$ in the phase transitions region of $TlInS_2$ crystal shows that this dependence has different forms for the samples taken from various technological batches. It is found in [1] that the different forms of $\varepsilon(T)$ result from the fact that $TlInS_2$ crystals relate to the berthollide class, i.e. the compounds with composition rearrangement occurring during the growth process. However, this peculiarity does not lead to smearing of the phase transitions, and the dependence $\varepsilon^{-1}(T)$ obeys the Curie-Weis law [2, 3] with a constant of $\approx 10^{-3}$ in the large frequency range going from kilohertz to submillimeter lengths. The neutron-diffraction research has also established [4] that $TlInS_2$ compound is an improper ferroelectric with incommensurate phase.

The temperature region, where instability of $TlInS_2$ crystal lattice is observed, is very sensitive to the trivalent cationic impurities of different ionic radius and coordination numbers. Moreover, for some impurities one observes the increase of phase transition temperatures while for others one obtains the decrease of them (the results of this comparative research have now been submitted for publication). It is also interesting to investigate the nature of these phase transitions in $TlInS_2$ crystals. The transition metals of iron group are the multicharged impurity ions and can form the deep centers of strong localization that are capable to strong interaction with highly polarizable $TlInS_2$ crystal lattice.

In this paper we present the results of study on dielectric, polarization and pyroelectric properties of $TlInS_2$<Mn> crystals.

2. Experimental Technique

The $TlInS_2$ crystals were grown by the modified Bridgman-Stockbarger method. It was not observed any anisotropy of dielectric properties in the plane of layer. The measurements have been carried out on the crystal faces cut out perpendicularly to the polar axis. The crystal faces were planished, polished and then covered by the silver paste. The dielectric constant ε and the tangent $tg\delta$ of the dielectric losses angle were measured by the alternating current bridge E7-8, E7-12, P5058 and Tesla BM560 at the frequencies 1kHz, 1MHz, 10kHz and 100kHz accordingly in the temperature region 150–250K.

The velocity of temperature scanning was 0.1 K/min. The dielectric-hysteresis loops have been studied at the frequency of 50Hz using modified Soyer-Tauer scheme. The pyroeffect has been investigated by the quasistatic method using universal voltmeter V7-30.

3. Results

The dielectric constant temperature dependencies $\varepsilon(T)$ of both $TlInS_2$ (curves 1, 2) and $TlInS_2$<Mn> crystals (curves 3, 4) are presented in fig. 1. The curves 1, 3 correspond to the cooling regime; the curves 2 and 4 are obtained at the heating regime. As it is seen from Figure 1, the well-known [3] typical sequence of the phase transitions was observed on $TlInS_2$ crystals (curves 1, 2). One sees the paraelectric-commensurate phase transitions at 216K, and two additional transitions at 200 and 204K. Last two transitions were most likely caused by the rearrangement of the modulated structure; their nature was widely discussed in [5]. The final transition to the polar phase occurs at 196K.

The dependence $\varepsilon(T)$ can be described by the Curie-Weis law with the Curie constant of $C^{+}=5.3\cdot 10^3$K in the temperature region $T–T_1$ (216)≤50°. The anomaly at 196K appears during the crystal cooling where all peaks are strong enough and there is no any signs of smearing. As one can see from the Figure 1, the dielectric hysteresis for $TlInS_2$ crystals is observed only at the temperature about 196K (and not at the maximum of the curves). The thermal hysteresis of the doped samples is situated at the temperature T_m, corresponding to the maximum of $\varepsilon(T)$ curve) and is about 2K (curves 3 and 4 in Figure1).

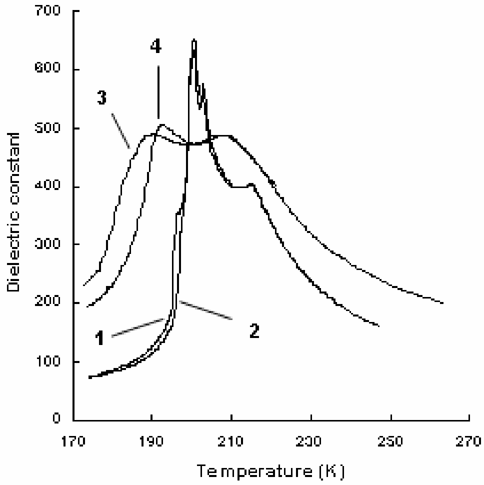

Fig.1. The dielectric constant $\varepsilon(T)$ temperature dependencies. Curves 1, 2 - the dependencies $\varepsilon(T)$ of $TlInS_2$ crystal (1-cooling; 2-heating); Curves 3, 4 – the dependencies $\varepsilon(T)$ of $TlInS_2$<Mn> crystal (3-cooling; 4-heating).

The dielectric constant temperature dependence $\varepsilon(T)$ is significantly different in this temperature region for $(TlInS_2)_{1-x}(Mn)_x$ crystals, where x=0.001. The dependence is strongly blurred, and the phase transitions move by 10K towards the lower temperature region. The region of incommensurate phase with two anomalies at 190K and 209K becomes wider. It is natural in this case to explain the reason of such radical change of the dependence $\varepsilon(T)$ for 0.1-mol% Mn doping.

It is known [6, 7] that the composition fluctuation is the main reason of smearing of phase transition temperatures. However, not all kind of defects and increase of their concentration can cause the smearing. According to [8] the smearing is determined by the defects having dipole moments that create the electric fields and electric field gradient in the adjoining regions of the crystal. In addition, since $TlInS_2$ is a semiconductor, the doping of impurities creates the corresponding centers of charge carrier localization that can create the local electric fields stimulating generation of the induced polarization near the phase transitions [9-11]. An important peculiarity of the ferroelectrics with smearing phase transitions is the fact that the dielectric constant at temperatures higher than T_m changes not in agreement with the Curie-Weis law of $\varepsilon^{-1}(T)=C^{-1}(T-T_0)$ but in accordance with the law of $\varepsilon^{-1}(T)= = A+B(T-T_0)^2$.

In $TlInS_2$<Mn> crystals was observed significant frequency dispersion and growth T_m with growth of frequency f. The increase T_m with growth of frequency is well described by the Vogel-Fulcher law (fig.2), interpretive as temperature of static freezing electrical dipoles or transition in a condition of dipole glass [12, 13].

The investigation of polarization properties of $TlInS_2$<Mn> shows that the dielectric hysteresis loops are observed below 175K and the maximum value of spontaneous polarization, P_s, for such loops reaches $4\cdot10^{-8}$C/cm^2. The value of P_s for non-doped $TlInS_2$ crystals is equal to $1.8\cdot10^{-7}$ C/cm^2. The value of Ps in the temperature region from 175 to 210K is $1.5\cdot10^{-8}$C/cm^2.

The investigation of the dielectric constant frequency dispersion has been carried out at the frequencies of 1kHz-1MHz. No temperature shift for the maximums of $\varepsilon(T)$ curves in $TlInS_2$ crystals was observed, while the shift of the smeared maximums of $\varepsilon(T)$ curves for $TlInS_2$<Mn> crystals is equal to 3K.

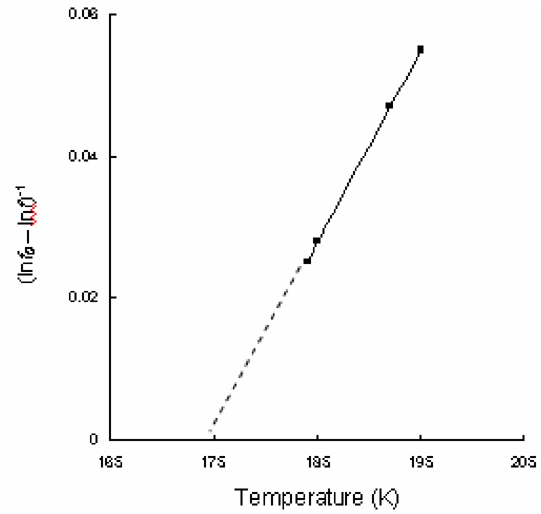

Fig.2. The dependence $(lnf_0 - lnf)^{-1}$ from T_m for $TlInS_2$<Mn>, illustrating performance of the Vogel-Fulcher law.

The temperature dependencies of the pyroelectric coefficient $\gamma(T)$ of $TlInS_2$ (curve 1) and $TlInS_2$<Mn> crystals (curve 2) are presented in 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 the pyroelectric current, A_0 is the area of the electrodes, dT/dt is the heating rate. The measurements were carried out on the samples, which were preliminary polarized in the external electric field. The dependence $\gamma(T)$ for the pure $TlInS_2$ crystal has one peak only with the maximum value of $1.4\cdot10^{-7}$ C/K$\cdot$cm^2 at 196K. Two anomalies at 190K and 174K are observed for $\gamma(T)$ of $TlInS_2$<Mn> crystal.

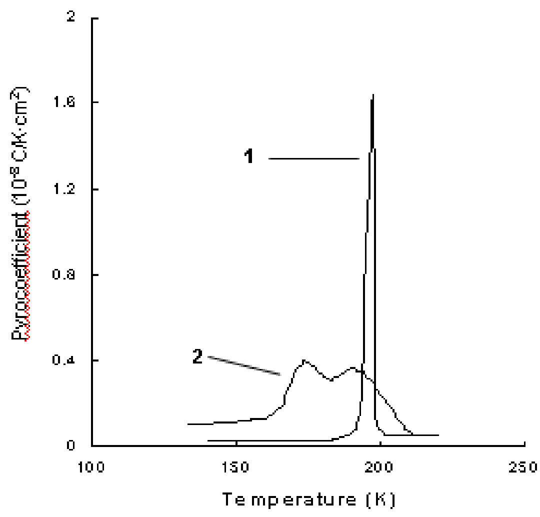

Fig. 3. The temperature dependence of the pyroelectric coefficient. Curve 1 - $TlInS_2$ crystal; Curve 2 - $TlInS_2$<Mn> crystal.

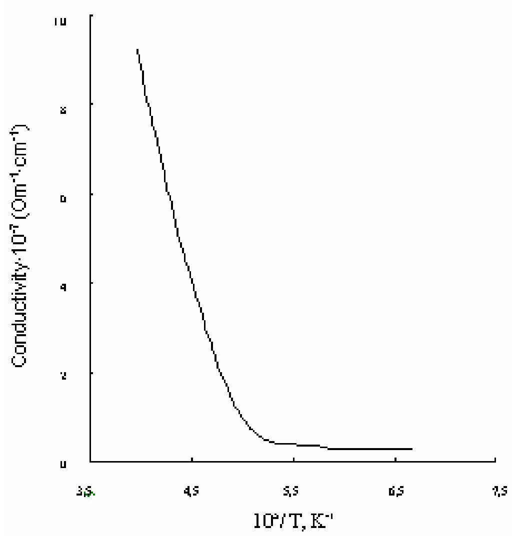

Fig. 4. The dependence of conductivity σ from *1/T* for $TlInS_2$<Mn> crystal.

The temperature dependence of conductivity on frequency 1 kHz is shown in fig. 4. It is visible, that the conductivity has thermoactivated character, and can be described by the Mott law: $\sigma=\sigma_o exp[-(U/kT)^v]$, where U - the energy of activation, k–Boltzmann constant, v-parameter depending on the mechanism of conductivity. It is known, that the parameter v is approximately equal 1 at the zoned mechanism of conductivity, and in a case of hopping conductivity it lays within the limits of $0,2<v<0,5$.

In an 175-190K interval of temperatures conductivity has thermoactivated character, is satisfactorily described by the above-stated Mott law with a parameter v equal 0,25, that corresponds thermoactivated hopping to the mechanism of conductivity. Thus on dependence fig.4 it is possible to pick out 3 temperature areas described by various mechanisms of conductivity. The high-temperature area corresponds to the zoned mechanism of conductivity. The temperature area 175-190K- thermoactivated hopping, and area is lower 175K–hopping to the mechanism of conductivity. The estimation of length of a jump shows, that this distance is approximately equal 100A^o that corresponds to jumps of carriers between nanodomain by inclusions.

4. Discussion and Conclusion

The analysis of figures 1-4 allows one to state that $TlInS_2$<Mn> crystals reveal all peculiarities that are typical for the relaxor ferroelectrics. The doping of $TlInS_2$ crystal by Mn cations leads to smearing of phase transitions, and the frequency dispersion of dielectric constant is observed. Moreover, the elongated dielectric hysteresis loop is observed in the smearing region of the phase transition, and the temperature dependence of the dielectric constant in the region of high temperatures is described not by the Curie-Weis law but according to the $(\varepsilon')^{-1}=A+B(T-T_0)^2$ functional form.

The smearing of phase transitions and other ferroelectric peculiarities of $TlInS_2$<Mn> crystal are undoubtedly caused by the structure disorder that leads to the appearance, in a wide temperature region, of local symmetry distortions and internal electric field. Although the phase transitions in $TlInS_2$ crystals are under investigation for a long period of time the satisfactory understanding of physical mechanisms of the processes taking place in the crystals and the unambiguous interpretation of the observed phenomena does not exist. It may be caused by the fact that, during the investigations of phase transitions in $TlInS_2$ crystals, not enough attention was paid to the semiconductor properties of these crystals. This is especially valid for the crystals doped by the cationic impurities. These impurities can form the capture levels (traps) at the bottom of the conduction band. One has to consider two processes: charge carrier localization on the local centers, and their influence on the phase transitions. This issue was considered by Mamin [9-11], where it was shown that the thermal filling of traps could lead to an intricate sequence of phase transitions as well as to the appearance of an unstable boundary state between the phases (incommensurate-commensurate).

The dependence $\gamma(T)$ shows the peak at 175K, and there is no peak of $\varepsilon(T)$ at this temperature (compare figures 1 and 3). According to [11] this peculiarity is typical for the relaxors. It may be explained by an assumption that the oscillation frequency of the induced polarization is determined by the characteristic relaxation time not only of the lattice subsystem as it takes place in usual ferroelectrics but also by the relaxation time of the electronic subsystem. Naturally, the characteristic time τ_η for the change of the order parameter η and the characteristic time τ_m for the change of the electron concentration m in the traps are significantly different $(\tau_\eta/\tau_m<<1)$. Using this assumption the author of [11] investigated the mentioned above problem by separation of fast and slow processes. As a result it has been established that the effective temperature T_{cm} of the phase transition is shifted to lower temperatures due to thermal filling of the capture levels. In our experiments this temperature corresponds to 175 K for the crystals of $TlInS_2$<Mn>. When the localized charges create the local electric fields 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 175–190K is observed as narrow and stretched. And according to the same reason, we did not observe the peculiarities in the dependence $\varepsilon(T)$ connected with phase transition at the temperature T_{cm}.

Thus, the doping of $TlInS_2$ crystals by Mn 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 (nanodomain) to the macrodomain (ferroelectric) state occurs at the temperature 175K. The jump in the temperature dependence $\gamma(T)$ corresponds to this transition.

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$TlInS_2$ <Mn> – YENİ RELAKSOR SEQNETOELEKTRİK

Göstərilmişdir ki, 0,1 at.% Mn aşkarlanmış $TlInS_2$ kristalı relaksor seqnetoelektriklər üçün xarakterik olan bütün xüsusiyyətlərə malik olur. Dayanıqlı relaksor (nanodomen) halının varlıq temperatur intervalı və seqnetoelektrik (makrodomen) halına keçid temperaturu piroelektrik xassələrində alınan anomaliya görə müəyyən edilmişdir.

$TlInS_2$ <Mn> - NEW RELAXOR FERROELECTRIC

О.А. Самедов

$TlInS_2$ <Mn> - НОВЫЙ РЕЛАКСОРНЫЙ СЕГНЕТОЭЛЕКТРИК

Показано, что $TlInS_2$, легированный щ,1 ат.% Mn проявляет все характерные особенности релаксорного сегнетоэлектрика. Установлена температурная область существования устойчивого релаксорного (нанодоменного) состояния и температура фазового перехода в сегнетоэлектрическое (макродоменное) состояние, сопровождаемое аномалиями поляризационных и пироэлектрических свойств.

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