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THE SPONTANEOUS RELAXOR-FERROELECTRIC TRANSITION OF *$TlInS_2$* WITH CATIONIC IMPURITIES

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Recent theoretical investigations predict that the thermal filling of trap centers could lead to an intricate sequence of phase transitions with unstable boundary state between the phases. This fact has motivated the experimental study of ferroelectric phase transitions in $TlInS_2$ <Cr> composites where the cationic impurities can form the capture levels (traps) at the bottom of the conduction band. In this paper the results of experimental investigation of dielectric, polarization and pyroelectric properties of $TlInS_2$ <Cr> composites are presented. It was shown that these composites display all peculiarities that are inherent for relaxor ferroelectrics.

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1. Introduction

The analysis of the dielectric constant temperature dependence ε (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 ε (T) result from the fact that $TlInS_2$ crystals relate to the berthollide class, i.e. the class of compounds with composition rearrangement occurring during the growth process. However, this peculiarity does not lead to smearing of the phase transitions, and, if we measure ε (T) at a chosen temperature using different frequencies, the dependence ε^{-1}(T) obeys the Curie-Weis law with a constant of $\approx 10^3$K in the wide frequency range going from kilohertz (300 Hz-300 KHz) to submillimeter lengths at 6-24 cm^{-1} [2, 3]. 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 radii and coordination numbers. Moreover, for some impurities one observes the increase of phase transition temperatures while for others one obtains the decrease of them [5]. As a result it is interesting to investigate the nature of these phase transitions in $TlInS_2$ crystals more attentively. The transition metals of iron group are the multicharged impurity ions and can form the deep centers of steady localization that are capable to strong interaction with highly polarizable $TlInS_2$ crystal lattice.

In this paper we present the results of a study on dielectric, polarization and pyroelectric properties of $TlInS_2$<Cr> 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 the layer. The measurements have

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been carried out on the crystal faces cut out perpendicularly to the polar axis. The crystal faces were polished and then covered by 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 1 kHz, 1 MHz, 10 kHz and 100 kHz accordingly in the temperature region 150 – 250K.

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

3. Results

The temperature dependencies of the dielectric constant ε (T) of both $TlInS_2$ (curves 1, 2) and $TlInS_2$<Cr> crystals (curves 3, 4) are presented in Fig. 1. The curves 1 and 3 correspond to the cooling regime; the curves 2 and 4 are obtained at the heating regime. All curves were measured at the frequency of 1 MHz. As it is seen from Fig. 1, the well-known [3] typical sequence of the phase transitions was observed on $TlInS_2$ crystals (curves 1, 2). One observes the paraelectric-commensurate phase transitions at 216 K, and two additional transitions at 200 and 204 K. Last two transitions were most likely caused by a rearrangement of the modulated structure. The nature of these transitions was discussed in detail in [6]. The final transition to the polar phase occurs at 196 K.

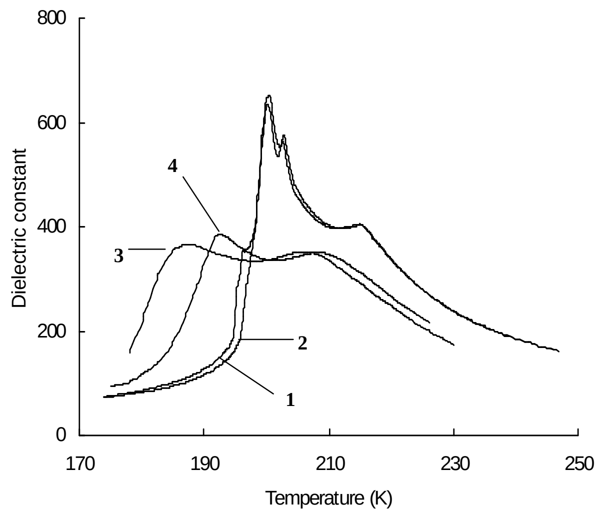

Fig. 1. The dielectric constant ε (T) temperature dependencies. Curves 1, 2 - the dependences ε (T) of $TlInS_2$ crystal (1 - cooling; 2 - heating); Curves 3, 4 - the dependences ε (T) of $TlInS_2$<Cr> crystal (3 - cooling; 4 - heating).

The dependence ε(T) can be described by the Curie-Weiss law with the Curie constant of $C^{+}=5.3 \times 10^{3}$ K in the temperature region $|T - T_i| \leq 50°$ where T_i =216 K. The anomaly at 196 K appears during the crystal cooling where all peaks are strong enough and there are no signs of smearing. As one can see from the Fig. 1, the dielectric hysteresis for $TlInS_2$ crystals is observed only at the temperature around 196 K (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 ε (T) curve) and has approximately 5 K width in temperature (curves 3 and 4 in Fig. 1).

The dielectric constant temperature dependence ε (T) is significantly different in this temperature region for $(TlInS_2)_{1-x}(Cr)_x$ crystals, where x = 0.001. The dependence is strongly blurred, and the phase transitions move by 8 K towards the lower temperature region. It is possible, in this case to explain the reason of such radical change of the dependence ε (T) for 0.1-mol % Cr doping.

It is known [7, 8] 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 [9] 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 could create the local electric fields stimulating generation of the induced polarization near the phase transitions [10-12]. An important peculiarity of the ferroelectrics with smearing phase transitions is the fact that their dielectric constant at temperatures higher than T_m changes not in agreement with the Curie-Weiss law of $\varepsilon^{-1}(T) = C^{-1}(T - T_0)$ but in accordance with the law of $\varepsilon^{-1}(T) = A + B(T - T_0)^2$.

The dependence $\varepsilon^{-1/2}(T)$ for $TlInS_2$<Cr> is shown in Fig. 2. The dielectric-hysteresis loops for $TlInS_2$<Cr> crystal are shown in the inserts of this figure. The first insert shows the measurements at 140 K, the second one shows the results for 180 K.

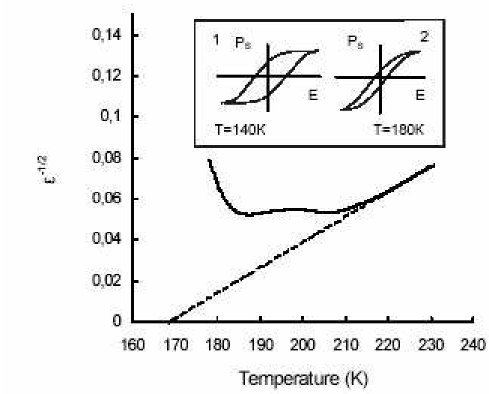

Fig. 2. The dependence $\varepsilon^{-1/2}$ (T) in $TlInS_2$<Cr> crystal.

The extrapolation of the dependence shown in Fig. 2 from the high temperatures crosses the temperature axis at 168 K. This value corresponds to the temperature of maximum for the temperature dependence of the low-temperature pyroelectric coefficient γ (T) (Fig. 3).

The investigation of polarization properties of $TlInS_2$<Cr> shows that the dielectric hysteresis loops are observed below 168 K and the maximum value of spontaneous polarization, P_s, for such loops reaches 6×10^{-8} C/cm^2. The value of P_s for nondoped $TlInS_2$ crystals is equal to $1.8 \cdot 10^{-7}$ C/cm^2. The value of P_S in the temperature region from 168 to 190 K is 1.5×10^{-8} C/cm^2.

A significant frequency dispersion, and the growth of T_m with increase of frequency, f, were observed in $TlInS_2$<Cr> crystals. This growth is well described by the Vogel-Fulcher law $f = f_0 \exp[-E/(T_m-T_f)]$, where f_0 and E are constants, T_f is the temperature of static freezing of electrical dipoles or the transition to dipole glass [13, 14] (Fig. 4). The obtained parameters for $TlInS_2$<Cr> are $f_0 \approx 10^{12}$ Hz, $E \approx 0.03 \pm 0.01$ eV.

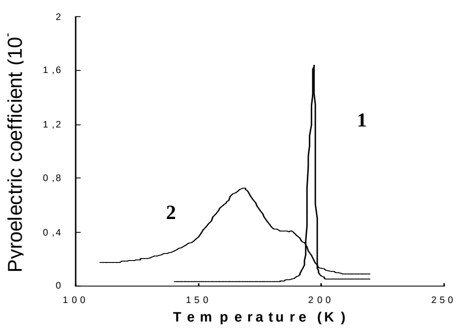

Fig. 3. The pyroelectric coefficient temperature dependence. Curve 1 - $TlInS_2$ crystal; Curve 2 - $TlInS_2$<Fe> crystal.

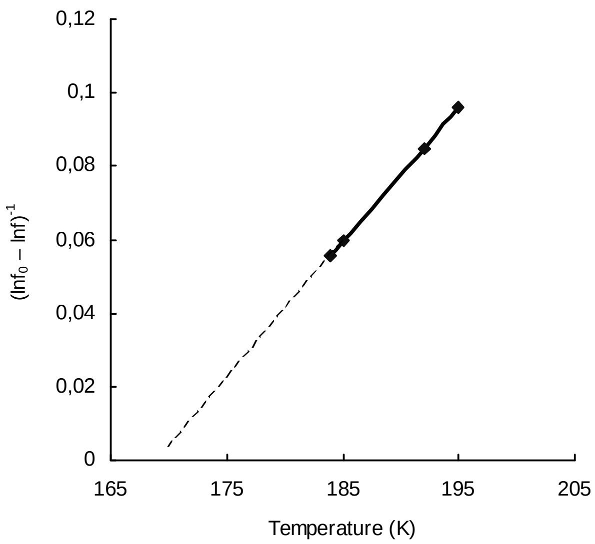

Fig. 4. The dependence $(\ln f_0 - \ln f)^{-1}$ from T_m for $TlInS_2$<Cr>, illustrating the validity of the Vogel-Fulcher law.

The temperature dependencies of the pyroelectric coefficient $\gamma(T)$ for $TlInS_2$ (curve 1) and for $TlInS_2$<Cr> 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 using the samples, that were preliminary polarized in the external electric field. The results are shown in Fig. 4. The dependence $\gamma(T)$ for the pure $TlInS_2$ crystal has one peak only with the maximum value of 1.4×10^{-7} C/Kcm^2 at 196 K. Two anomalies at 168 K and 190 K are observed for $\gamma(T)$ of $TlInS_2$<Cr> crystal.

4. Discussion and conclusion

The analysis of Figs. 1-4 allows one to state that $TlInS_2$<Cr> crystals reveal all peculiarities that are inherent for relaxor ferroelectrics. The doping of $TlInS_2$ crystal by Cr 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 transitions, 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 $TlInS_2$<Cr> 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 [10-12], where it was shown that the thermal filling of traps could lead to an intricate sequence of phase transitions as well as to appearance of an unstable boundary state between the phases (incommensurate-commensurate).

The dependence γ(T) shows the peak at 168 K, and there is no peak of ε(T) at this temperature (compare Figs. 1 and 3). According to [12] this peculiarity is typical for the relaxors. It may be explained assuming 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 ($\tau_\eta/\tau_m \ll 1$). Using this assumption the author of [12] investigated the mentioned above problem by separation of fast and slow processes. As a result it has been established that the effective temperature of the phase transition is shifted to lower temperatures due to thermal filling of the capture levels. In our experiments this temperature corresponds to 168 K for the crystals of $TlInS_2$<Cr> (Fig. 2). When the localized charges create the local electric fields the spontaneous polarization in the weak external fields in the separate microfields will be guided to different directions in compliance with space distribution of the localized charges. Therefore, the hysteresis loop in the temperature region 168 – 190 K is observed as narrow and stretched. And according to the same reason, we did not observe any peculiarity in the dependence ε (T) connected with phase transition at the temperature T_{cm} (the effective temperature of the phase transition).

Thus, doping of $TlInS_2$ crystals by Cr leads to the appearance of the temperature region in which the crystals show all peculiarities that are inherent for the relaxors. The phase transition from the relaxor (microdomain) to the macrodomain (ferroelectric) state occurs at the temperature 168 K. The jump in the temperature dependence γ (T) corresponds to this transition.

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