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Dielectric properties of $TlIn(S_{1-x}Se_x)_2$ polycrystals near phase transitions

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Abstract. Studies of polycrystalline $TlIn(S_{1-x}Se_x)_2$ samples under hydrostatic pressure were performed. Determined in this work were pressure coefficients near temperatures of ε(*T*) anomalies. Based on studying the temperature dependences of dielectric permittivity values for various hydrostatic pressures, (*p, T*) phase diagram was built. Phase transformations are found in the pressure range of $p > 550$ MPa.

Keywords: polycrystal, hydrostatic pressure, structural transformations.

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1. Introduction

A considerable interest to $TlInS_2$-type semiconductor crystals stems from their physical properties enabling these materials to be treated as a potential base for functional elements of electronics, pressure and temperature gauges, pyroelectric detectors [1]. $TlInS_2$ crystal is a layered ferroelectric semiconductor with a complex sequence of structural phase transformations and the presence of an incommensurate phase [2]. A number of works is devoted to detailed studies of its dielectric permittivity ε and spontaneous polarization in a broad temperature interval [3-9]. It was also found that at substitution of sulphur by selenium in $TlIn(S_{1-x}Se_x)_2$ the temperature interval of the incommensurate phase is reduced, and at $x = 0.05$ a Lifshitz-type polycritical point is observed in the (*x*, *T*) phase diagram [10, 11]. Up to date, dielectric properties of $TlIn(S_{1-x}Se_x)_2$ solid solutions in the vicinity of phase transitions have been studied quite incompletely. The aim of this work is to study temperature dependences of the dielectric permittivity in $TlIn(S_{1-x}Se_x)_2$ polycrystals ($x = 0.01$, 0.02, 0.03).

2. Experimental

Polycrystalline $TlIn(S_{1-x}Se_x)_2$ samples were prepared from the melt of the stoichiometric mixture of initial $TlInS_2$ and $TlInSe_2$ components. Dielectric permittivity measurements were performed in automated mode at the frequency of 1 MHz using an E7-12 ac bridge with temperature variation rate within 0.01–0.02 K/s. Samples of 4×4×2 mm size were used for the measurements, the contacts of silver paste being applied. The sample temperature was measured using a copper-constantan thermocouple. Hydrostatic pressure was applied using a high-pressure chamber, its value being controlled within ±1 MPa.

3. Results and discussion

Detailed studies of dielectric permittivity and spontaneous polarization of $TlInS_2$ layered crystals have revealed the presence of a number of anomalies at temperatures $T_i = 214$ K, $T_{i2} = 206$ K, $T_{c1} = 202$ K, $T_{c2} = 198$ K, and $T_c = 193$ K [1, 6-8], the anomalies at $T_i = 214$ K and $T_c = 193$ K corresponding to the paraelectric-to-incommensurate phase transition and transition to the ferroelectric phase, respectively. The mechanism of these transitions was discussed in [1, 5, 7]. The studies of anisotropy of the dielectric permittivity in $TlInS_2$ single crystals have shown the anomalies of ε in the vicinity of phase transitions are observed in all crystallographic directions. The highest values of the dielectric permittivity ε are observed in the direction parallel to the crystal layers ($\varepsilon_{||}$), while the values observed in the perpendicular direction ($\varepsilon_{\perp}$) are smaller, their ratio $\varepsilon_{||}/\varepsilon_{\perp}$ is close to 10 at $T_i = 214$ K.

This anisotropy of ε shows that in polycrystalline $TlInS_2$ one should also expect noticeable values of the dielectric permittivity, what we actually observed in the experiment.

Temperature dependences of the real ε′ and imaginary ε″ parts of the dielectric permittivity at atmospheric pressure for three compositions of $TlIn(S_{1-x}Se_x)_2$ polycrystals are shown in Fig. 1. In these dependences, an anomaly (maximum) is observed, the temperature of the ε′ maximum for $TlIn(S_{0.99}Se_{0.01})_2$ is T_m = 197 K, and for $TlIn(S_{1-x}Se_x)_2$ with x = 0.02 and x = 0.03, T_m is 193 K and 187 K, respectively. Beside this anomaly, the samples with the compositions x under investigation exhibit an additional anomaly (a kink) at a temperature above that of the maximum (see Fig. 1) corresponding to the paraelectric-to-incommensurate phase transition at T_i = 207 K for x = 0.01, T_i = 203 K for x = 0.02, and T_i = 197 K for x = 0.03. As shown in the earlier works [1, 5, 7], in $TlInS_2$ single crystal the transition to the ferroelectric phase is accompanied by a sharp decrease in the dielectric permittivity. The maximal values of the dielectric permittivity are achieved at the phase transitions at T_{i2} = 206 K and T_{c1} = 202 K. For $TlIn(S_{1-x}Se_x)_2$ polycrystalline samples, these anomalies converge to a broad maximum at $T = T_m$ and cannot be separated. The phase transition to the polar phase at $T = T_c$ should correspond to the low-temperature shoulder in the temperature dependence of the dielectric permittivity at $T < T_m$. For $TlIn(S_{1-x}Se_x)_2$ crystals these anomalies are observed at the temperatures T_c = 189 K for x = 0.01, T_c = 183 K for x = 0.02, and T_c = 178 K for x = 0.03. Hence, in $TlIn(S_{1-x}Se_x)_2$ polycrystals the sequence of paraelectric-to-incommensurate-to-ferroelectric transitions corresponds to a sequence of anomalies of dielectric permittivity at T_i, T_m, and T_c. It should be noted that due to a certain smearing of the dielectric permittivity anomalies with the increase of x, the identification of the anomalies and determination of their temperatures can be to a certain extent ambiguous. An effective additional tool that can be used is the study of external effects, one of which is hydrostatic pressure.

For polycrystalline $TlIn(S_{0.99}Se_{0.01})_2$, we carried out the studies of dielectric permittivity under high hydrostatic pressure. Temperature dependences of the dielectric permittivity of $TlIn(S_{0.99}Se_{0.01})_2$ single crystals at different hydrostatic pressure values are shown in Fig. 2. With pressure increase up to 550 MPa, the dielectric permittivity anomalies linearly shift towards higher temperatures. This is accompanied by a decrease in the dielectric permittivity maximum values, an increase of the Curie-Weiss constant, and an extension of the temperature interval of the existence of the incommensurate phase. Due to pressure-induced extension of the temperature range for the existence of the incommensurate phase, with the pressure increase up to 550 MPa the dielectric permittivity anomalies T_i, T_m, and T_c are revealed more distinctly (see curves 1 to 4 in Fig. 2).

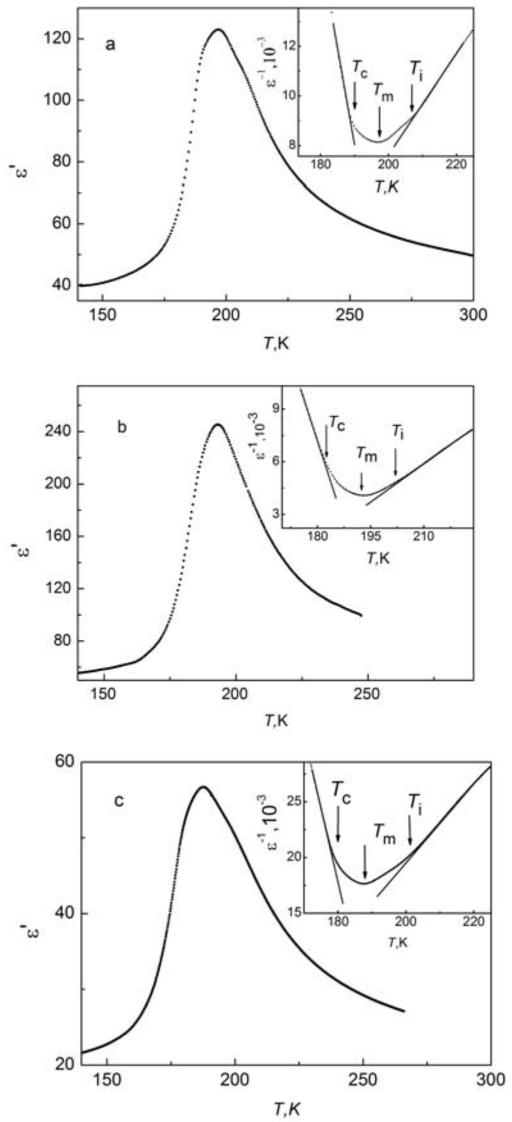

Fig. 1. Temperature dependence of the real part ε′ of the dielectric permittivity of $TlIn(S_{1-x}Se_x)_2$ crystals at the atmospheric pressure: (a) x = 0.01, (b) x = 0.02, (c) x = 0.03. The insets show the temperature dependences of ε^{-1} .

At pressures p > 550 MPa, the ε(T) dependence undergoes qualitative changes, namely, a sharp decrease in the maximal values of the dielectric permittivity and transformation of the anomalies (Fig. 2). This change in the temperature dependences of dielectric permittivity is caused by polycritical phenomena typical for $TlInS_2$, which were studied in [8]. At the pressure p = 650 MPa for $TlIn(S_{0.99}Se_{0.01})_2$ polycrystal, the anomalies of dielectric permittivity are revealed at temperatures T_1 = 218 K, T_2 = 247 K, and T_3 = 289 K. With further pressure increase, the $T_1(p)$ value decreases, while $T_2(p)$ and $T_3(p)$ essentially increase.

Based on studying the temperature dependences of the dielectric permittivity inherent to $TlIn(S_{0.99}Se_{0.01})_2$ polycrystals at a high hydrostatic pressure, the (p, T) phase diagram was built and shown in Fig. 3, and

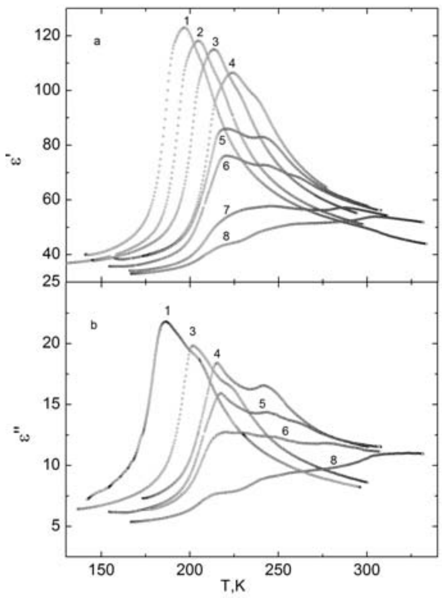

Fig. 2. Temperature dependence of the real ε′ (a) and imaginary ε″ (b) parts of the dielectric permittivity of $TlIn(S_{0.99}Se_{0.01})_2$ polycrystals at the hydrostatic pressure values of 0 (*1*), 190 (*2*), 350 (*3*), 550 (*4*), 580 (*5*), 610 (*6*), 680 (*7*), and 700 MPa (*8*).

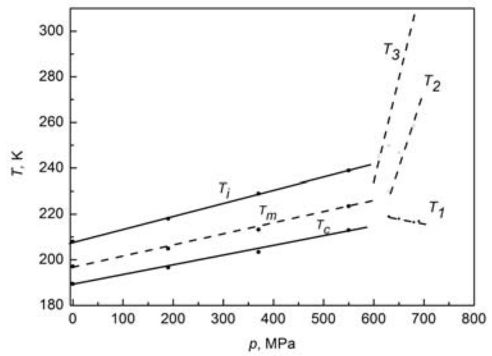

Fig. 3. (*p*, *T*) phase diagram for $TlIn(S_{0.99}Se_{0.01})_2$ polycrystal.

pressure coefficients for the phase transition temperature shift were determined with the following values for $TlIn(S_{0.99}Se_{0.01})_2$: dT_i/dp = 55 K/GPa, dT_m/dp = 47 K/GPa, dT_c/dp = 42 K/GPa, dT_1/dp = –39 K/GPa, dT_2/dp = 690 K/GPa, dT_3/dp = 938 K/GPa.

4. Conclusions

Studies of the temperature dependence of dielectric permittivity performed for $TlIn(S_{1-x}Se_x)_2$ polycrystals (x = 0.01, 0.02, 0.03) show the presence of anomalies ascribed to paraelectric-to-incommensurate-to-ferroelectric phase transitions. Isovalent substitution of S by Se in these materials reduces the phase transition temperatures. With the Se content increase up to x = 0.03, a slight trend to the convergence of the dielectric permittivity anomalies at T_i and T_m and divergence of those at T_m and T_c have been observed. Based on studying the temperature dependences for the dielectric permittivity of $TlIn(S_{0.99}Se_{0.01})_2$ crystal at a high hydrostatic pressure, its (*p*, *T*) phase diagram has been built.

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