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Effect of hydrostatic pressure on phase transitions in ferroelectric $TlInS_2$

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Studies of the layered ferroelectric $TlInS_2$ with an incommensurate phase at hydrostatic pressure ($p_{atm} \leq p \leq 660$ MPa) were performed. Based on the results of temperature dependence of the dielectric constant and dielectric loss, pyroelectric coefficient and spontaneous polarization at different pressures, a (p, T) phase diagram is obtained. A complex polycritical region is found in the range of $580 \leq p < 660$ MPa.

Keywords: layered crystal; phase transition; hydrostatic pressure

1. Introduction

Layered semiconductors are interesting to study since their characteristics and properties are determined by quasi-two-dimensionality and structural anisotropy. This class of materials includes $A^{III}B^{III}C_2^{VI}$ chalcogenides ($A = $ Tl, $B = $ In, Ga, $C = $ S, Se) with a specific mechanism of ferroelectricity, among which ferroelectric $TlInS_2$ is especially interesting, since it possesses an incommensurate (IC) phase (see [1,2], and references therein). The study of the (p, T) diagram of this crystal gives evidence for the existence of a triple point with the coordinates $p = 530$ MPa, $T = 245$ K [3,4]. However, no detailed data regarding polycritical phenomena in this crystal are available. Here we report the results of the studies of phase transformations in single crystals of $TlInS_2$ at hydrostatic pressures up to 660 MPa.

2. Experimental

$TlInS_2$ single crystals were grown in quartz ampoules by the Bridgman–Stockbarger technique, similar to details reported in [5]. Samples ranging from $5 \times 5 \times 0.25$ to $5 \times 5 \times 2\,mm^3$ in size

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were used for the measurements. The dielectric constant and the dielectric loss were investigated at field frequencies of 1 MHz and 1 kHz along the [100] and [001] crystallographic directions. Hysteresis loops were studied using a modified Sawyer–Tower scheme. Pyroelectric current studies were carried out by a quasistatic method. The hydrostatic pressure was generated in a high-pressure cell, described in [6].

3. Results and discussion

At atmospheric pressure, the temperature dependence of the dielectric constant, $\varepsilon(T)$, of $TlInS_2$ reveals anomalies in the interval 190–220 K, corresponding to a number of sequential phase transitions (PTs) (Figure 1). Detailed studies of the dielectric constant and spontaneous polarization in a broad temperature range show the evidence for the existence of a number of anomalies in $TlInS_2$ at 216, 206, 204 and 201 K and in the interval 190–195 K [7,8]. The mechanisms of

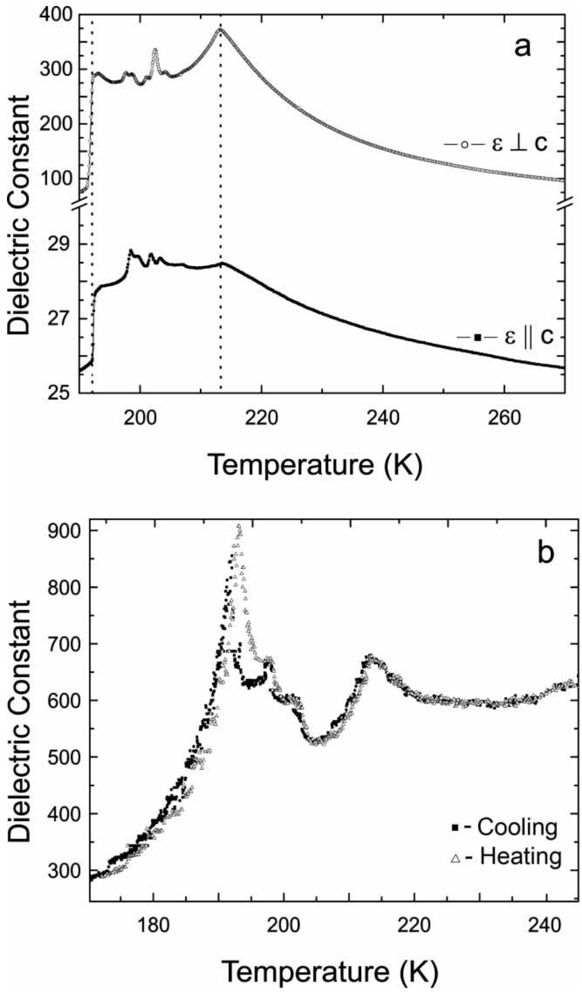

Figure 1. Temperature dependence of the dielectric constant of $TlInS_2$ (a) at the frequency of 1 MHz perpendicular and parallel to the [001] crystallographic direction in the cooling mode; (b) at the frequency of 1 kHz in cooling and heating modes.

these transitions were considered in [2,7,9]. The PT to the ferroelectric phase is associated with the displacement of Tl atoms in the (a, b) plane [1,2]. Ferroelectricity in $TlInS_2$-type layered crystals is caused by their specific electronic structure, namely the stereochemically active electron lone pair configuration of the Tl^+ ion [10]. Disturbances (impurities, structural defects) can lead to a splitting of the PTs between IC and commensurate phases in $TlInS_2$ at $T_{c1} = 204$ K and $T_{c2} = 201$ K [9]. According to this model, the anomaly at $T_{i2} = 206$ K corresponds to the formation of a new IC structure. The anomalous behaviour of $\varepsilon(T)$ in the temperature interval 190–195 K is explained as a result of coexistence of polar commensurate domains, appearing at temperatures $T_{c1} = 204$ K and $T_{c2} = 201$ K, and transitions at $T_{c1} = 204$ K and $T_{c2} = 201$ K correspond to IC–commensurate PTs to improper and proper ferroelectric phases [7]. The PTs at temperatures $T_i = 216$ K and $T_{i2} = 206$ K are explained as transitions to an IC phase of types I and II, respectively [7].

In the $\varepsilon(T)$ dependence of $TlInS_2$, anomalies at the temperatures $T_i = 214$ K, $T_{i2} = 206$ K, $T_{c1} = 202$ K, $T_{c2} = 198$ K, and $T_c = 193$ K were revealed (Figure 1). It should be noted that the T_{c1} and T_{c2} PT temperatures observed here differ by 2–3 K from those reported in [8], but coincide with the data of [3]. Such discrepancies are explained by the differences in the crystal growth procedure and were also reported earlier for the samples from different batches [2,11]. With increasing pressure to 550 MPa, the anomalies of the dielectric constant shift towards higher temperatures. The relevant pressure coefficients are determined: $\partial T_c/\partial p = 35$ K/GPa, $\partial T_{c1}/\partial p = 43$ K/GPa, $\partial T_{c2}/\partial p = 41$ K/GPa, $\partial T_i/\partial p = 56$ K/GPa, and $\partial T_{i2}/\partial p = 48$ K/GPa. In the pressure range $p > 580$ MPa, a qualitative change of the $\varepsilon(T)$ dependence is observed and attributed to polycritical phenomena.

The results of the pressure studies of the dielectric constant at constant temperatures are shown in Figure 2(a) and (b). Features, observed in the $\varepsilon(p)$ dependence, are related to the PTs T_{I-VII}, $T_{VII-VIII}$ at $T = 255$ K, T_{II-VII}, $T_{VII-VIII}$ at $T = 234$ K, and T_{II-VII}, $T_{VII-VIII}$ at $T = 230$ K. The corresponding PT points are shown in the (p, T) phase diagram (Figure 4).

Figure 3 shows the temperature dependences of the pyroelectric coefficient, γ, at various pressures, obtained in the heating mode at a rate 0.08–0.15 K/s, with the $TlInS_2$ sample being pre-polarized by an external electric field with the strength $E = 100$ V/mm. A maximum in the temperature dependence of the pyroelectric coefficient γ is observed, corresponding to a PT of a

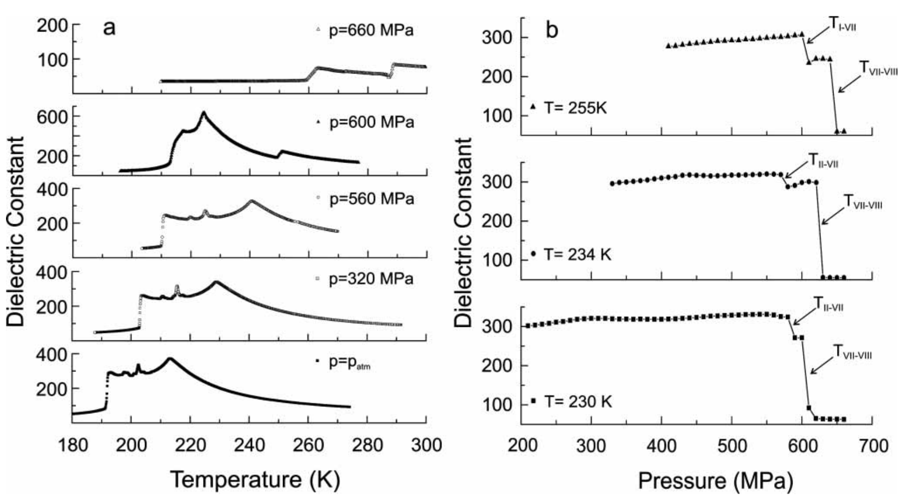

Figure 2. Temperature dependence of dielectric constant at the frequency of 1 MHz of $TlInS_2$: (a) in the cooling mode at various hydrostatic pressure values perpendicular to the [001] crystallographic direction; (b) isothermal studies of the dielectric constant $\varepsilon(p)$, $T =$ const.

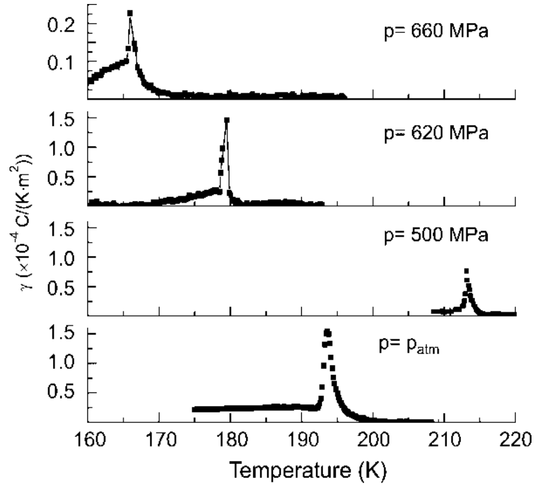

Figure 3. Temperature dependence of the pyroelectric coefficient γ of $TlInS_2$ at various pressures.

commensurate ferroelectric phase. The temperatures at which γ anomalies are detected agree with the temperature T_c of the V–VI transition, obtained from the $\varepsilon(T)$ dependence. We have found an anomaly of the pyroelectric coefficient γ at the pressure of 660 MPa (Figure 3), this being the evidence for the existence of a ferroelectric PT at $T = 166$ K. The points of the anomalies, corresponding to the ferroelectric PTs, are shown in the phase diagram (Figure 4). Note that we have observed hysteresis loops below the PT lines, of phase VI in the (p, T) phase diagram, in particular, in the temperature range $T \leq 194$ K at atmospheric pressure ($p = p_{atm}$) and in the range 80–178 K at the pressure $p = 640$ MPa.

Thus, the following PTs are revealed in the (p, T) diagram of $TlInS_2$ crystals (Figure 4) in the pressure range $p_{atm} \leq p \leq 660$ MPa: a transition I–II to the IC phase; a transition II–III to another IC phase, which we could observe only at the studies of the dielectric constant perpendicular to the layers; a III–IV IC–commensurate PT to an improper ferroelectric state; a IV–V IC–commensurate PT to a proper ferroelectric state; a transition V–VI to the ferroelectric state [7] as well as structural PTs: a first-order structural PT I–VII; a first-order structural PT VII–VIII; a

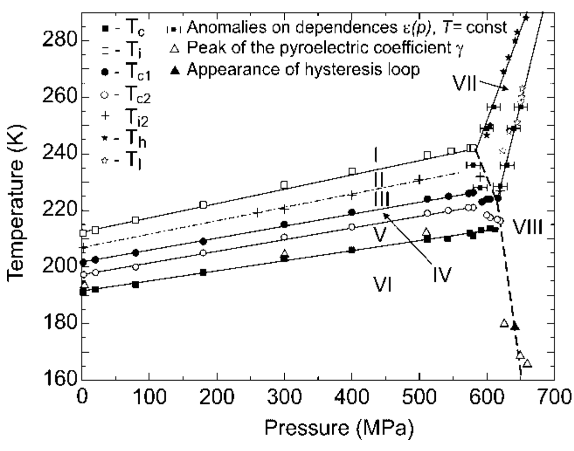

Figure 4. (p, T) phase diagram of $TlInS_2$.

structural ferroelectric PT VI–VIII from the polar phase to the non-polar high-pressure phase (an anomaly of the pyroelectric coefficient γ at pressure 660 MPa, Figure 3).

4. Conclusions

Based on the studies of temperature dependences of dielectric constant and dielectric loss, pyroelectric coefficient and spontaneous polarization at hydrostatic pressures ($p_{\mathrm{atm}} \leq p < 580$ MPa), a (p, T) phase diagram of $TlInS_2$ crystal is obtained. A pressure increase in the range $p_{\mathrm{atm}} \leq p <$ 580 MPa is shown to result in a shift of the anomalies of the dielectric constant towards higher temperatures; the variation of temperatures of the characteristic anomalies is observed to be linear, and the corresponding pressure coefficients are determined. A complex polycritical region is shown to exist in the range $580 \leq p < 660$ MPa.

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