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Optical properties of $TlInS_2$ layered crystal under pressure

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Studies of the optical properties of $TlInS_2$ layered ferroelectric with an incommensurate phase were performed. In the temperature range 190–220 K at atmospheric pressure, we observed rotation of the plane of the optical axes and a change of the angle between the optical axes of the crystal. The temperature dependences of birefringence and its anomalous part were investigated, the anomalies at $T_c = 192$ K and $T_i = 214$ K, corresponding to structural phase transitions, were revealed. Pressure increase in the range $p_{atm} \leq p < 470$ MPa is shown to result in a shift of the birefringence anomalies towards higher temperatures.

Keywords: layered crystal; phase transition; hydrostatic pressure

Introduction

Layered ferroelectrics are interesting for investigation since their properties are determined by quasi-two-dimensionality and strong structural anisotropy. This class of materials includes $A^{III}B^{III}C_2^{VI}$ chalcogenides (A = Tl, B = In, Ga, C = S, Se), among which the $TlInS_2$ ferroelectric crystal is especially interesting since it possesses a complex sequence of phase transitions (PTs) in the temperature interval 190–216 K and polycritical phenomena in the (p, T)-phase diagram in the pressure range $580 \leq p < 660$ MPa [1,2], as well as in the (x, T)-phase diagram [3]. The PT of $TlInS_2$ crystals into the ferroelectric phase is associated with the displacement of Tl atoms in the (a, b) plane [1,4]. The mechanism of existence of the ferroelectric state in $TlInS_2$-type layered crystals was studied in [5] and is explained by the existence of a specific electronic structure, namely the stereochemically active electron lone pair configuration of the Tl^+ ion.

Experimental

Here, we report on the studies of the optic angle and the rotation angle of the optical axes as functions of temperature as well as birefringence of $TlInS_2$ crystals at hydrostatic pressures up to

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470 MPa. $TlInS_2$ single crystals were grown by the Bridgman technique. Samples ranging from $5 \times 5 \times 0.25\,mm^3$ to $7 \times 1 \times 3.5\,mm^3$ in size were used for the measurements. The birefringence studies of the $TlInS_2$ single crystal were carried out in the temperature interval 170–300 K. The birefringence measurements were performed by the Senarmont technique at the laser wavelengths of 532 nm and 650 nm along the [001] crystallographic direction. The measurements were carried out in a high pressure optical cell. The temperature was measured by copper–constantan thermocouple.

Results and discussion

Studies of conoscopic interference patterns in the temperature range 180–293 K (Figure 1) enabled us to analyse the temperature behaviour of the optic angle and the rotation angle of the optical axes in the $TlInS_2$ crystal. Changes observed in the temperature interval 193–214 K are related to structural PTs. As seen from the dependences in Figure 1, a maximum at the temperature $T = 193$ K is observed, and in the range 193–214 K, an increase in the optic angle and a change of orientation of the plane of the axes are revealed with the temperature decrease.

To our knowledge, variation of the $TlInS_2$ crystal birefringence under hydrostatic pressure has not been studied before while conoscopic interference patterns were investigated only at atmospheric pressure. In general, our data are in agreement with those of Mamedov *et al.* [6] and Shim *et al.* [7].

In the temperature dependences of the birefringence of the $TlInS_2$ crystal at atmospheric pressure, anomalies at temperatures $T_i = 214$ K and $T_c = 192$ K are observed, corresponding to PTs into incommensurate and ferroelectric phases, respectively (Figures 2 and 3). One should note that cooling/heating temperature hysteresis for the anomaly at $T_c = 192$ K is $\Delta T \sim 2$ K, this being typical for a first-order PT. The anomalous part of the birefringence (Figure 3) was obtained from the temperature dependences shown in Figure 2 by subtracting the regular part which is a linear extrapolation of the temperature dependence of the birefringence in the paraelectric phase to the low-temperature region. Note that the temperature dependences of the anomalous part of birefringence (Figure 3), proportional to the spontaneous polarization and the order parameter, are in agreement with the data of Kashida and Y. Kobayashi [4] and Gomonnai *et al.* [8].

As can be seen from Figure 2, at the hydrostatic pressure increase to $p = 470$ MPa, the birefringence anomalies shift towards higher temperatures. The temperature dependences of the anomalous part of birefringence are shown in Figure 3. A decrease in the anomalous part of birefringence is observed with hydrostatic pressure, this being the evidence for the decrease in the spontaneous polarization value in the ferroelectric phase below T_c. Such behaviour is in agreement

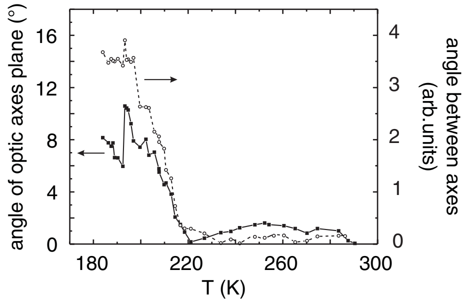

Figure 1. Temperature dependences of the angle of the optic axes plane and the angle between the optic axes of $TlInS_2$.

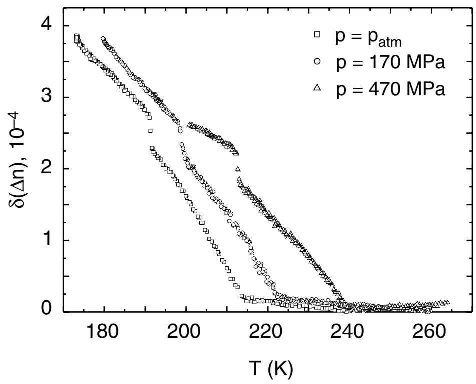

Figure 2. Temperature dependences of birefringence of $TlInS_2$ at different pressure values.

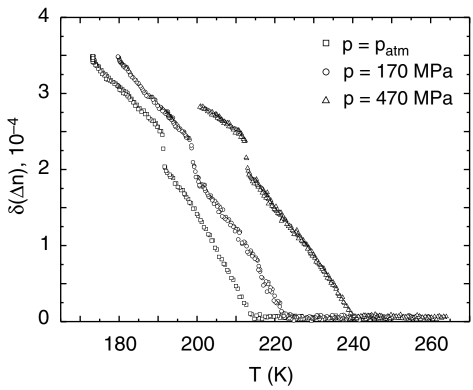

Figure 3. Temperature dependences of the anomalous part of birefringence of $TlInS_2$ at different pressure values.

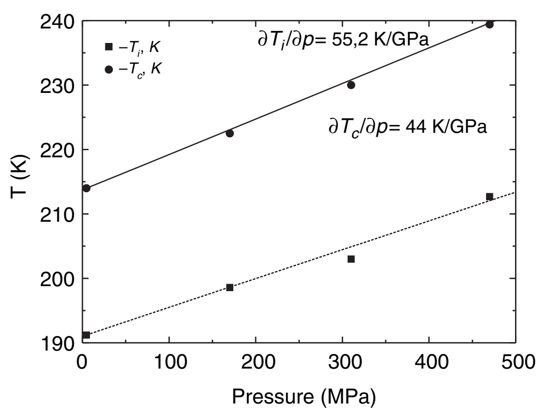

Figure 4. Pressure dependence of PT temperatures of $TlInS_2$, determined from birefringence.

with the pressure studies of the temperature dependence of spontaneous polarization determined on the base of the studies of pyroelectric current in the pressure range under investigation [8].

Based on the temperature dependences of birefringence at different hydrostatic pressure values, a pressure dependence of the PT temperatures was built (Figure 4).

Note that at atmospheric pressure, anomalies in the temperature dependence of the dielectric constant and the dielectric loss tangent of $TlInS_2$ are revealed at the temperatures $T_i = 214$ K, $T_{i2} = 206$ K, $T_{c1} = 202$ K, $T_{c2} = 198$ K and $T_c = 193$ K, corresponding to a number of sequential PTs [1–3,9]. It should be noted that the PT temperatures may differ by 2–3 K for different samples what is explained by the differences in the crystal growth procedure. Such deviations were also reported earlier for the samples from different batches [1,10]. The pressure behaviour of temperature dependences of dielectric characteristics was studied in [2,9] where the (p, T)-phase diagram was built for $TlInS_2$ crystals and the existence of hydrostatic pressure-induced structural PTs in the pressure range $580 \leq p < 660$ MPa was shown.

The temperature dependences of birefringence at different hydrostatic pressure values enabled us to determine the pressure coefficients of PT temperature variation $\partial T_c/\partial p = 44$ K/GPa and $\partial T_i/\partial p = 55.2$ K/GPa. Note that the pressure coefficient $\partial T_i/\partial p$ is in agreement with the data of Gomonnai *et al.* [2], while the $\partial T_c/\partial p$ value differs from the one obtained from the studies of dielectric characteristics at pressure variation which can be related to photo-induced changes of the temperature interval existing in the polar phase of the $TlInS_2$ crystal.

Conclusions

Based on the studies of temperature dependences of birefringence at hydrostatic pressure ($p_{atm} \leq p < 470$ MPa), a (p, T)-phase diagram of the $TlInS_2$ crystal is built. Pressure increase in the range $p_{atm} \leq p < 470$ MPa is shown to result in a shift of the anomalies of birefringence towards higher temperatures, the variation of temperatures of the characteristic anomalies is observed to be linear, the corresponding pressure coefficients being determined. The data on the temperature dependences of birefringence at different pressures are in agreement with the results obtained in [2].

Acknowledgements

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