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Anisotropy of thermal expansion of $TlGaSe_2$ crystals

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ABSTRACT

We study experimentally the temperature dependences of relative elongation in thallium gallium diselenide crystals, $TlGaSe_2$, in the temperature region 100–293 K. The eigenvalues of thermal expansion tensor are determined. The anisotropy of thermal expansion for $TlGaSe_2$ within the cleavage plane is revealed. We find that the temperature dependences of the relative elongations and the thermal expansion coefficients are characterized by a number of anomalies which correspond, most probably, to structural phase transitions among different polytypes. Relations between the anomalous temperature behavior of thermal expansion and the polytype structure of $TlGaSe_2$ are discussed.

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Ferroics; thallium-gallium diselenide; polytypes; thermal expansion; anisotropy

1. Introduction

$TlGaSe_2$ crystals belong to a layered type of $A^{III}B^{III}C_2^{VI}$ chalcogenide semiconductors (with A = Tl, B = In, Ga, and C = S, Se, Te). They reveal the monoclinic structure under normal conditions which is characterized by the point symmetry group 2/m [1]. Contrary to chain-like crystals like $TlInSe_2$ $TlGaTe_2$ and $TlInTe_2$ that belong to the tetragonal group 4/mmm, $TlInS_2$, $TlGaSe_2$ and $TlGaS_2$ exhibit a layered structure and remain monoclinic [1–3]. $TlGaS_2$ has the unit cell parameters $a = 10.772$ Å, $b = 10.771$ Å, $c = 15.636$ Å, $\beta = 100.6$ deg, and $Z = 16$ [2] at the ambient conditions. Since $a \approx b$, the structure of the crystalline lattice is pseudo-tetragonal. The crystal is mainly transparent in the infrared spectral range, with the transparency window extending from 0.61 to 20 μm [4].

$TlGaSe_2$ represents a promising material for detecting X- and γ-rays [5], possessing a high enough photoacoustic response [6]. Besides, it can be used in acoustooptics due to its notable acousto-optic figure of merit (260×10^{-15} s^3/kg [7,8]). Thallium-gallium diselenide has been studied well enough from the viewpoints of its electric conductivity and optical properties [9–12]. On the other hand, the behavior of $TlGaSe_2$ in the course of structural phase transitions (PTs) is, probably, one of the most interesting and unresolved problems. The main attention in this respect has been paid to the changes occurring in the structural [13–15], dielectric [16] and thermal expansion properties [17–19], as well as the Raman spectra [20]. In particular, it has been found that the $TlGaSe_2$ crystals undergo two PTs from an initial paraelectric phase into intermediate incommensurate phase and then to a ferroelectric phase. The latter is characterized by the point group 2, with the two-fold symmetry axis being parallel to the crystallographic axis c. The PTs mentioned above happen at the temperatures $T_i \approx 120$ K and $T_C \approx 110$ K. The PT into the ordered phase is of a weakly manifested first order. It is accompanied by a four-fold unit-cell multiplication along the direction c, while the PT into the incommensurate phase is of a second order, with the superstructure modulation wave vector being equal to $k = (\delta; \delta; 0.25)$, with $\delta = 0.02$ [21].

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Due to a widely accepted pseudo-tetragonality of the unit cell of $TlGaSe_2$, its thermal expansion coefficients have been studied only in the cleavage plane and along the direction perpendicular to this plane (see Refs. [13,15,18,19,22]). In other words, the anisotropy in the cleavage plane has been assumed to be negligibly small. This approximation hardly seems to be correct in a wide enough temperature range, including the low-temperature phases. Besides, basing on the thermal expansion characteristics and the unit-cell parameters, the authors [15] have supposed that the sequence of PTs in $TlGaSe_2$ is more complicated than that discussed above. In particular, additional anomalies have been observed at $T = 110$, 217 and 240 K [15]. Moreover, since the $TlGaSe_2$ crystals represent a layered-type material, they tend to exhibit a polytype structure due to weak van der Waals forces. This leads to stacking of layers, which results in different lattice parameters c^*. In fact, such structures have earlier been revealed in $TlInS_2$ and $TlGaSe_2$ crystals [23,24]. As a consequence, the lattice parameter c^* of $TlGaSe_2$ can be equal to $c^* = c$, $2c$, $3c$, $4c$, … No changes in the translational symmetry along the c axis has been found in the crystals with $c^* = 2c$, $8c$ and $10c$ in the temperature range $T = 90$–300 K (see Ref. [23]).

According to Ref. [23], the second-order PT in the polytype with $c^* = 2c$ manifests itself nearby the temperature point $T'_C \approx 124$ K. Notice that recently we have shown that the PTs occurring in the mixed polytype states can be revealed in the thermal expansion coefficients and the linear thermal expansion of $TlInS_2$ [25]. In the present work we study the anisotropy of thermal expansion in $TlGaSe_2$ in the course of its PTs.

2. Experimental procedures

We grew $TlGaSe_2$ using a Bridgman–Stockbarger technique. Our crystals had a stoichiometric composition and were dark red. As seen from Figure 1, their diameters were equal to ∼20 mm and the heights to ∼30 mm. The synthesis of $TlGaSe_2$ mixture was carried out in vacuumed (0.01 Pa) quartz ampoules, using purified and mechanically mixed initial components. The maximal synthesis temperature was about ∼1273 K. The initial substances were loaded into a quartz ampoule with an internal diameter of ∼20 mm, which was vacuumed down to 10–4 mm Hg and then soldered.

The $TlGaSe_2$ compound was prepared, using a melting method. The melt of the synthesized compound was crystallized under the condition of the horizontal position of the ampoule. The temperatures in the melt and annealing zones were equal to 1163–1183 and 843–893 K, respectively. The vertical temperature gradient in the crystallization zone was 2.0–6.5 K/mm, whereas the rate of movement of the ampoule from the melt zone to the annealing one amounted to 0.1–0.2 mm/h. We remind that the melting temperature of $TlGaSe_2$ is equal to 1091 K. The crystals thus obtained were cooled at the rate 20–30 deg/h.

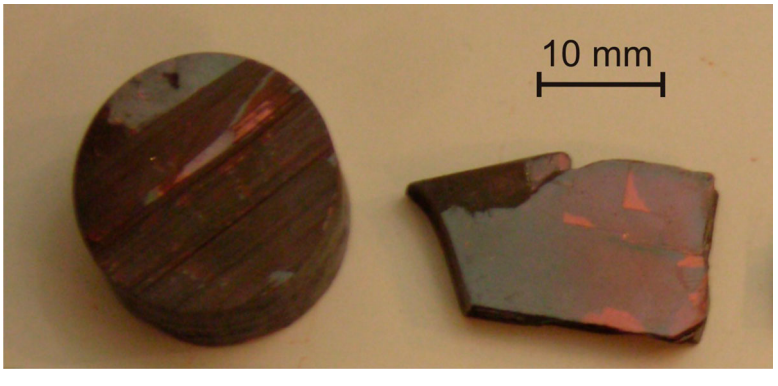

Figure 1. $TlGaSe_2$ crystals grown in the present work.

The relative thermal expansion is given by relation

$$\frac{\Delta L_i}{L_j^0} = \frac{L_i - L_i^0}{L_j^0}, \tag{1}$$

where L_i^0 and L_j^0 are the initial sizes of the sample respectively along the directions i and j, and L_i their thermally induced sizes. Then the linear thermal expansion coefficients can be written as

$$\alpha_{ij} = \frac{\partial(\Delta L_i / L_j^0)}{\partial T}. \tag{2}$$

In general, a symmetric second-rank polar tensor α_{ij} for the monoclinic crystals contains four different components:

$$\alpha_{ij} = \begin{vmatrix} \alpha_{XX} & \alpha_{XY} & 0 \\ \alpha_{XY} & \alpha_{YY} & 0 \\ 0 & 0 & \alpha_{ZZ} \end{vmatrix}. \tag{3}$$

It can be rewritten in the eigensystem $X'Y'Z'$ in the diagonal form

$$\alpha'_{ij} = \begin{vmatrix} \alpha'_{11} & 0 & 0 \\ 0 & \alpha'_{22} & 0 \\ 0 & 0 & \alpha'_{33} \end{vmatrix}, \tag{4}$$

using the system of equations

$$\begin{cases} \alpha_{XX} = \alpha'_{11}\cos^2\Theta + \alpha'_{22}\sin^2\Theta \\ \alpha_{YY} = \alpha'_{11}\sin^2\Theta + \alpha'_{22}\cos^2\Theta \\ \alpha_{XY} = \alpha'_{11}\sin^2(\Theta + 45) + \alpha'_{22}\cos^2(\Theta + 45) \end{cases}, \quad a_{ZZ} = \alpha'_{33}. \tag{5}$$

Here α_{XY} denotes the thermal expansion coefficient along the bisector of X and Y axes, and Θ the angle between the axes X and X' in the ab plane.

To study thermal expansion, we used a quartz capacitance dilatometer described in details in our recent works [25–28]. The temperature dependences of thermal elongations were studied in the interval 100–273 K in the heating run. Two sample of $TlGaSe_2$ were prepared in the shape of parallelepipeds. The first had its faces perpendicular to the Cartesian coordinate axes colour {7,6,0,0}, $Y \perp b$ and $X \perp$ (011), and the faces of the second sample were perpendicular to the bisector of X and Y axes. The sizes of these samples were 7.03 mm along the X-axis, 6.87 mm along the Y-axis, 2.11 mm along the Z-axis, and 5.0 mm along the bisector between the X and Y axes. The error of determination of the relative elongation did not exceed 2×10^{-5}, while the resultant error for the thermal expansion coefficients α_{ij} was about 5×10^{-6} K^{-1}.

3. Results and discussion

As seen from Figure 2, the relative linear expansion behaves almost monotonously in the temperatures region under study. However, small $\Delta L_Z/L_Z^0$ anomalies are observed at the temperatures $T_C \approx 106$ K and $T_i \approx 113$ K. Besides, a minimum in the temperature dependence of $\Delta L_Z/L_Z^0$ is observed in the region 124 K $< T'_C <$ 137 K. Notice that the latter point agrees with the temperature of the second-order PT observed for the polytype with $c^* = 2c$ [23]. As seen from Figures 2 and 3, both the relative elongations $\Delta L_Z/L_Z^0$ and $\Delta L_X/L_Y^0$, and the thermal expansion coefficients α_{ZZ} and α_{XY} manifest a kink-like behavior in the temperature region 200 K $< \Delta T_k <$ 240 K. These anomalies clearly manifest themselves in the temperature dependences of eigenvalues of the tensor α'_{ij} (see Figure 3). Note that anomalous behaviors of the lattice parameters and the thermal expansion coefficients evaluated on their basis in the temperature region mentioned above have been detected

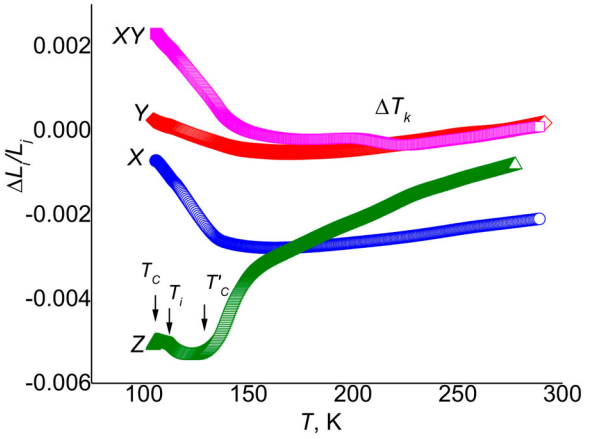

Figure 2. Temperature dependences of relative elongations for $TlGaSe_2$ crystals.

in Ref. [15]. Most probably, they are caused by some structural changes in the $TlGaS_2$ crystals, which are associated with higher c^* values.

With taking experimental errors into account, the thermal expansion coefficients α_{XX} and α_{YY} remain the same in the temperature region above 137 K (see Figure 3(a)). They are very small, with the absolute value equal to $(0.8 \pm 0.5) \times 10^{-5}K^{-1}$ (Figure 2(a)). These coefficients change their sign at the temperature ~161 K and become negative. On the other hand, they become different below the T'_C point, thus indicating increased anisotropy in the crystallographic plane *ab*. Both α_{XX} and α_{YY} coefficients, as well as α_{ZZ} and α_{XY} demonstrate anomalous behaviors at T_C, T_i and T'_C (see Figure 3(b)). Besides, Figure 3(b) testifies that α_{ZZ} and α_{XY} behave anomalously in the region ΔT_k.

All the anomalies mentioned above are well distinguishable in the temperature dependences of eigenvalues of the thermal expansion tensor. As seen from Figure 4(a), the anisotropy of thermal expansion in the *ab* plane exists in the overall temperature region under test. This anisotropy is expressed most distinctly below 175 K, as well as in the temperature region ΔT_k. In particular, the eigenvalues α'_{11} and α'_{22} differ appreciably at these temperatures. Close to the room temperature, the α'_{22} component is almost zero, although we have $\alpha'_{11} \approx \alpha'_{33} = (1.6 \pm 0.5) \times 19^{-5}K^{-1}$. The indicative surface of the thermal expansion tensor has a doughnut form (see Figure 5(a)). The α'_{22} becomes negative in the vicinity of T'_C (Figure 5(b)). The α'_{33} coefficient also becomes negative

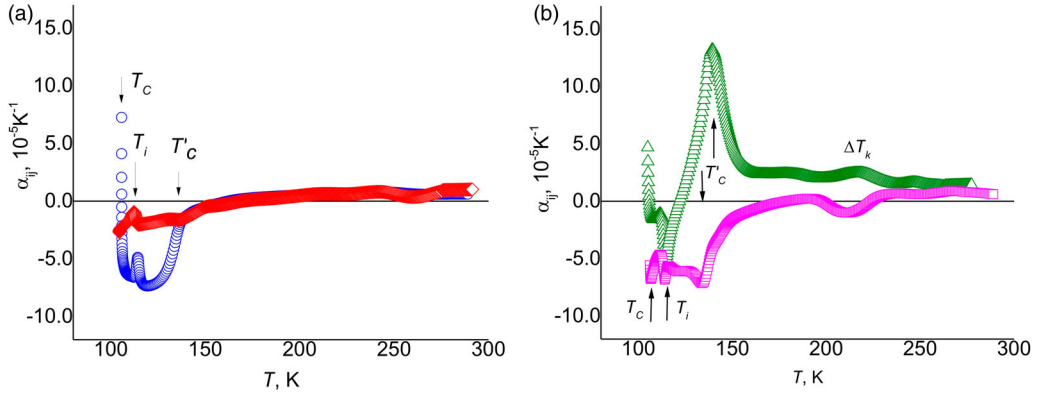

Figure 3. Temperature dependences of thermal expansion coefficients α_{ij}: (a) α_{XX} (circles) and α_{YY} (diamonds), and (b) α_{ZZ} (triangles) and α_{XY} (squares).

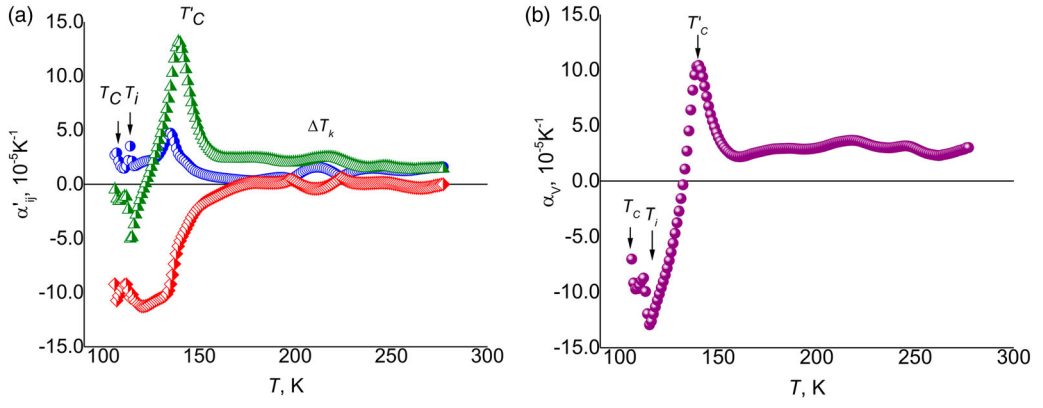

Figure 4. Temperature dependences of (a) thermal expansion coefficients α'_{11} (semi-open circles), α'_{22} (semi-open diamonds) and α'_{33} (semi open triangles), and (b) volume thermal expansion coefficient α_V.

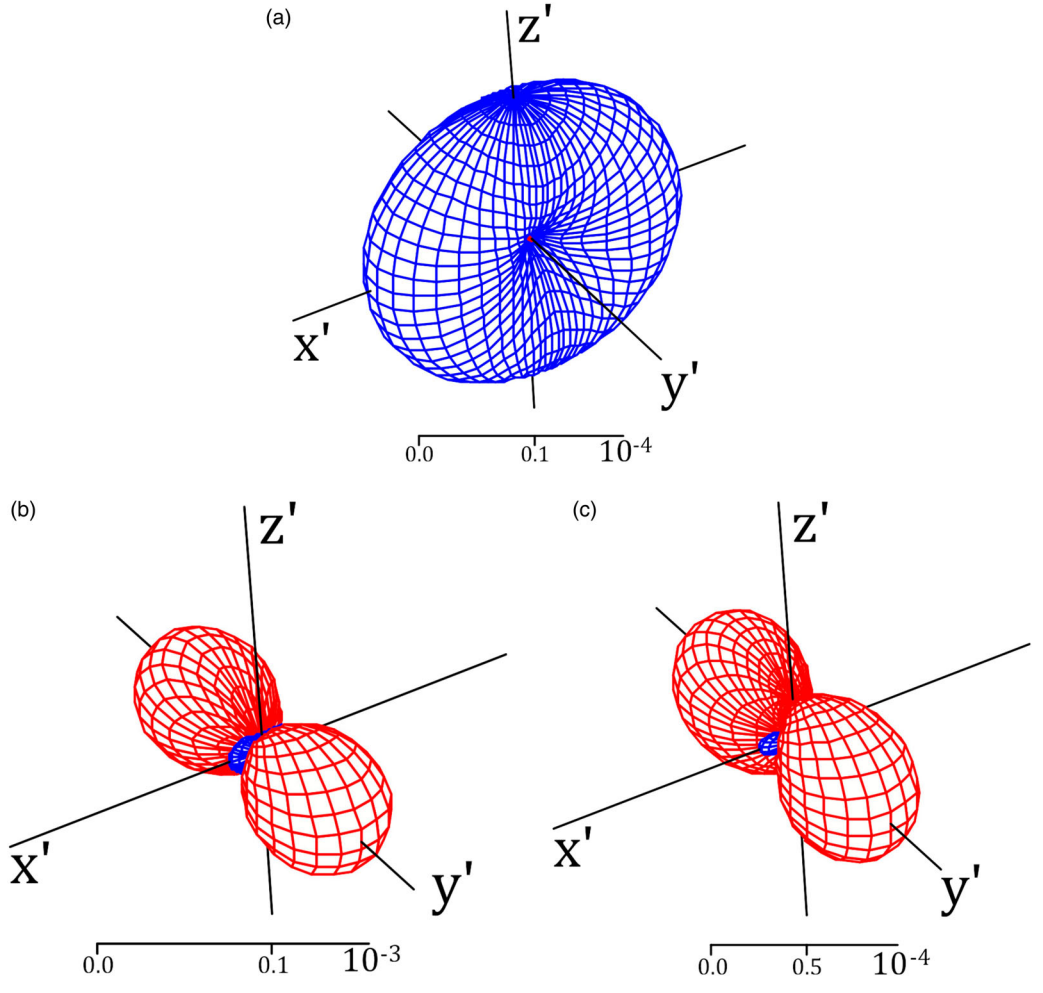

Figure 5. Indicative surfaces of thermal expansion tensor constructed at 273 K (a), 124 K (b) and 113 K (c).

when the temperature approaches the T_i and T_C points (see Figure 5(c)). The volume thermal expansion coefficient α_V calculated as behaves anomalously at the points T_C, T_i and T'_C. Moreover, it changes its sign below T'_C.

4. Conclusions

Basing on the experimental studies of temperature dependences of the relative elongations for $TlGaSe_2$ performed in the temperature region 100–293 K, we have obtained the dependences of eigenvalues of the thermal expansion tensor. It has been shown that the $TlGaSe_2$ crystals exhibit anisotropy of the thermal expansion not only along the directions parallel and perpendicular to the cleavage plane, but also within the cleavage plane itself. This anisotropy manifests itself in that the components α'_{11} and α'_{22} of the thermal expansion tensor are different.

Using the temperature dependences of the relative elongations and the thermal expansion coefficients, we have detected the anomalies which, most probably, correspond to the structural PTs among different polytypes. In particular, the anomalies found at $T_C \approx 106$ K and $T_i \approx 113$ K can be associated respectively with the ferroelectric and incommensurate PTs in the polytype with the lattice parameter $c^* = c$, while the anomaly in the region $124\ \text{K} < T'_C < 137\ \text{K}$ can be attributed to the PT in the polytype characterized by $c^* = 2c$.

Besides, we have observed the anomalous behavior of the thermal expansion parameters in the temperature region $200\ \text{K} < \Delta T_k < 240\ \text{K}$. Probably, it indicates that polytypes with some higher c^* values exist in the crystalline matrix. The latter should be characterized by some other structural changes.

Disclosure statement

No potential conflict of interest was reported by the authors .

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