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Phase Transition in a KPb_2Br_5 Crystal

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Abstract—Crystals of the KPb_2Br_5 compound are investigated using polarized light microscopy and calorimetry. The birefringence and the angle of rotation of the optical indicatrix are measured in the temperature range 270–620 K. It is found that the KPb_2Br_5 crystal undergoes a first-order ferroelastic phase transition at temperatures $T_{0}\uparrow = 519.5$ K and $T_{0}\downarrow = 518.5$ K with a change in the enthalpy $\Delta H = 1300 \pm 200$ J/mol. This transition is accompanied by both twinning and the symmetry change $mmm \longleftrightarrow P2_1/c$. It is revealed that the angle of rotation of the optical indicatrix exhibits an unusual behavior under variations in the temperature due to a strong temperature dependence of the birefringence. *© 2005 Pleiades Publishing, Inc.*

1. INTRODUCTION

The search for new active media for solid-state lasers operating in the middle-infrared range [1] has given impetus to investigations of the crystal family of compounds with the general formula APb_2X_5 (A = Cs, Rb, K, NH_4; X = Cl, Br). It is known [2] that, depending on the ratios between the ionic radii A/X and Pb/X, all these compounds can form two structural modifications, namely, the monoclinic modification $NH_4Pb_2Cl_5$ and the tetragonal modification $NH_4Pb_2Br_5$. According to the phase diagram, the region of existence of KPb_2Br_5 crystals lies along the boundary between the regions corresponding to these two structures and, hence, the KPb_2Br_5 compound can exist in both modifications. The KPb_2Br_5 monoclinic crystals ($P2_1/c$) are formed upon high-temperature crystallization, whereas the tetragonal crystals ($I4/mcm$) grow from aqueous solutions [2, 3]. X-ray diffraction investigations of KPb_2Br_5 crystals at room temperature have established that the monoclinic unit cell is similar to a rectangular unit cell with parameters a = 9.264 Å, b = 8.380 Å, c = 13.063 Å, and Z = 4. The monoclinic angle is relatively small: $\beta = 90.06(12)°$ [2]. Furthermore, Cola *et al.* [3] assigned these crystals to the orthorhombic system. Nothing definite is known about phase transitions from the monoclinic structural modification to the tetragonal modification. However, according to the differential thermal analysis performed in [3], KPb_2Br_5 crystals in the monoclinic modification undergo a phase transition at a temperature T_0 = 515 K with a weak thermal effect (≈400 J/mol). On the other hand, the x-ray diffraction patterns at higher temperatures (T = 593 K) did not exhibit any noticeable changes, except for insignificant shifts of the peaks and small variations in their intensities. All the aforementioned facts indicate that KPb_2Br_5 monoclinic crystals can undergo a structural phase transition at high temperatures.

The purpose of this work was to reveal the hypothetical structural phase transition, to determine its type, and to elucidate the nature and symmetry of the initial high-temperature phase. In order to solve these problems, the KPb_2Br_5 crystal was studied using polarized light microscopy and measurements of the heat capacity and birefringence over a wide range of temperatures.

2. SAMPLE PREPARATION AND EXPERIMENTAL TECHNIQUE

Crystals of the KPb_2Br_5 compound were grown by the Bridgman method from a batch of stoichiometric composition at a temperature T = 655 K. The initial potassium and lead bromides (special-purity grade) were dried under dynamic vacuum and then repeatedly purified through directional crystallization. A vertical one-zone furnace with a temperature gradient of no less than 5 K/mm served as the growth apparatus. Single crystals up to 15 mm in diameter and 40 mm in length were grown in evacuated silica tubes at a mean rate of 2–4 mm/day.

The thermodynamic properties were investigated on a DSM-2M differential scanning microcalorimeter. The DSM signals were recorded and processed using a computer. The measurements with powder samples were carried out in the temperature range 340–600 K.

The birefringence of the KPb_2Br_5 crystal was measured on the (001), (010), and (100) sections. The mea-

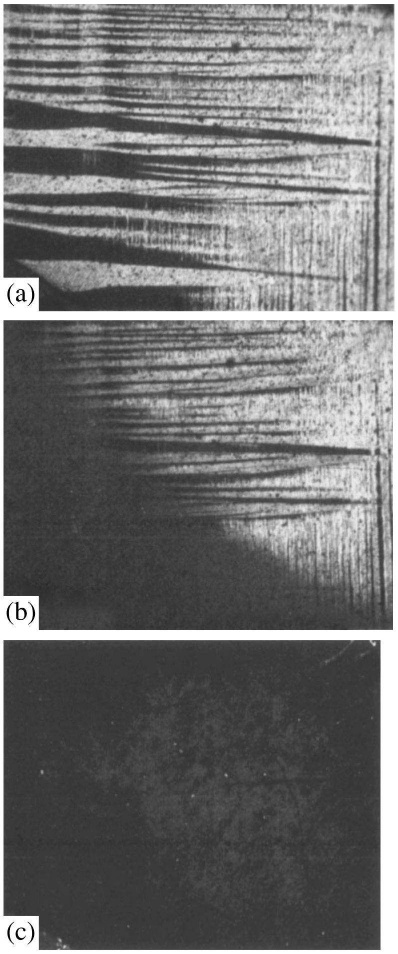

Fig. 1. Twinning of the KPb_2Br_5 crystal in the (010) section at temperatures T = (a) 518.5, (b) 519.5, and (c) 521.0 K.

surements were performed on a Berec compensator with an accuracy of $\cong 10^{-5}$ and a Senarmont compensator with a sensitivity of no less than $\cong 10^{-7}$ at a wavelength of 6328 Å. The former compensator was used to determine the birefringence magnitude, and the latter compensator made it possible to examine the temperature dependence of the birefringence. Observations in polarized light and measurements of the rotation angle of the optical indicatrix were carried out using an Axiolab polarizing microscope with an accuracy of ±0.5°. All the experiments were performed at temperatures ranging from 273 to 620 K.

3. EXPERIMENTAL RESULTS

Observations of the crystal plates in polarized light at room temperature revealed a streaky twin structure in the (010) section (Fig. 1). The structural components differ in the extinction positions by an angle 2φ. The twin boundaries are aligned parallel to the [100] and [001] directions. The width of twins is approximately equal to 10 μm. During heating, the twin pattern is observed up to a temperature of 519 K and then disappears. At temperatures above $T = 520$ K, the crystal is characterized by a uniform “straight” extinction and twins are absent. During cooling, twins again appear, but the pattern changes radically: there arise large-sized regions that occupy half the sample and differ in the extinction positions by an angle 2φ. The formation of these large-sized regions made it possible to measure the birefringence from the (010) section of the sample in a single-domain state. The original twin pattern is regained with time.

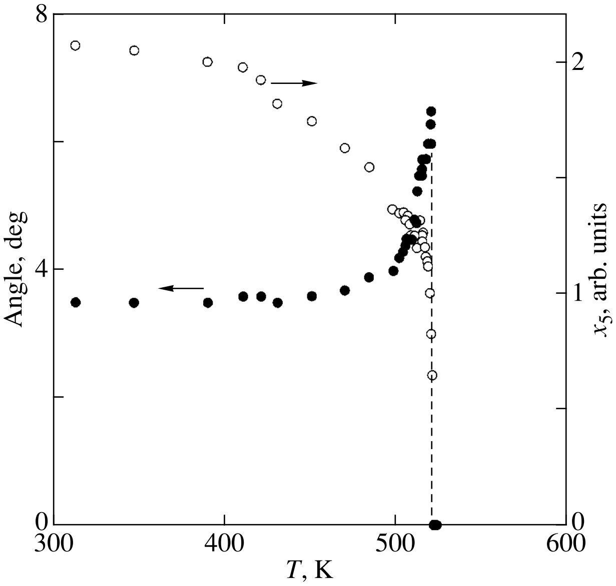

Fig. 2. Temperature dependences of the rotation angle of the optical indicatrix $\varphi(T)$ and the component $x_5(T)$ of the shear spontaneous strain in the KPb_2Br_5 crystal.

Figure 2 presents the angle of rotation of the optical indicatrix with respect to the [010] direction in a single twin as a function of temperature. The dependence $\varphi(T)$ exhibits an unusual behavior. At room temperature, the angle of rotation of the optical indicatrix is small and approximately equal to 4°. During heating, the angle of rotation initially remains constant, increases to 7° only in the vicinity of the phase transition, and then sharply decreases to zero. With a further increase in the temperature, the extinction of the sample remains unchanged. In the range 525–545 K, an unusual coloration of the crystal is observed in polarized light: the crystal becomes colored and changes its color (beginning with red) at each temperature. At temperatures above 550 K, the coloration disappears.

The temperature dependences of the birefringences Δn_a, Δn_b, and Δn_c are depicted in Fig. 3. At room temperature, the birefringences are approximately identical and relatively large (≈0.06) for the (100) and (010) sections and close to zero for the (001) section. As the temperature increases, the difference in the refractive indices initially changes linearly and insignificantly. At

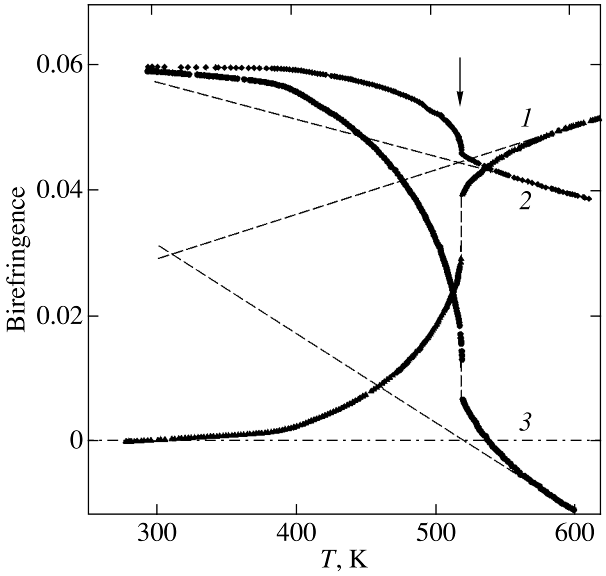

Fig. 3. Temperature dependences of the birefringence of the KPb_2Br_5 crystal: (*1*) Δn_c, (*2*) Δn_a, and (*3*) Δn_b.

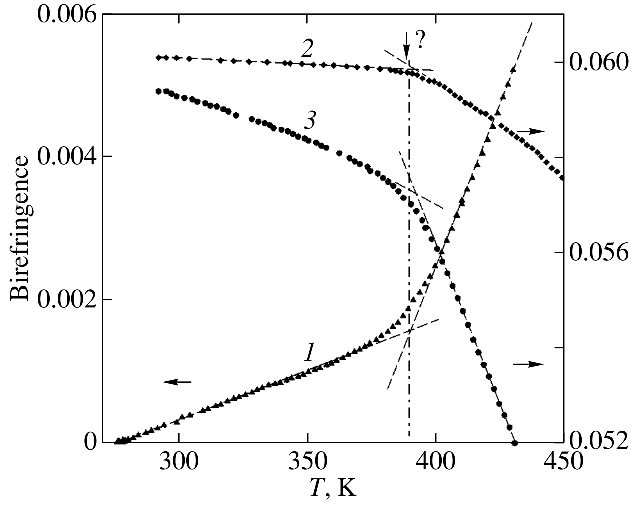

Fig. 4. Temperature dependences of the birefringence of the KPb_2Br_5 crystal at temperatures close to 400 K: (*1*) Δn_c, (*2*) Δn_a, and (*3*) Δn_b.

temperatures above $T \approx 390$ K, the dependences $\Delta n(T)$ exhibit an anomalous behavior for all the sections. It is worth noting that, at this temperature ($T \approx 390$ K), the dependences $\Delta n(T)$ for all three sections are characterized by a specific point (Fig. 4).

At temperatures $T_{0\uparrow} = 519.5$ K and $T_{0\downarrow} = 518.5$ K, the birefringence undergoes a jump with an insignificant temperature hysteresis ($\Delta T \approx 1$ K) (Fig. 3). As the temperature increases above 570 K, the temperature dependence of the birefringence exhibits a linear behavior. The dashed lines in Fig. 3 correspond to the extrapolation of the initial linear dependences of the birefringence. It can be seen from this figure that the KPb_2Br_5 crystal is characterized by pronounced pretransitional phenomena over a wide temperature range (≈60 K) above the phase transition point.

Slightly above the transition temperature, there is an "isotropic point" at which the birefringence Δn_b for the (010) section decreases to zero and then changes sign. It is in this temperature range that the continuous change in color of the crystal is observed in polarized light with a variation in the temperature. The birefringence of the crystal is characterized by a large dispersion (close to that of lithium niobate). This dispersion in the visible spectral range is approximately equal to 0.01. Hence, for each wavelength in the temperature range 525–545 K there is one zero point. Apart from the zero point for the (010) section, the zero point of the birefringence is observed for the (001) section below room temperature (Fig. 3).

Figure 5 shows the temperature dependence of the excess heat capacity associated with the phase transition according to the microcalorimetric data. The change in the enthalpy upon the phase transition was determined by integrating the function $\Delta C_p(T)$, where ΔC_p is the excess heat capacity. The obtained change in the enthalpy $\Delta H = 1300 \pm 200$ J/mol is nearly three times larger than that determined by the differential thermal analysis in [3] ($\Delta H \approx 400$ J/mol). This substantial difference in the values of ΔH can be caused by different accuracies of the methods used.

4. DISCUSSION

The investigations performed demonstrate that the KPb_2Br_5 crystal undergoes a phase transition at a temperature $T_0 \approx 519$ K. This transition is accompanied not only by a jump in the birefringence but also by a temperature hysteresis that is characteristic of first-order phase transitions. The twinning geometry and the angle of rotation of the optical indicatrix indicate that, at room temperature, the phase is monoclinic with the twofold axis parallel to the [010] direction. This is consistent with the symmetry group $P2_1/c$ [2]. Judging from the observations in polarized light, the high-temperature phase has orthorhombic symmetry. A considerable increase in the twin size upon repeated runs through the phase transition temperature T_0 suggests that the twin boundaries are sensitive to inhomogeneous internal stresses that arise upon the first-order phase transition and are responsible for the formation of a single-domain structure of the sample. Inhomogeneous strains relax with time, and the twins regain their original structure. Such a situation can be observed when the phase transition is ferroelectric in nature. These findings give grounds to assume that, at a temperature $T_0 \approx 519$ K, the crystal undergoes a first-order ferroelastic phase transition with the symmetry change

$mmm \longleftrightarrow P2_1/c$. This change in symmetry leads to the appearance of the component x_5 of the shear spontaneous strain and, hence, to the rotation of the optical indicatrix about the [010] axis.

It should be noted that no changes in the x-ray diffraction patterns above the phase transition temperature as compared to those at room temperature were revealed in [3]. This fact is not clear from the standpoint of the assumed symmetry change. The extinction laws are different for orthorhombic and monoclinic symmetries. Taking into account these circumstances, we repeated the experiment performed in [3]. For this purpose, we recorded the x-ray powder diffraction patterns at a temperature of 560 K and at room temperature and then compared them. According to our experimental data, a number of lines that do not satisfy the condition $(h + k + l) = 2n$ disappear at temperatures above the phase transition point. This suggests that the high-temperature phase of the KPb_2Br_5 crystal is orthorhombic and has the same unit cell but the cell is body-centered. The phase transition is not accompanied by a multiple change in the unit cell volume. This is typical of proper phase transitions. Most likely, the set of reflections observed in the x-ray diffraction pattern corresponds to a space group of the orthorhombic crystal system with a center of symmetry and a body-centered unit cell, i.e., to the space group *Immm* or *Imma*.

It is universally accepted that, upon proper ferroelectric phase transitions, the temperature dependence of the rotation angle of the optical indicatrix reflects the behavior of the shear spontaneous strain arising below the phase transition: $\varphi \sim x_s$. However, this is not always the case. As was shown by Aleksandrov *et al.* [4], this simplification holds true for small angles of rotation and for insignificant changes in the birefringence. In actual fact, upon transformation of the polarization tensor from one coordinate system to another coordinate system, we obtain $\tan 2\varphi = n^3 p_{55} x_5 / \Delta n_b$, where p_{55} is the photoelasticity coefficient, n is the averaged refractive index, and x_5 is the shear strain component. The angle of rotation of the optical indicatrix is small and, hence, $\tan\varphi \approx \varphi$. However, it can be seen from Fig. 3 that the birefringence for the (010) section in the phase transition range varies from a maximum value to zero and even reverses sign. Therefore, in order to determine the temperature dependence of the shear strain $x_5(T)$ for the KPb_2Br_5 crystal from optical experiments, we should take into account the two dependences $\Delta n_b(T)$ and $\varphi(T)$. Figure 2 depicts the dependence $(\Delta n_b \tan 2\varphi)(T)$, which reflects the behavior of the shear strain $x_5(T)$ for the KPb_2Br_5 crystal under the assumption that the phase transition is purely ferroelastic in nature.

The temperature dependences of the anomalous component of the birefringence in the range below the phase transition point T_0 are plotted in Fig. 6. These dependences were obtained by subtracting the extrapolated linear portions of the temperature dependences of the birefringence for the initial phase from the curves $\Delta n(T)$ depicted in Fig. 3. As can be seen from Fig. 6, the KPb_2Br_5 crystal is characterized by pronounced pretransitional effects over a wide temperature range (≈60 K) above the phase transition point. The phase transition is accompanied by a jump in the birefringence, and then the birefringence increases gradually. However, at temperatures below $T \approx 400$ K, the value of $\delta(\Delta n)(T)$ begins to decrease. It is known that, below the phase transition temperature, the anomalous component of the birefringence measured in the orthorhombic setting is proportional to the transition parameter squared; i.e., $\delta(\Delta n)(T) \sim \eta^2$. Figure 7 shows these dependences for all three sections of the KPb_2Br_5 crystal. The transition parameter is taken as the strain component x_5 calculated according to the above procedure (Fig. 2). It can be seen from Fig. 7 that all the experimental points fall on a linear dependence passing through the origin of the coordinates. This implies that

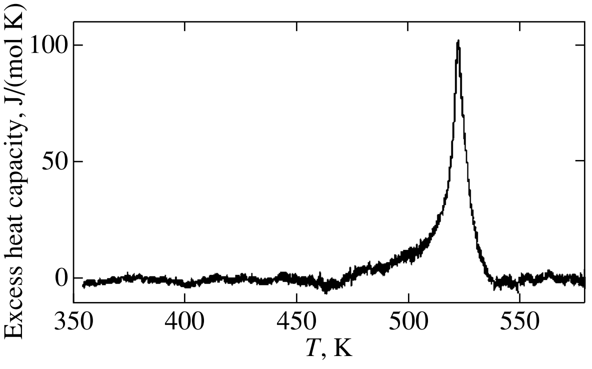

Fig. 5. Temperature dependences of the excess heat capacity of the KPb_2Br_5 crystal.

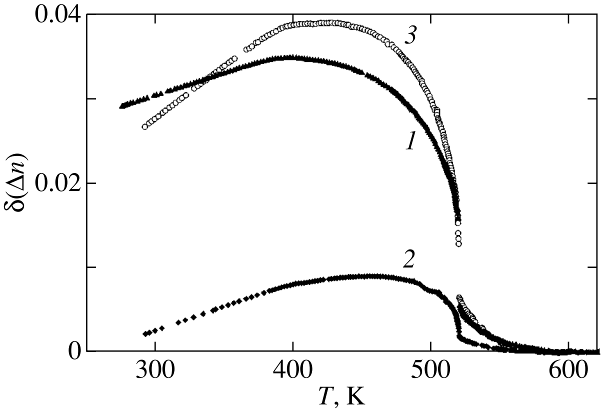

Fig. 6. Temperature dependences of the anomalous component of the birefringence for the KPb_2Br_5 crystal: (*1*) $\delta(\Delta n_c)$, (*2*) $\delta(\Delta n_a)$, and (*3*) $\delta(\Delta n_b)$.

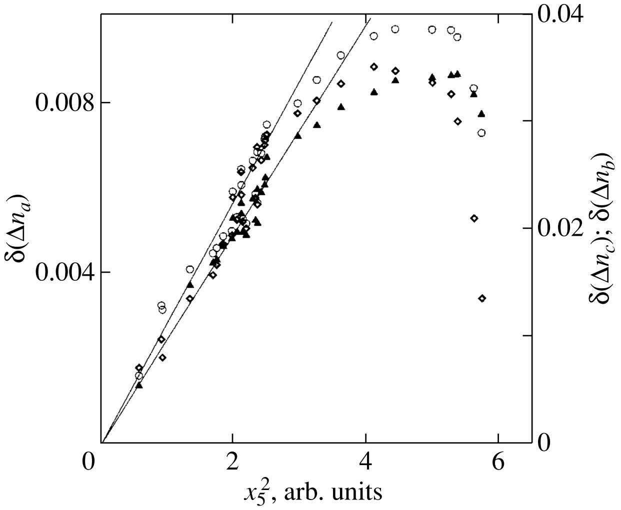

Fig. 7. Correlation between the anomalous component of the birefringence and the transition parameter squared at the corresponding temperatures. The point designations are the same as in Figs. 3, 4, and 6.

the anomalous birefringence is governed by the shear strain. However, at temperatures below 400 K, the anomalous birefringence considerably deviates from linear behavior.

5. CONCLUSIONS

Thus, the above investigations confirmed the assumption that the KPb_2Br_5 crystals undergoes a phase transition in the temperature range close to 515 K in which a weak thermal anomaly was revealed in [3]. This transition is not related to radical structural transformations that can occur upon the transition between two structural modifications of the crystal, namely, $P2_1/c$ and $I4/mcm$. The observed transition is accompanied by weak structural distortions and twinning typical of the change in crystal symmetry $mmm \longleftrightarrow P2_1/c$. The structural distortion is very small, and the monoclinic angle is determined within the limits of experimental error: $\beta = 90.06(12)°$ [2]. According to our experimental data, we can assume that the high-temperature phase is adequately described by the space group *Immm* or *Imma*.

The factors responsible for the inflection in the temperature dependences of the birefringence at a specific point in the vicinity of 390 K (Fig. 4) remain unclear. There are two possible variants. First, there can occur another phase transition. However, closer examination performed by differential scanning calorimetry did not reveal additional anomalies (Fig. 5). Second, the phase transition is pseudoproper in nature; i.e., there are two transition parameters that are linearly related but are characterized by different temperature dependences (as is the case with the $CsLiCrO_4$ compound [5]).

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