
LATTICE DYNAMICS
AND PHASE TRANSITIONS

Search for and Study of Phase Transitions in Some Representatives of the APb_2X_5 Family

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Abstract—Single crystals of KPb_2Cl_5 , $RbPb_2Cl_5$, and $RbPb_2Br_5$ are grown and studied using optical polarization methods. The heat capacity of the crystals is investigated by differential scanning microcalorimetry, and the birefringence and the angle of rotation of the optical indicatrix are measured. The measurements are performed in the temperature range 270–640 K. It is found that KPb_2Cl_5 undergoes a first-order ferroelastic phase transition at $T_{0\uparrow} = 530$ K, $T_{0\downarrow} = 528$ K, and $\Delta H = 1000 \pm 200$ J/mol. The transition is accompanied by twinning and a change in symmetry $mmm \rightleftharpoons P2_1/c$. The $RbPb_2Cl_5$ crystal remains monoclinic up to the melting temperature. The $RbPb_2Br_5$ compound belongs to the $I4/mcm$ tetragonal modification and does not undergo structural transformations.

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1. INTRODUCTION

Compounds of the general formula APb_2X_5 (where $A = Cs, Rb, K,$ or NH_4 and $X = Cl$ or Br) have been intensively studied recently as potential matrices for solid-state lasers operating in the IR range [1]. Depending on the ratio of the ionic radii A/X and B/X , these compounds can have structures of two types, monoclinic $P2_1/c$ or tetragonal $I4/mcm$ [2]. Studies of the monoclinic crystal KPb_2Br_5 [3] have revealed the existence of optical inhomogeneities at room temperature on the (010) cut in the form of a systematic twin band structure with components differing in the extinction positions by an angle 2φ and with boundaries along the [100] and [001] directions. This twin structure is formed in the course of a phase transformation occurring at high temperatures $T_{0\uparrow} = 519.5$ K and $T_{0\downarrow} = 518.5$ K. This is a first-order ferroelastic phase transition accompanied by a change in symmetry $mmm \rightleftharpoons P2_1/c$ and a considerable thermal anomaly $\Delta H = 1300 \pm 200$ J/mol.

The domain (twin) structure of these compounds is an unfavorable feature from the standpoint of potential use in optical devices. Information on the existence of phase transitions in other representatives of this crystal family is scarce. A polymorphic transformation in KPb_2Cl_5 was tentatively suggested as far back as 1960 [4]. Thermograms of this compound revealed a thermal anomaly at 524 K. Moreover, the existence of a phase transition in KPb_2Cl_5 at 543 K is reported in [5], where

differential thermal analysis (DTA) revealed a series of phase transitions in $RbPb_2Cl_5$ at 443, 573, and 613 K.

The purpose of this work was to investigate three representatives of the APb_2X_5 family, namely, KPb_2Cl_5 , $RbPb_2Cl_5$, and $RbPb_2Br_5$, in a search for and study of the possible phase transitions they can undergo. We made use of optical polarization methods and measurements of the heat capacity and birefringence in the temperature range 270–650 K.

2. SAMPLE PREPARATION AND EXPERIMENTAL TECHNIQUE

Crystals of KPb_2Cl_5 , $RbPb_2Cl_5$, and $RbPb_2Br_5$ were grown using the Bridgman method from a batch of stoichiometric composition. The melting temperature of the chlorides ($T = 717$ K) is slightly higher than that of the bromide ($T = 655$ K). The initial compounds $PbCl_2$, $PbBr_2$, KCl , and KBr (special-purity grade) were dried under pumping, followed by multiple purification through directed crystallization. The growth setup was a vertical single-zone furnace with a temperature gradient of no less than 5 K/mm. Single crystals of up to 15 mm in diameter and 40 mm in length were grown in evacuated quartz ampoules at an average rate of 2–4 mm/day.

The thermodynamic properties of the grown crystals were studied on a DSM-2M differential scanning microcalorimeter with computerized data acquisition

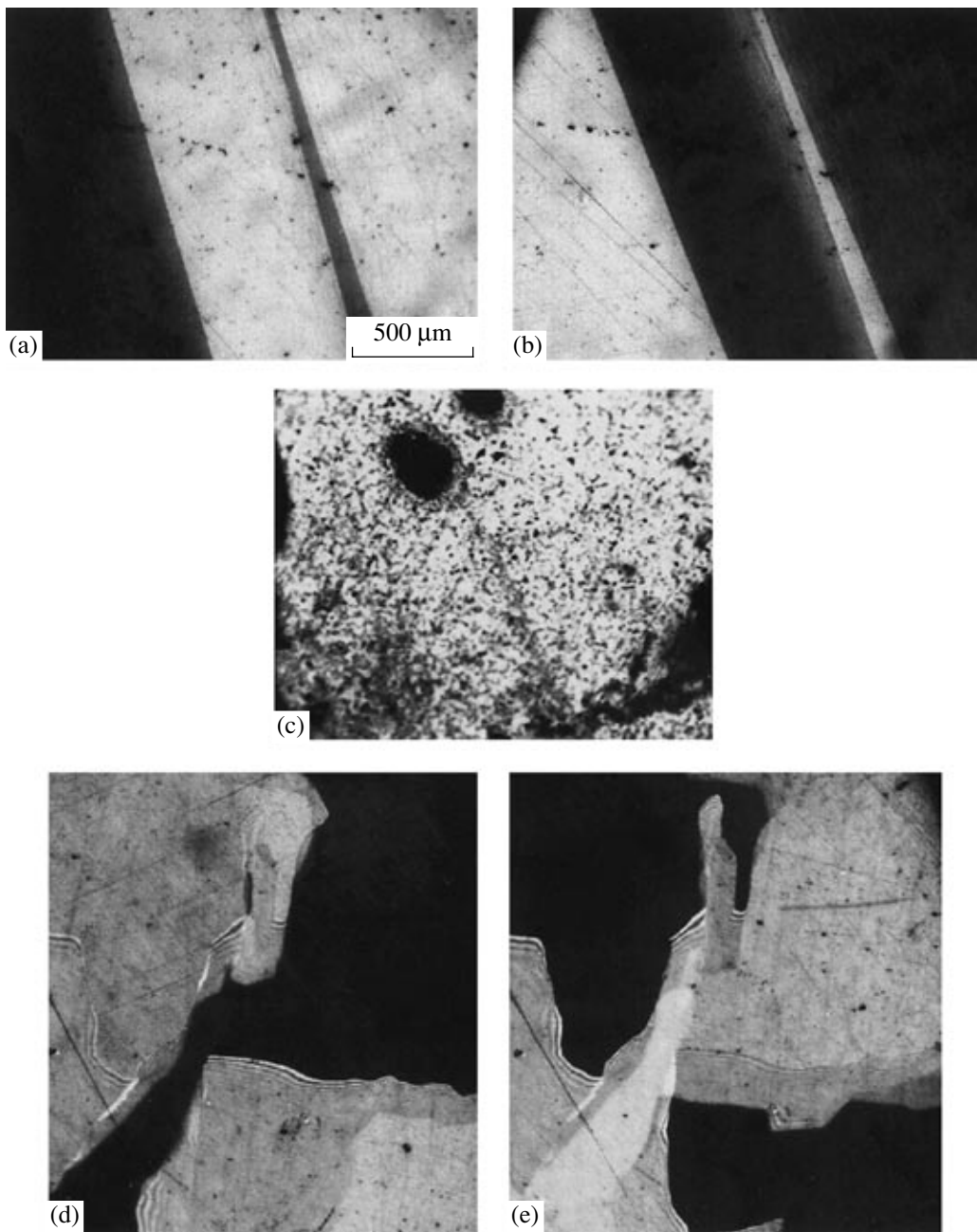


Fig. 1. Twinning of (a, b) KPb_2Cl_5 and (d, e) RbPb_2Cl_5 crystals on the (010) cut and (c) image of the KPb_2Cl_5 plate at a temperature of 635 K.

and treatment. The birefringence of the crystals was investigated on the (001), (010), and (100) cuts with a Berek compensator to within $\approx 10^{-5}$ and a Senarmont compensator with a sensitivity of no worse than $\approx 10^{-7}$ at a wavelength of 6328 Å. The first method was used to determine the absolute value of the parameter measured, while the second method permitted examining its temperature behavior. Optical polarization observations and measurements of the angle of rotation of the

optical indicatrix were performed with an Axiolab polarization microscope with an accuracy of $\pm 0.5^\circ$.

3. EXPERIMENTAL RESULTS

The studies performed with crystal plates of different orientations in polarized light showed RbPb_2Br_5 to differ strongly from the two other grown compounds. This is an optically uniaxial crystal revealing good extinction in cuts parallel to the optical axis in the tem-

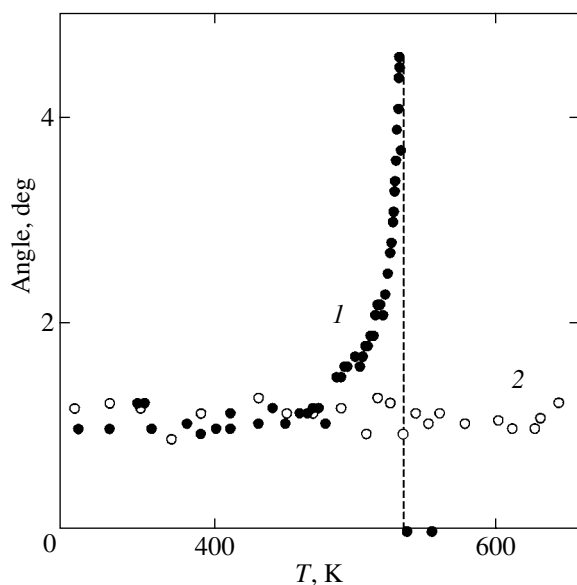


Fig. 2. Temperature dependences of the angle of rotation of the optical indicatrix $\phi(T)$ measured for (1) KPb_2Cl_5 and (2) RbPb_2Cl_5 crystals.

perature range 77–600 K. These observations are evidence both that RbPb_2Br_5 belongs to the tetragonal modification and that it does not undergo structural transformations.

The two other crystals are optically anisotropic with direct extinctions in the (100) and (001) cuts. In the (010) plates, one observes at room temperature a twin system with the components differing in their extinction positions by an angle $2\phi \approx 2^\circ\text{--}3^\circ$ (Fig. 1). The KPb_2Cl_5 compound reveals a twin band structure with boundaries along the [100] and [001] directions. The twins can differ in width, from small, of the order of a few micrometers, to large, up to a millimeter. The twin pattern persists up to 530 K and disappears thereafter. When cooled, twins appear again at 528 K. In the range 530–560 K, one observes in polarized light, just as in KPb_2Br_5 [3], an unusual pattern, namely, the plate in the extinction position becomes colored and each temperature point is characterized by a particular color, starting with red. Above 560 K, the coloring disappears, with the extinction becoming sharp, uniform, and direct. Above ~ 630 K, the crystal starts to decompose, beginning from the surface. Figure 1c shows how the sample looks at 635 K.

The RbPb_2Cl_5 plates cut in the (010) plane exhibit a slightly different twin structure. The polarization microscope reveals blocks with boundaries of irregular shape both in the plane of the plate and across it. At the same time, as in KPb_2Cl_5 , the twins differ in terms of the extinction position by an angle $2\phi \approx 2^\circ\text{--}3^\circ$ (Figs. 1d, 1e). When heated, these regions persist without changing up to 650 K.

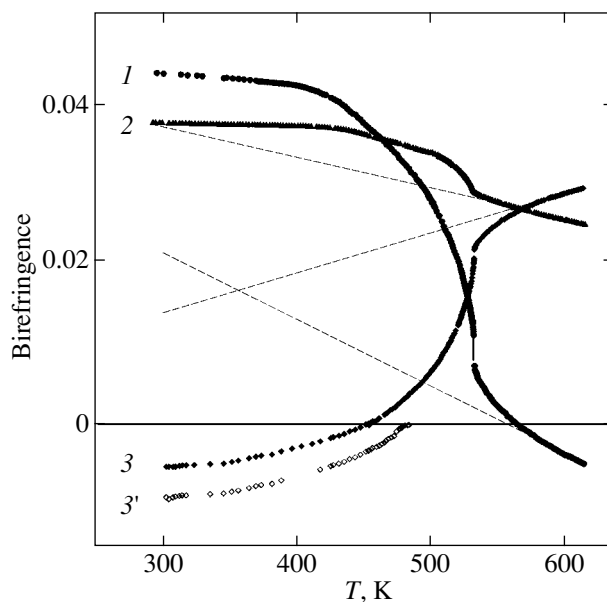


Fig. 3. Temperature dependences of the birefringence of the KPb_2Cl_5 crystal: (1) Δn_b , (2) Δn_a , and (3) Δn_c .

The temperature dependence of the angle of rotation of the optical indicatrix $\phi(T)$ about the [010] axis in a twin of KPb_2Cl_5 and RbPb_2Cl_5 crystals is presented in Fig. 2. Curve 1 plots the dependence $\phi(T)$ for the potassium crystal. This dependence is unusual. At room temperature, the angle ϕ is small ($1^\circ\text{--}2^\circ$). It remains constant under heating and increases to 5° close to the phase transition, after which it drops sharply to zero. Further heating does not change the extinction position of the sample.

Curve 2 (Fig. 2) displays the dependence $\phi(T)$ for the RbPb_2Cl_5 crystal. We readily see that the angle of misorientation of adjacent regions at room temperature is the same as in KPb_2Cl_5 and that it does not change up to the melting temperature.

Figure 3 sums up the results of the study of the behavior of the birefringence with variations in temperature for KPb_2Cl_5 along three crystallographic directions at a wavelength $\lambda = 6328 \text{ \AA}$. At room temperature, the birefringence Δn_a is approximately equal to Δn_b and is about 0.04, while for the third cut, it is rather small, $\Delta n_c = 0.0051$. Curve 3' shows the behavior of the birefringence $\Delta n_c(T)$ at the green wavelength of light. The crystal exhibits a strong birefringence dispersion in the visible range (~ 0.003). As the temperature increases, the difference between the refractive indices on all the cuts first varies linearly and insignificantly, but, above 450 K, the dependence $\Delta n(T)$ reveals an anomalous behavior. At $T_{0\uparrow} = 530 \text{ K}$ and $T_{0\downarrow} = 528 \text{ K}$, KPb_2Cl_5 exhibits a small jump in the birefringence with a temperature hysteresis ($\Delta T \approx 2 \text{ K}$) (Fig. 3). As heating is continued above 570 K, the birefringence of the crystal varies linearly with variations in the temperature.

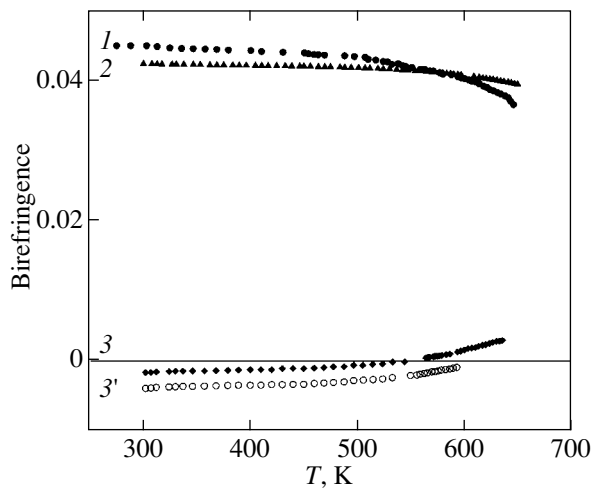


Fig. 4. Temperature dependences of the birefringence of the RbPb_2Cl_5 crystal: (1) Δn_b , (2) Δn_a , and (3) Δn_c .

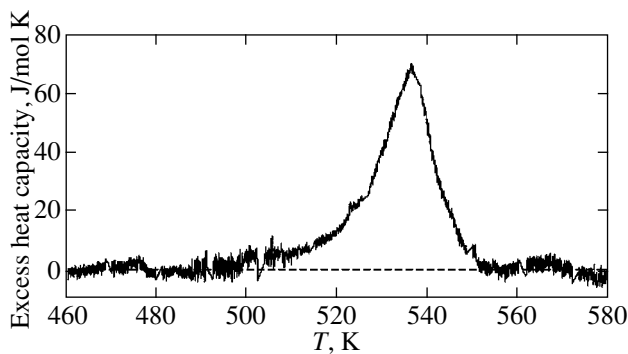


Fig. 5. Temperature dependence of the excess heat capacity of the KPb_2Cl_5 crystal.

Dashed lines in Fig. 3 plot the linear temperature dependences of the birefringence extrapolated from the starting phase. We clearly see that, over a wide temperature range above the phase transition, there occur strong pretransition processes extending over ≈ 60 K.

Slightly above the transition temperature T_0 , one observes an “isotropic” point in the (010) cut, where the birefringence Δn_b falls off to zero and subsequently reverses sign. It is in this temperature range that the polarization microscope reveals a continuous variation of the interference coloring of the (010) plate with variations in the temperature. Since the crystal exhibits a strong birefringence dispersion, each wavelength in the range 530–560 K can be determined from its zero point on the temperature scale. Besides on the (010) cut, a zero birefringence point exists on the (001) cut at temperatures of 450–500 K (Fig. 3). Similar phenomena were observed earlier in KPb_2Br_5 [3].

Figure 4 plots the results of the birefringence measurements performed with RbPb_2Cl_5 . Similar to KPb_2Cl_5 (Fig. 3), the birefringence on the (100) (Δn_a)

and (010) (Δn_b) cuts of this crystal are approximately equal in magnitude (curves 1, 2) and is about 0.04 at room temperature. On the third cut, the birefringence is small: $\Delta n_c = 0.0017$. The dispersion of the birefringence on the (001) cut is 0.0022 (curves 3, 3'). Heating gives rise to weak linear variations in the birefringence on all cuts up to a temperature of about 500 K. After this, the linearity breaks down to reveal a trend toward anomalous behavior. This pattern is most clearly pronounced in the dependence $\Delta n_b(T)$ (curve 1).

Figure 5 presents the results of DSM measurements in the form of the temperature dependence of the excess heat capacity accompanying the phase transition in KPb_2Cl_5 . The enthalpy change ΔH at the phase transition was determined by integrating the function $\Delta C_p(T)$, where ΔC_p is the excess heat capacity. The change in the enthalpy thus obtained is $\Delta H = 1000 \pm 200$ J/mol. The large error should be assigned to the decomposition the crystal starts to undergo at high temperatures (Fig. 1c).

4. DISCUSSION OF THE RESULTS

Our studies of three representatives of the APb_2X_5 family revealed a phase transition in KPb_2Cl_5 at $T_{0\uparrow} = 530$ K and $T_{0\downarrow} = 528$ K. Similar to the phase transition in KPb_2Br_5 observed earlier [3], this phase transition entails a jump in the birefringence and a temperature hysteresis characteristic of first-order transitions. The twinning geometry and rotation of the optical indicatrix suggest that the room-temperature phase is monoclinic with a twofold [010] axis, which fits the $P2_1/c$ symmetry group [5]. Observations made in polarized light show the high-temperature phase to be orthorhombic. This gives grounds to maintain that, at T_0 the crystal undergoes a first-order ferroelastic phase transition involving a change in symmetry $mmm \rightleftharpoons P2_1/c$ and a thermal anomaly with an enthalpy $\Delta H = 1000 \pm 200$ J/mol. This change in symmetry generates a spontaneous shear strain component x_5 , and the crystal breaks up into twins with the optical indicatrix turning about the (010) axis through an angle $\pm\phi$.

The curve $\phi(T)$ observed in [3] has an unusual shape (Fig. 2) for potassium bromide; it was assigned there to interaction between the polarization constant tensor components a_{ij} and to the large changes in birefringence $\Delta n_b(T)$ occurring close to the phase transition.

Figure 6 displays the anomalous part of the birefringence $\delta(\Delta n)$ of KPb_2Cl_5 , which was obtained by subtracting from the dependences $\Delta n(T)$ (Fig. 3) the linear part in the extrapolated birefringence of the starting phase. Within a wide temperature range above the phase transition, one observes intensive pretransition phenomena extending over ≈ 60 K that are characteristic of order–disorder-type transformations. The birefringence undergoes a small jump at the phase transition, followed by a smooth growth. The anomalous part

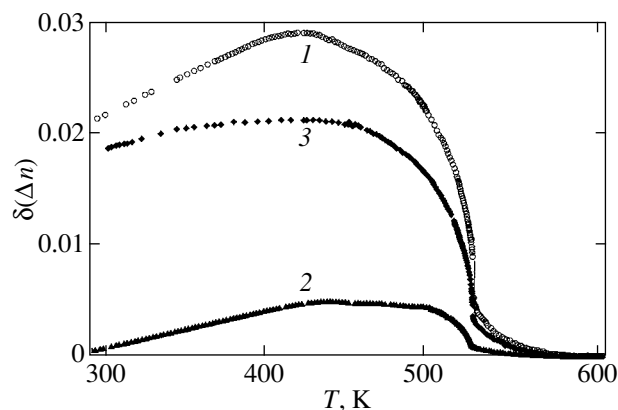


Fig. 6. Temperature dependences of the anomalous part of the birefringence of the KPb_2Cl_5 crystal: (1) $\delta(\Delta n_b)$, (2) $\delta(\Delta n_a)$, and (3) $\delta(\Delta n_c)$.

of the birefringence measured in orthorhombic geometry below the phase transition is usually proportional to the transition parameter squared: $\delta(\Delta n)(T) \sim \eta^2$ and therefore reflects its behavior with variations in the temperature. Similar to KPb_2Br_5 [3], however, in the potassium chloride, $\delta(\Delta n)$ reaches a maximum value at temperatures of 420–430 K, after which it again falls off. Just as for KPb_2Br_5 , the nature of this phenomenon remains unclear.

According to [5], at room temperature, RbPb_2Cl_5 has space symmetry group $P2_1/c$, much like KPb_2Cl_5 and KPb_2Br_5 [3]. In contrast to the potassium compounds, however, our studies of RbPb_2Cl_5 did not reveal a phase transformation to the orthorhombic phase up to the melting temperature. At the same time, the temperature dependence of the birefringence (Fig. 4) exhibits an anomalous pretransition behavior, similar to KPb_2Cl_5 (Fig. 3). Extrapolating the dependences $\Delta n(T)$ to high temperatures suggests that the transition in this compound could be expected to occur substantially above the melting temperature. Therefore, the orthorhombic symmetry in RbPb_2Cl_5 should be considered as a praphase. The compound crystallizes in the monoclinic phase with the subsequent formation of blocks differing in the sign of spontaneous strain and the angle of rotation of the optical indicatrix. For this reason, the blocks that form do not acquire a regular geometric shape, as is the case with potassium crystals, the latter crystals being associated with the loss of symmetry elements induced by the phase transition. This specific feature of the crystal may prove a favorable factor for the growth of single-crystal samples through proper choice of the growth conditions.

5. CONCLUSIONS

Thus, our studies confirmed the existence of a phase transition in KPb_2Cl_5 near $T = 530$ K, where a weak thermal anomaly was observed in [4, 5]. This transition is the first-order ferroelastic phase transition with a small temperature hysteresis accompanied by twinning characteristic of the change in symmetry $mmm \rightleftharpoons P2_1/c$. It is similar to the transition observed in KPb_2Br_5 [3], only its temperature is ten degrees higher than that of the bromide. Our studies showed that RbPb_2Cl_5 does not undergo a phase transition in the temperature range covered and that the series of thermal anomalies observed earlier [5] is not related to a symmetry change. Thus, the $\text{Cl} \rightarrow \text{Br}$ substitution in the APb_2X_5 family results in an insignificant lowering of the boundary of stability of the orthorhombic phase, whereas the $\text{K} \rightarrow \text{Rb}$ substitution of the A ion raises the boundary substantially by shifting it to the liquid aggregate state of the compound. The RbPb_2Br_5 compound belongs to the $I4/mcm$ tetragonal modification, and this structure is stable in the temperature range studied.

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REFERENCES

1. A. M. Tkachuk, S. E. Ivanova, L. I. Isaenko, A. P. Eliseev, S. Payne, R. Solarz, R. Page, and M. Nostrand, *Opt. Spektrosk.* **92** (1), 89 (2002) [*Opt. Spectrosc.* **92** (1), 83 (2002)].
2. Y. P. Beck, G. Clicqué, and H. Nau, *Z. Anorg. Allg. Chem.* **536**, 35 (1986).
3. S. V. Mel'nikova, L. I. Isaenko, V. M. Pashkov, and I. V. Pevnev, *Fiz. Tverd. Tela* (St. Petersburg) **47** (2), 319 (2005) [*Phys. Solid State* **47** (2), 332 (2005)].
4. T. N. Sumarokova, and T. P. Modestova, *Zh. Neorg. Khim.* **5**, 2479 (1960).
5. K. Nitsch, M. Dusek, M. Nikl, K. Polák, and M. Rodová, *Prog. Cryst. Growth Charact. Mater.* **30**, 1 (1995).

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