

LATTICE DYNAMICS  
AND PHASE TRANSITIONS

Investigation of the Influence of Gradual Substitution  $K \leftrightarrow Rb$   
on the Structure and Phase Transition  
in  $K_xRb_{1-x}Pb_2Br_5$  Solid Solutions

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**Abstract**—Single crystals of  $K_xRb_{1-x}Pb_2Br_5$  solid solutions have been grown and investigated using X-ray diffraction and polarized light microscopy in the temperature range 270–640 K. The regions of existence of the tetragonal ( $I4/mcm$ ) and monoclinic ( $P2_1/c$ ) phases have been determined. It has been demonstrated that the partial introduction of rubidium into  $KPb_2Br_5$  leads to an increase in the temperature of the ferroelastic phase transition ( $P2_1/c \longleftrightarrow mmm$ ), so that it approaches the melting temperature. In the solid solutions with  $x \approx 0.4$ – $0.5$ , the temperature region of existence of the orthorhombic phase is narrowed to  $\approx 1$ – $2$  K. It has been revealed that an increase in the potassium content in the material results in a considerable increase in the incorporation coefficient of  $Er^{3+}$  ions.

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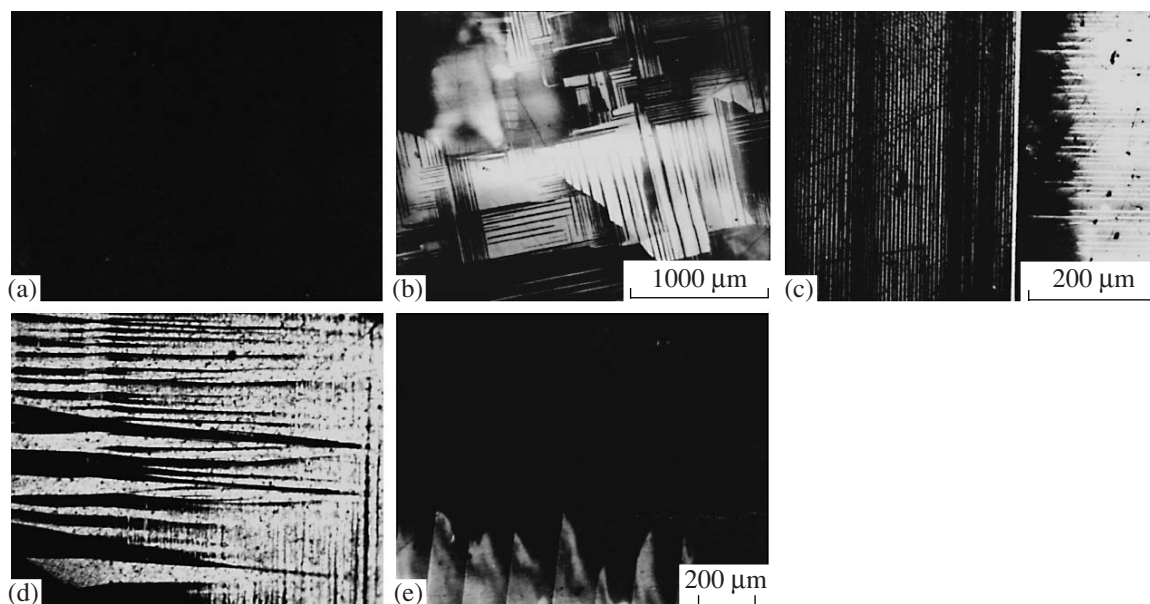
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## 1. INTRODUCTION

The use of laser diodes for selective pumping of active media based on crystals doped with rare-earth ions has stimulated the search for new crystalline matrices characterized by narrow phonon spectra, minimum thermal losses, and radiative processes with a high quantum yield. These crystals are of practical interest as active media for lasers operating in the middle-infrared and visible ranges, telecommunication amplifiers, and optic communication lines. The known matrices based on oxides, fluorides, and sulfides doped with rare-earth elements emit in the wavelength range up to 3.0, 4.5, and 6.0  $\mu\text{m}$ , respectively. Optical crystals of bromides and chlorides have attracted the particular attention of researchers due to their unique properties. The transparency window of these compounds covers the range from 0.3 to 20.0  $\mu\text{m}$  (for chlorides) or 30.0  $\mu\text{m}$  (for bromides). The presence of univalent cations in the structure allows one to assign crystals of the  $APb_2X_5$  ( $A = K, Rb; X = Cl, Br$ ) family to new laser matrices suitable for doping with rare-earth elements. These materials are not hygroscopic and exhibit a high chemical durability, a narrow phonon spectrum, and satisfactory mechanical properties [1].

It is known [2] that, depending on the ratios of the ionic radii  $A/X$  and  $B/X$ , these compounds can form two structural modifications, namely, the monoclinic and

tetragonal modifications. At room temperature,  $KPb_2Cl_5$ ,  $KPb_2Br_5$ , and  $RbPb_2Cl_5$  crystals have monoclinic symmetry  $P2_1/c$ . The  $KPb_2Br_5$  crystals can exist in both modifications. The  $KPb_2Br_5$  monoclinic crystals are formed upon high-temperature crystallization [2], whereas the tetragonal crystals grow from aqueous solutions [3]. The fourth representative of this family, namely,  $RbPb_2Br_5$ , has a tetragonal structure ( $I4/mcm$ ). Moreover, it is also known that, despite the transparency, the compounds under consideration strongly scatter transmitted light. In our earlier works [4, 5], we established that optical inhomogeneities, i.e., a system of twins formed upon the ferroelastic phase transition occurring at high temperatures, are observed in the (010) plates perpendicular to the twofold axis of monoclinic crystals. In the  $KPb_2Br_5$  crystals, the transition temperatures are  $T_{0\uparrow} = 519.5$  K and  $T_{0\downarrow} = 518.5$  K. In the  $KPb_2Cl_5$  crystals, the transition temperatures are somewhat higher:  $T_{0\uparrow} = 530$  K and  $T_{0\downarrow} = 528$  K. These are first-order phase transitions accompanied by the change in the symmetry  $P2_1/c \longleftrightarrow mmm$  and a considerable thermal anomaly  $\Delta H = 1300 \pm 200$  J/mol. The crystal with rubidium, i.e.,  $RbPb_2Cl_5$ , retains monoclinic symmetry up to a temperature of 640 K [5]. The temperature dependences of the birefringence of this crystal at temperatures close to 600 K indicate that there is a tendency toward an anomalous pretransition



**Fig. 1.** Images of the twin structures in the  $K_xRb_{1-x}Pb_2Br_5$  solid solutions with different potassium contents  $x =$  (a) 0, (b) 0.4, (c) 0.5 (without supercooling), (d) 1.0, and (e) 0.5 (with supercooling).

behavior. However, the phase transition in the crystal does not occur because of the melting at a lower temperature. For this reason, the twin boundaries have an irregular shape rather than are formed along specific crystallographic direction (as is the case in crystals with potassium). From the standpoint of the use of these compounds in optical devices, the presence of the domain (twin) structure is an undesirable factor. In this respect, the aim of the present study was to develop a method for preparing a single-domain crystal. For this purpose, we grew and investigated  $K_xRb_{1-x}Pb_2Br_5$  solid solutions.

## 2. SAMPLE PREPARATION AND EXPERIMENTAL TECHNIQUE

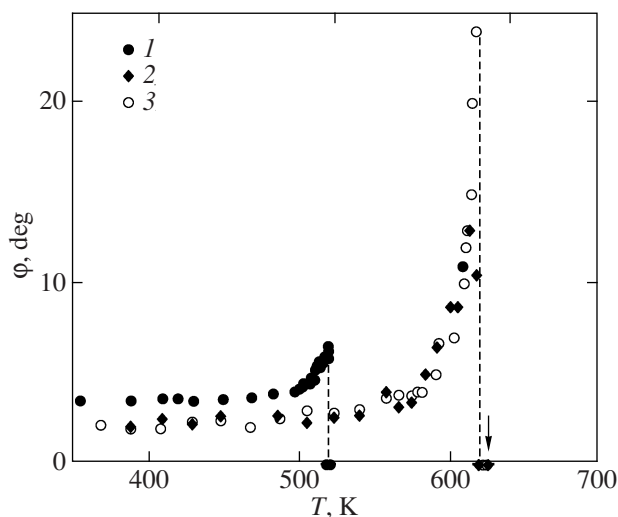
Single crystals of solid solutions were prepared using the bromide salts  $KPb_2Br_5$  and  $RbPb_2Br_5$  (special-purity grade) as the initial reactants. These compounds were additionally purified through repeated recrystallization with removal of contaminated parts. The components in a required ratio were placed in evacuated Pyrex tubes. The compounds were melted at a temperature of 619 K, and then the tube was rotated for a day to complete homogenization of the material. The crystals were grown by the Bridgman–Stockbarger method in a quartz growth container with a crystal sampler. The temperature gradient in the growth zone was equal to 2 K/mm, and the velocity of motion of the tube in the cold zone was 2–4 mm/day.

For the grown crystals with  $x = 0, 0.3, 0.4, 0.5, 0.7,$  and 1.0, the observations in polarized light and measurements of the rotation angle of the optical indicatrix

were carried out on an Axiolab polarizing microscope. Structural investigations were performed using single-crystal samples on a Bruker Nonius X8 X-ray diffractometer equipped with a CCD detector. The unit cell parameters of the compounds were determined with the APEX2 (Version 1.08) and SAINT (Version 7.03) program packages. The concentration of rare-earth elements and the potassium content  $x$  in the crystals were determined by electron probe X-ray microanalysis on a GXL-8100 setup.

## 3. EXPERIMENTAL RESULTS

The observations of the synthesized materials in polarized light have revealed that the grown crystals can have different symmetries depending on the ratio of the initial components. The single crystals with tetragonal symmetry are formed at  $x = 0–0.35$ . These are optically uniaxial crystals with a pronounced extinction in sections parallel to the optic axis. The crystals with these properties are retained in the range from 600 K to the liquid-nitrogen temperature (Fig. 1a). The crystals with monoclinic symmetry are formed at  $x = 0.35–1.00$ . They are optically anisotropic and characterized by “straight” extinctions in the (100) and (001) sections. At room temperature, a system of twins with components that differ in the extinction positions by an angle  $2\varphi \approx 3^\circ–4^\circ$  is observed in the (010) plates (Figs. 1b–1d). It can be seen from Fig. 1d that pure  $KPb_2Br_5$  ( $x = 1.0$ ) has a streaky twin structure with boundaries parallel to the [100] and [001] directions. The width of twins varies from 1 to 10  $\mu\text{m}$ . An increase in the rubidium content in the material leads to a change in the twin pat-

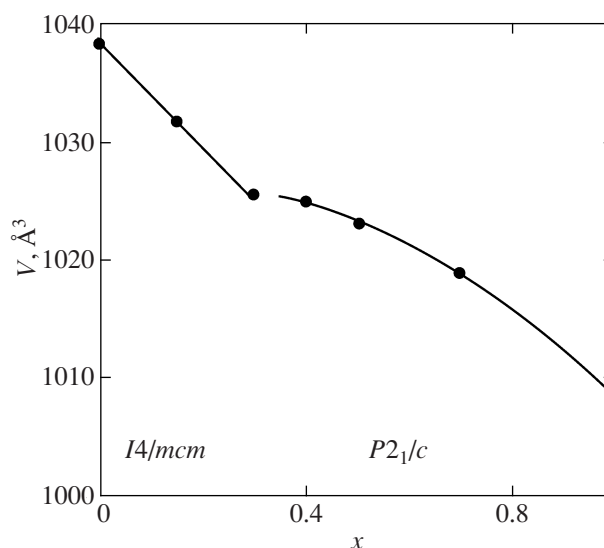


**Fig. 2.** Temperature dependences of the rotation angle of the optical indicatrix  $\varphi(T)$  for the  $K_xRb_{1-x}Pb_2Br_5$  crystals with different potassium contents  $x = (1)$  1.0,  $(2)$  0.5, and  $(3)$  0.4.

tern. The twinned regions become larger in size (Fig. 1b) ( $x = 0.4$ ).

The temperature dependences of the angle of rotation of the optical indicatrix  $\varphi(T)$  with respect to the  $[010]$  axis in a single twin of the monoclinic phase of the  $K_xRb_{1-x}Pb_2Br_5$  crystals are plotted in Fig. 2. Curve 1 indicates the dependence  $\varphi(T)$  for the potassium crystal ( $x = 1.0$ ). This dependence exhibits an unusual behavior. At room temperature, the angle of rotation of the optical indicatrix  $\varphi$  is approximately equal to  $4^\circ$ . During heating, the angle of rotation initially remains constant, increases to  $7^\circ$  only in the vicinity of the phase transition, and then sharply decreases to zero at the temperature  $T_{0\uparrow} = 520$  K. With a further increase in the temperature, the extinction of the plate remains unchanged. The crystal acquires orthorhombic symmetry. For the  $K_xRb_{1-x}Pb_2Br_5$  samples with  $x = 0.5$  (curve 3) and 0.4 (curve 2), the temperature dependences of the angle of rotation of the optical indicatrix exhibit a similar behavior, but the anomalies are shifted toward the high-temperature range. The phase transition to the initial orthorhombic phase in both compounds is observed at approximately the same temperature  $T_0 \approx 620$  K. The orthorhombic phase in these compounds exists in a narrow range 1–2 K and then melting occurs. The unusual dependence  $\varphi(T)$  (Fig. 2) was previously observed for potassium chloride [5] and explained by the interaction between the polarization constant tensor components  $a_{ij}$  and the large changes in the birefringence  $\Delta n_b(T)$  in the vicinity of the phase transition.

The results of X-ray diffraction investigations are presented in Fig. 3. These results confirm the above data obtained from optical observations. The crystals with  $x = 0-0.35(5)$  have tetragonal symmetry ( $I4/mcm$ ).

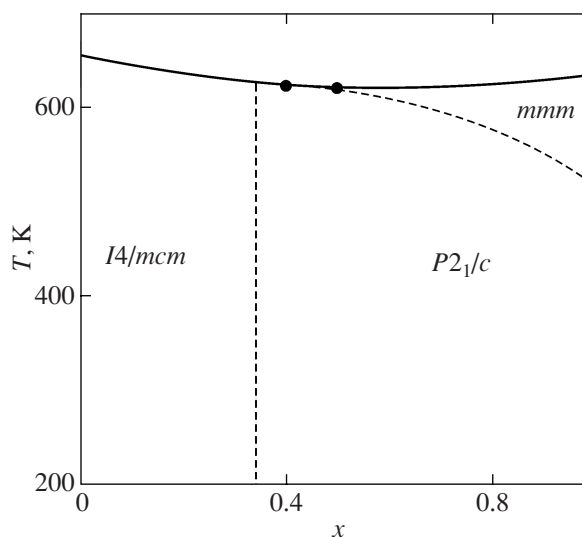


**Fig. 3.** Dependence of the unit cell volume of the  $K_xRb_{1-x}Pb_2Br_5$  crystals on the potassium content.

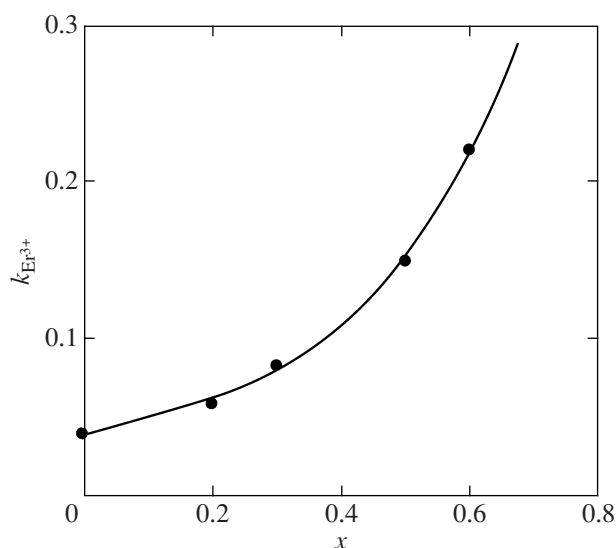
The crystals with  $x = 0.35(5)-1.00$  have monoclinic symmetry ( $P2_1/c$ ). Furthermore, it can be seen from Fig. 3 that an increase in the potassium content leads to a gradual decrease in the unit cell volume.

#### 4. DISCUSSION

The experimental results described above were used to construct the  $(T-x)$  phase diagram for the  $K_xRb_{1-x}Pb_2Br_5$  solid solutions (Fig. 4). This phase diagram involves the region of existence of the compounds with symmetry  $I4/mcm$ , the extended region of the monoclinic phase ( $P2_1/c$ ), and the small region corre-



**Fig. 4.**  $(T-x)$  phase diagram of the  $K_xRb_{1-x}Pb_2Br_5$  solid solutions.



**Fig. 5.** Dependence of the incorporation coefficient of  $\text{Er}^{3+}$  ions on the composition of the  $\text{K}_x\text{Rb}_{1-x}\text{Pb}_2\text{Br}_5$  solid solution.

sponding to the compounds with orthorhombic symmetry  $mmm$ . With an increase in the rubidium content, the line of the structural phase transitions  $P2_1/c \leftrightarrow mmm$  approaches the boundary of the transition to the liquid aggregate state but does not intersect it. Therefore, the region of existence of the orthorhombic phase for the compounds with  $x = 0.4\text{--}0.5$  narrows to 1–2 K.

Taking into account the aforementioned situation, we attempted to perform crystallization from a supercooled melt in the monoclinic phase without formation of the orthorhombic phase. This would make it possible to avoid the occurrence of the phase transition and the formation of ferroelastic twins. As a result of this experiment, we grew single crystals of good optical quality. The micrograph of the (010) section of the  $\text{K}_x\text{Rb}_{1-x}\text{Pb}_2\text{Br}_5$  crystal (with  $x = 0.5$ ) grown from the supercooled solution is displayed in Fig. 1e. The system of twins seen in the image is formed only in thin (no more than 0.5 mm) edges of the crystal.

It can be seen from Fig. 1a that, for the bromide compounds in the region of existence of the tetragonal phase with  $x = 0\text{--}0.35$ (5), there is a possibility of choosing the conditions for the growth of high-quality single crystals. They do not undergo phase transformations up to the melting temperature and crystallize without defects. However, the disadvantage of these compounds is a small coefficient of incorporation of rare-earth elements into the crystalline matrix. For example, the incorporation coefficient of  $\text{Er}^{3+}$  ions for pure  $\text{RbPb}_2\text{Br}_5$  is  $k \approx 0.04$ . This coefficient is one order of magnitude smaller than that for  $\text{KPb}_2\text{Br}_5$ , which complicates the preparation of effective IR laser materials. The results of investigations of the incorporation coefficient for  $\text{Er}^{3+}$  ions in the structure of the

$\text{K}_x\text{Rb}_{1-x}\text{Pb}_2\text{Br}_5$  solid solutions are presented in Fig. 5. The amount of the introduced rare-earth element was equal to 2 wt %. It can be seen from Fig. 5 that an increase in the potassium content in the structure results in a substantial increase in the incorporation coefficient  $k$ . In the range  $0.2 \leq x \leq 0.5$ , the concentration of rare-earth elements in the mixed crystals is sufficient for the effective generation of laser radiation.

## 5. CONCLUSIONS

Thus, the performed investigation has revealed the possibility of avoiding the formation of twins due to the change in the symmetry  $mmm \leftrightarrow P2_1/c$  upon the high-temperature ferroelastic transition in crystals of bromides  $\text{APb}_2\text{Br}_5$ . A partial replacement of potassium by rubidium leads to an increase in the phase transition temperature, which gradually approaches the melting temperature. In solid solutions with  $x \approx 0.4\text{--}0.5$ , the orthorhombic phase exists in a range of  $\approx 1\text{--}2$  K. Twinned regions become larger in size. The mixed crystals of the composition  $\text{K}_x\text{Rb}_{1-x}\text{Pb}_2\text{Br}_5$  at  $0.2 \leq x \leq 0.5$  exhibit positive properties of the pure  $\text{RbPb}_2\text{Br}_5$  and  $\text{KPb}_2\text{Br}_5$  compounds: they are characterized by low energies of crystal lattice vibrations. This makes it possible to generate laser radiation in the middle-infrared range up to 10  $\mu\text{m}$ . Moreover, there exist advantages over the pure compounds: these materials exhibit a combination of a large incorporation coefficient for rare-earth elements and a good optical quality of crystals. High-quality single crystals with a weight of  $\approx 70$  g were grown by crystallization from a supercooled melt.

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