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# MORPHOLOGY OF CRYSTAL GROWTH DURING II↔I PHASE TRANSFORMATION IN K0.945Rb0.055NO3 MONOCRYSTAL

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ARTICLE INFO	ABSTRACT
Article history:	K0,945Rb0,055NO3 monocrystals were grown from aqueous solutions of KNO3 and
Received: 2024-12-08	RbNO3 by isothermal crystallization method and the morphology of crystal
Received in revised form: 2025-01-13	growth during II $\leftrightarrow$ I phase transformations in these crystals was studied by
Accepted: 2025-01-16	optical microscopy. It was determined that two polymorphic transformations
Available online	_ occur in the studied crystal from room temperature to the melting temperature.
Keywords:	The structural transformations in these crystals are enantiotropic and of the
monocrystal,	monocrystal-monocrystal type. The equilibrium temperature between the
phase transformation,	interconverting II and I modifications is $T=455\pm0.5K$ .
rhombohedral modification	In the investigated sample, a repeated II $ ightarrow$ I phase transformation was studied,
	and the growth of the process was observed in a mono-nucleated manner in the
	[001] crystallographic direction. This transformation was accompanied by the
	movement of the non-linear boundary separating the phases.
	The transformation rate is as $\sqrt[n]{2-v_{[001]}} > 1-v_{[001]}$ . Experiments show
	that the rhombohedral modification existing between modifications I and II in
	potassium nitrate is not detected in the studied sample. Partial replacement of
	$K^{\scriptscriptstyle +}$ ions with $Rb^{\scriptscriptstyle +}$ ions increases the equilibrium temperature between modifica-
	tions II and I by about 55 K.

### 1. Introduction

The study of polymorphous transformations in nitrate compounds of alkali metals is of scientific and practical interest. Due to their high piezoelectric and ferroelectric properties, the technological capabilities of the compounds create great opportunities for their use as active elements (KNO3-III phase ferroelectric) in electronic devices (capacitors) [1, 2].

In addition, these compounds are strong oxidizing agents used in pyrotechnics, metallurgy, analytical chemistry and the preparation of pharmaceutical preparations [3]. Potassium salts are used in the production of conversion devices, memory elements and radiation heat transfer devices [4].

To study the mechanism of polymorphic transformations, it is necessary to study the morphology of new crystal growth during these transformations, the crystallographic directional relationships between the mutual transformation modifications, as well as the kinetics of the process. In this regard, it is convenient to use optically transparent crystals as a research object [5]. Nitrate compounds of alkali metals are such substances, and numerous research works have been devoted to the study of structural transformations in them, and a summary of the results obtained is given in [6].

This research work is devoted to the study of the regularities of polymorphic transformations in the  $K_{0.945}Rb_{0.055}NO_3$  crystal obtained as a result of partial replacement of K<sup>+</sup> ions with Rb<sup>+</sup> ions in KNO<sub>3</sub> crystals. Polymorphic transformations in this compound have not been studied previously.

Potassium nitrate exists in three different polymorphic forms at atmospheric pressure [7].

At ~299K, phase II,  $\alpha$ -KNO<sub>3</sub> has a rhombic (aragonitic) structure with lattice parameters a=5,414 Å, b=9,164 Å and c=6,431 Å, space group Pmcn [8, 9].

At temperatures T>403 K, phase I,  $\beta$ -KNO<sub>3</sub>, transforms into a rhombohedral (calcite) structure with lattice parameters a=5,42 Å and c=19,41 Å and space group R-3m [10]. On the other hand, during cooling, phase I first transforms into phase III (ferroelectric phase) at ~397 K, and then phase III transforms into phase II at ~383 K ( $\gamma$ -KNO<sub>3</sub>, rhombohedral structure with lattice parameters a=5,43 Å and c=9,112 Å, space group R-3m) [9, 10]. It has been determined that the temperature range corresponding to phase III expands at high pressure, and that phase III also appears upon heating and belongs to the space group R3m [11].

In rubidium nitrate four polymorphic transformations occur between room temperature and melting temperature. At a temperature of ~298K, phase IV has a trigonal lattice with lattice parameters a=10,479 Å, c=7,452 Å, and space group R3<sub>1</sub>m [12-14]. At T>437K, phase IV transforms into a cubic crystal III with lattice parameters a=4,36 Å, and space group Pm-3m [14]. At T>492K, the III  $\rightarrow$  II transformation occurs and the cubic lattice transforms into a hexagonal lattice with lattice parameters a=5,48 Å, c=10,71 Å, and a space group of R-3m [16]. At T>564K, modification II transforms into cubic modification I with lattice parameters a=7,32 Å, and space group *Fm-3m* [16].

## 2. Experimental part

The K<sub>0.945</sub>Rb<sub>0.055</sub>NO<sub>3</sub> crystals were obtained by isothermal crystallization from aqueous solutions of KNO<sub>3</sub> and RbNO<sub>3</sub> at room temperature. To achieve the perfection and purity of the obtained samples, potassium nitrate of the "CDA" brand and rubidium nitrate of the "XC" brand were subjected to multiple crystallizations.

For conducting research using an optical microscope, samples with dimensions of  $1 \times 0.5 \times 5$  *mm* were used. Because these measurements are suitable for conducting related studies, i.e. for observation under a microscope (figure 1).



Figure 1. K0,945Rb0,055NO3 monocrystals obtained from aqueous solution

In general, the samples were obtained in the form of flat plates and needlelike. The length of the needles was in the crystallographic direction [001]. The experiments were carried out on a MIN-8 polarization microscope equipped with a heater using a "Levenhuk C310 NK" type camera. Using a computer crystal growth was observed during polymorphic transformations [17, 18]. The temperature of the crystal was measured using a thermocouple touching it. The error of the temperature measurements was  $\pm 0.5^{\circ}$ C at 100°C. Temperature fluctuations should be minimal.

Temperature stability is important to prevent possible defects in the crystal.

During the morphological studies of the sample, first of all, the equilibrium temperature between modifications II and I was determined as  $T_0=(455\pm0,5)$  K. In the  $K_{0.945}Rb_{0.055}NO_3$  crystal, the II $\rightarrow$ I transformation occurs at a temperature  $T_{tr}>T_0$ , with the formation of a nucleus of a modification I crystal within a modification II crystal and its growth mainly in the [100] crystallographic direction (Fig. 2.b). Here  $T_{tr}$  is the transformation temperature, and  $T_0$  is the equilibrium temperature between the phases.

Polymorphic transformations always occur at temperatures  $T_{tr}>T_0$  and the temperature difference  $\Delta T = T_{tr} - T_0$  depends on the perfection of the parent crystal [6,19].

Experiments show that in the considered case the delay of transformation between modifications II and I is  $\Delta T \sim 2K$ .

As can be seen from Fig. 2.b, after the formation of the I-phase nucleus, it grows rapidly in the [100] direction within the parent crystal and after the growth in this direction is completed, it continues in both directions in the [001] crystallographic direction (Fig. 2. c-e). The growing nucleus is shown in the figure by an arrow. The growth rate in both directions is  $v_{[100]} > v_{[001]}$ .

After complete transformation, I modification crystal is obtained (Fig. 2.f). It showed that no further morphological changes occurred in the crystal under study until the melting temperature of the crystal.



Figure 2. Formation and growth of the nucleus of the I modification (T=455 K) crystal inside the II modification crystal during the II  $\rightarrow$  I phase transformation in the K<sub>0.945</sub>Rb<sub>0.055</sub>NO<sub>3</sub> crystal. a- II crystal, b- formation of the I crystal nucleus inside the II crystal and its rapid growth in the [100] direction, c-e- growth of the I crystal nucleus in both directions in the [001] direction, f- I crystal after the complete II  $\rightarrow$  I phase transformation (magnification ×90).

When the I-modification crystal is cooled to a temperature of 453K, the reverse transformation, that is, the I $\rightarrow$ II transformation, occurs at a temperature of T<sub>tr</sub> <T<sub>0</sub>. This process also occurs with the formation and growth of a II phase crystal nucleus within the I phase (Figure 3. a).

It was determined that during the experiments the boundary line separating the phases bent at an angle of 45°. This bending can be explained by the stress generated within the crystal during the phase transformation. After the reverse transformation was completed, the relatively low defect content of the II-modification crystal (Fig. 3.f) led to the observation of a repeated II $\rightarrow$ I transformation in the same sample. X-ray studies also showed that after the II-I-II transformation, the crystal completely restored its original state.



**Figure 3.** Formation and growth of the nucleus of the II modification (T=453K) crystal inside the I modification crystal during the I $\rightarrow$ II phase transformation in the K<sub>0,945</sub>Rb<sub>0,055</sub>NO<sub>3</sub> crystal. a- formation of the II crystal nucleus inside the I crystal and its rapid growth in the [100] direction, b-c- rapid growth of the II crystal nucleus in the [001] direction, d-e-45<sup>o</sup> bending of the boundary and rapid growth of the II crystal nucleus in the [001] direction, f- II crystal after the complete I $\rightarrow$ II phase transformation (magnification ×90).

The II $\rightarrow$ I phase transformation was again carried out in the investigated sample and the equilibrium temperature was determined. In this case, the transformation temperature in the crystal was not different as in the first transformation, the process occurred in the [001] direction and was mono embrionic (Fig. 4. b-d). The straightness of the boundary between the II and I phases is not preserved (Fig. 4. c, e,j), the transformation rate is  $[2 - v_{[001]} > 1 - v_{[001]}]$ . Experiments conducted on K<sub>0.945</sub>Rb<sub>0.055</sub>NO<sub>3</sub> samples show that the rhombohedral modification existing between modifications I and II in potassium nitrate is not detected in this case.



Figure 4. Formation and growth of the nucleus of the I modification (T=455 K) crystal within the II modification crystal during the second II→ I phase transformation in the K<sub>0.945</sub>Rb<sub>0.055</sub>NO<sub>3</sub> crystal. a- II crystal formation of microcracks on the crystal surface (gray lines), b- formation of the I crystal nucleus within the II crystal and its rapid growth in the [100] direction, c-d-e- rapid growth of the I crystal nucleus in the [001] direction, reduction of microcracks, f- I crystal after complete II → I phase transformation (magnification ×90).

### 3. Conclusion

It has been experimentally determined that polymorphic transformations in the  $K_{0.945}Rb_{0.055}NO_3$  crystal are enantiotropic in nature, are of the monocrystal-monocrystal type. During II $\leftrightarrow$ I transformations the growth of crystals of modifications I and II occurs through the formation and growth of a crystal nucleus within the parent crystal.

It was also determined that there is no intermediate modification between modifications I and II. The rhythmic growth observed in potassium nitrate crystals during the  $II \rightarrow I$  transformation [19, 20] is not detected in this case.

In the studied sample, a repeated II $\rightarrow$ I polymorph transformation was carried out, and between the temperatures of the first transformation and the second transformation any difference was not observed. It was determined that the process was monoemrionic and the growth proceeded mainly in the [001] direction. Partial replacement of K<sup>+</sup> ions with Rb<sup>+</sup> ions in potassium nitrate between modifications II and I increases the equilibrium temperature by about 55 K. This suggests that the phase transitions of mixed phases make these materials suitable for use in highly sensitive sensors. At the same time, their high heat capacity and stable phases make them suitable for thermal storage systems. Mixed nitrates are more stable and powerful combustible materials, and their crystals have high dielectric constants, making them suitable for capacitors and microelectronics.

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