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CRYSTAL GROWTH

Transformation Single Crystal ↔ Single Crystal in $K_{0.945}Rb_{0.055}NO_3$

R. B. Bayramli[a,*], E. V. Nasirov[b,], I. M. Magarramov[c,***], V. I. Nasirov[d,****], and U. S. Abdurahmanova[a,*****]**

[a] *Baku Engineering University, Baku, AZ-0101 Azerbaijan*
[b] *Military Institute Named After Heydar Aliyev, Baku, AZ-1018 Azerbaijan*
[c] *Military Scientific Research Institute, Baku, AZ-1065 Azerbaijan*
[d] *Azerbaijan State Pedagogical University, Baku, AZ-1000 Azerbaijan*
**e-mail: rabayramov@beu.edu.az*
***e-mail: emin-nasirov@inbox.ru*
****e-mail: izzetmeheremov@gmail.com*
*****e-mail: vaqif-nesir@mail.ru*
******e-mail: uabdurahmanova@beu.edu.az*

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Abstract—The results of microscopic and X-ray studies of polymorphic transformations II ↔ I in $K_{0.945}Rb_{0.055}NO_3$ are discussed. It is shown that the transformations II ↔ I in the studied crystal are enantiotropic in nature and occur with the formation and growth of nuclei of the daughter modification inside the matrix. The equilibrium temperature between the II and I modifications is $T_0 = 455 \pm 0.5$ K. It is determined that in $K_{0.945}Rb_{0.055}NO_3$ the transformation II ↔ I is of a single crystal–single crystal nature.

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INTRODUCTION

The study of polymorphic transformations in nitrate compounds of alkali metals is of scientific and practical interest. The technological potential of the compounds is aimed at their use as active elements in electrical devices (capacitors) due to their excellent piezoelectric and ferroelectric properties (KNO_3 is a ferroelectric, phase III), as well as in optical modulators [1, 2]. In addition, these compounds are strong oxidizers used in pyrotechnics, metallurgy, analytical chemistry, and pharmaceuticals [3]. Potassium salts are used in the production of converters, memory elements, and radiation heat transfer devices [4].

To investigate the mechanism of polymorphic transformations, it is necessary to study the morphology of the growth of new crystals during these transformations, the relationships between crystallographic directions during the mutual transformation of modifications, as well as the kinetics of the process. In this regard, the study of optically transparent crystals is convenient [5]. Such substances are nitrate compounds of alkali metals, the study of structural transformations in which is the subject of numerous research works. The results are summarized in [6].

This work is devoted to the study of polymorphic transformations in a single crystal $K_{0.945}Rb_{0.055}NO_3$ and to the elucidation of the effect of partial replacement of K^+ ions by Rb^+ ions on these processes. The crystal structure of individual phases and temperature transformations in these solid solutions have not been studied previously.

When heated at a temperature of ~401 K and at atmospheric pressure, KNO_3 undergoes a phase transformation from the orthorhombic phase (α-phase, *Pmcn*, aragonite type, $a = 5.414$, $b = 9.164$, $c = 6.431$ Å) to a trigonal phase (β-phase, $R\bar{3}m$, calcite type, $a = 5.42$, $c = 19.41$ Å). When the material is cooled, the transition from the β-phase to the α-phase occurs through the intermediate γ-phase ($R3m$, $a = 5.43$, $c = 9.112$ Å) (~397–383 K) before returning, upon further cooling [7, 8]. The γ-phase is known to exhibit ferroelectric properties [8, 9].

Between room temperature and the melting point, four polymorphic transformations occur in rubidium nitrate. At room temperature, the modification IV of rubidium nitrate has a lattice parameters $a = 10.48$, $c = 7.45$ Å, trigonal space group $P3_1$ [10–12]. At a temperature of $T > 437$ K, this modification transforms into a cubic modification III with the crystal lattice parameter $a = 4.30$ Å, space group $Pm\bar{3}m$ [13, 14]. At a temperature of $T > 492$ K, the III → II transformation occurs and the cubic lattice transforms into a trigonal lattice with parameters $a = 5.48$, $c = 10.71$ Å, space group $R\bar{3}m$ [10, 13, 14].

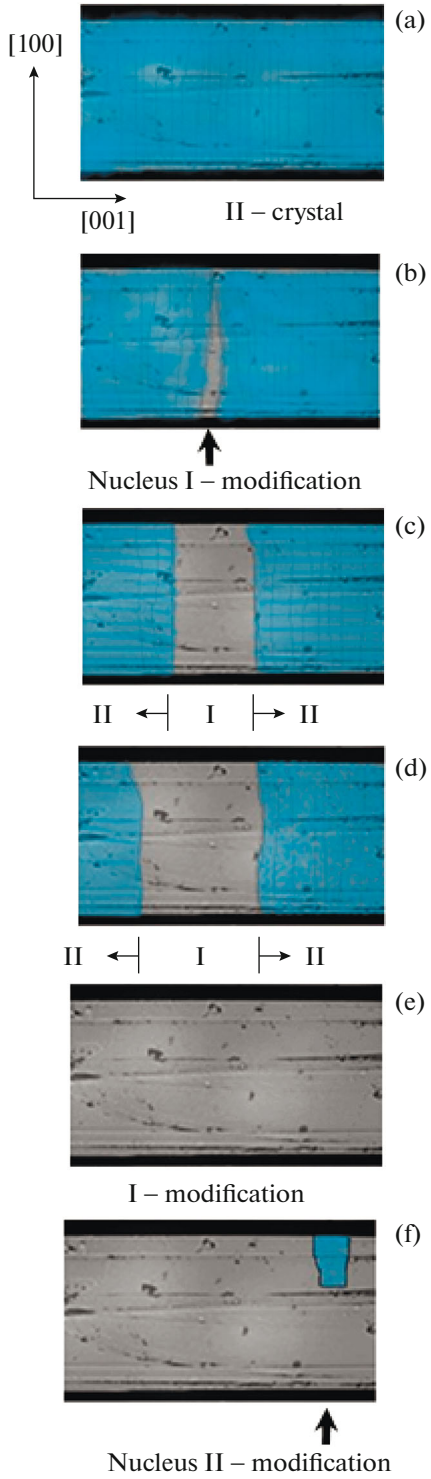

Fig. 1. Growth of crystals of modifications I and II during the transformation II ↔ I in $K_{0.945}Rb_{0.055}NO_3$: (a) matrix crystal II, (b) formation of a nucleus of modification II inside modification I, (c, d) the process of transformation II → I, (e) crystal I after complete transformation II → I, (f) formation of a nucleus of modification II inside modification I during the process of transformation I → II (magnification ×90).

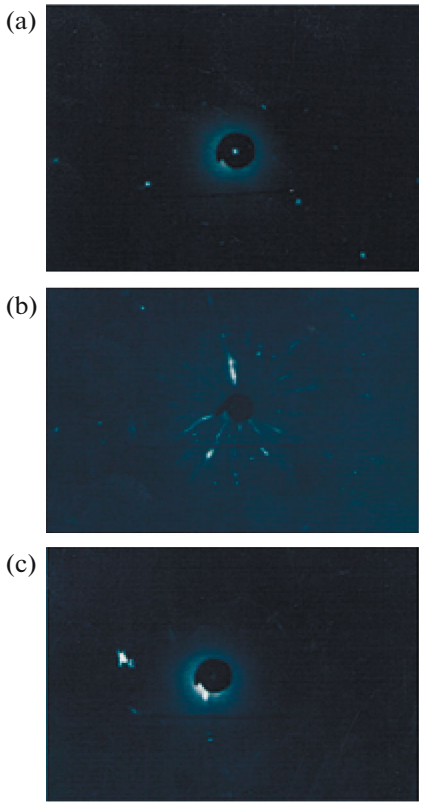

Fig. 2. Laue patterns of modifications II and I of the $K_{0.945}Rb_{0.055}NO_3$ crystal before (a) and after (b) the II → I transformation and after (c) the complete I → II transformation of crystal II.

EXPERIMENTAL

Single crystals of $K_{0.945}Rb_{0.55}NO_3$ were obtained from an aqueous solution at room temperature by isothermal crystallization. For perfection and chemical purity of the obtained crystals, potassium nitrate of analytical grade and rubidium nitrate of chemical grade were subjected to additional purification by multiple crystallization.

As a result, well-faceted crystals with an average size of 1 × 0.5 × 10 mm and a variety of external shapes were obtained. The resulting crystals were mainly needle-shaped, extending along the crystallographic direction [001].

Using an optical polarizing microscope MIN-8 equipped with a special heater, morphological studies were carried out, that is, visual observation of the crystal growth during polymorphic transformations [15]. These observations were conducted using a Levenhuk C310 NK film camera and recorded by a computer. The crystal temperature was measured with a thermocouple, the tip of which directly touched the surface of the sample. The accuracy of temperature measurement at 100°C reached ±0.5°.

First, the equilibrium temperature between modifications II and I was determined to be T_0 = 455 ±

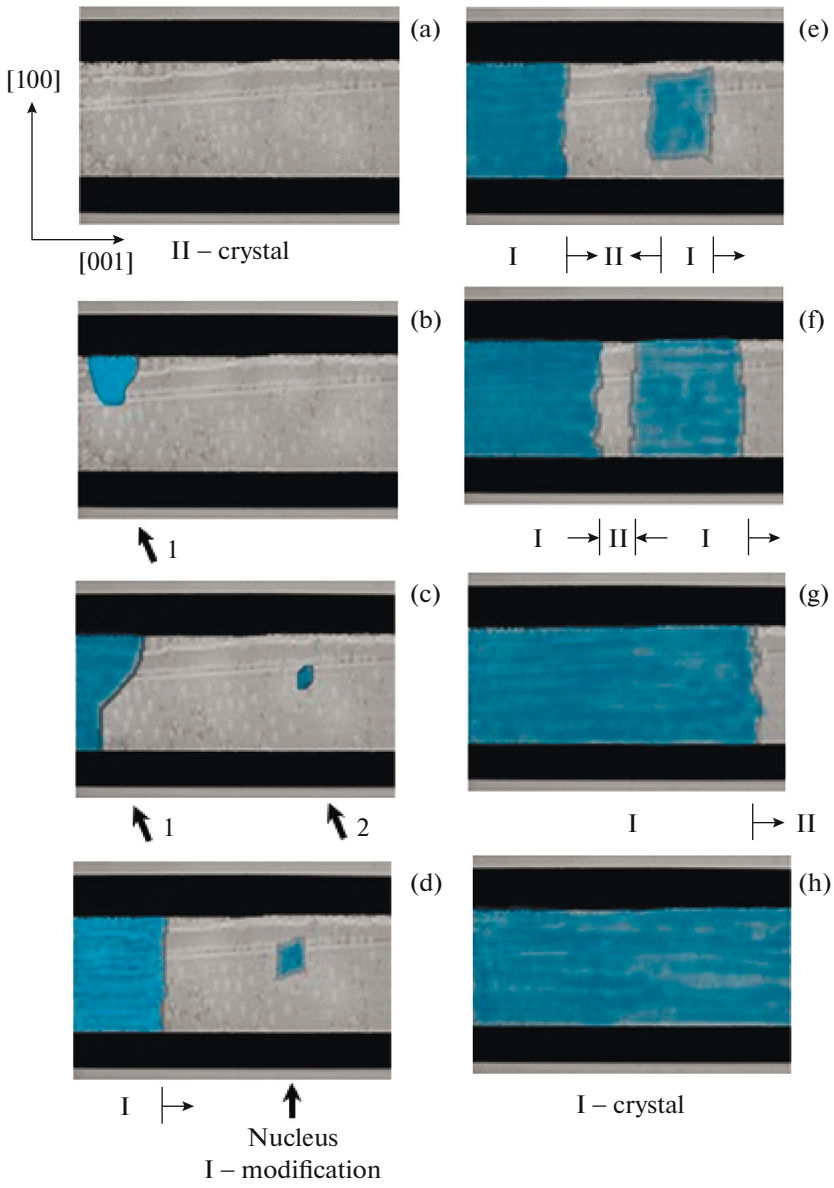

Fig. 3. Formation and growth of a binuclear crystal of modification I during the II → I transformations in $K_{0.945}Rb_{0.055}NO_3$: (a) matrix crystal II, (b) first nucleus of I modification I, (c) formation of the second nucleus, (d–g) the process of II → I transformation, (h) crystal after complete II → I transformation (magnification ×90).

0.5 K. Observations in an optical polarizing microscope show that the polymorphic transformation II → I in the crystal under study occurs at a temperature of $T_{tr} > T_0$. Here T_{tr} is the transformation temperature and T_0 is the phase equilibrium temperature. The determined temperature difference $\Delta T = T_{tr} - T_0$ [6, 16] depends on the perfection and on the prehistory of the matrix single crystal. The maximum deviation from the equilibrium temperature between modifications II and I is $\Delta T \sim 2$ K.

Above $T_{tr} > T_0$, a modification I nucleus is formed inside the crystal of modification II, which grows very quickly in the [100] direction of the matrix crystal, and when it reaches the other boundary of the matrix crystal, growth in this direction stops. Then, slow growth begins on both sides in the direction [001] of the matrix crystal (Fig. 1). Under fixed temperature conditions, the growth rate of modification I in the [100] direction is greater than in the [001] direction, that is, $\vartheta_{[100]} >> \vartheta_{[001]}$.

By comparing the Laue patterns obtained at room temperature (Fig. 2a), at $T = 460$ K (Fig. 2b) and after the complete transformation I → II (Fig. 2c), it can be concluded that a structural transformation of the single crystal ↔ single crystal type takes place.

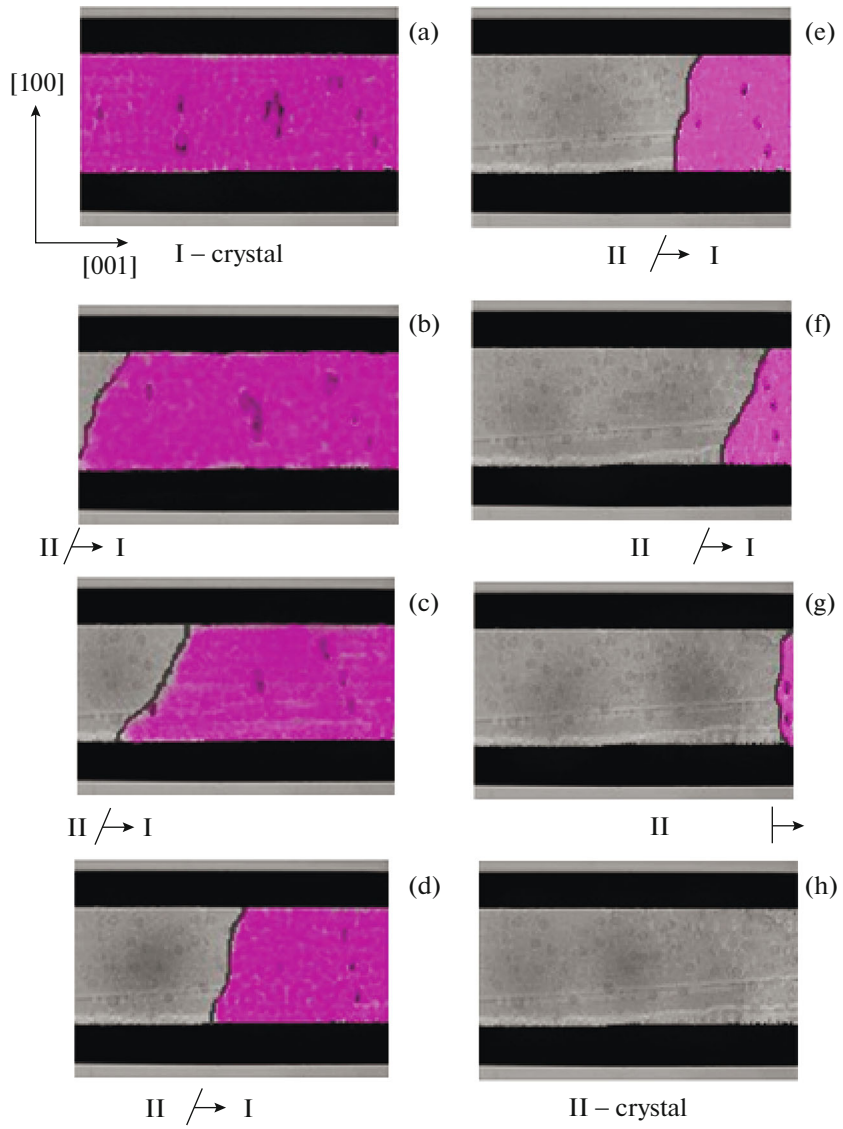

Fig. 4. Formation and growth of crystal II during the I → II transformation inside the matrix crystal: (a) matrix crystal I, (b) formation of the II-modification nucleus, (c–g) the process of I → II transformation, (h) crystal II after complete I → II transformation (magnification ×90).

As can be seen from Fig. 1e, when the crystal is cooled below the equilibrium temperature, the transformation I → II occurs, which is also accompanied by the formation and growth of a nucleus of modification II inside I. In another case, the process of transformation II → I in the studied crystal occurs with the growth of two nuclei of the I modification of the crystal (the nuclei in Fig. 3 are indicated by arrows).

When crystal I is cooled to 453 K, the transformation I → II occurs. The nucleus of modification II also initially grows in the [100] direction of the matrix crystal, and upon reaching its other boundary, the transformation process continues in the crystallographic direction [001] of the matrix crystal (Fig. 4). As shown in Fig. 4, the interface between phases II and I does is not linear, as in the II → I transformation. Our experiments on $K_{0.945}Rb_{0.055}NO_3$ samples did not reveal any signs of the existence of a ferroelectric phase III between modifications I and II in potassium nitrate.

CONCLUSIONS

Thus, it has been experimentally established that in $K_{0.945}Rb_{0.055}NO_3$ crystals, polymorphic transformations are enantiotropic in nature, and the growth of crystals of modifications I and II during II ↔ I transformations occurs with the formation and growth of nuclei of the daughter modification inside the matrix.

It has also been established that there is no intermediate modification between modifications I and II. The rhythmic growth observed in potassium nitrate

crystals during the II → I transformation [17–19] is not detected in these crystals. Polymorphic transformations occur according to the single crystal ↔ single crystal type. Partial replacement of K^+ ions by Rb^+ ions increases the equilibrium temperature between modifications II and I by approximately 55 K.

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CONFLICT OF INTEREST

The authors of this work declare that they have no conflicts of interest.

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