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Morphology of polymorphic transformations in a $K_{0.940}Cs_{0.060}NO_3$ single crystal

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The article considers the results of microscopic research on the growth morphology of crystals of modifications II and III during the transformation of II↔III into $K_{0.940}Cs_{0.060}NO_3$. The equilibrium temperature between modifications II and III was established, which is equal to $T_0 = 457 \pm 1$ K. Transformations II↔III in the crystal under study occur with the formation and growth of an embryo of a daughter modification inside the matrix.

Keywords: morphology of crystals, transformations in crystal, single crystal.

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Introduction

The study of the quantitative composition of the polymorphic transformation in nitrate compounds of alkali metals is of not only scientific but also practical interest since this process is associated with the technology of obtaining single crystals of a mixed composition with a polymorphic composition.

It is known that potassium nitrate at room temperature has a structure similar to aragonite (modification II) with symmetry *Pmcn* [1]. When the II-modification is heated at T>403 K, it turns into a structure very close to calcite (III-modification) with symmetry *R3m* [2]. The II→III transformation is enantiotropic. However, during cooling, two monotropic transformations are sometimes observed. Upon cooling near ~397 K, the III-modification can transform into a new structure (I-modification) with $R\bar{3}m$ symmetry, and only then at ~383 K does the I-modification transform into the II-modification.

Cesium nitrate at ambient temperature crystallizes in a rhombic pseudotrigonal syngony with $R\bar{3}m$ symmetry (II-modification) [4]. At a temperature of ~434 K, this modification turns into a cubic (I-modification) modification with $Pa3$ symmetry [5]. II↔I transformations in cesium nitrate are also enantiotropic. Crystallographic data on the storage of crystals is presented in Table 1.

Establishment of the mechanism of polymorphic transformations in single crystals of nitrate compounds of alkali metals, including potassium and cesium nitrates, has been the subject of studies [6-9]. A study of the morphology and kinetics of polymorphic transformations

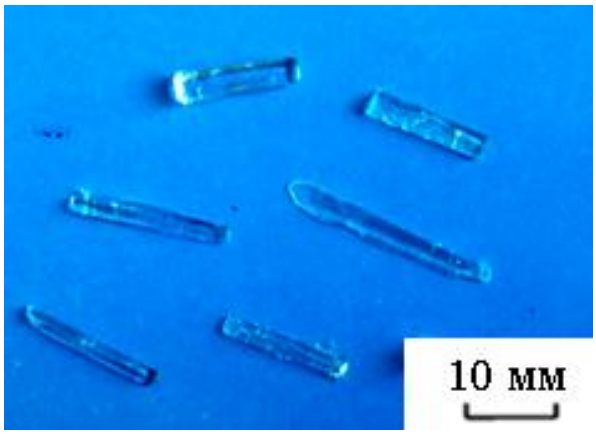
Table 1.

Crystallographic data of KNO_3 and $CsNO_3$ crystals

Substance	Symmetry	Crystal lattice parameters			Space group
		a, Å	b, Å	c, Å	
KNO_3	Rhombic	5.411	9.164	6.431	*Pmcn*
	Rhombohedral	5.43	-	9.112	$R\bar{3}m$
	Rhombohedral	5.42	-	19.41	$R\bar{3}m$
$CsNO_3$	Trigonal	10.87	-	7.76	$P3_1m$
	Cubic	8.98	-	-	*Pa3*

in cesium nitrate between modifications I and II revealed a new x-modification, the crystal structure of which was not determined [10]. The phase diagram of a mixture of potassium and silver nitrates [11] was determined, phase transitions in $K_{1-x}Ag_xNO_3$ [12] were established, and phase transitions in $K_{1-x}Rb_xNO_3$ were studied by Raman spectroscopy [13]. Structural transformations in rubidium and cesium [14] nitrates have been studied by molecular dynamics modeling. The phase diagram of the $RbNO_3$-$CsNO_3$ [15] system was compiled using the DSC method. Investigating solid solutions of $CsNO_3$ in $RbNO_3$, the disappearance of modifications I and II in the resulting compound was found at ~25 mol% $CsNO_3$ [16].

The purpose of this work is to study the effect of partial replacement of K^+ ions by Cs^+ ions and re-transformation on the nature of the polymorphic transformation in potassium nitrate. We obtained single crystals of $K_{0.940}Cs_{0.060}NO_3$ and carried out microscopic and X-ray studies [17]. $K_{0.940}Cs_{0.060}NO_3$ crystals were obtained from an aqueous solution at room temperature by the isothermal crystallization method. For the perfection and purity of the obtained single crystals, potassium nitrate CDA and cesium nitrate XC of chemically pure grade were subjected to additional purification by repeated crystallization. Well-faceted crystals with an average size



of 1×0.5×10 mm had various external shapes (Fig. 1).

Fig.1. Single crystals of $K_{0.940}Cs_{0.060}NO_3$ obtained from an aqueous solution.

The crystals obtained were mainly in the form of needles, elongated along the crystallographic direction [001]. Morphological studies were carried out using an optical polarizing microscope, «МИН-8», equipped with a special heater [8]. Observations of crystal growth during polymorphic transformations were carried out using a "Levenhuk C310 NK" camera and recorded by a computer. The crystal temperature was measured with a thermocouple, the tip of which directly touched the sample surface. The temperature measurement accuracy at 100 C reached $\pm 1^0$.

I. Experimental part

Observations in an optical polarization microscope show that at $T_{пр}$>457 K, II→III transformations occur in the crystal under study. Comparing the Lauegrams taken at room temperature and at a temperature of T = 460 K, we can see that in this case we have structural transformations of the single-crystal→single-crystal type.

First of all, we established the equilibrium temperature of phases III and II, which is equal to T_0= 457±1 K. Experiments show that transformations II→III always occur at a temperature T_{pr}>T_0 (T_{pr} is the transformation temperature, T_0 is the equilibrium temperature). The temperature difference $\Delta T = T_{pr} - T_o$, as was established in our previous studies, depends on the perfection of the crystal [18]. The maximum deviation of the transformation temperature from the equilibrium temperature between modifications II and III is $\Delta T = 2^o$.

At a temperature T_{pr} > 457 K, the embryo III - modification grows very rapidly in the direction [100]. When the growth of this embryo in the direction of [100] stops, i.e., it reaches another boundary of II - crystal, growth begins more slowly in the direction of [001] (Fig. 2, b). As it is seen, the process of transformation II→III in the crystal under study occurs with the formation and growth of three embryos III - modification of the crystal (Fig. 2, (c) embryos are indicated by arrows). One embryo was formed in the middle of the crystal, and the other two were at different ends of the crystal.

At a temperature of T < 457 K, III→II transformation occurs in the crystal under study. It also occurs with the formation and growth of the nucleus of modification II inside the crystal of modification III. The process of transformation III→II with two embryos is depicted in Fig. 2 d-f. There is a counter growth of two embryos in the direction [001] of the matrix crystal. Both embryos have a rectilinear boundary.

Experiments carried out in numerous samples of $K_{0.940}Cs_{0.060}NO_3$ show that the intermediate rhombohedral modification between the existing II and III modifications of potassium nitrate is not detected in this case.

In contrast to the first case, during the repeated transformation, the growth of the III modification during the II→III transformation occurs with the formation and growth of two embryos. The boundary of the first embryo on the left side of the crystal is perpendicular to the [001] crystallographic direction of the matrix crystal. In front of the second embryo, i.e., at the end of the crystal, it makes an angle of approximately ~40° with the direction [001]. The boundary of the second embryo on the right side makes an angle of approximately ~40° with the direction [001] of the matrix crystal.

The decrease in the number of embryos during the repeated transformation is apparently associated with the healing of defects in the matrix crystal during the first transformation and the disappearance of the third potential nucleus III the modification. Comparing Fig. 2 and 3, it is seen that the process is no worse during the second transformation than in the first one.

Conclusion

It has been experimentally established that in $K_{0.940}Cs_{0.060}NO_3$ crystals, polymorphic transformations are of an enantiotropic nature, and the growth of crystals of III and II modifications during II↔III transformations

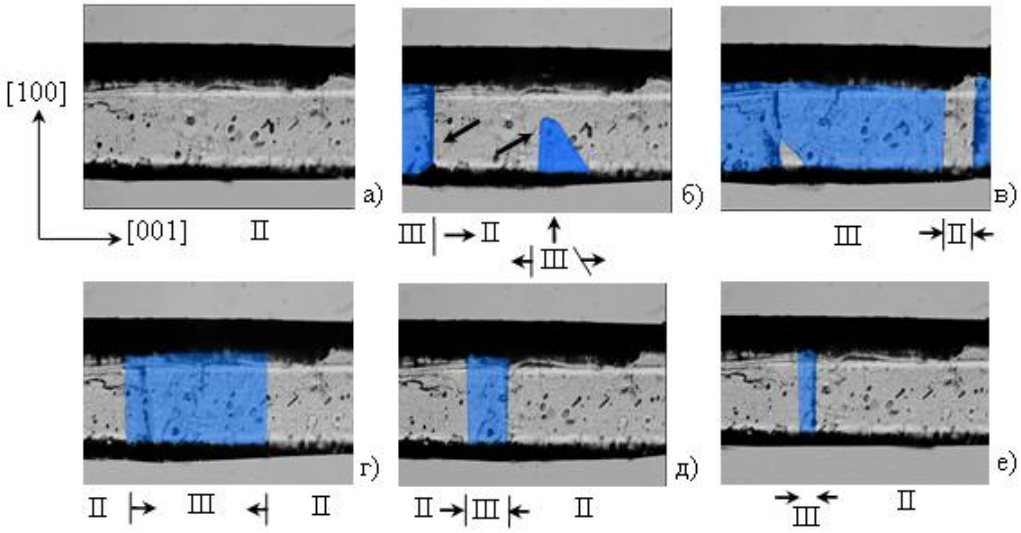


Fig.2. Optical micrograph of the formation and growth of III and II crystals during II↔III transformations (90 times of magnification) inside the crystal-matrix. a – crystal-matrix; b – formation and growth of two embryos of III – modification inside II – crystal; c – continuation of III – crystal in attachment [001]; d – formation of embryos of crystal II – modification inside III – crystal; e, f – continuation of crystal counter-growth II – modifications inside the crystal III – modifications.

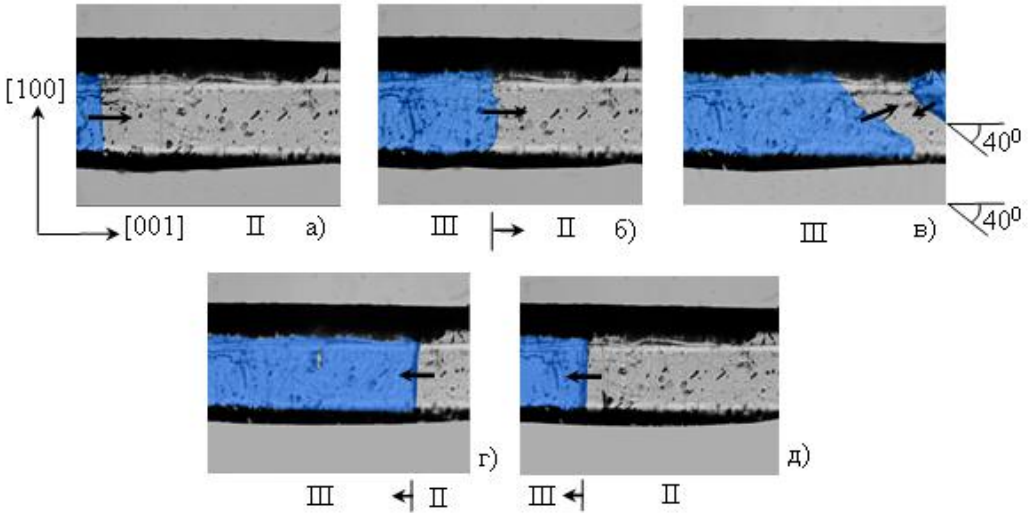


Fig. 3. Optical micrographs illustrating the formation and growth of III and II modifications of crystals during the repeated transformation of II↔III in a $K_{0.940}Cs_{0.060}NO_3$ single crystal (magnification ×90 times). a, b, c – growth of the embryos of III – modifications inside the II - crystal; d, e – reverse III→II transformations.

occur with the formation and growth of embryos of the daughter modification inside the matrix. It was also found that there is no intermediate modification between the III and II modifications. The rhythmic growth that we discovered in KNO_3 crystals during the II→III transformation [9] is not detected in this case. Partial replacement of potassium ions by cesium ions contributes to an increase in the equilibrium temperature between modifications II and III by about 50 K.

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[1] A. Edward, *A determination of the complete crystal structure of potassium nitrate*, Z. Krist., 80, 154-158, (1943); https://doi.org/10.1524/zkri.1931.80.1.154.
[2] P.E. Tahvonen, *X-ray investigation of molecular rotation in potassium nitrate crystal*, Ann. Acad. Sci. Fennical, ser. A, 44, 20 (1947).

[3] K. Nimmo, B.W. Lucas, *The crystal structures of γ- and β-KNO_3 and the α←γ←β phase transitions*, Acta. Cryst. B32, 1968 (1976).
[4] L. Pauling, J. Sherman *Note on the crystal structure of rubidium nitrate* Z. Kristallogr, 84. 213 (1933).
[5] U. Korhonen, *The Crystal Structure of $CsNO_3$, Ann. Acad. Sci. Fennical*., Ser.A, 1, 1 (1953).
[6] S.W. Kennedy, M. Odlyha *Polimorphic transformation II⟶III in potassium nitrate*. Multiple orientation. Aust. J. Chem., v. 27. p. 1121, (1974); https://doi.org/10.1071/CH9740209.
[7] E.W. Courtenay, S.W. Kennedy *Solition growth crystal system and transformation of crystals phase II $RbNO_3$*. Aust. J. Chem. ,27. 209, (1974).
[8] Y.G. Asadov. V.İ. Nasirov. G.A. Jabrailova, *Mophology of crystal at polymorphic transformation in KNO3, $AgNO_3$ and NH_4NO_3 single crystals*, J. Crystal Crowth, 15, 45 (1972). https://doi.org/10.1016/0022-0248(72)90318-1.
[9] Y. Shinnaka, S. Yamomoto, *X-ray study of orientational disorder in cubic $RbNO_3$*. J. Phys. Soc. Jpn., 50. 2091, (1981).
[10] Ch.M. Alekperov, V.I. Nasirov, F.G. Maharramova, Yu.G. Asadov, *Morphology and kinetics of crystal growth during polymorphic transformations in $RbNO_3$ and $CsNO_3$ single crystals*, Preprint, Azerb., 4, 38, (1996);
[11] H. Zamali, M. Jemal *Phase diagrams of binary systems: $AgNO_3$-KNO_3 and $AgNO_3$-$NaNO_3$*. J. Phase Equilibria, 16, 235 (1995); https://doi.org/10.1007/BF02667307.
[12] S.V. Baryshkov, E.V. Charnaya, E.V. Stukova, et al., *Dielectric properties of crystalline binary mixtures KNO_3-$AgNO_3$ in nanoporous silicate matrices*, SSP, 52, 365, (2010); https://journals.ioffe.ru/articles/viewPDF/1734
[13] Xu. Kangcheng, *Application of Raman in phase eqibilibirium studies: the structures of substitutional solid solutions of KNO_3 by $RbNO_3$*, J. Mater. Sci., 34, 3447 (1999); https://doi.org/10.1023/A:1004649603036.
[14] J. Liu, C. Duan, M. Ossovski, W. Mei, R.W. Smith, J.R. Hardy *Molecular dynamics stimulation of phase transition in $RbNO_3$ and $CsNO_3$*. J. Sol. State. Chem., 160, 222, (2001); https://doi.org/10.1006/jssc.2001.9226.
[15] E.A. Secco, R.A. Secco *Heats of solution/substitution in $TlNO_3$ and $CsNO_3$ crystals and in $RbNO_3$ and $CsNO_3$ crystals from heats of transition: The complete phase diagrams of $TlNO_3$-$CsNO_3$ and $RbNO_3$-$CsNO_3$ systems.* J. Phys. and Chem. of Solids, 63(3), 433 (2002); https://doi.org/10.1016/S0022-3697(01)00157-3.
[16] E.S. Schlemper, W.C. Hamilton *Phase formation in the system $RbNO_3$-$CsNO_3$*. J. Phys. Chem. Sol., 45, 4498 (1966).
[17] V.I. Nasirov, A.F. Khazieva, Yu.G. Asadov *Polymorphic single crystal ↔single crystal transformations in $Rb_{0.975}Cs_{0.025}NO_3$*. Cryst. Reports, 56, 1077, (2011); https://doi.org/10.1134/S1063774511050208.
[18] Yu.G. Asadov, V.I. Nasirov, *Study of the kinetics of polymorphic transformation in potassium nitrate single crystals*, Crystallography, 17, 991 (1972).

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Морфологія поліморфних перетворень у монокристалах $K_{0.940}Cs_{0.060}NO_3$

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У статті розглянуто результати мікроскопічних досліджень морфології росту кристалів II і III модифікацій при перетворенні II↔III в $K_{0,940}Cs_{0,060}NO_3$. Встановлено температуру рівноваги між II та III модифікаціями, яка дорівнює T_0 = 457 ± 1 K. Перетворення II↔III в досліджуваному кристалі відбуваються з утворенням і ростом зародка дочірньої модифікації всередині матриці.

Ключові слова: морфологія кристалів, перетворення в кристалі, монокристал.