Characteristic Features of Polymorphic Transformations in Solid Solutions of Nitrate Compounds of Alkali Metals

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Abstract— Optical microscopic and X-ray studies were conducted on KNO_3-$RbNO_3$, KNO_3-$CsNO_3$ and KNO_3-$AgNO_3$ solid solution monocrystals grown by isothermal crystallization, and as a result of these studies a number of properties characteristic of polymorphic transformations were identified in these samples. As a result of morphological studies, it was determined that polymorphic transformations in these samples occur with the formation and growth of a new crystal nucleus within the parent crystal. The nucleus of the newly formed phase crystal always first grows in the [100] crystallographic direction, and after growth in this direction is complete, in the [001] direction. In all cases, the crystal growth in the [100] direction is greater than that in the [001] direction. Overall, the results obtained and the good agreement of these results with M. Folmer's two-dimensional nucleation mechanism of crystal growth from the liquid phase indicate that crystal growth occurs by a two-dimensional mechanism during polymorphic transformations in the studied samples.

Keywords— polymorphic transformations, solid solutions, equilibrium temperature, monocrystalline, activation energy

I. INTRODUCTION

The study of polymorphous transformations in nitrate compounds of alkali metals is of scientific and practical interest. The strong piezoelectric and ferroelectric properties of these compounds create great opportunities for their use as active elements (KNO_3 - III phase ferroelectric) in electrical devices (as capacitors) [1, 2]. In addition, these compounds are strong oxidizing agents used in pyrotechnics, metallurgy, analytical chemistry and the preparation of pharmaceuticals [3]. Potassium salts are substances used in the production of conversion devices, memory elements and radiation heat transfer devices [4].

To investigate 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 interconversion modifications, as well as the kinetics of the process. Therefore, it is convenient to use optically transparent crystals as research objects [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 obtained results of these researches is presented in [6].

Optical microscopic and X-ray diffraction studies were carried out on KNO_3-$RbNO_3$, KNO_3-$CsNO_3$ and KNO_3-$AgNO_3$ solid solution monocrystals grown by isothermal crystallization and as a result, some properties characteristic of polymorphic transformations were identified in these samples. In this work, these properties are given by examples of different compositions. First of all, it should be noted that each of the nitrate compounds of alkali metals has two or more polymorphic modifications. The crystallographic data of these compounds are given in Table 1.

TABLE I. STRUCTURAL DATA OF NITRATE COMPOUNDS OF ALKALI METALS, TEMPERATURE RANGE OF EXISTENCE AND MELTING TEMPERATURES OF POLYMORPHIC MODIFICATIONS.

№	Substance	Modification	Symmetry	Temperature range of the modification. T, K	Space group	Melting point, T_m, K	Reference
1	KNO_3	II III I	rhombic rhombohedral rhombohedral	300-400 400-610 383-397	Pmcn R-3m R3m	610	7, 8, 9, 10, 11
2	$RbNO_3$	I II III IV	cubic rhombohedral cubic rhombic	564-587 492-564 437-492 437<	Fm3m R-3m Pm-3m $R3_1m$	587	12, 13, 14, 15, 16
3	$AgNO_3$	II I	rhombic hexagonal	300-432 432-483	$P222_1$	483	8, 17, 18
4	$CsNO_3$	II I	trigonal cubic	300-434 434-687	P3/m Pa3	687	19, 20, 21, 22

II. EXPERIMENTAL PART

The studied solid solution monocrystals were obtained in the needle-shaped and flat plates, the length of these needles was in the [001] crystallographic direction, and the size of the flat plate-shaped crystals was 1×0.5×5 mm^3. Figure 1 shows the images of the monocrystals obtained from the solution.

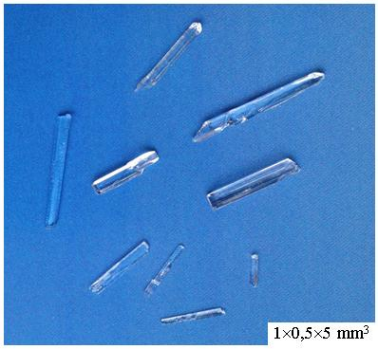


Fig. 1. $K_{0,985}Cs_{0,015}NO_3$ monorystals obtained from solution in water.

Morphological studies were carried out on a MIN-8 polarizing microscope equipped with a heater using a "Levenhuk C310 NK" type camera.

Crystal growth during polymorphic transformations was observed using a computer [6, 23]. The temperature of the crystal was measured using a copper-constantan thermocouple touching it. The error of temperature measurements was about $\pm 0{,}5^0C$ at 100^0C.

The studies conducted using an optical microscope show that polymorphic transformations in the investigated samples always occur at the temperature of $T_{tr}>T_0$ above the equilibrium temperature of phases, with a temperature delay of $\Delta T=T_{tr}-T_0$-temperature. Here T_{tr} is the transformation temperature, T_0 is the equilibrium temperature between modifications.

The temperature delay is 5-8 K in KNO_3, while in solid solutions it is 1-2 K. In some cases, plated crystal growth is difficult or not observed in these samples. In this case, the boundary separating the polymorphic modifications is non-linear. However, X-ray studies show that in this case, a monocrystal-monocrystal transition is observed in the sample. The value of the temperature delay depends on the initial state and perfection condition of the crystal structure. Partial replacement of K^+ ions in KNO_3 by Cs^+, Ag^+, Rb^+ ions in the initial approach has a positive effect on the perfection of the parent crystal.

It was determined that as a result of morphological studies in these samples, polymorphic transformations, accompanied by the replacement of the rhombic structure with the rhombohedral structure, occur with the formation and growth of a new crystal nucleus within the parent crystal. The nucleus of the newly formed phase crystal always first grows in the [100] crystallographic direction, and after the growth in this direction is completed, the process continues in the [001] direction. In all cases, the crystal growth in the [100] direction is greater than that in the [001] direction.

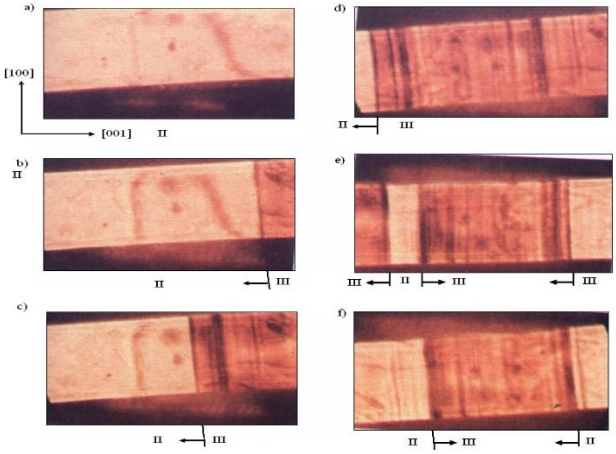


Fig. 2. The process of formation and growth of a new crystal nucleus within the parent crystal during polymorphic transformation in $K_{0,975}Rb_{0,025}NO_3$ crystal (magnification 90 times).

Figure 2 shows the formation and growth of a new crystal nucleus within the parent crystal during the polymorphic transformation in the $K_{0,975}Rb_{0,025}NO_3$ crystal.

For example, Figure 3 presents the process of growth of a newly formed crystal with its own faces within the parent crystal during polymorphic transformation in the $Rb_{0,95}Cs_{0,05}NO_3$ crystal.

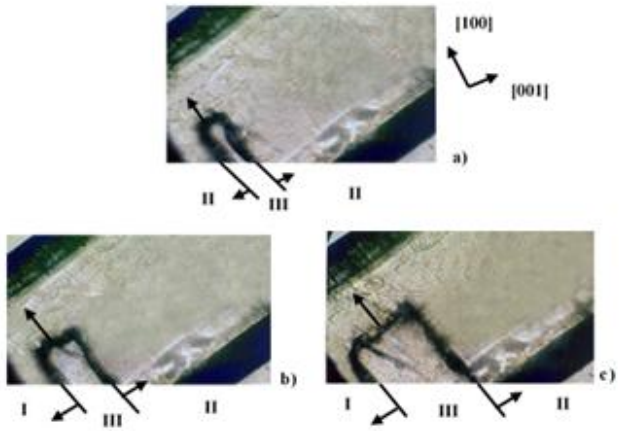
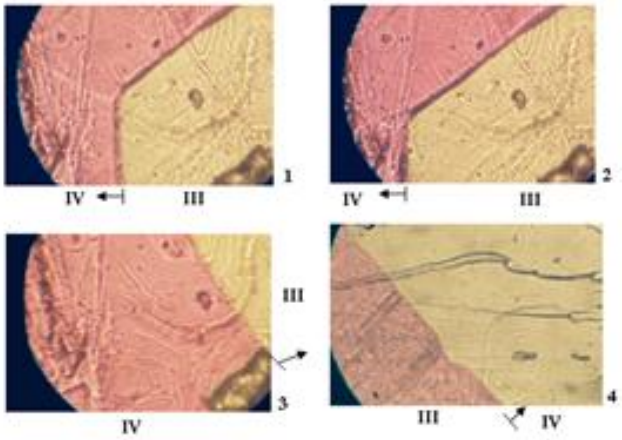


Fig. 3. The growth of a newly formed crystal with its own faces within the parent crystal during polymorphic transformation in $Rb_{0,95}Cs_{0,05}NO_3$ crystal (magnification 90 times).

During the polymorphic transformation in needle-shaped crystals, crystal growth occurs with the movement of the linear boundary between phases (fig. 4). Partial replacement of K^+ ions in KNO_3 by Cs^+, Ag^+, Rb^+ ions causes a changing of the equilibrium temperature between the interconverting modification crystals.

The transformation temperature increases, polymorphous transformations occur. Experiments show that the equilibrium temperature between the rhombic and rhombohedral phases in KNO_3 is 402 K, while in its solid solutions this temperature is 50-58 K higher.

Fig. 4. Growth stages of III and II modification crystals during II→III



transformations in $K_{0,975}Ag_{0,025}NO_3$ crystals. (magnification 90 times).

It is known that in KNO_3, during the II→I polymorphic transformation the rhythmic growth of the I-modification crystal and the formation of a rhombohedral III modification crystal between the I and II modifications during the crystal cooling are observed [24]. However, in the considered solid solutions, rhythmic growth during the II→I transformation and rhombohedral III modification between the I and II modifications during the cooling process were not observed.

The temperature dependence of the growth rate of the crystal of modification I during the II→I polymorphic transformation was studied using an optical microscope in the samples by the method given in [24-26].

Using the MATLAB program, it was determined that in all examples this dependence obeys the following empirical law.

$$\upsilon=(a\Delta T+b\Delta T^2+c\Delta T^3)\cdot 10^{-2}\text{cm/sec}.$$

The constants a, b, c in the equation have different values for different samples. Table 2 represents the values of these constants for three samples.

TABLE II. VALUES OF CONSTANTS a, b, c INCLUDED IN THE EMPIRICAL FORMULA

Substance	Transformation	Constants		
		a, deg^{-1}	b, deg$^{-}_{2}$	c, deg^{-3}
$K_{0,985}Rb_{0,015}NO_3$	II→III	-0,1482	0,5575	-0,01013
$K_{0,965}Rb_{0,035}NO_3$	II→III	-0,40098	0,671	0,001935
$K_{0,955}Rb_{0,045}NO_3$	II→III	0,0319	0,5163	0,0102

As mentioned, $\Delta T=T_{tr}-T_0$- is temperature delay, T_{tr}- is transformation temperature, T_0-is equilibrium temperature between modifications. Figure 5 shows the experimental results of velocity measurements on the $K_{0,985}Rb_{0,015}NO_3$ crystal and the results obtained from the empirical formula. As can be seen from the figure 5, the results obtained from the empirical formula and the experiment agree well with each other.

The results obtained from the process rate measurements show that partial replacement of K^+ ions in KNO3 by Cs^+, Ag^+, Rb^+ ions leads to an increase in the rate of polymorphic transformation. This replacement is approximately ten times greater than the corresponding rate in KNO_3.

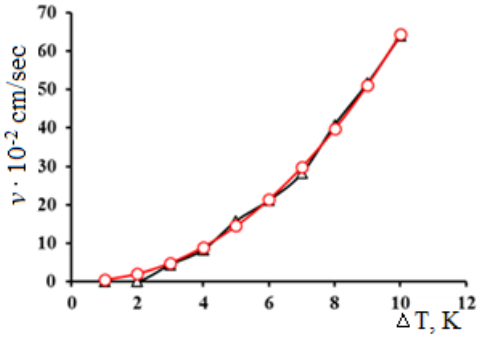


Fig. 5. Experimental "Δ" results of the velocity measurements in $K_{0,985}Rb_{0,015}NO_3$ crystal and results obtained from the empirical "o" formula.

The obtained experimental results agree well with Folmer's equation for two-dimensional embryonic growth from the liquid phase [27].

$$\upsilon = k_1 \exp(-k_2/T) \exp(-k_3/\Delta T) \quad (1)$$

Here $k_1=Bvd$ is coefficient independent of temperature in the first approximation. $\nu= 10^{12}$-10^{13}sec^{-1} is the oscillation frequency of molecules, d– is the interatomic distance in the growth direction, $B=10^7$ is the number of molecules passing from the liquid phase to the surface of the growing crystal (the number of molecules passing from the parent crystal to the surface of the newly growing crystal in the case of polymorphic transformation), $\kappa_2 = \frac{E}{R}$ is a constant which determines the energy required for molecules to pass from the liquid phase to the surface of the newly growing crystal. In the expression of $\kappa_2 = \frac{E}{R}$, E– is the activation energy per mole, R– is universal gas constant.

Here ΔT- expresses the supercooling (here it represents heating). k_3– is the energy required to form a two-dimensional nucleus of a crystal and is expressed as follows:

$$\frac{k_3}{T_0\Delta T} = \frac{\omega M\rho^2 NT}{2q\delta dR}\cdot\frac{1}{T_0\left(T_{çev}-T\right)} = \frac{\text{const}}{T_0\Delta T} \quad (2)$$

In the equation of (2) M is the weight of the molecules, ρ is the energy of the growing face, N is Avogadro's number, q is the transformation heat, T_0 is the equilibrium temperature between modifications, ΔT is the superheat (in this case it is temperature delay), δ is the density, and d is the interplanar distance in the crystal in the growth direction.

If the velocity measurements are made over a narrow temperature range, the ratio of $\frac{k_2}{T}$ can be considered practically independent of temperature. In this case, the dependence $\ln\vartheta \sim f\frac{1}{T_0\Delta T}$ should be linear. If we write the value of $\frac{k_3}{T_0\Delta T}$ from (2) in (1) and take its logarithm, we get the following expression

$$\ln \upsilon = \ln \kappa_1 - \frac{E}{RT_0} - \frac{\omega M \rho^2 N T_0}{2qd\delta R} \cdot \frac{1}{T_0 \Delta T}$$

The dependence of ln(υ) on $\frac{1}{T_o \Delta T}$ is a linear function. From the dependence ln(υ)= $f\left(\frac{1}{T_o \Delta T}\right)$, the k_2 and k_3 coefficients of the polymorphic transformation in each sample were found and the activation energy of the process was calculated. The good agreement of the results obtained by experiments and the Folmer equation allows us to say that crystal growth in polymorphic transformations in the investigated crystals occurs by a two-dimensional nucleation mechanism, as in the liquid phase.

Morphological and X-ray studies show that the polymorphic transformations in the studied samples are enantiotropic, monocrystal-monocrystal type, and crystallographic directional relationships are maintained between the mutually transforming modification crystals. The figure 6 shows the lauegrams which represent the monocrystal→monocrystal transformations in $K_{0,985}Cs_{0,015}NO_3$ crystals.

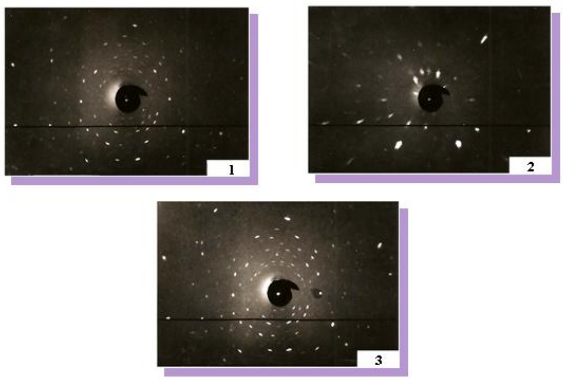


Fig. 6. Lauegrams of the $K_{o.985}$ $Rb_{o.015}$ NO_3 crystal before and after the transformation. 1- II crystal at room temperature, 2- I crystal after II→I transformation, 3- I crystal after I→II transformation.

III. Conclusion

Thus, the researches show that crystal growth during polymorphic transformations in solid solutions of nitrate compounds of alkali metals occurs with the formation and growth of a new crystal nucleus within the parent crystal. The process is enantiotropic and monocrystal-monocrystal type. Partial replacement of K^+ ions in KNO_3 by Cs^+, Ag^+, Rb^+ ions leads to an increase in the rate of polymorphic transformation, the equilibrium temperature between phases and a decrease in the activation energy of the process.

The good agreement of the obtained results with Folmer's two-dimensional nucleation mechanism of crystal growth from the liquid phase indicates that crystal growth occurs by a two-dimensional mechanism during polymorphic transformations in these solid solution crystals.

The phase transitions of mixed phases make these materials highly sensitive sensors, while their high heat capacity and stable phases make them suitable for thermal storage systems. Mixed nitrates can be used as more stable and powerful combustible substances, and their crystals have high dielectric constant and can be used in capacitors and microelectronics.

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