

THE INVESTIGATION OF KINETICS OF II→III POLYMORPHOUS TRANSFORMATION IN $\text{KNO}_3+x\% \text{RbNO}_3$ ($x=2.5, 5, 10\%$) SINGLE CRYSTALS

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The growth velocity of III modification in the dependence on temperature at II→III transformation in $\text{KNO}_3+x\% \text{RbNO}_3$ ($x=2.5, 5, 10\%$) single crystals has been measured by the method of optical microscopy. It is shown that the growth velocity of III modification at polymorphous transformation increases with ΔT increase and it is described by empirical formulas. The transformation process energy activation is calculated and it is shown that it decreases with x increase.

The some investigators are paid the attention to polymorphous transformation of potassium and rubidium nitrates in both ways specially and in the connection of some system studies at taking participation of these compounds.

The three different modifications of potassium nitrate have been established in temperature region from room one up to melting point one. At room temperature the potassium nitrate has the aragonite structure (II-modification) with $Pnma$ symmetry [1], at temperature $T_{tr}>400K$ the II modification transforms into III modification with $R3c$ symmetry [2]. According to [3] I-modification with $R3m$ symmetry takes place between II and III modifications. Rubidium nitrate has the four modifications: the rhombohedral structure (IV-modification) with $P3_1$ symmetry [4] at room temperature, at $T_{tr}>437K$ temperature IV-modification transforms into III- cubic one with $Fm3m$ symmetry [5], at $T_{tr}>492K$ this modification transforms into rhombohedral II-modification with $R3m$ [6] and finally, at temperature $T_{tr}>564K$ II-modification transforms into cubic one with $Fm3m$ symmetry [7]. Many works are dedicated to establishing of polymorphous transformation establishing in single crystals of alkali metal nitrate compounds including in potassium and rubidium nitrates [8-12].

It is shown that in these crystals the structural transformations take place mainly with germ origin and growth of daughter modification inside matrix one.

The other transformation mechanism types are revealed.

What is the polymorphous transformation mechanism in solid solutions of these compounds? In order to answer this question we have carried out the series of investigations for study of polymorphous transformation mechanism in argentine nitrate solid solutions in potassium nitrate [13,14]. The present paper is the continuation of these works and is dedicated to investigation of polymorphous transformation kinetics in rubidium nitrate solid solutions in potassium nitrate consisting 2,5; 5,0 and 10% RbNO_3 .



Fig.1. $\text{KNO}_3+5\% \text{RbNO}_3$ single crystals obtained from water solution

From water solution at room temperature we have obtained the well faceted perfect single crystals of II-modification $\text{KNO}_3+x\% \text{RbNO}_3$ ($x=2,5; 5,0; 10\%$) with sizes $1 \times 0,5 \times 10 \text{mm}$ in average which are suitable for microscopic investigations (fig.1). In the work the big attention is paid to perfection and purity of investigated crystals. The potassium nitrates of «ЧДА» mark and rubidium nitrate of «XЧ» mark are endured by additional purification by the way of multiple recrystallization. The obtained crystals have the form of needles extended in crystallographic direction [001] or in the form of plane plate.

The investigation is carried out in polarized microscope of МИН-8 mark with heating table providing the total thermostating of investigated crystals. The crystal temperature is measured by thermocouple the ends of which directly touch the sample surface. The measurement accuracy of temperature at 100°C achieves $\pm 0,5^\circ$.

Firstly the equilibrium temperatures of II and III phases are fixed: for $\text{KNO}_3+2,5\% \text{RbNO}_3$ $T_0=381K$, $\text{KNO}_3+5\% \text{RbNO}_3$ $T_0=372K$ and $\text{KNO}_3+10\% \text{RbNO}_3$ $T_0=369K$.

The growth velocity of III modification $\text{KNO}_3+x\% \text{RbNO}_3$ ($x=2,5; 5,0; 10\%$) at transformation of II→III as ΔT function ($\Delta T=T_{tr}-T_0$, where T_{tr} is transformation temperature, T_0 is modification equilibrium temperature) is measured after finding of equilibrium temperatures of II and III modifications. The growth velocity is measured on the one and the same edge (hkl) of growing crystal on technique supposed in [3].

The crystal of $1 \times 0,5 \times 15 \text{mm}$ dimension is put on cover glass and after on microscope heating table at $T_1>T_0$ temperature. The section of length 1mm is emphasized in crystal with the help of scanning reticle. After some time, which is necessary for equality of sample temperature and table, the boundary of growing modification achieves the risk of reticle fixing the beginning of main section, the stopwatch is switched off. After passing modification boundary 1mm the stopwatch is switched off and sample is transferred on another microscope where heating table temperature is $T_2>T_1>T_0$. Thus the growth velocity of the one and the same edge of III modification at II→III in $\text{KNO}_3+x\% \text{RbNO}_3$ ($x=2,5; 5,0; 10\%$) as ΔT function is measured consequently. The interface of II and III modifications on motion of which the growth velocity at II→III transformation as temperature function is shown on fig.2.

The measuring results are given in table 1. The experimental data obtained from six crystals of each composition and treated with the help of least-squares procedure give the functional dependence of growth velocity

of daughter modification inside matrix one on temperature at polymorphous II→III transformation in the form:

$$v = (a\Delta T + b\Delta T^2 + c\Delta T^3) 10^{-2} \text{ mm/sec}$$

where $\Delta T = T_{tr} - T_0$.

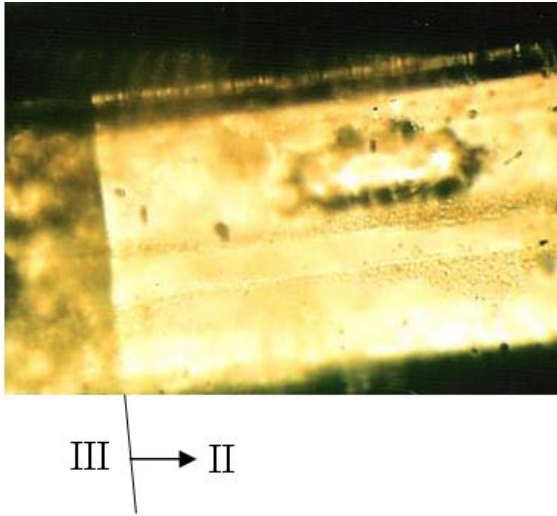


Fig.2. Transformation process of II→III into $\text{KNO}_3+5\% \text{RbNO}_3$.

The numerical values of a, b, c constants of crystal growth velocity at II→III transformation in

$\text{KNO}_3+x\% \text{RbNO}_3$ ($x=2,5; 5,0; 10\%$) as ΔT function are given in the table 2.

The plots of growth velocity of III modification crystals at II→III transformation in the dependence on temperature constructed on experimental data for investigated crystals are shown on fig.3.

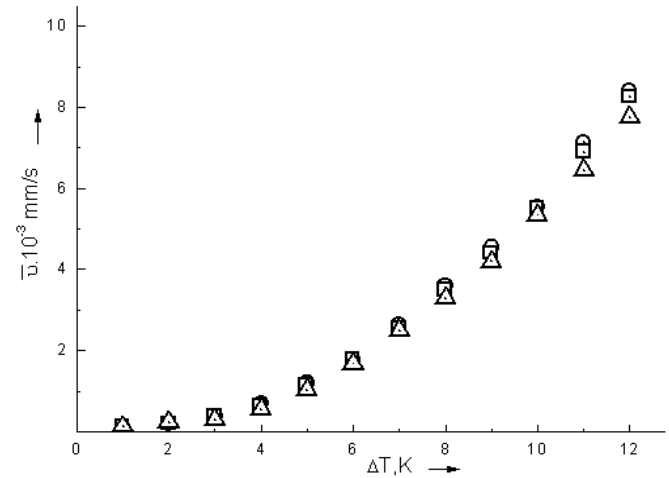


Fig.3. The dependence of crystal rate of increase of III modification at II→III transformation of $\text{KNO}_3+x\% \text{RbNO}_3$ ($x=2,5; 5,0; 10\%$) on temperature Δ - $x=10\%$, \square - $x=5,0\%$, \odot - $x=2,5\%$.

Table 1.

The measuring results of crystal rate of increase of III-modification at polymorphic transformation of II→III into $\text{KNO}_3+x\% \text{RbNO}_3$ ($x=2,5; 5,0; 10\%$) single crystals.

$\Delta T, K$	$x = 0,00$		$x = 2,5\%$		$x = 5,0\%$		$x = 10\%$	
	$\bar{v}_{exp} 10^{-2}$ mm/sec	$v_{\Delta T} 10^{-2}$ mm/sec	$\bar{v}_{exp} 10^{-2}$ mm/sec	10^{-2} mm/sec	$\bar{v}_{exp} 10^{-2}$ mm/sec	$v_{\Delta T} 10^{-2}$ mm/sec	$\bar{v}_{exp} 10^{-2}$ mm/sec	$v_{\Delta T} 10^{-2}$ mm/s
1			0,118	0,1077	0,127	0,121	0,113	0,107
2			1,501	1,475	1,428	1,428	1,363	1,377
3			4,286	4,104	4,364	4,025	3,781	3,811
4			8,347	8,053	7,610	7,086	7,696	7,446
5	0,03	0,05	13,242	13,120	12,656	12,825	11,988	12,314
6	0,73	0,67	19,365	19,508	19,328	12,020	17,975	18,191
7	1,54	1,48	27,016	27,148	25,984	26,434	25,615	25,314
8	2,57	2,47	36,384	36,036	35,876	35,065	33,816	33,601
9	3,52	3,65	46,985	46,171	45,155	44,905	42,975	43,049
10	4,68	5,00	56,124	57,267	54,267	55,63	53,436	53,66
11	5,97	6,52	71,036	70,293	69,126	68,998	65,261	65,429
12	7,38	8,22	84,245	84,035	81,484	81,648	78,496	78,496

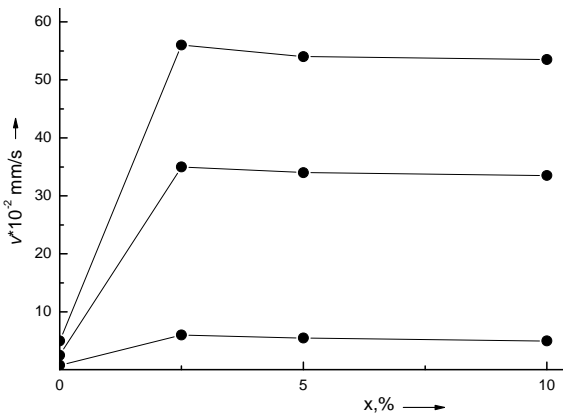


Fig.4. The dependence of crystal rate of increase of III modification at II→III transformation on $1/(T_0\Delta T)$ into $\text{KNO}_3+x\% \text{RbNO}_3$.

As it is seen from the table 1 and fig.4 the growth velocity of III crystal modification inside II one increases in the investigated crystals with temperature increase. It decreases when x values increase. From table 1 it is also seen that growth velocity of III modification crystal in potassium nitrate is measured beginning from $\Delta T=5K$ and in $\text{KNO}_3+x\% \text{RbNO}_3$ from $\Delta T=1K$. This is connected with the fact that delay temperature at II→III transformation in potassium nitrate is approximately $\sim 5K$ and for $\sim 1K$, i.e. II→III transformation takes place almost without delay in investigated crystals.

From fig.4 it is seen that $x=0$, i.e. the growth velocity of III modification is $\bar{v}=4,68 \cdot 10^{-2} \text{ mm/sec}$ in potassium nitrate at $\Delta T=10 K$ temperature and at the same temperature for $\text{KNO}_3+x\% \text{RbNO}_3$ ($x=2,5; 5,0; 10\%$) it increases in more than 10 times. The increase of x values leads to decrease of

growth velocity. The experimental data are well described by formula obtained by M. Folmer [15] in the supposition that the increase of two-dimensional germs appearing on crystal edges takes place by the way of consequent attachment of separate atoms or molecules:

$$v = k_1 \exp\left(-\frac{k_2}{T_0}\right) \exp\left(-\frac{k_3}{T_0 \Delta T}\right)$$

where κ_1 in first approximation can be accepted as independent one on temperature and equal to $\kappa_1 = Bvd$ (v is molecule oscillation frequency, d is interatomic spacing on the surface of growing crystal, B is molecule number transiting from matrix crystal to surface of growing crystal), $\kappa_2 = E/R$ is constant taking into consideration the energy threshold for molecule transition from matrix crystal to the crystal surface of growing modification, κ_3 is formation work of two-dimensional germ of new modification, T_0 is temperature of equilibrium modification.

Table 2.

The numerical values of a , b , c constant in empirical formula of crystal rate of increase of III-modification at transformation of II→III into $\text{KNO}_3 + x\% \text{RbNO}_3$ ($x=2,5; 5,0; 10\%$)

Coefficient	Samples		
	$x = 2,5\%$	$x = 5\%$	$x = 10\%$
a	-0,523	-0,491	-0,456
b	0,631	0,612	0,588
c	-0,00032	-0,00034	-0,00028

From fig.5 it is seen that $\ln v$ dependence on $1/(T_0 \Delta T)$ presents itself the linear function, i.e. experimental points lie

on direct line. As the character of $\ln v$ dependence on $1/(T_0 \Delta T)$ for all investigated compositions is similar one, so this dependence on fig.5 is given for only one composition $\text{KNO}_3 + 2,5\% \text{RbNO}_3$.

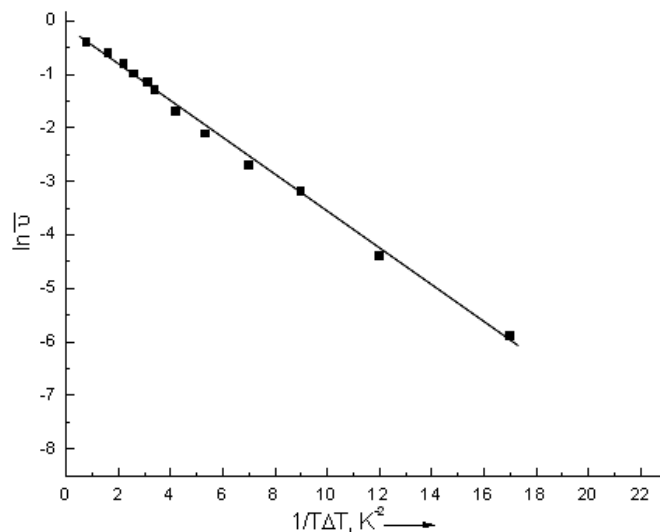


Fig.5. The logarithm dependence of crystal rate of increase of III modification at II→III transformation on $1/(T_0 \Delta T)$ into $\text{KNO}_3 + 2,5\% \text{RbNO}_3$.

From direct lines κ_2 and κ_3 values are found and activation energy of II→III transformation process for $\text{KNO}_3 + 2,5\% \text{RbNO}_3$ $E=21,2$ kcal/mol; for $\text{KNO}_3 + 5\% \text{RbNO}_3$ $E=20,8$ kcal/mol; for $\text{KNO}_3 + 10\% \text{RbNO}_3$ $E=20,63$ kcal/mol have been calculated. The obtained data show that energy activation of transformation process decreases with x increase in investigated crystals.

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$\text{KNO}_3 + x\% \text{RbNO}_3$ ($x=2,5, 5, 10\%$) MONOKRİSTALLARINDA II→III ÇEVİRİLMƏSİNİN KİNETİKASININ TƏDQIQI

Optik mikroskopik metodu ilə $\text{KNO}_3 + x\% \text{RbNO}_3$ ($x=2,5, 5, 10\%$) monokristallarda II→III çevrilməsi zamanı III modifikasiya kristallarının böyümə sürətinin temperaturdan aşağı tədqiq olunmuşdur. Müəyyən edilmişdir ki, ΔT artdıqca II→III çevrilməsi zamanı III modifikasiya kristalının böyümə sürəti artır və o empirik düsturlarla ifadə olunur. Prosesin aktivləşmə enerjisi hesablanmış və müəyyən edilmişdir ki, x artdıqca o da artır.

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**ИССЛЕДОВАНИЯ КИНЕТИКИ ПОЛИМОРФНОГО II→III ПРЕВРАЩЕНИЯ В МОНОКРИСТАЛЛАХ
 $\text{KNO}_3+x\% \text{RbNO}_3$ ($x=2.5, 5, 10\%$)**

Методом оптической микроскопии измерена скорость роста III модификации в зависимости от температуры при превращении II→III в монокристаллах $\text{KNO}_3+x\% \text{RbNO}_3$ ($x=2.5, 5, 10\%$). Показано, что с повышением ΔT скорость роста III модификации при полиморфном превращении II→III увеличивается, и она описывается эмпирическими формулами. Вычислена энергия активации процесса превращения и показано, что с увеличением x она уменьшается.

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