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Kinetics of IV → III polymorphic transformation in $Rb_{1-x}Cs_xNO_3$ ($x = 0.025, 0.05, 0.1$) single crystals

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Optical microscopy was used to measure the growth rate of III-modification crystals as a function of temperature during the IV → III transformation in $Rb_{1-x}Cs_xNO_3$ ($x = 0.025, 0.05, 0.1$) single crystals. It is shown that the growth rate of III-modification crystals depending on temperature during the IV → III transformation is described by the empirical formula: $\upsilon_{\mathrm{IV}\to\mathrm{III}} = (-0.486\Delta T + 0.592\Delta T^2 - 0.0015\Delta T^3) \cdot 10^{-2}$ cm/s, $\upsilon_{\mathrm{IV}\to\mathrm{III}} = (-0.49\Delta T + 0.563\Delta T^2 - 0.0018\Delta T^3) \cdot 10^{-2}$ cm/s, $\upsilon_{\mathrm{IV}\to\mathrm{III}} = (-0.437\Delta T + 0.484\Delta T^2 - 0.0014\Delta T^3) \cdot 10^{-2}$ cm/s where $\Delta T = T_{\mathrm{tr}} + T_0$. The activation energy of the process IV → III transformation was calculated, which is equal to $E = 85.5$ kJ/mol, $E = 82.8$ kJ/mol, $E = 84.8$ kJ/mol.

Keywords: Crystals, polymorphic transformations, activation energy.

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1. Introduction

Semiconductor compounds are widely studied due to their various physical properties. The study of structural transformations occurring in these materials under the action of external influences is important for studying their other physical properties [1–5]. In complex oxides, various phase transitions can be observed. Ferroelectric–paraelectric and ferromagnetic–paramagnetic phase transitions in these materials are widely studied [6–9]. Among complex oxides, nitrates occupy very special place. The structural phase transitions that occur in them have been understudied.

It is known that in the temperature range from room temperature to the melting point, rubidium nitrate has four, and cesium nitrate two different modifications [10–12]. Structural data of individual modifications and temperature intervals of their existence are given in Table 1.

The works [13,14] present the results of studies of the morphology and kinetics of crystal growth during polymorphic transformations in rubidium and cesium nitrates. Based on the obtained data on morphology and kinetics, the new modification was revealed in the crystals under study. As a result of the research, the commonality of the mechanism of crystal growth of a new modification inside the matrix in rubidium and cesium nitrates has been established.

According to the work data [15] at sufficiently high pressures, the high-temperature phases I and II of rubidium nitrate disappear, while phase III remains as the high-temperature phase. In the same way, phases I and II disappear from solid-state solutions of cesium nitrate in rubidium nitrate at cesium salt concentration ~ 25 mol% [16]. In the work [17] the phase behavior of cesium nitrate under irradiation with γ-quanta was studied by ultrasonics methods.

To elucidate the mechanism of polymorphic transformations in solid-state solutions of cesium nitrate in rubidium nitrate, we have planned a series of studies on the morphology and kinetics of crystal growth, and this work is one of them. It is dedicated to the study of the crystal growth kinetics of the III-modification as a function of temperature during the transformation of IV → III into $Rb_{1-x}Cs_xNO_3$ ($x = 0.025, 0.05, 0.1$).

2. Experiment details

The growth rate of the III-modification crystal nucleus inside the crystal of the IV-modification was measured on the same face (hkl) of the growing crystal by the methodology proposed in the work [18], i.e., the growth rate was measured at different temperatures in selected areas in the same crystal with size of $1 \times 0.5 \times 10$ mm (Fig. 1).

In order for the crystal to be in the thermostatically-controlled state, the heating element was tightly closed with the heat-insulating cap. The temperature of the crystal was measured by thermocouple, the solder connection of which touched the surface of the crystal. The measurement accuracy at 100° was ~ 0.5°.

With the help of an ocular grid, the section with the length of 1 mm was distinguished in the crystal. After measuring the velocity on one of the microscopes at a

Table 1. Structural data of modifications of rubidium and cesium nitrates and their temperature ranges of existence

Substance	Modification	Symmetry	Lattice parameters			Spatial group	Temperature interval of existence, T, K	Literature
			a, Å	b, Å	c, Å			
$RbNO_3$	I	Cubic	7.32			$Fm3m$	564–587	[1]
	II	Rhombohedral	5.48		10.71	$R3m$	492–564	[2]
	III	Cubic	4.35			$Fm3m$	437–492	[3]
	IV	Rhombohedral	10.48		7.45	$P3_1$	Below 437	[4]
$CsNO_3$	I	Rhombic	10.87		7.76	$P3/m$	434–687	[5]
	II	Cubic	8.98			$Pa3$	Below 434	[6]

Table 2. The results of measurements of the growth rate of the crystal of the III-modification during the polymorphic transformation IV → III into $Rb_{1-x}Cs_xNO_3$ ($x = 0.025, 0.05, 0.1$)

ΔT, K	$\frac{1}{T_0\Delta T}$ $\times 10^{-4}$ K^2	$Rb_{0.975}Cs_{0.025}NO_3$			$Rb_{0.95}Cs_{0.05}NO_3$			$Rb_{0.90}Cs_{0.10}NO_3$		
		$\bar{\vartheta}_{exp} \cdot 10^{-2}$, cm/s	$\vartheta_{calc} \cdot 10^{-2}$, cm/s	$\ln \vartheta$	$\bar{\vartheta}_{exp} \cdot 10^{-2}$, cm/s	$\vartheta_{calc} \cdot 10^{-2}$, cm/s	$\ln \vartheta$	$\bar{\vartheta}_{exp} \cdot 10^{-2}$, cm/s	$\vartheta_{calc} \cdot 10^{-2}$, cm/s	$\ln \vartheta$
1	15.1	0.98	0.104	−4.68	0.064	0.071	−7.35	0.063	0.045	−7.7
2	12.7	1.35	1.38	−4.30	0.98	1.26	−4.62	1.15	1.051	−4.55
3	8.48	3.67	3.83	−3.30	3.65	3.55	−3.31	3.23	3.007	−3.5
4	6.36	7.45	7.43	−2.59	5.64	6.93	−2.82	5.28	5.90	−2.82
5	5.08	12.84	12.18	−2.05	12.4	11.4	−2.08	9.37	8.77	−2.43
6	4.24	18.15	18.07	−1.70	16.8	16.9	−1.78	14.68	14.49	−1.93
7	3.63	24.65	25.09	−1.40	22.2	23.5	−1.50	20.81	20.17	−1.60
8	3.18	35.6	33.23	−1.09	32.5	31.2	−1.12	24.97	26.76	−1.31
9	2.82	41.82	42.48	−0.87	39.3	39.8	−0.93	33.89	34.25	−1.07
10	2.54	50.98	52.84	−0.67	46.7	49.6	−0.76	43.46	42.63	−0.85

temperature of $T_1 = T_0 + \Delta T_1$, the sample was transferred to the warm stage of another microscope at a temperature of $T_2 = T_0 + \Delta T_2$, where $\Delta T_2 > \Delta T_1$. Here, T_0 is temperature of equilibrium between III- and IV-modifications, ΔT is temperature of transformation delay. For single crystals $Rb_{1-x}Cs_xNO_3$ ($x = 0.025, 0.05, 0.1$) the equilibrium temperature between phases of IV- and III-modifications is $T_0 = 397$ K. Thus, the growth rate of the same crystal face of the III-modification was measured sequentially on the same crystal during the transformation of IV → III. The experimental data obtained are given in Table 2.

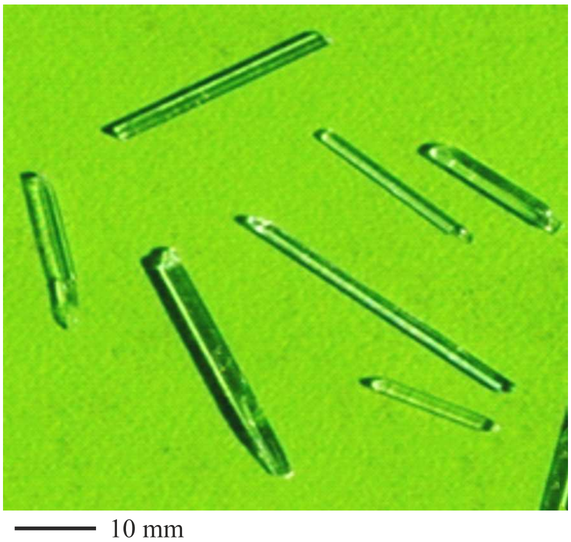

Figure 1. Single crystals $Rb_{1-x}Cs_xNO_3$ ($x = 0.025, 0.05, 0.1$) obtained from an aqueous solution at room temperature.

3. Results and discussion

The experimental data obtained from 3 crystals and processed using the „MATLAB“ [19] program give the functional dependence of the crystal growth rate of the III-modification on temperature in the form $\upsilon_{IV \to III} = (-0.486\Delta T + 0.592\Delta T^2 - 0.0015\Delta T^3) \cdot 10^{-2}$ cm/s for $Rb_{0.975}Cs_{0.025}NO_3$, $\upsilon_{IV \to III} = (-0.49\Delta T + 0.563\Delta T^2 - 0.0018\Delta T^3) \cdot 10^{-2}$ cm/s for $Rb_{0.95}Cs_{0.05}NO_3$ and $\upsilon_{IV \to III} = (-0.437\Delta T + 0.484\Delta T^2 - 0.0014\Delta T^3) \cdot 10^{-2}$ cm/s for $Rb_{0.90}Cs_{0.10}NO_3$, where $\Delta T = T_{tr} - T_0$. Figure 2 shows the diagrams of the crystal growth rate of the III-modification versus temperature, constructed from the experimental data and the given empirical formula. As can be seen from Table 2, at $\Delta T = 1$ K, the crystal growth rate of the III-modification during the IV → III transformation

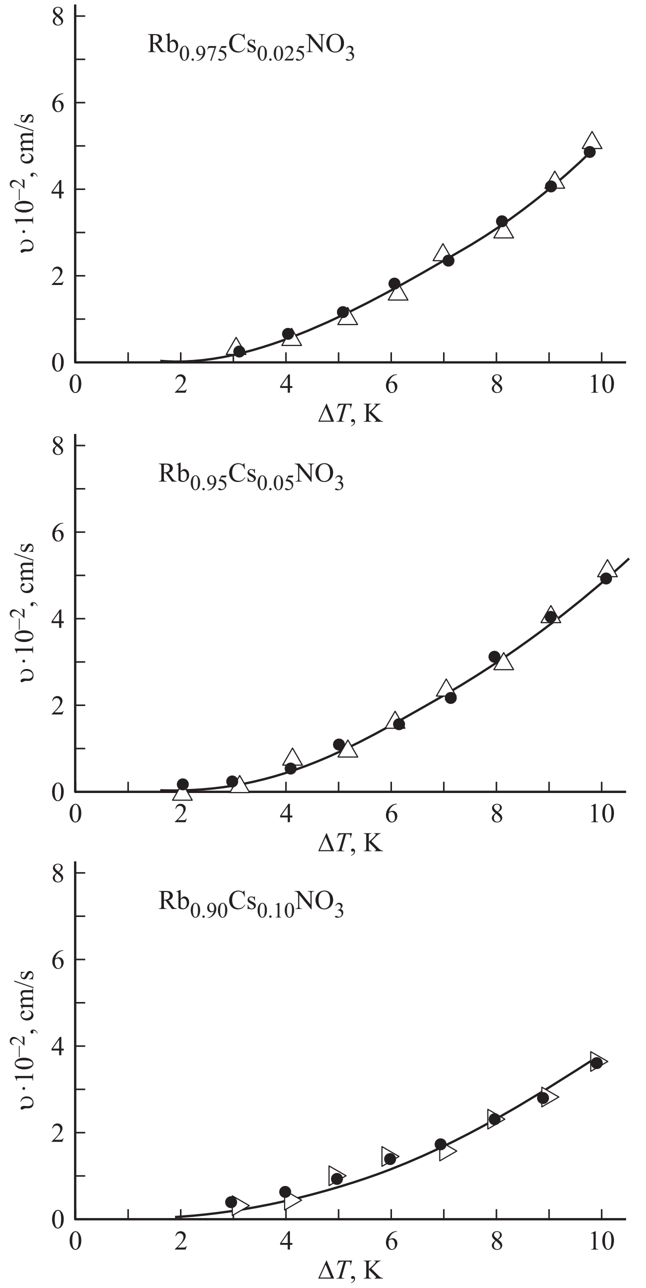

Figure 2. Dependence of a IV-crystal growth rate during transformation IV → III of $Rb_{1-x}Cs_xNO_3$ ($x = 0.025, 0.05, 0.1$): triangles — empirical data, circles — experimental data.

is negligibly small. As the temperature rises, the crystal growth rate of the III-modification increases.

According to the work data [13] at $\Delta T = 5\,K$ in rubidium nitrate, the growth rate of a III-crystal is $\upsilon = 2.46$ cm/s, but in our case $\upsilon = 12.8$ cm/s for $Rb_{0.975}Cs_{0.025}NO_3$, $\upsilon = 11.4$ cm/s for $Rb_{0.95}Cs_{0.05}NO_3$ and $\upsilon = 8.77$ cm/s for $Rb_{0.90}Cs_{0.10}NO_3$. This indicates that the partial replacement of Rb^{1+} ions in rubidium nitrate by Cs^{1+} ions leads to an increase in the crystal growth rate of the III-modification during the transformation IV → III.

The experimental data are well described by the formula obtained by M. Volmer [20] under the assumption that the growth of two-dimensional nuclei that appear on the face of the crystal occurs by sequential addition of individual atoms

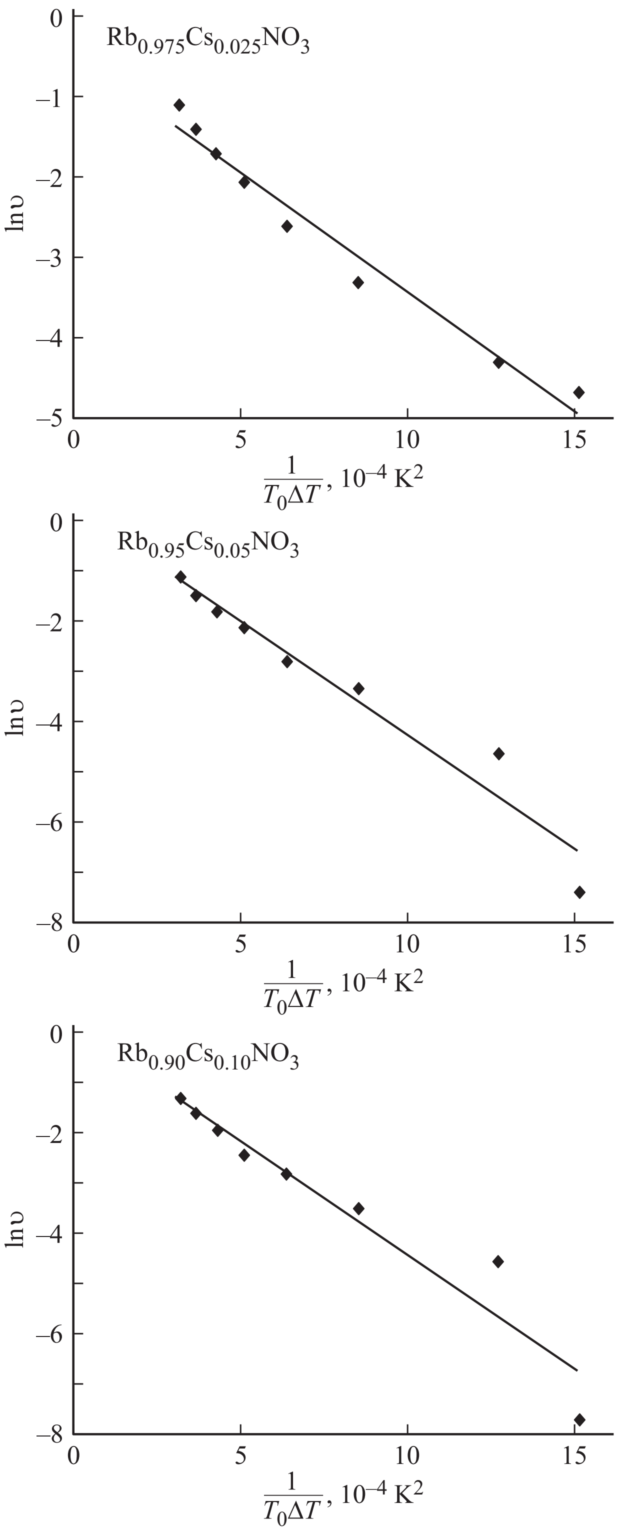

Figure 3. Dependence of $\ln\upsilon$ on $\frac{1}{T_0\Delta T}$ in $Rb_{1-x}Cs_xNO_3$ ($x = 0.025, 0.05, 0.1$).

Table 3. Activation energy and constants k_2, k_3 for polymorphic transformation IV → III in crystals $Rb_{1-x}Cs_xNO_3$ ($x = 0.025$, 0.05, 0.1)

Composition	Polymorphic transformation	k_2, deg	k_3, deg^2	Energy of activation, kJ/mol
$Rb_{0.975}Cs_{0.025}NO_3$	IV → III	10292	5433	85.5
$Rb_{0.95}Cs_{0.05}NO_3$	IV → III	10508	4491.7	82.8
$Rb_{0.90}Cs_{0.10}NO_3$	IV → III	10205	6620	84.8

or molecules:

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

where k_1 — in the first approximation can be taken independent of temperature and equal to $k_1 = B\nu d$ (ν — oscillation frequency of molecules, d — interatomic distance, B — number of molecules passing from the matrix crystal to the surface of the growing crystal), $k_2 = E/R$ — constant taking into account the energy threshold for the transition of molecules from the matrix crystal to the surface of the growing modification, k_3 — formation work of a two-dimensional nucleus of new modification, T_0 — equilibrium temperature.

It can be seen from Fig. 3 that the dependence of $\ln \nu$ is a linear function, i.e., experimental points fit on the straight line. From these straight lines, the values k_2 and k_3 were found and the activation energy of the IV → III transformation process for samples of $Rb_{1-x}Cs_xNO$ ($x = 0.025$, 0.05, 0.1) was calculated (see Table 3).

4. Conclusion

Analysis of the experimental data showed that with increasing temperature in the studied crystals of $Rb_{1-x}Cs_xNO_3$, the growth rate of the crystal of the III-modification at IV → III transformation increases due to partial substitution of Rb^+ ions in rubidium nitrate by Cs^+ ions. It should be noted that in the case of the $Rb_{1-x}Cs_xNO_3$ crystal, the activation energy of the IV → III transformation is less than in nitrate rubidium ($E = 99.2$ kJ/mol).

Conflict of interest

The authors declare that they have no conflict of interest.

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