KINETICS OF IV→III POLYMORPHOUS TRANSFORMATION IN $Rb_{0,95}Cs_{0,05}NO_3$ SINGLE CRYSTALS

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The crystal growth velocity of III-modification on temperature at IV→II transformation in $Rb_{0,95}Cs_{0,05}NO_3$ single crystals is measured by optical microscopy. It is shown that crystal growth velocity of III-modification in the dependence on temperature at empiric formula $\upsilon=(-0.49\Delta T+0.563\Delta T^2-0.0018\Delta T^2)\cdot 10^{-2}$cm/sec where $\Delta T=T_{trans}+T_0$. The activation energy of transformation process IV→III which is equal to E=23,72 kcal/mol has been calculated.

It is known that four rubidium nitrate and two cesium nitrate different modifications are established in temperature interval from room temperature up to melting point. The structural data of separate modifications and their temperature intervals of are given in table 1.

Table 1

Structural data of modifications of rubidium and cesium nitrates and their temperature intervals of existence

Substance	Modification	Symmetry	Lattice parameters			Space group	Temperature interval of existence, T, K	Reference
			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	$P3_1$	Less than 437	[4]
$CsNO_3$	I	Rhombohedral	10,87		7,76	P3/m	434-687	[5]
	II	Cubic	8,98			Pa3	Less than 434	[6]

The investigation results of morphology and crystal growth kinetics at polymorphous transformations in rubidium and cesium nitrates are given in works [7,8]. On the base of obtained data the new modification in investigated crystals has been revealed. As a result of investigations the community of crystal growth mechanism of new modification inside matrix one in rubidium and cesium nitrates.

According data [9] at enough high pressures the high-temperature phases I and II of rubidium nitrates disappear and III phase stays as a high-temperature one. Thus I and II phases disappear from solid solutions of cesium nitrate in rubidium nitrate at cesium salt concentration ~25mol% [10].

We are planning the series of investigations on morphology and kinetics of crystal growth for revealing of mechanism of polymorphous transformations in solid solutions of cesium nitrate in rubidium nitrate and the present work is dedicated to the one of such problems. This work is dedicated to investigation of kinetics of crystal growth of III-modification as temperature function at IV→III transformation in $Rb_{0,95}Cs_{0,05}NO_3$.

The crystal growth velocity of III-modification inside crystal of IV-modification is measured on the same face (hkl) of growing crystal by technique given in [11], i.e. the measurement of growth velocity is carried out at different temperatures on chosen regions in the same crystal of 1·0,5·10 dimension. The heating furnace is tightly closed by heat-insulated cap, thus the crystal is in temperature-controlled state. The crystal temperature is measured by thermocouple the junction of which is on crystal surface. The measurement accuracy at 100K is ~0,5K.

The region of length 1mm is isolated in crystal with help of graticule. After velocity measurement on the one of microscopes at $T_1=T_0+\Delta T_1$ temperature the sample is transferred on heating table of other microscope having the temperature $T_2=T_0+\Delta T_2$ where $\Delta T_2>\Delta T_1$. Here T_0 is equilibrium temperature between III and IV modifications; ΔT is temperature of transformation delay. The equilibrium temperature between crystals of IV and III modifications is T_0=397K. Thus, the velocity of the one and the same crystal face of III modification is measured continuously on the one and the same crystal at IV→III transformation. The obtained experimental data are given in table 2.

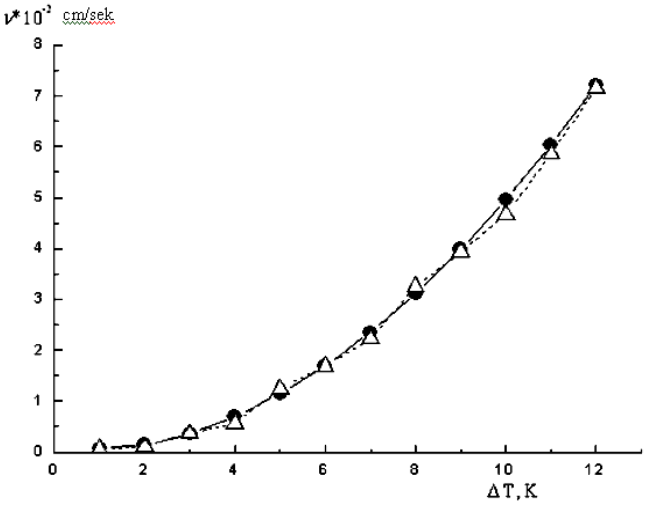

Fig.1. ● is empiric data, Δ is experimental data

Experimental data obtained from four crystals and treated with the help of methods of least squares, give the functional dependence of crystal growth velocity of III modification on temperature in the form:

$$\upsilon = (-0{,}49\Delta T + 0{,}563\Delta T^2 - 0{,}0018\Delta T^3)\cdot 10^{-2}\ cm/sec$$

where $\Delta T = T_{trans} - T_0$. The plots of crystal growth velocity of III modification on temperature constructed on experimental data and data of given empiric formula, are shown on fig.1.

Table 2.

The measuring results of crystal growth velocity of III modification at polymorphous transformation IV→III in $Rb_{0,95}Cs_{0,05}NO_3$.

ΔT, K	$\upsilon_{emp}\cdot 10^{-2}$ cm/sec	$\bar{\upsilon}_{exp}\cdot 10^{-2}$ cm/sec
1	0,071	0,064
2	1,26	0,98
3	3,55	3,65
4	6,93	5,64
5	11,4	12,4
6	16,9	16,8
7	23,5	22,2
8	31,2	32,5
9	39,8	39,3
10	49,6	46,7
11	60,3	58,5
12	72,1	71,6

As it is seen from table 2 *at* ΔT=1K the crystal growth velocity value of III modification at IV→III transformation is extremely small. The crystal growth velocity of III modification increases with temperature growth.

According data [7] at ΔT=5K in rubidium nitrate the crystal growth velocity of III modification is υ=2,46 cm/sec, but in our case is υ=11,4cm/sec. This proves the fact that the partial exchange of Rb^{1+} ions in rubidium nitrate by cesium ions Cs^{1+} leads to increase of values of crystal growth velocity of III modification at IV→III transformation.

Experimental data are well described by the formula obtained by *M*. Folmer [10] in suppositionthat the growth of two-dimensional germs appearing on crystal edge takes place by the way od continulos attachment of separate atoms or molecules:

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

where κ_1 can be accepted as independent one on temperature in first approximation and is equal to $\kappa_1 = Bvd$ (v is molecule oscillation frequency, d is interatomic space, B is molecule number transferring from matrix material on growing crystal surface $k_2 = \frac{E}{R}$ is constant taking into consideration the energy threshold for molecule transferring from matrix crystal on the surface of growing modification, κ_3 is formation work of two-dimension germ of new modification, T_0 is equilibrium temperature. From fig.2 it is seen that lnυ dependence on $\frac{1}{T_0\Delta T}$ presents itself the linear function, i.e. experimental points are on the direct line.

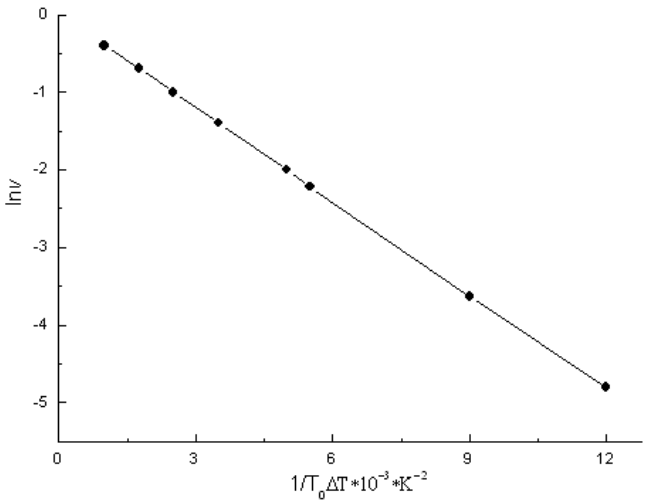

Fig.2. The lnυ dependence on $\frac{1}{T_0\Delta T}$ at IV→III transformation in $Rb_{0,95}Cs_{0,05}NO_3$.

From direct lines we founds the κ_2 and κ_3 values which are equal to 10508 degree и 4491,7 degree^2 and activation energy of transformation process IV→III for $Rb_{0,95}Cs_{0,05}NO_3$ which is equal to 20,8 kcal/mol.

For comparison let's note that activation energy of IV→III transformation in rubidium nitrate is E=23,72 kcal/mol, i.e. the partial exchange of Rb^{1+} ions in rubidium nitrate by Cs^{1+} ions leads to decrease of activation energy of polymorphous transformation.

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$Rb_{0,95}Cs_{0,05}NO_3$ MONOKRİSTALLARINDA IV→III POLİMORF ÇEVRİLMƏNİN KİNETİKASI

Optik mikroskop vasitəsilə $Rb_{0,95}Cs_{0,05}NO_3$ monokristallarında IV→III polimorf çevrilmə zamanı III-modifikasiya kristalının temperaturdan asılı olaraq böyümə sürəti ölçülmüşdür. Müəyyən edilmişdir ki, IV→III çevrilmə zamanı III-modifikasiya kristalının böyümə sürətinin temperatur asılılığı $\upsilon=(-0{,}49\Delta T+0{,}563\Delta T^2-0{,}0018\Delta T^3)\cdot 10^{-2}$sm/san, empirik düsturu ilə ifadə oluna bilər. Burada $\Delta T=T_{çev}-T_0$-dir. IV→III çevrilmənin aktivləşmə enerjisi hesablanmış və E=23,72 kkal/mol alınmışdır.

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КИНЕТИКА ПОЛИМОРФНЫХ ПРЕВРАЩЕНИЙ IV→III В $Rb_{0,95}Cs_{0,05}NO_3$ МОНОКРИСТАЛЛАХ

Методом оптической микроскопии измерена скорость роста кристаллов III-модификации от температуры при превращении IV→III в монокристаллах $Rb_{0,95}Cs_{0,05}NO_3$, Показано, что скорость роста кристаллов III-модификации в зависимости от температуры при превращении IV→II описывается эмпирической формулой $\upsilon=(-0{,}49\Delta T+0{,}563\Delta T^2-0{,}0018\Delta T^2)\cdot 10^{-2}$см/сек., где $\Delta T=T_{пр}+T_0$. Вычислена энергия активации процесса IV→III превращения, которая равна E=23,72 ккал/моль.

Received: 10.07.09