

UDC 621.315.592

THE KINETICS OF POLYMORPHIC TRANSFORMATION IN $K_{1-x}Cs_xNO_3$ ($x=0,015; 0,035; 0,045$) SINGLE CRYSTALS

V.I.Nasirov¹, R.B.Bairamov^{1,2}

(Presented by Academician of ANAS B.H.Tagiev)

Through the optical microscope in $K_{1-x}Cs_xNO_3$ ($x=0,015; 0,035; 0,045$) single crystals the speed of polymorphic transformation has been measured and during II→III transformation for temperature dependence the rate of growth of II crystal in $v = a\Delta T + b\Delta T^2 + c\Delta T^3$ form dependence on empirical has been identified. The activation energy of the process in all the samples were calculated.

Keywords: crystal, single crystals, polymorphic transformation, modification, kinetics, activation energy

Introduction

In order to study the polymorphic transformation mechanisms during that transformation the growth morphology of modification crystals, crystallographic direction of the relations between them as well as to explore the process of kinetics are important.

The transformation speed of one modification crystals to another modification crystals are the distinguishing factor from the fluctuations in aggregate state of matter. The speed of polymorphic transformation by depending on more factors, as well as temperature and pressure can be changed. The speed of polymorphic transformation depend on the size of crystal and by moving away from the balance temperature between two modification, this speed is getting increase. In terms of structure the speed of polymorphic transformation depending on energy intake height which prevents transformation. More precisely, for realization of this transformation is required certain activation energy. So, the transformation speed depending on the number of atoms which is higher from activation energy presented in

temperature, it means $e^{-\frac{E}{kT}}$ formed factor (there E - is an activation energy of the process. Therefore, in order to clarify the essence of the process it is important to measure of the speed of polymorphic transformation and evaluate activation energy. Specially introduced for this object in

$K_{1-x}Cs_xNO_3$ ($x=0,015; 0,035; 0,045$) crystals by measuring the speed of II→III polymorphic transformation, the activation energy of the process has been calculated.

The study of polymorphic transformation in nitrate compounds of alkaline metals has a great scientific and practical significance. On the one hand the lack of complete theory of structure requires the collection of numerous experimental facts. On the other hand the studied substances is widely applied in explosive objects, especially pyrotechnics, drugs.

Experimental part

There occurs two polymorphic transformation in each potassium and cesium nitrate crystals from room temperature to melting temperature. These transformations relating to enantiotropic characters. But during the cooling the potassium nitrate the two monotropy transformation, III→I and I→II transformation has been observed. According to experiments conducted by us there are not existing I modification [1] $K_{1-x}Cs_xNO_3$ crystals observed between in KNO_3 II and III modifications [2]. The crystal structure, crystal lattice parameters, space group of polymorphic modifications of potassium and cesium nitrate crystals and informations on existence has been issued in table 1.

Table 1

**The crystals and temperature existing fields of polymorphic modifications of
crystallography potassium and cesium nitrate**

Substance	Modification	Symmetry	The crystal lattice parameters				Sp. gr.	Modification existing temperature	References
			a, Å	b, Å	c, Å	α			
KNO_3	II	Rhombic	4,411	9,17	6,42		$Pnma$	300-400	3
	III	Rhombohedral	7,148	-	-	$44^{\circ}35'$	$R\bar{3}m$	400-610	4
	I	Rhombohedral	4,36	-	-	$76^{\circ}56'$	$R\bar{3}m$	383-397	5
$CsNO_3$	II	Trigonal	10,87	-	7,76		$P3/m$	300-434	6
	I	Cubic	8,98	-	-		$Pa3$	434-687	7

The II modification of the studied crystals has been obtained at a room temperature distillate through isothermal crystallization method in water from liquid of KNO_3 and $CsNO_3$. In order to achieve the cleanliness of the examples the obtained crystals was subjected to re-crystallization. During the experiment was used from needle-shaped crystals. The size of the examples were $1 \times 0,5 \times 10$ mm.

The measurements were conducted in optical polarization microscopy through offered method in [8] by special heating equipment in the same (hkl) plane of new growing crystals in inside of base crystal. The accuracy of the temperature of the crystal has been measured through thermocouple being $373K \pm 1K$. By conducting the measurement in each six crystal of the examples implemented by "MATLAB" program and during II→III transformation for temperature dependence of growing speed of the crystal inside the base crystal the following empirical dependence has been determined:

$$v = a\Delta T + b\Delta T^2 + c\Delta T^3$$

There $\Delta T = T_{trans} - T_0$, T_{trans} -polymorphic transformation temperature, is a balance temperature between T_0 – II and III modifications. In $K_{1-x}Cs_xNO_3$ ($x=0,015$; $0,035$; $0,045$) crystals during II→III polymorphic transformation for III-dependence of growing speed of modification crystals the obtained results has been issued and in obtained empirical expression the points of a , b , c constants has been issued in table 2.

Results

The obtained practical results show that, when the temperature is increasing, the speed of transformation II→III in studied crystals is getting high. As it seems from the table 2 the results obtained from experiment and empirical formula well combined with each other. In figure 1 for only one example $v=f(\Delta T)$ the formula of dependence has been issued for points calculated from obtained experiment and empirical formula. In addition to that in studied solid liquids the speed of II→III transformation, is high from clear KNO_3 . So, at $\Delta T=10K$ temperature at KNO_3 being II→III transformation $4,68 \cdot 10^{-2} \frac{cm}{sec}$ [7], in studied crystals: $K_{0,985}Cs_{0,015}NO_3$ $62,78 \cdot 10^{-2} \frac{cm}{sec}$, $K_{0,965}Cs_{0,035}NO_3$ in $63,123 \cdot 10^{-2} \frac{cm}{sec}$ and $K_{0,955}Cs_{0,045}NO_3$ in $65,181 \cdot 10^{-2} \frac{cm}{sec}$. The partial replacement of K^{+1} ions with Cs^{+1} ions in potassium nitrate it caused to ~ 14 times growth of II→III polymorphic transformation in obtained example. The polymorphic transformation speed in given temperature depending on the number of atoms which is high than activation energy. In viewed case the increasing of transformation speed in potassium nitrate the replacement energy of K^{+1} ions with Cs^{+1} ions can lead to the increase of the amount of ions being higher than activation energy.

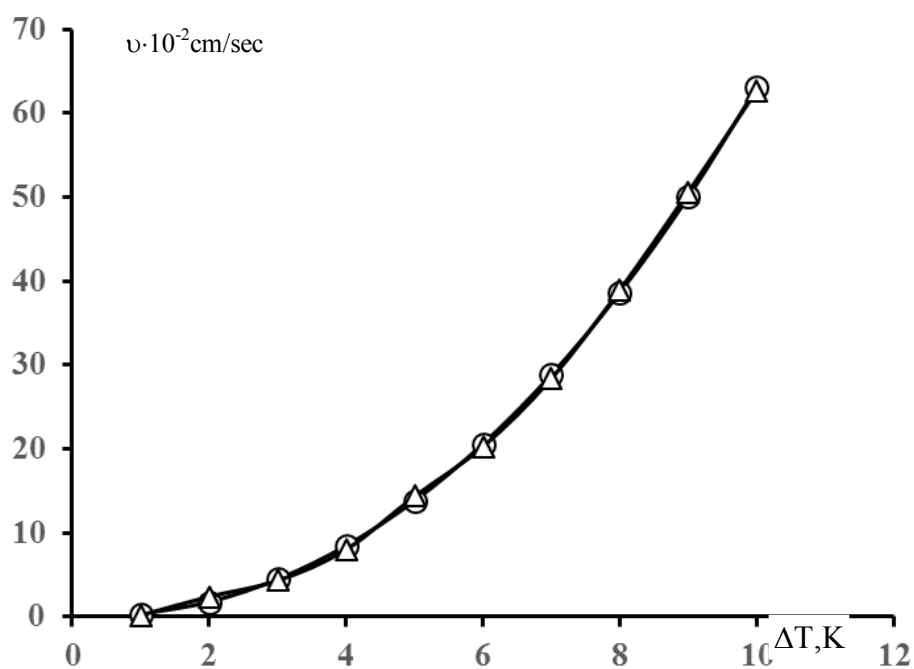


Fig.1. In $K_{0.985}Cs_{0.015}NO_3$ crystal $v=f(\Delta T)$ dependence graphic Δ -practical results, O-calculated results of empirical formula

Table 2

The results obtained from speed measurement in $K_{1-x}Cs_xNO_3$ ($x=0,015; 0,035; 0,045$) crystals

$\Delta T, K$	$x=0,015$			$x=0,035$			$x=0,045$		
	T_o, K	$\bar{v}_{tac} \cdot 10^{-2}$ cm/sec	$\bar{v}_{hes} \cdot 10^{-2}$ cm/sec	T_o, K	$\bar{v}_{tac} \cdot 10^{-2}$ cm/sec	$\bar{v}_{hes} \cdot 10^{-2}$ cm/sec	T_o, K	$\bar{v}_{tac} \cdot 10^{-2}$ cm/sec	$\bar{v}_{hes} \cdot 10^{-2}$ cm/sec
1	450 ± 1	0,145	0,282	452 ± 1	0,215	0,390	455 ± 1	0,212	0,654
2		2,380	1,745		3,613	2,123		3,816	2,559
3		4,283	4,446		4,860	5,195		5,852	5,738
4		7,984	8,446		8,640	9,599		9,723	10,213
5		14,340	13,805		15,73	15,331		15,633	16,010
6		20,256	20,583		21,922	22,386		22,724	23,151
7		28,372	28,841		30,482	30,759		31,318	31,659
8		38,940	38,640		40,915	40,446		42,728	41,558
9		50,623	50,038		52,218	51,440		53,042	52,870
10		62,780	63,097		63,123	63,737		65,181	65,621
	$a=-0,2863 \text{ deg}^{-1}$ $b=0,5593 \text{ deg}^{-2}$ $c=0,01003 \text{ deg}^{-3}$			$a=-0,2830 \text{ deg}^{-1}$ $b=0,674 \text{ deg}^{-2}$ $c=-0,0008326 \text{ deg}^{-3}$			$a=0,036666 \text{ deg}^{-1}$ $b=0,6136 \text{ deg}^{-2}$ $c=0,003894 \text{ deg}^{-3}$		

The results of speed measurement in potassium nitrate is well combined with equation [8] given by M.Folmer for two-dimensional embryonic growth from liquid phase:

$$v = \kappa_1 \exp\left(-\frac{\kappa_2}{T}\right) \left(-\frac{\kappa_3}{T_0 \Delta T}\right)$$

When this equation is being applied to crystal growth during polymorphic transformation k_2 -for passing from base crystal to growth crystal considering the required energy limit being stable to, $\frac{E}{R}$. There E , ending to 1mola activation energy, R -universal gas is stable.

In equation T_0 - is a balance temperature between modification, ΔT -temperature delay, being $k_1=Bvd$, there v -is a frequency of oscillation of molecules, d - the distance between atoms, B -is a number of molecule passing from base crystal to the surface of growing crystal, k_3 - is an energy spent for the creation of a two-dimensional crystal embryos. The Folmer equation $K_{1-x}Cs_xNO_3$ crystals the results obtained from speed measurement is well combined and the dependence of $\ln v$ from $\frac{1}{T_0 \Delta T}$ gives a straight line (table 3).

Table 3

In $K_{1-x}Cs_xNO_3$ ($x=0,015; 0,035; 0,045$) crystals for II→III, transformation ΔT , T_0 , $1/T_0 \Delta T$ and $\ln(v)$ points

$\Delta T, K$	$x=0,015$			$x=0,035$			$x=0,045$		
	T_0, K	$\frac{1}{T_0 \Delta T} \cdot 10^{-3} K^{-2}$	$\ln(\bar{v})$	T_0, K	$\frac{1}{T_0 \Delta T} \cdot 10^{-3} K^{-2}$	$\ln(\bar{v})$	T_0, K	$\frac{1}{T_0 \Delta T} \cdot 10^{-3} K^{-2}$	$\ln(\bar{v})$
1	450 ± 1	2,22	-6,536	452 ± 1	2,21	-6,142	455 ± 1	2,19	-6,156
2		1,1	-3,738		1,106	-3,32		1,09	-3,266
3		0,79	-3,15		0,73	-3,024		0,736	-2,838
4		0,55	-2,527		0,553	-2,448		0,549	-2,33
5		0,44	-1,942		0,442	-1,849		0,439	-1,856
6		0,37	-1,597		0,368	-1,522		0,366	-1,508
7		0,31	-1,26		0,316	-1,118		0,313	-1,161
8		0,27	-0,943		0,276	-0,905		0,44	-0,850
9		0,25	-0,68		0,245	-0,649		0,244	-0,634
10		0,22	-0,465		0,221	-0,46		0,219	-0,428

According to the trend line k_2 and k_3 ratios by determining the activation energy of II→III transformation were calculated. The obtained results has been given in table 4.

Table 4

$K_{1-x}Cs_xNO_3$ ($x=0,015; 0,035; 0,045$) for solid liquid crystals in II→III transformation the points of k_2 , k_3 ratios and activation energy

Composition	k_2, deg	k_3, deg^2	Activation energy $E, \text{kJ/mol}$
$K_{0,985}Cs_{0,015}NO_3$	12131	6156,6	100,8
$K_{0,965}Cs_{0,035}NO_3$	12209	5844	101,45
$K_{0,955}Cs_{0,045}NO_3$	12336	5561	102,5

As it seems from table 4 in potassium nitrate when the amount of replacement of K^{+1} ions with Cs^{+1} ions the activation energy of II→III transformation is getting higher. For comparison, it should be noted that, the activation energy of KNO_3 [1] II→III is $97,8 \frac{kJ}{mol}$. Here it can be concluded that, in KNO_3 in obtained crystals the partial replacement of K^{+1} ions with Cs^{+1} ions caused to activation energy of II→III polymorphic transformation.

REFERENCES

1. Асадов Ю.Г., Насиров В.И. // Кристаллография. 1970, т.15, №6, с.1204.

2. Nəsirov V.İ., Bayramov.R.B., Nəsirov E.V.// Repub. Conf. VIII problems of modern physics. materials. December 24-25, Baku, 2014, p.213
3. Edward D.A. // Z. Krist. 1943,v.80, p.154.
4. Tahvonen P.E. // Ann. Acad. Sci. Fennic., ser. A., 1947. v.44. p.20.
5. Bridgman P.W. // Pros. Ammer. Acad., Arts., 1916. v.52. p.57.
6. Fischmeister N.F. // J.Inorg.Nucl.Chem., 1956, v.3, p.182.
7. Korhonen U. // Ann. Acad. Sci. Fennical 1953, A1. p.150.
8. Асадов Ю.Г., Насиров В.И. // Кристаллография, 1972, т.17, № 5, с.991.
9. Volmer M. Kinetik der phasen // Drezden and Leipzig, 1934, v.3, p.38

¹Institute of Physics of ANAS
²Qafqaz University
 rabayramov@qu.edu.az

$K_{1-x}Cs_xNO_3$ (x=0,015; 0,035; 0,045) MONOKRİSTALLARINDA POLİMORF ÇEVİRİLMƏLƏRİN KİNETİKASI

V.İ.Nəsirov, R.B.Bayramov

Optik mikroskop vasitəsilə $K_{1-x}Cs_xNO_3$ (x=0,015; 0,035; 0,045) monokristallarında polimorf çevrilmələrin sürəti ölçülmüş və II→III çevrilmə zamanı II kristalın böyümə sürətinin temperatur asılılığı üçün $v = a\Delta T + b\Delta T^2 + c\Delta T^3$ formasında empirik asılılıq müəyyən edilmişdir. Nümunələrin hamısında prosesin aktivləşmə enerjisi hesablanmışdır.

Açar sözlər: kristal, monokristal, polimorf çevrilmə, modifikasiya, kinetika, aktivləşmə enerjisi

КИНЕТИКА ПОЛИМОРФНЫХ ПРЕВРАЩЕНИЙ В МОНОКРИСТАЛЛАХ $K_{1-x}Cs_xNO_3$ (x=0,015; 0,035; 0,045)

В.И.Насиров, Р.Б.Байрамов

Методом оптической микроскопии исследована кинетика полиморфных превращений в монокристаллах $K_{1-x}Cs_xNO_3$ (x=0,015; 0,035; 0,045) и установлена эмпирическая зависимость скорости роста кристалла III–модификации при превращении II→III в зависимости от температуры в виде: $v = a\Delta T + b\Delta T^2 + c\Delta T^3$. Вычислена энергия активации процесса для каждого образца.

Ключевые слова: кристалл, монокристалл, полиморфные превращения, модификация, кинетика, энергия активации