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KINETICS OF STRUCTURAL PHASE TRANSFORMATIONS IN $K_{0.945}Ag_{0.055}NO_3$ and $K_{0.945}Cs_{0.055}NO_3$ MONOCRYSTALS

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ABSTRACT

In this work have been presented the result of investigation of $K_{0,945}Ag_{0,055}NO_3$ and $K_{0,945}Cs_{0,055}NO_3$ single crystals were grown from aqueous solution of KNO_3, $AgNO_3$ and $CsNO_3$ using isothermal crystallization method. Then, structural and phase transformations in samples were studied by X-ray and optical microscopy methods. It has been determined that in $K_{0,945}Ag_{0,055}NO_3$ monocrystal at T>393K temperature, in $K_{0,945}Cs_{0,055}NO_3$ monokrystal at T>455K temperature the rhombic (II) → hexagonal (III) transformation occurs with the formation and growth of the III - modification crystal embryo within II – modification. The results obtained from the kinetic studies were determined that the temperature dependence of the conversion rate of II → III in $K_{0,945}Ag_{0,055}NO_3$ and $K_{0,945}Cs_{0,055}NO_3$ single crystals can be expressed by an empirical formula of $\upsilon = (a\Delta T + b\Delta T^2 + c\Delta T^3) \cdot 10^{-2} \frac{cm}{sec}$. $\Delta T = T_t - T_0$ is temperature delay, $T_t -$ is transformation temperature and $T_0 -$ is equilibrium temperature between interconverting modification crystals. Based on the results of velocity measurements, the activation energy of II→III polymorphic transformations were calculated.

$K_{0,945}Ag_{0,055}NO_3$ və $K_{0,945}Cs_{0,055}NO_3$ MONOKRİSTALLARINDA QURULUŞ FAZA ÇEVRİLMƏLƏRİNİN KİNETİKASI

XÜLASƏ

İzotermik kristallaşma üsulu ilə KNO_3, $AgNO_3$ və $CsNO_3$-ün suda məhlulundan $K_{0,945}Ag_{0,055}NO_3$ və $K_{0,945}Cs_{0,055}NO_3$ monokristalları yetişdirilmiş, rentgenoqrafik və optik mikroskopiya üsulları ilə həmin nümunələrdə quruluş faza çevrilmələri tədqiq olunmuşdur. Müəyyən edilmişdir ki, $K_{0,945}Ag_{0,055}NO_3$ monokristalında T>393K temperaturda, $K_{0,945}Cs_{0,055}NO_3$ monokristalında isə T>455K temperaturda rombik (II) → heksaqonal (III) çevrilməsi II – modifikasiya daxilində III - modifikasiya kristalı rüşeyiminin yaranması və böyüməsi ilə gedir.

Kinetik tədqiqatlardan alınan nəticələr MATLAB proqramı əsasında işlənərək müəyyən edilmişdir ki, $K_{0,945}Ag_{0,055}NO_3$ və $K_{0,945}Cs_{0,055}NO_3$ monokristallarında II → III çevrilmə sürətinin temperatur asılılığı $\upsilon = (a\Delta T + b\Delta T^2 + c\Delta T^3) \cdot 10^{-2} \frac{sm}{san}$ emprik düsturu ilə ifadə oluna bilər. Burada $\Delta T = T_ç - T_0$ temperatur yubanması olub, $T_ç -$çevrilmə, $T_0 -$qarşılıqlı çevrilən modifikasiya kristalları arasında tarazlıq temperaturudur. Sürət ölçmələrinin nəticələri əsasında II → III polimorf çevrilmənin aktivləşmə enerjisi hesablanmışdır.

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

КИНЕТИКА СТРУКТУРНЫХ ФАЗОВЫХ ПРЕВРАЩЕНИЙ В МОНОКРИСТАЛЛАХ $K_{0,945}Ag_{0,055}NO_3$ и $K_{0,945}Cs_{0,055}NO_3$

РЕЗЮМЕ

Монокристаллы $K_{0,945}Ag_{0,055}NO_3$ и $K_{0,945}Cs_{0,055}NO_3$ были выращены на водных растворах KNO_3, $AgNO_3$ и $CsNO_3$ методом изотермической кристаллизации. После этого структурные и фазовые превращения в этих образцах были изучены методами рентгеновской и оптической микроскопии. Установлено, что в монокристалле $K_{0,945}Ag_{0,055}NO_3$ при температурах T>393K, в монокристалле $K_{0,945}Cs_{0,055}NO_3$ при температурах T>455K происходит переход ромбическое (II) → гексагональное (III) превращение с образованием и ростом III – модификация кристаллического зародыша внутри II – модификации.

Результаты кинетических исследований были обработаны на основе программы MATLAB и установлено, что температурная зависимость скорости конверсии II → III в монокристаллах $K_{0,945}Ag_{0,055}NO_3$ и $K_{0,945}Cs_{0,055}NO_3$ может быть выражена эмпирической формулой $\upsilon = (a\Delta T + b\Delta T^2 + c\Delta T^3) \cdot 10^{-2}\,\frac{\text{см}}{\text{сек}}$. Здесь $\Delta T = T_{\text{п}} - T_0$ температурная задержка, $T_{\text{п}}$- температура превращения, а T_0 − температура равновесия между кристаллами взаимопревращающихся модификаций. По результатам измерений скорости рассчитана энергия активации полиморфных превращений II → III.

Ключевые слова: монокристалл, полиморфное превращение, модификация, кинетика, энергия активации.

Introduction

The investigation of structural transformations in potassium salts is of great scientific importance. Thus, the potassium salt crystals can be used as various converting devices, memory elements and heat radiation sensors. The structural transformation studies in the crystal and solid solutions of this substance can allow to determine its behavior in case of large dynamic loading (in the area of large deformation, explosions) or to eliminate the structural transformations during the application of this material. In addition, the results of the experiments can be applied in the methods of obtaining nanostructured materials.

The study of structural phase transformations in nitrate compounds of alkali metals, including potassium and silver nitrate crystals, is of great scientific and practical importance. Despite numerous experimental results, there is still no complete theory of the polymorphic transformation process. On the other hand, these substances are used for different purposes in different areas of our life. This includes the wide applications of these substances in explosives, glass production, drug preparation, robotics, solid rocket fuel preparation and other fields. In addition, these substances are used in the preparation of various converter devices, as memory elements and heat radiation transmitters [1, 2]. These investigations require studying the growth morphology of the modification crystals that are mutually transformed during these transformations. That is why the kinetics of structural transformations in $K_{0,945}Ag_{0,055}NO_3$ and $K_{0,945}Cs_{0,055}NO_3$ crystals have been studied in this work. The first two crystals are rhombic at room temperature and rhombohedral after structural transformation. *$CsNO_3$* has a trigonal lattice at room temperature, and a cubic lattice after transformation. All three of these transformations are enantiotropic and they are single crystal-single crystal type [3-9]. The crystallographic results of the polymorphic modifications of all three crystals and the temperature ranges of existence are represented in table 1.

Table 1. Crystallographic parameters of polymorphic modifications of KNO_3, $AgNO_3$ and $CsNO_3$ and temperature ranges of existence

Compound	Symmetry	Lattice parameters			Phase group	Existence temperature T,K	Reference
		a, Å	b, Å	c, Å			
KNO_3	Rhombic	5,411	9,164	6,431	*Pmcn*	300-400	3, 4
	Rhombohedral	5,43	-	9,112	$R\bar{3}m$	400-610	3, 4
	Rhombohedral	5,42	-	19,41	$R\bar{3}m$	397-383	5, 6
$AgNO_3$	Rhombic	6,997	7,325	10,118	Pbca	300-432,5	3, 7
	Rhombohedrik	5,203		8,522	$R\bar{3}m$	432,5-438	3, 7
$CsNO_3$	Trigonal	10,87	-	7,76	*P3/m*	300-434	3, 8
	Cubic	8,98	-	-	*Pa3*	434-687	9

In order to investigate the mechanism of structural transformations in the solid solutions of the compounds mentioned, a number of experiments were conducted and the results based on experiments was investigated [11-13].

Research method and research

Single crystals of $K_{0,945}Ag_{0,055}NO_3$ and $K_{0,945}Cs_{0,055}NO_3$ solid solutions were obtained by isothermal crystallization method from aqueous solutions of "ЧДА" type KNO3, AgNO3 and CsNO3 compounds, respectively. The samples were needle-shaped and planar plate-shaped. The length of the needle is oriented in the [001] crystallographic direction. The crystallization process was repeated several times in order to obtain perfect crystals. Among the obtained crystals, $1\times0.5\times10 mm^3$ crystals were selected for conducting microscopic studies.

Researches were carried out using a "Levenhuk C 310" type film camera in a MIN-8 brand polarizing microscope equipped with a special heater. The temperature of the crystal was measured using a copper-constantan thermocouple. The accuracy of the measurements was $\pm1^0C$ at 100^0C. Since the velocity measurements were carried out around the equilibrium temperature of the interconverting modification crystals, that temperature was determined first. It was determined that this temperature was 393 $\pm$1K for $K_{0,945}Ag_{0,055}NO_3$ and 455 $\pm$1K for $K_{0,945}Cs_{0,055}NO_3$.The temperature dependence of the new crystal growth rate during structure transformations was carried out by the method given in the work of [10].

During the experiments, the following were strictly observed:

1. The speed of movement of the boundary separating two modifications was measured only in the [001] crystallographic direction.
2. Only the rate of single-crystal-single-crystal conversion was measured.
3. During the experiment crystals of the same size and shape grown under the same conditions were used.

Measurements were made on six samples of each composition and the results obtained are given in table 2.

Table 2. Results from velocity measurements on $K_{0,945}Ag_{0,055}NO_3$ and $K_{0,945}Cs_{0,055}NO_3$ crystals

	$K_{0,945}Ag_{0,055}NO_3$			$K_{0,945}Cs_{0,055}NO_3$		
ΔT,K	T_o,K	$\overline{\upsilon}_t \cdot 10^{-2}$ cm/sec	$\overline{\upsilon}_h \cdot 10^{-2}$ cm/sec	T_o,K	$\overline{\upsilon}_t \cdot 10^{-2}$ cm/sec	$\overline{\upsilon}_h \cdot 10^{-2}$ cm/sec
1		0,056	0,472		0,215	0,340
2		2,514	1,883		3,912	2,157
3		4,342	4,273		5,918	5,429
4		6,523	7,681		9,650	10,138
5		12,635	12,150		14,513	16,263
6	**393±1**	18,240	17,717	**455±1**	23,420	23,783
7		24,438	24,425		32,226	32,679
8		32,525	32,314		44,745	42,432
9		40,521	41,423		55,322	54,519
10		52,241	51,793		66,356	67,423

In figures 1 and 2 the graps of results obtained by the experiments and the empirical formula are represented for the temperature dependence of the rate of structural transformations in $K_{0,945}Ag_{0,055}NO_3$ and $K_{0,945}Cs_{0,055}NO_3$ crystals, respectively. The experimental results are met with the theoretical calculations and it can be observed in graphs.

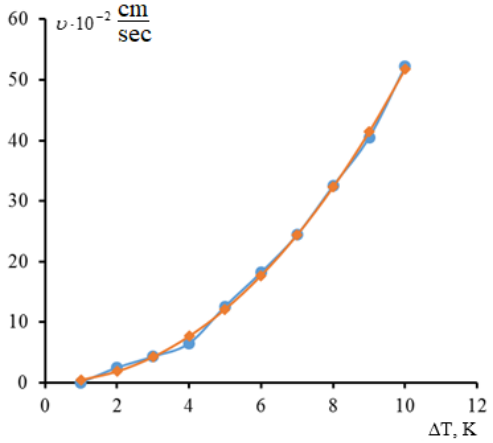

Figure 1. Graph of temperature dependence of growth rate of III-modification crystal in II→III transformation in $K_{0,945}Ag_{0,055}NO_3$ crystal. •-empirical datas; ◊-experimental datas

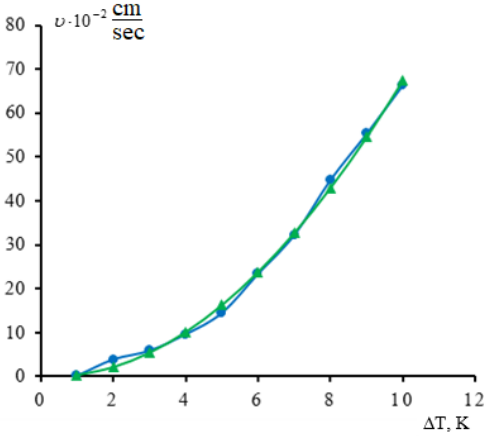

Figure 2. Graph of temperature dependence of growth rate of III-modification crystal in II→III transformation in $K_{0,945}Cs_{0,055}NO_3$ crystal. •-empirical datas; Δ- experimental datas

Conclusion

The conclusion of the obtained results showed that the mentioned partial replacement leads to an increase in the conversion speed. At a temperature of 10K this speed is is $52 \cdot 10^{-2}$cm/sec in $K_{0,945}Ag_{0,055}NO_3$, and $66 \cdot 10^{-2}$cm/sec in $K_{0,945}Cs_{0,055}NO_3$. /sec, while in KNO_3 is $5x10^{-2}$cm/sec as shown in table 2. In other words, as a result of this substitution, the rate of structure transformation has increased approximately 10 times. We think that partial replacement of K^+ ions by Ag^+ and Cs^+ ions in KNO_3 causes the energy barrier height to decrease. So, the speed is determined by the factor of $\upsilon \approx e^{\frac{E}{kT}}$, where E is the activation energy of the process. The activation energy is calculated based on the velosity mesurement results.

In order to evaluate the process of polymorphic transformation in terms of energy, the equation [14] given by M. Folmer for crystal growth from the liquid phase with a two-dimensional mechanism has been used:

$$\upsilon = \kappa_1 \, exp(-\frac{\kappa_2}{T_0}) \, exp(-\frac{\kappa_3}{T_0 \Delta T})$$

When this equation is applied to crystal growth during polymorphic transformation, k_2-is a constant that takes into account the energy limit necessary for the transfer of molecules from the parent crystal to the surface of the newly grown crystal and it is equal to $\frac{E}{R}$. Here E is the activation energy per 1 mole, R is the universal gas constant. In the equation T_0- is the equilibrium temperature between modifications, ΔT – is the temperature delay. k_1=Bνd and ν- is oscillation frequency of molecules, d- is interatomic distance, B- is number of molecules passing from parent crystal to growing crystal surface, k_3- is energy used for generation of two-dimensional crystal embryo. The Folmer equation also agrees well with the results obtained from velocity measurements on $K_{0,945}Ag_{0,055}NO_3$ and $K_{0,945}Cs_{0,055}NO_3$ crystals and the dependence slope of lnυ on $\frac{1}{T_0 \Delta T}$-is a straight line. According to the inclination of that straight line, k_2 and k_3 coefficients were determined, and the activation energy of II→III transformation was calculated in the studied crystals. The obtained results are given in table 3.

Table 3. Values of coefficients k_2, k_3 and activation energy in II→III transformation for $K_{0,945}Ag_{0,055}NO_3$ and $K_{0,945}Cs_{0,055}NO_3$ single crystals.

Content	k_2,deg^{-1}	k_3,deg^{-2}	Activation energy E, kJ/mol
$K_{0,945}Ag_{0,055}NO_3$	10877,5	4028,4	90,38
$K_{0,945}Cs_{0,055}NO_3$	12392,8	4121,9	102,98

As can be seen from Table 3, the rate of rhombic→hexagonal transformation in the $K_{0,945}Ag_{0,055}NO_3$ crystal increases as the temperature increases and the partial replacement of K+ ions by Ag+ ions in KNO_3 leads to a decrease in the activation energy. So, while the activation energy of the rhombic→hexagonal transformation for potassium nitrate is 97.8 kJ/mol, for $K_{0,945}Ag_{0,055}NO_3$ is 90.38 kJ/mol. On the other hand, the activation energy is 102.98 kJ/mol in the II→III transformation in the $K_{0,945}Cs_{0,055}NO_3$ crystal.

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