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STRUCTURE SPACE CONVERSIONS IN $K_{0,955}Cs_{0,045}NO_3$ SOLID SOLUTION CRYSTAL

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$K_{0,955}Cs_{0,045}NO_3$ monocrystals have been achieved by the use of isothermal crystallization and polymorph conversions have been analyzed in the samples obtained with optical microscope and x-ray methods. It has been determined that $K_{0,955}Cs_{0,045}NO_3$ crystal has an orthorhombic cage space group of which is Pmcn with a=5,4199Å, b=6,4363Å, c=9,1648Å, parameters at a room temperature. At T>455K temperature, this orthorhombic cage is converted into rhombohedral cage space group of which is $R\bar{3}m$ with a=5,4250Å, c=9,8360Å parameters. It has been clear that II↔III conversion in analyzed crystals occurs with the formation and growth of newly created crystal embryo within the main crystal. New modification embryo firstly grows in [100] crystallographic direction of the main crystal and after the growth ends in this direction, it continues in [001] crystallographic direction of the crystal. $K_{0,955}Cs_{0,045}NO_3$ II→III conversion is of monocrystal↔monocrystal type and is characterized as enantiotropic.

Keywords: *crystal, single crystals, polymorphic, polymorphic transformation, modification*

Introduction

The issue of structure stability of substances including crystals depending on external situations is one of the main problems of solid-state physics. As crystals are frequently used in different spheres of science and technology, this problem turns out to be actual. From this perspective, researches on mechanism of structural conversions because of temperature are both scientifically and practically important. Thus, these conversions are closely related to technologies of materials.

The article is on mechanism of II↔III polymorph conversions in $K_{0,955}Cs_{0,045}NO_3$ crystals and the morphology of crystal growth, crystal structure, and cage stabilities of the very crystals have been determined with the aid of optical microscope and roentgenographic methods. It is worth mentioning that learning of polymorph conversions in nitrate compounds of alkali is both scientifically and practically important as these substances are used in pyrotechnics, medicine materials and so on.

It is known that both KNO_3 and $CsNO_3$ undergo two polymorph conversions from room temperature until the melting point [1-4]. While cooled, one more structural conversion is observed in KNO_3 [5]. Crystallographic information of these modifications is given in Table 1.

Many researches have been conducted on structural conversions of nitrate compounds of alkali including potassium and caesium [6-9]. Different authors have done various researches on hard solutions of these substances [10-12]. $K_{1-x}Ag_xNO_3$, $K_{1-x}Rb_xNO_3$, $Rb_{1-x}Cs_xNO_3$, $Rb_{1-x}Ag_xNO_3$ hard solution crystals have been grown and analyzed by us and interesting solutions have been gotten [13-15]. Being the continuation of the mentioned researches, this article is on the research of structure space conversions in, $K_{0,955}Cs_{0,045}NO_3$ crystals with the aid of optical microscope and x-ray methods.

Experimental method

The analyzed sample has been obtained from water solution of KNO_3 and $CsNO_3$ compounds at room temperature using the isothermal crystallization method. The samples were generally taken in a plane board shape and needle-shaped form. The dimensions of the needle were 1×0,5×10 mm in the crystallographic direction (Fig. 1).

Table 1

Structural data for different modifications of KNO_3 and $CsNO_3$ and the temperature ranges of their existence

Composition	Symmetry	Lattice parameters				Sp.gr.	Modification existing temperature T,K
		a, Å	*b*, Å	*c*, Å	α		
KNO_3	Rhombic	4,411	6,42	9,17		*Pnma*	300-400
	Rhombohedral	7,148	-	-	$44^0 35^/$	$R\bar{3}m$	400-610
		4,35	-	-	$76^0 56^/$	$R\bar{3}m$	383-397
$CsNO_3$	Trigonal	10,87	-	7,76		*P3/m*	300-434
	Cubic	8,98	-	-		*Pa3*	434-687

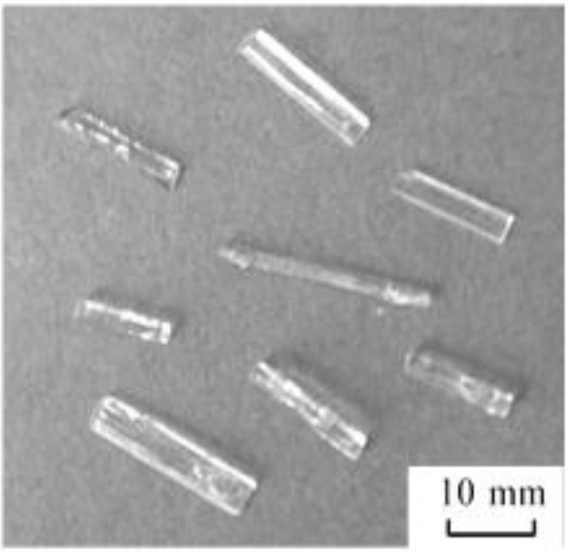

Fig. 1. $K_{0.955}Cs_{0.045}NO_3$ single crystals obtained from an aqueous solution

Morphological researches were conducted with heater provided МИН-8 type polarization microscope and the conversion process was filmed on a computer with the usage of “Levenhuk C310 NK” brand film camera. The tip of thermocouple with ±0,5 K accuracy at 373 K touched directly on the surface of the sample. Before the morphological researches were conducted, the balance temperature was determined among II and III modification crystals. T_0=455±1K was determined for that temperature.

Experiments conducted with optical microscopes showed that II→III polymorph conversions in $K_{0,955}Cs_{0,045}NO_3$ mono crystal always happen at $T>T_0$ temperature. The process is observed with the appearance and growth of rhombohedral crystal embryo in orthorhombic crystal. As it is clear from the Figure 2, III crystal embryo that is formed within the main crystal in the course of II→III conversion mainly grows in the crystallographic direction (compare photo 2 and 3).

After the first embryo is formed, more three embryos of III modification crystal are formed within the main crystal (photo 4). The very embryos are shown with arrows in the photo. The growth of the following embryos happen in [100] and [001] directions. However, in all cases $\upsilon_{[100]}>\upsilon_{[001]}$ is observed. Photo 5 shows that four of III crystal embryos take part in II→III conversion process. In the conclusion, unique III modification crystal is formed (photo 6). When the crystal is cooled, counter conversion is observed at $T<T_0$ temperature. This process also happens with the formation and growth of II modification crystal embryo within III modification crystal (photo 7).

The analysis of experimental outcomes reveal the fact that II→III polymorph conversions in $K_{0,955}Cs_{0,045}NO_3$ crystals are observed with the formation and growth of newly formed embryos within the main crystals. Partial replacement of K^+ ions with Cs^+ ions in potassium nitrate result with ~50K increase in conversion temperature.

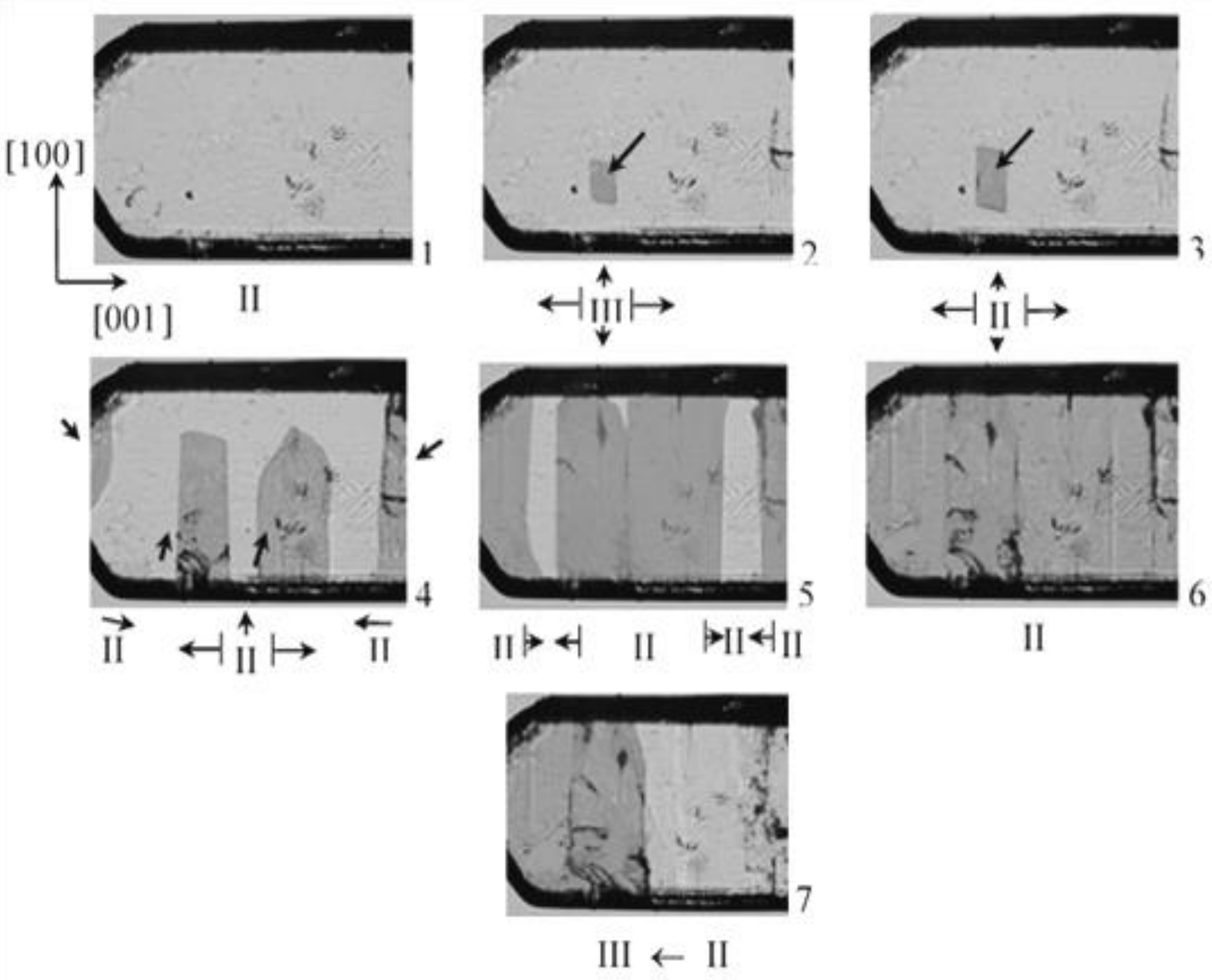

Fig. 2. Optical micrographs of the growth of crystals III and II at the II↔III polymorphic transformation in $K_{0.955}Cs_{0.045}NO_3$ (magnification of 90)

Roentgenographic researches in $K_{0,955}Cs_{0,045}NO_3$ crystals were conducted in D8 ADVANCE type roentgen diffractometer of Bruker company (Germany) at CuK_α (λ=1,5406 Å) radiation in 300≤T≤600K temperature interval in TTK 723K temperature chamber in 40 kV, 40 mA regime. The indexation of obtained diffraction reflections was realized on the base of TOPAS and EVA programs. As the applied roentgen diffractometer was considered for powder, the obtained mono crystals were turned into powder and researches were conducted in $10^0 \leq 2\theta \leq 80^0$ angle intervals. The diffraction reflections observed at a room temperature (T=300K) were indexed in orthorhombic cage space group of which was *Pmcn* with *a*=5,4199Å, *b*=6,4363Å, *c*=9,1648Å parameters. In the following stages of experiments, temperature was increased and shootings were realized in a isothermal condition after each 10K. Before each shooting, the crystal was kept in stable temperature for 30 minutes.

The experiments showed that the structure of researched crystal change in T>455K temperature and orthorhombic cage is converted into a this orthorhombic cage is converted into rhombohedral cage space group of which is $R\bar{3}m$ with *a*=5,4250Å, *c*=9,8360Å parameters. When the crystal is cooled, the counter process - rhombohedral - orthorhombic conversion – is observed. The following structural conversions are observed in 300÷600K temperature interval in $K_{0,955}Cs_{0,045}NO_3$ crystals that were obtained as a result of partial replacement of K^+ ions with Cs^+ ions.

Orthorhombic		Rhombohedral
a=5,4199Å *b*=6,4363Å *c*=9,1648Å sp.gr. *Pmcn*	T>455K → T<455K ←	*a*=5,4250Å *c*=9,8360Å sp.gr. $R\bar{3}m$

Conclusions

Thus, II↔III polymorph conversion in $K_{0,955}Cs_{0,045}NO_3$ crystals is of monocrystal↔monocrystal type and is characterized as enantiotropic. The conversion process happens with the formation and growth of newly formed crystal embryos. Partial replacement of K^+ ions with Cs^+ ions result with ~50K increase in conversion temperature. Numerous experiments have proved that interval I modification no longer exist beteen III and II modifications as it is shown in the sample.

The analysis of Table 2 shows that (221), (202), (310), (014), (400), (351) planes of orthorhombic modification coincide with (104), (202), (210), (300), (220) and (132) planes of rhombohedral modification. It can be said that solid crystallographic direction exists between II and III modification in the course of II↔III conversion in $K_{0,955}Cs_{0,045}NO_3$ crystals.

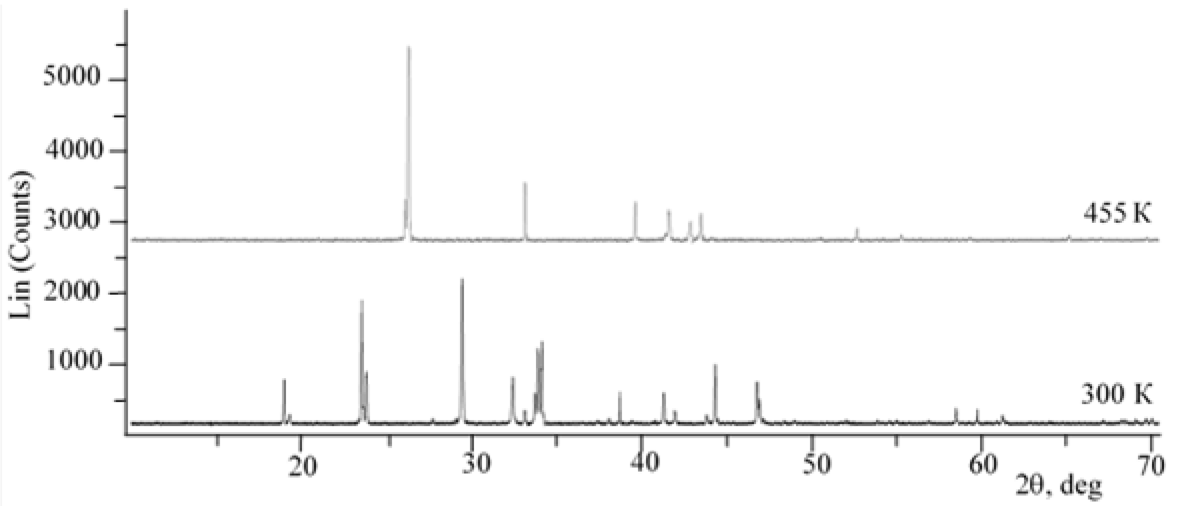

Fig. 3. Diffraction patterns of $K_{0.955}Cs_{0.045}NO_3$ crystal at different temperatures

Table 2

Calculated diffraction patterns of a $K_{0,955}Cs_{0,045}NO_3$ crystal, recorded at different temperatures (*CuK*$_\alpha$ radiation, λ=1,5406 Å, 40kV, 40mA)

T_{exp}, K	2θ, deg.	d_{exp}, Å	I/I_0, %	hkl	Unit-cell parameters
1	2	3	4	5	6
300	19,029	4,6602	9,9	110	Orthorhombic *a*=5,4199 Å *b*=6,4363 Å *c*=9,1648 Å sp.gr. *Pmcn*
	23,551	3,7746	38,5	111	
	23,817	3,73295	15,2	021	
	29,035	3,03639	100	012	
	32,339	2,7607	39,7	102	
	32,414	2,75983	14,3	031	
	33,077	2,706	11,9	200	
	33,662	2,66036	40	130	
	33,622	2,64808	59,5	022	
	34,014	2,63358	52,5	022	
	38,609	2,33006	12,3	220	
	40,69	2,21562	3,3	032	

1	2	3	4	5	6
	41,169	2,19091	22,7	221	
	43,669	2,07112	8,8	202	
	44,132	2,0544	26,5	132	
	46,565	1,94882	25,1	113	
	46,712	1,94302	16,7	023	
	51,595	1,7703	3,7	310	
	58,162	1,58483	5,9	014	
	59,457	1,55337	6	330	
	60,856	1,52096	6	114	
	60,979	1,5182	6,7	024	
	67,692	1,38303	44	204	
	67,866	1,37992	4,5	062	
	68,565	1,36755	7,5	214	
	69,407	1,353	4,5	400	
	75,316	1,26082	3,3	351	
455	20,938	4.23939	2,3	101	Rhombohedral a=5,4250 Å, c=9,8360 Å, sp.gr. $R\bar{3}m$
	26,211	3,39716	100	102	
	27,177	3,27867	2,8	003	
	32,996	2,71249	25,3	110	
	37,878	2,37518	1,5	112	
	39,405	2,28483	20	201	
	41,412	2,17863	11,9	104	
	42,618	2,11969	11	202	
	43,255	2,08996	8,2	113	
	50,26	1,82181	1,6	114	
	51,417	1,77574	1,3	210	
	52,31	1,74749	7,1	211	
	53,936	1,69858	1,2	204	
	54,929	1,6702	2,3	122	
	58,927	1,56606	1,5	300	
	64,698	1,43961	3,3	124	
	69,217	1,35625	1,6	220	
	75.404	1,25958	1,7	132	

REFERENCES

1. *Edvard D.A.* // Z.Kristallogr., 1931, v.80, p.154.
2. *Tahvonen P.E.* // Ann. Acad. Sci. Fennical. 1947, No.44, p.20.
3. *Finbak G., Hassel O.* // J. Phys. Chem. 1937, v.B37, p.75.
4. *Korhonen U.*// Ann. Acad. Sci. Fennical., Ser.A, 1953, v.1, No.15, p.1
5. *Bridgman P.W.* // Pros. Am. Acad. Arts. 1916, v.51. p.579.
6. *Kennedy S.W., Odlyha M.* // Aust. J. Chem. 1974, v.27, No.5, p.1121
7. *Asadov Yu.G., Nasirov V.I.* // Kristallografiya, 1970, v.15, No.6, p.1204
8. *Courtenay E.W., Kennedy S.W.* // Aust. J. Chem. 1974, v.27, No.1, p.209.
9. *Asadov Yu.G., Nasirov V.I., Jabrailova G.A.* // J. Crystal Growth, 1972, v.15, p.45.
10. *Zamali H., Jemal M.* // J.Phase Equilibria. 1995, v.16, p.235.
11. *Baryshnikov S.V., Charnaya E.V., Milinskii A.Yu., Stukova E.V., Michel D.* // Physics of Solid State, 2010, v.52, No.2, p.392.
12. *Kangchen Xu.* // J. Materials Science, 1999, v.34, No.14, p.3447.
13. *Nasirov V.I., Hazieva A.F., Asadov Yu.G.* // Cryst. Reports. 2011, v.56, No.5, p.1077.
14. *Nasirov V.I., Bairamov R.B.* // Reports of ANAS. 2016, v.72, No.1, p.29.
15. *Nasirov V.I., Bairamov R.B., Nasirov E.V.* // Cryst. Reports. 2015, v.60, No.7, p.1.

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$K_{0,955}Cs_{0,045}NO_3$ BƏRK MƏHLUL KRİSTALINDA QURULUŞ FAZA ÇEVRİLMƏLƏRİ

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İzotermik kristallaşma metodu ilə $K_{0,955}Cs_{0,045}NO_3$ monokristalları alınmış və optik mikroskopiya və rentgenoqrafiya üsulları ilə alınan nümunələrdə polimorf çevrilmələr tədqiq olunmuşdur. Müəyyən edilmişdir ki, $K_{0,955}Cs_{0,045}NO_3$ ktistalı otaq temperaturunda parametrləri *a*=5,4199Å, *b*=6,4363Å, *c*=9,1648Å, fəza qrupu *Pmcn* olan ortorombik qəfəsə malikdir. T>455K temperaturda bu ortorombik qəfəs kristal qəfəsinin parametrləri *a*=5,4250Å, *c*=9,8360Å, fəza qrupu $R\bar{3}m$ olan romboedrik qəfəsə çevrilir. Müəyyən edilmişdir ki, tədqiq olunan kristallarda II↔III çevrilməsi ana kristal daxilində yeni yaranan kristal rüşeyiminin əmələ gəlməsi və böyüməsi ilə baş verir. Yeni modifikasiya rüşeyimi əvvəlcə ana kristalın [100] kristalloqrafik istiqamətində böyüyür və bu istiqamətdə böyümə başa çatdıqdan sonra kristalın [001] kristalloqrafik istiqamətində davam edir. $K_{0,955}Cs_{0,045}NO_3$ II→III çevrilməsi monokristal↔monokristal tipli olub, enantiotrop xarakter daşıyır.

Açar sözlər: *kristal, monokristal, polimorfizm, polimorf çevrilmə, modifikasiya*

СТРУКТУРНЫЕ ФАЗОВЫЕ ПРЕВРАЩЕНИЯ В ТВЕРДОТЕЛЬНОМ РАСТВОРЕ $K_{0,955}Cs_{0,045}NO_3$

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Методом изотермической кристаллизации получены монокристаллы $K_{0,955}Cs_{0,045}NO_3$, в которых методами оптической микроскопии и рентгенографии исследованы полиморфные превращения. Установлено, что кристалл $K_{0,955}Cs_{0,045}NO_3$ при комнатной температуре имеет орторомбическую решетку (пр.гр.*Pmcn*) с параметрами *a*=5,4199Å, *b*=6,4363Å, *c*=9,1648Å. При температуре T>455K орторомбическая решетка превращается в ромбоэдрическую (пр.гр. $R\bar{3}m$) с параметрами кристаллической решетки *a*=5,4250Å, *c*=9,8360Å. Показано, что превращения II↔III в исследуемых кристаллах происходят с образованием и ростом зародышей дочерней модификации внутри матричного кристалла. Зародыши новой модификации сначала возникают в кристаллографическом направлении [100], а после завершения роста в этом направлении процесс продолжается в направлению [001]. Превращение II→III в $K_{0,955}Cs_{0,045}NO_3$ носит энантиотропный характер.

Ключевые слова: *кристалл, монокристалл, полиморфные превращения, модификация*