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Crystal physics**POLYMORPHISM OF RUBIDIUM NITRATE IN ATMOSPHERE OF ARGON****V.I.Nasirov, N.M.Namazova, G.G.Huseynov, A.S.Amirov**

(Presented by Academician of NAS of Azerbaijan M.I.Aliyev)

Polymorphism of rubidium nitrate in the atmosphere of argon was studied by the method of high-temperature X-ray diffraction. New cubic modification with the parameter $a = 3,617 \text{ \AA}$, pr. gr. P23 is discovered at the temperature $T = 600 \text{ K}$.

Keywords: crystal, mono crystal, polymorphic transformation, modification, structure, x-ray diffraction

Introduction

It is known that four different modifications are determined at rubidium nitrate in the temperature range from ambient ($\sim 300\text{K}$) to the melting temperature ($T_m = 587\text{K}$) [1-4]. At room temperature, the IV-modification has a rhombohedral lattice with symmetry $P31$ [1]. At the temperature $T > 437\text{K}$ rhombohedral modification is converted into cubic III-modification with symmetry $Rm3m$ [2]. At the temperature $T > 492\text{K}$ III-cubic modification turns into rhombohedral II-modification with the symmetry $R3m$ [3] and in its turn, at the temperature $T > 564\text{K}$ this modification is converted into cubic I modification with the symmetry $Fm\bar{3}m$ [4].

It should be noted that numerous works by different authors written at different times were devoted to polymorphic transformations in rubidium nitrate. For example, the structural phase transitions in rubidium nitrate is studied at work [5] of molecular dynamics simulation and effect of pressure on the structural transformations in RbNO_3 is studied and in 2,8 GPa V- orthorhombic phase with parameters: $a = 5,66 \text{ \AA}$, $b = 5,181 \text{ \AA}$, $c = 4,798 \text{ \AA}$ is found at work [6]. At [7] the I and II modifications disappear under pressure 103 atm. in RbNO_3 and the III-cubic modification remains as the high-temperature modification. The studies of the mechanism of polymorphic transformations [8-9] showed that the conversion $\text{IV} \leftrightarrow \text{III} \leftrightarrow \text{II} \leftrightarrow \text{I}$ in RbNO_3 occurs with the formation and growth of crystal nuclei of the subsidiary modifications within the matrix and wherein monocystal $\leftrightarrow$ monocystal transfor-

mation is observed. It should also be noted that the analysis of literature data on the morphology and the kinetics of polymorphic transformations in rubidium nitrate discloses existence of a new x- modification between the III and IV modifications [10].

The polymorphic transformations in RbNO_3 have enantiotropic character. Thermal transformations in RbNO_3 were studied at the work [2] with the methods of optical microscopy and X-ray measurement of electrical conductivity. It is shown that there are hard crystallographic orientational relations in the transformation of $\text{IV} \leftrightarrow \text{III} \leftrightarrow \text{II} \leftrightarrow \text{I}$ between crystal lattices IV, III, II, and II and I modifications.

The objective of these studies is establishing the influence of the environment on the mechanism of polymorphic transformations in rubidium nitrate. As we know, such studies are conducted for the first time.

Experimentation method

Well-faceted perfect single crystals RbNO_3 have been acquired from the aqueous solution at room temperature by slow evaporation. The crystals have a needle shape drawn out in the crystallographic direction [001] or flat plates. Crystal size averaged $1,0,5,10 \text{ mm}$. Rubidium nitrate of the mark "chemically pure" were purified additionally by repeated recrystallization. The samples in the form of fine powder are made for X-ray studies of these single crystals. The researches are conducted on the powder diffractometer of D8 ADVANCE type of the company «Bruker» under the regime of 40kV, 40mA, $\text{CuK}\alpha$ - radiation ($\lambda = 1,5406 \text{ \AA}$) in tem-

perature cell of TNK 723K type. The studies were conducted in the temperature range $300\text{K} < T < 600\text{K}$. Registration of diffraction reflections were carried out in the angular range $10^\circ \leq 2\theta \leq 80^\circ$. The identification of the received diffraction data RbNO_3 were conducted by the program TOPAS. The crystallographic parameters were specified under the program EVA.

The results of researches and their discussion

The diffractograms with clear diffraction reflections were obtained from powder samples of the crystals RbNO_3 at room temperature ($T = 300\text{ K}$) and under standard pressure (see fig. 1).

Calculation of interplanar distances (d) and indication of obtained diffraction data showed that they comply with the hexagonal lattice with parameters $a = 10,458\text{Å}$, $c = 7,798\text{Å}$ pr. gr. $P3m1$. After recording and their processing, the heating furnace of the chamber was included and diffractograms were recorded at differ-

ent temperatures (Fig. 1). Before each radiography specimen was kept at a fixed temperature for 30 minutes.

It was determined upon the changes in the intensity of the structure-sensitive images that disappear during these structural transformations that at $T > 437\text{K}$ room temperature hexagonal -IV- modification is converted into cubic III- modification with unit cell parameters $a = 4,372\text{Å}$, pr. gr. $Fm\bar{3}m$, and at $T > 492\text{K}$ diffraction reflections belonging to the III- modification disappear and new reflections belonging to non-cubic, as shown in [3], and the tetragonal lattice of the II modification with the parameters $a = 6,193\text{Å}$, $c = 8,74\text{Å}$, pr. gr. $I4$ appear. At temperature $T \geq 564\text{K}$ the II-tetragonal modification is turned to cubic I- modification with the parameter $a = 7,32\text{Å}$, pr.gr. $Fm\bar{3}m$.

The diffraction image of the crystal investigated at different temperatures is shown in figure 1, and their crystallographic data are given in table 1.

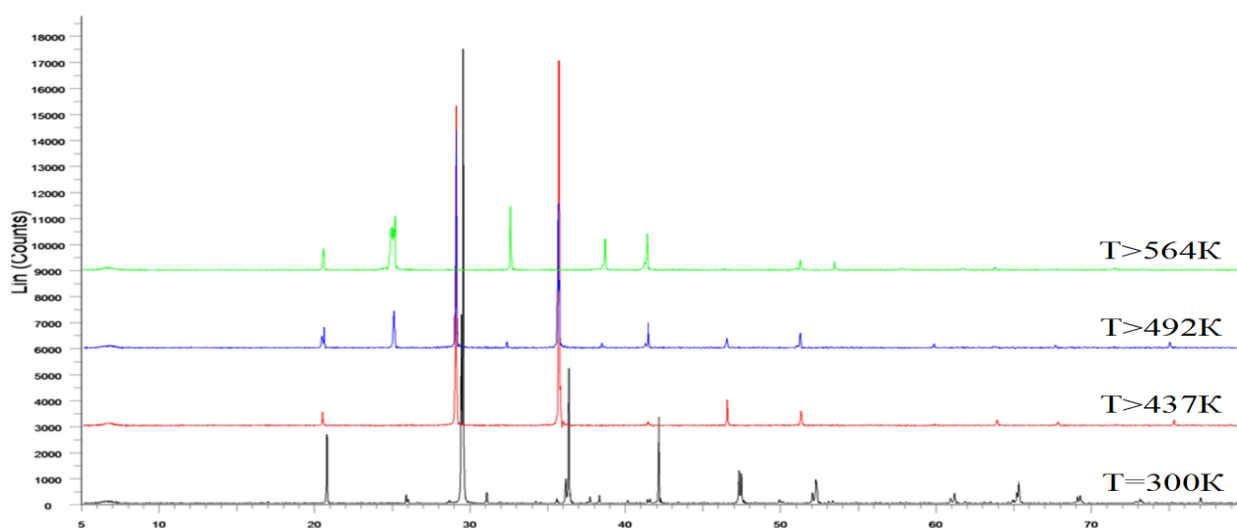
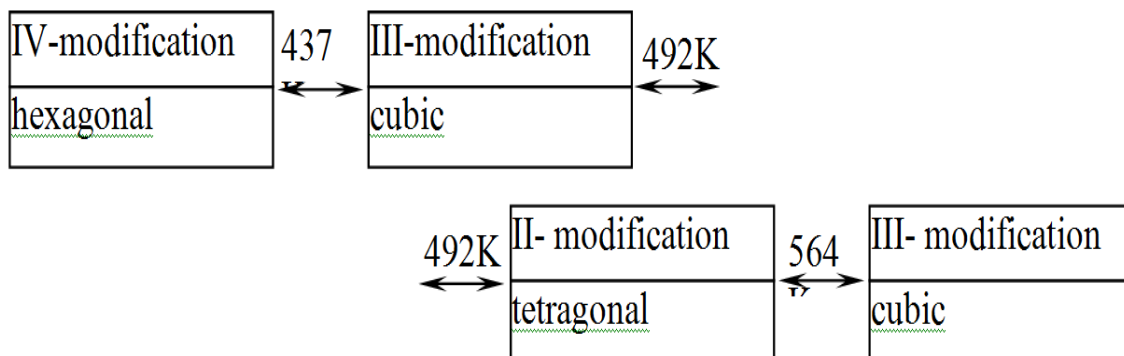


Fig. 1. X-ray diffractometric record of RbNO_3 at normal air pressure and at different temperatures

Table 1

Temperature, K	Modification	Crystal system	Parameters of the crystal lattice , Å		Space group
			a	c	
300	IV	hexagonal	10,458	7,450	$P3m1$
437	III	cubic	4,372	-	$Fm\bar{3}m$
492	II	tetragonal	6,193	8,740	$I4$
564	I	cubic	7,320	-	$Fm\bar{3}m$

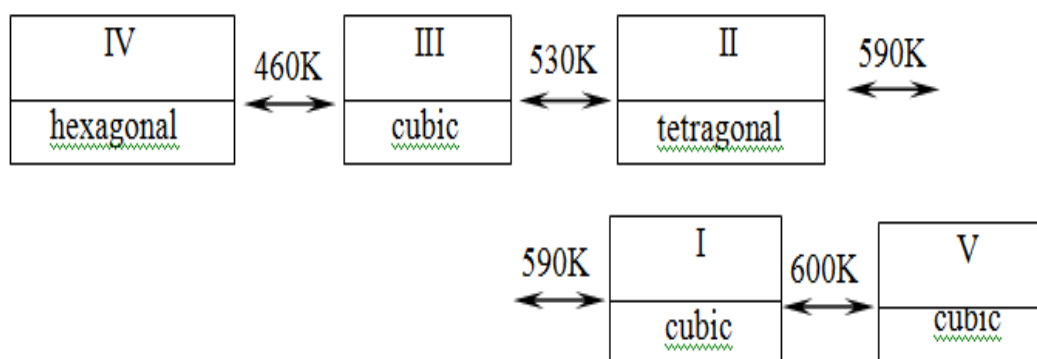
Thus, in the structural phase RbNO_3 transmission occurs as follows:



As it is seen from the above diagram the transformation process has an enantiotropic character. Since the opposite $\text{I} \rightarrow \text{II} \rightarrow \text{III} \rightarrow \text{IV} \rightarrow \text{V}$ transformation happens, i.e., the sample is returned to its original state during cooling of the sample.

The similar studies were conducted in crystals RbNO_3 located under argon conditions. For this purpose, the prepared powders were placed in cell with goniometer head and inlet valve was closed on after the injection of argon. Temperature diffractograms were obtained in the temperature range $300\text{K} \leq T \leq 600\text{K}$ through every 50 K. The analysis of obtained diffrac-

tograms showed that all four polymorphs obtained for RbNO_3 in a conventional environment are stored in argon environment too. But the transition temperatures change substantially (see fig. 2, table 2), and differing from the air version, a new cubic subcell with the parameter of crystal lattice $a=3,657\text{\AA}$, pr.gr. P23 occurs at $T = 600\text{ K}$. Melting of the investigated pattern happens at temperature $T = 602\text{K}$. Thus structural phase transformations into rubidium nitrate happen according to the following scheme in the argon environment:



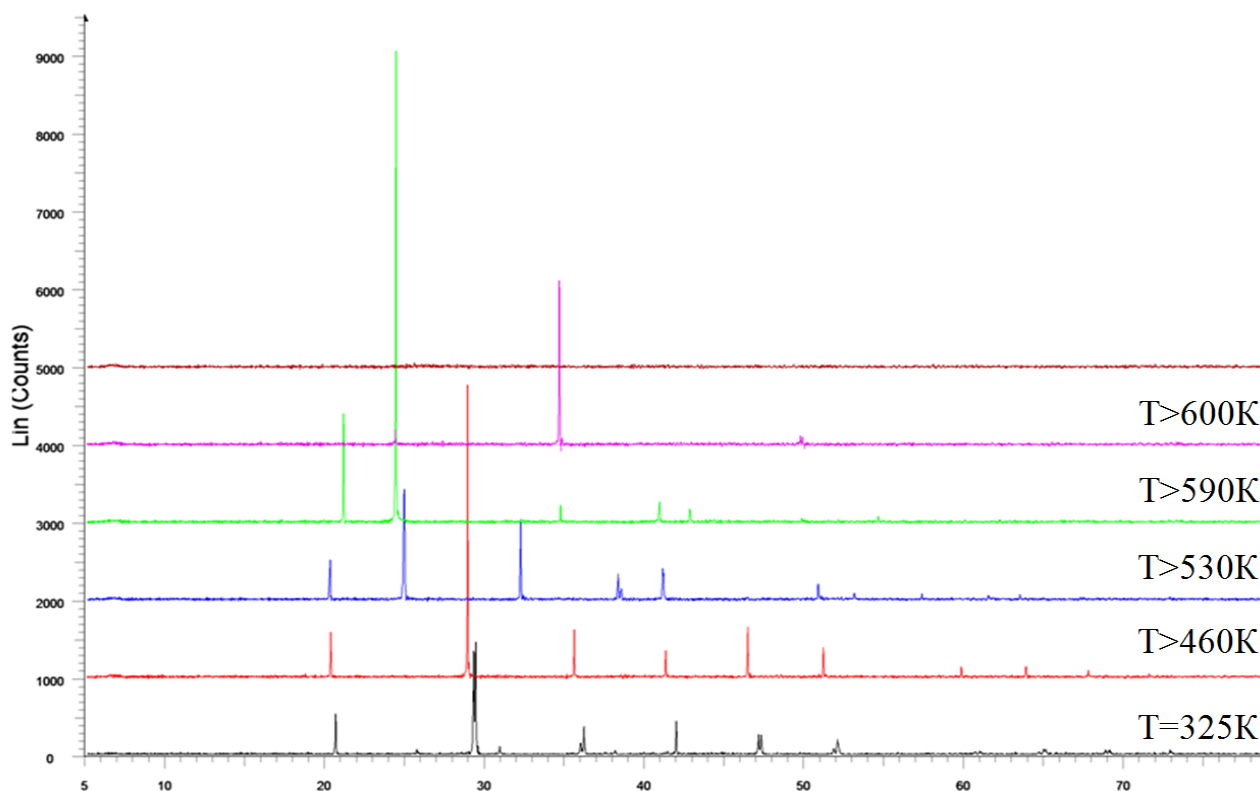


Fig.2. X-ray diffractometric record of RbNO_3 in argon atmosphere and at different temperatures

The diffraction image obtained in the present case is given in figure 2.

The crystallographic data are obtained from X-ray studies conducted in rubidium nitrate in argon atmosphere shown in table 2.

Table 2

Crystallographic data of polymorphous modifications of nitrate rubidium in argon atmosphere

Temperature, K	Modification	Crystal system	Parameters of the crystal lattice, Å		Space group
			<i>a</i>	<i>c</i>	
325	IV	hexagonal	10,474	7,443	$P3m1$
460	III	cubic	4,370	-	$Pm\bar{3}m$
530	II	Tetragonal	6,193	8,740	-
590	I	cubic	7,320	-	$Fm\bar{3}m$
600	V	cubic	3,657	-	$P23$

Conclusion

The analysis of the results shows that the temperatures of the respective transformations of rubidium nitrate in argon increases compared with the temperature obtained the air environment, the elementary cell parameters do not differ greatly. New modification appointed as the V modification by us and not known up to the present time is revealed at $T = 600$ K. The parameters and space group of the crystal lattice of this modification are determined. The experiments show that there are x- modification, as described in [10] among the IV and the third III modifications

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ARQON ATMOSFERİNDƏ RUBİDİUM NİTRATDA POLİMORFİZM

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Yüksək temperaturlu rentgen difraksiyası metodu ilə arqon mühitində rubidium nitratda polimorfizm öyrənilmişdir. $T=600$ K temperaturda parametri $a=3,617 \text{ Å}$, fəza qrupu P23 olan yeni kub quruluşlu modifikasiya müəyyən edilmişdir.

Açar sözlər: kristal, monokristal, polimorf çevrilmə modifikasiya, struktur, rentgendifraksiyası

ПОЛИМОРФИЗМ НИТРАТА РУБИДИЯ В АТМОСФЕРЕ АРГОНА

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Методом высокотемпературной рентгеновской дифракции исследован полиморфизм нитрата рубидия в атмосфере аргона. При температуре $T=600\text{K}$ обнаружена новая кубическая модификация с параметром $a=3,617 \text{ Å}$, пр.гр. P23.

Ключевые слова: кристалл, монокристалл, полиморфные превращения, модификация, структура, рентгенодифракция