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TRANSITION POLYMORPHIC II→III IN $K_{0,975}Rb_{0,025}NO_3$ SINGLE CRYSTALS

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The growth rates of the III phase have been measured as a function of the temperature during the II→III transition in $K_{0,975}Rb_{0,025}NO_3$. It was found that the growth rate of the III phase (II→III transition) has been described by the empirical equation $\upsilon = \left(-0{,}523\Delta T + 0{,}631\Delta T^2 - 0{,}00032\Delta T^3\right)\cdot 10^{-2}\,\frac{mm}{sek}$, where $\Delta T=T_{trans}-T_0$.

A number of researchers gave attention to the structural transformation of the rubidium and compounds. There are three different modification of the potassium nitrate in the temperature range from room temperature to the melting temperature. At room temperature the potassium nitrate has the structure of aragonite (modification II) with Pnma symmetry [1]. At T_{trans}>400 K the modification II turn into the modification III with R3c symmetry [2]. According to [3], there is modification I between the modification II and III. At room temperature the rubidium nitrate has rhombohedra structure (modification IV) with $P3_1$ symmetry [4], at T_{trans}>437K the modification IV turns into the modification III with Fm3m cubic symmetry [5], at T_{trans}>492K the modification turns into rhombohedra modification II with R3m symmetry [6], and finally, at T_{trans}>564K the modification II turns into cubic modification with Fm3m symmetry [7]. Many works [8-12] deal with the identification of structural transformation mechanism in alkali metal nitrate compounds, including the rubidium and potassium nitrates. There are rhythmic, step-by step, dendrite, elastic growth under structural transformations which resemble the crystal growth from liquid and gaseous media without seed, except that in the case of structural transformation, new ordered crystals grow from strictly ordered matrix single crystal (non-diffusion process), and ordered phases grow from liquid and gaseous media (by means of diffusion) through disordered medium. It has been shown that in these crystals the structural transformations occupy with the formation and growth of daughter modification nucleus within matrix modification. In addition, the conditions under which the crystal grows from solid phase are fundamentally different from the conditions of crystal growth from solution, melt or vapor. In the case of crystal growth from solid phase, growing crystal faces do not collide with free atoms or molecules, but they should capture particles from adjacent layers of the surrounding matrix with crystalline structure where each of the atoms or molecules has well-defined position. As a result, the crystal growth occurs due to gradual movement of the boundaries between two un-joining areas of the lattice, and the decrease of free surface energy will be a driving force for such movement.

In order to clarify the mechanism of structural transformations in solid solution of these compounds, we have undertaken a series of stadies to investigate single crystals $K_{1-x}Ag_xNO_3$ (x=0.025, 0.05, 0.1) [13-15]. This work is a continuation of the series of works devoted to investigation of the kinetics of crystals under structural transformations in $K_{0,975}Rb_{0,025}NO_3$.

Experiments were carried out by method of optical microscopy. From aqueous solution at the room temperature, well faceted $K_{0,975}Rb_{0,025}NO_3$ single crystals (modification II) with average size of 1x0.5x10mm suitable for microscopic studies were obtained. For perfection and purity of the obtained crystals were subjected to aft purification by repeated multiple recrystallization. The crystals have various external forms. We used crystals with a flat plate spare or needle along [001] crystallographic

direction (Fig.1). Kinetically studies were carried out using the polarizing microscope MIN-8 with warm stage. Temperature was measured by thermocouple which tips touched directly with the sample surface.

Fig.1.
$K_{0,975}Rb_{0,025}NO_3$ single crystals obtained from aqueous solution.

The temperature measurement accuracy at 100^0C reached $\pm 1^0$C. At the warm stage providing full thermosetting of the investigated crystals, we first of all carefully measured the temperature of equilibrium of phases II and III, which is equal to T_0=381K. To measure the growth rates of the phases as a function of temperature only, υ(T), we carried out the following experiment: We measured the growth rate at various temperature on chosen parts in the very same crystal of dimensions 5 to 10 mm. The heating oven was closely surrounded by a thermally insulating cover in such a way that the crystal was under thermally stabilized conditions. The region of study was arbitrarily chosen using the graduated eyepiece. After measuring the rate on one of the microscopes at the temperature $T_1=T_0+\Delta T_1$ the sample was transferred to the heated stage of the other microscope, having a temperature $T_2= T_0+\Delta T_2$, where $\Delta T_1<\Delta T_2$, and the measurement was repeated over the section $A'B'C'D'$.After this time a temperature $T_3= T_0+\Delta T_3$ was established in the first microscope,where $\Delta T_2<\Delta T_3$, and the measurement was repeated for the region $A''B''C''D''$, etc. Between measurement regions of the investigated crystal there were regions $MNAB, CDA'B', C'D'A'B'$, etc.since the phase separation boundary moved a certain distance during the time to transfer the crystal from one microscope to the other and establish the fixed temperature. This is illustrated in Fig.2.

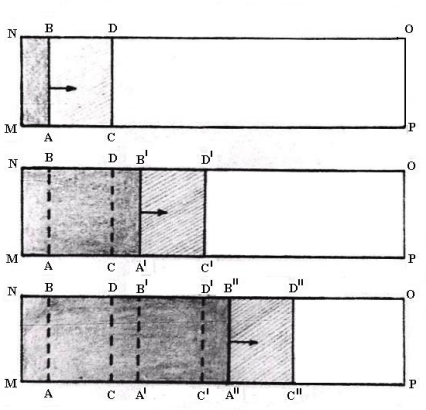

Fig. 2.
Schematic illustration of the growth rate of the III phase during the II→III transformation in the same crystal.

Thus we measured the growth rate of the same face of the growth rate of the same face of the III phase sequentially in the same crystal during the II→III transformation in $K_{0,975}Rb_{0,025}NO_3$ as a function of T.

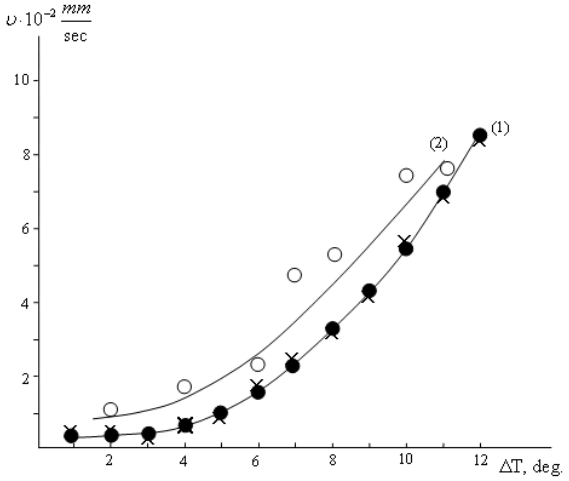

Fig.3.
Temperature dependence of the growth rate of the III phase during II→III transformation in $K_{0,975}Rb_{0,025}NO_3$.1) Dependence of the growth rate of the III phase on temperature during the II→III transformation in the same crystal;dark circles are experimental values and the crosses are emrirical values; 2) dependence of the growth rate of the III phase on temperature during the II→III transformation different crystals (the growth rate of the new phase in different crystals as a function of temperature gives the large scatter).

The experimental data analyzed using least squares gave a functional dependence of the form $\upsilon = \left(-0{,}523\Delta T + 0{,}631\Delta T^2 - 0{,}00032\Delta T^3\right)\cdot 10^{-2}\,\frac{mm}{sek}$, for the growth rate as a function of temperature, where $\Delta T=T_{trans}-T_0$. In Fig.3 (curve 1) we show a graph of the growth

rate of the new phase as a function of temperature, constructed from experimental data and calculated from the empirical equation.

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$K_{0,975}Rb_{0,025}NO_3$ MONOKRİSTALLARINDA II→III POLİMORF ÇEVRİLMƏ

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Optik mikroskopiya üsulu ilə $K_{0,975}Rb_{0,025}NO_3$ kristallarında II→III çevrilməsi zamanı III modifikasiya kristalının böyümə sürəti temperaturdan asılı olaraq ölçülmüş və böyümə sürəti üçün $\upsilon = \left(-0{,}523\Delta T + 0{,}631\Delta T^2 - 0{,}00032\Delta T^3\right)\cdot 10^{-2}\,\frac{mm}{sek}$ empirik asılılığı müəyyən edilmişdir, burada $\Delta T=T_{çev}-T_0$.

ПОЛИМОРФНОЕ II→III ПРЕВРАЩЕНИЕ В МОНОКРИСТАЛЛАХ $K_{0,975}Rb_{0,025}NO_3$

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Методом оптической микроскопии была измерена скорость роста кристаллов III модификации при II→III (полиморфном) превращении в монокристаллах $K_{0,975}Rb_{0,025}NO_3$ в зависимости от температуры. Определена эмпирическая зависимость скорости роста кристалла III-модификации от температуры: $\upsilon = \left(-0{,}523\Delta T + 0{,}631\Delta T^2 - 0{,}00032\Delta T^3\right)\cdot 10^{-2}\,\frac{mm}{sek}$, где $\Delta T=T_{пр}-T_0$.

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