Polymorphic Single Crystal ↔ Single Crystal Transition in $K_{0.975}Rb_{0.025}NO_3$

Yu. G. Asadov and E. V. Nasirov

Institute of Physics, Azerbaijan National Academy of Sciences, Baku, Azerbaijan
e-mail: yusifasadov@rambler.ru

Received December 21, 2009

Abstract—Polymorphic transformations in $K_{0.975}Rb_{0.025}NO_3$ single crystals have been investigated by optical microscopy and X-ray diffraction. The equilibrium temperature between modifications II and III has been determined. It is established that the crystal growth at $II \leftrightarrow III$ polymorphic transitions is accompanied by the formation and growth of daughter-modification nuclei in the matrix crystal.

DOI: 10.1134/S1063774510050330

A number of researchers have considered the structural transformations of potassium and rubidium nitrates both in the pure form and when studying some systems containing these compounds. An analysis of the systematic features of polymorphic transformations in these compounds is not only interesting from scientific point of view, but it is also important for practice, since this process is closely related to the technology of single crystals of mixed compositions with polymorphic properties.

At room temperature, potassium nitrate is known to have a structure similar to aragonite (modification II) with the $Pnma$ symmetry [1]. Upon heating, at $\sim 403$ K, modification II is transformed into a structure that is very similar to calcite (modification III) with the $R3c$ symmetry [2]. The $II \rightarrow III$ transformation is enantiotropic. However, sometimes two monotropic transformations are also observed upon cooling. During this process, at $\sim 397$ K, modification III can pass into a new structure (modification I) with the $R3m$ symmetry [3]; only then, at $\sim 383$ K, is modification I transformed into modification II. Rubidium nitrate undergoes three polymorphic transformations in the temperature range of 437–564 K. At

![Fig. 1. $K_{0.975}Rb_{0.025}NO_3$, single crystals grown from an aqueous solution.](image1)

![Fig. 2. Optical micrographs illustrating the formation and growth of a modification-III nucleus in a matrix crystal of modification II (magnification ×90).](image2)
room temperature, RbNO₃ has an orthorhombic structure (modification IV) with a $P3 \cdot (P3_2)$ symmetry [4]; at the temperature $T_{tr} > 437$ K, modification IV passes into cubic modification III with the $Fm\overline{3}m$ symmetry [5]; at $T_{tr} > 492$ K, this modification is transformed into rhombohedral modification II with the $R3m$ symmetry [6]; and, finally, at $T > 564$ K, modification II is transformed into cubic modification I with the $Fm\overline{3}m$ symmetry [7].

It was shown in [8] that, at sufficiently high pressures, rubidium nitrate phases I and II disappear and only phase III remains as a high-temperature phase. Phases I and II disappear in the same way in solid solutions of cesium and rubidium nitrates at a cesium salt concentration of ~25 mol % [9].

Many studies [10–14] have been devoted to the mechanism of polymorphic transformations in single crystals of alkali metal nitrates (including potassium and rubidium nitrates). The phase diagram of a mixture of potassium and silver nitrates was determined in [15], phase transitions in $K_{1-x}Ag_xNO_3$ were established in [16], and the phase transitions in $K_{1-x}Rb_xNO_3$ were studied by Raman spectroscopy in [17].