

Solution-Growth, Crystal System and Transformation of Crystals of Phase II RbNO_3

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Abstract

It has proved possible to grow small single crystals of phase II of rubidium nitrate above 220°C. These are used to examine the crystal system and polymorphic transformation of this phase. Rhombohedral symmetry has been deduced from polarized light microscopy. The crystals undergo a regular shape change in the transformations II \rightarrow I \rightarrow II. This implies a coordinated structural rearrangement which can be related to a lattice deformation.

The symmetry of phase II of crystalline rubidium nitrate is of interest especially because this phase represents an intermediate degree of lattice deformation linking the face-centred cubic NaCl-related phase I,¹ stable above 284°C, to a primitive cubic CsCl-related phase III² stable below 219°C. The polymorphism of RbNO_3 therefore affords not only a test of the kind of lattice deformation which links the NaCl-related and CsCl-related cubic structures in complex compounds; but also a test of whether the planes of the triangular oxy-ions can be reoriented during structure changes while the general arrangement (e.g. of cations) is merely deformed. This information is necessary where concepts of change of coordination in crystals are to be extended to compounds of complex ions, for example for discussion of a possible martensitic mechanism for the aragonite-calcite transformation.³ Even partial information on RbNO_3 II is therefore of value. The difficulty of producing single crystals of an intermediate phase at rather high temperature has prevented X-ray investigation of the structure. Morphology and fast extinction direction between crossed polars can however be used as tests of symmetry if microscopic crystals are available, at least to the extent of distinguishing between crystal systems. Small single crystals have now been grown.

Wallerant⁴ deduced from optical study of melt-grown sheets that form II was rhombohedral, calcite-type; and Finbak and Hassel⁵ found that the X-ray powder pattern was consistent with this. However, Brown and McLaren⁶ suggested that their own powder diffraction patterns could equally well be indexed as tetragonal. Iversen and Kennedy⁷ found, that in the sequence RbNO_3 I \rightarrow II \rightarrow III, the orientation

¹ Kennedy, S. W., *Phys. Status solidi (A)*, 1970, **2**, 415.

² Korhonen, U., *Ann. Acad. Sci. fenn. (A)*, 1951, **1**, No. 102.

³ Kennedy, S. W., and Kriven, W. M., *J. Mater. Sci.*, 1972, **7**, 1092.

⁴ Wallerant, F., *Bull. Soc. fr. Minér. Cristallogr.*, 1905, **28**, 325.

⁵ Finbak, C., Hassel, O., and Strømme, L. G., *Z. phys. Chem. (B)*, 1937, **37**, 468.

⁶ Brown, R. N., and McLaren, A. C., *Acta crystallogr.*, 1962, **15**, 974.

⁷ Iversen, A. J., and Kennedy, S. W., *Acta crystallogr. (B)*, 1973, **29**, 1554.

relation was $[100]_{\text{I}} \parallel [100]_{\text{III}}$, $(010)_{\text{I}} \parallel (110)_{\text{III}}$. This could be explained more conventionally if phase II were indeed tetragonal. A tetragonal structure ($\text{NH}_4\text{NO}_3\text{V}$) is already known in the nitrates. It has low positive birefringence.⁴ In the present work RbNO_3 was crystallized above 219°C.

Experimental

The starting material was Johnson–Matthey rubidium nitrate. The solvent was a mixture of polyethylene glycols synthesized by the iodine method,⁸ and having a boiling range of 155–163°C at a pressure of 267 N m⁻². Numerous other high-boiling solvents were tried but found unsuitable because of decomposition or rapid evaporation.

Batches of crystals were grown on glass cover slips from the solution by evaporation of the solvent. They were examined on a polarizing microscope fitted with a transparent heating stage, at magnifications of 256 and 400. That the crystals were RbNO_3 was confirmed by their transformation to phase I and III as expected, and by X-ray powder photographs at room temperature. The crystals were small, with edge-length 14–30 μm , but suitable for microscopy.

Results

Many well formed crystals were rhombohedral in appearance. The obtuse rhombohedral angle measured from photomicrographs was 98°. The fast extinction direction bisected this rhombohedral angle and the birefringence was high. Some other crystals, oriented so that they were permanently extinct (optic axis normal to the stage), were approximately equilateral triangular, or hexagonal, in projection. This morphology and extinction direction are consistent with rhombohedral (or monoclinic pseudo-rhombohedral) rather than tetragonal symmetry, and are typical of the morphology of calcite-type structures, such as NaNO_3 . The shape then corresponds to the four-molecule ‘morphological rhombohedron’⁹ of such structures. The observed rhombohedral angle α is in substantial agreement with a value of 96° calculated from the lattice parameters⁵ at 250°C. Some difference in value may be expected because of variation of α with temperature, for this structure has anomalously high thermal expansion along the threefold axis.

The tetragonal morphology of most similar general appearance would be the tetragonal dipyramid. The interedge angle on the $\{011\}$ faces for the tetragonal cell would be 61°, quite different from the angle observed.

By use of the single crystals it has been possible to detect a regular shape change caused by the transformations $\text{II} \rightarrow \text{I} \rightarrow \text{II}$. In general a regular shape change is valuable evidence of the persistence, over substantial distances, of coordinated displacements of atoms in the mechanism of structure-change. In RbNO_3 the volume change $\Delta V_{\text{II} \rightarrow \text{I}}$ is less than the experimental precision.¹⁰ It might be expected that because of thermal motion, the rhombohedral arrangement would approach cubic near the transformation temperature and that the rhombohedral angle could approach 90°. In practice it was observed that the rhombohedral crystals superheat slightly and then change quite suddenly to a rectangular (or square) shape as seen in projection, corresponding to the cubic symmetry of I. On returning to II the orthogonal shape was retained by means of transformation-twinning. Lamellae (earlier observed to be

⁸ Perry, S. Z., and Hibbert, H., *Can. J. Res. (B)*, 1936, **14**, 77.

⁹ Henry, N. F. M., Lipson, H., and Wooster, W. A., ‘The Interpretation of X-ray Diffraction Photographs’ (Macmillan: London 1960).

¹⁰ Salhotra, P. P., Subbarao, E. C., and Venkateswarlu, P., *Phys. Status solidi*, 1968, **29**, 859.

internally twinned¹) had traces parallel to $\langle 100 \rangle_1$. During this sudden cooperative structure change the planes of the anions reorient. This is another example of the *large* regular shape change of a crystal, previously seen at a NaCl-type \rightarrow CsCl-type transformation,¹¹ and is the first in a structure containing complex ions. Further measurements of shape change, and of orientations of lamellae and twins, and of lattice orientations would show what lattice deformation links the structures.

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¹¹ Fraser, W. L., and Kennedy, S. W., *Acta crystallogr. (B)*, 1972, **28**, 3101.