

POLYMORPHISM OF KNaNbOF₅ CRYSTALS

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X-ray crystallography is used to analyze the concomitant polymorphism of KNaNbOF₅ crystals. The second β -modification of the compound, crystallizing in the tetragonal crystal system is found for the first time: space group $P4/nmm$, $a = 5.9352(2)$ Å, $c = 8.5487(5)$ Å, $V = 301.14(2)$ Å³, $Z = 2$, $R1 = 0.0095$. Parameters of the orthorhombic noncentrosymmetric structure of the α -phase, previously described by Poeppelmeier et al. (*J. Am. Chem. Soc.*, **129**, 13963-13969 (2007)), are refined and a comparative analysis of both structures is performed. The structures are characterized by the complete ordering of oxygen and fluorine atoms, the Nb–O distance in the α -phase (1.738(1) Å) being noticeably longer than that in the β -phase (1.709(2) Å). In β -KNaNbOF₅, alternating NbOF₅ and NaOF₅ octahedra share vertices, while in α -KNaNbOF₅, they share both vertices and edges. The existence of the non-polar centrosymmetric β -modification of KNaNbOF₅ cancels the assumption of the substantial contribution of potassium cations to the polar structure of α -KNaNbOF₅.

Keywords: potassium-sodium oxopentafluoronioate, crystal structure, O/F order, concomitant polymorphism.

INTRODUCTION

Nonlinear physical properties typical of noncentrosymmetric crystals are an important spur in the search and synthesis of such materials. The generation of the second optical harmonics (SHG) is first of all due to the anionic group in the crystal lattice [1], which should be noncentrosymmetric by its nature. This condition is satisfied by oxofluoride polar $[\text{MO}_x\text{F}_{6-x}]^{2-}$ anions d^0 of transition metals ($x = 1$, $M = \text{V, Nb, Ta}$; $x = 2$, $M = \text{Mo, W}$), in which the central atom is shifted from the octahedron center to oxygen ligands [2, 3]. This primary distortion is added by the secondary one resulting from the interaction of polyhedra with the outer-sphere environment. The selection of the outer-sphere cation makes it possible to order polyhedra in the lattice with producing noncentrosymmetric structures, as in the case of $[\text{NbOF}_5]^{2-}$ with organic cations: $[\text{HNC}_6\text{H}_6\text{OH}]_2[\text{Cu}(\text{NC}_5\text{H}_5)_4(\text{NbOF}_5)_2]$ [2] and $\text{Cd}(\text{py})_4\text{NbOF}_5$ ($\text{py} = \text{NC}_5\text{H}_5$) [3]. The orthorhombic modification of KNaNbOF₅ [4] is the first example of a noncentrosymmetric structure with acentric $[\text{NbOF}_5]^{2-}$ anions surrounded by inorganic cations, which has nonlinear optical (SHG) properties. However, the authors of this work still had doubts about the determination of the absolute structure. The crystals of this compound were first synthesized by Antokhina et al. [5], however, during their synthesis the second modification of KNaNbOF₅, to the crystal structure of which this paper is devoted, was not revealed. (The first information on the structure of the α -phase was presented as the report [6]).

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EXPERIMENTAL

All precursors for the synthesis of KNaNbOF_5 were of chemically pure grade. Single crystals of the complex were obtained as a result of slow evaporation in air of the niobium(V) oxide solution ($\text{Nb}_2\text{O}_5 \cdot x\text{H}_2\text{O}$) in concentrated (40%) HF added by stoichiometric amounts of (KCl + NaCl) or (KF + NaF). We started from 10 g of niobium oxide dissolved in 23-25 ml of 40% HF solution on heating. During slow evaporation in air transparent colorless cubic crystals formed at the initial crystallization steps; further crystallization resulted in the appearance of plate-like crystals. The structural study has shown that the plates are orthorhombic KNaNbOF_5 crystals (α -phase) described previously [4, 5], while the cubes turned out to be the crystalline compound of the same composition in the tetragonal form (β -phase). The composition of the latter was confirmed by a chemical analysis for alkali elements and fluorine. The fluorine concentration was determined by distillation in the form of H_2SiF_6 followed by titration with $\text{Th}(\text{NO}_3)_4$; sodium and potassium were determined by atomic absorption. For KNaNbOF_5 calculated (wt %): K 14.70, Na 8.65, F 35.71. Found (wt %): K 14.2 \pm 0.7, Na 8.4 \pm 0.5, F 35.3 \pm 0.5.

X-ray diffraction data on both phases were collected at room temperature on a single crystal SMART APEX II (Bruker AXS) diffractometer with a CCD detector. Experimental absorption corrections were introduced using the SADABS program [7] by a multi-scan method. The structure model was found by direct methods and refined using the SHELXTL program complex [8]. Table 1 lists the experimental parameters and structure refinement results. Atomic coordinates and their equivalent isotropic thermal parameters are given in Table 2; interatomic distances and bond angles are given in Table 3.

Additional information on the structural data of the studied complex can be received from Karlsruhe, 763444 Eggenstein-Leopoldschafen, Germany (fax: (49) 7247-808-666; e-mail: crysdata@fiz-karlsruhe.de) or at the site <http://www.fiz-karlsruhe.de/home.html> upon request of depositary numbers 423273 for the α -phase and 423274 for the β -phase.

TABLE 1. Crystallographic Data, Parameters of the Experiment and Structure Refinement for α - and β - KNaNbOF_5

Formula	KNaNbOF_5	
	$Pna2_1$ (α -phase)	$P4/nmm$ (β -phase)
Space group	$Pna2_1$ (α -phase)	$P4/nmm$ (β -phase)
Crystal dimensions, mm	0.30 \times 0.27 \times 0.10	0.29 \times 0.27 \times 0.22
$a, b, c, \text{\AA}$	11.8856(11), 5.9261(6), 8.1616(8)	5.9352(2), 5.9352(2), 8.5487(5)
$V, \text{\AA}^3$	574.9(1)	301.14(2)
Z	4	2
$d, \text{g/cm}^3$	3.073	2.934
μ, mm^{-1}	2.913	2.780
Radiation	$\text{MoK}\alpha$	
$2\theta_{\text{max}}, \text{deg}$	59	59
Tot./indep. refl.	5082/1517	2735/279
$R_{\text{int}}, R_{\text{sigma}}$	0.018, 0.017	0.020, 0.010
h, k, l range	$-16 < h < 15, -7 < k < 8, -11 < l < 11$	$-8 < h < 8, -7 < k < 7, -11 < l < 11$
	Refinement	
Weight scheme coeff.	0.0205, 0.1285	0.0093, 0.170
Extinction coeff.	0.0237(8)	0.137(4)
Number of refined param.	84	22
$R1$ (over all refl.)	0.0126	0.0095
$wR2$	0.0334	0.0235
$GOOF$	1.098	1.013
Flack-parameter	0.11(3)	—
$(\Delta\rho)_{\text{max}}/(\Delta\rho)_{\text{min}}, \text{e/\AA}^3$	0.34/-0.40	0.19/-0.31
$(\Delta/\sigma)_{\text{max}}$	0	0

TABLE 2. Relative Coordinates and Equivalent Parameters of Thermal Atomic Motion in the Structure of the β -Phase of KNaNbOF_5

Atom	x	y	z	q	U_{eq}	Atom	x	y	z	q	U_{eq}
Nb	0.25	0.25	0.73505(2)	0.125	0.0145(1)	O	0.25	0.25	0.5351(2)	0.125	0.0352(5)
K	0.75	0.25	0	0.125	0.0240(2)	F1	0.25	0.25	0.9865(2)	0.125	0.0289(4)
Na	0.25	0.25	0.2660(1)	0.125	0.0180(2)	F2	0.4795(1)	0.0205(1)	0.7719(1)	0.5	0.0303(2)

TABLE 3. Interatomic Distances and Bond Angles in the Structure β - KNaNbOF_5

Bond	$d, \text{\AA}$	Bond	$d, \text{\AA}$	Angle	ω, deg	Angle	ω, deg
Nb–O	1.709(2)	Na–O	2.301(2)	F1–Nb–F2	80.72(3)	F1 ^{iv} –Na–F2 ^v	81.90(3)
Nb–F1	2.150(2)	Na–F1	2.389(2)	F2–Nb–O	99.28(3)	F2 ^v –Na–O	98.10(3)
Nb–F2	1.9515(9)	Na–F2	2.2937(9)	F2–Nb–F2 ⁱ	88.51(1)	F2 ^{vi} –Na–F2 ^v	88.86(1)
				F2–Nb–F2 ⁱⁱⁱ	161.44(5)	F2 ^{vi} –Na–F2 ^{vii}	163.79(7)

Symmetric transformations: (i) $1/2-y, x, z$; (ii) $y, 1/2-x, z$; (iii) $1/2-x, 1/2-y, z$; (iv) $x, y, z-1$; (v) $-y, x-1/2, 1-z$; (vi) $1-x, -y, 1-z$; (vii) $y+1/2, 1-x, 1-z$.

RESULTS AND DISCUSSION

First of all, let us stop on differences in the synthesis procedures for the studied complex, which were proposed by the authors of [4] and [5]. In the first case [4], quite small portions of the precursors were used: 0.0223 g of KF and 0.1000 g of Na_2NbOF_5 (obtained as a result of the interaction of Nb_2O_5 in 48% HF and NaF) in 1 ml of deionized water. The experiment was conducted under pressure for 24 h at 150°C (hydrothermal synthesis), the yield of transparent plate-like crystals being small. In the second case [5] the initial F/Nb ratio was 5 (it is unclear, how the authors controlled it because for the complete dissolution of starting niobium oxide in 40% HF the excess of the latter is required). Then alkali metal fluorides were used in the ratio Na:K:Nb = 1:1:1 or an aqueous solution of NaNbOF_4 and KF. One way or another, the formation of another polymorphic modification (β - KNaNbOF_5) was not observed.

The method that we propose seems to be much simpler and it leads to the formation of two types of single crystals: cubes and plates. Usually, polymorphic forms of a compound are obtained when different synthesis procedures are used. If it happens under the same chemistry and reaction conditions (which is close to our experiment), the authors of [3] call this process concomitant polymorphism. Thus, α - and β -forms that we obtained are concomitant polymorphic forms.

Parameters of the refined structure of the α -phase (Table 1) show that the results that we obtained are of higher quality than those in [4], where $R_{\text{int}} = 0.098$, $R_{\text{sigma}} = 0.054$, $R1 = 0.043$, $wR2 = 0.113$, although its authors worked with the sample cooled to 153 K. Moreover, the Flack parameter $x = 0.27(10)$ given in this work has a low degree of sensitivity to inversion, which does not provide a reliable interpretation of the obtained parameter. In our case, the standard deviation below 0.04, and hence, the degree of sensitivity to inversion is high, as it is described in [9]. Although chemical elements in the structure of the α -phase do not exhibit strong anomalous scattering, based on our structural data it is possible to state that the studied sample is not strictly chiral and has a low concentration of the alternative inverted component.

Crystals of the β -phase are described by the centrosymmetric tetragonal symmetry group $P4/nmm$. Table 2 lists atomic coordinates related to the origin of coordinates in the center of symmetry (second setting in [10]). The structure, as in the case of the α -phase, is composed of NbOF_5 and NaOF_5 octahedra with complete ordering in the arrangement of oxygen and fluorine atoms. However, their arrangement is quite another in β - KNaNbOF_5 . Thus, although in both phases, niobium octahedra are linked only with sodium octahedra, and on the contrary, in the α -phase, they share both vertices and edges, while in the β -phase only vertices are shared.

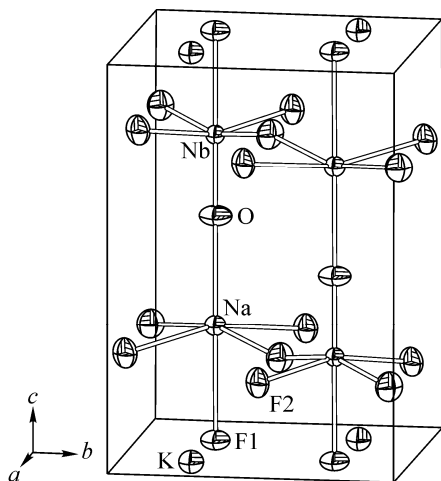


Fig. 1. Crystal lattice content in the structure of β -KNaNbOF₅.

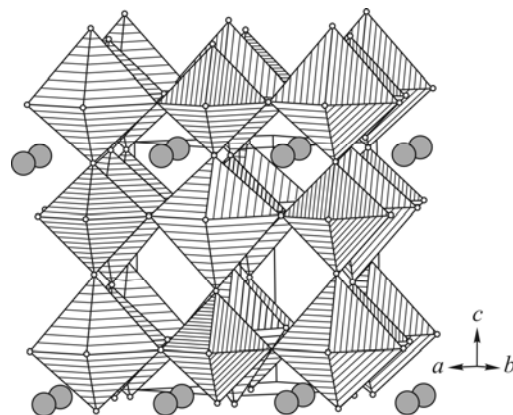


Fig. 2. Structure of the β -KNaNbOF₅ crystal in the elpasolite representation. NbOF₅ octahedra have a smaller size.

Therefore, the β -phase has the octahedral arrangement similar to that in elpasolites, however, the octahedra are not regular (Fig. 1). In both types of the octahedra, Na and Nb atoms are shifted towards oxygen along the 4-fold axis; interatomic distances are as follows: Na–O 2.301(2) Å, Nb–O 1.709(2) Å, Na–F1 2.389(2) Å, Nb–F1 2.150(2) Å, Na–F2 2.2937(9) Å, and Nb–F2 1.9515(9) Å (Table 3).

A significant difference from elpasolites is the 50% filling of interoctahedral voids with potassium ions (Fig. 2). This filling is strictly ordered; potassium cations fill alternatively next-but-one the layers of voids, the layers being perpendicular to the c axis of the cell. Hence, the potassium cuboctahedron is composed of only fluorine atoms with distances: K–F1 $4 \times 2.9698(1)$ Å and K–F2 $8 \times 2.8700(6)$ Å. These differences in the structure of two polymorphic modifications of KNaNbOF₅ crystals make impossible the phase transition between them; on heating up to the phase decomposition temperature they remain unchanged.

The authors of [4] considered the primary electronic distortions of [NbOF₅]²⁻ polyhedra and secondary ones related to the lattice interaction in the noncentrosymmetric structure of the α -phase of KNaNbOF₅ and in the centrosymmetric structure of CsNaNbOF₅. As a result, they drew the conclusion that the shorter Nb–O distance and only two bonds of oxygen with the neighboring cations in the first structure (unlike three cationic contacts in the second one) were more strained and the metal-oxygen bonding was strengthened, which, in their opinion, resulted in the preference for the noncentrosymmetric structure. From Fig. 3 it is seen that the oxygen atom in α -KNaNbOF₅ lies practically in one plane with K, Na, and Nb ions (angles Na–O–K 90.21(5)°, Na–O–Nb 139.41(8)°, Nb–O–K 128.83(7)°); here the K–O, Na–O, and Nb–O distances are 2.869(1) Å, 2.359(2) Å, and 1.738(1) Å respectively, i.e. the oxygen atom is three-coordinated at two contacts with the outer-sphere cations, as described in [4] (all numerical values for the α -phase were taken from our determination).

In the considered structure of the β -phase of KNaNbOF₅, the oxygen atom is two-coordinated at one contact with the outer-sphere cation, namely the sodium cation. The Nb–O bond is noticeably shorter than that in the α -phase with the corresponding elongation of the Nb–F1 distance. It should be noted that the mentioned Nb–O distances well correlate with the stretching vibrational frequency of this bond: for α -KNaNbOF₅ it is 933 cm⁻¹, for β -KNaNbOF₅ it is 978 cm⁻¹. Thus, an even smaller number of the cationic contacts of the oxygen atom and higher strain of the Nb–O bond (and correspondingly, a larger distortion of the NbOF₅ octahedron) do not lead to the formation of the noncentrosymmetric structure of KNaNbOF₅, as could be expected in accordance with the conclusions of [4]. As in the case of concomitant polymorphic modifications of Cd(py)₄NbOF₅ (py = pyridine) with ordered (*A*) and disordered (*B*) linear chain structures, the formation of one or another structure is most likely to be affected by thermodynamic and kinetic factors [3].

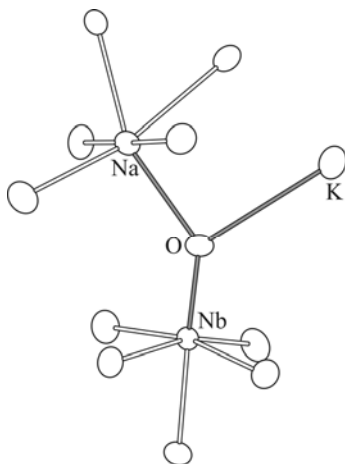


Fig. 3. Oxygen atom surrounded by cations in the structure of α -KNaNbOF₅.

CONCLUSIONS

Thus, the co-existence of two polymorphic (concomitant) α - and β -modifications of KNaNbOF₅ indicate the kinetic preference for the centrosymmetric of the β -phase of KNaNbOF₅ because its crystallization rate is much higher than that of the α -form. Both structures are ordered. It is noteworthy that all so far known inorganic compounds with ordered oxofluoride anions of transition metals contain sodium cations preferably interacting with fluoride ions [11]. The ordered noncentrosymmetric structure determining the nonlinear optical (SHG) properties of α -KNaNbOF₅ is the only one at present.

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