JOURNAL OF SOLID STATE CHEMISTRY 53, 136–139 (1984)

BRIEF COMMUNICATIONS

Chemical Preparation and X-Ray Structure Determination of $K_{0.30}NbF_3$

R. MASSE, S. ALÉONARD, AND M. T. AVERBUCH-POUCHOT

Laboratoire de Cristallographie, Centre National de la Recherche Scientifique, Laboratoire associé à l'USMG, 166X, 38042 Grenoble Cédex, France

Received October 4, 1983; in revised form December 13, 1983

The preparation and crystal structure of $K_{0.30}NbF_3$ single crystals are described. The compound is orthorhombic with $a = 7.540(3)$, $b = 13.06(2)$, $c = 7.750(3)$ Å, space group $C222_1$. The structure refines to $R = 0.044$ with 455 reflections. The framework derives from the Magneli hexagonal tungsten bronze and is similar to the $K_{0.25}VF_3$ orthorhombic phase.

Introduction

Nb_6F_{15} is the only known niobium cluster fluoride (*1*). The niobium cluster chloride $K_4Nb_6Cl_{18}$ was obtained by reduction of Nb_3Cl_8 in LiCl, KCl, Nb mixtures (*2*) and by electrochemical reduction of a LiCl, KCl, eutectic melt containing Nb_3Cl_8 and niobium anode (*3*). We have tried to apply these two syntheses to prepare potassium niobium cluster fluoride compounds: first, a direct reaction between molten K_2NbF_7 and niobium metal; second, electrochemical reduction of a LiF, KF eutectic melt with a soluble niobium anode. Reactions in LiF, KF, or K_2NbF_7 molten fluorides between Nb^0 and fluorides lead to the production of bronze materials. The electrochemical reduction leads to a compound of ideal formula $KNbF_3$, probably with a small quantity of oxygen on the fluorine site: $KNbF_{3-x}O_x$.

Experimental

Pure K_2NbF_7 (0.760 g) is mixed with 0.116 g of niobium metal (puratronic JMC) and 0.012 g of graphite ($5K_2NbF_7 + 2.5\ Nb^0 + 2C$) in a dry box under argon atmosphere. This mixture is evacuated and sealed in a platinum tube and then heated for a week at 850°C. Thereafter, the sample is cooled rapidly down to 500°C, then to 200°C. Two forms of crystals grew on graphite aggregates: thick blue-black crystals with a hexagonal section, and blue transparent hexagonal needles. Both correspond to the same material (verified by X-ray analysis). The needles result from the rapid growth of seeds fixed on graphite aggregates when the temperature of the sample is lowered from 850 to 500°C (Fig. 1).

An investigation with a precession camera (Mo$K\alpha$ = 0.711 Å) of a thick crystal (or a needle) gives a pseudohexagonal cell: a =

0022-4596/84 $3.00

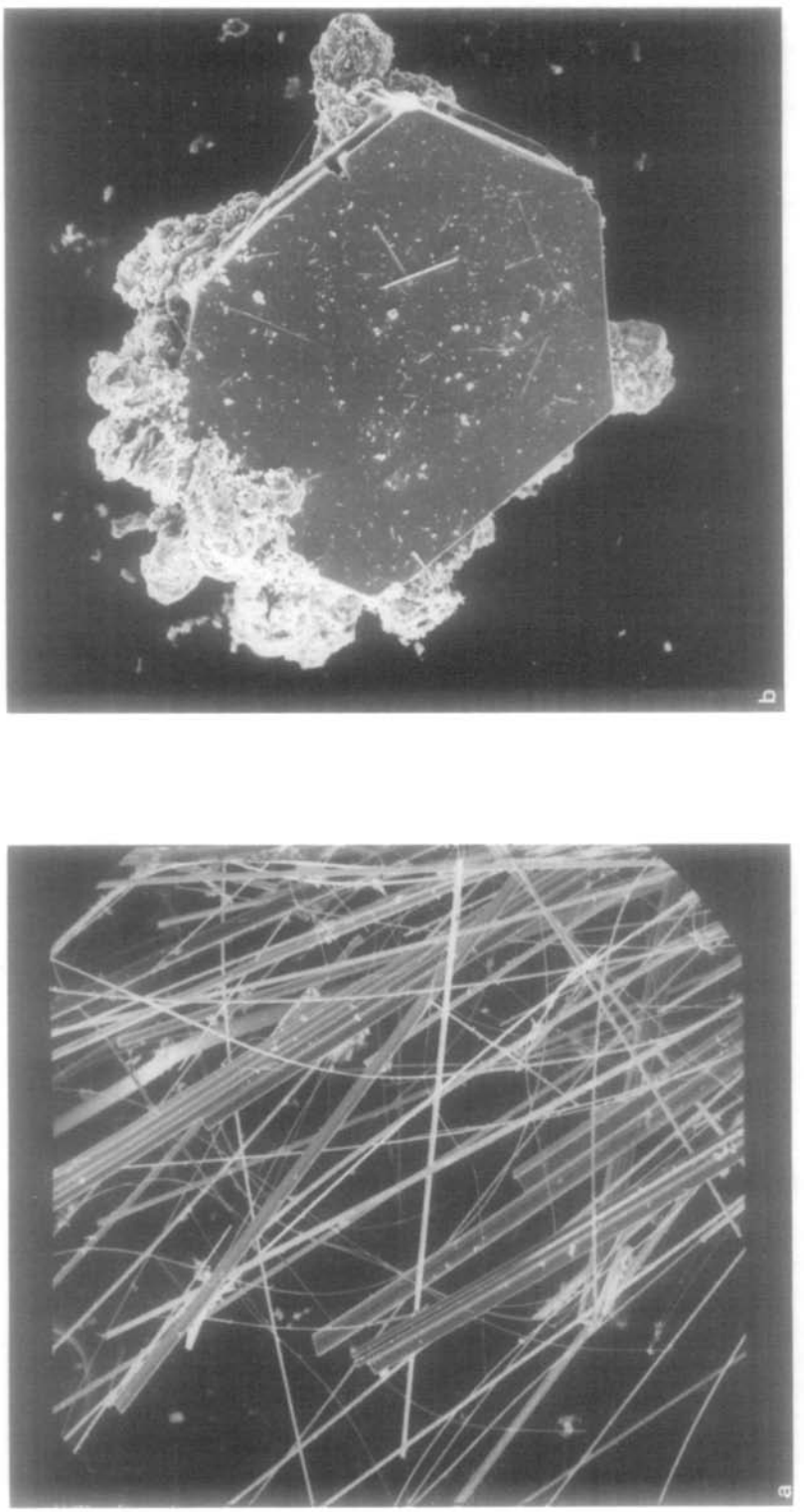

FIG. 1. Crystals of the $K_{0.30}NbF_3$ orthorhombic phase grown with needle or prismatic shape. Images obtained with a scanning electron microscope. (a) Scale: 1 cm/41.6 μm. (b) Scale: 1 cm/62.5 μm.

7.54 Å, c = 3.87 Å. Numerous additional weak reflections appear after long exposures, leading to an orthohexagonal cell with a doubling of c. The true cell is orthorhombic with a = 7.540(3) Å, b = 13.06(2) Å, c = 7.750(3) Å, V = 763.2 Å^3. The space group is $C222_1$, Z = 12, d_x = 4.20.

A crystal of prismatic shape and approximate dimensions 0.26 × 0.16 × 0.16 mm^3 was used for data collection. Five hundred ninety independent reflections were collected in ω scan with an automatic four-circle diffractometer, Philips PW 1100, using Mo$K\alpha$ radiation (0.7107 Å). The θ range was 3 to 30°, the scan speed 0.02°/sec, and the scan width 1.40°. The background was measured during 10 sec at the starting and final position of each scan. No absorption correction was made (μMo$K\alpha$ = 48.6 cm^{-1}).

The crystal structure was solved and refined using the SDP system (Version RSX 11M, September 1977; Enraf-Nonius) with Patterson and Fourier techniques. Full matrix refinement in the space group $C222_1$ gave $R = \Sigma||F_0| - |F_c||/\Sigma F_0 = 0.044$ with 455 independent reflections, satisfying the condition $F_0^2 > 4\,\sigma(F_0^2)$, $\sigma(F_0^2)$ = counting statistics. Sixteen reflections with $|F_0| - |F_c| > 25$ on a scale ranging from 0 to 1735 were also omitted. The final difference Fourier map was featureless (±0.5 e Å^{-3}). A list of observed and calculated structure factors will be sent on request (R.M.).

Results and Discussion

The formula established by this structural determination is $K_{3.64}Nb_{12}F_{36}$ or $12K_{0.30}NbF_3$. Atomic, isotropic, and anisotropic thermal parameters of $K_{0.30}NbF_3$ are given in Table I. The structure is derived from the Magneli hexagonal tungsten bronze type. The interatomic distances and angles of the two NbF_6 octahedra are given in Table II together with the K–F distances.

TABLE I

ATOMIC, ISOTROPIC,[a] AND ANISOTROPIC[b] THERMAL PARAMETERS OF $K_{0.30}NbF_3$

Atom	Position in $C222_1$	x	y	z	B_{eq}	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
Nb1	4*a*	−0.0038(4)	0.0000(0)	0.0000(0)	1.93(3)	0.01054(18)	0.00205(5)	0.0082(2)	0.0000(0)	0.0000(0)	−0.0008(5)
Nb2	8*c*	0.2515(3)	0.2518(2)	0.0013(5)	1.91(2)	0.00728(9)	0.00313(4)	0.0081(1)	−0.0024(1)	−0.0003(4)	−0.0005(4)
K	4*b* (3.64)	0.0000(0)	0.497(2)	0.2500(0)	16.8(9)	0.039(3)	0.0116(9)	0.14(1)	0.0000(0)	0.01(2)	0.0000(0)
F1	8*c*	0.5020(15)	0.2095(4)	0.473(1)	2.01(20)	0.0048(6)	0.0025(3)	0.0135(15)	−0.0051(17)	−0.012(3)	0.002(1)
F2	8*c*	0.6850(13)	0.3964(6)	−0.042(1)	2.17(25)	0.0137(15)	0.0025(4)	0.0071(15)	−0.0008(14)	−0.001(2)	0.001(1)
F3	8*c*	0.6872(7)	0.3947(4)	0.494(2)	1.08(13)	0.0022(6)	0.0009(2)	0.0088(9)	0.0016(7)	0.003(3)	−0.001(2)
F4	8*c*	0.7715(11)	0.2625(9)	0.256(2)	3.40(26)	0.0127(15)	0.0098(8)	0.0026(7)	−0.0015(19)	−0.005(3)	−0.005(3)
F5	4*b*	0.0000(0)	−0.0119(11)	0.250(0)	4.12(39)	0.0417(36)	0.0039(7)	0.0007(9)	0.0000(0)	−0.008(6)	0.000(0)

[a] $^+B_{eq} = \frac{4}{3}\sum_{ij} a_i a_j \beta_{ij}$.

[b] $T = \exp - (h^2\beta_{11} + k^2\beta_{22} + l^2\beta_{33} + hk\beta_{12} + hl\beta_{13} + kl\beta_{23})$. Standard deviations are in parentheses.

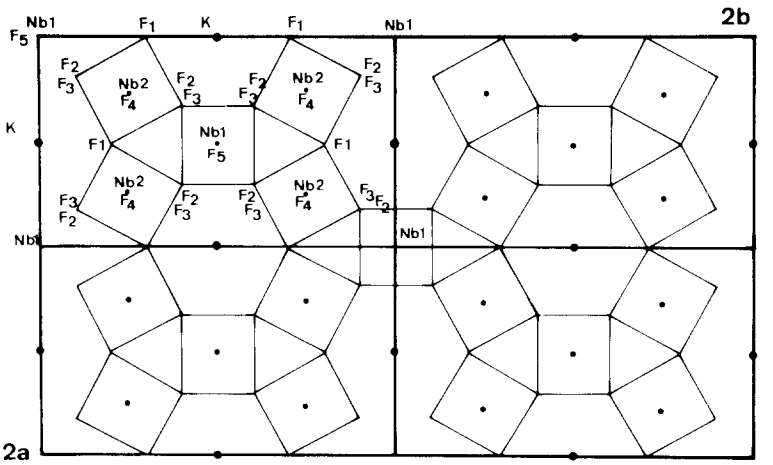

FIG. 2. Projection on the (a,b) plane of the $K_{0.30}NbF_3$ simplified structure. Four cells are drawn to illustrate the channels containing the potassium atoms.

Numerous phases of vanadium fluorobronzes have been pointed out in the literature (*4–6*). Orthorhombic phases of K_xVF_3, Rb_xVF_3, Tl_xVF_3 are described by Hong *et al.* (*5*). Very precise studies by high-resolution electron microscopy made by Langley *et al.* (*7*) and Rieck *et al.* (*8, 9*) provide excellent support for the comparison between K_xVF_3, α_{II}, orthorhombic phase, and $K_{0.30}NbF_3$ and an understanding of the possible detailed structure. In Fig. 2, we can see the pseudohexagonal arrangement of slightly distorted NbF_6 octahedra with channels containing 3.64 potassium per cell. This model is similar to that given by Rieck *et al.* (*9*) for $K_{0.25}VF_3$.

TABLE II

INTERATOMIC DISTANCES (Å) IN $K_{0.30}NbF_3$: SELECTED ANGLES (°)

Nb1–F2	1.993(10)	(×2)	F2–Nb2–F3	169.9(5)	
Nb1–F3	1.953(6)	(×2)	F2–Nb2–F4	94.8(4)	
Nb1–F5	1.947(1)	(×2)	F2–Nb2–F4	83.9(4)	
			F3–Nb2–F4	95.2(5)	
F2–Nb1–F2	88.6(6)		F3–Nb2–F4	86.1(5)	
F2–Nb1–F3	169.2(4)	(×2)	F4–Nb2–F4	178.5(1)	
F2–Nb1–F3	91.9(2)	(×2)			
F2–Nb1–F5	95.6(4)	(×2)	K–F1	3.27 (2)	(×2)
F2–Nb1–F5	83.2(4)	(×2)	K–F1	3.45 (2)	(×2)
F3–Nb1–F3	89.7(4)		K–F2	3.54 (1)	(×2)
F3–Nb1–F5	95.2(5)	(×2)	K–F2	3.19 (1)	(×2)
F3–Nb1–F5	86.0(5)	(×2)	K–F3	3.31 (1)	(×2)
F5–Nb1–F5	178.3(2)		K–F3	3.39 (1)	(×2)
			K–F4	3.52 (2)	(×4)
Nb2–F1	1.992(10)		K–F5	3.778(1)	(×2)
Nb2–F1	1.952(9)				
Nb2–F2	2.026(9)				
Nb2–F3	1.924(7)				
Nb2–F4	2.011(12)				
Nb2–F4	1.898(13)				
F1–Nb2–F1	178.2(2)				
F1–Nb2–F2	91.2(3)				
F1–Nb2–F3	89.2(2)				
F1–Nb2–F4	89.2(3)				
F1–Nb2–F4	90.1(3)				
F1–Nb2–F2	87.1(4)				
F1–Nb2–F3	92.5(2)				
F1–Nb2–F4	90.2(4)				
F1–Nb2–F4	90.4(4)				

References

1. H. SCHÄFER, H. G. SCHNERING, K. J. NIEHUES, AND H. G. NIEDER-VAHRENHOLZ, *J. Less-Common Met.*, 9–95 (1965).
2. A. SIMON, H. V. VON SCHNERING, AND H. SCHÄFER, *Z. Anorg. Allg. Chem.* **361,** 235 (1968).
3. R. MASSE AND A. SIMON, *Mater. Res. Bull.* **16,** 1007 (1981).
4. C. CROS, R. FEURER, M. POUCHARD, AND P. HAGENMULLLER, *Rev. Chim. Miner.* **11,** 585 (1974).
5. Y. S. HONG, R. F. WILLIAMSON, AND W. O. J. BOO, *Inorg. Chem.* **18,** 2123 (1979).
6. Y. S. HONG, R. F. WILLIAMSON, AND W. O. J. BOO, *Inorg. Chem.* **19,** 2229 (1980).
7. R. LANGLEY, D. RIECK, H. EICK, L. EYRING, R. F. WILLIAMSON, AND W. O. J. BOO, *Mater. Res. Bull.* **13,** 1297 (1978).
8. D. RIECK, R. LANGLEY, AND L. EYRING, *J. Solid State Chem.* **45,** 259 (1982).
9. D. RIECK, R. LANGLEY, AND L. EYRING, *J. Solid State Chem.* **48,** 100 (1983).