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$Ba_5Nb_3O_3F_{18}(HF_2)$: Synthesis and Crystal Structure

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Single crystals of $Ba_5Nb_3O_3F_{18}(HF_2)$ are grown by hydrothermal synthesis. The crystal structure is established from single-crystal X-ray diffraction data: S. G. $P6_3/m$, $Z = 2$, $a = 11.935(1)$ Å, and $c = 7.852(1)$ Å ($R = 0.0249$, $R_w = 0.0255$ for 819 independent reflections and 57 parameters). The tridimensional network is built up from NbX_7 (X = O, F) pentagonal bipyramids connected by Ba^{2+} ions. The location of anions (O^{2-}, F^-, and $[HF_2]^-$) is discussed from bond valence calculations.

Introduction

We report here the synthesis and the crystal structure of $Ba_5Nb_3O_3F_{18}(HF_2)$. This phase was encountered in the course of a general study of barium complex oxide fluorides of transition metals (*1–4*). As in $Ba_4Nb_2O_3F_{12}$ (*3*) and $Ba_3Nb_2O_2F_{12} \cdot 2H_2O$ (*4*), the structure of the title compound is built up from NbX_7 (X = O, F) pentagonal bipyramids; the location of O^{2-}, F^-, and $[HF_2]^-$ is discussed from bond valence calculations.

Preparation

Crystals of $Ba_5Nb_3O_3F_{18}(HF_2)$ were prepared by hydrothermal synthesis in HF solution from dry BaF_2 and NbO_2F in a stoechiometric ratio: 1 g of this mixture was introduced with 5 cm^3 HF 5 *M* in a teflon bomb (Berghof), heated 48 hr at 200°C (the pressure is close to 15 MPa), and then slowly cooled (6°/hr). The solid phase was filtered off, washed with ethanol, and air dried. Very few crystals (colorless needles) of this new oxide fluoride were obtained. The fluorine chemical analysis ($F_{exp} = 27.22 \pm 2.0\%$, $F_{theo} = 27.24\%$) was conducted by pyrohydrolysis and confirmed the presence of $[F–H–F]^-$ anions in the framework.

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X-Ray Data Collection

A crystal of approximate size $0.07 \times 0.02 \times 0.02$ mm^3, with boundary faces ± ⟨001⟩, ⟨100⟩, ⟨010⟩ was selected for the structural study. The experimental conditions of the X-ray data collection are listed in Table I. The lattice parameters were refined by the double scan technique from the positions of 32 reflections in the vicinity of 30° (2θ). The intensity data showed the systematic absences characteristic of $P6_3/m$ and $P6_3$ space groups ($00l : l = 2n + 1$).

Determination of the Structure

Calculations were made with the SHELX-76 program (*5*). Atomic scattering factors for Ba^{2+}, Nb^{5+}, and F^- ions, $\Delta f'$ and $\Delta f''$, were taken from "International Tables for X-ray Crystallography" (*6*) and from (*7*) for O^{2-}. In the space group $P6_3/m$, the Patterson method allowed us to locate three Ba and one Nb positions. Subsequent

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TABLE I

$Ba_5Nb_3O_3F_{18}(HF_2)$: Operating Conditions of the Intensity Data Collection (Siemens AED 2 Four-Circle Diffractometer)

Symmetry	Hexagonal
Space group	$P\,6_3/m$
a (Å)	11.935(1)
c (Å)	7.852(1)
V (Å^3)	968.6
Z	2
Formula weight (g)	1394.39
D_{calc} (g/cm^3)	4.78
Temperature (°C)	20
Radiation	MoK_α (graphite monochromatized)
Crystal volume (10^{-4} mm^3)	2.41
Scanning mode	$\omega/2\theta$
Aperture (mm)	3.5 × 3.5
Range registered	
θ_{max}(°)	45
h, k, l max	−14, 17, 11
Absorption coefficient (cm^{-1})	μ = 118.13
Absorption correction	Gaussian method
Transmission factors:	
T_{max}, T_{min}	0.6336, 0.5483
R_{int}	0.0213
Reflections measured	Two independent sets—177 standards
Total	2486
Independent	1202
Used in refinement ($I > 3\sigma(I)$)	819
Number of refined parameters	57
Secondary extinction	0.00024 (6)
Weighting scheme	$w = 0.92/(\sigma^2(F) + 5.66\ 10^{-4}F^2)$
Electron density in final Fourier difference map maximum, minimum (e^-/Å^3)	2.0, −1.7
R, R_w	0.0249, 0.0255

Fourier difference synthesis revealed six noncationic sites. The structural model was then classicaly refined. However, as in various oxide fluorides (*1–4*), it was impossible to distinguish between O^{2-} and F^- from X-ray diffraction data, but the bond valence method (*8*) showed unambiguously their relative positions; Table II presents the calculated valence for the six noncationic sites: F atoms of the $[F{-}H{-}F]^-$ anions are located on site 6 (quoted FH); the disorder of six O^{2-} and six F^- on the two 6*h* positions corresponding to the sites 4 and 5 (quoted OF1 and OF2) is explained by the intermediate value of their calculated valence. Hydrogen atoms of $[HF_2]^-$ groups were impossible to locate even if the data set used for the Fourier difference synthesis was limited to lower values of 2θ.

With absorption correction, anisotropic thermal parameters and weighting scheme, the final refinement cycle converged to $R = 0.0249$ and $R_w = 0.0255$. The Fourier difference synthesis was then featureless with maxima and minima in the range ± 2 e^-/Å^3. Calculations in the $P6_3$ space group did not improve the result. Tables IIIa and b present final atomic coordinates and thermal parameters, while the main interatomic distances and angles are given in Table IV (F_o and F_c tables will be sent upon request).

TABLE II

$Ba_5Nb_3O_3F_{18}(HF_2)$: CALCULATED VALENCE S FOR THE ANIONIC SITES[a]

	Ba1	Ba2	Ba3	Nb	Σ_S
			Site 1		
O^{2-}		0.26	0.26–0.19	0.63	1.34
F^-		0.19	0.20–0.15	0.57	1.11
			Site 2		
O^{2-}		0.31	0.36	0.69	1.36
F^-		0.24	0.27	0.62	1.13
			Site 3		
O^{2-}	0.13		0.32	0.81	1.26
F^-	0.10		0.24	0.72	1.06
			Site 4		
O^{2-}	0.45–0.45			0.75	1.65
F^-	0.34–0.34			0.68	1.36
			Site 5		
O^{2-}			0.27–0.17	1.43	1.87
F^-			0.20–0.13	1.28	1.61
			Site 6		
O^{2-}		0.24	0.11–0.11–0.11		0.57
F^-		0.18	0.09–0.09–0.09		0.45

[a] For the sites i, $S_i = \Sigma_j \exp [(R_{ij} - d_{ij})/b]$ with $b = 0.37$ and R_{ij} for oxygen and fluorine are, respectively, 2.29 and 2.19 for Ba^{2+} and 1.911 and 1.87 for Nb^{5+}

Description of the Structure

The structure (Fig. 1) is built up from isolated $NbOF_6$ pentagonal bipyramids represented in Fig. 2. As reported in Table I, the shortest Nb–X distance is normally found for Nb–OF2 (1.779(8) Å), OF2 being the site with the highest rate of O^{2-}, as in other $NbOF_6$ similar polyhedra (1.851 Å in $Ba_3Nb_2O_2F_{12} \cdot 2H_2O$ (*4*), 1.704 Å in $Ba_4Nb_2O_3F_{12}$ (*3*)); the mean distance Nb–X is very close to the sum of the ionic radii (*9*). As quoted above, the 6h positions, labeled OF1 and OF2, are occupied in a disordered fashion by six O^{2-} and six F^- ions.

Ba^{2+} cations (Ba1, Ba2, and Ba3) are, respectively, in a 12-, 11-, and 11-fold coordi-

TABLE IIIa

$Ba_5Nb_3O_3F_{18}(HF_2)$: FRACTIONAL ATOMIC COORDINATES AND THERMAL PARAMETERS

Atom	Position	x	y	z	B_{eq} (Å^2)
Ba1	2b	0	0	0	1.40(3)
Ba2	2c	1/3	2/3	1/4	0.92(3)
Ba3	6h	0.6401(1)	0.5605(1)	1/4	0.93(3)
Nb	6h	0.2819(1)	0.3285(1)	1/4	0.99(4)
F1	12i	0.3921(3)	0.4901(3)	0.0989(5)	1.2(2)
F2	6h	0.2434(5)	0.8359(5)	1/4	1.5(3)
F3	12i	0.2261(4)	0.2776(3)	0.4900(5)	1.4(2)
OF1	6h	0.1411(6)	0.1413(5)	1/4	2.3(3)
OF2	6h	0.7015(6)	0.1152(6)	1/4	1.7(4)
FH	4f	1/3	2/3	0.8907(10)	1.6(3)

TABLE IIIb

$Ba_5Nb_3O_3F_{18}(HF_2)$: ANISOTROPIC THERMAL PARAMETERS U_{ij} (Å^2 × 10^4)

	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Ba1	226(3)	226(3)	82(3)	113(1)	0	0
Ba2	99(2)	99(2)	151(4)	50(1)	0	0
Ba3	123(2)	128(2)	109(2)	68(2)	0	0
Nb	135(3)	96(3)	110(3)	31(2)	0	0
F1	170(15)	124(14)	140(16)	50(12)	41(13)	4(13)
F2	155(22)	142(23)	233(27)	53(20)	0	0
F3	196(16)	175(16)	126(16)	70(13)	19(14)	20(13)
OF1	306(31)	102(23)	219(29)	−71(21)	0	0
OF2	206(30)	49(23)	366(38)	56(23)	0	0
FH	242(22)	242(22)	110(33)	121(11)	0	0

Note. The form of anisotropic thermal parameter is

$$T = \exp - [2\pi^2(h^2a^{*2}U_{11} + k^2b^{*2}U_{22} + l^2c^{*2}U_{33} + 2hka^*b^*U_{12} + 2hla^*c^*U_{13} + 2klb^*c^*U_{23})].$$

nation and ensure the connection between the isolated NbX_7 groups, so that the structure is tridimensional. The mean distances in each barium polyhedron are very close (2.820, 2.780, and 2.851 Å, respectively for Ba1, Ba2, and Ba3) and are in good agreement with the sum of the ionic radii (*9*).

Ba1 is at the center of a cubooctahedron,

TABLE IV

$Ba_5Nb_3O_3F_{18}(HF_2)$: SELECTED INTERATOMIC DISTANCES (Å) AND ANGLES (°)

	NbX₇ Pentagonal bipyramid						
Nb	OF2	F3	F3	OF1	F2	F1	F1
OF2	**1.779(8)**	2.840(7)	2.840(7)	2.829(8)	3.800(5)	2.700(7)	2.700(7)
F3	97.7(5)	**1.990(3)**	3.769(6)	2.361(6)	2.766(4)	3.842(2)	2.412(5)
F3	97.7(5)	142.6(3)	**1.990(3)**	2.361(6)	2.766(4)	2.412(5)	3.842(2)
OF1	96.2(5)	72.3(4)	72.3(4)	**2.015(4)**	3.049(9)	3.904(4)	3.904(4)
F2	166.5(4)	86.5(3)	86.5(3)	97.3(4)	**2.047(7)**	2.665(6)	2.665(6)
F1	88.5(4)	141.6(2)	72.7(4)	145.0(2)	80.5(3)	**2.079(3)**	2.373(5)
F1	88.5(4)	72.7(4)	141.6(2)	145.0(2)	80.5(3)	69.6(4)	**2.079(3)**

⟨Nb–X⟩ = 1.997 Å

Ba1 Polyhedron	⟨Ba1–X⟩ = 2.820 Å
6 × Ba1–OF1	2.587(5)
6 × Ba1–F3	3.054(4)
Ba2 Polyhedron	⟨Ba2–X⟩ = 2.780 Å
3 × Ba2–F2	2.720(7)
6 × Ba2–F1	2.796(3)
2 × Ba2–FH	2.821(8)
Ba3 Polyhedron	⟨Ba3–X⟩ = 2.851 Å
1 × Ba3–F2	2.670(7)
2 × Ba3–F3	2.714(7)
1 × Ba3–OF2	2.780(8)
2 × Ba3–F1	2.790(4)
2 × Ba3–F1	2.896(4)
1 × Ba3–OF2	2.938(5)
2 × Ba3–FH	3.088(10)
$[F–H–F]^-$ group	F–F = 2.21(2) Å

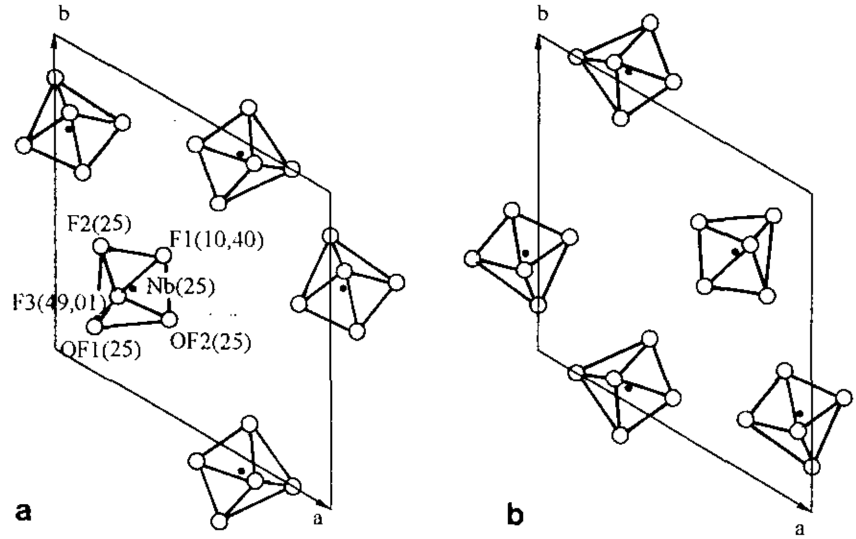

FIG. 1. $Ba_5Nb_3O_3F_{18}(HF_2)$: Partial projection on the (001) plane showing the location of the isolated NbX_7 (X = O, F) pentagonal bipyramids inside the unit cell, for $z < 1/2$ (a) and $z > 1/2$ (b) (numbers indicate the z-coordinate (×100) of the atoms).

the hexagonal basis of which being constituted by six F3 (at 3.054(4) Å) and the two top triangular faces by six OF1 (at 2.587(5) Å), as shown in Fig. 3. Each Ba1 polyhedron links together six NbX_7 bipyramids by sharing one edge OF1–F3 (Fig. 4).

In the case of Ba2, the polyhedron, represented in Fig. 5, is constituted by a trigonal prism $Ba2F1_6$, tricaped by three F2. Under and above the two triangular faces of the prism, two FH, owned by two different $[F–H–F]^-$ groups, are located at 2.821(8) Å. Inside a $[F–H–F]^-$ group, the distance F–F is equal to 2.21(2) Å, which is very close to those observed in other compounds as in $BaF(HF_2)$ (2.269 Å) (*10*) and in KHF_2 (2.25 Å) (*11*). Each Ba2 polyhedron shares three faces F1–F1–F2 with three different bipyramids NbX_7 (Fig. 4) and each group $[F–H–F]^-$ connects two Ba2 polyhedra along the c axis.

At last, the Ba3 polyhedron is very similar as that of Ba2 but not as regular: the trigonal prism $Ba3F1_4F3_2$ is tricaped by one F2 and two OF2 and the $[F–H–F]^-$ group is located

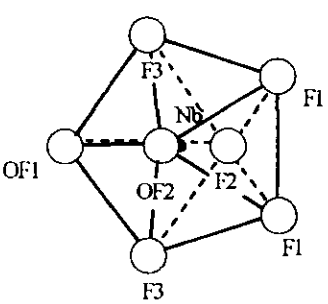

FIG. 2. $Ba_5Nb_3O_3F_{18}(HF_2)$–NbX_7 (X = O, F) pentagonal bipyramid.

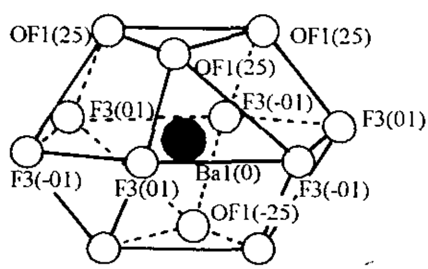

FIG. 3. $Ba_5Nb_3O_3F_{18}(HF_2)$: Ba1 cubooctahedron (numbers indicate the z coordinate (×100) of the atoms).

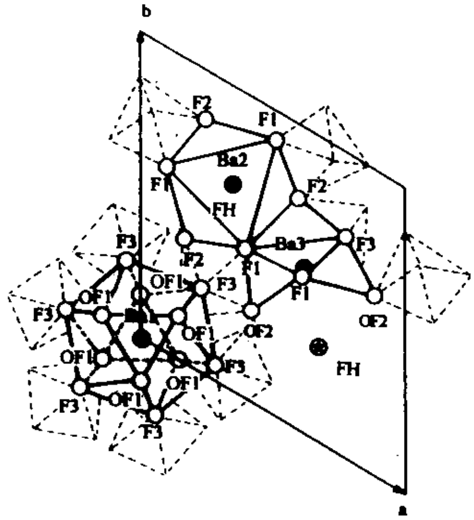

FIG. 4. $Ba_5Nb_3O_3F_{18}(HF_2)$: Partial projection on the (001) plane showing the connections between the Ba polyhedra and the NbX_7 groups (dotted).

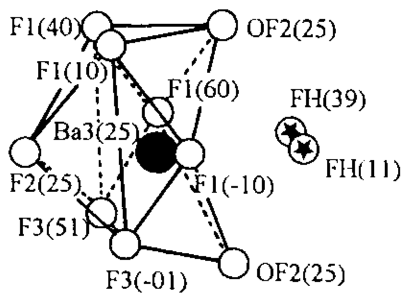

FIG. 6. $Ba_5Nb_3O_3F_{18}(HF_2)$: Ba3 polyhedron constituted by a trigonal prism $Ba3F1_4F3_2$, tricaped by one F2 and two OF2. One $[F–H–F]^-$ ion is located at the opposite of F2 (numbers indicate the z-coordinate (× 100) of the atoms).

at the opposite of F2 (Fig. 6). Each Ba3 polyhedron links together five NbX_7 pentagonal bipyramids by sharing one triangular face F1–F1–OF2 with the first one, one edge F1–F3 with two others, and only two corners (OF2 and F2) with the two last (Fig. 4).

It is worthy of note that the longest distances Ba2–X and Ba3–X are those relative to the $[F–H–F]^-$ group as in the case of

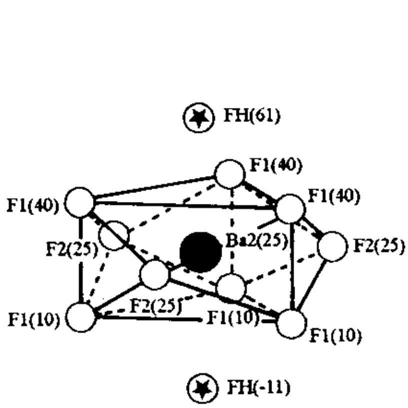

FIG. 5. $Ba_5Nb_3O_3F_{18}(HF_2)$: Ba2 polyhedron constituted by a trigonal prism $Ba2F1_6$, tricaped by three F2. Under and above the triangular faces $F1_3$, are located $[F–H–F]^-$ ions (numbers indicate the z-coordinate (× 100) of the atoms).

$BaF(HF_2)$ (2.76 Å) (10). In fact, a NbX_7 group shares all its corners with the barium cations: one edge OF1–F3 with Ba1, one face F1–F1–F2 with Ba2, and one other face F1–F1–OF2 with Ba3.

Conclusion

$Ba_5Nb_3O_3F_{18}(HF_2)$ is a new example of oxide fluoride with a $[F–H–F]^-$ anion; its tridimensional structure is constituted by isolated NbX_7 pentagonal bipyramids linked together by Ba^{2+} cations. Such groups NbX_7 have been already observed in two others oxide fluorides of barium and niobium (*3*, *4*) synthesized by the same method. To our knowledge and up to now, the $[F–H–F]^-$ ions were only found in MHF_2 (M = NH_4, Na, K, Li) and $M'F(HF_2)$ (M' = Ba, Sr).

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