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Synthesis and Crystal Structure of $Ba_4Nb_2O_3F_{12}$

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Single crystals of $Ba_4Nb_2O_3F_{12}$ were grown by hydrothermal synthesis. The structure is determined from X-ray diffraction data: space group $C2/c$, $Z = 12$, $a = 22.672(2)$ Å, $b = 13.075(1)$ Å, $c = 14.996(1)$ Å and $\beta = 114.234(5)°$ ($R = 0.0227$ and $R_w = 0.0282$ for 6886 independent reflections and 288 parameters). The network is built up from separated $[Nb_4O_7F_{14}]^{8-}$ blocks of four *cis*-oxygen linked distorted octahedra ($2 \times NbO_2F_4$ and $2 \times NbO_3F_3$) and from isolated $NbOF_6$ pentagonal bipyramids. All these entities are three-dimensionally connected by classically coordinated Ba^{2+} ions.

Introduction

Hydrothermal synthesis is a powerful tool to produce single crystals of oxyfluorides as shown in the case of the BaF_2–TiO_2–HF_{aq} system (*1*, *2*). We report here the preparation of $Ba_4Nb_2O_3F_{12}$ and its structure determination from single crystal X-ray diffraction data.

Preparation

Single crystals were prepared by hydrothermal synthesis (*1*) from BaF_2 and NbO_2F. Typical conditions of preparation are gathered in Table I. Small colorless platelets are filtered off and air-dried.

Determination of the Structure

A small single crystal was chosen for the data collection (platelet with boundary faces ± ⟨100⟩, ⟨$\bar{1}$02⟩, ⟨010⟩, ⟨263⟩, ⟨12$\bar{2}$⟩).

Table II gathers the operating conditions of the data collection. The lattice parameters—$a = 22.672(2)$ Å, $b = 13.075(1)$ Å, $c = 14.996(1)$ Å and $\beta = 114.234(5)°$—were refined by the double scan technique from the positions of 32 reflections near 30° (2θ). The intensity data show the systematic absences characteristic of $C2/c$ or Cc space groups ($hkl: h + k = 2n + 1$; $h0l: l = 2n + 1$). All the calculations were performed with the SHELX 76 program (*3*). Atomic scattering factors for ions, including $\Delta f'$ and $\Delta f''$ values are taken from "International Tables for X-Ray Crystallography" (*4*). The heavy Ba and Nb cations were located in the space group $C2/c$ by using the Patterson function. All the anions were found on subsequent Fourier difference maps. As in $BaTiOF_4$ (*1*) and Ba_2TiOF_6 (*2*), it was impossible to distinguish between O^{2-} and F^- by X-ray diffraction. The bond valence method (*5*) made it possible to clear up this question and showed O^{2-} unambiguously sites in Table III. Atomic coordinates and anisotropic thermal parameters were then refined, lead-

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TABLE I

$Ba_4Nb_2O_3F_{12}$: Operating Conditions of Crystal Growth

Volume of platinum tube	2.62 cm^3
Filling rate	0.55
H_2O, volume	1.8 cm^3
Ba/Nb molar ratio	1/1
BaF_2 mass	1.947 g
NbO_2F mass	1.598 g
P_{init} (RT)	1000 bars
Heating rate	200°/hr
Temp. max. (T_f)	590°C
Stay at T_f	50 hr
P_{final} at T_f	2010 bars
Natural cooling rate	

ing to the final values of R and R_w: 0.0227 and 0.0282 respectively. In these conditions, the final Fourier difference map was featureless.

Table IV a-b presents the atomic coordinates and thermal parameters (structure factors will be sent upon request) and Table V shows selected interatomic distances and angles. Calculations in the noncentric Cc space group did not improve the results.

Description of the Structure

As shown in Fig. 1, it can be seen as a stacking of two types of cationic planes

TABLE II

$Ba_4Nb_2O_3F_{12}$: Operating Conditions of the Intensity Data Collection (Siemens AED 2 Four-Circle Diffractometer)

Symmetry	Monoclinic
Space group	$C2/c$
a (Å)	22.672 (2)
b (Å)	13.075 (1)
c (Å)	14.996 (1)
β (°)	114.234 (5)
V (Å^3)	4053.6
Z	12
Formula weight (g/mol)	1011.15
D_{calc} (g/cm^3)	4.96
Temperature	20°C
Radiation	MoK_α (graphite monochromatized)
Crystal volume (10^{-3} mm^3)	1.44
Scanning mode	$\omega/2\theta$
Aperture (mm)	3.5 ×3.5
Range registered:	
θ_{max} (°)	35
h, k, l_{max}	34, 20, 24
Absorption coefficient	μ = 133.0 cm^{-1}
Absorption correction	Gaussian method
Transmission factors:	
T_{max}, T_{min}	0.4777, 0.1286
R_{int}	0.0185
Reflections measured:	
total	9815 (648 standards)
independent	8507
used in refinement ($I > 3\sigma(I)$)	6886
Number of refined parameters	288
Weighting scheme	$w = 1.00/(\sigma^2(F) + 2.1910^{-3}F^2)$
Secondary extinction coefficient	0.00004 (1)
Electron density in final Fourier difference map:	
maximum, minimum (e$^-$/Å^3)	3.1, −2.1
R,R_w	0.0227, 0.0282

TABLE III

$Ba_4Nb_2O_3F_{12}$: CALCULATED VALENCES V FOR THE OXIDE SITES ($V_i = \Sigma_j v_{ij}$ WITH $v_{ij} = \exp[(R_{ij}-d_{ij})/b]$)[a]

Site		v_{X-Ba}			v_{X-Nb}		$V_x = \Sigma_i v_{xi}$	
		$X = O^{2-}$	$X = F^-$		$X = O^{2-}$	$X = F^-$	$X = O^{2-}$	$X = F^-$
O1	Ba6	0.33	0.25	Nb2	1.75	1.57	**2.08**	1.82
O2	Ba6	0.17	0.13	Nb1	0.82	0.73	**2.08**	1.84
				Nb3	1.09	0.98		
O3	Ba3	0.20	0.15	Nb1	1.61	1.44	**1.90**	1.67
	Ba5	0.09	0.08					
O4	Ba1	0.04	0.03	Nb3	1.55	1.38	**1.97**	1.70
	Ba2	0.26	0.20					
	Ba6	0.12	0.09					
O5				2 × Nb1	2 × 1.04	2 × 0.93	**2.08**	1.86

[a] $b = 0.37$ and R_{ij} for oxygen and fluorine, respectively, are 2.29 and 2.19 for Ba^{2+} and 1.911 and 1.87 for Nb^{5+} (5).

TABLE IVa

$Ba_4Nb_2O_3F_{12}$: FRACTIONAL ATOMIC COORDINATES AND THERMAL PARAMETERS

	x	y	z	B_{eq}[Å^2]
Ba1	0.4155(1)	0.0063(1)	0.6119(1)	0.88(1)
Ba2	0.4063(1)	0.1619(1)	0.3407(1)	0.80(1)
Ba3	0.4232(1)	0.6607(1)	0.6106(1)	0.94(1)
Ba4	0.4172(1)	0.3319(1)	0.6114(1)	0.80(1)
Ba5	0.5870(1)	0.5058(1)	0.1434(1)	0.88(1)
Ba6	0.7600(1)	0.3242(1)	0.1678(1)	0.79(1)
Nb1	0.7628(1)	0.3614(1)	0.5871(1)	0.80(1)
Nb2	0.5610(1)	0.1662(1)	0.6026(1)	0.69(1)
Nb3	0.7608(1)	0.0425(1)	0.1111(1)	0.67(1)
F1	0.4568(1)	0.1653(1)	0.5386(1)	0.99(12)
F2	0.5407(2)	0.1631(1)	0.4559(2)	1.12(13)
F3	0.4568(1)	0.4953(2)	0.5473(2)	1.04(12)
F4	0.3683(1)	0.3344(2)	0.4102(2)	1.17(13)
F5	0.1751(1)	0.1394(2)	0.2873(2)	1.40(13)
F6	0.3544(2)	0.1673(2)	0.6170(2)	1.39(14)
F7	0.2855(2)	0.3649(2)	0.5256(2)	1.56(14)
F8	0.4505(2)	0.3337(2)	0.2998(2)	1.21(13)
F9	0.3653(2)	−0.1746(2)	0.6376(2)	1.51(15)
F10	0.6443(1)	0.4853(2)	0.3583(2)	1.42(13)
F11	0.2749(2)	0.4550(2)	0.2231(2)	1.54(14)
F12	0.5465(2)	0.3129(2)	0.5495(2)	1.76(16)
F13	0.4316(2)	−0.0199(2)	0.4384(2)	2.39(19)
F14	$\frac{1}{2}$	0.4552(3)	$\frac{3}{4}$	3.05(26)
F15	0.5441(2)	0.2553(3)	0.6994(2)	2.40(17)
F16	0.2812(1)	0.2219(2)	0.2056(2)	1.38(13)
F17	0.4538(2)	−0.0699(3)	0.3037(2)	2.54(18)
F18	0.1894(2)	0.4717(2)	0.8149(2)	1.58(14)
F19	$\frac{1}{2}$	−0.1148(3)	$\frac{3}{4}$	2.66(23)
O1	0.1430(2)	0.3210(3)	0.1517(3)	1.66(16)
O2	0.2205(2)	0.4520(2)	0.0062(2)	1.16(14)
O3	0.1851(2)	−0.0993(4)	0.5659(3)	2.78(22)
O4	0.3057(2)	0.1144(3)	0.3946(3)	1.57(16)
O5	$\frac{1}{4}$	$\frac{1}{4}$	0	4.14(47)

TABLE IVb

$Ba_4Nb_2O_3F_{12}$: ANISOTROPIC THERMAL PARAMETERS U_{ij} (Å^2 × 10^4)

	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
Ba1	140(1)	88(1)	120(1)	2(1)	69(1)	5(1)
Ba2	106(1)	106(1)	84(1)	9(1)	32(1)	−6(1)
Ba3	150(1)	105(1)	132(1)	−10(1)	88(1)	−13(1)
Ba4	113(1)	87(1)	98(1)	2(1)	38(1)	−6(1)
Ba5	127(1)	103(1)	90(1)	6(1)	29(1)	2(1)
Ba6	96(1)	114(1)	96(1)	5(1)	47(1)	5(1)
Nb1	110(1)	105(1)	69(1)	7(1)	18(1)	−30(1)
Nb2	86(1)	106(1)	72(1)	−3(1)	33(1)	−4(1)
Nb3	91(1)	86(1)	80(1)	−12(1)	38(1)	−5(1)
F1	102(10)	156(11)	117(10)	−23(8)	45(9)	−30(8)
F2	215(13)	136(11)	82(10)	−11(7)	68(10)	−6(9)
F3	163(12)	134(10)	109(11)	22(8)	68(9)	−7(9)
F4	160(12)	152(11)	147(11)	3(8)	77(10)	−5(9)
F5	191(13)	112(10)	164(11)	24(8)	7(10)	2(9)
F6	158(12)	143(11)	269(14)	−4(9)	129(11)	2(9)
F7	171(13)	266(13)	151(12)	−95(10)	61(10)	35(11)
F8	193(13)	118(10)	161(12)	3(8)	87(10)	−3(9)
F9	187(13)	189(12)	252(14)	79(10)	145(12)	90(10)
F10	146(12)	188(11)	210(13)	18(10)	76(10)	−71(10)
F11	223(14)	177(11)	188(12)	65(9)	86(11)	−12(10)
F12	364(17)	97(10)	218(13)	−19(9)	131(13)	−11(11)
F13	534(24)	84(10)	240(15)	2(10)	109(15)	27(13)
F14	505(35)	234(22)	228(22)	0	−108(21)	0
F15	206(14)	548(21)	143(12)	−176(13)	54(11)	77(14)
F16	196(13)	203(11)	120(10)	−43(9)	59(9)	47(10)
F17	263(16)	511(21)	190(14)	166(14)	92(12)	−75(15)
F18	306(16)	143(11)	176(12)	67(9)	122(11)	37(11)
F19	454(32)	193(19)	206(20)	0	−75(20)	0
O1	119(14)	323(17)	162(14)	4(12)	31(11)	−10(13)
O2	151(13)	146(12)	134(12)	−73(10)	46(10)	2(10)
O3	122(15)	646(29)	285(19)	258(20)	78(14)	58(18)
O4	166(14)	232(15)	209(15)	18(12)	88(12)	−58(12)
O5	1126(72)	287(28)	209(25)	121(22)	323(36)	418(38)

Note. The form of the anisotropic thermal parameter is

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

perpendicularly to the *a* direction. One kind, called A, contains Nb2 and all the Ba cations except Ba6; the second, B, contains Nb1, Nb3, and Ba6. The stacking sequence along the *a*-axis is then ABAABA. Two successive blocks ABA are exchanged by a twofold axis parallel to [010] at $x = \frac{1}{2}$ (or 0) and $z = \frac{1}{4}$, involving a doubling of the cell parameter in the [100] direction.

Inside each block ABA, the two cationic planes A are associated by a 2_1 axis parallel to [010] at $z = \frac{1}{4}$.

In the A planes (see Fig. 2), isolated $(NbOF_6)^{3-}$ pentagonal bipyramids are found (centered by Nb2) with a very short Nb2–O1 bond (1.704 (4) Å) at the opposite of a long Nb2-F1 distance (2.154(2)Å) (see Table V). Such a coordination was found in K_3NbOF_6

TABLE V

$Ba_4Nb_2O_3F_{12}$: SELECTED INTERATOMIC DISTANCES (Å) AND ANGLES (°)

$Nb1O_3F_3$ Octahedron

Nb1	O3	O5	F16	O2	F18	F9
O3	*1.735(5)*	2.868(3)	2.822(4)	2.846(3)	2.824(5)	3.900(6)
O5	104.2(3)	*1.898(2)*	2.890(2)	2.735(2)	3.855(0)	2.763(3)
F16	98.7(3)	96.4(2)	*1.977(1)*	3.893(2)	2.667(3)	2.580(3)
O2	99.6(3)	89.6(2)	158.7(1)	*1.985(2)*	2.671(4)	2.780(4)
F18	97.0(3)	158.5(1)	83.5(3)	83.5(3)	*2.026(4)*	2.536(4)
F9	170.2(4)	85.0(2)	76.5(3)	83.6(3)	74.0(3)	*2.180(4)*

⟨Nb1–*X*⟩ = 1.967 Å

$Nb3O_2F_4$ Octahedron

Nb3	O4	O2	F11	F7	F5	F10
O4	*1.750(5)*	2.794(3)	2.856(3)	2.795(3)	2.748(4)	3.861(6)
O2	100.7(.3)	*1.879(3)*	2.968(3)	2.763(4)	3.895(1)	2.933(5)
F11	101.0(.3)	101.7(.2)	*1.947(2)*	3.868(1)	2.695(3)	2.615(3)
F7	96.0(.3)	90.7(.3)	156.5(.1)	*2.003(3)*	2.572(4)	2.669(4)
F5	92.2(.3)	164.2(.1)	84.6(.3)	78.7(.3)	*2.054(3)*	2.507(4)
F10	165.5(.4)	93.4(.3)	79.4(.3)	80.1(.3)	73.4(.3)	*2.142(4)*

⟨Nb3–*X*⟩ = 1.962 Å

$Nb2OF_6$ Pentagonal bipyramid

Nb2	O1	F17	F15	F13	F12	F2	F1
O1	*1.704(4)*	2.916(4)	2.802(4)	2.672(4)	2.729(4)	2.907(4)	3.854(5)
F17	102.9(3)	*2.016(3)*	2.425(5)	2.366(4)	2.868(2)	3.759(4)	2.706(4)
F15	97.3(3)	73.9(4)	*2.018(5)*	3.871(1)	2.394(5)	3.816(4)	2.683(4)
F13	90.7(3)	71.4(3)	145.3(1)	*2.037(3)*	3.858(4)	2.365(5)	3.069(4)
F12	92.8(3)	144.0(1)	72.1(4)	141.4(2)	*2.051(2)*	2.381(5)	2.760(4)
F2	101.0(3)	134.9(2)	139.2(2)	70.7(3)	70.9(3)	*2.053(3)*	2.663(2)
F1	174.6(3)	80.8(3)	80.0(3)	94.1(2)	82.0(3)	78.5(2)	*2.154(2)*

⟨Nb2–*X*⟩ = 2.005 Å

Ba1 Polyhedron

Ba1-F6	2.537(4)	Ba1-F2	2.785(4)
Ba1-F19	2.684(3)	Ba1-F13	2.793(4)
Ba1-F1	2.693(3)	Ba1-F17	2.828(5)
Ba1-F9	2.720(4)	Ba1-O2	2.944(4)
Ba1-F17	2.769(3)	Ba1-F18	3.035(5)

⟨Ba1–*X*⟩ = 2.779 Å

Ba2 Polyhedron

Ba2-F8	2.633(4)	Ba2-F9	2.801(3)
Ba2-F1	2.708(3)	Ba2-F2	2.819(4)
Ba2-F13	2.727(3)	Ba2-F16	2.837(3)
Ba2-F4	2.766(3)	Ba2-F18	3.008(3)
Ba2-O4	2.784(6)	Ba2-F19	3.019(2)

⟨Ba2–*X*⟩ = 2.810 Å

Ba3 Polyhedron

Ba3-F3	2.598(5)	Ba3-F8	2.645(4)
Ba3-F10	2.606(4)	Ba3-F2	2.764(3)
Ba3-F8	2.618(5)	Ba3-F12	2.775(4)
Ba3-F9	2.638(5)	Ba3-O3	2.888(6)

⟨Ba3–*X*⟩ = 2.691 Å

TABLE V—*Continued*

		Ba4 Polyhedron	
Ba4-F6	2.600(4)	Ba4-F7	2.757(5)
Ba4-F3	2.646(4)	Ba4-F15	2.789(5)
Ba4-F14	2.691(2)	Ba4-F15	2.812(5)
Ba4-F1	2.747(3)	Ba4-F10	2.895(4)
Ba4-F4	2.755(3)	Ba4-F5	3.072(4)
⟨Ba4–*X*⟩ = 2.776 Å			
		Ba5 Polyhedron	
Ba5-F3	2.618(4)	Ba5-F5	2.856(2)
Ba5-F8	2.666(6)	Ba5-F10	2.951(5)
Ba5-F3	2.702(3)	Ba5-F11	3.018(5)
Ba5-F4	2.714(3)	Ba5-F14	3.049(3)
Ba5-F12	2.718(6)	Ba5-O3	3.148(8)
⟨Ba5–*X*⟩ = 2.844 Å			
		Ba6 Polyhedron	
Ba6-F6	2.554(5)	Ba6-F5	2.766(3)
Ba6-F4	2.656(3)	Ba6-F16	2.779(4)
Ba6-O1	2.698(4)	Ba6-F18	2.874(3)
Ba6-F11	2.700(4)	Ba6-O4	3.077(4)
Ba6-F7	2.702(3)		
⟨Ba6–*X*⟩ = 2.756 Å			

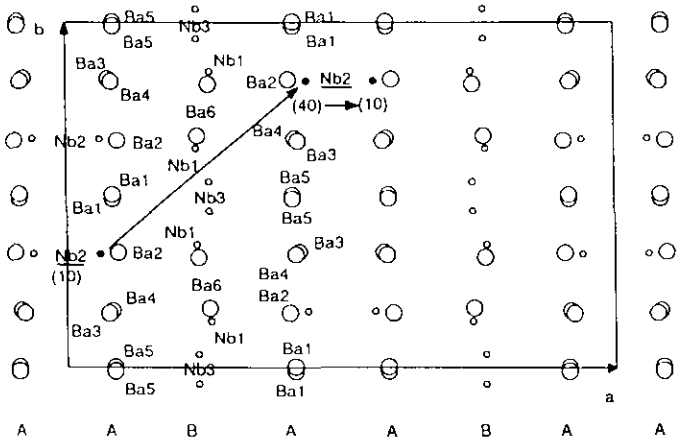

FIG. 1. $Ba_4Nb_2O_3F_{12}$: [001] view of the structure constituted by a stacking of two types of cationic planes (A and B) perpendicular to the a direction. The sequence along the *a*-axis is then ABAABA. Numbers indicate the *z* coordinate (× 100) of three Nb2 atoms, which are exchanged by a 2 and a 2_1 axis:

Nb2 (10)	→	Nb2 (40)	→	Nb2 (10)
	2_1 axis parallel to [010] at $x = \frac{1}{4}$ and $z = \frac{1}{4}$		2 axis parallel to [010] at $x = \frac{1}{2}$ and $z = \frac{1}{4}$	

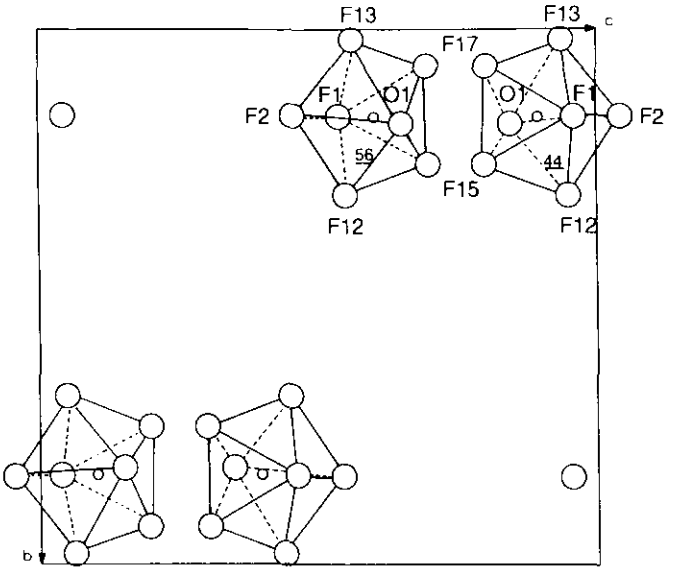

FIG. 2. $Ba_4Nb_2O_3F_{12}$: [100] view of an A plane showing the isolated $(Nb2OF_6)^{3-}$ pentagonal bipyramids (underlined numbers indicate the x coordinate ($\times$ 100) of Nb2 atoms (small circles)).

(6). The other distances Nb2-F are quite equivalent (ranging from: 2.016 (3) Å to 2.053 (3) Å).

In the B planes, isolated $(Nb_4O_7F_{14})^{8-}$ blocks of four *cis*-oxygen-linked distorted $(Nb(O,F)_6)$ octahedra are located. These entities are constituted by two $(Nb3O_2F_4)$ and two $(Nb1O_3F_3)$ octahedra. As shown in Fig. 3, in every $(Nb_4O_7F_{14})^{8-}$ block, the two Nb1 centered octahedra are cis-linked by O5 atoms and each Nb1 octahedron is cis-linked to a Nb3 octahedron by O2 atoms. From Table V, it can be seen that all the distances Nb–X are in good agreement with previous knowledge of niobium structural chemistry. However, it is worthy of note that the shortest bonds, Nb1–O3 and Nb3–O4 (1.735 (5) Å and 1.750 (5) Å, respectively), are opposite the longest distances, Nb1–F9 and Nb3–F10 (2.180 (4) Å and 2.142 (4) Å respectively) and are quite perpendicular to the B plane. The other distances are ranging from 1.898 (2) Å to 2.026 (4) Å for Nb1 and from 1.879 (3) Å to 2.054 (3) Å for Nb3.

For all the Ba^{2+} ions, we observe a clear cut for the Ba–X distances near 3.15 Å, the next neighbors lying at distances longer than 3.34 Å. The coordination number is classically 10 for Ba1, Ba2, Ba4, and Ba5, 8 for Ba3, and 9 for Ba6 (see Table V), each Ba^{2+} ion ensuring the three dimensional connection between the $(Nb_4O_7F_{14})^{8-}$ blocks and the $(NbOF_6)$ pentagonal bipyramids. It can be noted that F3, F4, F6, F8, F14, and F19 do not take part in the niobium coordination polyhedra but achieve the Ba^{2+} environment.

Conclusion

$Ba_4Nb_2O_3F_{12}$ is a three dimensional oxyfluoride which exhibits two kinds of coordination polyhedra for Nb atoms: the octahedral form with (NbO_2F_4) and (NbO_3F_3) formulations and the pentagonal bipyramid

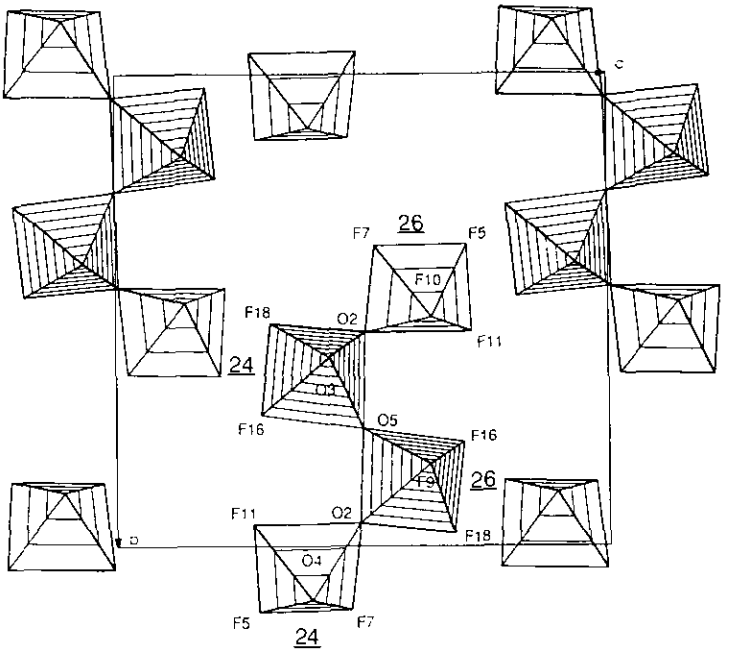

FIG. 3. $Ba_4Nb_2O_3F_{12}$: [100] view of a B plane showing the $(Nb_4O_7F_{14})^{8-}$ blocks constituted by four *cis*-oxygen linked distorted $(Nb(O,F)_6)$ octahedra. (Nb1 octahedra are the more hatched—underlined numbers indicate the x coordinate ($\times$ 100) of Nb atoms).

$(NbOF_6)$. Four (NbX_6) octahedra are *cis*-oxygen connected to form separated $[Nb_4O_7F_{14}]^{8-}$ condensed blocks while $(NbOF_6)$ pentagonal bipyramids are isolated. The Ba atoms supply the three dimensional connections between the Nb polyhedra.

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