Synthesis and Crystal Structure of a New Acentric Oxyfluoride: Ba$_2$TiOF$_6$

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Ba$_2$TiOF$_6$ is a new oxyfluoride obtained in single-crystal form by hydrothermal synthesis. The structure was solved by X-Ray diffraction data from a single crystal using 2688 independent reflections (R = 0.018 − R_w = 0.020). Ba$_2$TiOF$_6$ crystallizes in the monoclinic system (S.G.: Cc, acentric) with a = 11.446(2) Å, b = 9.304(2) Å, c = 7.252(1) Å, β = 126.67(2)°, and Z = 4. The structure is built up from TiO$_2$F$_4$ octahedra sharing opposite oxygen atoms to form infinite kinked chains running along the c axis. These chains [TiOF$_4$]$_n^{2n-}$ are separated from each other by barium and "independent" fluorine ions. The structure, described in term of two subnetworks of cationic tetrahedra FBa$_4$, is compared with some silicate frameworks. © 1992 Academic Press, Inc.

Introduction

Our recent study in the system BaF$_2$–TiO$_2$–HF$_{aq}$ evidenced a new oxyfluoride BaTiOF$_4$ (*1*). We present here the structure determination of an other oxyfluoride Ba$_2$TiOF$_6$, also isolated in single-crystal form by hydrothermal synthesis. Ba$_2$TiOF$_6$ is a new example of compound with titanyl bond and "independent" fluorine ions. The location of the O^{2-} anions is discussed using the bond valence method.

Preparation

Very few crystals of Ba$_2$TiOF$_6$ are grown by hydrothermal synthesis, in a sealed platinum tube, from BaF$_2$ and TiOF$_2$ (stoichiometric ratio) in HF aqueous solutions (*2*). Experimental conditions are given in Table I. These colorless crystals are rather distorted rhomboedra. They are accompanied by BaTiF$_6$ needles. After natural cooling of the bomb, the crystals are washed with ethanol, filtered, and air dried.

Ba$_2$TiOF$_6$ can also be synthesized in powder form by solid-state reaction between stroichiometric amounts of anhydrous BaF$_2$ and TiOF$_2$ (T = 873 K, sealed gold tube).

X-Ray Data Collection

A small crystal, limited by faces ±($1\overline{1}0$, $1\overline{1}1$, $1\overline{1}0$, $1\overline{1}1$), is chosen for the structural determination.

The experimental conditions of the X-Ray data collection on a Siemens AED2 four-circle diffractometer are listed in Table II. The lattice parameters a = 11.446(2) Å, b = 9.304(2) Å, c = 7.252(1) Å, β = 126.67(2)° were refined from high-angle reflections by the double-scan technique from the positions of 31 reflections in the vicinity of 30° (2θ). The intensity data show the sys-

TABLE I

Ba_2TiOF_6: Operating Conditions of
Crystal Growth

Volume of plantinum tube	3.08 cm³	Heating rate	5°C/mn
Filling rate	0.60	Temp. max (T_f)	350°C
HF (30% volume)	1.49 cm³	Time at T_f	48 hr
[Ba_2TiOF_6]	5 mole/liter	Natural cooling rate	
$P_{initial}$(RT)	750 bars	$P_{final}(T_f)$	1350 bars

tematic absences characteristic of $C2/c$ or Cc (acentric) space groups ($hkl: h + k = 2n + 1$; $h0l: l = 2n + 1$). However, some $h0l$ reflections forbidden by $C2/c$ or Cc space groups are found with very small intensities. For instance, the intensity of the higher forbidden reflection (-201) is less than 0.5% of the strongest reflection (021). These weak reflections originate from a double-reflection process, called "Renninger effect." It can be established either by changing the wavelength, or, for a fixed wavelength, by changing the crystal orientation (3). To clarify unambiguously the origin of these weak reflections, a series of complementary experiments was performed. The higher reflections were checked by the so-called ψ-scan rotation: the measured intensities are found strongly ψ-dependent (for a rotation of 5°, the peaks disappear), indicating the occurence of other reflection(s) on the Ewald sphere. So we conclude to a strong Renninger effect and confirm the $C2/c$ or Cc space groups.

Structure Determination

All the calculations are performed with the Shelx-76 program (4). Atomic scattering factors for ions, $\Delta f'$ and $\Delta f''$ are taken from "International Tables for Crystallography" (5). Direct or Patterson methods in the $C2/c$ space group were unable to give any clear proposition, whereas, a starting model with two positions for the barium atoms was obtained directly by the application of direct methods using the acentric Cc space group.

Then, successive refinements and Fourier difference synthesis allowed us to complete the structure: titanium atoms are located on one site and anions on seven different sites, giving the formulation Ba_2TiOF_6. The second harmonic generation test (SHG: 1.06 μm/0.532 μm), performed on a polycrystalline sample, is positive and confirms the acentric space group Cc.

As in $BaTiOF_4$ (1), it is impossible to de-

TABLE II

Ba_2TiOF_6: Crystallographic and
Experimental Data

Symmetry	monoclinic
Space group	Cc (acentric-No. 9)
a(Å)	11.446(2)
b(Å)	9.304(2)
c(Å)	7.252(2)
β(°)	126.67(2)
V(Å³)	619.4(4)
Z	4
Formula weight (g)	452.57
D_{calc}(g/cm³)	4.85
Crystal size (10^{-3} mm³)	3.8
Radiation	MoKα (graphite monochromatized)
Scanning mode	$\omega/2\theta$
Aperture (mm)	3.5 × 3.5
Range registered:	
θ_{max}(°)	35
hkl max	18 14 11
Absorption coefficient	μ = 139.08 cm⁻¹
Absorption correction	gaussian method
Transmission factors:	
T_{max}, T_{min}	0.280 0.132
Reflections measured	two independent sets
total	5720
independent	2860
used in refinement ($I > 3\sigma(I)$)	2688
Number of refined parameters	90
Weighting scheme	w = 1.00 (σ^2(F) + $0.710^{-3}F^2$)
Secondary extinction	0.0039(1)
Electron density in final Fourier difference map:	
maximum height	3.1 e⁻.Å⁻³
minimum height	−5.0 e⁻.Å⁻³ (close to Ba sites)

TABLE III

Ba$_2$TiOF$_6$: Experimental Bond Valence(s) for the Anionic Sites (Calculated from Reference 6(b))

Atom	Ba	Ti	Σs
F1	0.21	0.70	1.09
	0.18		
F2	0.24		
	0.16	0.64	1.14
	0.10		
F3	0.19		
	0.19	0.60	1.13
	0.15		
F4	0.17		
	0.14	0.66	1.07
	0.10		
F5	0.32		
	0.23		0.98
	0.23		
	0.20		
F6	0.33		
	0.28		1.04
	0.24		
	0.19		
O	0.19	1.28	2.02
	0.08	0.47	

termine by X-ray refinement the position of O^{2-} anions. The bond valence method (6) allowed us to clear up this question and showed unambiguously the O^{2-} site (Table III). With absorption correction, secondary extinction and weighting scheme, the final stage of refinement, for all atomic coordinates and anisotropic thermal parameters, converged to $R = 0.018$ and $R_w = 0.020$. In these conditions, the Fourier difference map lets appear a negative peak (-5.0 e$^-$/Å^3), located near the Ba sites. However, this peak is significantly lowered if the data collection is limited successively to $2\theta = 60°$ and $2\theta = 55°$: its intensity is respectively close to -3.2 e$^-$.Å^{-3} and -2.3 e$^-$.Å^{-3}. Tables IVa and b present the final atomic coordinates and thermal parameters (structure factor tables will be sent upon request). The main interatomic distances and angles are given in Table V.

Description of the Structure

The structure of Ba$_2$TiOF$_6$ is built up from infinite kinked chains of *trans* connected TiO$_2$F$_4$ octahedra running along the c-axis (Fig. 1). In each chain, the octahedra are linked together, via corner-sharing, by oxygen atoms, like in BaTiOF$_4$ (1). The bridging angle Ti–O–Ti is 143.5(2)°. These chains [TiOF$_4$]$_n^{2n-}$ are separated from each other by barium and "independent" fluorine ions. The term "independent" means that F$^-$ ions do not belong to TiO$_2$F$_4$ octahedra; this was previously encountered in some other compounds (7–12). Ba^{2+} cations (Ba1 and Ba2) are respectively in an 11- and 10-fold coordination. Each Ba^{2+} links together two different chains [TiOF$_4$]$_n^{2n-}$.

The TiO$_2$F$_4$ octahedra are almost regular with F–F distances ranging from 2.665(3) to 2.751(3) Å and F–O distances from 2.585(5) to 2.770(4) Å (Table V). However, within these octahedra, the Ti atoms are displaced from the center by about 0.19 Å. This marked off-center position leads to the sequence of short (titanyl) and long Ti–O distances along the c-axis, Ti–O = 1.724(4) and Ti–O = 2.095(4) Å. The four Ti–F distances are quite equivalent, Ti–F1 = 1.891(2) to Ti–F3 = 1.952(2) Å. The coordination polyhedron around Ti atoms is very similar to

TABLE IV-a

Ba$_2$TiOF$_6$: Fractional Atomic Coordinates and Thermal Parameters

Atom	x	y	z	B$_{eq}$(Å^2)
Ba1	0	0.1715(0)	0	0.57(3)
Ba2	0.7016(0)	0.8779(0)	0.6567(0)	0.53(3)
Ti	0.3263(1)	−0.0065(1)	0.0856(1)	0.54(5)
F1	0.2275(3)	0.1689(2)	0.9509(4)	0.9(2)
F2	0.5133(2)	0.0870(3)	0.2648(4)	0.9(2)
F3	0.4203(2)	0.8186(2)	0.2633(4)	0.7(2)
F4	0.1445(2)	0.0941(2)	0.4787(4)	0.8(2)
F5	0.8858(2)	0.9582(3)	0.1085(4)	1.0(3)
F6	0.1995(2)	0.3539(3)	0.2831(4)	0.8(3)
O	0.3321(3)	0.0641(3)	0.3653(4)	0.9(2)

TABLE IV-b

Ba_2TiOF_6: Anisotropic Thermal Parameters $U_{ij}(Å^2 \times 10^4)$

Atom	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Ba1	91(1)	96(1)	98(1)	−20(1)	56(1)	−22(1)
Ba2	91(1)	91(1)	86(1)	−3(1)	56(1)	−8(1)
Ti	88(2)	87(2)	100(2)	6(1)	57(2)	14(1)
F1	177(10)	137(9)	186(10)	62(7)	123(9)	60(6)
F2	137(9)	152(8)	221(10)	−36(7)	128(8)	−56(7)
F3	105(7)	117(7)	117(7)	15(6)	52(6)	17(6)
F4	113(8)	142(7)	156(9)	1(6)	85(7)	4(7)
F5	124(8)	208(9)	107(8)	−36(7)	40(7)	32(7)
F6	119(8)	143(7)	116(8)	−43(6)	50(7)	−29(7)
O	242(12)	159(9)	102(8)	−39(8)	142(9)	−29(7)

those observed in the potassium titanyl phosphate $KTiOPO_4$ (13).

Within the Ba1 and Ba2 coordination polyhedra, the distances Ba–O and Ba–F are in good agreement with the sum of the ionic radii (Table V) (14).

This classical description of Ba_2TiOF_6 structure is based on the anionic coordination of Ti^{4+} cations. By this way, the framework is described as constituted of [TiOF$_4$]$_n^{2n-}$ isolated chains separated by Ba^{2+} and F^- ions.
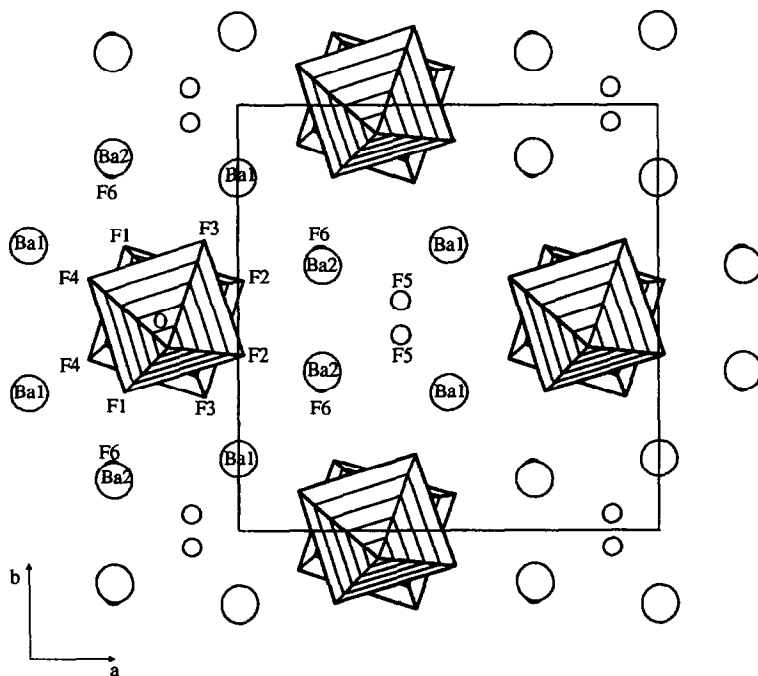

FIG. 1. Ba_2TiOF_6: [001] view of the structure showing the trans chains of TiO_2F_4 octahedra running along the c-axis, separated by Ba atoms (large circles) and F atoms (small circles).

TABLE V

Ba$_2$TiOF$_6$: Main Interatomic Distances (Å) and Bond Angles (°) for the Coordination Polyhedra

TiO$_2$F$_4$ Octahedron

Ti	O	F1	F4	F2	F3	O
O	1.724(4)	2.721(4)	2.734(5)	2.738(3)	2.657(4)	3.817(2)
F1	97.6(1)	1.891(2)	2.676(3)	2.751(3)	3.828(3)	2.668(4)
F4	97.3(1)	89.3(1)	1.915(2)	3.808(3)	2.665(3)	2.729(3)
F2	97.1(1)	92.3(1)	165.2(1)	1.925(2)	2.712(4)	2.585(5)
F3	92.4(1)	169.8(2)	87.1(1)	88.8(1)	1.952(2)	2.770(4)
O	176.8(2)	83.9(1)	85.6(1)	79.9(1)	86.3(1)	2.095(4)

⟨Ti–F⟩ = 1.921   ⟨Ti–O⟩ = 1.910
d$_{Shannon}$ = 1.890   d$_{Shannon}$ = 1.955

Ba1O$_2$F$_9$ Polyhedron

Ba1–F6	2.590(2)	Ba1–F3	2.904(3)
Ba1–F5	2.606(3)	Ba1–F4	2.907(3)
Ba1–F5	2.738(3)	Ba1–O	2.908(3)
Ba1–F6	2.810(2)	Ba1-F4	3.028(2)
Ba1–F1	2.831(4)	Ba1–O	3.231(3)
Ba1–F2	2.880(3)		

⟨Ba1–F⟩ = 2.810   ⟨Ba1–O⟩ = 3.070
d$_{Shannon}$ = 2.855   d$_{Shannon}$ = 2.920

Ba2F$_{10}$Polyhedron

Ba2–F6	2.663(3)	Ba2–F5	2.788(3)
Ba2–F6	2.704(3)	Ba2–F3	2.800(2)
Ba2–F2	2.717(3)	Ba2–F3	2.810(2)
Ba2–F5	2.736(3)	Ba2–F4	2.839(2)
Ba2–F1	2.769(3)	Ba2–F2	3.032(3)

⟨Ba2–F⟩ = 2.786
d$_{Shannon}$ = 2.805

F5Ba$_4$ Tetrahedron

F5	Ba1	Ba2	Ba1	Ba2
Ba1	2.606(3)	4.932(3)	4.830(1)	3.895(1)
Ba2	134.8(1)	2.736(3)	3.895(1)	4.279(3)
Ba1	129.3(1)	90.7(1)	2.738(3)	4.219(1)
Ba2	92.4(1)	101.5(1)	99.6(1)	2.788(3)

⟨F5–Ba⟩ = 2.717

F6Ba$_4$ Tetrahedron

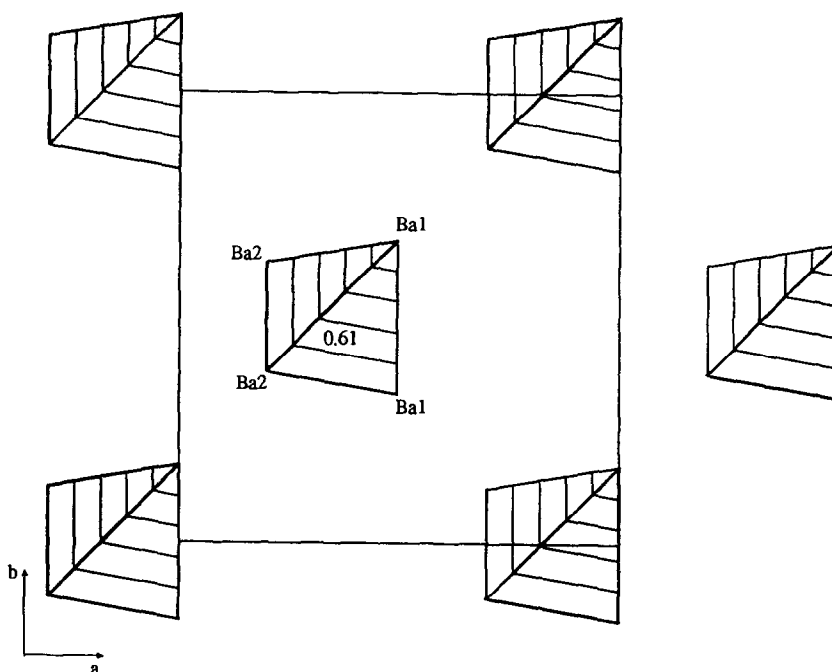| F6	Ba1	Ba2	Ba2	Ba1
Ba1	2.590(2)	4.589(2)	4.309(2)	4.822(2)
Ba2	121.7(1)	2.663(3)	4.279(1)	3.895(1)
Ba2	108.9(1)	105.7(1)	2.704(3)	4.219(1)
Ba1	126.4(1)	90.7(1)	99.8(1)	2.810(2)

⟨F6–Ba⟩ = 2.692

FIG. 2. F5 subnetwork: [001] view of the chains constituted by tetrahedra $[F5Ba_2]^{3+}$ linked together via opposite edge-sharing. The number indicates the z-coordinate of the F5 atom in the tetrahedron.

However, it is worthy of note that only F1, F2, F3, and F4 belong to the octahedra: F5 and F6, called independent, are only bonded to Ba^{2+} cations. This remark leads us to propose a second description based on the cationic coordination of the two independent fluorine anions F5 and F6. So, we are going to study successively these two subnetworks.

Each F5 ion is surrounded by four Ba^{2+} (two Ba1 and two Ba2), forming a tetrahedron. These tetrahedra are linked together via opposite edge-sharing so that they build up $[F5Ba_2]_n^{3n+}$ chains running along [001] (Fig. 2). Such chains have already been observed in crystal chemistry of silicates, even if edge-sharing of $[SiO_4]$ tetrahedra is energetically very unfavorable. This framework, called "fibrous form," was first synthesized in 1954 (15).

Each F6 anion is also tetrahedrally coordinated (two Ba1 and two Ba2), and the framework formed by the tetrahedra is three-dimensional. These tetrahedra are linked together, via corner-sharing, so that every Ba^{2+} is common to two tetrahedra, giving the composition $[F6Ba_2]^{3+}$. However, this 3D subnetwork, can be described by a fundamental chain, which is very usual for some 3D framework silicates, called tectosilicates (15). In Ba_2TiOF_6, this characteristic chain $[F6Ba_3]_n^{5n+}$, formed by the regular repetition of two tetrahedra is running along the [101] direction (Fig. 3). According to the classification of F. Liebau (15), this kind of arrangement is called an "unbranched zweir [101] framework." With this same notation, high-temperature tridymite SiO_2 would be specified as "an unbranched zweir [100] framework." Both arrangements can be described by the following structural formula: $\{uB, \frac{3}{\infty}\}$ $[^2M_2X_4]$. In the case of tridymite, M = Si, X = O, whereas, in Ba_2TiOF_6, M = F and X = Ba. This formula can describe the cristobalite form, too.
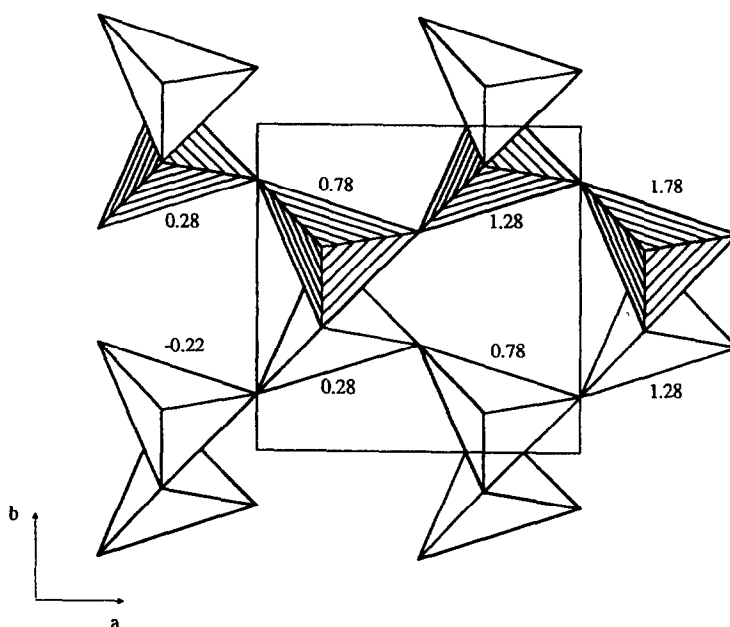
However, these 3D frameworks differ not

FIG. 3. F6 subnetwork: [001] view of the 3D framework constituted by tetrahedra [F6Ba$_2$]$^{3+}$, showing a fragment of a fundamental chain {uB, $\frac{3}{z}$} [^{2}F$_2$Ba$_4$] (shaded) and the pseudo-hexagonal tunnels. Numbers indicate the z-coordinates of F6 atoms in the tetrahedra.

only in the relative orientation of the tetrahedra within the repeat unit, but also in the chain-linking process. In Ba$_2$TiOF$_6$ structure, each chain is connected to four other chains in such a way that the resulting 3D subnetwork delimits pseudo-hexagonal tunnels parallel to the [001] axis (Fig. 3).

The two subnetworks, 1D (F5) and 3D (F6), are connected together: the chains [F5Ba$_2$]$_n^{3n+}$ are located inside the channels of the [F6Ba$_2$]$^{3+}$ three-dimensional framework. Each tetrahedron F5Ba$_4$ links together two fundamental chains by sharing one face with one F6Ba$_4$ tetrahedron, belonging to the first chain, and one edge with one F6Ba$_4$ tetrahedron of the second chain (Fig. 4). The connection of the face-sharing tetrahedra F6Ba$_4$ and F5Ba$_4$ leads to a distance F5–F6 of 2.676(3) Å.

These tetrahedra F5Ba$_4$ and F6Ba$_4$ are almost regular with F–Ba distances ranging from 2.606(3) to 2.788(3) Å for the F5Ba$_4$ tetrahedron and from 2.590(2) to 2.810(2) Å

for F6Ba$_4$, very similar to those observed in the forms I (9) and Ib (16) of Ba$_3$AlF$_9$ compound. It is worthy of note that the longest bonds Ba–F are observed for the three barium atoms (one Ba1 and two Ba2) owned by the two face-sharing tetrahedra.

The interconnection of the two subnetworks delimits pseudo pentagonal channels running along [001] wherein the chains [TiOF$_4$]$_n^{2n-}$ are located (Fig. 5).

Conclusion

Ba$_2$TiOF$_6$ is a new oxyfluoride with independent fluorine ions. So, its formula can be alternatively written Ba$_2$F$_2$(TiOF$_4$).

Ba$_2$TiOF$_6$ crystallizes in the polar space group Cc and second harmonic generation tests show that the phase matching condition is fulfilled at room temperature. In this scope and taking into account the possible applications, different investigations have
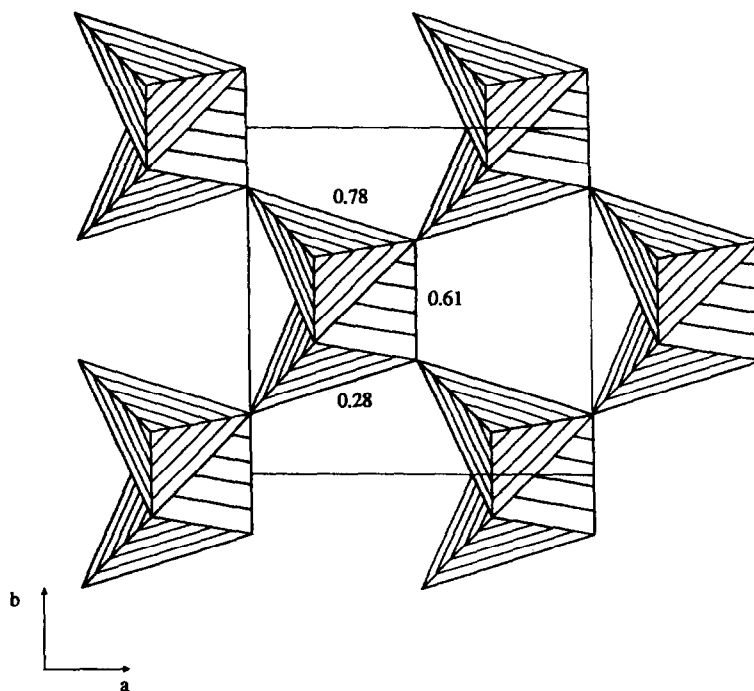
FIG. 4. Interconnection of the two subnetworks, 1D (F5) and 3D (F6), showing the pseudo-pentagonal tunnels. Numbers indicate the z-coordinates of F5 and F6 atoms within the tetrahedra.
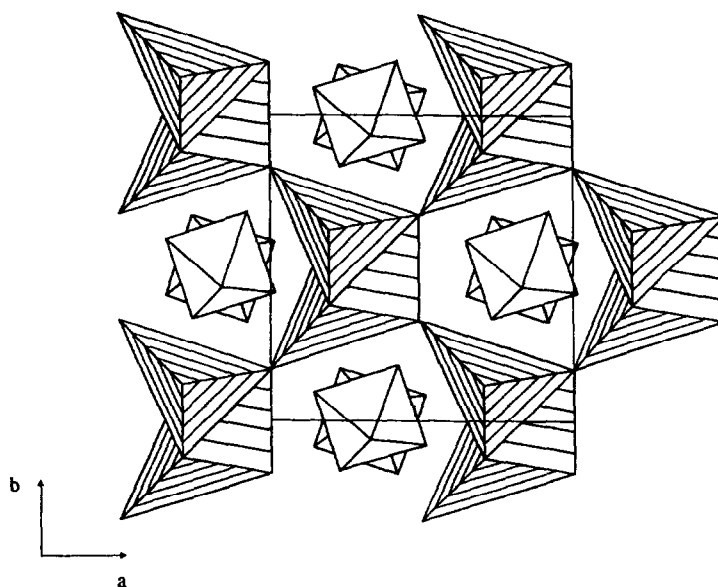

FIG. 5. Ba_2TiOF_6: [001] view of the structure showing the location of $[TiOF_4]_n^{2n-}$ chains inside the pseudo-pentagonal channels delimited by the interconnection of the two subnetworks, 1D (F5) and 3D (F6).

been undertaken and will be reported in a forthcoming paper.

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