Synthesis and single-crystal structural study of an original low-temperature form α of $BaTbF_6$

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$BaTbF_6$ is the first terbium(IV) fluoride for which a polymorphic phase transition at high temperature is evidenced. Whereas its high temperature form is isostructural with β-$BaZrF_6$, the crystal structure of its low-temperature polymorph has been determined from single-crystal X-ray diffraction data and refined to conventional $R = 0.044$ ($R_w = 0.053$) for 2880 independent reflections and 149 variable parameters. α-$BaTbF_6$ crystallizes in the triclinic system with space group $P\bar{1}$ and unit-cell parameters $a = 7.344(1)$, $b = 8.4476(6)$, $c = 8.6770(9)$ Å, $\alpha = 101.63(8)$, $\beta = 96.89(1)$, $\gamma = 114.62(1)°$ and $Z = 4$.

The three-dimensional structure may be regarded as a stacking along the c direction of alternated corrugated layers of Ba polyhedra and layers of Tb polyhedra built from $[Ba_4F_{30}]^{22-}$ and $[Tb_4F_{26}]^{10-}$ tetrameric complex anions respectively. The $[Tb_4F_{26}]^{10-}$ complex anion results from the association of four square antiprisms by sharing corners and edges.

A large number of $M^{II}M'^{IV}F_6$ compounds have been studied and a summary of the different structural types of $MM'F_6$ compounds is given in ref. 1 which shows that several of them are dimorphic. The compound $BaZrF_6$ is of special interest owing to its significance in fluoride glasses recrystallization studies.[2] This compound is also polymorphic, showing three polymorphs among which the γ-$BaZrF_6$ form is stabilized by a small amount of water.[3] Finally and belonging to this large family of $MM'F_6$ compounds, $BaTbF_6$ was first characterized by Feldner and Hoppe who referred to a unique form of unknown structure.[4] A recent study carried out in our laboratory has shown that this compound is also dimorphic with a high temperature form, β-$BaTbF_6$,[5] isostructural with β-$BaZrF_6$[6] whereas the form referred to by Feldner and Hoppe is the low-temperature form α-$BaTbF_6$.

This paper reports the crystal structure determination of the low-temperature form α-$BaTbF_6$ carried out from single-crystal X-ray data.

Experimental

Polycrystalline samples of α-$BaTbF_6$ were obtained by heating overnight at 550 °C stoichiometric mixtures of BaF_2 and TbF_4 in a nickel boat under a pure fluorine atmosphere. This compound provides a strong stabilization of the 4+ oxidation state of terbium and can be further heated to higher temperature *e.g.* 700 °C without decomposition. Instead, heat treatment results in the high-temperature form β-$BaTbF_6$ which is isostructural with β-$BaZrF_6$.[6] Crystallization of α-$BaTbF_6$ cannot be carried out directly but occurs *via* the high-temperature polymorph which appears at *ca.* 637 ± 5 °C.[5]

Single crystals of α-$BaTbF_6$ with a platelet-like shape were obtained by annealing at 625 °C for 24 h a β-$BaTbF_6$ sample heated overnight at 600 and 700 °C successively with intermediate grinding.

As the presence of Tb^{III} in the sample is conceivable in this material, this was checked on a powdered sample by utilizing the luminescence properties of Tb^{3+}. A powdered sample was obtained by crushing single crystals and a luminescence spectrum was recorded under excitation at 337.1 nm using a nitrogen laser. This wavelength ensures the promotion of Tb^{3+} ions to the $^5D_3$ excitation state from which a blue emission is expected ($^5D_3 \rightarrow {}^7F_J$) when the Tb^{3+} concentration is very low (typically <0.1%), (for higher concentrations the emission is green rather than blue). The absence of any blue emission is therefore a good indication for a negligible amount of Tb^{3+}, if any. Although this experiment was not carried out on the crystal selected for structural study it can be safely assumed that the crystal is representative of the sample.

Structure determination and refinement

A small colourless platelet-like crystal was mounted on a Pyrex rod using epoxy paste. Unit-cell dimensions were determined

Table 1 Crystallographic data and data collection parameters for α-$BaTbF_6$

chemical formula	α-$BaTbF_6$
M_w	410.25
symmetry	triclinic
space group	$P\bar{1}$ (no. 2)
unit-cell parameters:	
a/Å	7.344(1)
b/Å	8.4475(6)
c/Å	8.6770(9)
α/°	101.63(8)
β/°	96.89(1)
γ/°	114.62(1)
V/Å^3	466.5(1)
Z	4
D_c/g cm^{-3}	5.84(1)
data collection temperature/K	293
crystal size/mm	$0.03 \times 0.03 \times 0.02$
radiation (λ/Å)	Mo-Kα ($\lambda = 0.71069$ Å)
μ (Mo-Kα)/cm^{-1}	240.7
transmission factors	0.902–0.996
scan mode	ω–2θ
scan width/°	$0.80 + 0.35 \tan \theta$
scan aperture/mm	$2.70 + 0.40 \tan \theta$
θ range/°	$1 \leqslant \theta \leqslant 40$
index ranges	$-13 \leqslant h \leqslant 13$, $-15 \leqslant k \leqslant 15$, $0 \leqslant l \leqslant 15$
period of intensity control/s, σ	3600, 0.02
number of measured reflections	6057
observed reflections with $I > 3\sigma(I)$	2880
number of variables	149
weighting scheme	$w = 1.0$ for $F_o < 0.80\ F_{o\ max}$ $w = (0.80\ F_{o\ max}/F_o)^2$ for $F_o \geqslant 0.80\ F_{o\ max}$ $w = 0.0$ for $F_o{}^2 < 3\sigma(F_o{}^2)$
secondary extinction parameter	$7.8(9) \times 10^{-8}$
R, R_w	0.044, 0.053
goodness of fit s	0.879
max., min. electron density in final difference Fourier synthesis/e Å^{-3}	3.53 close to Tb(2) −3.56 close to Tb(1)

Table 2 Atomic coordinates and thermal parameters for α-BaTbF$_6$

atom	Wyckoff position	x	y	z	$B_{\mathrm{iso}}/\mathrm{Å}^2$
Tb(1)	2i	0.18367(8)	0.25951(7)	0.28111(7)	0.430(8)
Tb(2)	2i	0.22918(8)	0.78338(7)	0.06120(7)	0.387(7)
Ba(1)	2i	0.2988(1)	0.31428(9)	0.76950(9)	0.66(1)
Ba(2)	2i	0.7072(1)	0.2311(1)	0.45645(9)	0.72(1)
F(1)	2i	0.095(1)	0.236(1)	0.027(1)	1.0(1)
F(2)	2i	0.119(1)	0.383(1)	0.496(1)	1.0(1)
F(3)	1d	1/2	0	0	1.3(2)
F(4)	2i	0.087(1)	0.754(1)	0.258(1)	1.2(1)
F(5)	2i	0.292(1)	0.534(1)	0.288(1)	1.1(1)
F(6)	1c	0	1/2	0	1.2(2)
F(7)	2i	0.527(1)	0.108(1)	0.726(1)	1.0(1)
F(8)	2i	0.396(1)	0.638(1)	0.001(1)	1.1(1)
F(9)	2i	0.310(1)	0.177(1)	0.469(1)	1.2(1)
F(10)	2i	0.869(1)	0.284(1)	0.199(1)	1.1(1)
F(11)	2i	0.082(1)	0.960(1)	0.703(1)	1.4(2)
F(12)	2i	0.236(1)	0.041(1)	0.145(1)	1.2(1)
F(13)	2i	0.497(1)	0.630(1)	0.702(1)	1.4(2)

accurately by centering on 25 reflections with $15° \leqslant 2\theta \leqslant 40°$ and subsequent least-squares refinement of the measured setting angles. Single-crystal X-ray diffraction intensities were collected with an Enraf-Nonius CAD4 four-circle diffractometer under the conditions given in Table 1. Lorentz and polarization corrections were applied followed by an empirical absorption correction deduced from psi scan series on $1\bar{3}2$, $\bar{1}24$ and 012 reflections.

The Ba and Tb atomic positions were determined from the Patterson function and refined in the centric space group $P\bar{1}$. Atomic scattering factors for the ions and anomalous dispersion terms were taken from ref. 7. As no scattering factors were available for the Tb^{4+} ion, we used the values for isoelectronic Gd^{3+}. Refinement of the cationic atomic coordinates and isotropic thermal parameters led to $R=0.116$ for the 2880 reflections taken into account. Then thirteen independent fluorine atoms were located from a difference-Fourier synthesis. Subsequent full-matrix least-squares refinements and use of isotropic thermal parameters led to $R=0.068$. A final refinement of the atomic coordinates and anisotropic thermal parameters including a secondary extinction parameter resulted in a conventional $R=0.044$ ($R_w=0.053$). All computer programs used for data collection, reduction and refinement were from

Table 3 Selected distances (Å) and angles (°) in α-BaTbF$_6$

Tb(1)	**F(5)**	**F(11)**	**F(13)**	**F(9)**	**F(2)**	**F(1)**	**F(12)**	**F(10)**
F(5)	**2.10(1)**	3.95(1)	2.48(2)	3.71(1)	2.57(1)	2.73(1)	3.93(1)	2.82(2)
F(11)	140.1(4)	**2.10(1)**	4.03(1)	2.71(1)	2.72(1)	3.23(1)	2.81(1)	2.52(2)
F(13)	72.3(5)	146.5(4)	**2.11(1)**	2.53(1)	3.50(1)	3.19(1)	2.58(2)	4.36(1)
F(9)	121.5(4)	79.2(4)	72.9(4)	**2.15(2)**	2.65(2)	4.17(1)	2.71(1)	4.28(1)
F(2)	74.5(4)	79.4(3)	110.6(3)	75.9(4)	**2.15(1)**	3.97(1)	4.19(1)	2.74(1)
F(1)	79.6(3)	98.2(3)	96.6(4)	149.9(4)	133.6(4)	**2.17(1)**	2.58(1)	2.46(1)
F(12)	132.9(4)	82.1(4)	74.0(3)	77.1(4)	149.6(4)	72.8(4)	**2.19(1)**	4.04(2)
F(10)	76.6(3)	67.0(4)	146.1(4)	137.1(3)	72.6(3)	64.3(3)	121.1(3)	**2.45(2)**

<Tb(1)—F> 2.18 Å

Tb(2)	**F(8)**	**F(4)**	**F(12)**	**F(7)**	**F(10)**	**F(6)**	**F(3)**	**F(1)**
F(8)	**2.10(1)**	3.64(1)	4.02(1)	2.68(1)	2.81(1)	2.64(1)	2.82(1)	4.16(1)
F(4)	120.0(5)	**2.10(2)**	2.65(1)	2.55(1)	3.97(1)	2.57(1)	4.10(1)	2.70(1)
F(12)	147.2(3)	77.4(4)	**2.13(1)**	2.80(2)	3.38(1)	4.00(1)	2.53(2)	2.58(1)
F(7)	78.1(3)	73.6(3)	81.5(4)	**2.15(1)**	4.16(1)	3.73(1)	2.71(1)	4.23(1)
F(10)	82.3(4)	136.8(3)	103.9(4)	149.6(3)	**2.16(1)**	2.72(1)	2.81(1)	2.46(1)
F(6)	76.1(2)	73.7(3)	136.6(2)	119.1(2)	77.6(2)	**2.18(1)**	4.29(1)	2.65(1)
F(3)	80.1(2)	137.8(2)	70.2(2)	75.6(2)	78.4(3)	148.0(1)	**2.28(1)**	3.93(1)
F(1)	138.6(3)	74.5(3)	70.0(3)	140.9(3)	66.2(3)	71.5(2)	116.6(3)	**2.34(1)**

<Tb(2)—F> 2.18 Å

Ba(1)	**F(4)**	**F(11)**	**F(9)**	**F(8)**	**F(13)**	**F(8)**	**F(2)**	**F(1)**	**F(7)**	**F(5)**
F(4)	**2.62(1)**	3.12(2)	4.12(1)	4.90(1)	4.28(1)	3.73(1)	2.93(1)	2.70(1)	5.12(2)	5.40(1)
F(11)	73.0(3)	**2.63(1)**	3.17(1)	4.02(1)	5.19(1)	5.14(1)	4.25(2)	3.23(1)	2.94(1)	4.79(1)
F(9)	102.9(3)	73.7(3)	**2.66(1)**	4.51(1)	3.53(1)	5.19(1)	2.65(2)	5.26(1)	2.89(1)	3.08(1)
F(8)	86.9(3)	98.8(3)	115.7(3)	**2.66(1)**	3.98(2)	3.29(2)	5.38(1)	3.48(1)	2.68(1)	2.90(1)
F(13)	107.7(3)	155.8(3)	82.9(3)	96.5(3)	**2.68(2)**	2.77(1)	2.78(1)	5.03(1)	4.55(2)	2.48(2)
F(8)	136.6(4)	142.2(4)	143.4(3)	74.1(3)	60.7(3)	**2.80(1)**	4.28(1)	3.27(1)	5.15(1)	4.04(1)
F(2)	64.4(3)	101.1(3)	57.3(3)	155.3(2)	60.1(3)	98.4(3)	**2.85(1)**	5.02(1)	4.96(2)	4.21(1)
F(1)	58.7(3)	71.7(3)	144.3(3)	78.1(3)	130.2(3)	70.5(2)	122.2(3)	**2.87(1)**	4.66(1)	5.41(1)
F(7)	137.1(2)	64.2(3)	62.5(3)	57.7(3)	109.8(3)	130.0(2)	119.7(3)	108.3(3)	**2.88(2)**	2.79(1)
F(5)	157.8(3)	119.8(3)	67.3(2)	62.9(3)	52.7(3)	90.5(2)	94.3(3)	140.2(2)	57.8(3)	**2.89(1)**

<Ba(1)—F> 2.76 Å

Ba(2)	**F(5)**	**F(7)**	**F(13)**	**(F10)**	**F(2)**	**F(4)**	**F(9)**	**F(2)**	**F(11)**	**F(7)**
F(5)	**2.66(1)**	5.01(1)	3.51(1)	4.87(1)	3.96(1)	2.87(2)	3.08(1)	2.57(1)	5.39(1)	2.79(1)
F(7)	139.9(3)	**2.66(1)**	3.91(1)	3.63(1)	4.65(1)	4.45(2)	3.37(1)	5.37(1)	2.94(1)	3.88(1)
F(13)	82.5(3)	94.4(3)	**2.67(1)**	3.23(2)	4.58(1)	5.15(2)	2.53(1)	2.78(1)	4.92(2)	4.72(2)
F(10)	130.7(3)	85.5(3)	74.0(3)	**2.69(1)**	2.74(1)	4.78(1)	4.82(1)	3.41(1)	2.52(2)	4.16(1)
F(2)	95.4(3)	120.6(3)	117.6(3)	61.0(3)	**2.69(1)**	2.93(1)	5.41(1)	3.14(2)	2.72(1)	4.89(1)
F(4)	64.8(3)	112.2(3)	147.1(4)	125.1(3)	65.6(3)	**2.70(1)**	4.51(1)	4.16(2)	3.92(1)	2.55(1)
F(9)	68.9(3)	59.9(3)	55.4(4)	123.9(3)	162.9(3)	111.0(3)	**2.77(2)**	4.21(2)	5.36(2)	2.89(1)
F(2)	55.2(3)	151.3(3)	60.0(2)	75.6(3)	68.3(3)	96.4(3)	96.3(3)	**2.88(1)**	4.97(1)	4.91(1)
F(11)	148.8(3)	63.1(3)	122.3(3)	53.1(3)	57.5(2)	88.0(4)	139.4(2)	117.6(3)	**2.94(1)**	5.05(1)
F(7)	58.9(3)	86.7(2)	112.9(3)	169.9(3)	118.6(3)	53.0(3)	59.9(3)	114.1(2)	117.4(4)	**2.98(1)**

<Ba(2)—F> 2.76 Å

Table 4 Main intercationic distances (Å)

Tb(1)···Tb(1)	5.354(1)	Tb(1)···Tb(2)	3.826(1)
Tb(2)···Tb(2)	6.069(1)	Tb(1)···Tb(2)	5.611(1)
Tb(2)···Tb(2)	4.364(1)	Tb(1)···Tb(2)	4.255(1)
Tb(2)···Tb(2)	4.560(1)	Tb(1)···Tb(2)	5.066(1)
Ba(1)···Ba(1)	4.354(1)	Ba(1)···Ba(2)	4.450(1)
Ba(1)···Ba(1)	6.478(1)	Ba(1)···Ba(2)	4.539(1)
Ba(2)···Ba(2)	4.112(1)	Ba(1)···Ba(2)	4.608(1)
Ba(2)···Ba(2)	4.612(1)	Ba(1)···Ba(2)	4.665(1)
Ba(2)···Ba(2)	6.416(1)		

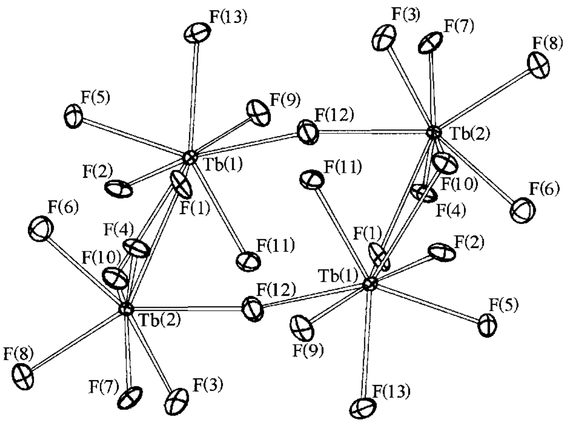

Fig. 1 Perspective view of the $[Tb_4F_{26}]^{10-}$ complex anion. ORTEP drawing[11] showing 50% probability displacement ellipsoids.

the CAD4 SDP package.[8] Final positional and thermal parameters are given in Table 2 and important interatomic distances are listed in Tables 3 and 4. Atomic coordinates, thermal parameters, and bond lengths and angles have been deposited at the Cambridge Crystallographic Data Centre (CCDC). See Information for Authors, *J. Mater. Chem.*, 1997, Issue 1. Any request to the CCDC for this material should quote the full literature citation and the reference number 1145/42.

Description of the structure and discussion

In α-$BaTbF_6$, both crystallographically independent Tb(1) and Tb(2) terbium(IV) ions are surrounded by eight fluorine ions forming strongly distorted square antiprisms as revealed by the bond lengths and angles (Table 3). The square faces of the square antiprisms are delimited by F(5)F(13)F(9)F(2) and F(1)F(12)F(11)F(10) for Tb(1) and by F(4)F(7)F(8)F(6) and F(1)F(12)F(3)F(10) for Tb(2) (Fig. 1 and 2).

In spite of equal average Tb—F distances (2.18 Å) close to that expected from Shannon's ionic radii[9] ($d_{\text{Shannon}} = 2.21$ Å) it is worth noting that a longer distance appears in each of the Tb^{IV} coordination polyhedra, *viz.* Tb(1)—F(10) 2.45 Å and Tb(2)—F(1) 2.34 Å. It is also interesting that the fluorine ions corresponding to the two longest distances are involved in a common edge, F(1)···F(10), between both Tb(1) and Tb(2) polyhedra associated in a binuclear $[Tb_2F_{14}]^{6-}$ entity. Simultaneously this F(1)···F(10) shared edge is also the shortest F···F distance in the structure. Such a feature is general and has also been observed, for instance, in $[Zr_2F_{12}]^{4-}$ and $[Zr_2F_{13}]^{5-}$ complex anions in α-$BaZrF_6$[10] and γ-$BaZrF_6$,[3] respectively. This clearly illustrates the difference between terminal and bridging fluoride ions.

In α-$BaTbF_6$, two identical $[Tb_2F_{14}]^{6-}$ entities related by

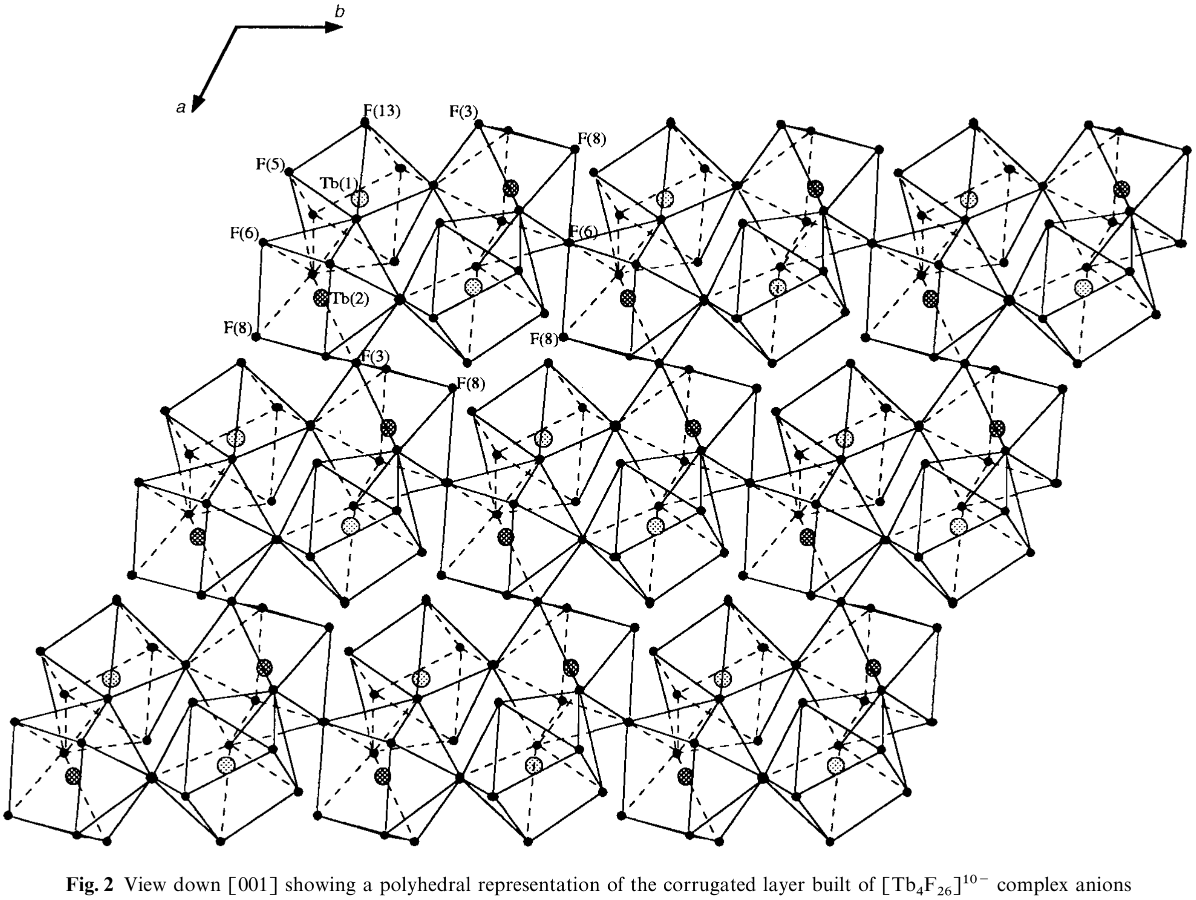

Fig. 2 View down [001] showing a polyhedral representation of the corrugated layer built of $[Tb_4F_{26}]^{10-}$ complex anions

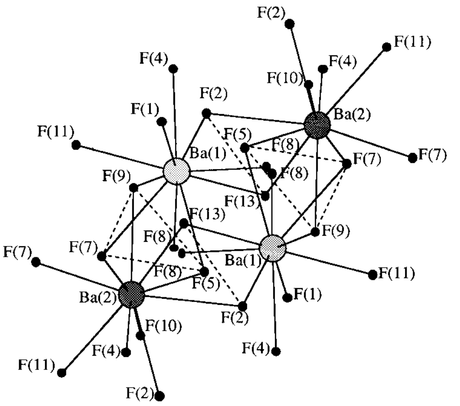

Fig. 3 Perspective view of the tetrameric structural unit $[Ba_4F_{30}]^{22-}$ complex anion

a center of symmetry are connected together by sharing corners involving F(12) fluorine atoms to form the true basal structural unit $[Tb_4F_{26}]^{10-}$ shown in Fig. 1. These $[Tb_4F_{26}]^{10-}$ units are further joined by sharing corners involving both F(3) and F(6) to form layers expanding in parallel with the $(x0y)$ plane (Fig. 2).

Both Ba(1) and Ba(2) atoms are surrounded by ten fluorine ions with distances ranging from 2.62 to 2.89 Å and from 2.66 to 2.98 Å, respectively, and leading to identical average Ba—F distances of 2.76 Å. These two Ba polyhedra are joined together by sharing a face involving F(5), F(7) and F(9) to form a binuclear complex anion $[Ba_2F_{17}]^{13-}$ (Fig. 3). Two identical binuclear complex anions $[Ba_2F_{17}]^{13-}$ related by a center of symmetry are, in turn, connected together by sharing edges F(2)···F(13) to form the tetrameric structural unit $[Ba_4F_{30}]^{22-}$ shown in Fig. 3. These $[Ba_4F_{30}]^{22-}$ units are further linked together by edge sharing involving F(2)···F(2), F(2)···F(4), F(7)···F(7) and F(7)···F(11) to form infinite corrugated layers expanding in parallel with the $(x0y)$ plane (Fig. 4). More accurately, each $[Ba_4F_{30}]^{22-}$ tetrameric unit is linked to four other identical tetrameric units by sharing two F(7)···F(11) and one F(7)···F(7) edge along the *b* direction and by sharing two F(2)···F(4) and one F(2)···F(2) edge along the *a* direction. These corrugated layers are then held together by sharing F(8)···F(8) edges along the *c* direction to form a three-dimensional framework. All the F(8)···F(8) edges are parallel

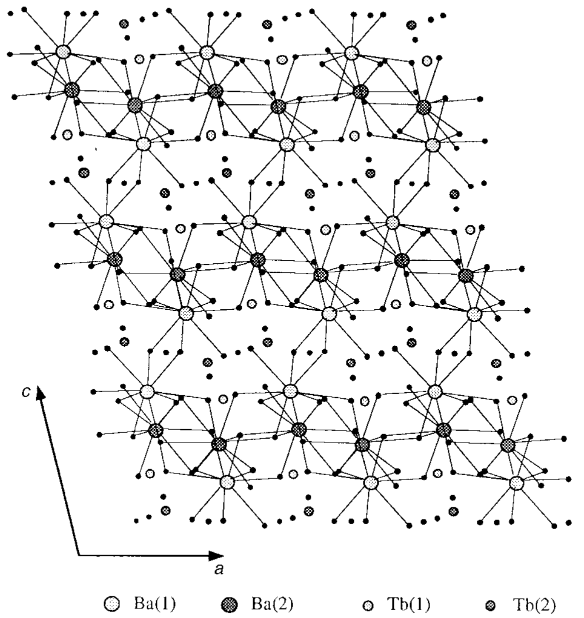

Fig. 5 Projection down [010] of the overall structure of α-BaTbF$_6$

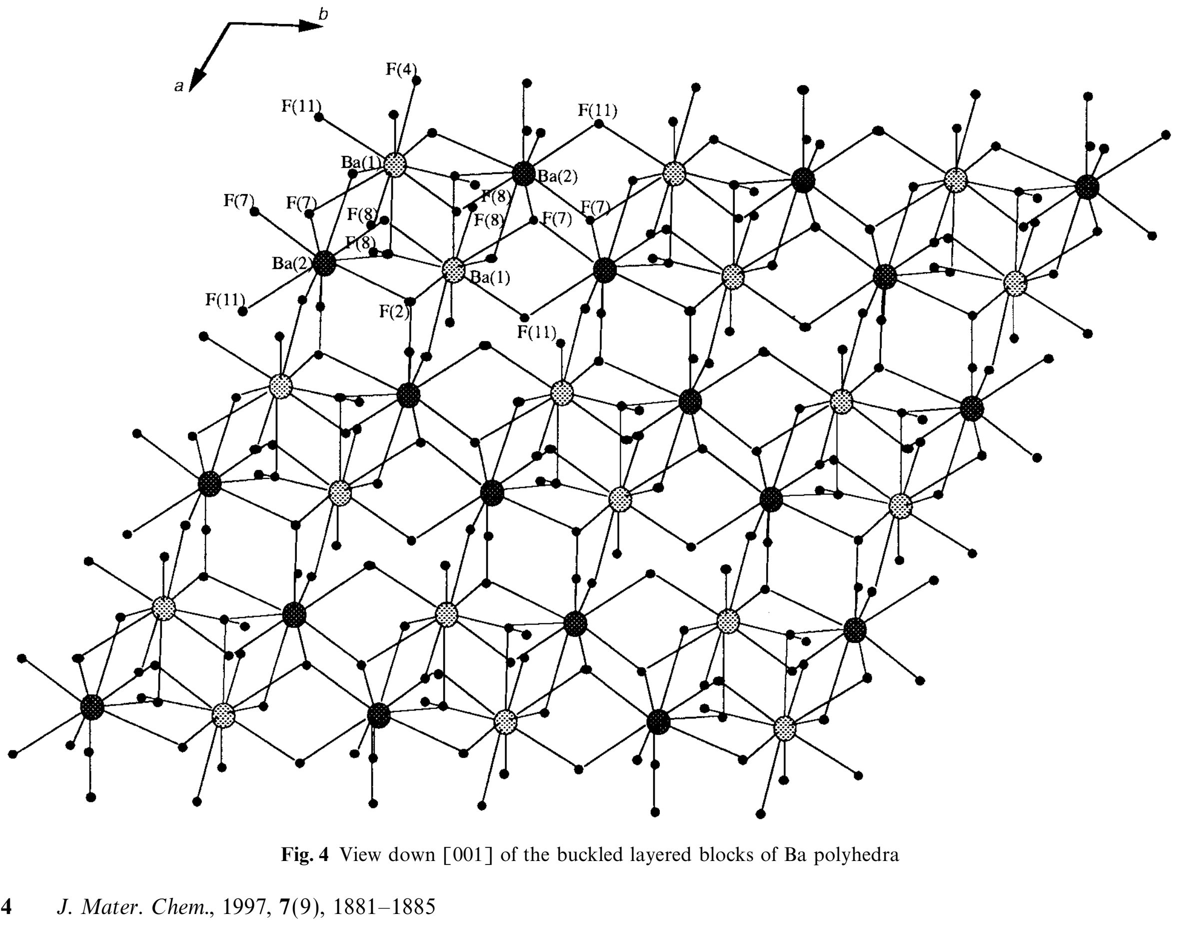

Fig. 4 View down [001] of the buckled layered blocks of Ba polyhedra

to each other and lie in the (001) plane. The overall three-dimensional structure may be regarded as a stacking along the *c* direction of alternated corrugated layers of Ba polyhedra and layers of Tb ones as shown in Fig. 5. The linkage between the three-dimensional network of Ba polyhedra and the layers of $[TbF_8]^{4-}$ square antiprisms involves corners, edges and face-sharing in such a way that the edges shared between the layers of Ba polyhedra lie in the plane of the corrugated layer of $[TbF_8]^{4-}$ square antiprisms between the tetrameric $[Tb_4F_{26}]^{10-}$ units. The corners shared are F(1), F(8), F(10) and F(11); the common edges F(1)—F(4), F(2)—F(5), F(2)—F(9), F(4)—F(7), F(5)—F(13), F(7)—F(8) and F(9)—F(13) whereas the shared triangular face is delimited by F(2), F(10) and F(11).

Apart from β-$BaTbF_6$,[5] $CsTbF_5$[12] and Li_2TbF_6,[13] this fluoride is only the fourth tetravalent terbium(IV) compound to be structurally characterised by single-crystal X-ray diffraction data. This work is a part of an extensive investigation devoted to the constitution of a database for crystal structures of tetravalent terbium complex fluorides.

References

1 D. Babel and A. Tressaud, in *Inorganic solid fluorides, Chemistry and Physics*, ed. P. Hagenmuller, Academic Press Inc., New York, 1985, ch. 3, Crystal chemistry of fluorides.

2 P. W. France, M. G. Drexhage, J. M. Parker, M. W. Moore, S. F. Carter and J. V. Wright, in *Fluoride Glass Optical Fibres*, Blackie, Glasgow/London, 1990.

3 A. Le Bail and A. M. Mercier, *J. Solid State Chem.*, 1992, **101**, 229.

4 K. Feldner and R. Hoppe, *Rev. Chim. Miner.*, 1983, **20**, 351.

5 E. Largeau, M. El-Ghozzi, J. Metin and D. Avignant, *Acta Crystallogr., Sect. C*, 1997, **53**, 530.

6 B. Mehlhorn and R. Hoppe, *Z. Anorg. Allg. Chem.*, 1976, **425**, 180.

7 *International Tables for X-ray Crystallography*, Kynoch Press, Birmingham, 1974, vol. IV.

8 B. A. Frenz, in *Computing in Crystallography*, ed. H. Shenk, R. Olthof-Hazckamp, H. Van Koningsveld and G. C. Bassi, Delft, 1982.

9 R. D. Shannon, *Acta Crystallogr., Sect. A*, 1976, **32**, 751.

10 J. P. Laval, R. Papiernik and B. Frit, *Acta Crystallogr., Sect. B*, 1978, **34**, 1070.

11 C. K. Johnson, ORTEP, Report ORNL 3794, Oak Ridge National Laboratory, Oak Ridge, 1965.

12 V. Gaumet and D. Avignant, *Acta Crystallogr., Sect. C*, 1997, in press.

13 P. Dugat, M. El-Ghozzi and D. Avignant, personal communication.

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