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Crystal structure of $BaTe_2F_{10}$

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Abstract

$BaTe_2F_{10}$ crystallizes with monoclinic symmetry (space group $C2/c$) and unit cell parameters $a = 1731.1(3)$ pm, $b = 483.16(8)$ pm, $c = 1023.3(2)$ pm, $\beta = 111.60(1)°$, $Z = 6$. Its structure was solved and refined to $R_1 = 0.048$ and $wR_2 = 0.125$ on the basis of 1354 independent reflections registered from a single crystal with an automatic four-circle diffractometer. The Te^{IV} atoms are five-fold coordinated and their lone-pairs are stereochemically active. The Ba atoms are 12-fold coordinated. This very simple structure corresponds to an approximate fcc packing of Ba atoms and isolated TeF_5E polyhedra forming alternate layers, and can be described as a regular repetition along the $0x$ direction of $BaTe_2F_{10}E_2$ three-layer-wide sheets with the $KOsF_6$ structure (CsCl), shifted $1/2\ \langle 1\ 1\ 0\rangle_{CsCl}$ one from the other.

Structural relationships with the $KTeF_5$ structure have been established.

Keywords: Crystal structure; Barium tellurium fluorides; Structural relationships

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1. Introduction

During a study of the BaF_2–TeF_4 system, a very hygroscopic white phase with the composition $BaTe_2F_{10}$ was synthesized. This report describes a study of its crystal structure.

2. Experimental details

2.1. Preparation of $BaTe_2F_{10}$

An intimate mixture of $BaF_2 + 2TeF_4$ was heated at 300 °C for 24 h in a sealed platinum tube. BaF_2 was a commercial product (Aldrich) and TeF_4 was prepared by the thermal decomposition of $NaTeF_5$ in the way described previously [1]. Because of the air sensitivity of most of the compounds, all the experiments were performed in a glove box under a strictly dried and deoxygenated argon atmosphere. Single crystals of this new phase were obtained by slowly cooling the mixture from 330 °C to 250 °C in a sealed platinum tube.

2.2. Crystallographic studies

One such single crystal, prismatic and of size $0.14 \times 0.07 \times 0.05$ mm^3, was selected for crystallographic study and sealed in a glass capillary to avoid hydrolysis. It was mounted on a P4 Siemens four-circle diffractometer for determination of its crystallographic features. The symmetry was monoclinic with the refined parameters: $a = 1731.1(3)$ pm, $b = 483.16(8)$ pm, $c = 1023.3(2)$ pm and $\beta = 111.60(1)°$ (powder data recorded on a Siemens D5000, Cu Kα radiation). The extinction conditions corresponded to the $C2/c$ or Cc space group. The indexed powder pattern is reported in Table 1.

Taking into account the lack of structural information concerning the fluorotellurates(IV), we decided to determine the crystal structure of $BaTe_2F_{10}$, recording the diffraction intensities of the single crystal under the conditions listed in Table 2.

2.3. Determination of the structure

The location of Ba and Te atoms was determined by direct methods with the SHELXS-86 program on the basis of the $C2/c$ space group [2]. After refinement of their position using SHELXL-93 [3], the anionic sites were localized by Fourier-difference calculations. After refinement of the atomic coordinates and isotropic thermal factors of all the atoms, anisotropic temperature factors, an extinction coefficient and a weighting scheme were successively introduced. Absorption corrections by the psi-scan method were also performed with the XEMP program [4], considering the crys-

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Table 1
Powder X-ray pattern of $BaTe_2F_{10}$ ($\lambda = 154.06$ pm)

$h\,k\,l$	d_{calc} (pm)	d_{obs} (pm)	I/I_0
2 0 0	804.0	803.0	4
0 0 2	475.7	475.7	4
1 1 0	462.8	462.9	3
1 1 −1	434.6	434.7	14
4 0 0	402.4	402.3	10
1 1 1	399.8	399.9	5
4 0 −2	384.9	385.0	89
3 1 −1	367.1	367.1	8
3 1 0	359.0	358.9	100
2 0 2	356.1	356.2	67
1 1 −2	350.8	350.8	96
1 1 2	315.4	315.4	3
3 1 1	311.5	311.4	4
6 0 −2	282.3	282.4	2
5 1 −1	281.3	281.2	5
1 1 −3	275.6	275.5	1
3 1 −3	273.5	273.6	2
5 1 −2	271.7	271.7	3
6 0 0	268.2	268.1	28
5 1 0	268.0		
4 0 2	263.1	263.1	5
2 0 −4	255.1	255.1	11
1 1 3	249.6	249.6	8
0 2 0	241.6	241.6	8
0 0 4	237.9	237.9	2
0 2 1	234.2	234.2	5
3 1 −4	225.5	225.4	3
6 0 −4	223.4	223.4	5
7 1 −2	218.8	218.9	95
2 2 −2	217.3	217.3	8
5 1 −4	213.3	213.2	30
3 1 3	213.1		
4 2 −1	210.9	210.8	5
5 1 2	207.8	207.8	30
7 1 0	207.7		
4 2 −2	204.6	204.6	27
1 1 4	203.0	203.0	27
2 2 2	199.92	199.90	15
2 2 −3	197.12	197.12	7
4 2 1	194.85	194.87	3
8 0 −4	192.47	192.43	14
4 2 −3	190.75	190.77	6
3 1 −5	188.44	188.44	3
6 2 −1	184.89	184.86	5

Table 2
Crystal data and structure refinement conditions for $BaTe_2F_{10}$

Formula weight (g)	582.51	
Temperature	293(2) K	
Wavelength	71.073 pm	
Crystal system	Monoclinic	
Space group	*C*2/*c*	
Unit cell dimensions	$a = 1731.1(3)$ pm	$\alpha = 90°$
	$b = 483.16(8)$ pm	$\beta = 111.602(9)°$
	$c = 1023.3(2)$ pm	$\gamma = 90°$
Volume	$795.8(2) \times 10^6$ pm^3	
Z	4	
Density (calculated)	4.862 mg m^{-3}	
Absorption coefficient	12.31 mm^{-1}	
F(000)	1000	
Crystal size	$0.14 \times 0.07 \times 0.05$ mm^3	
2θ range for data collection	8.20° to 60.08°	
Index ranges	$-24 \leqslant h \leqslant 14 \quad -6 \leqslant k \leqslant 1 \quad -14 \leqslant l \leqslant 14$	
Reflections collected	1354	
Independent reflections	1000 [R(int) = 0.0270]	
Refinement method	Full-matrix least-squares on F^2	
Data/restraints/parameters	1000/0/61	
Goodness-of-fit on F^2	1.115	
Final *R* indices [$I > 2\sigma(I)$]	$R_1 = 0.0406$, $wR_2 = 0.1188$	
R indices (all data)	$R_1 = 0.0476$, $wR_2 = 0.1254$	
Extinction coefficient	0.0013(3)	
Largest diff. peak and hole	2922 and −1855 e nm^{-3}	

Table 3
(a) Atomic coordinates ($\times 10^4$), equivalent isotropic temperature factor B_{eq} (pm$^2 \times 10^{-4}$) (esd are given in parentheses) *

Atom	*x*	*y*	*z*	B_{eq}
Ba	0	9615(1)	2500	1.32(3)
Te	1582(1)	4463(1)	660(1)	1.13(3)
F1	735(4)	5633(9)	8785(5)	1.76(6)
F2	1669(4)	1060(11)	9628(5)	2.34(7)
F3	619(3)	2427(10)	536(5)	1.89(5)
F4	1064(3)	7033(11)	1542(5)	2.32(7)
F5	2008(4)	2494(12)	2407(5)	2.29(7)

* $B_{eq} = \frac{4}{3} \times 2\pi^2(U_{11} + U_{22} + U_{33})$.

(b) Anisotropic displacement factors U_{ij} (pm$^2 \times 10^{-1}$) (esd are given in parentheses) *

Atom	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
Ba	23(1)	12(1)	15(1)	0	8(1)	0
Te	17(1)	12(1)	14(1)	−1(1)	6(1)	1(1)
F1	29(3)	20(2)	18(2)	4(2)	6(2)	6(2)
F2	39(3)	18(2)	32(3)	−9(2)	16(2)	2(3)
F3	22(2)	19(2)	31(2)	3(2)	10(2)	−8(2)
F4	36(3)	26(3)	26(2)	−3(2)	18(2)	6(3)
F5	33(3)	29(3)	24(2)	9(2)	−2(2)	3(3)

* The exponent takes the form $-2\pi^2(h^2a^{*2}U_{11} + \dots\dots + 2hka^*b^*U_{12}]$.

tal as an ellipsoid. The refinement finally converged to R_1 and wR_2 values of 0.048 and 0.125, respectively, when all reflections were taken into account and of 0.041 and 0.119 when only reflections with $I > 2\sigma(I)$ were considered.

Various refinements on the basis of the non-centrosymmetric space group *Cc* did not lead to significant improvements of the *R* factors.

No electron density peak greater than 2922 e nm^{-3} persisted and all the structure parameters and bond distances were quite normal. The atomic coordinates and thermal coefficients are reported in Table 3 and the main bond lengths and angles in Table 4.

3. Description of the structure

Each tellurium atom (Fig. 1) is surrounded by five anions at distances ranging from 190 to 202 pm (⟨Te—F⟩ = 195.3 pm). These anions constitute a nearly perfect square pyramid, which in fact can be described as a distorted octahedron

Table 4
Main interatomic distances (pm), angles (°) and bond valences in $BaTe_2F_{10}$ (esds are given in parentheses; notations are those indicated in Figs. 1 and 2)

Te	F1	F2	F3	F4	F5	V_{ij}
F1	**202.0(5)**	268.7(5)	243.4(5)	275.2(5)	386.2(5)	0.667
F2	84.08	**199.0(5)**	242.1(5)	384.6(5)	277.5(5)	0.724
F3	76.63	76.90	**189.9(5)**	245.5(5)	246.4(5)	0.924
F4	87.99	156.20	79.45	**193.8(4)**	191.9(5)	0.832
F5	156.98	90.42	80.35	88.17	**191.7(5)**	0.881
V_{ij}						4.028

⟨Te–F⟩ = 195.3 pm.

Ba	$F1^1$	$F1^2$	$F1^3$	$F1^4$	$F2^1$	$F2^2$	$F3^1$	$F3^2$	$F3^3$	$F3^4$	$F4^1$	$F4^2$	V_{ij}
$F1^1$	**271.8(5)**	291.3(5)	483.3(5)	564.3(6)	303.6(4)	507.3(5)	339.2(5)	284.1(5)	378.2(5)	531.4(5)	465.1(5)	437.4(5)	0.240
$F1^2$	64.72	**271.8(5)**	564.3(6)	483.3(5)	507.3(6)	303.6(5)	284.2(4)	339.2(5)	531.4(5)	378.2(5)	437.4(5)	465.1(5)	0.240
$F1^3$	177.49	117.81	**292.3(5)**	292.3(5)	268.7(5)	487.3(5)	508.0(5)	473.0(5)	243.4(5)	445.6(5)	327.5(5)	286.9(5)	0.138
$F1^4$	117.82	177.49	59.72	**292.3(5)**	487.3(5)	268.7(5)	473.0(5)	508.0(5)	445.6(5)	243.4(5)	286.9(5)	327.5(5)	0.138
$F2^1$	127.82	64.92	54.65	112.62	**292.6(6)**	582.3(5)	425.6(5)	425.5(5)	242.1(5)	535.8(5)	453.3(5)	308.3(5)	0.137
$F2^2$	64.92	127.82	112.62	54.65	167.22	**292.6(6)**	425.5(5)	425.6(5)	535.8(5)	242.1(5)	308.3(5)	453.3(5)	0.137
$F3^1$	60.12	73.52	120.08	107.56	92.97	92.95	**293.6(4)**	521.2(5)	563.5(5)	309.5(5)	554.1(5)	280.8(5)	0.133
$F3^2$	73.52	60.12	107.56	120.07	92.95	92.97	124.92	**293.6(4)**	309.5(5)	563.5(5)	280.5(5)	554.1(5)	0.133
$F3^3$	81.63	133.76	96.25	47.96	126.99	47.64	62.22	140.02	**305.4(5)**	578.6(5)	292.2(5)	444.2(8)	0.097
$F3^4$	133.76	81.63	47.90	96.25	47.64	126.99	140.02	62.22	142.32	**305.4(5)**	444.8(5)	292.2(5)	0.097
$F4^1$	118.49	107.92	61.22	71.22	66.32	107.33	59.62	159.32	60.69	100.94	**269.0(5)**	477.4(5)	0.258
$F4^2$	107.92	118.49	71.22	61.22	107.33	66.32	159.32	59.60	100.94	60.69	124.72	**269.0(5)**	0.258
V_{ij}													2.006

⟨Ba–F⟩ = 287.5 pm.

Table 5
Comparison of the main average bond lengths (pm) and angles (°) in TeF_5E polyhedra

TeF_5	TeF_4 [4]	$KTeF_5$ [5]	$CsTeF_5$ [6]	$PbTeF_6$ [7]	$BaTe_2F_{10}$
$Te–F_{ax}$	180	186	181	188	190
$Te–F_{eq}$	203	195	193	203	197
$F_{ax}–F_{eq}$	252	242	240	252	244
$F_{eq}–F_{eq}$	285	271	269	283	253
$F_{ax}–Te–F_{eq}$	82.0	78.9	79.8	80.4	78.3
$F_{eq}–Te–F_{eq}$	88.8	87.8	88.2	88.3	87.7

TeF_5E whose one corner is occupied by the stereochemically active lone-pair E of the central tellurium atom. Such an environment is quite classical in the stereochemistry of Te^{IV} and is observed in crystal structures like TeF_4 [5], $KTeF_5$ [6], $CsTeF_5$ [7] and $PbTeF_6$ [8] (see values in Table 5). The results of a bond valence calculation realized by Brown's

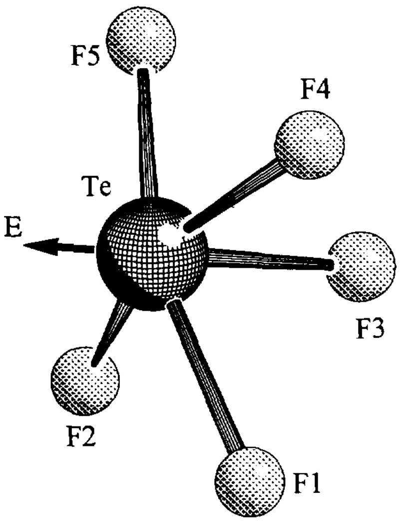

Fig. 1. The TeF_5E polyhedron in $BaTe_2F_{10}$.

method [9,10] indicate nearly perfect electrostatic equilibrium around the tellurium(IV) atoms ($\Sigma V_{ij} = 4.03$).

Each barium atom is surrounded by four anions at distances ranging from 269 to 272 pm and eight anions at slightly longer distances in the range 292–305 pm. The corresponding rather irregular polyhedron can be considered as a distorted cuboctahedron and is represented in Fig. 2. The sum of the bond valences $\Sigma V_{ij} \approx 2.006$ also indicates a good electrostatic balance around Ba^{2+}.

Projections of the structure on to the xOz and xOy planes are shown in Fig. 3. One can see that this structure is very simple and corresponds to a slightly distorted cubic close packing of barium atoms and independent TeF_5E polyhedra. In fact, as clearly shown in Fig. 3, it can be described as the regular stacking along Ox of alternate (1 0 0) square layers

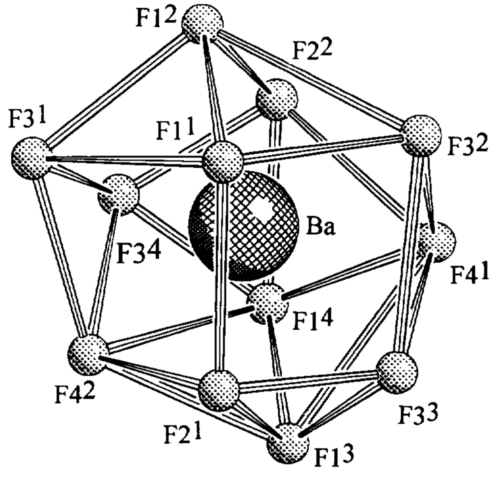

Fig. 2. The BaF_{12} polyhedron in $BaTe_2F_{10}$.

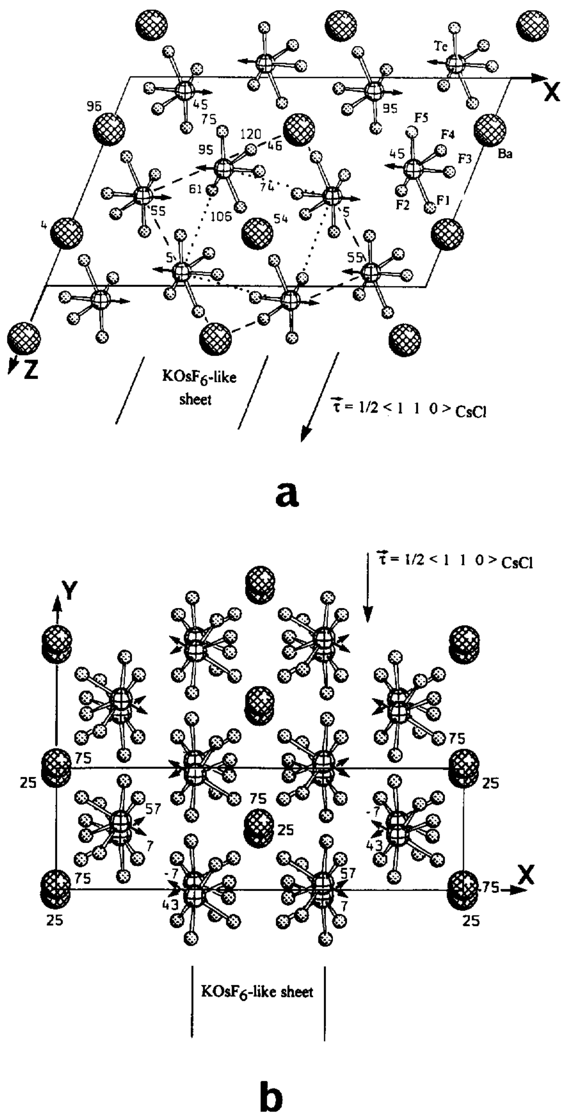

Fig. 3. Projection of the $BaTe_2F_{10}$ structure: (a) on to the xOz plane; (b) on to the xOy plane. The dashed and dotted lines respectively visualize the fcc subcell and the distorted CsCl ($KOsF_6$-like) cell.

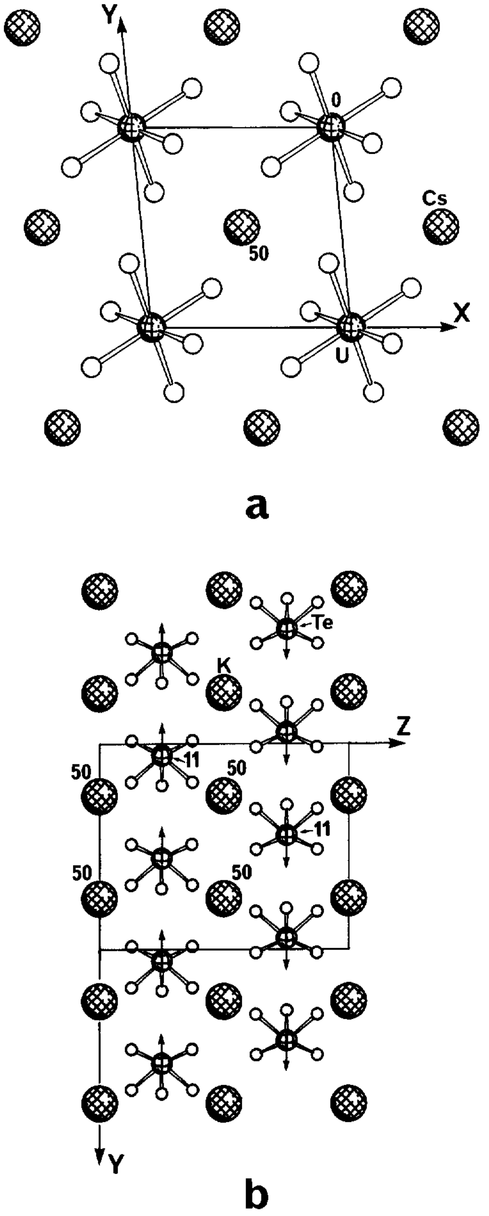

Fig. 4. Two $KOsF_6$-related structures: (a) $CsUF_6$ [12]; (b) $KTeF_5$.

of Ba atoms on the one hand and independent TeF_5E octahedra on the other hand, according to the sequence ...–Ba–TeF_5E–TeF_5E–.... It is interesting to note that this structure corresponds to the regular repetition along 0*x* of $BaTe_2F_{10}E_2$ three-layer-wide sheets. These sheets derive from a $KOsF_6$-type structure (rhombohedrally distorted CsCl type), as shown by a comparison of Figs. 3 and 4(a). In $BaTe_2F_{10}$, these sheets are shifted 1/2 $\langle 1\ 1\ 0\rangle_{CsCl}$ one from the other.

As in many other fluorinated compounds of tellurium(IV) ($Te_2O_3F_2$ [11], $PbTeF_6$ [8] etc.), all the lone-pairs E of tellurium atoms point towards the intersheet space, their relative shifts avoiding them being directly one in front of the other and thus increasing the stability of the packing of the TeF_5E octahedra.

In the same way, the $KTeF_5$ structure can be considered as a distorted $KOsF_6$ structure, i.e. as a regular primitive cubic array of K atoms where the cubic sites are all occupied by TeF_5E octahedra [Fig. 4(b)]. Here again, the stereochemical activity of the lone-pairs E of Te atoms imposes an alternate displacement of the TeF_5E octahedra out of the ideal 1/2 1/2 1/2 cubic sites and thus a distortion of the ideal CsCl-like structure.

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