ELSEVIER

Journal of Fluorine Chemistry 89 (1998) 223–228

JOURNAL OF FLUORINE CHEMISTRY

Comparative study of the crystal–chemical behaviour of Zr^{4+}, Tb^{4+} and U^{4+} ions in MF_2–$M'F_4$ systems (M = Ca, Sr, Ba, Cd; M′ = Zr, Tb, U)

E. Largeau *, M. El-Ghozzi

Laboratoire des Matériaux Inorganiques, UPRES A-6002 CNRS, Université Blaise Pascal, 63177 Aubiere, France

Received 24 October 1997; accepted 20 January 1998

Abstract

Investigations on MF_2–TbF_4 (M = Ca, Sr, Ba, Cd) systems showed the existence of new compounds with original structures for MF_2/TbF_4 molar ratios equal to 2, 1, 0.5, 0.33 and emphasized the particular crystal–chemical behaviour of the Tb^{4+} ion.

Keywords: Tetravalent terbium-fluoride

1. Introduction

In spite of recent crystal structure determinations of tetravalent terbium fluorides [1–7] carried out from single-crystals, the 4+ oxidation state of terbium remains little known. This lack of information arises from the difficulty to stabilize the tetravalent state which constrains the experimenter to synthesize such compounds under a fluorine atmosphere. Nevertheless Tb(IV) fluorinated compounds are of great interest for investigation of optical and magnetic properties due to the $4f^7$ electronic configuration and its $^8S_{7/2}$ ground state. So an understanding of the crystal–chemical behaviour of this cation becomes essential. Investigations on MF_2–TbF_4 (M = Ca, Sr, Ba, Cd) were carried out and brought out the existence of eight new intermediate compounds with new structures. Both α-$BaTbF_6$ and β-$BaTbF_6$ structures have been refined from single-crystal data whereas that of Cd_2TbF_8 has been solved *ab initio* from X-ray powder diffraction data and refined using Rietveld's procedure. The singular crystal–chemical behaviour of the Tb^{4+} ion in these MF_2–TbF_4 systems was brought out by comparison with the MF_2–ZrF_4 and MF_2–UF_4 systems.

2. Synthesis

Accurate synthesis conditions were deduced from previous experiments [1–3]. All compounds were obtained by heating twice, overnight, at temperatures ranging from 450°C to 750°C, stoichiometric mixtures of starting MF_2 (M = Ca, Sr, Ba, Cd) and TbF_4 fluorides in a nickel boat under a pure fluorine gas flow. Single-crystals were only obtained for both α- and β-$BaTbF_6$ and $SrTbF_6$ compounds.

3. Results

In order to bring out a better understanding of the crystal–chemical behaviour of Tb^{4+}, all phases containing this ion presented below were compared with compounds of identical stoichiometry, if they exist, in MF_2–ZrF_4 and MF_2–UF_4 systems. Tetravalent zirconium and uranium ions were chosen for their ionic radii close to and on either side of Tb^{4+} and their various coordination numbers ranging from 6 to 8 and 7 to 11, respectively.

It is worth noticing that previous works on tetravalent terbium fluorides [1,2,8] revealed a favored capacity for the Tb^{4+} ion to assume eight-coordination. Until now this trend seems to be an outstanding feature of the crystal–chemical behaviour of this tetravalent lanthanide and was not followed only for M_3TbF_7 (M = NH_4, Cs, Rb, K) [9–11] where this lanthanide is surrounded by seven fluoride ions in a dynamical distribution.

Fig. 1 displays the different definite compounds which have been found and allows a brief comparison between Tb^{4+} and both Zr^{4+} and U^{4+}. Despite apparent similarities concerning the $MF_2/M'F_4$ molar ratios for which phases occur in these systems, many tetravalent terbium phases exhibit

* Corresponding author.

0022-1139/98/$19.00
PII S0022-1139(98)00133-X

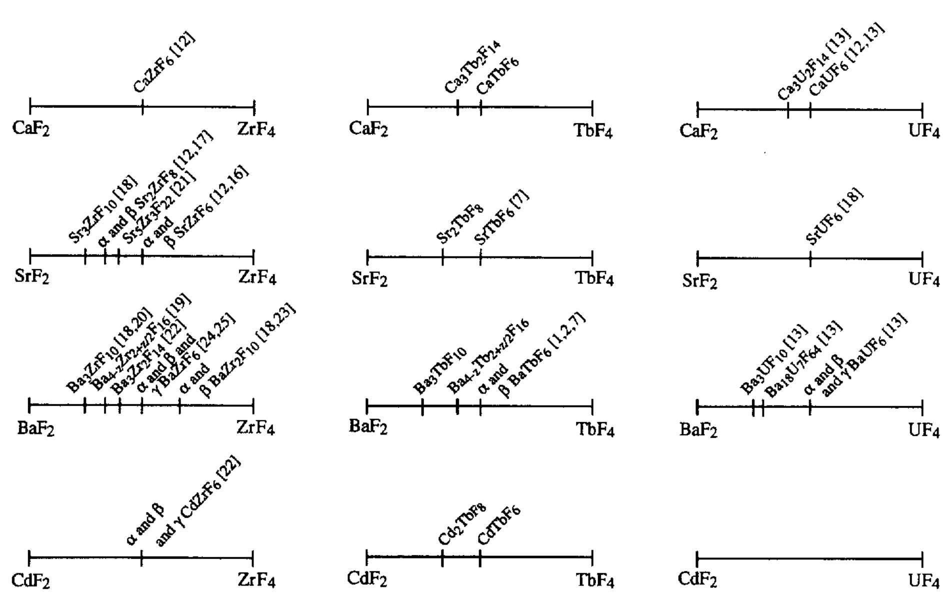

Fig. 1. Phase relationships in MF_2–$M'F_4$ systems (M = Ca, Sr, Ba, Cd; M′ = Zr, Tb, U).

unprecedented structures and isostructural compounds have been found only when the tetravalent cations are in eight-coordination.

3.1. CaF_2–TBF_4 system

The first new compound in this system was $CaTbF_6$. It was synthesized at 700°C and appeared as a white powder. Its X-ray powder diffraction pattern displayed in Fig. 2 does not show any direct relation with either $CaZrF_6$ [12] which has an ordered ReO_3 structure or $CaUF_6$ which exhibits a disordered tysonite structure [12,13]. In the two latter compounds the tetravalent cations are 6- and 11-coordinate, respectively, which may explain the absence of isotypy with $CaTbF_6$.

The X-ray powder diffraction pattern of $CaTbF_6$ was indexed using the TREOR90 [14] program and revealed for this compound tetragonal symmetry and unit cell parameters $a = 5.273$ Å and $c = 7.715$ Å and possible $P4_2/mcm$, $P4_2cm$ or $P4c2$ space groups.

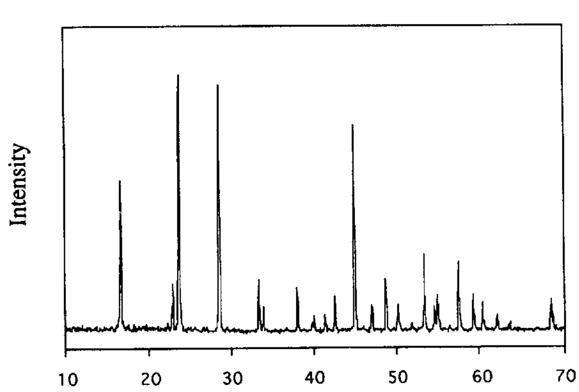

Fig. 2. X-ray powder diffraction pattern of $CaTbF_6$.

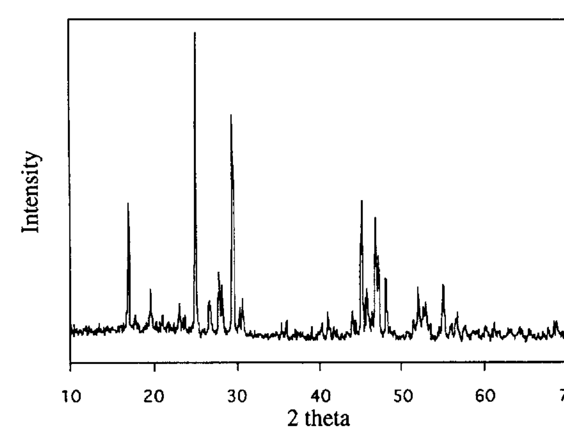

Fig. 3. X-ray powder diffraction pattern of $Ca_3Tb_2F_{14}$.

The other new compound characterized in this system was $Ca_3Tb_2F_{14}$. Its X-ray powder diffraction pattern shown in Fig. 3 is different from all other compounds observed in the MF_2–$M'F_4$ systems. We note that this uncommon stoichiometry was previously only observed in $Ca_3U_2F_{14}$ [13] a low-temperature tysonite related structure and $Ag_3Zr_2F_{14}$ [15] where the zirconium is surrounded by seven fluorine ions in a pentagonal bipyramid. Due to the coordination numbers of the tetravalent cation in these two compounds, no isotypy between these compounds and $Ca_3Tb_2F_{14}$ could be expected according to the aforementioned assumption. This is effectively observed.

3.2. SrF_2–TBF_4 system

Two phases were synthesized in this system but the first, $SrTbF_6$, was known [7]. It is isotypic with the homologous α-$SrZrF_6$ and belongs to the β-$BaZrF_6$ type [16]. In this

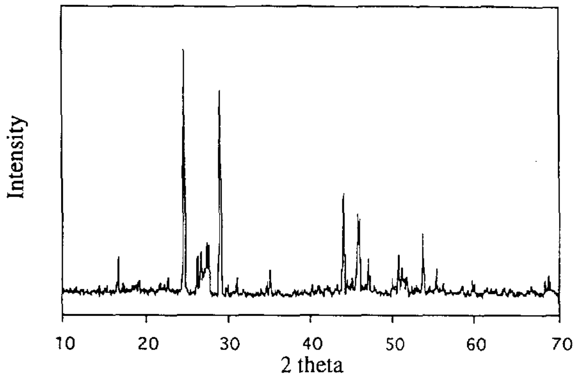

Fig. 4. X-ray powder diffraction pattern of Sr_2TbF_8.

structural type, $[TbF_8]^{4-}$ dodecahedra are linked by opposite edges to form infinite chains parallel to the [100] direction. Sr atoms are surrounded by 10 fluorine ions. $SrUF_6$ [12,13] has a rather different structure since it exhibits a disordered tysonite type like $CaUF_6$.

A new fluoride Sr_2TbF_8 was also synthesized at 650°C and was always obtained with a low crystallization rate (Fig. 4). This compound does not exhibit isotypy with other fluorides and more particularly with α- and β-Sr_2ZrF_8 [17] and $Ba_{4-z}Zr_{2+z/2}F_{16}$ [18,19]. Therefore Sr_2TbF_8 may be considered as a new structural type.

No other compound was found in this system whereas Sr_3ZrF_{10} [20,21] has been found in the SrF_2–ZrF_4 system. Moreover $Sr_5Zr_3F_{22}$ was recently [21] obtained under hydrothermal conditions but no homologue has been observed with terbium.

3.3. BaF_2–TBF_4 system

Barium provides the more complex MF_2–$M'F_4$ systems ($M' = Zr^{4+}, Tb^{4+}$ and U^{4+}). Three $BaUF_6$ polymorphs [13] deriving from the tysonite structure with a more or less extended ordering have been found in the BaF_2–UF_4 system. Other phases such as Ba_3UF_{10} and $Ba_{18}U_7F_{64}$ [13] were found and are also related to the tysonite type. These structural types exhibit high coordination of the tetravalent cations probably requiring participation of f orbitals. According to the general trend which tends to demonstrate that Tb^{4+} never adopts coordination number higher, than 8 such structures cannot be expected for Tb^{4+}, as confirmed by X-ray diffraction characterization of these phases.

On the contrary, many analogies have been observed between BaF_2–ZrF_4 and BaF_2–TbF_4 systems. Comparison of the X-ray diffraction patterns of Ba_3TbF_{10}, Ba_3ZrF_{10} and Pb_3ZrF_{10} [20] reveals an isotypy between these three fluorides. From a single-crystal structure determination [20] carried out on the lead compound the structure can be described as an ordered intergrowth of $(Pb_2F_4)_n$ fluorite columns and $(Pb_4Zr_2F_{16})_n$ columnar clusters built of two isolated square antiprisms sharing faces with four $[PbF_{11}]$ complex polyhedra.

Both BaF_2–ZrF_4 and BaF_2–TbF_4 systems exhibit a single-phase domain $Ba_{4-z}Zr_{2+z/2}F_{16}$ [19]. The crystal structure of this last compound refined from single-crystal data for $z = 0.232$ showed the three-dimensional framework as a stacking of two kinds of slab: partly disordered anion excess ReO_3 type and regular perovskite.

Another compound of the greatest interest is $BaTbF_6$ mentioned for the first time by Feldner and Hoppe [7] who reported that the structure was unknown. At present it is well established that this compound is a low temperature form subsequently called α-$BaTbF_6$ [1,2]. Its structure was refined from single-crystal X-ray diffraction data. It may be regarded as a stacking along the *c* direction of alternated layered blocks of Ba polyhedra and layers of Tb polyhedra built of $[Ba_4F_{30}]^{22-}$ and $[Tb_4F_{26}]^{10-}$ tetrameric complex anions respectively. The $[Tb_4F_{26}]^{10-}$ complex anion (Fig. 5) results from the association of four square antiprisms by sharing corners and edges [2]. α-$BaTbF_6$ undergoes a phase transition at about 637±5°C to an orthorhombic form β-$BaTbF_6$ [1] isotypic with β-$BaZrF_6$ (Fig. 6). It is worth noticing that $BaTbF_6$ is the first representative for which a structural phase transition has been observed with a quenchable high temperature form.

Whereas in the BaF_2–ZrF_4 system several intermediate compounds have been found on the rich ZrF_4 side, no other phase was observed in the BaF_2–TbF_4 system. In spite of numerous studies carried out on the BaF_2–ZrF_4 system, the $Ba_3Zr_2F_{14}$ fluoride was mentioned only once [22] and never confirmed [18,23]. Both α-$BaZr_2F_{10}$ and β-$BaZr_2F_{10}$ have been obtained by recrystallization of fluoride glasses [24]. Both compounds, as for α-$BaZrF_6$ [25], have structures built from seven coordinate zirconium polyhedra which are uncommon for Tb^{4+}. Finally γ-$BaZrF_6$ [26], for which the

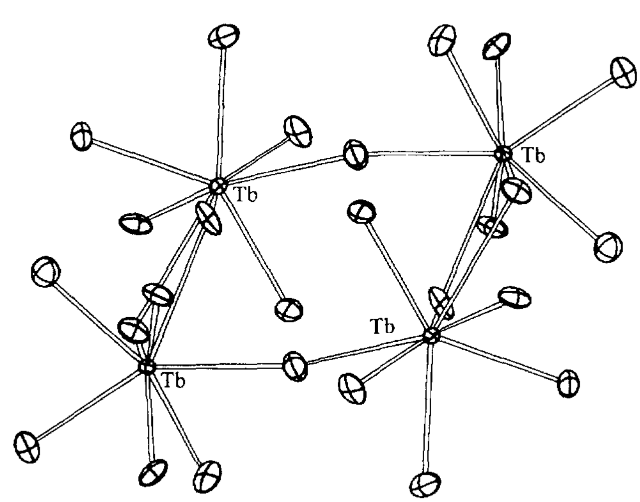

Fig. 5. $[Tb_4F_{26}]^{10-}$ complex anions in α-$BaTbF_6$ structure.

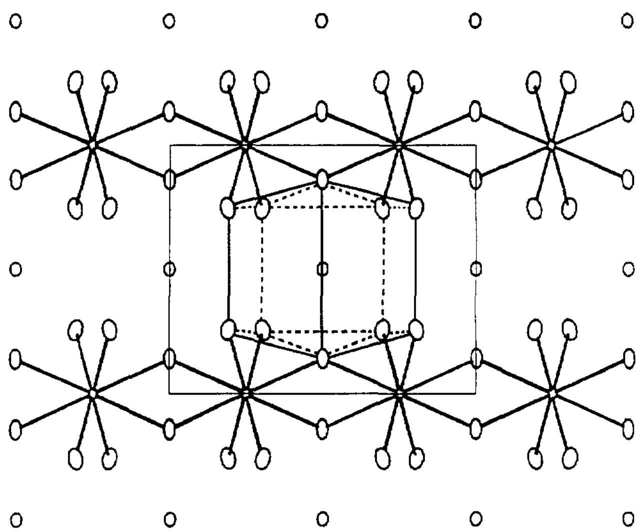

Fig. 6. Infinite chains built up of edge-sharing $[TbF_8]^{4-}$ dodecahedra in β-$BaTbF_6$ and $SrTbF_6$.

structure presents two crystallographically independent eight-coordinated zirconium atoms, is stabilized by the presence of structural H_2O molecules and is formed during an hydrothermal synthesis. Our synthetic procedure carried out under pure F_2 gas excludes the obtaining of a hydrated compound. Therefore we cannot expect to obtain such a phase with tetravalent terbium under our experimental conditions.

3.4. CdF_2–TBF_4 system

Two new compounds have been found in the CdF_2–TbF_4 system namely $CdTbF_6$ and Cd_2TbF_8. $CdTbF_6$ exhibits a complex X-ray powder diffraction pattern (Fig. 7) which cannot be related to those of α-, β- or γ-$CdZrF_6$ [22], which suggests that this compound has a new structural type.

Cd_2TbF_8 was obtained by heating twice overnight at 650°C a stoichiometric mixture $2CdF_2$–$1TbF_4$. As no single-crystal of this compound could be obtained the structure was solved *ab initio* from the X-ray powder diffraction data. The data used for structure determination were recorded at room temperature on a SIEMENS D500 diffractometer using a scan step of 0.02° over the 2θ range 10–120° and a counting time

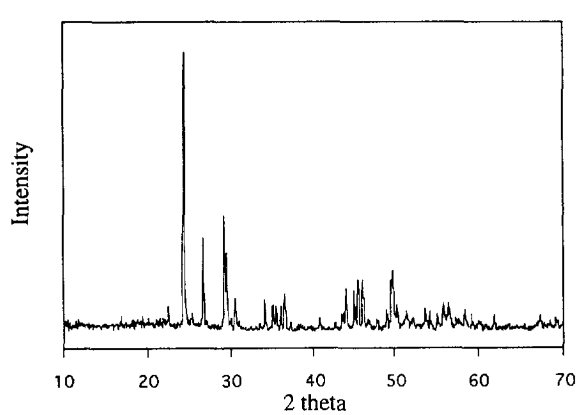

Fig. 7. X-ray powder diffraction pattern of $CdTbF_6$.

Table 1
Details of Rietveld refinement for Cd_2TbF_8

Space group	$I\bar{4}$
Cell parameters	$a=5.145(1)$ Å $c=11.184(1)$ Å
2θ range (°)	10–120
Step scan (°2θ)	0.02
Time/step (s)	20
Number of reflections	168
Number of refined parameters	22
Profile function	pseudo-voigt
Profile parameters	$U=0.0275$ $V=-0.0261$ $W=0.0151$
Discrepancy factors	$R_p=11.3$; $R_{wp}=13.3$ $R_B=4.956$; $R_F=4.953$ $\chi^2=1.97$

Table 2
Positional and thermal parameters for Cd_2TbF_8

	x	y	z	Biso (Å²)
Tb	0	0	0	0.485
Cd	0	0	0.6733(1)	0.545
F1	0.664(2)	0.296(1)	0.332(2)	1.642
F2	0.267(1)	0.198(2)	0.439(1)	2.050

Table 3
Main distances in Cd_2TbF_8

Tb–F: 2.081(2) Å	Tb–F: 2.315(2) Å
Cd–F: 2.117(1) Å	Cd–F: 2.304(2) Å
Cd–F: 2.226(2) Å	

of 20 s per step. An automatic indexation of the X-ray powder diffraction pattern using TREOR90 [14] reveals tetragonal symmetry and unit cell parameters $a=5.145$ Å, $c=11.184$ Å. Systematic extinctions were consistent with either $I4/mmm$, $I422$, $I4mm$, $I\bar{4}2m$, $I\bar{4}m2$, $I4/m$, $I4$ or $I\bar{4}$ space groups. The heavy Cd and Tb atoms were located from the Patterson function computed with the SHELXS-97 [27] program on the whole data set. The anionic positions were deduced from a Fourier difference synthesis and the best refinement was obtained in the acentric $I\bar{4}$ space group (Table 1). The structure refinement was performed with the Rietveld profile method [28,29] using the program FULLPROF [30]. Table 2 shows the positional and thermal parameters for Cd_2TbF_8; Table 3 shows the main distances in Cd_2TbF_8.

Fig. 8 displays the observed and difference patterns represented up to 120°.

The structure is built of $[Cd_2TbF_{16}]^{8-}$ entities (Fig. 9) formed by a $[TbF_8]^{4-}$ dodecahedron sharing opposite edges with two $[CdF_6]^{4-}$ octahedra. These complex anions are further linked by sharing terminal vertices to form a three-dimensional framework (Figs. 10 and 11).

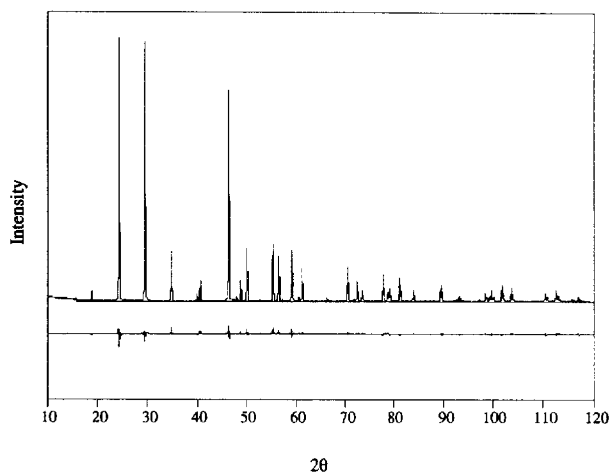

Fig. 8. Observed and difference X-ray powder diffraction patterns of Cd_2TbF_8.

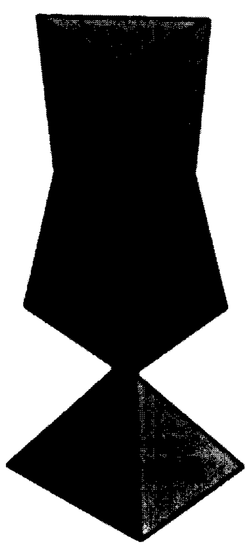

Fig. 9. $[Cd_2TbF_{16}]^{8-}$ complex anions in Cd_2TbF_8.

4. Conclusion

Preliminary investigations carried out on the MF_2–TbF_4 systems showed eight new compounds out of which new structural types were investigated. Comparison of these compounds with homologous phases of uranium or zirconium (other tetravalent cations not investigated here) reveal a singular crystal–chemical behaviour of the Tb^{4+} ion which confirms the great capability of this ion to adopt eight-coordination. The general trend which is coming out from this preliminary phases relationships in MF_2–TbF_4 systems tends to demonstrate that when all the tetravalent crystallographically independent cations are in eight-coordination then both Zr and Tb homologous compounds are present in these systems whereas when only the Zr representative of a given stoichiometry appears, this has probably the meaning that some of the Zr^{4+} ions should be in six- or seven-coordination.

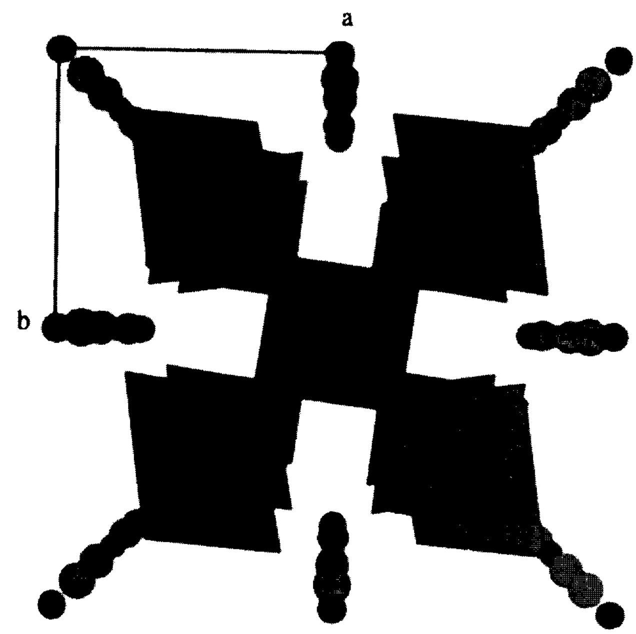

Fig. 10. Structure of Cd_2TbF_8 viewed along the [001] direction.

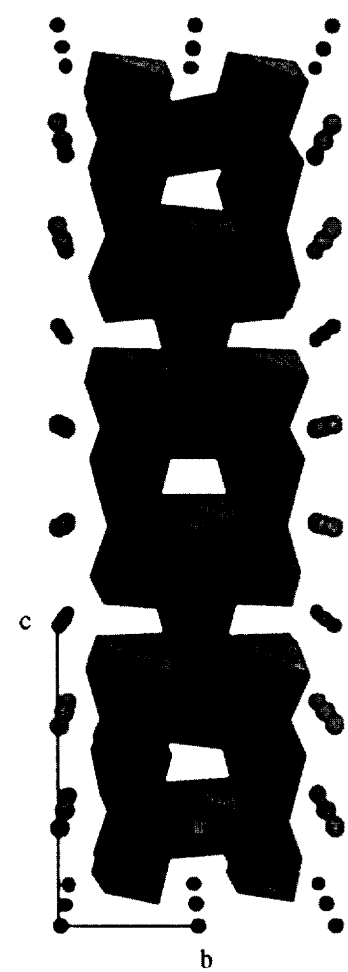

Fig. 11. Structure of Cd_2TbF_8 viewed along the [100] direction.

References

[1] E. Largeau, M. El-Ghozzi, J. Metin, D. Avignant, Acta Crystallogr. C 53 (1997) 530.

[2] E. Largeau, V. Gaumet, M. El-Ghozzi, D. Avignant, J.C. Cousseins, J. Mater. Chem. 7 (1997) 1881.

[3] V. Gaumet, E. Largeau, D. Avignant, Eur. J. Solid State Inorg. Chem. (1997) submitted for publication.

[4] V. Gaumet, D. Avignant, Acta Crystallogr. C 53 (1997) to appear.

[5] A.I. Popov, M.D. Val'Kovskii, P.P. Fedorov, Y.M. Kiselev, Russ. J. Inorg. Chem. 36 (4) (1991) 476.

[6] M. Guillot, M. El-Ghozzi, D. Avignant, G. Ferey, J. Solid State Chem. 97 (1992) 400.

[7] K. Feldner, R. Hoppe, Rev. Chim. Min. 20 (1983) 351.

[8] D. Avignant, E. Largeau, V. Gaumet, P. Dugat, M. El-Ghozzi, J. Alloys Compounds (1997) submitted for publication.

[9] R. Hoppe, K.M. Rödder, Z. Anorg. Allg. Chem. 312 (1961) 277.

[10] Z. Hu, G. Kaindl, D. Vandré, R. Hoppe, G. Wortmann, J. Alloys Compounds 205 (1994) 263.

[11] V. Gaumet, Thesis, University of Clermont-Ferrand, 1996.

[12] D. Babel, A. Tressaud, Crystal chemistry in fluorides, in: P. Hagenmuller (Ed.), Inorganic Solid Fluorides, Chemistry and Physics, Academic Press, San Diego, 1985.

[13] A. Mikou, Thesis, University of Limoges, 1986.

[14] P.E. Werner, L. Eriksson, M. Westdahl, J. Appl. Crystallogr. 18 (1985) 367.

[15] B.G. Muller, Z. Anorg. Allg. Chem. 553 (1987) 196.

[16] J.P. Laval, D. Mercurio-Lavaud, B. Gaudreau, Rev. Chim. Min. 11 (1974) 742.

[17] I.D. Ratnikova, Yu.M. Korenev, A.V. Novoselova, Russ. J. Inorg. Chem. 25 (1980) 452.

[18] J.P. Laval, B. Frit, B. Gaudreau, Rev. Chim. Min. 16 (1979) 509.

[19] J.P. Laval, B. Frit, Acta Crystallogr. B 36 (1980) 2533.

[20] J.P. Laval, B. Frit, Mater. Res. Bull. 14 (1979) 1517.

[21] A. Le Bail, Eur. J. Solid State Inorg. Chem. 33 (1996) 1211.

[22] A.A. Babitsyna, T.A. Emel'yanova, A.P. Chernov, Russ. J. Inorg. Chem. 34 (1989) 1798.

[23] T. Grande, S. Aasland, S. Julsrud, J. Non-Cryst. Solids 140 (1992) 73.

[24] J.P. Laval, J. Non-Cryst. Solids 161 (1993) 123.

[25] J.P. Laval, R. Papiernik, B. Frit, Acta Crystallogr. B 34 (1978) 1070.

[26] A. Le Bail, A.M. Mercier, J. Solid State Chem. 101 (1992) 229.

[27] G.M. Sheldrick, Z. Dauter, K.S. Wilson, H. Hope, L.C. Sieker, Acta Crystallogr. D 49 (1993) 18.

[28] H.M. Rietveld, Acta Crystallogr. 22 (1967) 151.

[29] H.M. Rietveld, J. Appl. Crystallogr. 2 (1969) 65.

[30] J. Rogrigues Carvajal, FULLPROF: a program for the Rietveld refinement and pattern matching analysis, Abstracts of the Satellite Meeting on Powder Diffraction of the XV Congress of the International Union of Crystallography, Toulouse, France, 1990, p. 127.