

Crystal chemistry of Te(IV) fluorinated compounds

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Abstract

After a short review of the main results of our activities in the field of fluorinated compounds, a comparison of the crystal structures of the $M_xTe_y(IV)F_z$ compounds is developed.

Considering only the shortest bonds (in the range 1.80–2.10 Å) the co-ordination polyhedra for Te atoms are quasi systematically TeF_3E square pyramids or more rarely TeF_4E disphenoids. With increasing M/Te ratio, the fluorinated network changes from bi-dimensional $Te_{1.5}F_{6.5}$ layers of corner-sharing TeF_4E and TeF_5E polyhedra in $RbTe_3F_{13}$, to independent TeF_5E units in the $MTeF_5$ compounds, via finite Te_4F_{18} groups of four basic units, in KTe_2F_9 . Such an evolution emphasises the depolymerising character of the M atoms.

In all these structures the electronic lone pairs E of Te atoms are stereochemically active, pointing towards the empty spaces of the various networks: cavities, tunnels or inter-sheet spaces. © 2001 Elsevier Science B.V. All rights reserved.

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1. Introduction

Crystal structure determination of fluorinated materials by X-ray, electron or neutron diffraction experiments, has now become a quasi-routine scientific activity, correctly carried out in most of the concerned laboratories. On the contrary, the subtle analysis, the vivid description and consequently the full exploitation of the information collected are far from being as well performed, and deserve a more constant interest from our scientific community.

We have been involved for many years in this particularly fascinating field of solid state chemistry (whose predictive character is not the least interesting) by systematically comparing new structures solved with listed structural types, and by elaborating original defect models, in close relation with nonstoichiometry and with short- or long-range order.

In the case of fluoroindates and fluoroscandates $M_xIn(Sc)F_{3+x}$ of monovalent metals we have shown, for the first time, that indium or scandium atoms, in addition to the classical octahedral co-ordination, can accept a seven-fold co-ordination (pentagonal bipyramid), and we have constructed a structural classification of these compounds [1–6].

In the case of fluorozirconates, more than 40 crystalline phases have been identified and structurally characterised

[7–24]. Several homologous structural series have been described, as for example, the anion-excess fluorite-related M_mX_{2m+2} and M_mX_{2m+4} series [14], or the square antiprism layer structures [28]. An accurate analysis of the structure of α - ZrF_4 [29], β - $BaZr_2F_{10}$ [17] and β - $BaZrF_6$ [9], has allowed a significant breakthrough in the understanding of BaF_2 – ZrF_4 glasses [17,25–27].

We have been strongly involved in the characterisation of structural defects in anion-excess fluorine-related phases like $M_{1-x}^{II}M'_x{}^{II+}F_{2+\alpha x}$ or $(M, M')(O, F)_{2+x}$ complex oxide-fluorides and $M(N, F)_{2+x}$ nitridefluorides.

In the nonstoichiometric disordered phases, the defects (interstitial anions, anion vacancies, relaxed anions) constitute finite clusters. We have shown that depending on the nature of the fluorite matrix and of the dopant cation, three kinds of clusters are observed: small 1:0:n clusters, cuboctahedral 8:12:0 or 8:12:1 clusters, and columnar $2n + 2:4n:2$ or $2n + 2:3n:2$ clusters. The stability of these clusters depends more on the relative size of dopant and host cations than on their charge [30–42]. These clusters interact in the highly doped phases so as to constitute more or less well ordered superstructures as for example the incommensurate or semi-commensurate vernier phases M_mX_{2m+1} [43,44].

In mixed anion phases a O/F or N/F order is systematically observed: the smaller and lower charged anions are always located in the densest part of the structure, and only a strict order can justify the existence of abnormally vernier phases such as Bi_3NF_6 [45] and $Lu_3O_5F_2$ [46].

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More recently, we have undertaken a systematic study in the solid state of the MF–TeF₄ (M: Li, Na, K, Rb, Cs, Tl, NH₄), MF₂–TeF₄ (M: Ba, Pb) and TeO₂–TeF₄ systems.

In the case of the TeO₂–TeF₄ system [47], two original oxidefluorides TeOF₂ [48] and Te₂O₃F₂ [49] have been synthesised. Both compounds exhibit strong structural relationships with respectively the α - and β -TeO₂ polymorphs. In both structures, bond valence calculations indicate a perfect O/F order: O atoms logically occupy the equatorial positions in the anionic polyhedra and are bridging atoms; F atoms, on the contrary, occupy axial positions and are non-bridging.

In the MF₂–TeF₄ systems, in addition to a fluorite-type solid solution, which in the case of M: Pb is an excellent anionic conductor, two stoichiometric phases, with compositions MTeF₆ and MTe₂F₁₀, have been found and studied structurally.

In the MF–TeF₄ systems, three kinds of stoichiometric compounds have been isolated: MTeF₅ (M: Li, Na, K, Rb, Cs, Tl, NH₄), MTe₂F₉ (M: K), MTe₃F₁₃ (M: Rb) and perhaps MTe₄F₁₇ (M: Cs) [50]. It is interesting to note that, in the TeO₂–TeF₄ system, as well as in three MF–TeF₄ systems (M: K, Rb, Cs), very large glassy domains (about 55–95 mol% TeF₄) have been observed, demonstrating the strong glass-forming character of TeF₄. The structural study of such glasses, particularly the oxidefluorides, which exhibit glass transition at temperatures lower than 0°C, would be of fundamental interest.

2. The M_xTe_yF_z crystal structures

In all the known structures the Te atoms are fivefold coordinated (square pyramid) approximately at the centre of a distorted octahedron whose one open corner is occupied by its stereochemically active electronic lone pair E (Fig. 1a). Such a basic building unit, which is also present in the TeF₄ crystal structure [51], and whose geometry does not notably change with the nature of the M cation or of the network

formed seems, therefore, to be the most striking feature in the crystal chemistry of Te(IV) in fluorinated media.

In the KTe₂F₉ [52] and RbTe₃F₁₃ [50] structures, respectively, one half and two thirds of the Te atoms are fourfold co-ordinated (distorted disphenoid) approximately at the centre of a distorted trigonal bipyramid whose one equatorial corner is occupied by the lone pair E (Fig. 1b).

All the Te–F distances are short, in the range 1.81–2.08 Å. Because of the stereochemical activity of the lone pair E:

- in the TeF₅E octahedra, the Te–F_{ax} bond is systematically shorter than the four Te–F_{eq} ones, and the F–Te–F angles are always less than 90°;
- in the TeF₄E trigonal bipyramids, the two Te–F_{eq} bonds are shorter than the two Te–F_{ax} ones, and the F_{ax}–Te–F_{ax}, F_{eq}–Te–F_{eq} and F_{ax}–Te–F_{eq} angles are always less than the ideal respective values: 180, 120 and 90°.

In the case of the TeF₄E polyhedra observed in the KTe₂F₉ [52] and RbTe₃F₁₃ [50] crystal structures, if we take into account the two extra anions at distances 2.52–2.65 Å, the co-ordination polyhedra can then be considered as very distorted pentagonal bipyramids TeF₆E, whose one equatorial corner is occupied by the lone pair E (Fig. 1b).

Let us see now how the spatial distribution and the linking of these basic structural units develop when

- for a given stoichiometry the nature of the M cation changes;
- the Te/M ratio increases.

2.1. Te/M = 1

This corresponds to the MTeF₅ [53–58] and MTeF₆ [59,60] crystal structures. In all these structures the TeF₅E basic units are independent.

As shown in a forthcoming paper [61], all the MTeF₅ structures are made up of a mix in equal number of independent M⁺ cations and (TeF₅E)[–] anions, and they are all topologically related to the CsCl type, i.e. the TeF₅E units are located within M₈ more or less distorted cubic cavities. Such a cavity is emphasised, in Fig. 2, which represents the KTeF₅ crystal structure (orthorhombic symmetry, space group Pbcm [54]). It is worth noting that in each case:

- due to the strong stereochemical activity of the lone pairs E, the TeF₅E units are set off-centre toward an edge of the M₈ cavities.
- the distortion of the two primitive cubic arrays is all the more important since the geometrical fit between the (TeF₅E)[–] anions and the M⁺ cations is bad.

In the PbTeF₆ structure [59], which can be related to the ReO₃ type, the three-dimensional network consists of double columns of edge- and corner-sharing PbF₇E polyhedra, connected one to each other by sharing corners with independent TeF₅E units.

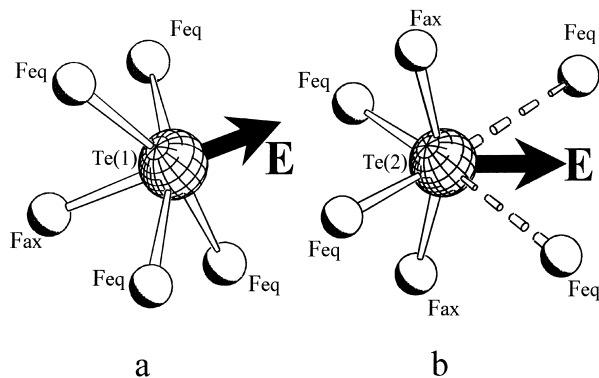


Fig. 1. Spatial view of (a) the TeF₅E polyhedron (KTe₂F₉, MTeF₅ and RbTe₃F₁₃) (b) the TeF₄₊₂E polyhedron (KTe₂F₉ and RbTe₃F₁₃).

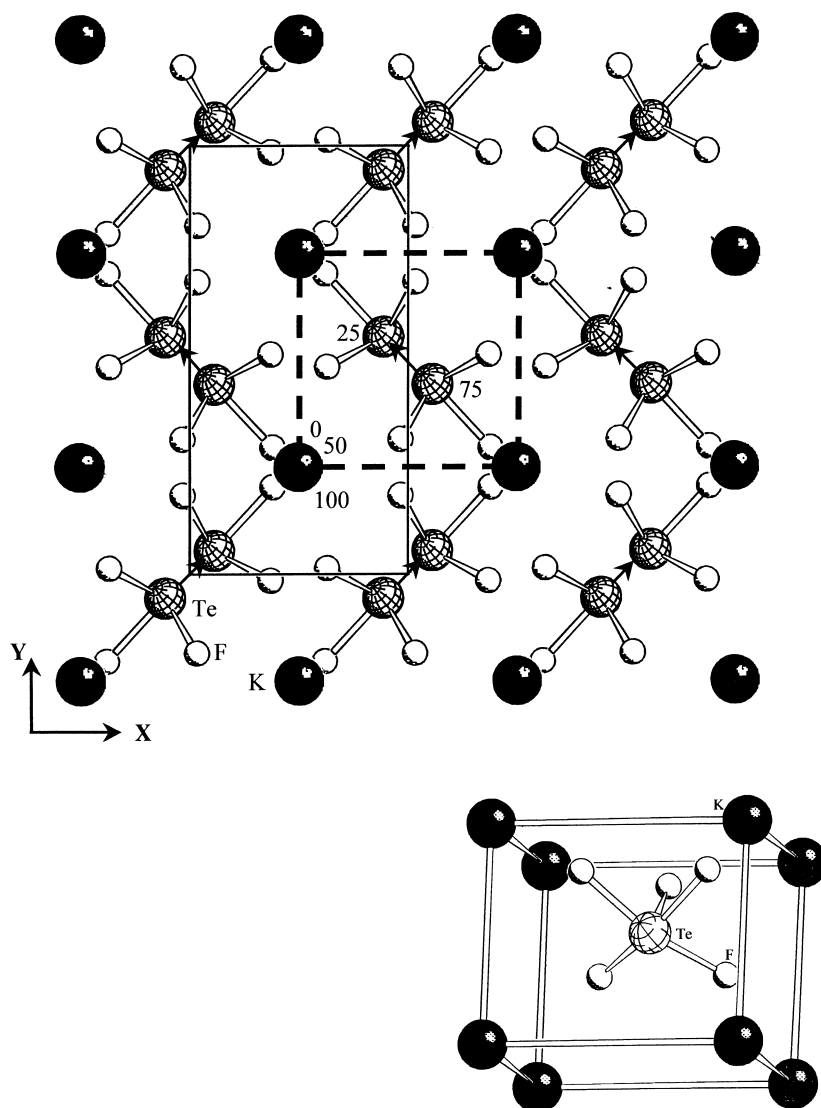


Fig. 2. Projection along [0 0 1] of the KTeF_5 crystal structure showing the K_8 cubic cavities. Arrows visualise the direction toward which point the lone pairs E (in the upper level).

In the BaTeF_6 structure [60], which is related to the tysonite (LaF_3) type, the Ba atoms and the TeF_5E units are distributed at the corners of a distorted fcc array. By sharing triangular faces the BaF_{11} polyhedra constitute infinite columns connected by rows of independent TeF_5E units.

2.2. $\text{Te}/\text{M} = 2$

This corresponds to the KTe_2F_9 and $\text{BaTe}_2\text{F}_{10}$ crystal structures.

The $\text{BaTe}_2\text{F}_{10}$ structure (space group $\text{C}2/c$, $a = 17.311 \text{ \AA}$, $b = 4.832 \text{ \AA}$, $c = 10.233 \text{ \AA}$, $\beta = 111.60^\circ$, $Z = 6$) [62] is very simple and corresponds to a slightly distorted cubic close packing of Ba atoms and independent TeF_5E units. As clearly shown in Fig. 3a, it can be described as the

regular and alternate stacking along [1 0 0] of 4^4 plane nets of Ba atoms and layers of TeF_5E polyhedra, according to the sequence $\dots\text{Ba}-\text{TeF}_5\text{E}-\text{TeF}_5\text{E}-\text{Ba}\dots$. In fact, it corresponds to the regular repetition along [1 0 0] of $\text{BaTe}_2\text{F}_{10}\text{E}_2$ three-layer-wide sheets, deriving from the KOsF_6 structure (rhombohedrally distorted CsCl type), each sheet being shifted $1/2(110)\text{CsCl}$ one from the other.

If we only take into account the shortest Te–F distances, the KTe_2F_9 crystal structure (space group P-1, $a = 4.757 \text{ \AA}$, $b = 9.333 \text{ \AA}$, $c = 9.467 \text{ \AA}$, $\alpha = 108.82^\circ$, $\beta = 95.79^\circ$, $\gamma = 96.11^\circ$, $Z = 2$) [52], corresponds to the same sequence of $4^2 \times 3^3$ plane nets of K atoms and of layers of TeF_4E and TeF_5E independent units (Fig. 3b). Such an analogy justifies the close geometrical relationships which exist between the two unit cells: $a(\text{BaTe}_2\text{F}_{10}) \approx 2c(\text{KTe}_2\text{F}_9)$, $b(\text{BaTe}_2\text{F}_{10}) \approx a(\text{KTe}_2\text{F}_9)$, $c(\text{BaTe}_2\text{F}_{10}) \approx b(\text{KTe}_2\text{F}_9)$ and

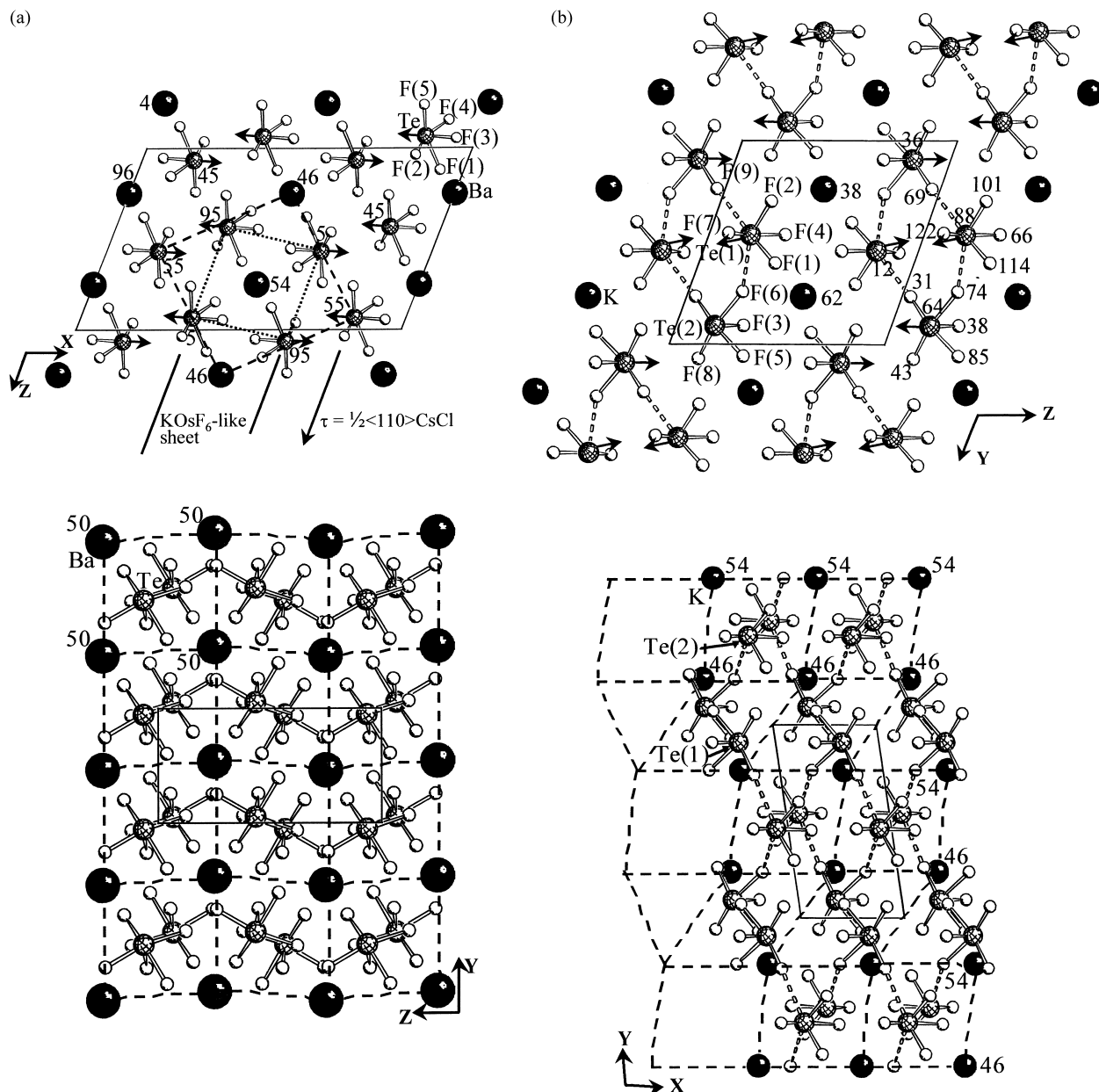


Fig. 3. Comparison of the crystal structures of (a) BaTe₂F₁₀; (b) KTe₂F₉. Arrows visualise the direction toward which point the lone pairs E.

$V(\text{BaTe}_2\text{F}_{10}) \approx V(\text{KTe}_2\text{F}_9)$. The doubling of a , and, therefore, of the unit cell volume in BaTe₂F₁₀ results from the periodic shift ($\tau = 1/2 \langle 110 \rangle \text{CsCl}$, see Fig. 3a) of the KOsf₆-like sheets, not observed in the KTe₂F₉ structure. Despite this analogy, the two structures are different. Whereas in the BaTe₂F₁₀ structure the TeF₅E units are independent, in the KTe₂F₉ one, the TeF₄E and TeF₃E units are connected one to another via F(6) and F(9) anions (see Fig. 3b) producing discrete Te₄F₁₈ units.

2.3. $Te/M = 3$

This case is limited to the RbTe₃F₁₃ crystal structure [50].

As shown in Fig. 4, in this structure the Rb atoms and independent TeF₅E and TeF₄E units are distributed at the corners of a face centred orthorhombic array. That it corresponds to the regular stacking along [0 0 1] of alternate square 4⁴ plane nets of Rb atoms and of layers of independent TeF₅E and TeF₄E units, according to the sequence $\dots \text{Rb}-\text{Te}(2)\text{F}_4\text{E}-\text{Te}(1)\text{F}_5\text{E}-\text{Te}(2)\text{F}_4\text{E}-\text{Rb} \dots$. If we take into account the two weak bonds (Te(2)F = 2.65 Å), the structure can, therefore, be described as a succession along [0 0 1] of 4⁴ square layers of Rb atoms and of two independent Te_{1.5}F_{6.5} sheets of corner-sharing Te(1)F₅E and Te(2)F₄E units, separated by the lone pairs E.

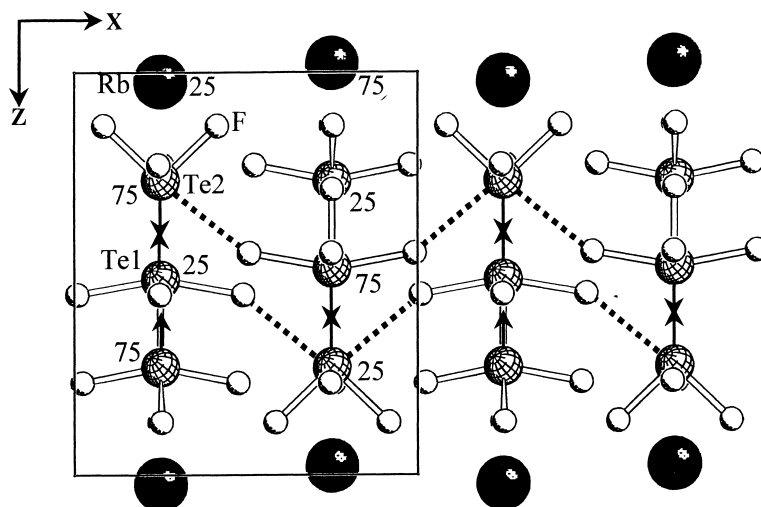


Fig. 4. Projection onto [0 1 0] of the $\text{RbTe}_3\text{F}_{13}$ crystal structure. Broken lines indicate the weak $\text{Te}(2)\text{-F}$ bonds, and arrows visualise the direction toward which point the lone pairs E.

3. Conclusions

In all the fluorinated compounds, as in all the corresponding complex oxides or oxidefluorides, the lone pairs E of $\text{Te}(\text{IV})$ atoms are stereochemically active and fill the empty spaces of the various networks: cavities, tunnels, inter-sheet spaces.

With increasing M/Te ratio, the fluorinated network changes from infinite $\text{Te}_{1.5}\text{F}_{6.5}$ layers of corner-sharing TeF_5E and TeF_4E polyhedra in $\text{RbTe}_3\text{F}_{13}$ to independent TeF_5E units in the MTeF_5 structures, via finite Te_4F_{18} groups of four basic units in KTe_2F_9 . Such an evolution clearly

emphasises the depolymerising role of the M atoms. A similar evolution should be observed in the corresponding fluorinated glasses. Moreover, it is worth pointing out that as soon as $M/\text{Te} > 1$, the two constituents KF and TeF_4 tend to segregate structurally in alternate sheets, the thickness of the TeF_x sheets increasing with the M/Te ratio. From this point of view, the determination of the $\text{CsTe}_4\text{F}_{17}$ crystal structure would be of great interest. It is also interesting to note the great analogies of the infinite chains of TeF_5E and TeF_4E polyhedra which, by crossing constitute the Te_3F_{13} sheets (Fig. 4), with the zigzag chains TeF_4 present in the TeF_4 structure [51] (Fig. 5).

Acknowledgements

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References

- [1] J.C. Champarnaud-Mesjard, B. Frit, B. Gaudreau, *Rev. Chim. Min.* 15 (1978) 328.
- [2] S. Kacim, J.C. Champarnaud-Mesjard, B. Frit, *Rev. Chim. Min.* 19 (1982) 199.
- [3] S. Turrell, S. Hafsi, P. Barbier, J.C. Champarnaud-Mesjard, *J. Mol. Struct.* 143 (1986) 17.
- [4] S. Turrell, M. Toussaint, G. Turrell, J.C. Champarnaud-Mesjard, G. Cuveiller, *J. Mol. Struct.* 143 (1986) 121.
- [5] J.C. Champarnaud-Mesjard, B. Frit, *J. Less Common Metals* 167 (1991) 319.
- [6] J.C. Champarnaud-Mesjard, B. Frit, *Eur. J. Solid State Inorg. Chem.* 29 (1992) 161.
- [7] J.P. Laval, D. Mercurio-Lavaud, B. Gaudreau, *Rev. Chim. Min.* 11 (1974) 742.
- [8] P. Joubert, B. Gaudreau, *Rev. Chim. Min.* 12 (1975) 289.
- [9] J.P. Laval, R. Papiernik, B. Frit, *Acta Cryst. B* 34 (1978) 1070.
- [10] R. Papiernik, B. Gaudreau, B. Frit, *J. Sol. State Chem.* 25 (1978) 143.

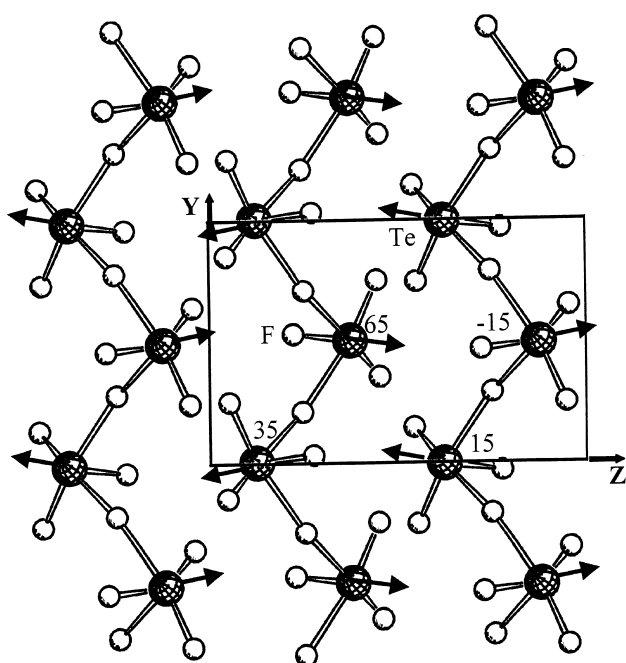


Fig. 5. Projection of the TeF_4 crystal structure down [1 0 0], showing the chains of corner-sharing TeF_5E polyhedra.

- [11] J.P. Laval, B. Frit, B. Gaudreau, *Rev. Chim. Min.* 16 (1979) 509.
- [12] J.P. Laval, B. Frit, *Mater. Res. Bull.* 15 (1980) 45.
- [13] J.P. Laval, B. Frit, *Acta Cryst. B* 36 (1980) 1769.
- [14] B. Frit, J.P. Laval, *J. Solid State Chem.* 39 (1981) 85.
- [15] C. Depierreux, R.M. Awadallah, J.P. Laval, B. Frit, *Rev. Chim. Min.* 20 (1983) 96.
- [16] R. Papiernik, D. Mercurio, J.P. Laval, B. Frit, *Stud. Inorg. Chem.* 3 (1983) 652.
- [17] J.P. Laval, B. Frit, J. Lucas, *J. Solid State Chem.* 72 (1988) 181.
- [18] J.P. Laval, A. Abaouz, *J. Solid State Chem.* 96 (1992) 324.
- [19] J.P. Laval, A. Abaouz, *J. Solid State Chem.* 100 (1992) 90.
- [20] J.P. Gervais, L. Fournes, J. Grannec, P. Gravereau, J.P. Laval, P. Hagemuller, *Mater. Res. Bull.* 29 (1994) 405.
- [21] A. Taoudi, A. Mikou, J.P. Laval, *Eur. J. Solid State Inorg. Chem.* 33 (1996) 687.
- [22] A. Taoudi, A. Mikou, J.P. Laval, *Eur. J. Solid State Chem.* 33 (1996) 1051.
- [23] A. Abaouz, A. Taoudi, J.P. Laval, *J. Solid State Chem.* 130 (1997) 277.
- [24] A. Le Bail, J.P. Laval, *Eur. J. Solid State Inorg. Chem.* 35 (1998) 357.
- [25] J.P. Laval, B. Frit, J. Lucas, *Mater. Sc. Forum* 6 (1985) 457.
- [26] B. Boulard, A. Le Bail, J.P. Laval, C. Jacobini, *J. Mol. Struct.* 143 (1986) 121.
- [27] C.C. Phifer, C.A. Angell, J.P. Laval, J. Lucas, *J. Non Cryst. Sol.* 94 (1987) 315.
- [28] A. Mikou, J.P. Laval, B. Frit, *Rev. Chim. Min.* 24 (1987) 315.
- [29] R. Papiernik, D. Mercurio, B. Frit, *Acta Cryst. B* 38 (1982) 2347.
- [30] J.P. Laval, B. Frit, *J. Solid State Chem.* 49 (1983) 237.
- [31] J.P. Laval, C. Depierreux, B. Frit, G. Roullet, *J. Solid State Chem.* 54 (1984) 260.
- [32] J.P. Laval, A. Mikou, B. Frit, J. Pannetier, G. Roullet, in: *Proceedings of the 6th Riso International Symposium, 1985*, p. 201.
- [33] J.P. Laval, A. Mikou, B. Frit, J. Pannetier, *J. Solid State Chem.* 61 (1986) 5.
- [34] J.P. Laval, A. Mikou, B. Frit, G. Roullet, J. Pannetier, *Rev. Chim. Min.* 24 (1987) 165.
- [35] J.P. Laval, A. Mikou, B. Frit, G. Roullet, *Sol. St. Ion.* 28 (1988) 1300.
- [36] J.P. Laval, A. Abaouz, B. Frit, G. Roullet, W.T.A. Harrison, *Eur. J. Solid State Inorg. Chem.* 25 (1988) 425.
- [37] J.P. Laval, A. Abaouz, B. Frit, *J. Solid State Chem.* 81 (1989) 271.
- [38] J.P. Laval, A. Abaouz, B. Frit, J. Pannetier, *Eur. J. Solid State Inorg. Chem.* 26 (1989) 23.
- [39] T. Vogt, E. Schweda, J.P. Laval, B. Frit, *J. Solid State Chem.* 83 (1989) 324.
- [40] J.P. Laval, A. Abaouz, B. Frit, A. Le Bail, *Eur. J. Solid State Inorg. Chem.* 27 (1990) 545.
- [41] J.P. Laval, A. Abaouz, B. Frit, A. Le Bail, *J. Solid State Chem.* 85 (1990) 133.
- [42] M. El Omari, J.M. Reau, J. Senegas, J.P. Laval, B. Frit, *J. Fluorine Chem.* 58 (1992) 17.
- [43] R. Papiernik, B. Frit, *Acta Cryst. B* 42 (1986) 342.
- [44] B. Frit, J.P. Laval, J. Strahle, *Aust. J. Chem.* 49 (1996) 883.
- [45] H. Hofmann, E. Schweda, J. Strahle, J.P. Laval, B. Frit, M.A. Estermann, *J. Solid State Chem.* 114 (1995) 73.
- [46] J.P. Laval, A. Taoudi, A. Abaouz, B. Frit, *J. Solid State Chem.* 119 (1995) 125.
- [47] A. Ider, B. Frit, J.P. Laval, J. Carre, P. Claudy, J.M. Letoffe, *Thermochem. Acta* 258 (1995) 117.
- [48] L. Guillet, A. Ider, J.P. Laval, B. Frit, *J. Fluorine Chem.* 93 (1999) 33.
- [49] A. Ider, J.P. Laval, B. Frit, J. Carre, J.P. Bastide, *J. Solid State Chem.* 123 (1996) 68.
- [50] L. Guillet, Thesis, University of Limoges, 1999.
- [51] A.J. Edwards, F.I. Hewaidy, *J. Chem. Soc. A* 68 (12) (1968) 2977.
- [52] L. Guillet, J.P. Laval, B. Frit, *J. Fluorine Chem.* 85 (1997) 177.
- [53] A. Du Bois, W. Abriel, *Mater. Res. Bull.* 24 (1989) 633.
- [54] S.H. Mastin, R.R. Ryan, L.B. Asprey, *Inorg. Chem.* 9 (1969) 2100.
- [55] L. Guillet, J.P. Laval, B. Frit, *J. Fluorine Chem.* 103 (2000) 13.
- [56] J.C. Jumas, M. Maurin, E. Phillipot, *J. Fluorine Chem.* 10 (1977) 219.
- [57] Y.E. Gorbunova, S.A. Linde, V.I. Pakhomov, Yu.V. Kokounov, M.P. Gustyakova, Yu.A. Buslaev, *Koord. Chem.* 12 (1986) 703.
- [58] W. Abriel, *Mater. Res. Bull.* 24 (1989) 1515.
- [59] A. Ider, J.P. Laval, B. Frit, J. Carré, J.P. Bastide, *J. Fluorine Chem.* 78 (1996) 15.
- [60] A. Ider, M. El Farissi, J.P. Laval, *J. Fluorine Chem.* 99 (1999) 161.
- [61] L. Guillet, J.P. Laval, B. Frit, *Acta Cryst. B*, in press.
- [62] J.P. Laval, B. Frit, A. Ider, M. El Farissi, *J. Fluorine Chem.* 77 (1996) 15.