Te3O5F2: a new metastable tellurium IV oxyfluoride with an acentric complex structure

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$Te_3O_5F_2$: a new metastable tellurium IV oxyfluoride with an acentric complex structure

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Abstract

The crystal structure of a new metastable tellurium (IV) oxyfluoride $Te_3O_5F_2$ [non-centrosymmetric $P2_1$ space group] is unusually complex with 15 different Te polyhedra. It is built of giant cylindrical columns of oxide units connected via weak Te-F bonds. A strict O/F order is evidenced and a structural comparison with $Sb_3O_2F_5$ shows that these two phases derive, by a different mechanism, from the anion-excess fluorite superstructure type. Surprisingly, in these two structures is observed a full gradation of various polyhedra of tellurium (IV) or antimony (III) with the oxygen atom ensuring a strong framework at the centre of these structures (cylinders for Te phase and layers for Sb one), and more and more F anions moved away at the periphery of these strong units, connecting these units *via* weak Te-F or Sb-F bonds. This well illustrates the different roles played by oxygen and fluorine atoms in the oxyfluorides of cations presenting an electronic lone pair E ($5s^2$ in the case of Te^{4+} cation), in relation with the non-linear properties of these phases.

Keywords: tellurium IV oxyfluoride, crystal structure, anionic ordering, electronic lone pair.

1. Introduction:

The investigation by thermal analysis and X-ray diffraction techniques within the TeO_2–TeF_4 system [1] had allowed to establish the phase diagram of this system, to isolate an extended glass domain (0.25-0.83 mole% TeF_4) with a vitreous transition temperature T_g varying from about 180°C to -20°C and to characterize two crystalline Te^{IV} oxidefluorides with the respective formulae $TeOF_2$ [2] and $Te_2O_3F_2$ [3] with original structure types. $Te_2O_3F_2$ crystallizes with the triclinic symmetry (P-1 space group) and $TeOF_2$ with the monoclinic $P2_1$ acentric space group. The bond valence calculations show a perfect O/F order and a stereochemical activity of the lone pair E of the Te^{4+} cations is in both structures. In $Te_2O_3F_2$ $Te_2O_4F_2E$, bipolyhedral units constitute by sharing O corners, independent twisted sheets, similar to those described in β-TeO_2. In $TeOF_2$, quasi-independent helical chains of TeO_2F_3E polyhedra share O corners. All the F atoms are non-bridging and orientated, together with the E lone pairs, toward the interlayer space. A structural relationship of $Te_2O_3F_2$ with the β-TeO_2 structure and of $TeOF_2$ with the α-TeO_2 structure has been established.

The present paper deals with the synthesis and the structural determination on single crystal of a third metastable oxyfluoride $Te_3O_5F_2$, unknown until now and closer to Te dioxide, this last oxide being the basis of many phases of great interest for their non-linear optical properties. Oxyhalides of cations presenting a stereoactive electronic lone pair are also the subject of a great interest in the same field.

The acentric structure of $Te_3O_5F_2$ is unusually complex and has unique features, related to a long range O/F order. It is compared to other complex phases comprising a cation with an electronic lone pair E.

2. Experimental

A small number of single crystals in shape of small cleaved rods were obtained randomly as a by-product in the pseudo-binary InF_3-TeO_2 for compositions close to InF_3-$3TeO_2$ heated about 400 °C in a Pt sealed tube and water-quenched. InF_3 (Aldrich, >99.9% purity) and TeO_2 (prepared in the laboratory by calcination of orthotelluric acid H_6TeO_6 in a Pt container at 550°C during 1 day) were mixed in a glove box under dry N_2 atmosphere. The analysis of these single crystals by EDX shows that, in fact, they don't contain indium and are likely a tellurium oxyfluoride, hypothesis confirmed by the structural study determining without ambiguity a composition $Te_3O_5F_2$. Attempts to synthesize this phase by solid state reaction between $Te_2O_3F_2$ and TeO_2 in Au or Pt sealed tubes about 350-400°C fail likely because of the thermal instability and the high vapor pressure of the Te^{IV} fluoride and oxyfluorides in this temperature range (see the TeO_2–TeF_4 diagram [1]). Synthesis by dissolution of a Te salt in HF and recrystallisation was also unsuccessful. It is likely that these single crystals result from a chemical transport process with InF_3 acting as a fluorinating agent on initial TeO_2. That explains the non-reproducibility of the reaction and the formation of only few crystals inside the Pt-sealed tubes. This new phase is likely metastable and exists in a very narrow thermal domain.

The diffraction pattern is recorded on a 4-circle P4-Siemens diffractometer equipped with a graphite monochromator and a scintillation counter using the *XSCANS* program [4]. Absorption correction by a psi-scan method uses the program *XEMP* [5]. The structure is solved by direct methods using *SHELXS-86* and refined with *SHELXL-2018/3* [6], using the *WINGX* integrator *V2018-3* [7]. The pictures are drawn using *DIAMOND* software [8].

3. Results and discussion

Although the quality of the single crystals was rather weak, we have tried to determine, as well as possible, the structure of this phase. However, if all the cationic and anionic positions and the isotropic thermal displacements are determined with enough accuracy, the anisotropy of the thermal displacements is well refined only for the cationic sites but remains slightly non-definite/negative for several anions. The examination of the diffraction spots shows that there is no clear twinning of the crystals but rather a beginning of decomposition of this metastable phase during the cooling process, in spite of a water quenching of the sealed tubes. That generates some diffuse scattering around many diffraction reflections, likely responsible of the difficulty to refine the anisotropic thermal vibration factors of the anions. However, the refined structure is perfectly logical, although very complex; all the interatomic distances are normal and the R1 factor stabilizes at 6.29% in the acentric space group $P2_1$, selected without any doubt with the $|E^2-1|$ criterion = 0.745(18) (0.968 for centric, 0.736 for ideal acentric symmetry). After complete refinement, the absolute structure has to be inverted, the fractional contribution of the inverted component of a "racemic twin" (Flack parameter) being 1.09 (17) [9].

The crystal data and structural refinement data are gathered in table 1. The refined atomic coordinates in table S1, the main bond lengths in table S2 and the anisotropic thermal factors of Te in table S3 are reported as supplementary material in annexes. To confirm the validity of the refinement and determine the O/F anionic ordering, the bond valences are calculated with the program *VALIST* [10] using the Brown and Altermatt method [11, 12] and are gathered in Table 2.

Considering the difficulty of synthesis of this phase, the interest of its very original crystal structure and its potential physical properties, the main features of the crystal structure of $Te_3O_5F_2$ are described in the present paper.

Table 1: Crystal data and structure refinement for $Te_3O_5F_2$.

Elementary formula	$Te_3O_5F_2$
Formula weight	500.80 $g.mol^{-1}$
Temperature	293(2) K
Wavelength	0.7107 Å
Crystal system, space group	Monoclinic, $P2_1$
Unit cell dimensions	a = 16.547(4) Å
	b = 6.360(2) Å β = 119.04(2)°
	c = 16.938(4) Å
Volume	1558.4(8) $Å^3$
Z, Calculated density	10, 5.336 g/cm^3
Absorption coefficient	13.953 mm^{-1}
F(000)	2140
Crystal size	0.08 x 0.05 x 0.04 mm
Theta range for data collection	2.40 to 30.00°
Reflections collected / unique	5203 / 5171 [R(int) = 0.092]
Refinement method	Full-matrix least-squares on F^2
Completeness to theta = 25.242°	58.1 %
Data / restraints / parameters	5171 / 1 / 278
Goodness-of-fit on F^2	1.020
Final R indices [I>2sigma(I)]	R1 = 0.0629, wR2 = 0.1245
R indices (all data)	R1 = 0.1103, wR2 = 0.1449
Extinction coefficient	0.00028(6)
Largest diff. peak and hole	1.64 and -1.65 $e.Å^{-3}$
Estimated min. and max. transmission	0.464 and 0.579

3.1 Description of the structure

The structure of $Te_3O_5F_2$ is unusually complex for a structure containing a single type of cation with a single valence. Indeed, the acentric unit cell, of space group $P2_1$ and volume V = 1558.4 $Å^3$, includes 15 independent cationic sites, 25 O sites and 10 F sites.

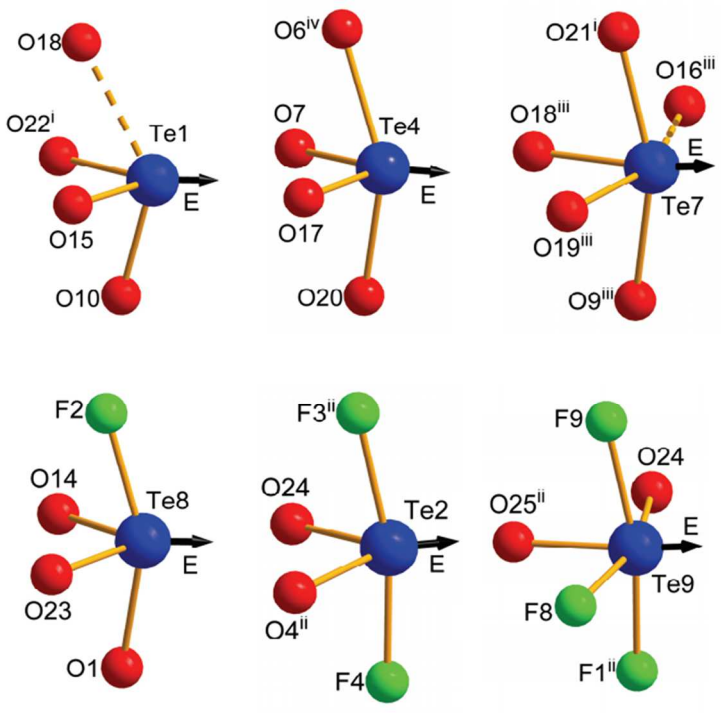
Table 2: Bond valences of cations and anions and Te IV polyhedra in $Te_3O_5F_2$., (calculated using Brown and Altermatt approach with R = 1.955 Å, B = 0.44 for Te - O bonds, R = 1.87 Å and B = 0.37 for Te - F bonds [11, 12]).The Te polyhedra incorporate weak Te-O and Te-F bonds <3.26 Å.

Te1	**Te2**	**Te3**	**Te4**	**Te5**	**Te6**	**Te7**	**Te8**	**Te9**	**Te10**
3.86	4.03	3,98	3.99	3.93	4.08	4.08	3.92	4.05	4.00
$TeO_{3+3}F$	TeO_2F_{2+2}	TeO_{4+3}	$TeO_{4+2}F_{0+1}$	$TeO_{3+3}F_{0+2}$	TeO_{4+4}	TeO_{4+2}	$TeO_{3+3}F_{1+1}$	TeO_2F_{3+1}	$TeO_{3+3}F_{0+1}$
Te11	**Te12**	**Te13**	**Te14**	**Te15**	**O1**	**O2**	**O3**	**O4**	**O5**

3.91	4.02	3.88	3.77	4.24	2.23	2.26	2.01	2.11	1.95
TeO_2F_{3+2}	$TeO_{3+1}F_{1+2}$	$TeO_{3+3}F_{0+1}$	TeO_4F_{0+3}	$TeO_{4+3}F_{0+1}$					
O6	**O7**	**O8**	**O9**	**O10**	**O11**	**O12**	**O13**	**O14**	**O15**
2.06	2.16	1.92	2.04	2.21	2.05	2.26	2.14	1.99	2.13
O16	**O17**	**O18**	**O19**	**O20**	**O21**	**O22**	**O23**	**O24**	**O25**
1.74	1.97	1.96	2.00	1.98	1.91	2.31	1.94	2.19	2.18
F1	**F2**	**F3**	**F4**	**F5**	**F6**	**F7**	**F8**	**F9**	**F10**
0.89	0.73	0.82	0.77	0,79	0,79	0,91	0,89	0,77	0,71

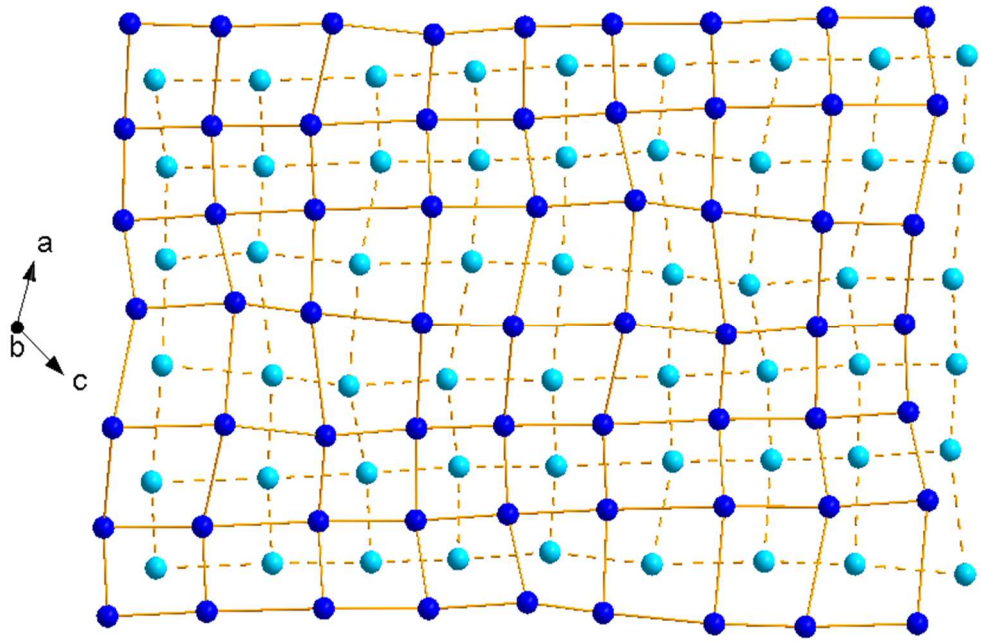
By limiting the distances Te - O and Te - F to 2.3 Å, classical polyhedra TeO_3, TeO_4, TeO_3F, TeO_2F_2 and TeO_2F_3 are described, as some examples shown on Fig. 1, but the bond valences calculated on this basis are often far from the real charge of the cations and anions. A second calculation, performed in adding the Te - O and Te - F weaker bonds between 2.2 and 3.26 Å, gives much better calculated bond valences and confirms that all the Te cations have a +4 charge and true coordination numbers ranging from 6 and 8, as reported in Table 2. The bond valences, calculated for the anions and reported in the same Table, show a perfect O / F anionic order in this structure and confirm the reasonable accuracy of the refined anionic positions, in spite of the limited quality of the single crystal.

Fig. 1: Main classical polyhedra of Te^{4+} (with Te - O and Te - F <2.45 Å). The electronic E lone pair of Te^{4+} is represented by an arrow.

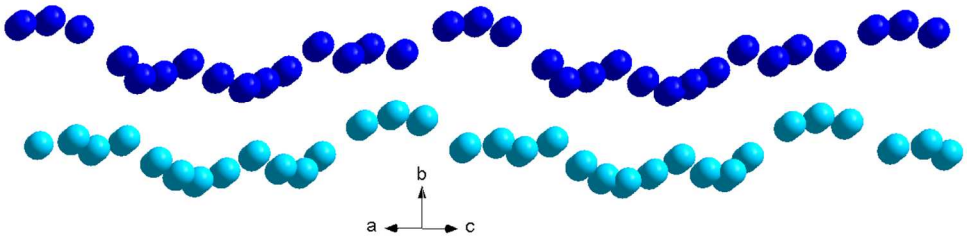


The network of tellurium atoms derives from a face-centered cubic lattice (*fcc*) rather distorted and quite wavy (Figs. 2a and b).

Fig. 2: a: projection along [010] showing the cationic very distorted *fcc* fluorite network of $Te_3O_5F_2$. dark blue = Te at $y_{av.}$~0.20 (0.05-0.41); light blue = Te at $y_{av.}$~ 0.70 (0.55-0.91). **b:** view along [101] axis, showing the wavy plane nets of Te cations: the most distorted parts correspond to the cations mainly connected to F anions and located at the boundaries between adjacent cylindrical columns.



a



b

This network includes, in its most regular part, very short Te - Te distances when the cations are connected *via* O - O edges, for example Te12 - Te4 = 3.172 Å (as in the Te_2O_6 units of α-TeO_2) or Te10 - Te8 = 3.379Å. When the connections operate through O - O common vertices, these distances Te - Te are logically longer and range between about 3.6 and 4 Å. Finally, much longer Te - Te distances (4.4 to 5.5 Å) correspond to cations only connected *via* very weak Te - F bonds ($2.64 \leq$ Te - F ≤ 3.3 Å).

It can therefore be distinguished a "strong" network corresponding to quasi-cylindrical columns as shown in the projection of fig. 3, with their central part consisting only of tellurium atoms and oxygen atoms and intercationic connections mainly ensured *via* O –O edges. Each column includes a group of 15 tellurium atoms indefinitely repeated along the [0 1 0] axis of the column.

Fig. 3: Projection onto the (010) plane of a right non-circular cylindrical column of Te IV cations only interconnected *via* O anions, forming a strong network. All the F peripheral anions are connected *via* weak Te-F bonds with the adjacent cylindrical units.

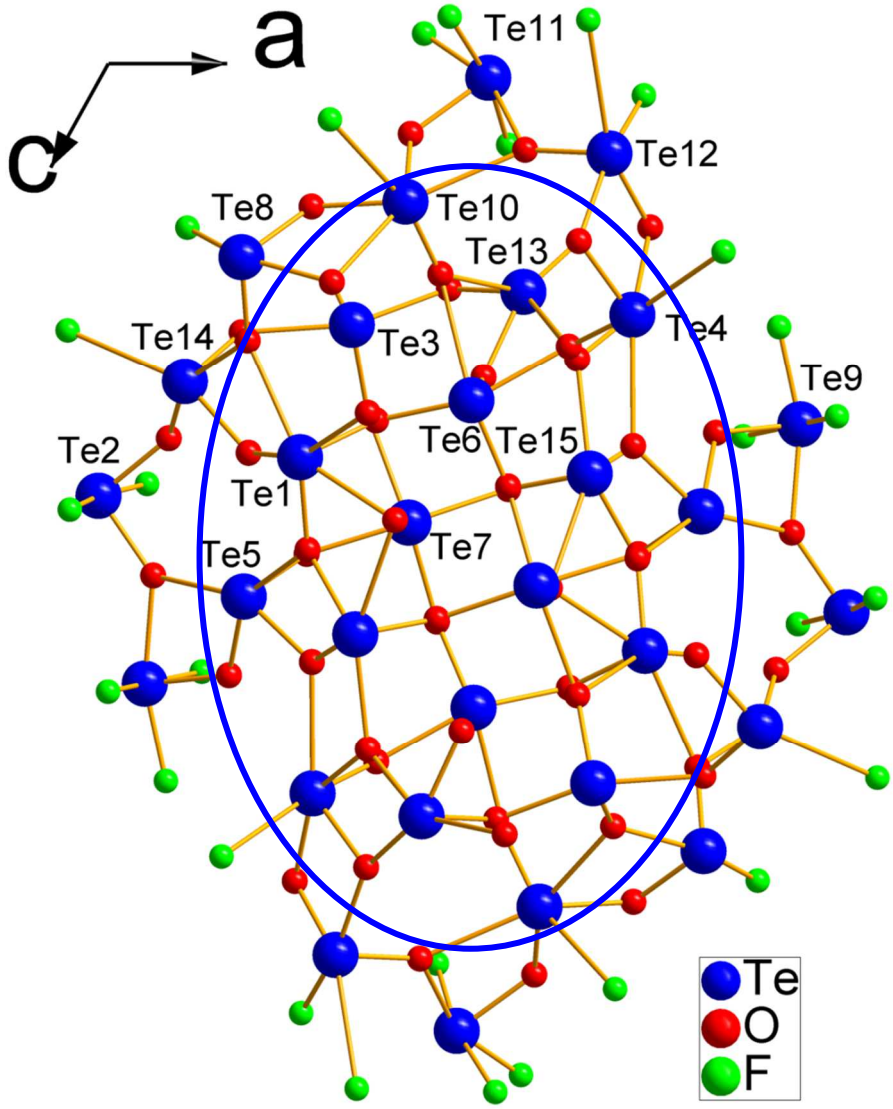
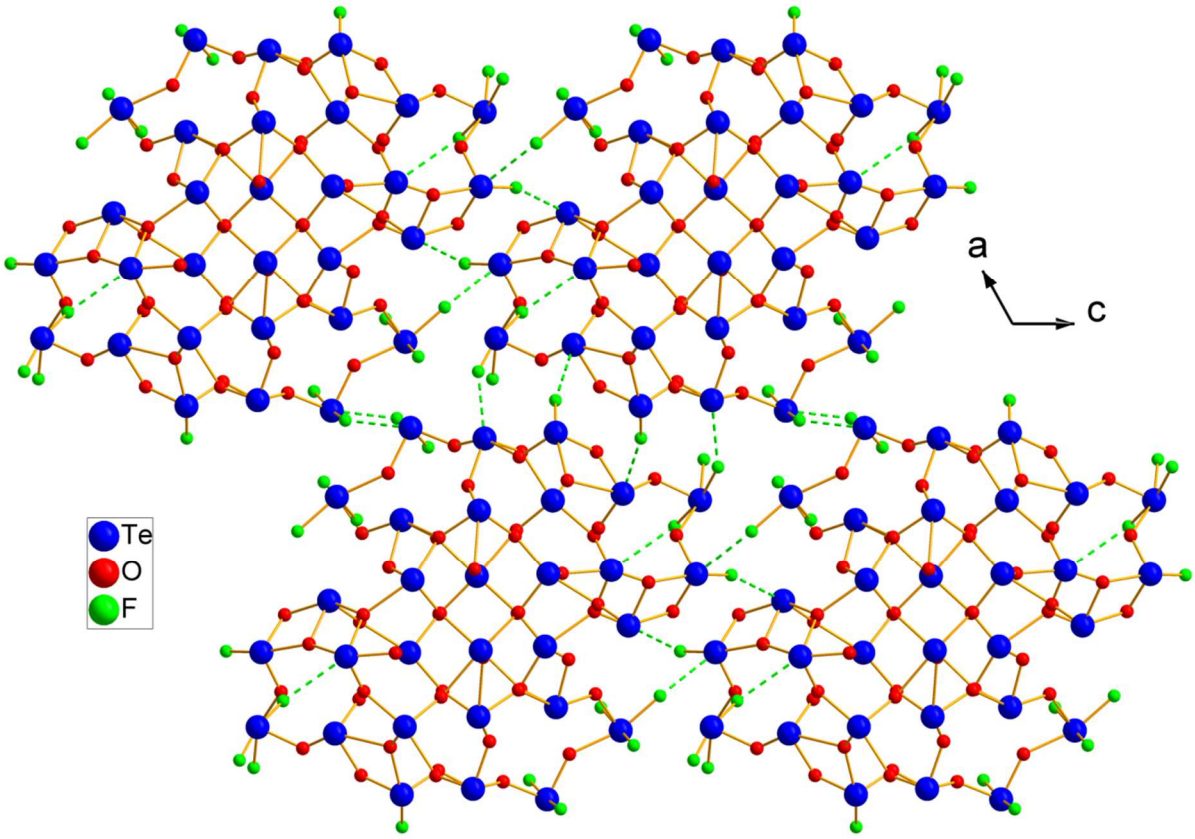


Fig. 4: Projection onto the (010) plane of the pseudo-hexagonal distribution of the cylindrical strong units of fig. 3, showing their interconnection *via* weak Te - F bonds (2.64 Å ≤ Te - F ≤ 2.9 Å) represented by dotted lines.


a
c
Te
O
F

The peripheral part of the columns, made up of oxyfluorinated polyhedra, is much more relaxed: all F^- anions, located in "quasi-terminal" positions, that is to say linked only to one Te^{4+} atom by a very short bond (~1.9 Å), are repelled to the periphery, in contact with the "intercolumnar" space. These “terminal” F^- anions also ensure, by very weak Te - F bonds the cohesion with the contiguous cylindrical columns. The Figure 4 represents by dotted lines the weak bonds Te - F <2.9 Å which mainly interconnect the strong cylindrical columns. Another series of very weak connections (3 Å <Te - F <3.3 Å) operates secondarily. The structure of each cylindrical column can therefore be considered almost independently of the others and their packing is almost hexagonal, in agreement with the monoclinic unit cell which derives from hexagonal symmetry with $a \sim c = a_{hex}$, $b = c_{hex}$ and $\beta = \gamma_{hex} \sim 119°$.

However, examination of the fig. 2a also shows that the *fcc* cationic network is not completely broken at the level of the intercolumnar space and that its continuity is ensured between adjacent columns.

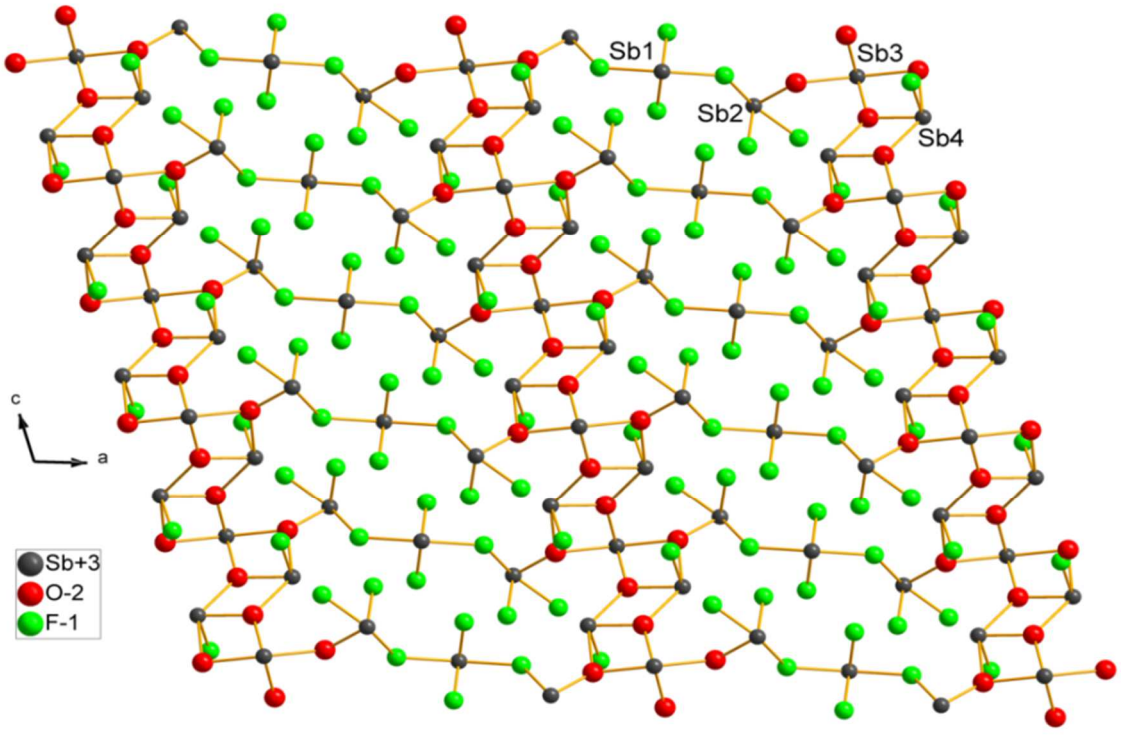
The segregation of the anions O and F with two quite distinct roles constitutes the main feature of the O / F order in this oxyfluoride and partially explains the complexity of this structural type. It can also be noted that a large part of the anions O is located in the tetrahedral sites of this network, site occupied by the anions in the fluorite structure. This last point will be developed in a next paragraph.

3.2 Comparison with other complex phases comprising a cation with an electronic lone pair E:

Few oxyfluorinated, fluorinated or oxide phases based on a single cation as complex as $Te_3O_5F_2$ have been described. The main one that can be compared is $Sb_3O_2F_5$ [13-15], isoformulary with an inversion of the relative proportions of oxygen and fluorine.

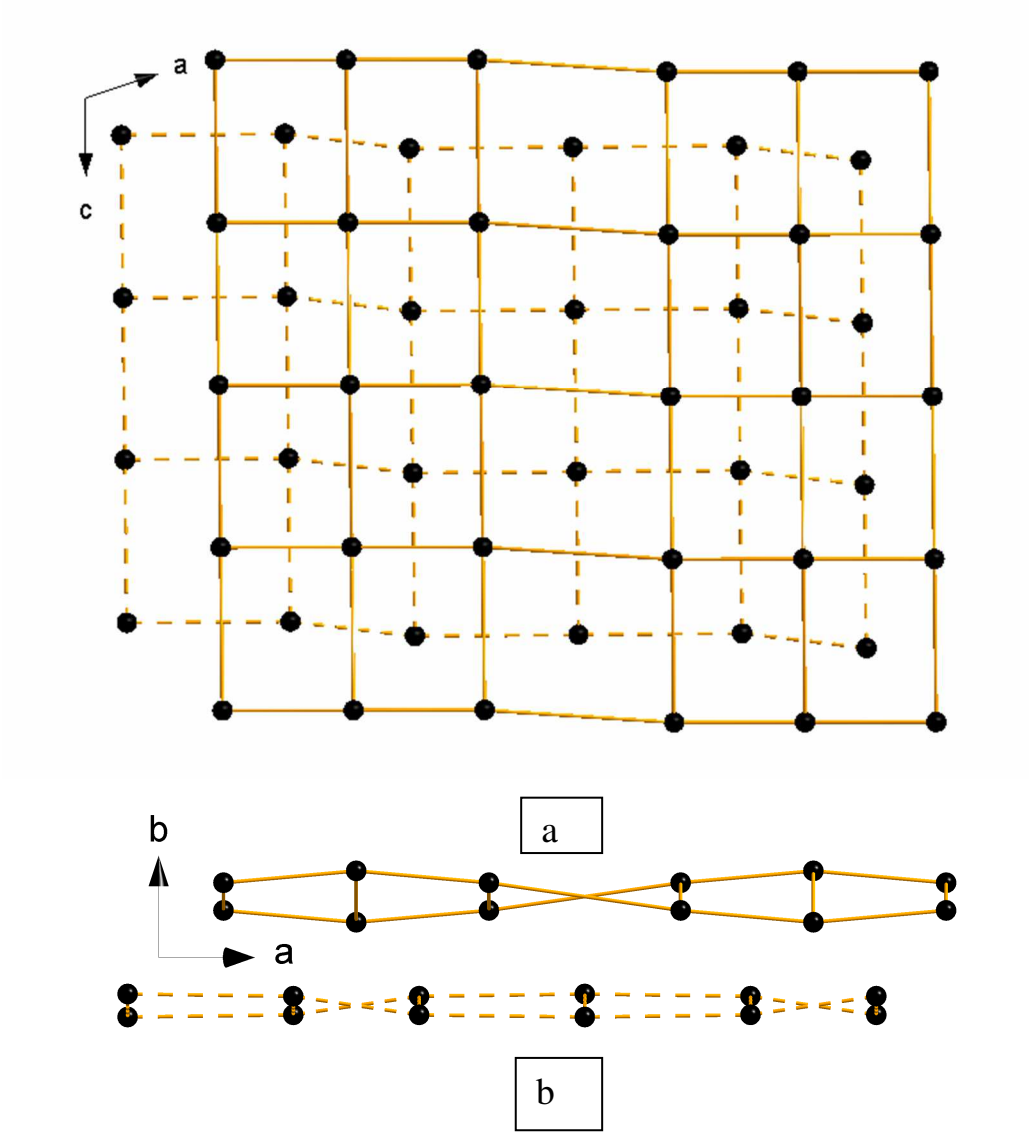
The $Sb_3O_2F_5$ phase has only four Sb, five F and two O sites. Unlike $Te_3O_5F_2$, $Sb_3O_2F_5$ is centrosymmetric with space group P 2 / c and a much lower cell volume (679 $Å^3$ against 1558 $Å^3$ for $Te_3O_5F_2$). In this structure, the anionic order is also established in a very particular way: it can be observed along the direction [1 0 0] a successive transition from purely fluorinated layers, composed of SbF_4 polyhedra, to purely oxygenated layers composed of SbO_4 polyhedra, *via* layers of mixed $SbOF_3$ and SbO_3F polyhedra (Fig. 5). As also in $Te_3O_5F_2$ (Table 2), Ali and Johnsson [14] show by BVS calculations for the Sb oxyfluorides, a slight hypervalence in a strong Sb and O framework and a slight hypovalence in the Sb - F framework.

Fig. 5: Projection onto (010) plane of the $Sb_3O_2F_5$ structure.



As in $Te_3O_5F_2$, the cationic framework in $Sb_3O_2F_5$ (Fig. 6) derives from a distorted and wavy *fcc* lattice, comprising shorter Sb – Sb distances in the most oxygenated layers (Sb - Sb = 3.35 and 3.95 Å) and looser connections in the purely fluorinated layers (Sb - Sb = 3.68; 4.05; 4.22 and 4.64 Å).

Fig. 6: a: Sb double cationic layer in $Sb_3O_2F_5$, homologous of Figs. 2 a and b of $Te_3O_5F_2$. **b**: view along (011) plane of the Sb wavy cationic layers of $Sb_3O_2F_5$.



It can be observed in the two structures a modulation of the O / F order between two extreme areas, fully oxygenated and fully or partially fluorinated, preserving in both cases the distorted *fcc* cationic network. The main difference consists in the formation in

$Te_3O_5F_2$ of "oxide" zones of cylindrical shape, separated by fluorinated side walls and in $Sb_3O_2F_5$ of successive "oxide" and "fluoride" layers and therefore of an O / F order in two-dimensional sheets.

Most of the oxyfluorides of cations presenting a stereoactive electronic lone pair E also have a strict anionic order: in the two varieties of SbOF, L [16] and M [17], the SbO_3F units constitute, by pooling of O-O edges, respectively chains and folded layers. The two types of anions play a different role: the oxygen atoms provide the strong connections within layers or chains and the fluorine atoms are essentially quasi-terminal anions, nevertheless ensuring weak inter-chain connections (Sb-F = 2.8 to 3.2 Å) as also observed in $TeOF_2$ [2].

A strict anionic order also exists in BiOF [18], Sn_2OF_2 [19] and Sn_4OF_6 [20]. Oxyfluorides having a molecular character such as $SeOF_2$ [21] and XeO_2F_2 [22] also exhibit a strict O / F order with M - O bonds significantly stronger than M – F bonds. Brown [23], studying the characteristics of the MX_3E, MX_4E and MX_5E polyhedra in oxides and mixed oxyfluorides of Sn II, Sb III, Te IV, I V and Xe VI, already distinguished three kinds of bonds, resp. strong, intermediate and weak, e. g. in TeF_4. He noticed that oxygen preferably occupies, e. g. in IOF_4^-, the apical position strongly linked to I^{5+} and observed in $KXeO_3F$ [24] the presence of three Xe-O bonds forming a strong unit XeO_3, the F anions providing, through moderately weak bonds, a bridging between these strong units to form an infinite polyion: - [F - XeO_3 - F' - XeO_3 - F] -. In summary, in the oxyfluorides of elements with an unengaged electronic pair, there is usually a strict O / F order, especially when these anions are likely to play a different structural role, depending on their charge. This is the case in the major part of these phases which include, through the formation of strong units (layers or chains) resulting from the spatial distribution of the lone pairs E, a well-structured strong part and a looser peripheral part. Quite naturally, the

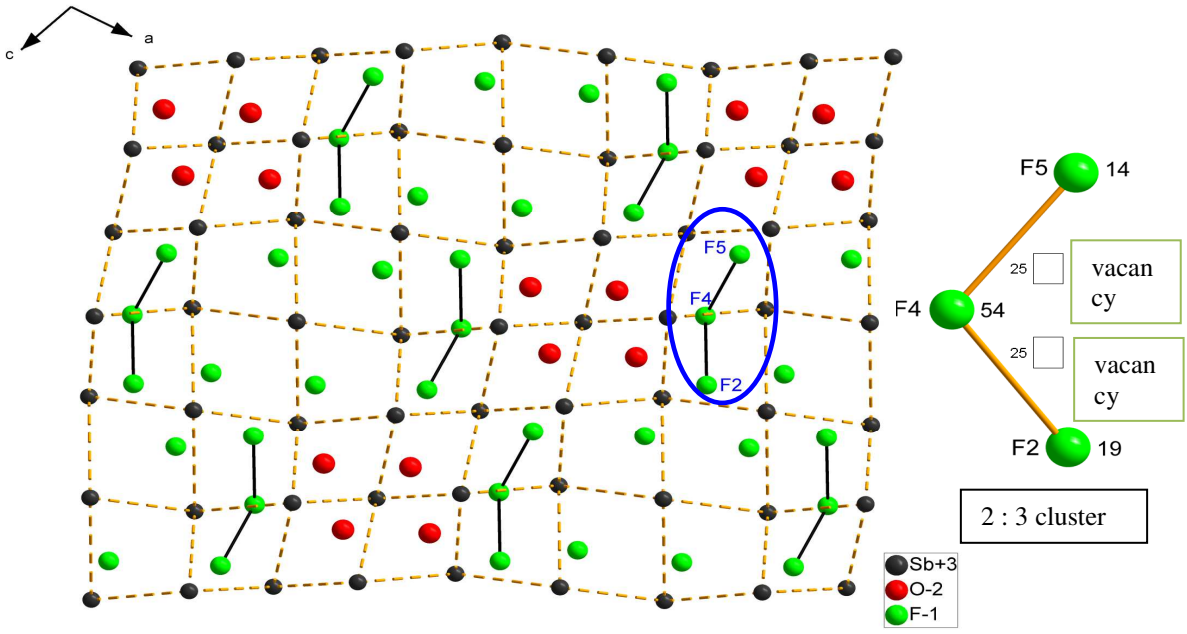
oxygen atoms provide the strong central bonds and fluorine atoms the weaker peripheral bonds.

3.3 Comparison with fluorite structure:

If one consider that fluorite structure has a cationic *fcc* network, $Sb_3O_2F_5$ and $Te_3O_5F_2$ are also in this case. A second characteristic of the cubic Fm-3m fluorite structure CaF_2 or UO_2 is the occupancy by the F or O anions of the anionic site (¼, ¼, ¼) with each anion located at the centre of a tetrahedron of cations at (0, 0, 0). The two lattices of $Te_3O_5F_2$ and $Sb_3O_2F_5$ comprise a parameter *b* homologous to that of fluorite (*b* = 6.360 and 5.927 Å respectively against 5.462 Å for CaF_2) with cations forming a distorted *fcc*-type network developed in the (0 1 0) plane of the two structures. The Te^{4+} and Sb^{3+} cations are located in parallel layers homologous to the fluorite cationic layers with *y* = ½ and 0 and a large part of the anions is located inside the tetrahedron formed by four adjacent cations at y ~ ¼ and ¾. However, due to the stereochemical activity of the electronic lone pair E of these cations, the anions systematically move away from the centre of these tetrahedra and the coordination [8] of these cations in the ideal fluorite structure is reduced to [4] or [6] strong or intermediate Te(Sb) – O and Te(Sb) – F bonds but completed to [6] [7] or [8] by incorporating weak Te(Sb) – O and Te(Sb) – F bonds.

It can be noticed in the structure of $Sb_3O_2F_5$ (Fig. 7) the presence of groups of four O^{2-} and four F^- anions in normal anionic site (sometimes very shifted) and three anions F5, F2 and F4 respectively occupying the inner of two contiguous Sb tetrahedra. This last arrangement is reminiscent of an anion-excess fluorite-type structure.

Fig. 7: Projection onto the (010) plane of the structure of $Sb_3O_2F_5$ showing its relationship with anion-excess fluorite structure family by formation of 2 : 3 anionic clusters (2 vacancies and 3 F_i interstitials, in Willis notation).



This generic type of structure actually covers several different mechanisms of accommodation of the anionic excess, transforming an ideal MX_2 fluorite to an anion-excess phase, as e.g. other $MX_{2.33}$ phases Ca_2LnF_7 [25], Pb_2InF_7, [26], Sr_2RhF_7 [27], U_3O_7 [28].

In $Sb_3O_2F_5$, it can be proposed a mechanism such as two anions in normal site are replaced by three interstitial anions according to the following diagram:

12 SbOF $\Longrightarrow$ $Sb_{12}(O_8 \square_4)(F_8 \square_4) Fi_{12}$ [Fi = F5, F2, F4] or 12 MX_2 $\Longrightarrow$ 12 $MX_{2.33}$.

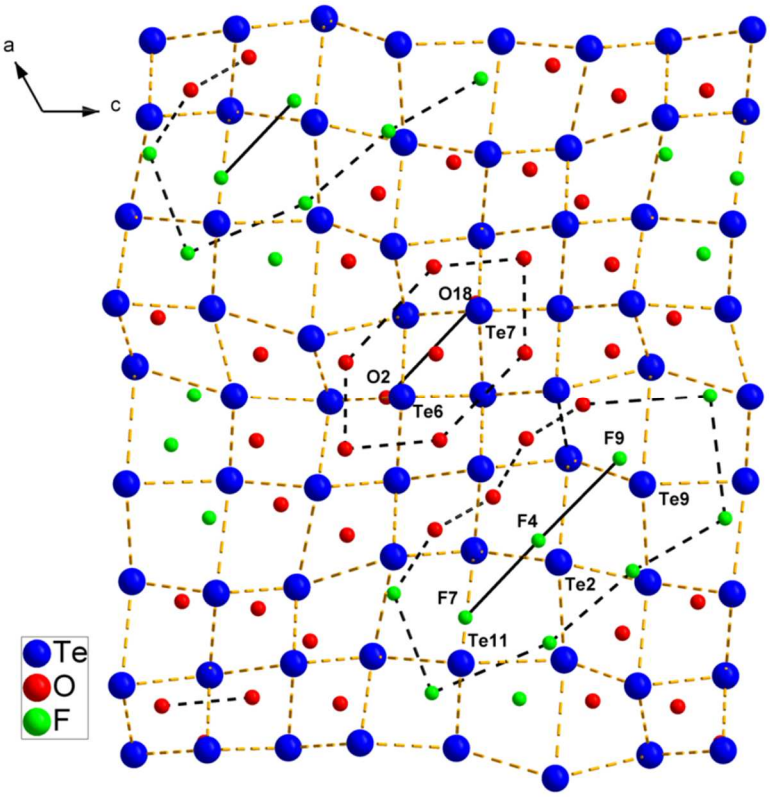
This simple mechanism explains the anionic excess leading from a composition MX_2 to $MX_{2.33}$.

Using Willis notation, the defect (or "anionic cluster") allowing to accommodate the anionic excess can be called **2: 3** (2 anion vacancies, 3 interstitials F_i). The distortion of the fluorite network, inherent in the phases comprising a cation with an electronic lone pair E, does not make it possible to really distinguish one of the two types of interstitials F' or F" defined by Willis [29].

The defect highlighted in $Sb_3O_2F_5$ is similar to the homologous defect described in $Lu_3O_2F_5$ [30] which is the basis of the series of ordered anion-excess fluorite phases

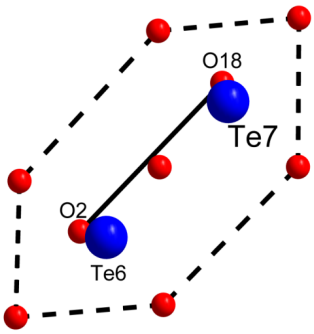
M_nX_{2n+1} called "vernier" phases or "infinitely adaptable" phases in which the local densification due to the insertion of the anionic excess in (2: 3) clusters is “absorbed” by a progressive shift of the adjacent anionic rows, according to the principle of the "vernier" effect [31, 32]. In $Lu_3O_2F_5$ also, the F sub-network is the only one concerned by the densification but the strict O / F order, different from that described in $Sb_3O_2F_5$, plays an important role in the stabilization of the structure (Fig. 8). However, the structure of $Lu_3O_2F_5$ is closer to a classical fluorite structure than that of $Sb_3O_2F_5$ and *a fortiori* that of $Te_3O_5F_2$ due, as already noticed, to the distortion resulting from the stereochemical influence of the electronic lone pair E of Sb^{3+} and Te^{4+}.

Fig. 8: Projection onto (010) plane of the structure of $Te_3O_5F_2$ showing its relationship with anion-excess fluorite structure family.

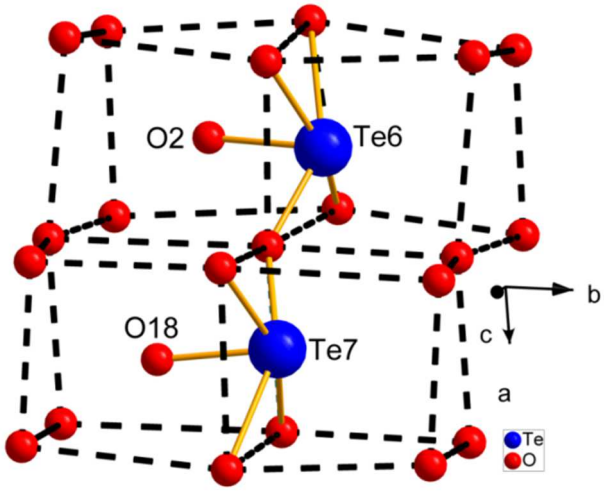


In $Te_3O_5F_2$, the O^{2-} anions mainly occupy the tetrahedral anionic fluorite site, with much more pronounced displacements than in $Sb_3O_2F_5$, by reference to the fluorite structure (Fig. 8). The defect structure is much more complex; two different types of anionic clusters can be described:

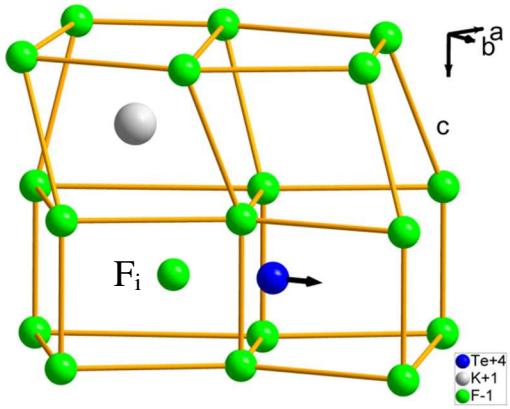
Fig. 9: Comparison between the defect affecting O anions around Te6 and Te7 cations in $Te_3O_5F_2$ (**a:** and **b:**) and affecting F anions around Te in the anion-excess fluorite $KTeF_5$ (**c:**); F cluster in$Te_3O_5F_2$ (**d:**).



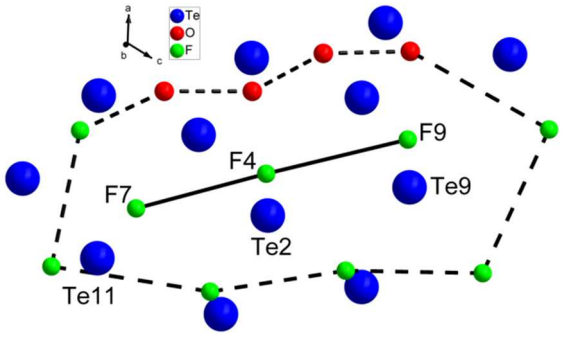
a



b



c



d

-The first only affects the oxygen network at the centre of each cylindrical unit defined above (around atoms Te6 and Te7) (Fig. 9a). It corresponds to the formation of two neighbouring polyhedra TeO_5 linked by vertex to form a bipolyhedron Te_2O_9 (Fig. 9b). This arrangement reminds the structure of $KTeF_5$ [33] in which a TeF_5E polyhedron is described. This polyhedron derives from a TeF_8 cube with an additional anion occupying the centre of a neighbouring cubic vacancy (Fig. 9c).

-The second affects the "intercolumnar" fluorinated network (around the atoms Te11, Te2 and Te9). It consists of three interstitial anions (F7, F4, F9) lined up at the same *y* coordinate (Fig. 9d). These F_i anions repel all the concentric O and F anions from their normal site.

4. Conclusion:

In the system TeO_2-TeF_4 system, a new metastable tellurium (IV) oxyfluoride$Te_3O_5F_2$ is structurally characterized in spite of the weak quality of the single crystals. Its structure, unusually complex with 15 different Te polyhedra, is built of giant cylindrical columns of oxide units interconnected *via* weak Te-F bonds. A strict O / F order is evidenced and a structural comparison with $Sb_3O_2F_5$ shows that these two phases derive, by a different mechanism, from the anion-excess fluorite superstructure type. Interestingly, in both structures is observed a full gradation of various polyhedra of antimony or tellurium from purely oxide to oxyfluoride and / or purely fluoride polyhedra. The oxygen atoms ensure a strong framework at the centre of these structures and the fluorine atoms are pushed back at the periphery forming loose connections between adjacent strong units or even in "terminal" position in the "intercolumnar" space, that is to say linked only to one Te^{4+}cation.This illustrates well the different roles of oxygen and fluorine atoms in these ordered oxyfluorides.

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Annexes:

Table S1: Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters ($Å^2$x 10^3) for $Te_3O_5F_2$. U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U(eq)
Te(1)	7670(3)	3847(4)	6275(2)	24(1)
Te(2)	9779(3)	937(4)	5764(2)	17(1)
Te(3)	7919(3)	8992(4)	8014(2)	19(1)
Te(4)	4685(3)	2326(4)	8146(2)	17(1)
Te(5)	12584(2)	2858(4)	5557(2)	15(1)
Te(6)	13981(3)	9198(4)	12977(3)	27(1)
Te(7)	5952(3)	9501(4)	5405(2)	22(1)
Te(8)	9658(3)	3164(4)	8904(2)	17(1)
Te(9)	8016(3)	1207(5)	3304(2)	24(1)
Te(10)	8089(3)	3535(4)	9629(2)	18(1)
Te(11)	12076(3)	1417(4)	8743(2)	19(1)
Te(12)	6004(3)	2607(4)	262(2)	18(1)
Te(13)	13885(3)	3110(4)	11555(2)	18(1)
Te(14)	9508(3)	7302(5)	7265(2)	19(1)
Te(15)	14151(3)	9023(4)	6055(3)	27(1)
O(1)	8420(30)	1580(40)	8571(19)	14(5)
O(2)	13980(30)	2070(40)	12700(20)	19(6)
O(3)	12990(30)	4970(40)	11520(20)	17(6)
O(4)	9340(30)	9920(50)	6500(20)	26(7)
O(5)	9150(30)	9120(40)	7910(20)	15(5)
O(6)	14980(30)	4700(40)	12430(20)	19(6)
O(7)	5790(30)	1000(50)	9110(20)	27(7)
O(8)	7260(30)	5070(50)	8690(20)	25(7)
O(9)	15010(30)	500(40)	5850(20)	19(6)
O(10)	8320(30)	6510(50)	6340(20)	24(6)
O(11)	7050(30)	3940(50)	330(20)	24(6)
O(12)	13780(30)	1640(40)	6390(20)	21(6)
O(13)	11550(30)	890(50)	9500(30)	33(8)
O(14)	9140(30)	4740(40)	9530(20)	19(6)
O(15)	6980(30)	5270(40)	6740(20)	15(5)
O(16)	7180(30)	310(50)	6870(20)	25(7)
O(17)	5210(30)	4310(40)	7710(20)	15(5)

O(18)	6130(30)	2390(50)	5440(20)	24(6)
O(19)	5030(30)	130(50)	4150(20)	26(7)
O(20)	5060(30)	4140(50)	9300(20)	27(7)
O(21)	13020(30)	4750(40)	5000(20)	18(6)
O(22)	13070(30)	40(40)	4960(20)	15(5)
O(23)	9010(30)	4550(50)	7780(20)	24(7)
O(24)	8660(30)	630(50)	4710(20)	25(7)
O(25)	7100(30)	9800(50)	3450(30)	29(7)
F(1)	8400(30)	8240(50)	3200(20)	51(8)
F(2)	10530(30)	5560(50)	9310(20)	49(8)
F(3)	10030(30)	7880(50)	5570(20)	46(7)
F(4)	9290(40)	3640(50)	5950(30)	50(9)
F(5)	12790(30)	3660(40)	9650(20)	34(6)
F(6)	5930(30)	5030(50)	970(20)	42(7)
F(7)	11010(30)	3260(40)	8170(20)	35(6)
F(8)	7110(40)	1190(60)	2020(30)	57(9)
F(9)	7350(40)	3730(60)	3410(30)	64(10)
F(10)	11200(40)	9120(60)	7920(30)	68(11)

Table S2: Shorter bond lengths [Å] for $Te_3O_5F_2$.

Te(1)-O(15)	1.89(3)
Te(1)-O(10)	1.98(3)
Te(1)-O(22)#1	1.99(3)
Te(1)-O(18)	2.43(4)
Te(1)-O(23)	2.48(4)
Te(2)-O(4)#2	1.84(3)
Te(2)-O(24)	1.85(4)
Te(2)-F(4)	1.99(3)
Te(2)-F(3)#2	2.05(3)
Te(3)-O(1)#3	1.88(3)
Te(3)-O(16)#3	1.91(4)
Te(3)-O(3)#4	2.11(3)
Te(3)-O(5)	2.13(3)
Te(4)-O(17)	1.88(3)
Te(4)-O(7)	1.95(4)
Te(4)-O(20)	2.09(3)
Te(4)-O(6)#5	2.13(3)
Te(4)-Te(12)#6	3.170(5)
Te(5)-O(21)	1.88(3)
Te(5)-O(25)#7	1.94(3)
Te(5)-O(12)	1.95(4)
Te(5)-O(22)	2.38(3)
Te(6)-O(2)#3	1.88(3)
Te(6)-O(19)#8	1.99(4)
Te(6)-O(15)#4	2.00(3)
Te(6)-O(17)#4	2.16(2)
Te(7)-O(18)#3	1.86(3)
Te(7)-O(19)#3	1.97(4)
Te(7)-O(21)#1	2.12(3)
Te(7)-O(9)#9	2.13(3)
Te(7)-O(16)#3	2.38(4)
Te(8)-O(23)	1.89(3)
Te(8)-O(14)	1.93(3)
Te(8)-F(2)	1.98(4)
Te(8)-O(1)	2.10(3)
Te(9)-O(25)#2	1.87(4)

Te(9)-F(8)	1.96(4)
Te(9)-F(9)	2.00(4)
Te(9)-F(1)#2	2.03(3)
Te(9)-O(24)	2.12(3)
Te(10)-O(8)	1.81(4)
Te(10)-O(13)#4	1.98(3)
Te(10)-O(14)	1.99(3)
Te(10)-O(1)	2.45(2)
Te(11)-O(13)	1.89(3)
Te(11)-F(7)	1.94(4)
Te(11)-F(5)	2.01(3)
Te(11)-F(10)#2	2.06(5)
Te(11)-O(11)#7	2.20(4)
Te(12)-O(11)	1.87(4)
Te(12)-O(20)#10	1.89(4)
Te(12)-F(6)	2.00(3)
Te(12)-O(7)#10	2.08(3)
Te(13)-O(3)	1.87(3)
Te(13)-O(6)	1.98(4)
Te(13)-O(2)	1.98(2)
Te(13)-O(7)#4	2.34(3)
Te(14)-O(5)	1.87(2)
Te(14)-O(10)	1.89(4)
Te(14)-O(4)	2.04(3)
Te(14)-O(23)	2.28(3)
Te(15)-O(9)#3	1.87(3)
Te(15)-O(12)#3	1.95(3)
Te(15)-O(22)#3	1.96(4)
Te(15)-O(6)#11	2.29(3)

Symmetry transformations used to generate equivalent atoms:

#1 -x+2,y+1/2,-z+1 #2 x,y-1,z #3 x,y+1,z

#4 -x+2,y+1/2,-z+2 #5 -x+2,y-1/2,-z+2 #6 x,y,z+1

#7 -x+2,y-1/2,-z+1 #8 x+1,y+1,z+1 #9 x-1,y+1,z

#10 x,y,z-1 #11 -x+3,y+1/2,-z+2 #12 -x+3,y-1/2,-z+2

#13 x+1,y-1,z #14 x-1,y-1,z-1

Table S3 : Anisotropic displacement parameters ($Å^2$ x 10^3) for $Te_3O_5F_2$. The anisotropic displacement factor exponent takes the form: $-2\pi^2[h^2a^{*2}U^{11} + ... + 2 h k a^* b^* U^{12}]$

	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
Te(1)	36(3)	19(1)	30(2)	9(1)	25(3)	12(2)
Te(2)	11(3)	19(1)	17(2)	1(1)	3(2)	-2(2)
Te(3)	22(3)	16(1)	20(2)	0(1)	12(2)	-1(2)
Te(4)	13(3)	18(1)	19(2)	2(1)	7(2)	1(2)
Te(5)	12(3)	16(1)	14(1)	-1(1)	4(2)	0(1)
Te(6)	25(3)	13(1)	50(2)	-1(2)	25(3)	-1(2)
Te(7)	24(3)	13(1)	35(2)	0(1)	21(3)	-1(2)
Te(8)	14(3)	21(1)	15(1)	2(1)	5(2)	2(2)
Te(9)	24(3)	28(2)	19(2)	6(1)	10(2)	-5(2)
Te(10)	17(3)	19(1)	15(2)	2(1)	5(2)	1(2)
Te(11)	13(3)	23(1)	17(2)	3(1)	4(2)	-1(2)
Te(12)	13(3)	24(1)	14(1)	-5(1)	6(2)	-3(2)
Te(13)	13(3)	26(1)	12(1)	-3(1)	3(2)	2(2)
Te(14)	10(3)	31(2)	13(1)	-1(1)	2(2)	6(2)
Te(15)	23(3)	17(1)	49(2)	11(2)	24(3)	7(2)

•$Te_3O_5F_2$: a new metastable tellurium IV oxyfluoride with an acentric complex structure

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The crystal structure of $Te_3O_5F_2$ is unusually complex with 15 different Te polyhedra. It is built of giant cylindrical columns of oxide units connected *via* weak Te-F bonds. A strict O/F order is evidenced. It derives from anion-excess fluorite type.