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New oxyfluorotellurates(IV): $M\text{TeO}_3\text{F}$ (M = Fe^{III}, Ga^{III} and Cr^{III})

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The crystal structures of the new isomorphous compounds iron(III) oxyfluorotellurate(IV), FeTeO_3F, gallium(III) oxyfluorotellurate(IV), GaTeO_3F, and chromium(III) oxyfluorotellurate(IV), CrTeO_3F, consist of zigzag chains of $M\text{O}_4\text{F}_2$ distorted octahedra alternately sharing O–O and F–F edges and connected *via* TeO_3 trigonal pyramids. A full O/F anionic ordering is observed and the electronic lone pair of the Te^{IV} cation is stereochemically active.

Comment

In recent years, a systematic investigation of tellurium(IV) fluorides and oxyfluorides has been performed in our laboratory in order to develop our knowledge in four directions: (i) synthesis of new phases of potential interest for their nonlinear optical properties; (ii) characterization of new structure types in order to determine the influence of the electronic lone pair of Te^{IV} atoms (E) on their structural framework, especially in fluorides and oxyfluorides, compounds very sensitive to the stereochemical activity of this electronic lone pair; (iii) determination of the main rules governing the O/F anionic long-range or short-range ordering in oxyfluorides; and (iv) crystal growth in hydrofluoric acid medium of tellurates and oxyfluorotellurates(IV), which could be promising for nonlinear optics.

Following on from the structural characterization of the TeOF_2 (Guillet *et al.*, 1999), $\text{Te}_2\text{O}_3\text{F}_2$ (Ider *et al.*, 1996) and $\text{KTe}_3\text{O}_6\text{F}$ (Laval *et al.*, 2002) phases, this paper deals with the syntheses and crystal structure determination of a new isomorphous series of oxyfluorides, $M\text{TeO}_3\text{F}$, with M = Fe^{III}, Ga^{III} and Cr^{III}.

The Te atom is bonded to three O atoms at distances of *ca* 1.9 Å (Tables 1 and 2). It occupies the center of a trigonal pyramid with the stereochemically active electronic lone pair E pointing in the direction of the fourth corner (Fig. 1). If three weak extra bonds with lengths of *ca* 2.7 Å are considered, the anionic polyhedron can be described as a distorted octahedron. The lone pair E occupies the volume formed between the Te atom and the weakly bonded anions. The M atom is sixfold coordinated, slightly shifted from the center of a distorted $M\text{O}_4\text{F}_2$ octahedron (Fig. 2, and Tables 1 and 2). Bond-valence calculations (Brown, 1981) are consistent with the description $M^{\text{III}}\text{Te}^{\text{IV}}(\text{O}^{2-})_3\text{F}^-$ showing a full O/F ordering (Tables 3 and 4).

FeTeO_3F, GaTeO_3F and CrTeO_3F [with lattice parameters refined on the basis of powder X-ray diffraction data of a = 5.028 (1) Å, b = 5.073 (1) Å, c = 12.307 (2) Å and β = 97.40 (4)°, using the refinement program *CHEKCELL* (Laugier & Bochu, 2000)] are isomorphous, with 'zigzag' chains of $M\text{O}_4\text{F}_2$ (M = Fe^{III}, Ga^{III} and Cr^{III}) distorted octahedra sharing alternately O–O and F–F edges and interconnected *via* TeO_3 trigonal pyramids (Fig. 3*a*). A projection on to (010) shows large tunnels parallel to [010], towards which point the lone pairs E (Fig. 3*b*). The description considering the Te anionic environment as a distorted octahedron (Fig. 1) allows an interesting comparison with the α-PbO_2 (Fig. 4) structure (Hyde & Andersson, 1989). Indeed, the structure of $M\text{TeO}_3\text{F}$ (M = Fe^{III}, Ga^{III} and Cr^{III}; Fig. 3*a*) is thus based on parallel zigzag chains of corner-sharing octahedra, two adjacent chains being shifted by $a/2$ along the [001] direction. The idealized $M\text{TeO}_3\text{F}$ structure appears as a superstructure of α-PbO_2 with doubling of the c axis (Table 5). However, the hexagonal close packed (hcp) anionic array and

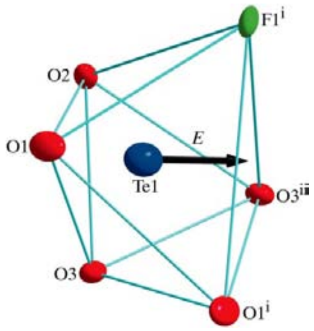

Figure 1
The anionic polyhedron (distorted octahedron) around the Te atom in the FeTeO_3F structure. The arrow indicates the direction towards which the lone pair E points. The Ga and Cr analogs are isomorphous. [Symmetry codes: (i) $-x + \frac{1}{2}, y - \frac{1}{2}, -z + \frac{3}{2}$; (ii) $-x + \frac{3}{2}, y - \frac{1}{2}, -z + \frac{3}{2}$.]

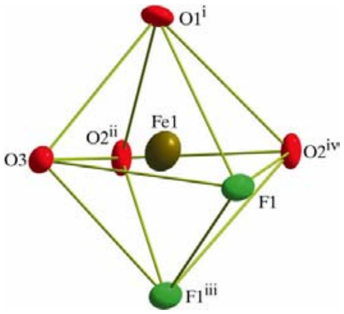

Figure 2
The coordination polyhedron of the Fe atom in FeTeO_3F. [Symmetry codes: (i) $-x+\frac{1}{2}, y-\frac{1}{2}, -z+\frac{3}{2}$; (ii) $-x+\frac{3}{2}, y-\frac{1}{2}, -z+\frac{3}{2}$; (iii) $-x+1, -y+2, -z+1$; $-z + 1$; (iv) $x - \frac{1}{2}, -y + \frac{3}{2}, z - \frac{1}{2}$.]

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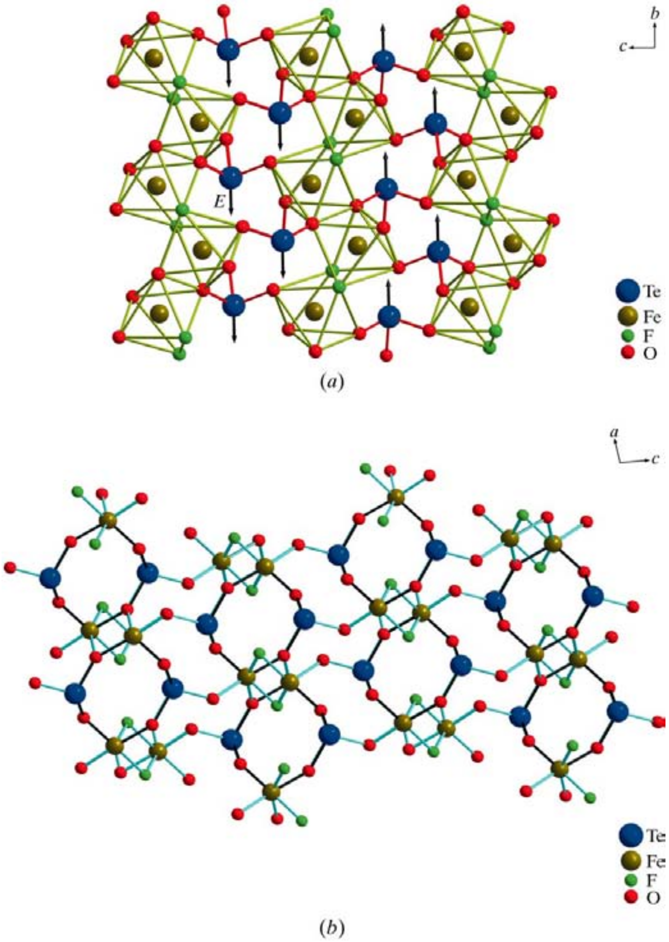

Figure 3
(*a*) The (100) layer of 'zigzag' $(FeO_3F)_n$ chains of FeO_4F_2 octahedra connected *via* TeO_3. (*b*) A projection on to (010), showing the tunnels towards which the lone pairs *E* point.

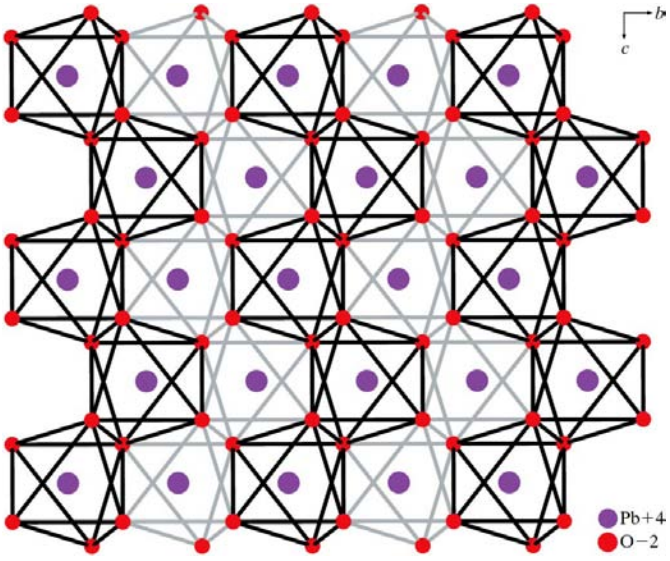

Figure 4
The ideal structure of α-PbO_2 for comparison with the structure of $FeTeO_3F$ (see Fig. 3*a*).

the positions of the cations are more distorted than in α-PbO_2 as a consequence of the cationic ordering, of the difference in size between M^{III} and Te^{IV} cations, and of the stereochemical activity of the lone pair *E*. A strong monoclinic distortion of the lattice also occurs in the $MTeO_3F$ phases, but the analogy is worth noting.

The new $MTeO_3F$ structure type is important because it shows that oxyfluorotellurates associating the Te^{IV} cation with trivalent cations presenting octahedral coordination can adopt a structure type derived from a classical oxide such as α-PbO_2, with a distorted hcp anionic array and full cationic ordering in parallel zigzag rows. It also corresponds to an intergrowth of *M*OF and TeO_2 slabs with F^- anions only bonded to M^{III} cations. There is no strong Te—F bond, sensitive to hydrolysis, so this kind of phase is air stable and could be of interest for applications in optical devices. Moreover, the unusual environment of M^{III} cations, interconnected by alternate F–F and O–O edges, offers the potential of promising magnetic properties.

Experimental

Fe_2O_3, Cr_2O_3 and Ga_2O_3 were commercial products (Aldrich, 99.9%) and TeO_2 was prepared by decomposition of commercial H_6TeO_6 (Aldrich, 99.9%) at 823 K under flowing oxygen. $FeTeO_3F$ and $GaTeO_3F$ were prepared in two steps: first an intimate mixture (mol%) of $\frac{1}{2}Fe_2O_3$–$4TeO_2$ (or $\frac{1}{2}Ga_2O_3$–$2TeO_2$) was dissolved in hydrofluoric acid (40%) in a Teflon beaker and heated at 453 K, and then, after slow evaporation, the product was crushed and heated in a sealed platinum tube. The temperature was progressively increased to 723 K (923 K for the Ga phase) (5 K min^{-1}), kept stable for 96 h, slowly decreased to 673 K (0.05 K min^{-1} for Fe and 0.1 K min^{-1} for Ga) and finally stabilized for 10 h. After that, the tube was water-quenched to room temperature. Green crystals of $FeTeO_3F$ and colorless crystals of $GaTeO_3F$, air stable and suitable for X-ray diffraction study, were obtained. The chromium phase was obtained in powder form by direct heating of a Cr_2O_3–CrF_3–$3TeO_2$ mixture in a sealed platinum tube. The temperature was progressively increased to 973 K (5 K min^{-1}) and kept stable for 96 h. The tube was then water-quenched.

Compound (I)

Crystal data

$FeTeO_3F$
$M_r = 250.45$
Monoclinic, $P2_1/n$
$a = 5.0667$ (7) Å
$b = 5.0550$ (7) Å
$c = 12.3975$ (15) Å
$\beta = 97.630$ (13)°

$V = 314.72$ (7) Å^3
$Z = 4$
Mo $K\alpha$ radiation
$\mu = 13.73$ mm^{-1}
$T = 293$ (2) K
0.10 × 0.04 × 0.02 mm

Data collection

Nonius KappaCCD diffractometer
Absorption correction: multi-scan (*SADABS*; Bruker 2004)
$T_{min} = 0.337$, $T_{max} = 0.763$

10518 measured reflections
903 independent reflections
757 reflections with $I > 2\sigma(I)$
$R_{int} = 0.058$

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.021$
$wR(F^2) = 0.036$
$S = 0.99$
903 reflections

56 parameters
$\Delta\rho_{max} = 0.88$ e Å^{-3}
$\Delta\rho_{min} = -0.95$ e Å^{-3}

Table 1
Selected bond lengths (Å) for (I).

Te1—O3	1.870 (2)	Fe1—O1^{i}	1.923 (2)
Te1—O1	1.884 (2)	Fe1—O3	1.941 (2)
Te1—O2	1.904 (2)	Fe1—O2^{ii}	1.965 (2)
Te1—O1^{i}	2.695 (2)	Fe1—F1	1.974 (2)
Te1—O3^{ii}	2.746 (2)	Fe1—F1^{iii}	2.040 (2)
Te1—F1^{i}	2.850 (3)	Fe1—O2^{iv}	2.054 (2)

Symmetry codes: (i) $-x+\frac{1}{2}, y-\frac{1}{2}, -z+\frac{3}{2}$; (ii) $-x+\frac{3}{2}, y-\frac{1}{2}, -z+\frac{3}{2}$; (iii) $-x+1, -y+2, -z+1$; (iv) $x-\frac{1}{2}, -y+\frac{3}{2}, z-\frac{1}{2}$.

Compound (II)

Crystal data

$GaTeO_3F$
$M_r = 264.32$
Monoclinic, $P2_1/n$
$a = 5.0625\ (7)$ Å
$b = 4.9873\ (7)$ Å
$c = 12.1662\ (15)$ Å
$\beta = 97.952\ (13)^\circ$

$V = 304.22\ (7)$ Å^3
$Z = 4$
Mo $K\alpha$ radiation
$\mu = 18.29$ mm^{-1}
$T = 293\ (2)$ K
0.10 × 0.04 × 0.02 mm

Data collection

Nonius KappaCCD diffractometer
Absorption correction: multi-scan (*SADABS*; Bruker 2004)
$T_{min} = 0.257$, $T_{max} = 0.697$

8547 measured reflections
867 independent reflections
831 reflections with $I > 2\sigma(I)$
$R_{int} = 0.036$

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.017$
$wR(F^2) = 0.042$
$S = 1.21$
867 reflections

56 parameters
$\Delta\rho_{max} = 1.25$ e Å^{-3}
$\Delta\rho_{min} = -1.71$ e Å^{-3}

Table 2
Selected bond lengths (Å) for (II).

Te1—O3	1.865 (2)	Ga1—O1^{i}	1.918 (2)
Te1—O1	1.884 (2)	Ga1—O3	1.911 (2)
Te1—O2	1.918 (2)	Ga1—O2^{ii}	1.923 (2)
Te1—O1^{i}	2.632 (2)	Ga1—F1	1.929 (2)
Te1—O3^{ii}	2.731 (2)	Ga1—F1^{iii}	2.009 (2)
Te1—F1^{i}	2.830 (2)	Ga1—O2^{iv}	1.987 (2)

Symmetry codes: (i) $-x+\frac{1}{2}, y-\frac{1}{2}, -z+\frac{3}{2}$; (ii) $-x+\frac{3}{2}, y-\frac{1}{2}, -z+\frac{3}{2}$; (iii) $-x+1, -y+2, -z+1$; (iv) $x-\frac{1}{2}, -y+\frac{3}{2}, z-\frac{1}{2}$.

Table 3
Bond valences for (I).

	Fe1	Te1	V_{ij}
O1	0.600	1.286/0.144	2.03
O2	0.536/0.421	1.218	2.18
O3	0.576	1.335/0.125	2.04
F1	0.417/0.349	0.071	0.84
V_{ij}	2.90	4.18	–

Table 4
Bond valences for (II).

	Ga1	Te1	V_{ij}
O1	0.602	1.286/0.17	2.06
O2	0.594/0.499	1.173	2.27
O3	0.613	1.354/0.13	2.10
F1	0.480/0.386	0.096	0.96
V_{ij}	3.17	4.21	–

Table 5
Comparison of lattice parameters (Å) of $FeTeO_3F$ and α-PbO_2.

$FeTeO_3F$	α-PbO_2
$a = 5.067$	$a = 4.989$
$b = 5.055$; $\beta = 97.63$	$c = 5.466$
$c = 12.398 = 2 \times 6.199$	$b = 5.947$
Monoclinic, $P2_1/n$	Orthorhombic, *Pbcn*

For both compounds, data collection: *KappaCCD Server Software* (Nonius, 1997); cell refinement: *DIRAX*/*LSQ* (Duisenberg *et al.*, 2000); data reduction: *EVALCCD* (Duisenberg *et al.*, 2000); program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *DIAMOND* (Brandenburg, 2001); software used to prepare material for publication: *SHELXL97*.

Supplementary data for this paper are available from the IUCr electronic archives (Reference: SQ3115). Services for accessing these data are described at the back of the journal.

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