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

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The crystal structures of the new isomorphous compounds iron(III) oxyfluorotellurate(IV),  $\text{FeTeO}_3\text{F}$ , gallium(III) oxyfluorotellurate(IV),  $\text{GaTeO}_3\text{F}$ , and chromium(III) oxyfluorotellurate(IV),  $\text{CrTeO}_3\text{F}$ , consist of zigzag chains of  $\text{MO}_4\text{F}_2$  distorted octahedra alternately sharing O–O and F–F edges and connected *via*  $\text{TeO}_3$  trigonal pyramids. A full O/F anionic ordering is observed and the electronic lone pair of the  $\text{Te}^{\text{IV}}$  cation is stereochemically active.

### Comment

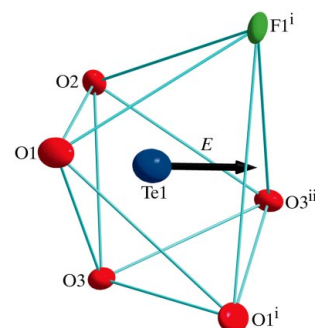
In recent years, a systematic investigation of tellurium(IV) fluorides and oxyfluorides has been performed in our laboratory in order to develop our knowledge in four directions: (i) synthesis of new phases of potential interest for their nonlinear optical properties; (ii) characterization of new structure types in order to determine the influence of the electronic lone pair of  $\text{Te}^{\text{IV}}$  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  $\text{TeOF}_2$  (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  $M = \text{Fe}^{\text{III}}$ ,  $\text{Ga}^{\text{III}}$  and  $\text{Cr}^{\text{III}}$ .

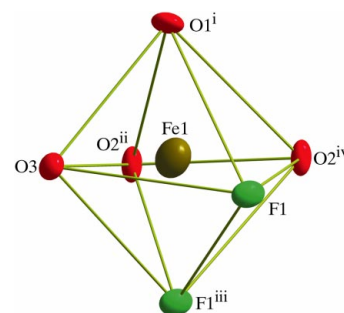
The Te atom is bonded to three O atoms at distances of *ca* 1.9 Å (Tables 1 and 2). It occupies the center of a trigonal pyramid with the stereochemically active electronic lone pair  $E$  pointing in the direction of the fourth corner (Fig. 1). If three weak extra bonds with lengths of *ca* 2.7 Å are 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  $\text{MO}_4\text{F}_2$  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).

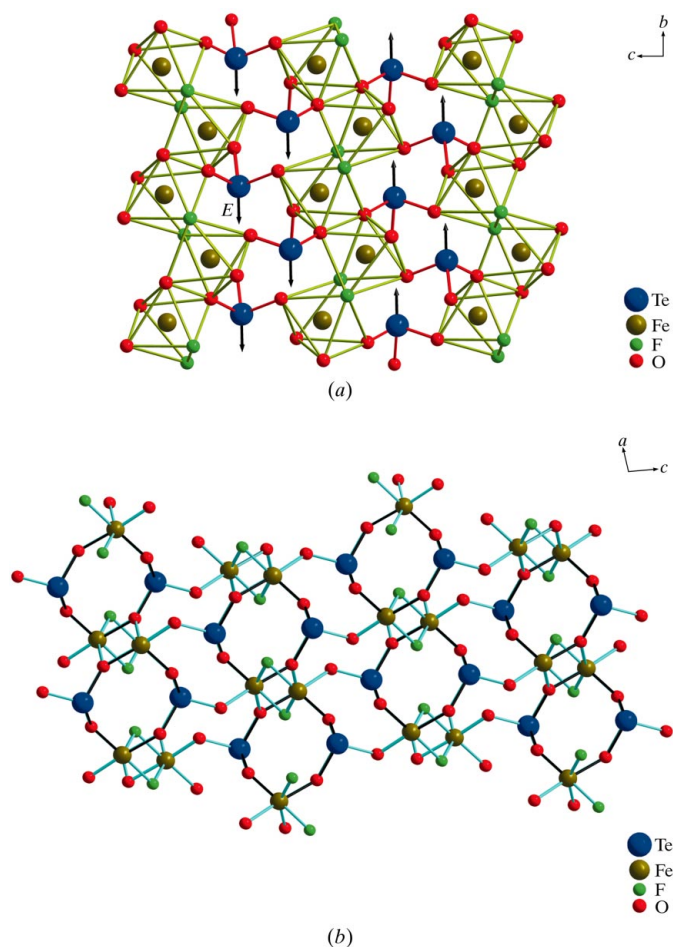
$\text{FeTeO}_3\text{F}$ ,  $\text{GaTeO}_3\text{F}$  and  $\text{CrTeO}_3\text{F}$  [with lattice parameters refined on the basis of powder X-ray diffraction data of  $a = 5.028$  (1) Å,  $b = 5.073$  (1) Å,  $c = 12.307$  (2) Å and  $\beta = 97.40$  (4)°, using the refinement program *CHEKCELL* (Laugier & Bochu, 2000)] are isomorphous, with 'zigzag' chains of  $\text{MO}_4\text{F}_2$  ( $M = \text{Fe}^{\text{III}}$ ,  $\text{Ga}^{\text{III}}$  and  $\text{Cr}^{\text{III}}$ ) distorted octahedra sharing alternately O–O and F–F edges and interconnected *via*  $\text{TeO}_3$  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  $\alpha\text{-PbO}_2$  (Fig. 4) structure (Hyde & Andersson, 1989). Indeed, the structure of  $M\text{TeO}_3\text{F}$  ( $M = \text{Fe}^{\text{III}}$ ,  $\text{Ga}^{\text{III}}$  and  $\text{Cr}^{\text{III}}$ ; 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  $\alpha\text{-PbO}_2$  with doubling of the  $c$  axis (Table 5). However, the hexagonal close packed (hcp) anionic array and



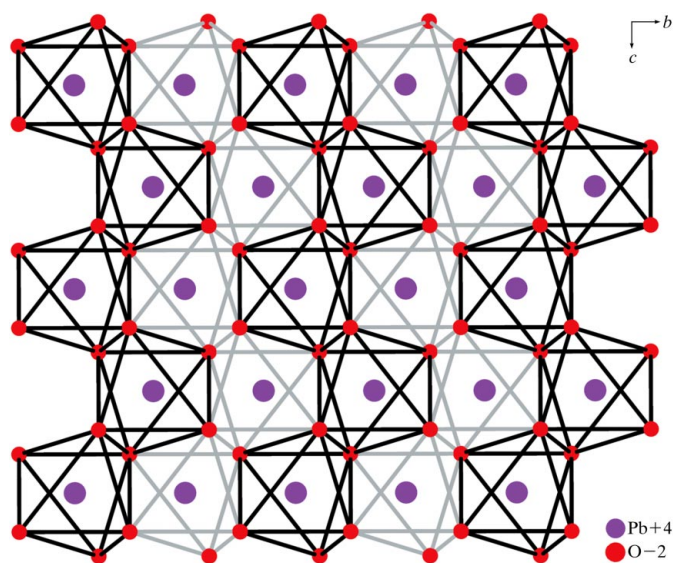
**Figure 1**  
The anionic polyhedron (distorted octahedron) around the Te atom in the  $\text{FeTeO}_3\text{F}$  structure. The arrow indicates the direction towards which the lone pair  $E$  points. The Ga and Cr analogs are isomorphous. [Symmetry codes: (i)  $-x + \frac{1}{2}, y - \frac{1}{2}, -z + \frac{3}{2}$ ; (ii)  $-x + \frac{3}{2}, y - \frac{1}{2}, -z + \frac{3}{2}$ .]



**Figure 2**  
The coordination polyhedron of the Fe atom in  $\text{FeTeO}_3\text{F}$ . [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)  $x - \frac{1}{2}, -y + \frac{3}{2}, z - \frac{1}{2}$ .]



**Figure 3**  
 (a) The (100) layer of 'zigzag'  $(\text{FeO}_3\text{F})_n$  chains of  $\text{FeO}_4\text{F}_2$  octahedra connected via  $\text{TeO}_3$ . (b) A projection on to (010), showing the tunnels towards which the lone pairs  $E$  point.



**Figure 4**  
 The ideal structure of  $\alpha\text{-PbO}_2$  for comparison with the structure of  $\text{FeTeO}_3\text{F}$  (see Fig. 3a).

the positions of the cations are more distorted than in  $\alpha\text{-PbO}_2$  as a consequence of the cationic ordering, of the difference in size between  $M^{\text{III}}$  and  $\text{Te}^{\text{IV}}$  cations, and of the stereochemical activity of the lone pair  $E$ . A strong monoclinic distortion of the lattice also occurs in the  $M\text{TeO}_3\text{F}$  phases, but the analogy is worth noting.

The new  $M\text{TeO}_3\text{F}$  structure type is important because it shows that oxyfluorotellurates associating the  $\text{Te}^{\text{IV}}$  cation with trivalent cations presenting octahedral coordination can adopt a structure type derived from a classical oxide such as  $\alpha\text{-PbO}_2$ , with a distorted hcp anionic array and full cationic ordering in parallel zigzag rows. It also corresponds to an intergrowth of  $MOF$  and  $\text{TeO}_2$  slabs with  $\text{F}^-$  anions only bonded to  $M^{\text{III}}$  cations. There is no strong  $\text{Te}-\text{F}$  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  $M^{\text{III}}$  cations, interconnected by alternate  $\text{F}-\text{F}$  and  $\text{O}-\text{O}$  edges, offers the potential of promising magnetic properties.

## Experimental

$\text{Fe}_2\text{O}_3$ ,  $\text{Cr}_2\text{O}_3$  and  $\text{Ga}_2\text{O}_3$  were commercial products (Aldrich, 99.9%) and  $\text{TeO}_2$  was prepared by decomposition of commercial  $\text{H}_6\text{TeO}_6$  (Aldrich, 99.9%) at 823 K under flowing oxygen.  $\text{FeTeO}_3\text{F}$  and  $\text{GaTeO}_3\text{F}$  were prepared in two steps: first an intimate mixture (mol%) of  $\frac{1}{2}\text{Fe}_2\text{O}_3-4\text{TeO}_2$  (or  $\frac{1}{2}\text{Ga}_2\text{O}_3-2\text{TeO}_2$ ) 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) ( $5\text{ K min}^{-1}$ ), kept stable for 96 h, slowly decreased to 673 K ( $0.05\text{ K min}^{-1}$  for Fe and  $0.1\text{ K min}^{-1}$  for Ga) and finally stabilized for 10 h. After that, the tube was water-quenched to room temperature. Green crystals of  $\text{FeTeO}_3\text{F}$  and colorless crystals of  $\text{GaTeO}_3\text{F}$ , air stable and suitable for X-ray diffraction study, were obtained. The chromium phase was obtained in powder form by direct heating of a  $\text{Cr}_2\text{O}_3-\text{CrF}_3-3\text{TeO}_2$  mixture in a sealed platinum tube. The temperature was progressively increased to 973 K ( $5\text{ K min}^{-1}$ ) and kept stable for 96 h. The tube was then water-quenched.

## Compound (I)

### Crystal data

$\text{FeTeO}_3\text{F}$   
 $M_r = 250.45$   
 Monoclinic,  $P2_1/n$   
 $a = 5.0667(7)\text{ \AA}$   
 $b = 5.0550(7)\text{ \AA}$   
 $c = 12.3975(15)\text{ \AA}$   
 $\beta = 97.630(13)^\circ$

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

### Data collection

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

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

### Refinement

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

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

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

Te1—O3	1.870 (2)	Fe1—O1 <sup>i</sup>	1.923 (2)
Te1—O1	1.884 (2)	Fe1—O3	1.941 (2)
Te1—O2	1.904 (2)	Fe1—O2 <sup>ii</sup>	1.965 (2)
Te1—O1 <sup>i</sup>	2.695 (2)	Fe1—F1	1.974 (2)
Te1—O3 <sup>iii</sup>	2.746 (2)	Fe1—F1 <sup>iii</sup>	2.040 (2)
Te1—F1 <sup>i</sup>	2.850 (3)	Fe1—O2 <sup>iv</sup>	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 <sub>3</sub> F	$V = 304.22 (7) \text{ \AA}^3$
$M_r = 264.32$	$Z = 4$
Monoclinic, $P2_1/n$	Mo $K\alpha$ radiation
$a = 5.0625 (7) \text{ \AA}$	$\mu = 18.29 \text{ mm}^{-1}$
$b = 4.9873 (7) \text{ \AA}$	$T = 293 (2) \text{ K}$
$c = 12.1662 (15) \text{ \AA}$	$0.10 \times 0.04 \times 0.02 \text{ mm}$
$\beta = 97.952 (13)^\circ$	

### Data collection

Nonius KappaCCD diffractometer	8547 measured reflections
Absorption correction: multi-scan (SADABS; Bruker 2004)	867 independent reflections
$T_{\min} = 0.257, T_{\max} = 0.697$	831 reflections with $I > 2\sigma(I)$
	$R_{\text{int}} = 0.036$

### Refinement

$R[F^2 > 2\sigma(F^2)] = 0.017$	56 parameters
$wR(F^2) = 0.042$	$\Delta\rho_{\max} = 1.25 \text{ e \AA}^{-3}$
$S = 1.21$	$\Delta\rho_{\min} = -1.71 \text{ e \AA}^{-3}$
867 reflections	

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

Te1—O3	1.865 (2)	Ga1—O1 <sup>i</sup>	1.918 (2)
Te1—O1	1.884 (2)	Ga1—O3	1.911 (2)
Te1—O2	1.918 (2)	Ga1—O2 <sup>ii</sup>	1.923 (2)
Te1—O1 <sup>i</sup>	2.632 (2)	Ga1—F1	1.929 (2)
Te1—O3 <sup>iii</sup>	2.731 (2)	Ga1—F1 <sup>iii</sup>	2.009 (2)
Te1—F1 <sup>i</sup>	2.830 (2)	Ga1—O2 <sup>iv</sup>	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<sub>3</sub>F and  $\alpha$ -PbO<sub>2</sub>.

FeTeO <sub>3</sub> F	$\alpha$ -PbO <sub>2</sub>
$a = 5.067$	$a = 4.989$
$b = 5.055; \beta = 97.63$	$c = 5.466$
$c = 12.398 = 2 \times 6.199$	$b = 5.947$
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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