

Two new types of oxyfluorotellurates(IV): ScTeO_3F and InTeO_3F

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In the course of a general study of oxyfluorotellurates(IV), materials likely to exhibit interesting nonlinear optical properties, the crystal structures of the new phases scandium tellurium trioxide fluoride, ScTeO_3F , and indium tellurium trioxide fluoride, InTeO_3F , belonging to two different structural types and also differing from that of the recently published $M\text{TeO}_3\text{F}$ ($M = \text{Fe}$, Ga and Cr) series, have been determined. The ScTeO_3F structure can be described as an intergrowth of two different layers of scandium octahedra connected *via* isolated TeO_3 groups. The scandium ions occupy two different sites with ..2 and 2.. site symmetry. The Te, F and O atoms are on general positions of the $Pnma$ space group. The InTeO_3F structure consists of zigzag sheets of InO_3F octahedra. The In, Te, O and F atoms are all located on general positions of the $P2_1/a$ space group. TeO_3F polyhedra are inserted between the zigzag sheets of InO_3F octahedra and with them form double $(\text{InTeO}_3\text{F})_n$ layers. Therefore, InTeO_3F is a true layer structure, unlike the previous types. In all these phases, the electronic lone pair of the Te^{IV} atom is stereochemically active and a full O/F anionic ordering is observed.

Comment

In recent years, many tellurates(IV) of transition metals or heavy metals have generated interest for their excellent nonlinear optical properties. Therefore, a general study of the structural and physical properties of some homologous oxyfluorotellurates(IV) and oxyfluoroiodates(V) has been undertaken. Indeed, few fluorides and oxyfluorides of tellurium(IV) and iodine(V) were known because of the highly hygroscopic character of most of these phases. In the present series of studies, the compounds are generally more thermally stable and moisture resistant. Following our characterization of the new series $M\text{TeO}_3\text{F}$ ($M = \text{Fe}$, Ga and Cr ; Laval *et al.*, 2008) and NaIO_2F_2 (Laval & Jennene Boukharrata, 2008), the present paper describes the syntheses and crystal structures of

two phases, *viz.* ScTeO_3F and InTeO_3F , belonging to two new structure types that differ from that of the $M\text{TeO}_3\text{F}$ ($M = \text{Fe}$, Ga and Cr) series.

In ScTeO_3F , the Te^{IV} ion is bonded to three O atoms (O1, O2 and O3) and occupies the center of a tetrahedron whose fourth corner corresponds to the direction of the stereochemically active lone pair E (Fig. 1 and Table 1). If weak bonds are considered, Te1 is connected to two additional O atoms at more remote distances.

Atoms Sc1 and Sc2 occupy two different sixfold-coordinated sites. Atom Sc1 occupies the center of an ScO_6 irregular octahedron with two shorter and four slightly longer Sc1—O bonds (Fig. 2*a* and Table 1). Atom Sc2 is located at the center of an almost regular ScF_4O_2 octahedron in which the F atoms occupy the square base and the O atoms the two apices (Fig. 2*b*). Sc^{III} cations are generally six-coordinated by O atoms in oxides and can be sevenfold coordinated in mixed oxyfluorides, for example in ScOF belonging to the ZrO_2 baddeleyite type (Vlasse *et al.*, 1979). The ScO_6 octahedra are often irregular with a low point symmetry and Sc—O distances generally ranging from 2.0 to 2.25 Å or longer. The octahedra evidenced in ScTeO_3F are in agreement with those described in most Sc oxide phases.

The ScTeO_3F structure results from the stacking of two types of scandium layers interconnected *via* layers of isolated TeO_3 polyhedra.

The first type of layer consists of Sc1O_6 octahedra sharing O1···O1 edges in the [100] direction, so forming 'zigzag' chains (Fig. 3*a*). These chains are similar to those observed in

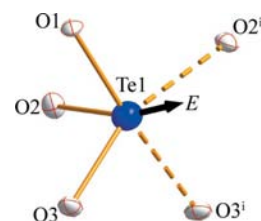


Figure 1

The tellurium coordination in ScTeO_3F . The arrow indicates the direction towards which the lone pair E points. [Symmetry code: (i) $x + \frac{1}{2}, y, -z$.]

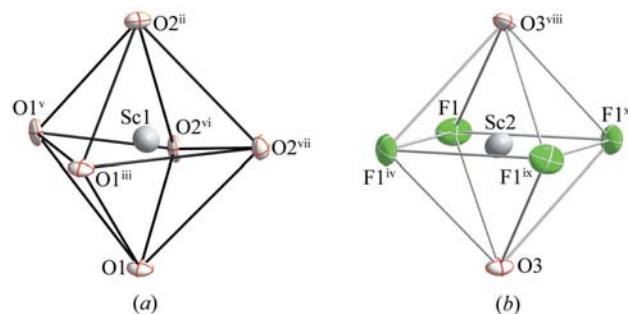


Figure 2

(*a*) The coordination polyhedron of Sc1 in ScTeO_3F . [Symmetry codes: (ii) $-x + \frac{1}{2}, -y + 1, z + 1$; (iii) $-x, -y + 1, -z + 1$; (v) $-x + \frac{1}{2}, -y + 1, z$; (vi) $x + \frac{1}{2}, y, -z + 1$; (vii) $x, y, z + 1$.] (*b*) The coordination polyhedron of Sc2 in ScTeO_3F . [Symmetry codes: (iv) $x - \frac{1}{2}, y, -z + 1$; (viii) $x, -y + \frac{1}{2}, -z + \frac{1}{2}$; (ix) $x - \frac{1}{2}, -y + \frac{1}{2}, z - \frac{1}{2}$; (x) $x, -y + \frac{1}{2}, -z + \frac{1}{2}$.]

the MoOCl_3 structure (Hyde & Andersson, 1989) and to the zigzag chains of MO_4F_2 octahedra, alternately sharing $\text{O}\cdots\text{O}$ and $\text{F}\cdots\text{F}$ edges, in the MTeO_3F ($M = \text{Fe}, \text{Ga}$ and Cr) series (Laval *et al.*, 2008). Along the $[001]$ direction, successive parallel chains are interconnected *via* O1 and O2 corners of TeO_3 polyhedra, so forming layers perpendicular to the $[010]$ direction. In the MTeO_3F ($M = \text{Fe}, \text{Ga}$ and Cr) type, zigzag chains of octahedra are also interconnected *via* TeO_3 polyhedra, giving a structure related to the $\alpha\text{-PbO}_2$ classical type of hcp framework (Hyde & Andersson, 1989). However, this last interconnection occurs on one side *via* one O3 corner and on the other side *via* O1 and O2 corners belonging to three different chains of the same type. In ScTeO_3F , the O3 atoms of the TeO_3 polyhedra are shared with Sc2 atoms belonging to a second completely different type of layer.

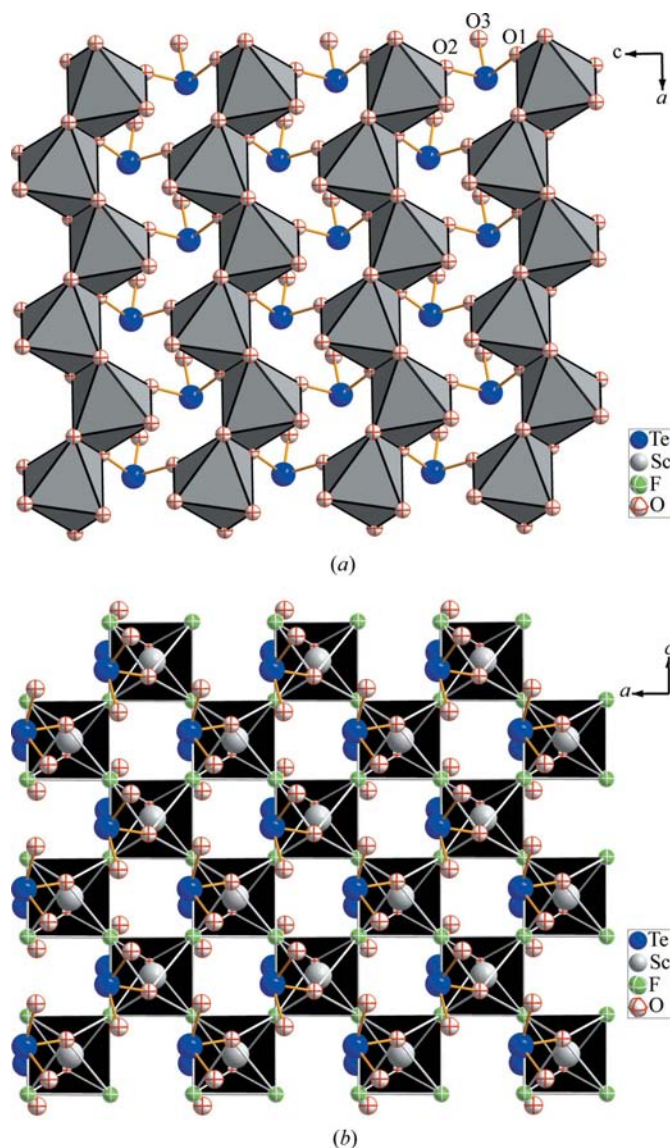


Figure 3
(a) A projection on to (101) , showing the $\text{Sc}_1\text{O}_{4n+2}$ chains linked through $\text{O}-\text{Te}-\text{O}$ bridges. (b) A projection on to (101) , showing the layer of $\text{Sc}_2\text{O}_2\text{F}_4$ octahedra (SnF_4 -type network).

This second type of layer (Fig. 3b), perpendicular to the $[010]$ axis, consists of F1 corner-connected tilted $\text{Sc}_2\text{O}_2\text{F}_4$ octahedra forming a square 4^4 plane net similar to the plane net of SnF_6 octahedra described in the SnF_4 type (Wells, 1975). Two TeO_3 isolated units are connected to each Sc2 atom above and below the empty square holes of the 4^4 plane net through O3 corners. However, the Te1 atoms are not located above and below the center of these square holes, which would give overly long $\text{Te1}-\text{O3}$ bonds, like, for example, the $\text{Ca}-\text{O}$ bonds in CaTiO_3 perovskite (Hyde & Andersson, 1989), but rather are shifted along the $[100]$ direction towards the Sc2 atoms, sitting above and below an $\text{F1}\cdots\text{F1}$ edge of each $\text{Sc}_2\text{O}_2\text{F}_4$ octahedron. This shift allows a stronger connection between the Sc2 and Te1 polyhedra *via* O3 corners and releases the volume necessary for the active lone pair of Te^{IV} to be directed towards the center of the empty square holes.

Therefore, the Te atoms, located between the scandium layers, provide the connection between the $\text{Sc}_1\text{O}_{4n+2}$ chains through $\text{O1}-\text{Te1}-\text{O2}$ bridges, so forming mixed $\text{Sc}_1\text{O}_{4n+2}-\text{Te}_1\text{O}_{4n+2}$ layers, and also provide the linking of both types of layers through $\text{Te1}-\text{O3}$ bonds (Fig. 4). This constitutes the main difference from the MTeO_3F ($M = \text{Fe}, \text{Ga}$ and Cr) type: the chains of MO_4F_2 octahedra, interconnected by TeO_3

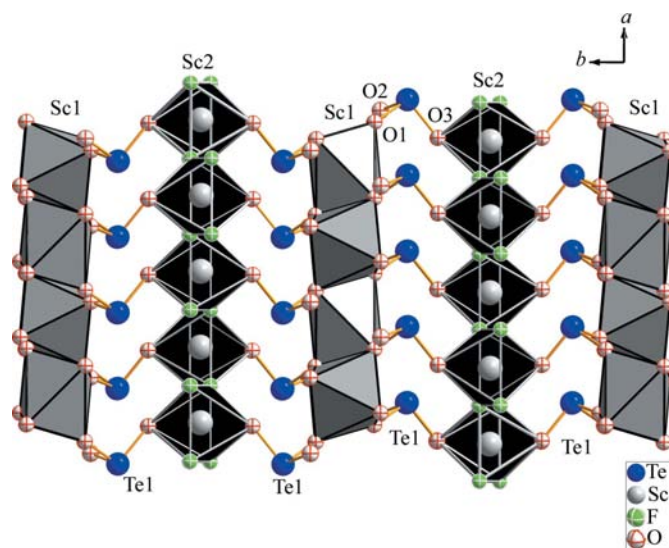


Figure 4
A projection on to (110) , showing the connection between the two scandium layers.

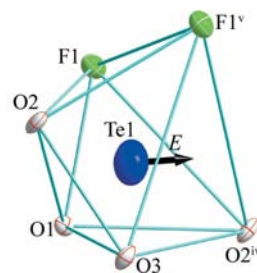


Figure 5
The tellurium coordination in InTeO_3F . The arrow indicates the direction towards which the lone pair E points. [Symmetry codes: (iv) $x + \frac{1}{2}, -y + \frac{1}{2}, z$; (v) $-x + \frac{3}{2}, y + \frac{1}{2}, -z + 1$.]

polyhedra, are replaced by alternate chains of ScO_6 and layers of ScO_2F_4 octahedra, these chains and layers being also interconnected by TeO_3 polyhedra.

In the InTeO_3F structure, the Te atom is surrounded by four O and two F atoms (Fig. 5). Three O atoms are strongly

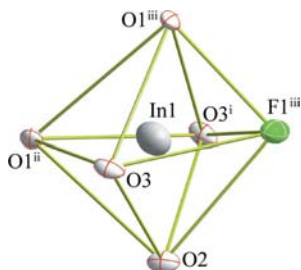


Figure 6
The coordination polyhedron of In1 in InTeO_3F . [Symmetry codes: (i) $x - \frac{1}{2}, -y + \frac{3}{2}, z$; (ii) $-x + \frac{3}{2}, y + \frac{1}{2}, -z + 2$; (iii) $x, y + 1, z$.]

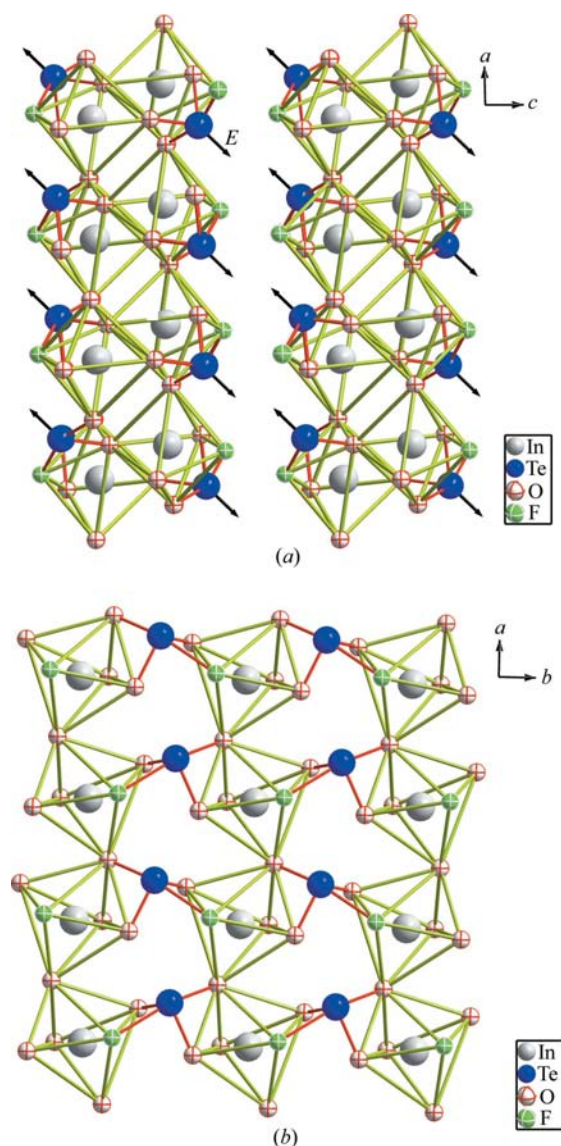


Figure 7
(a) A projection on to (101), showing the zigzag sheets of InO_5F and the interlayer spaces. (b) A projection on to (110), showing a single sheet of InO_5F octahedra connected through TeO_3F units.

bonded at distances less than 2 Å, while the first Te—F bond is somewhat longer, and the fourth O ($\text{O}2^{\text{iv}}$) and the second F ($\text{F}1^{\text{v}}$) atoms are weakly bonded at much longer distances (Table 3). The corresponding complete polyhedron can be described as a distorted TeO_4F_2 octahedron. The stereochemically active lone pair E is located between the two longest bonds. Taking into account only the four shortest bonds, TeO_3F is a square pyramid whose vertex is occupied by the lone pair E , but in a first approximation, it can also be described as a TeO_3 trigonal bipyramid, like those in the other $M\text{TeO}_3\text{F}$ structures. The In atom is sixfold coordinated. It is slightly shifted from the center of a distorted InO_5F octahedron (Fig. 6).

The InTeO_3F structure consists of zigzag sheets of InO_5F octahedra separated by spaces into which the stereochemically active lone pair E of the Te atom is directed (Fig. 7a). Each sheet is formed by isolated chains of tilted InO_5F octahedra sharing O-atom corners and connected by TeO_3F polyhedra (Fig. 7b). Contrary to the two other $M\text{TeO}_3\text{F}$ types in which TeO_3 polyhedra connect single sheets of M octahedra, in InTeO_3F , the TeO_3F polyhedra form with the zigzag sheets of InO_5F octahedra independent double (InTeO_3F)_n sheets, with the lone pairs pointing to the space between successive sheets. Therefore, InTeO_3F is a true layer structure, different from the two other $M\text{TeO}_3\text{F}$ types, with only weak Te—O and Te—F bonds connecting the double sheets (Fig. 8).

Bond valence calculations (Brown, 1981) show O-atom valences ranging from 2.04 to 2.14 and from 2.00 to 2.23, and F valences as 0.96 and 0.82 in ScTeO_3F (Table 2) and InTeO_3F (Table 4), respectively. It must be noted that, in most oxyfluorides, the calculated anionic valences are sometimes

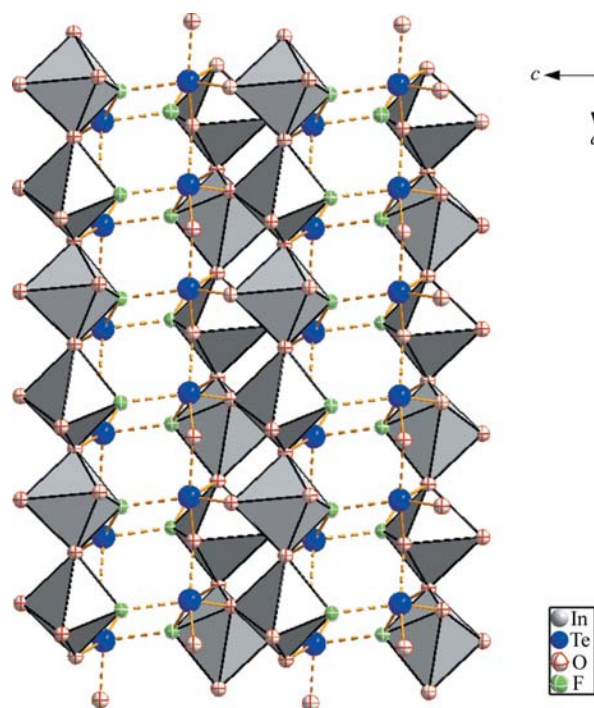


Figure 8
The three-dimensional framework of InTeO_3F , taking into account the weak Te—O and Te—F bonds.

imprecise. The discrepancies can be attributed to imperfect electrostatic equilibrium in some cases, to the empirical character of the constants used in Brown's equation and to a poor knowledge of the ionic radii of rare elements (*e.g.* scandium), based on a limited number of solved structures. In spite of these limitations, the calculated valences of atoms Sc1, Sc2, In1 and Te1 are very close to their ideal values, which are consistent with a full O/F ordering in both ScTeO₃F and InTeO₃F.

In conclusion, these three structure types differ in the manner of connection of the *M*(O,F)₆ octahedra and in the respective O/F distribution in these octahedra, but they have an interesting common feature: in the *M*TeO₃F (*M* = Fe, Cr and Ga) type, in ScTeO₃F and to a first approximation in InTeO₃F, the fluoride anions are not directly bonded to the tellurium cations, which are threefold coordinated by O atoms only. This feature draws these compounds closer to Te oxides than to the Te fluorides or oxyfluorides described previously, the latter phases being characterized by four- or fivefold coordination (Guillet *et al.*, 1999, 2001; Ider *et al.*, 1996, 1999). This may also explain the unusually high thermal and chemical stability of these phases compared with the main oxyfluoro-tellurates(IV) already known.

Experimental

ScTeO₃F was prepared by a solid-state reaction. A mixture of Sc₂O₃ (Aldrich, 99%), ScF₃ (Aldrich, 99%) and TeO₂ (1:1:3) was heated in a platinum sealed tube. The temperature was progressively increased to 1123 K, held for 48 h and water-quenched to room temperature. TeO₂ was prepared by decomposition of commercial H₆TeO₆ (Aldrich, 99.9%) at 823 K under flowing oxygen. For the preparation of InTeO₃F, a mixture of InF₃ (Aldrich, 99.9%) and TeO₂ (1.8:1) was heated in a sealed platinum tube as follows: the temperature was increased from 298 to 943 K (5 K min⁻¹), held at this temperature for 106 h, decreased slowly to 673 K (0.1 K min⁻¹) and held at this temperature for 164 h. The tube was then water-quenched. Transparent tablet-shaped single crystals, air-stable and suitable for X-ray diffraction study, were obtained in both cases.

ScTeO₃F

Crystal data

ScTeO ₃ F	$V = 700.6$ (2) Å ³
$M_r = 239.56$	$Z = 8$
Orthorhombic, <i>Pnna</i>	Mo <i>K</i> α radiation
$a = 5.7740$ (5) Å	$\mu = 10.13$ mm ⁻¹
$b = 22.062$ (5) Å	$T = 293$ (2) K
$c = 5.5000$ (12) Å	$0.1 \times 0.08 \times 0.04$ mm

Data collection

Nonius KappaCCD diffractometer	17528 measured reflections
Absorption correction: multi-scan (SADABS; Bruker 2004)	1019 independent reflections
$T_{\min} = 0.363$, $T_{\max} = 0.667$	895 reflections with $I > 2\sigma(I)$
	$R_{\text{int}} = 0.045$

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.018$	57 parameters
$wR(F^2) = 0.035$	$\Delta\rho_{\text{max}} = 0.98$ e Å ⁻³
$S = 1.18$	$\Delta\rho_{\text{min}} = -1.00$ e Å ⁻³
1019 reflections	

Table 1

Selected bond lengths (Å) for ScTeO₃F.

Te1—O2	1.854 (2)	Sc1—O1 ⁱⁱⁱ	2.142 (2)
Te1—O3	1.876 (2)	Sc1—O1	2.174 (2)
Te1—O1	1.912 (2)	Sc2—F1 ^{iv}	2.017 (2)
Te1—O3 ⁱ	2.664 (2)	Sc2—F1	2.047 (2)
Te1—O2 ⁱ	2.766 (2)	Sc2—O3	2.057 (2)
Sc1—O2 ⁱⁱ	2.022 (2)		

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

Table 2

Bond valences for ScTeO₃F.

Atoms	Sc1	Sc2	Te1	V_{ij}
O1	$2 \times 0.453/2 \times 0.415$	—	1.192	2.06
O2	2×0.627	—	1.396/0.119	2.14
O3	—	2×0.570	1.314/0.156	2.04
F1	—	$2 \times 0.498/2 \times 0.459$	—	0.96
V_{ij}	2.99	3.05	4.18	—

Table 3

Selected bond lengths (Å) for InTeO₃F.

In1—O3 ⁱ	2.097 (4)	Te1—O2	1.868 (4)
In1—O2	2.112 (4)	Te1—O1	1.917 (4)
In1—O1 ⁱⁱ	2.122 (4)	Te1—O3	1.968 (4)
In1—O1 ⁱⁱⁱ	2.157 (4)	Te1—F1	2.273 (4)
In1—F1 ⁱⁱⁱ	2.157 (4)	Te1—O2 ^{iv}	2.674 (4)
In1—O3	2.260 (4)	Te1—F1 ^v	2.782 (3)

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

Table 4

Bond valences for InTeO₃F.

Atoms	Te1	In1	V_{ij}
O1	1.176	0.552/0.502	2.23
O2	1.343/0.152	0.567	2.06
O3	1.025	0.59/0.38	2.00
F1	0.336/0.110	0.373	0.82
V_{ij}	4.14	2.96	—

InTeO₃F

Crystal data

InTeO ₃ F	$V = 344.35$ (9) Å ³
$M_r = 309.42$	$Z = 4$
Monoclinic, <i>P2₁/a</i>	Mo <i>K</i> α radiation
$a = 7.9395$ (11) Å	$\mu = 15.03$ mm ⁻¹
$b = 5.3867$ (8) Å	$T = 293$ (2) K
$c = 8.0529$ (12) Å	$0.06 \times 0.04 \times 0.02$ mm
$\beta = 91.058$ (13)°	

Data collection

Nonius KappaCCD diffractometer	7758 measured reflections
Absorption correction: multi-scan (SADABS; Bruker 2004)	1187 independent reflections
$T_{\min} = 0.406$, $T_{\max} = 0.740$	1044 reflections with $I > 2\sigma(I)$
	$R_{\text{int}} = 0.045$

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.029$	56 parameters
$wR(F^2) = 0.086$	$\Delta\rho_{\text{max}} = 4.37$ e Å ⁻³
$S = 1.06$	$\Delta\rho_{\text{min}} = -2.73$ e Å ⁻³
1187 reflections	

The residuals of electron density are minimal for ScTeO_3F , but for InTeO_3F , a residual density peak of $4.37 \text{ e } \text{\AA}^{-3}$ persists 0.6 \AA from Te1. It clearly cannot correspond to an extra atom but more likely to an imperfect absorption correction, resulting from the much more irregular shape and poorer quality of the single crystal of InTeO_3F . However, the structural results do not seem adversely affected, as attested by the reasonable R factors, interatomic distances and bond valences.

For both compounds, data collection: *COLLECT* (Nonius, 1997); cell refinement: *DIRAX/LSQ* (Duisenberg, 1992); data reduction: *EVALCCD* (Duisenberg *et al.*, 2003); program(s) used to solve structure: *SHELXS97* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008); molecular graphics: *DIAMOND* (Brandenburg, 1999); software used to prepare material for publication: *SHELXL97*.

Supplementary data for this paper are available from the IUCr electronic archives (Reference: SQ3138). Services for accessing these data are described at the back of the journal.

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