

Orthorhombic aluminium oxyfluoride,  
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Crystals of the title compound were extracted from the bulk of grown SrAlF<sub>5</sub> crystals as unexpected inclusions that were identified as the long sought after aluminium oxyfluoride. The structure of AlOF is built up from tetrahedral and octahedral polyhedra. Each tetrahedron is bisected by a mirror plane, with the Al atom and two vertex anions in the plane. All tetrahedral vertices are positions of competing oxide and fluoride ions and are shared with octahedra. These shared vertices belong to two octahedral edges which join the octahedra to form infinite zigzag chains. The chains are strung along twofold screw axes that run parallel to the unit-cell *b* axis. The remaining two octahedral vertices are occupied only by fluoride ions. A small deficiency in the occupation of the octahedral Al position was suggested by the refinement. However, the stoichiometry of the compound is AlOF within experimental uncertainty. The Al–F(O) distances are separated into three groups with average values of 1.652 (3) (tetrahedra), 1.800 (2) (octahedra) and 1.894 (2) Å (octahedra). This structure differs widely from the reported tetragonal phase Al<sub>1–x</sub>O<sub>1–3x</sub>F<sub>1+3x</sub> (*x* = 0.0886) [Kutoglu (1992). *Z. Kristallogr.* **199**, 197–201], which consists solely of octahedral structural units.

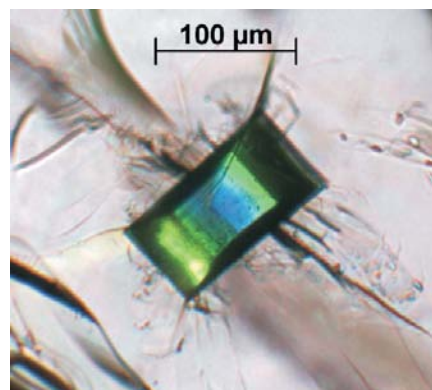
## Comment

Aluminium oxyhalides, especially the bromides and iodides, are frequently present in industrial processes, often as so-called unwanted by-products. An example of their occurrence is the deterioration of discharge lamps, where polycrystalline alumina is preferred over quartz as the material for the envelope of the lamp. During operation there is some corrosion of the alumina wall. This is believed to be due to the formation of AlX<sub>3</sub> and AlOX, where X is a halogen (Swihart & Catoire, 2000). Another occurrence of aluminium oxyhalides is the cathode surface in the aluminium electrolysis cell

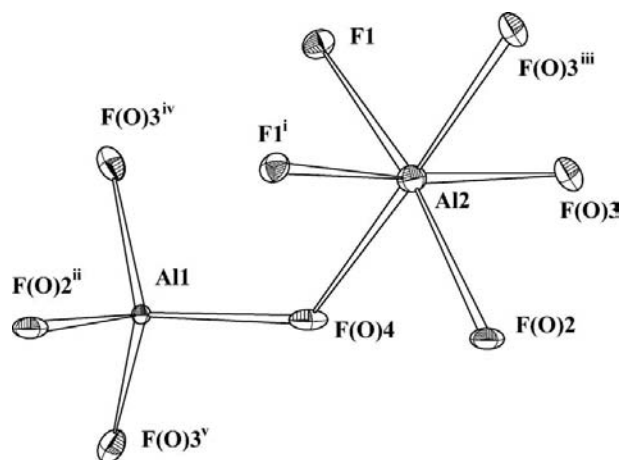
(Sharapova *et al.*, 2005). Petrographic analysis of cell materials has revealed oxyfluoride glasses with variable compositions of AlOF<sub>1–x</sub> and with index of refraction *n* = 1.33–1.362. Although the crystalline aluminium oxyhalides AlOCl, AlOBr and AlOI are known (Rouxel, 1962; Hagenmuller, Rouxel & le Neindre, 1961; Hagenmuller, Rouxel *et al.*, 1961; Schafer *et al.*, 1958), the corresponding compound AlOF is absent from the FIZ/NIST Inorganic Crystal Structure Database (Release 2008; ICSD, 2008). Some authors have tried to prepare AlOF using the procedure commonly used to prepare the other AlOX compounds, namely the reaction of AlF<sub>3</sub> with As<sub>2</sub>O<sub>3</sub> in a sealed evacuated glass ampoule at elevated temperatures. However, the stoichiometric compound was not formed at temperatures up to 750 K (Siegel & Johnson, 1964). The crystal structure of tetragonal Al<sub>1–x</sub>O<sub>1–3x</sub>F<sub>1+3x</sub> (*x* = 0.0886) with the rutile structure has been reported (Kutoglu, 1992).

During examination of SrAlF<sub>5</sub> single crystals synthesized from the melt using the Bridgman technique, some crystalline inclusions into the basal crystalline body were detected. Optical polarization investigations revealed considerable variation within the grown crystals, with a rough extinction due to blockings, systematic distortions and crystal inclusions. The inclusions have the form of small faceted crystals, distributed randomly over the bulk of the matrix substance (Fig. 1). The birefringence of the inclusions is greater by an order of magnitude than that of the matrix SrAlF<sub>5</sub> crystal, indicating that the inclusions may be grown crystals with another composition. Such inclusions are believed to be the consequence of a small excess of AlF<sub>3</sub> included in the reaction mixture, as they were not present if a rigorously stoichiometric loading of the components was implemented for the synthesis.

It has been observed that during repeated thermal cycling to 800 K, the matrix substance becomes more and more cracked near the inclusions. We were therefore readily able to pull some inclusions out of the matrix SrAlF<sub>5</sub> crystal for subsequent experiments. They were found to be without damage, transparent, and with ideal orthorhombic faceting and straight extinctions. The value of the birefringence ( $\Delta n_b = n_a - n_c$ ) in a pinacoid with a thickness of 40 µm is 0.0113. The temperature dependence of the birefringence shows that the



**Figure 1**  
Photograph of the AlOF inclusion into the SrAlF<sub>5</sub> crystal body.

**Figure 2**

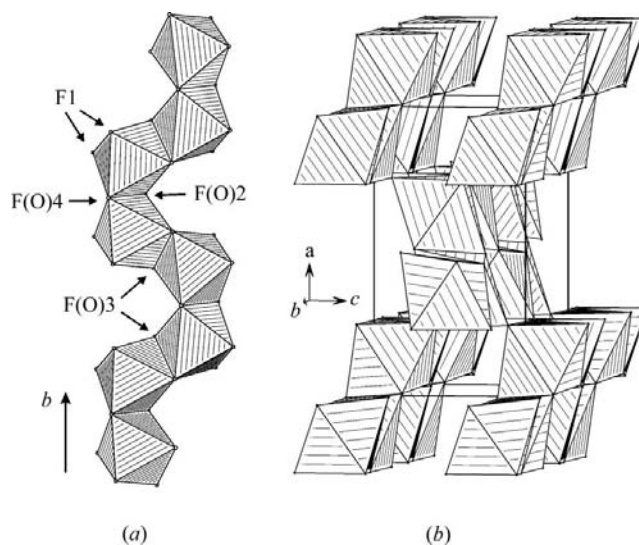
The asymmetric unit of the AIOF structure, showing the atom-labelling scheme. Symmetry-equivalent anions are shown to complete the Al coordination polyhedra. The labels point to several symmetry-related positions of the specified atoms. [Symmetry codes: (i)  $\frac{1}{2} - x, 1 - y, \frac{1}{2} + z$ ; (ii)  $x - \frac{1}{2}, \frac{1}{2} - y, \frac{3}{2} - z$ ; (iii)  $1 - x, 1 - y, 1 - z$ ; (iv)  $x - \frac{1}{2}, y, \frac{1}{2} - z$ ; (v)  $x - \frac{1}{2}, \frac{1}{2} - y, \frac{1}{2} - z$ .]

optical anisotropy of the included crystals varies only slightly up to 800 K with no appreciable anomalies.

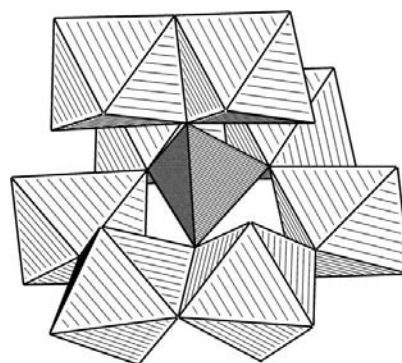
The structure of the included AIOF crystals consists of  $\text{AlF}(\text{O})_6$  octahedra and  $\text{AlF}(\text{O})_4$  tetrahedra (Fig. 2). Connecting *via* their edges, the octahedra line up in a zigzag chain along the unit-cell *b* axis (Fig. 3*a*) and common edges are formed from the competitive F/O sites only. Each chain is connected to four adjacent chains *via* the F1 vertices (Fig. 3*b*). In addition, every F/O ion is the vertex of a tetrahedron which joins three adjacent octahedral chains in the same manner (Fig. 4). As a result, the tetrahedra have common vertices with the octahedra and do not connect to one another.

The interionic distances are strictly separated into three groups. The Al–F(O) distances are  $2 \times 1.650$  (2), 1.652 (3) and 1.658 (3) Å in the tetrahedron, but 1.885 (2),  $2 \times 1.896$  (2) and 1.900 (2) Å in the octahedron, and the Al–F distances in the octahedron are 1.792 (2) and 1.808 (2) Å. Tetrahedral distortions are minimal, with tetrahedral angles in the range 107.44 (13)–110.23 (9)°. The interior octahedral angles differ from 90° by as much as 10.5°. By contrast, in the reported tetragonal phase  $\text{Al}_{1-x}\text{O}_{1-3x}\text{F}_{1+3x}$  ( $x = 0.0886$ ; Kutoglu, 1992), the basic structural elements are octahedra which are joined *via* edges and form infinite columns along the *c* direction of the unit cell. Each column is connected *via* all its vertices to four adjacent columns. The Al–F(O) distances are 1.980 (1) and 1.982 (1) Å.

We attempted to refine the site-occupancy factors (s.o.f.) for all ions in the structure. The refinement revealed that ions Al1 and F1 occupy their positions completely, while the Al2 position appears to possess some deficiency. Separate refinements of s.o.f.(Al2) and s.o.f.(O and F) with charge-balance retention have shown that, to within two standard uncertainties, s.o.f.(O) = 72% and s.o.f.(F) = 26% in all positions except F1. Meanwhile, s.o.f.(Al2) = 0.977 (4) and the *R* factor was lowered slightly to 0.0297. Based on this refinement, we may

**Figure 3**

The octahedral ordering in AIOF crystals, showing (a) the octahedral chain in the structure,  $(\bar{1}01)$  plane projection, and (b) the unit cell completed with the octahedral chains.

**Figure 4**

The connections of the tetrahedron (centre, shaded darker) in the structure.

assign to the crystal under investigation the composition  $\text{Al}_{0.987}\text{O}_{0.96}\text{F}_{1.04}$ , with about 2% deficiency of Al2 in the octahedral position. Nevertheless, within the range of three standard uncertainties, the composition of the compound is AIOF. Consequently, in the final refinement, the Al2 site was treated as fully occupied and the mixed F/O sites were fixed at 25% F and 75% O. We cannot, however, rule out a slight nonstoichiometry in this compound.

## Experimental

$\text{AlF}_3$  (99.99%) and  $\text{SrF}_2$  (99.99%) were used as starting reagents. Due to the high volatility of  $\text{AlF}_3$ , it was added in a 2–5% excess to the starting reaction mixture. The crystallization temperature was 1140 K. The excess of  $\text{AlF}_3$  appears to be necessary for the formation of the AIOF inclusions; when exact stoichiometric amounts of the reagents were used, no inclusions formed in the product  $\text{SrAlF}_5$  crystals. The optical quality of the grown transparent single crystals of  $\text{SrAlF}_5$  was studied using an Axioskop 40 Pol polarizing microscope with high permittivity and contrast objective 'Plan-Neofluar' (Zeiss).

## Crystal data

AIOF	$V = 346.44 (14) \text{ \AA}^3$
$M_r = 61.98$	$Z = 12$
Orthorhombic, <i>Pnma</i>	Mo $K\alpha$ radiation
$a = 8.825 (2) \text{ \AA}$	$\mu = 1.08 \text{ mm}^{-1}$
$b = 8.408 (2) \text{ \AA}$	$T = 299 \text{ K}$
$c = 4.669 (1) \text{ \AA}$	$0.15 \times 0.08 \times 0.04 \text{ mm}$

## Data collection

Bruker SMART APEXII 4K CCD area-detector diffractometer	2858 measured reflections
Absorption correction: multi-scan (SADABS; Sheldrick, 2004)	441 independent reflections
$T_{\min} = 0.818, T_{\max} = 0.958$	337 reflections with $I > 2\sigma(I)$
	$R_{\text{int}} = 0.055$

## Refinement

$R[F^2 > 2\sigma(F^2)] = 0.031$	49 parameters
$wR(F^2) = 0.078$	$\Delta\rho_{\max} = 0.46 \text{ e \AA}^{-3}$
$S = 1.02$	$\Delta\rho_{\min} = -0.55 \text{ e \AA}^{-3}$
441 reflections	

A transparent colourless crystal inclusion was chosen for structure studies. Neither Patterson function nor direct methods produced a correct structure solution. Repeated electron-density syntheses with a cull of 'atoms' which acquired heightened displacement parameters, new maxima substitution and variation of atom types allowed us to isolate octahedral and tetrahedral configurations among the maxima disposition and then to define the elemental composition. The analysis indicated that Al is the only metal in the structure. Subsequent refinement of the structural model required the introduction of oxide ions which occupy positions in competition with the fluoride ions. The model refined well under the assumption that the Al, fluoride and oxide ions take part in the compound in equal amounts. The F and O ions compete everywhere in an F:O ratio of 1:3, except in the case of the F1 position, where the O does not admix.

Data collection: *SMART* (Bruker, 2001); cell refinement: *SAINTE-Plus* (Bruker, 2001); data reduction: *SAINTE-Plus*; program(s) used to solve structure: *SHELXTL* (Sheldrick, 2008); program(s) used to refine structure: *SHELXTL*; molecular graphics: *SHELXTL*; software used to prepare material for publication: *SHELXTL*.

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: SQ3190). Services for accessing these data are described at the back of the journal.

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