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The Crystal Structures of Er_3OFS_3 and $Er_3OF_3S_2$: Two Erbium Oxide Fluoride Sulfides with Condensed Tetrahedral $[ZEr_4]$ Units (Z = O and F)

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Dedicated to Professor Martin Jansen on the Occasion of his 65th Birthday

Abstract. The two new compounds Er_3OFS_3 and $Er_3OF_3S_2$ vary mostly in their fluoride and sulfide content. The fluoride-poor erbium(III) oxide fluoride sulfide Er_3OFS_3 crystallizes in the tetragonal space group *I*4/*mmm* (*a* = 374.86(2), *c* = 2068.41(9) pm, *Z* = 2) with two crystallographically different Er^{3+} cations. $(Er1)^{3+}$ is surrounded by six S^{2-} anions in the shape of a slightly distorted octahedron, whereas $(Er2)^{3+}$ exhibits a coordination number of eight (4 × O^{2-}/F^- and 4 × S^{2-} arranged as a square antiprism). In the crystal structure of Er_3OFS_3 edge-sharing tetrahedral $[ZEr_4]^{10.5+}$ units (Z^{n-} = 50% O^{2-} + 50% F^-) form condensed $^2_\infty[OFEr_2]^{3+}$ layers. These layers alternate with $^2_\infty[ErS_3]^{3-}$ sheets, built up of $[ErS_6]^{9-}$ octahedra, which are connected via four common edges, to complete the three-dimensional crystal structure of Er_3OFS_3. The fluoride-rich erbium(III) oxide fluoride sulfide $Er_3OF_3S_2$ crystallizes in the orthorhombic space group *Ccce* (*a* = 538.31(2), *b* = 1892.03(9), *c* = 538.27(2) pm, *Z* = 4). Two crystallographically distinct Er^{3+} cations are present in its crystal structure. $(Er1)^{3+}$ is surrounded by eight Z^{n-} anions (Z = 25% O^{2-} + 75% F^-) in the shape of a twisted square antiprism, while $(Er2)^{3+}$ holds a coordination number of nine (4 × O^{2-}/F^- and 5 × S^{2-} arranged as a monocapped square antiprism), copying the coordination geometry of the Er^{3+} cations in PbFCl-type ErFS. The three-dimensional structure of $Er_3OF_3S_2$ is built up of S^{2-} sheets and $^2_\infty[OF_3Er_3]^{4+}$ double layers, which are formed by strongly contorted tetrahedral $[ZEr_4]^{10.75+}$ units (Z^{n-} = 25% O^{2-} + 75% F^-). The crystals of this compound show a prominent superstructure in the tetragonal space group *I*4/*mmm* with *a* = 380.59(3), c = 1892.03(9) pm and *Z* = 2. In the crystal structures of both title compounds, the light anions O^{2-} and F^- occupy one crystallographically unique *Wyckoff* position in a statistic allocation. Subject to the O/F content in the formulae, the ratio of O^{2-} : F^- is 1 : 1 in Er_3OFS_3 and 1 : 3 in $Er_3OF_3S_2$.

Keywords: Erbium; Oxides; Fluorides; Sulfides; Crystal Structures

Introduction

Oxide fluoride sulfides of the rare-earth metals demonstrate an interesting research topic, since they are closely related to rare-earth metal oxide sulfides, which are currently used in technical applications, for example as phosphors in X-ray imaging detectors [1–3]. Although, the mere oxide sulfides appear yet in many different formulae and structure types (*e. g.* M_2O_2S, M_2OS_2 or $M_{10}OS_{14}$, M = rare-earth metal [4–7]) substitution of oxygen by fluorine (*e. g.* MFS, M = La – Nd, Gd – Lu [8]) or plain insertion of fluoride anions into rare-earth metal oxide sulfides (*e. g.* $Ce_6O_2F_8S_3$ [9], Dy_3OF_5S [10]) may result in many new materials with special characteristics. Remarkably, in the crystal structures of almost all rare-earth metal compounds comprising light anions (Z^{n-} = F^-, O^{2-} or N^{3-}), condensed $[ZM_4]^{m+}$ tetrahedra provide an important building block, which is responsible for several physical properties. For example, layers of edge-sharing $[OM_4]^{10+}$ tetrahedra can cause magnetic frustration [11] or work as energy preserving hosts for luminescence [12, 13]. Even the nowadays so prominent high-T_C-superconductors with the formula type $M(O_{1-x}F_x)FeAs$ [14–16] exhibit this kind of layers, although there, these $\{M(O_{1-x}F_x)\}$ layers serve only as spacers. However, not just the light-anion part of the crystal structure, but also the interaction of light and heavy anions, as well as the coordination geometry around the rare-earth cations account for property variations in light-anion derivatives of rare-earth metal sulfides. For instance optical characteristics of lanthanum oxide sulfides compared to those of lanthanum oxide fluoride sulfides vary significantly [17], which is not least due to the different surroundings for the La^{3+} cations within these compounds. To obtain a good understanding of structure-property relationships, a precise description of the atomic arrangement is essential. Thus, it is potentially feasible to gain a tool to "design" desired materials.

In this paper, the crystal structures of two new erbium(III) oxide fluoride sulfides are presented, to show the diversities of two, at the first glance, quite similar compounds. On the one hand the fluoride-poor but sulfur-rich Er_3OFS_3 and on the other hand the fluoride-rich but sulfur-poor $Er_3OF_3S_2$.

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Experimental Section

Synthesis

Both title compounds accrued as unintentionally formed by-products, due to some oxygen contamination of the reaction mixtures. In attempts to synthesize ErFS, quite a few transparent, pinkish, flake-shaped crystals of $Er_3OF_3S_2$ developed in a reaction of elemental erbium (99.9 % ChemPur, Karlsruhe, Germany) and sulfur (99.999 % ChemPur, Karlsruhe, Germany) with erbium trifluoride (99.9 % ChemPur, Karlsruhe, Germany) in silica-covered, arc-welded tantalum capsules after five days at 850 °C. NaCl (99.9 % E. Merck, Darmstadt, Germany) as fluxing agent helped to grow crystals, which were large enough for single crystal X-ray diffraction. A pure sample of $Er_3OF_3S_2$ was obtained by annealing a mixture of erbium metal (99.9 % ChemPur, Karlsruhe, Germany), ErF_3 (99.9 % ChemPur, Karlsruhe, Germany), Er_2O_3 (99.9 % ChemPur, Karlsruhe, Germany) and elemental sulfur (99.999 % ChemPur, Karlsruhe, Germany) in a molar ratio of 4:3:1:6 for seven days at 850 °C in silica-jacketed, gastightly sealed tantalum ampoules. This procedure is not limited to erbium, as in that way phase-pure samples of $M_3OF_3S_2$-type oxide fluoride sulfides with M = Y, Ho – Yb can be synthesized as well [18]. The other compound Er_3OFS_3 arose as transparent, orange, slat-shaped crystals from a product lump after a reaction of Er_2S_3 (made from elemental erbium metal and sulfur, according to [19]), ErF_3 (99.9 % ChemPur, Karlsruhe, Germany), As_2S_3 (99.9 % E. Merck, Darmstadt, Germany) and CsI (99.9 % E. Merck, Darmstadt, Germany) as fluxing agent in evacuated silica ampoules at 700 °C within 7 days. Attempts to synthesize the pure material Er_3OFS_3 without As_2S_3 as fluxing agent and additional Er_2O_3 (99.9 % ChemPur, Karlsruhe, Germany) as oxygen source were not successful so far.

X-Ray Crystallography

Intensity data sets for single crystals of Er_3OFS_2 and $Er_3OF_3S_3$ were collected on a Nonius Kappa-CCD diffractometer using graphite-monochromatized Mo-Kα radiation (wavelength: λ = 71.07 pm). Numerical absorption corrections were performed with the help of the program HABITUS [20]. The structure solutions and refinements were carried out by using the program package SHELX-97 [21]. Details of the data collections and the structure refinements [22] are summarized in Table 1, atomic positions and coefficients of the isotropic thermal displacement parameters [23] are given in Table 2, interatomic distances and selected bond angles are listed in Table 3. Further details of the crystal structure investigations are available from the Fachinformationszentrum (FIZ) Karlsruhe, D-76344 Eggenstein-Leopoldshafen, Germany (Fax: +497247-808-666; E-mail: crysdata@fiz-karlsruhe.de), on quoting the depository numbers CSD-420552 for Er_3OFS_3, and CSD-420551 for $Er_3OF_3S_2$.

Electron-Beam Microprobe Analysis

The chemical compositions of Er_3OFS_2 and $Er_3OF_3S_3$ were approved by electron-beam microprobe analysis. An energy dispersive X-ray analysis (EDX) was performed on a Cameca SX 100 device to get a general composition for the crystals already used in the X-ray diffraction measurements. To affirm the presence of oxygen and fluorine and to obtain experimental data about the correct O^{2-} : F^- ratios a wavelength dispersive X-ray analysis (WDX) was carried out as well.

Results and Discussion

The crystal structures of the erbium(III) oxide fluoride sulfides Er_3OFS_3 and $Er_3OF_3S_2$ share some general features. On the one hand the light anions O^{2-} and F^- in both compounds occupy a common crystallographic site in a statistic way. Neither a crystallographic symmetry reduction, nor bond valence calculations [24, 25] give hints of any ordering in the O^{2-} and F^- positions. Furthermore, in theory the empirical formulae of the title compounds Er_3OFS_3 and $Er_3OF_3S_2$ can be derived from 3 × ErFS = $Er_3F_3S_3$ (PbFCl-type structure [26]) by substitution of two fluoride anions with one oxygen anion: $Er_3F_3S_3 - 2\ F^- + O^{2-} = Er_3OFS_3$ or one sulfur anion with one oxygen anion: $Er_3F_3S_3 - S^{2-} + O^{2-} = Er_3OF_3S_2$, respectively. This formal consideration can even be extended, regarding the crystal parameters. A-ErFS crystallizes in the tetragonal space group *P*4/*nmm* (*Z* = 2) with *a* = 374.61(3), *c* = 681.34(5) pm [8], whereas the lattice constants of likewise tetragonal Er_3OFS_3 are *a* = 374.86(2), *c* = 2068.41(9) pm (*Z* = 2) in space group *I*4/*mmm*. $Er_3OF_3S_2$ shows a superstructure with *a* = 380.59(3), *c* = 1892.03(9) pm (*Z* = 2) in space group *I*4/*mmm*, which implies a tripling in the [001] direction for both erbium(III) oxide fluoride sulfides as compared to A-type ErFS. But a closer look into the crystal structures of Er_3OFS_3 and $Er_3OF_3S_2$ proves that further similarities are only moderate.

Nevertheless, the relationship between ErFS and Er_3OFS_3 can not be denied. In the crystal structure of the sulfur-rich Er_3OFS_3 (space group *I*4/*mmm*: *a* = 374.86(2), *c* = 2068.41(9) pm, *Z* = 2) light-anion centred tetrahedral $[ZEr_4]^{10.5+}$ units (Z = 50% O^{2-} + 50% F^-) (Fig. 3) form condensed $^2_\infty[ZEr_{4/4}]^{1.5+}$ (≡ $^2_\infty[OFEr_2]^{3+}$) layers by sharing four common edges (Fig. 1). These layers are strongly related to the $^2_\infty[FEr_{4/4}]^{2+}$ sheets that form the PbFCl-type crystal structure of A-ErFS, together with S^{2-} anions. In Er_3OFS_3 the $^2_\infty[OFEr_2]^{3+}$ building units spread out parallel to the (001) plane. In addition, they alternate along [001] with $^2_\infty[ErS_{4/4}S_{2/1}]^{3-}$ (≡ $^2_\infty[ErS_3]^{3-}$) layers to complete the three-dimensional arrangement (Fig. 2). This second sort of layers is built up by octahedral $[ErS_6]^{9-}$ units, sharing four common *trans*-oriented edges (Fig. 1). In the tetragonal crystal system an octahedral $[ErS_6]^{9-}$ building block has more degrees of freedom than a polyhedron with ideal octahedral symmetry $4/m\,\bar{3}\,2/m$ (O_h) (Fig. 3). This is reflected in slightly variable interatomic distances between cations and anions in the $[ErS_6]^{9-}$ units: $d((Er1)^{3+}–(S1)^{3+})$ = 265.1 pm (4×) and $d((Er1)^{3+}–(S2)^{2-})$ = 265.4 pm (2×) (Table 3). The mean value of approximately 265 pm is in good agreement with interatomic distances found in other erbium(III) sulfides, *e. g.* D-type Er_2S_3 ($d(Er^{3+}–S^{2-})$ = 261 – 283 pm for the Er^{3+} cations with CN = 6) [19]. As a result of the different two-dimensional building blocks, two crystallographically unique Er^{3+} cations need to be present: the above described $(Er1)^{3+}$ cations, with six adjacent S^{2-} anions, and $(Er2)^{3+}$ cations, which participate in the $^2_\infty[OFEr_2]^{3+}$ layers and hold a coordination number of eight. The latter are surrounded by four S^{2-} anions and four light Z^{n-} anions (Z^{n-} = 50% O^{2-} + 50% F^-) in the shape of a square antiprism (Fig. 3). Thus, the coordination sphere of the $(Er2)^{3+}$ cations resembles the surrounding area of the Er^{3+} cations in PbFCl-type ErFS, although, compared to ErFS where the Er^{3+} cations show a coordination number of nine, the capping S^{2-} anion is missing in Er_3OFS_3. The interatomic distances for Er^{3+} cations and Z^{n-} anions ($d((Er2)^{3+}–Z^{n-})$ = 231.7 pm, 4×) within these $[ErZ_4S_4]^{11-}$ polyhedra (Z^{n-} = 50% O^{2-} + 50% F^-) lie in-between the values found in erbium(III) fluoride sulfide ($d(Er^{3+}–F^-)$ = 244 pm in A-ErFS [8]) and erbium(III) oxide sulfide ($d(Er^{3+}–O^{2-})$ = 225 – 229 pm in Er_2O_2S [7]). This indicates that the light-anion site is simultaneously occupied by O^{2-} as well as F^- anions, which is also necessary to achieve electroneutrality in this compound. Therefore, the ratio of the mixed occupation was fixed at 50% O^{2-} : 50% F^-, although, a free refinement of the occupancy factors of O^{2-} against F^- results in a ratio of 36% O^{2-} : 64% F^-. Keeping in mind that the deviation is about 14% and a refinement of O^{2-} against F^- from X-ray data is not very reliable, the value for the refined ratio ranges within the

tolerance. Furthermore, the ratio of one oxygen and one fluorine atom per formula unit is also confirmed by wavelength dispersive X-ray analysis (WDX), which results in the formula $Er_{3.08}O_{0.98}F_{0.65}S_{2.80}$. Therefore, the empirical formula Er_3OFS_3 is approved within the error of measurement. The coordination sphere for $(Er2)^{3+}$ is finally completed by four S^{2-} anions, which are 289.2 pm afar. This value is slightly larger than the space between erbium and sulfur for the sixfold coordinated $(Er1)^{3+}$ cations, but still in the range of general interatomic $d(Er^{3+}–S^{2-})$ distances [19]. So far, this structure type, in which $^{2}_{\infty}[ZM_{4/4}]$ and $^{2}_{\infty}[MX_{4/4}X_{2/1}]$ sheets (M = metal cations; Z = O^{2-}, F^{-}; X = S^{2-}, Cl^{-}) pile up, is only known for compounds with two different cationic species, *e. g.* $Bi_xCa_yO_2S_3$, $Bi_xCd_yO_2Cl_3$ [27, 28] and $U_2ErO_2S_3$ [29]. Thus, Er_3OFS_3 is the first example for this structure type with only one kind of metal cations, but a combination of two sorts of light anions.

The second erbium(III) oxide fluoride sulfide $Er_3OF_3S_2$ crystallizes in the orthorhombic crystal system (space group *Ccce*) with a = 538.31(2), b = 1892.03(9) and c = 538.27(2) pm. As in the crystal structure of the aforementioned compound, edge-sharing light-anion centred $[ZEr_4]^{10.75+}$ units (Z = 25% O^{2-} + 75% F^{-}) form condensed $^{2}_{\infty}[ZEr_{4/4}]^{1.75+}$ layers. However, two of these two-dimensional building blocks are further linked via more common edges to form $^{2}_{\infty}[ZEr_{2/8}Er_{2/4}]^{+}$ ($\equiv$ $^{2}_{\infty}[OF_3Er_3]^{4+}$) double layers (Fig. 4). Therefore, one sort of Er^{3+} cations, $(Er1)^{3+}$, is coordinated exclusively by eight of the light anions, whereas the other one, $(Er2)^{3+}$, carries five S^{2-} as well as four Z^{n-} anions (Z = 25% O^{2-} + 75% F^{-}) in the shape of a monocapped distorted square antiprism, alike the coordination for Er^{3+} cations in PbFCl-type ErFS (Fig. 5). As the space group *Ccce*, a subgroup of *I*4/*mmm* (Scheme 1), indicates, the coordination polyhedra in $Er_3OF_3S_2$ have lower symmetries as the ones in Er_3OFS_3. Thus, the tetrahedral $[ZEr_4]^{10.75+}$ units in $Er_3OF_3S_2$ with $d(Z^{n-}–Er^{3+})$ = 228.9, 229.8, 230.3 and 286.1 pm are better described as trigonal pyramids or even monocapped triangles (Fig. 5), which is a quite common coordination feature for fluoride anions. In addition, the nine interatomic distances (CN(Er2) = 7 + 2) in the capped antiprisms $[(Er2)Z_4S_5]^{12-}$ range from $d(Er^{3+}–Z^{n-})$ = 228.9 (2×), 286.1 (2×) to $d(Er^{3+}–S^{2-})$ = 278.9 (4×), 283.4 pm (1×), whereas in the $[(Er1)Z_8]^{7-}$ polyhedra the distances unite ($d(Er^{3+}–Z^{n-})$ = 229.8 (4×) and 230.3 pm (4×), Table 3), but the shape of the polyhedron is somewhere between a square antiprism and a square prism (Figs. 5 and 6) with a rotation angle of α_t = 20.2° between the two square planes (ideal prism: α_t = 0°, ideal antiprism: α_t = 45°). Like in Er_3OFS_2 the light-anion site (Z) in $Er_3OF_3S_2$ ($\equiv$ $Er_3Z_4S_2$) is occupied by O^{2-} as well as F^{-} anions. To obtain electroneutrality in this compound one out of four light anions (Z) has to be oxygen. Therefore, the occupancy of the mixed O^{2-}/F^{-} site was fixed at Z^{n-} = 25% O^{2-} : 75% F^{-}, which is in very good agreement with an O^{2-}/F^{-} ratio of 27% : 73% experimentally determined by wavelength dispersive X-ray analysis (WDX). Compounds with the same composition $M_3X_4S_2$ are already known for M = Sm, Eu, Yb [18, 30], but in these cases the light-anion site (Z) is exclusively occupied by F^{-} anions and electroneutrality is achieved by a mixed valence (M^{2+}/M^{3+}) of the metal cations. Thus, M^{3+} cations (M = Sm, Eu, Yb) represent the central atom within the $[MF_4S_5]^{11-}$ units, similar to $(Er2)^{3+}$ in $Er_3OF_3S_2$, whereas M^{2+} cations are surrounded by eight F^{-} anions in the shape of an ideal square prism (Fig. 6), alike the coordination of Ca^{2+} in the fluorite-type structure of CaF_2 [31]. These mixed-valent rare-earth metal compounds crystallize in the tetragonal crystal system with space group *I*4/*mmm* (*e. g.* a = 384.61(3), c = 1884.2(4) pm for M = Yb), in which the light anions (F^{-}) occupy the *Wyckoff* site 8*g*. For $Er_3OF_3S_2$, which bears strictly trivalent cations along with a mixture of two different anions (O^{2-}/F^{-}) on the light-anion site, a related superstructure in space group *I*4/*mmm* with a = 380.59(3), c = 1892.03(9) pm is observed, but in this symmetry the light anions (O^{2-}/F^{-}) are assigned to the *Wyckoff* site 16*n*. Thus, the light-anion site has to be half-occupied only as well as mixed allocated. Former attempts by different research groups to properly refine the crystal structures of various $M_3OF_3S_2$ representatives in orthorhombic space groups without any face centering of the translation symmetry (*e. g.* $M_3OF_3S_2$, M = La, Ce in *Pnmm* [17]) or even without inversion symmetry (*e. g.* $M_3OF_3S_2$ with M = Y, Ho and Tm in *P*222 [18, 32]) remained unsatisfying. However, a symmetry reduction to space group *Ccce*, according to the *Bärnighausen* tree [33] seen in Scheme 1, provides a better description of the crystal structure, in which at least the underoccupation is resolved. It can be easily understood, why there has to be a loss in symmetry for $Er^{(III)}{}_3OF_3S_2$ in contrast to $Yb^{(III)}{}_2Yb^{(II)}F_4S_2$, by comparing the two different anionic surroundings for the eightfold coordinated $(Er1)^{3+}$ and $(Yb1)^{2+}$ cations, respectively (Fig. 6). In the square prisms $[Yb^{(II)}F_8]^{6-}$ the gap between F^{-} anions amounts to $d(F^{-}\cdots F^{-})$ = 272 pm (4×) within the quadratic area and 311 pm (4×) within the rectangular faces. Substitution of the Yb^{2+} cations with the smaller Er^{3+} cations causes a shrinking of the thickness of the $^{2}_{\infty}[OF_3Er_3]^{4+}$ double layers, which reduces the $Z^{n-}\cdots Z^{n-}$ distance considerably. Although, the spacing $d(Z^{n-}\cdots Z^{n-})$ (Z = 25% O^{2-} : 75% F^{-}) within the square plane of the $[Er^{(III)}X_8]^{7-}$ polyhedra levels off (273 pm), the interspacing of $Z^{n-}\cdots Z^{n-}$ in the rectangular faces would amount only to about 242 pm, which is far smaller than twice the anionic radius of $r(O^{2-})$ = 138 pm or $r(F^{-})$ = 131 pm [34, 35]. Hence, due to electrostatic repulsion the quadratic faces are twisted, and the shape of the $[ErZ_8]^{7-}$ polyhedra (Z = 25% O^{2-} : 75% F^{-}) is no longer a square prism, but a hybrid between square prism and square antiprism, in which a distance $d(Z^{n-}\cdots Z^{n-})$ of 259 pm is maintained. Although, this is still a little bit smaller than double the ionic radii, such short distances between two fluoride anions are also known for other compounds, *e. g.* ErF_3 with $d(F^{-}\cdots F^{-})$ = 250 pm [36] or $ErF[MoO_4]$ with $d(F^{-}\cdots F^{-})$ = 255 pm [37]. In the special case of edge-fused planar $[FM_3]^{8+}$ triangles as found in B-type YFS and C-type LuFS $d(F^{-}\cdots F^{-})$ can even range between 230 and 235 pm [38]. Nevertheless, for $Er_3OF_3S_2$ the coordination geometry of the Er^{3+} cations can no longer be supported in the tetragonal space group *I*4/*mmm*, thus, the symmetry in $Er_3OF_3S_2$ has to be reduced. Since this is merely triggered by the light anions, the tetragonal superstructure is highly prominent and the real orthorhombic symmetry (*Ccce*) can be simply overlooked. Therefore, it is suspected that the tetragonal mixed-cationic representatives of the $Yb_3F_4S_2$-type structure, which contain alkaline-earth as well as rare-earth metals on one crystallographic position in space group *I*4/*mmm* (*e. g.* $EAM_2F_4S_2$ with *EA* = Ca, Sr and M = Sm, Ce [39]) and in which the light anions (F^{-}) also half-occupy the *Wyckoff* site 16*n*, are actually orthorhombic. Besides, it is assumed that the compounds described in [39] therefore contain some oxygen along with fluorine. Usually the cell determination on a single-crystal diffractometer results in the tetragonal supercell, which makes it difficult to refine the cell parameters from single-crystal data. Unfortunately, there are not enough crystallites of $Er_3OF_3S_2$ to properly determine the unit cell from X-ray powder diffraction data so far.

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References

[1] I. Kandarakis, D. Cavouras, *Appl. Radiat. Isot.* **2001**, *54*, 821.
[2] I. Kandarakis, D. Cavouras, *Nucl. Instrum. Methods Phys. Res. A* **2001**, *460*, 412.
[3] I. Kandarakis, D. Cavouras, *Eur. Radiol.* **2001**, *11*, 1083.
[4] F. Lissner, Th. Schleid, *J. Less-Common Met.* **1991**, *175*, 309.
[5] F. Lissner, Th. Schleid, *Z. Kristallogr.* **1993**, *205*, 117.
[6] Th. Schleid, *Z. Anorg. Allg. Chem.* **1991**, *602*, 39.
[7] H. A. Eick, *J. Am. Chem. Soc.* **1958**, *80,* 43.
[8] Th. Schleid, H. Grossholz, *Z. Anorg. Allg. Chem.* **2001**, *627*, 2693.
[9] H. Grossholz, Th. Schleid, *Z. Kristallogr.* **2000**, *Suppl. 17*, 118.
[10] H. Grossholz, Th. Schleid, *Z. Anorg. Allg.Chem.* **2002**, *268*, 1012.
[11] S. Strobel, A. Choudhury, P. K. Dorhout, C. Lipp, Th. Schleid, *Inorg. Chem.* **2008**, *47*, 4936.
[12] T. Jüstel, H. Nikol, C. Ronda, *Angew. Chem.* **1998**, *110*, 3250; *Angew. Chem. Int. Ed.* **1998**, *37*, 3048.
[13] H. A. Höppe, *Angew. Chem.* **2009**, *121*, 3626; *Angew. Chem. Int. Ed.* **2009**, *48*, 3572.
[14] H. Takahashi, K. Igawa, K. Arii, Y. Kamihara, M. Hirano, H. Hosono, *Nature* **2008**, *453*, 376.
[15] Y. Kamihara, T. Watanabe, M. Hirano, H. Hosono, *J. Am. Chem. Soc.* **2008**, *130*, 3296.
[16] D. Johrendt, R. Pöttgen, *Angew. Chem.* **2008**, *120*, 4860.
[17] D. Pauwels, A. Demourgues, H. Laronze, P. Gravereau, F. Guillen, O. Isnard, A. Tressaud, *Solid State Sci.* **2002**, *4*, 1471.
[18] H. Grossholz, Ph.D. Thesis, Universität Stuttgart, Stuttgart, **2003**.
[19] Th. Schleid, F. Lissner, *Z. Anorg. Allg. Chem.* **1992**, *615*, 19.
[20] W. Herrendoff, H. Bärnighausen, HABITUS: Program for the optimization of the crystal shape for numerical absorption correction in X-SHAPE (version 2.06, Fa. Stoe, Darmstadt 1999), Karlsruhe, Gießen, **1993, 1996**.
[21] G. M. Sheldrick, SHELX-97: Program package for solution and refinement of crystal structures from X-ray diffraction data, Göttingen, Germany, **1997**.
[22] Th. Hahn, A. J. C. Wilson, *International Tables for Crystallography, Vol. C*, 2nd ed., Kluwer Academic Publishers, Boston, Dordrecht, London, **1992**.
[23] R. X. Fischer, E. Tillmanns, *Acta Crystallogr.* **1988**, *C 44*, 775.
[24] N. E. Brese, M. O'Keeffe, *Acta Crystallogr.* **1991**, *B 47*, 192.
[25] I. D. Brown, R. D. Shannon, *Acta Crystallogr.* **1973**, *A 29*, 266.
[26] W. Nieuwenkamp, J. M. Bijvoet, *Z. Kristallogr.* **1932**, *81*, 469.
[27] L. G. Sillén, A. S. Gjoerling-Husberg, *Z. Anorg. Allg Chem.* **1941**, *248*, 121.
[28] L. G. Sillén, *Z. Anorg. Allg. Chem.* **1941**, *246*, 331.
[29] S. Jaulmes, M. Julien-Prouzol, M. Guittard, T. Vovan, P. Laruelle, J. Flahaut, *Acta Crystallogr.* **1986**, *C 42*, 1109.
[30] Th. Schleid, *Z. Anorg. Allg. Chem.* **2000**, *626*, 2429.
[31] W. L. Bragg, *Proc. R. Soc. London A* **1914**, *89*, 468.
[32] H. Grossholz, H. Müller-Bunz, Th. Schleid, unpublished.
[33] H. Bärnighausen, *MATCH-Comm. Math. Chem.* **1980**, *9*, 139.
[34] R. D. Shannon, *Acta Crystallogr.* **1976**, *A 32*, 751.
[35] R. D. Shannon, C. T. Prewitt, *Acta Crystallogr.* **1969**, *B 25*, 925.
[36] K. Krämer, H. Romstedt, H. U. Güdel, P. Fischer, A. Murasik, M. T. Fernandez-Diaz, *Eur. J. Solid State Inorg. Chem.* **1996**, *33*, 273.
[37] I. Hartenbach, S. Strobel, P. K. Dorhout, Th. Schleid, *J. Solid State Chem.* **2008**, *181*, 2828.
[38] Th. Schleid, *Z. Anorg. Allg. Chem.* **1999**, *625*, 1700.
[39] A. Demourgues, A. Tressaud, H. Laronze, P. Macaudière, *J. Alloys Compds.* **2001**, *323*, 223.
[40] R. Hoppe, *Adv. Fluorine Chem.* **1970**, *6*, 387.
[41] R. Hoppe, *Izv. Jugoslav. Centr. Krist. [Zagreb]* **1973**, *8*, 21.
[42] R. Hoppe, in *Crystal Structure and Chemical Bonding in Inorganic Chemistry, Vol. 127* (Eds. C. J. M. Rooymans, A. Rabenau), Amsterdam, **1975**.

Figure Captions and Scheme

Figure 1 View at the condensed $^{2}_{\infty}[OFEr_2]^{3+}$ layers (*left*) and $^{2}_{\infty}[ErS_3]^{3-}$ sheets (*right*), which spread out parallel to the (001) plane in the crystal structure of Er_3OFS_3. Dotted lines indicate the linking edges. The light-anion site is occupied by 50% O^{2-} + 50% F^-.

Figure 2 Part of the crystal structure of Er_3OFS_3, showing the stacking of the $^{2}_{\infty}[OFEr_2]^{3+}$ and $^{2}_{\infty}[ErS_3]^{3-}$ layers (O^{2-}/F^- = 50% O^{2-} + 50% F^-).

Figure 3 Coordination polyhedra around the two crystallographically different Er^{3+} cations (*top*) and the diverse anions (*bottom*) in Er_3OFS_3.

Figure 4 Section of the crystal structure of $Er_3OF_3S_2$, showing the stacking of the $^{2}_{\infty}[OF_3Er_3]^{4+}$ double layers (O^{2-}/F^- = 25% O^{2-} + 75% F^-).

Figure 5 Coordination polyhedra around the two crystallographically different Er^{3+} cations (*top*) and the S^{2-} and Z^{n-} anions (Z^{n-} = 25% O^{2-} + 75% F^-) (*bottom*) in $Er_3OF_3S_2$.

Figure 6 Light-anion surrounding of the $(Er1)^{3+}$ cations, as viewed onto the quadratic plane (*left*) and onto the rectangular faces (*mid*) of the polyhedron, along with a comparison of the two different anionic surroundings for the eightfold coordinated $(Er1)^{3+}$ cations in $Er_3OF_3S_2$ (*mid*) and $(Yb1)^{2+}$ cations in $Yb_3F_4S_2$ (*right*).

Scheme 1 *Bärnighausen* symmetry tree, displaying the group-subgroup relationship between the tetragonal supercell and the real orthorhombic unit cell of $Er_3OF_3S_2$.

Table 1. Crystallographic data for Er_3OFS_3 and $Er_3OF_3S_2$.

		Er_3OFS_3	$Er_3OF_3S_2$
Crystal system		tetragonal	orthorhombic
Formula units		$Z = 2$	$Z = 4$
Space group		*I*4/*mmm*	*Ccce*
Lattice parameters,	*a* in pm	374.86(2)	538.31(2)
	b in pm	= *a*	1892.03(9)
	c in pm	2068.41(9)	538.27(2)
Calculated density, D_x in $g \cdot cm^{-3}$		7.232	7.741
Molar volume, V_m in $cm^3 \cdot mol^{-1}$		87.516	82.536
F(000)		538	1084
Index range, $\pm h / \pm k / \pm l$		4 / 4 / 26	6 / 24 / 7
Theta range, θ_{max}		27.95	23.20
Absorption coefficient, μ in mm^{-1}		43.89	46.22
Data corrections		background, polarization, and Lorentz factors; numerical absorption correction with the program *HABITUS* [20]	
Reflections, collected / unique		1725 / 139	4624 / 333
R_{int} / R_σ		0.097 / 0.028	0.042 / 0.019
Structure solution and refinement		program package *SHELX-97* [21], scattering factors according to *International Tables, Vol. C* [22]	
R_1 for n reflections with $\lvert F_o \rvert \geq 4\sigma(F_o)$		0.029 (n = 130)	0.031 (n = 248)
R_1 / wR_2 for all reflections		0.031 / 0.057	0.041 / 0.096
Goodness of Fit (GooF)		1.155	1.157
Extinction, *g*		0.0023(3)	0.0075(6)
Residual electron density, ρ in $e^- \cdot 10^{-6}$ pm^{-3}, min. / max.		−1.78 / 2.29	−2.36 / 2.21

Table 2. Atomic coordinates and equivalent isotropic thermal displacement parameters U_{eq}[a)] for Er_3OFS_3 and $Er_3OF_3S_2$.

Er_3OFS_3		*x / a*	*y / b*	*z / c*	U_{eq} in pm^2
Er1	(2*a*)	0	0	0	178(5)
Er2	(4*e*)	0	0	0.31582(5)	194(4)
O/F[b)]	(4*d*)	0	$^1/_2$	$^1/_4$	109(25)
S1	(2*b*)	0	0	$^1/_2$	253(19)
S2	(4*e*)	0	0	0.1284(3)	143(10)
$Er_3OF_3S_2$		*x / a*	*y / b*	*z / c*	U_{eq} in pm^2
Er1	(4*a*)	0	$^1/_4$	$^1/_4$	198(4)
Er2	(8*f*)	0	0.59419(4)	$^1/_4$	101(4)
O/F[c)]	(16*i*)	0.1996(9)	0.6848(3)	0.0512(9)	284(14)
S	(8*f*)	0	0.4444(2)	$^1/_4$	55(6)

[a)] U_{eq} is defined as one third of the trace of the orthogonalized U_{ij} tensor [20];

[b)] fixed mixed occupation: O = 50%; F = 50%;

[c)] fixed mixed occupation: O = 25%; F = 75%.

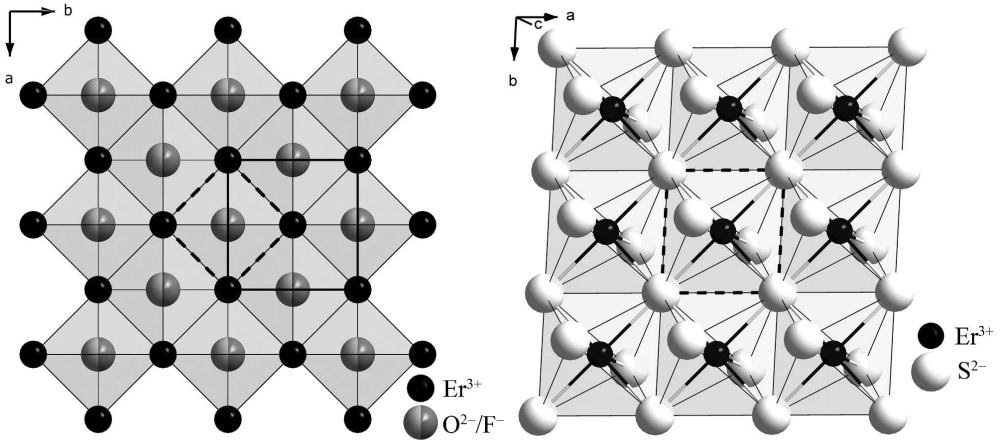
Table 3. Selected interatomic distances (*d*/pm, esd = ±0.1) and bond angles (∢/deg, esd = ±0.1) for Er_3OFS_3 (*top*) and $Er_3OF_3S_2$ (*bottom*).

Er_3OFS_3					
distances			angles		
Er1 – S1	4×	265.1	S1 – Er1 – S1	4×	90
Er1 – S2	2×	265.4	S2 – Er1 – S1	8×	90
			S2 – Er2 – S2	4×	80.8
Er2 – O/F	4×	231.7	S2 – Er2 – O/F	8×	73.2
Er2 – S2	4×	289.2	O/F – Er2 – O/F	4×	69.8
			Er2 – O/F – Er2	4×	110.2
			Er2 – O/F – Er2	2×	108.0
$Er_3OF_3S_2$					
distances			angles		
Er1 – O/F	4×	229.8	O/F – Er1 – O/F	4×	68.1
Er1 – O'/F'	4×	230.3	O/F – Er1 – O/F	4×	92.7
			S – Er2 – S	4×	86.1
Er2 – O/F	2×	228.9	S – Er2 – S'	8×	74.9
Er2 – O'/F'	2×	286.1	O/F – Er2 – O/F	1×	85.0
Er2 – S	2×	278.9	O'/F' – Er2 – O'/F'	1×	105.4
Er2 – S'	2×	278.9	O/F – Er2 – O'/F'	4×	63.5
Er2 – S"	1×	283.4	Er1 – O/F – Er1'	1×	111.6
			Er1 – O/F – Er2	1×	121.0
			Er1' – O/F – Er2	1×	120.8
			Er2 – O/F – Er2'	1×	94.7
			Er1 – O/F – Er2'	1×	100.8
			Er1' – O/F – Er2'	1×	100.7

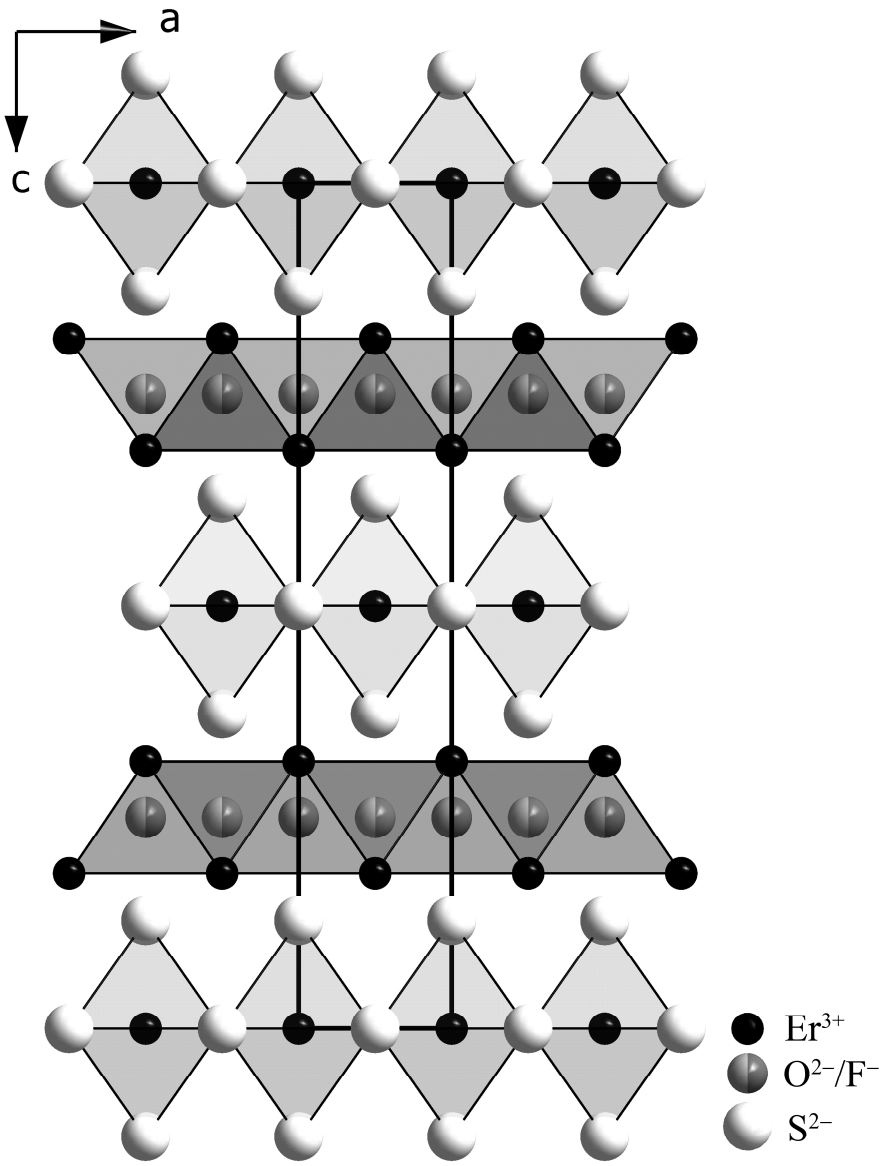
Table 4. Motifs of mutual adjunction [40–42] for Er_3OFS_3 (*top*) and $Er_3OF_3S_2$ (*bottom*).

Er_3OFS_3	O/F	S1	S2	CN
Er1	0 / 0	4 / 4	2 / 1	6
Er2	4 / 4	0 / 0	4 / 4	8
CN	4	4	5	

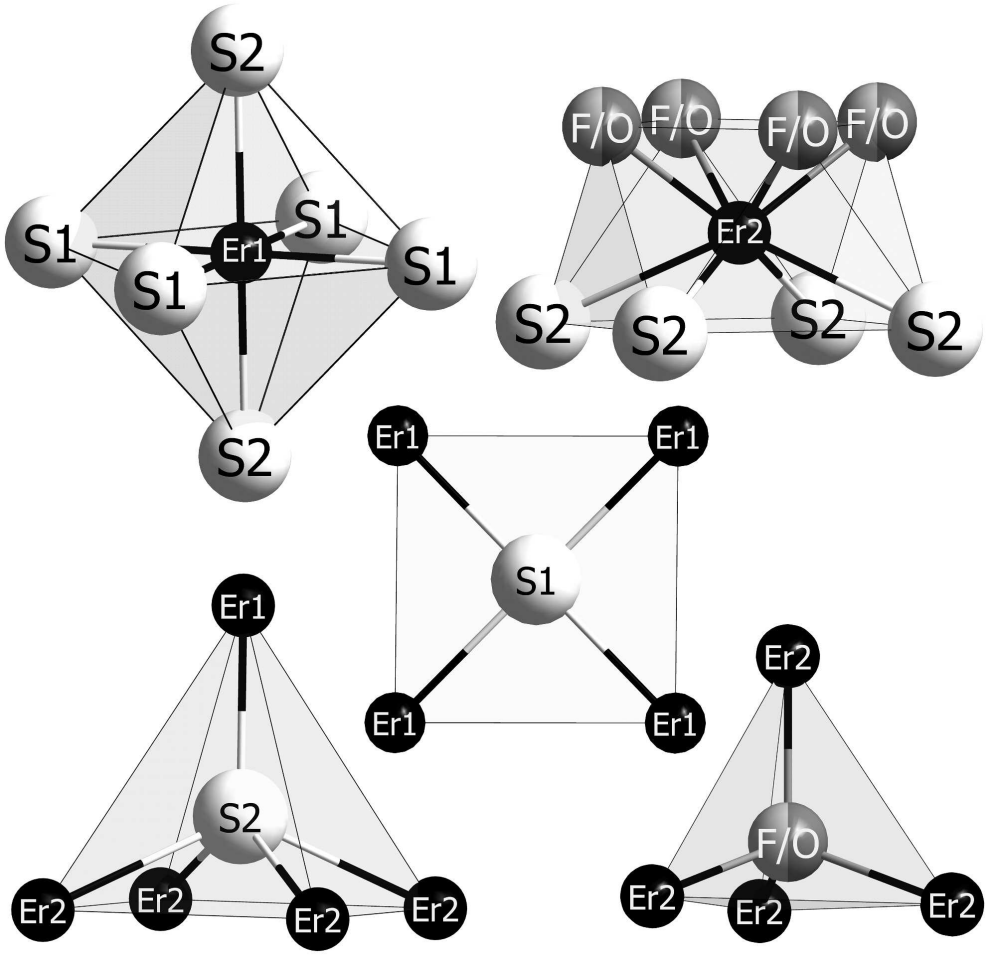
$Er_3OF_3S_2$	O/F	S	CN
Er1	8 / 2	0 / 0	8
Er2	2+2 / 1+*1*	5 / 5	7+2
CN	3+*1*	5	



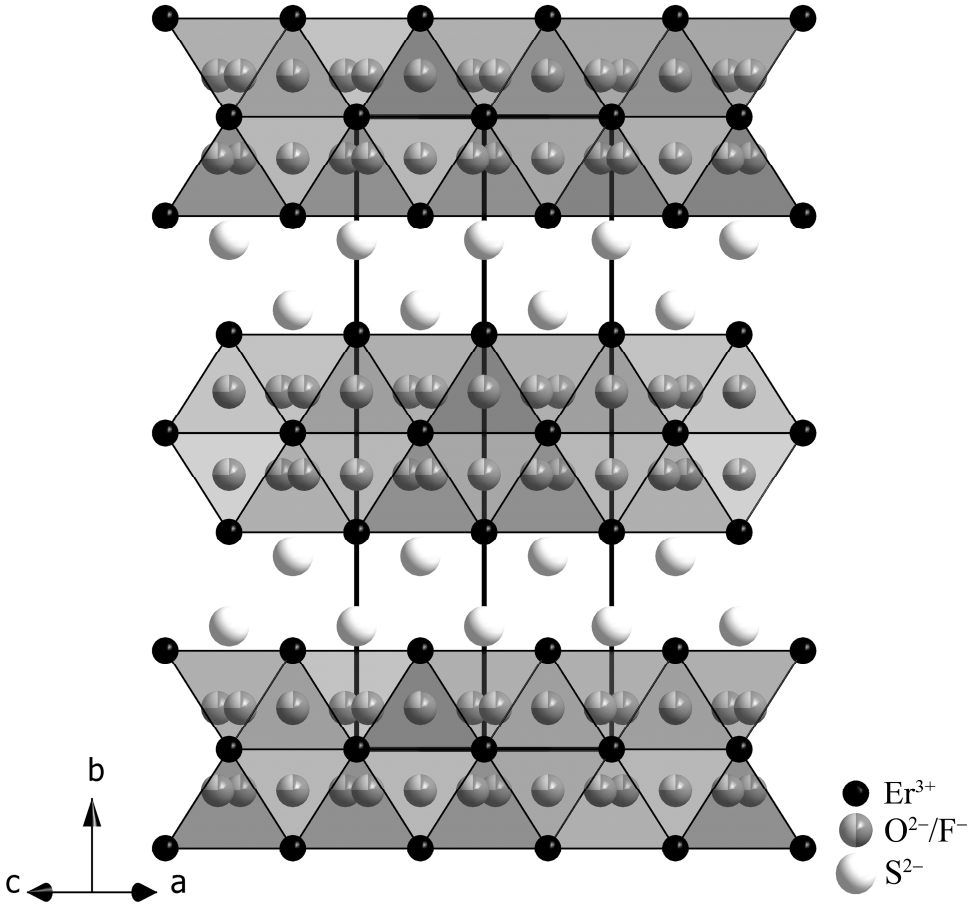
View at the condensed [OFEr2]3+ layers (left) and [ErS3]3− sheets (right), which spread out parallel to the (001) plane in the crystal structure of Er3OFS3. Dotted lines indicate the linking edges. The light-anion site is occupied by 50% O2− + 50% F−.
170x79mm (600 x 600 DPI)



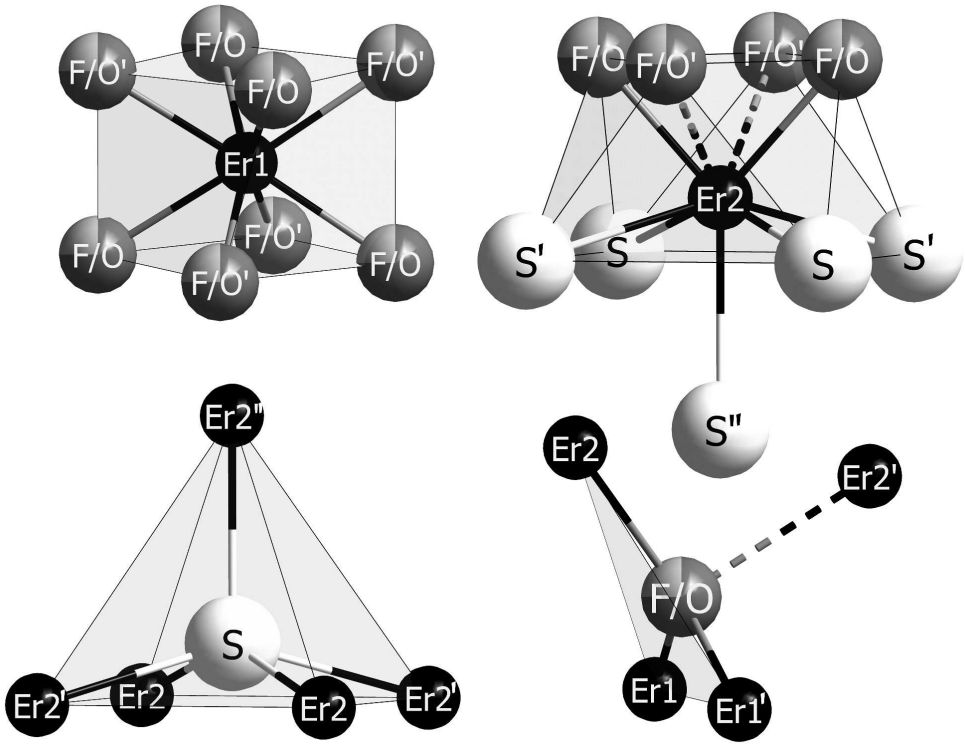
Part of the crystal structure of Er3OFS3, showing the stacking of the [OFEr2]3+ and [ErS3]3– layers (O2–/F– = 50% O2– + 50% F–).
170x219mm (600 x 600 DPI)



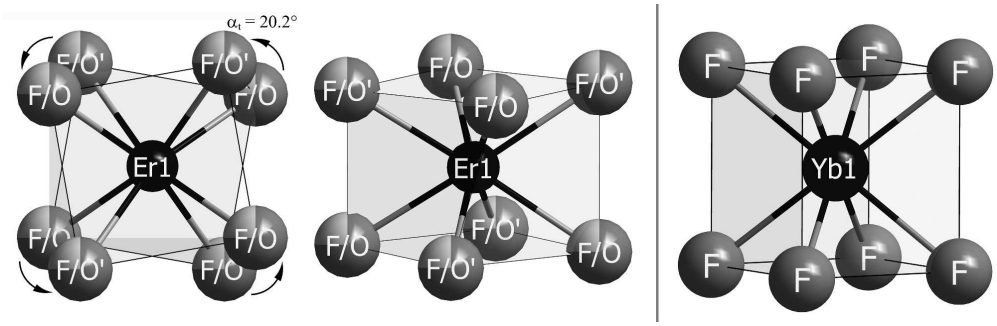
Coordination polyhedra around the two crystallographically different Er3+ cations (top) and the diverse anions (bottom) in Er3OFS3.
170x168mm (600 x 600 DPI)



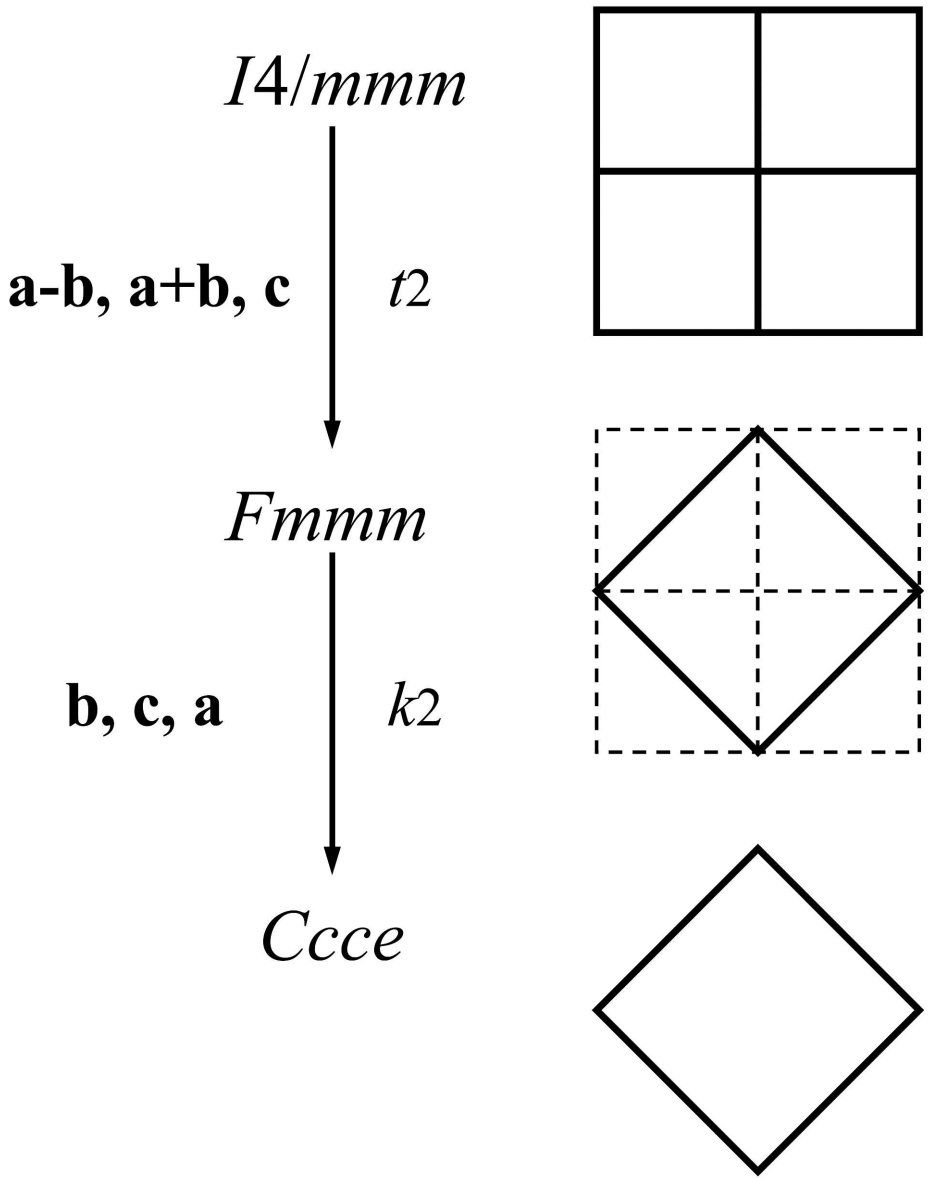
Section of the crystal structure of Er3OF3S2, showing the stacking of the [OF3Er3]4+ double layers (O2−/F− = 25% O2− + 75% F−).
170x158mm (600 x 600 DPI)



Coordination polyhedra around the two crystallographically different Er3+ cations (top) and the S2– and Zn– anions (Zn– = 25% O2– + 75% F–) (bottom) in Er3OF3S2.
170x133mm (600 x 600 DPI)



Light-anion surrounding of the (Er1)3+ cations, as viewed onto the quadratic plane (left) and onto the rectangular faces (mid) of the polyhedron, along with a comparison of the two different anionic surroundings for the eightfold coordinated (Er1)3+ cations in Er3OF3S2 (mid) and (Yb1)2+ cations in Yb3F4S2 (right).
170x54mm (600 x 600 DPI)



Bärnighausen symmetry tree, displaying the group-subgroup relationship between the tetragonal supercell and the real orthorhombic unit cell of Er3OF3S2.
170x211mm (600 x 600 DPI)