About Lanthanoid Fluoride Selenide Oxoselenotantalates with the Composition $Ln_3F_2Se_2TaO_4$ (Ln = La – Nd)

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Dedicated to Professor Bernd Harbrecht on the Occasion of his 70th Birthday

Abstract. After solid-state reactions of the light lanthanoid metals, their oxides and fluorides as well as selenium in sealed tantalum ampoules with sodium chloride as a fluxing agent at 850 °C for 8 days needle-shaped single crystals of $Ln_3F_2Se_2TaO_4$ (Ln = La – Nd) were obtained. They crystallize in the orthorhombic space group *Pnma* analogous to $La_3F_2Se_2NbO_4$ with a = 1133–1120 pm, b = 400–393 pm and c = 1812–1778 pm (Ln = La – Nd) for Z = 4 as the first known quinary lanthanoid(III) oxoselenotantalates(V) with fluoride and selenide anions. The three crystallographically different Ln^{3+} cations are all surrounded by nine anions (O^{2-}, F^- and Se^{2-}) each. Tantalum resides in an octahedral chalcogen coordination by forming *trans*-vertex oxygen-connected $[TaO_5Se]^{7-}$ polyhedra, which build up chains $\frac{1}{\infty}\{[TaO^V_{2/2}O^t_{3/1}Se^t_{1/1}]^{5-}\}$ along [010]. The sites of the four crystallographically different oxygen atoms and the two distinct fluoride anions were established by bond-valence calculations. One fluorine and three oxygen atoms are surrounded tetrahedrally by cations, while another fluoride and oxide anion exhibit just triangular non-planar coordination spheres. The two independent Se^{2-} anions have five or six cationic neighbors.

Introduction

During the attempted flux-supported synthesis of cubic Cu_3NbSe_4[1] *Ibers* et al. obtained yellow needles of orthorhombic $La_3F_2Se_2NbO_4$[2] as undesired by-product. Own experiments with the aim of lanthanoid(III) fluoride selenides (LnFSe) have shown to produce oxide-fluoride selenides, when the lanthanoid metal is contaminated with oxygen, and even of fluoride selenide oxoselenotantalates, when carelessly cleaned tantalum ampoules are used as container material. So we were able to synthesize isostructural compounds $Ln_3F_2Se_2TaO_4$ with tantalum instead of niobium for the lanthanoids from lanthanum to neodymium as the first quinary lanthanoid oxoselenotantalates, which contain fluoride and selenide anions. Even without the latter oxygen-contaminated tantalum capsules turn into a powerful tantalum-oxide sources, whenever lanthanoid oxides are around, and the serendipitous formation of LnTaO_4 single crystals (Ln = La – Nd, Sm – Lu)[3] might serve as proof for this finding. So the compounds with the composition $Ln_3F_2Se_2TaO_4$ were found as by-products of synthesis experiments with fluoride- and selenide-containing reactant mixtures in with oxide-polluted tantalum capsules. On the other hand clean tantalum tubing was used successfully for the synthesis of ternary and quaternary compounds like LnFS,[4–6] LnFSe,[7–9] Ln_2F_4Se,[10] Ln_3OFS_3,[11] $Ln_3OF_3S_2$,[11] Ln_3OF_5S,[6,12,13] $Ln_6O_2F_8S_3$,[14] Ln_2OF_2Se,[15–17] Ln_3OFSe_3,[18] $Ln_3OF_3Se_2$,[18] $Ln_5OF_5Se_4$,[19–21] $Ln_6O_2F_8Se_3$,[16] or $Ln_6O_4F_4Se_3$[22] (Ln = La – Lu), because fluoride-containing melts do react destructively with otherwise very versatile fused silica ampoules at the typical conversion temperatures.

For the quaternary selenium-free lanthanoid fluoride oxotantalates there is a cubic compound known with the formula $NdFTa_2O_6$[23] and for the fluoride-free lanthanoid oxoselenotantalates the orthorhombic representatives $Ln_2Se_2Ta_3O_8$ (Ln = La – Nd)[24] exist. With an ionic radius of 78 pm for C.N. = 6, Ta^{5+} has about the same size as Nb^{5+} [25] owing the lanthanoid contraction. So for many tantalum compounds analogous niobium compounds should be accessible and the other way around. In the niobium case a quaternary fluoride-free lanthanoid oxoselenoniobate such as $Sm_3Se_2NbO_4$[26] is known, without its tantalum counterpart. At the time, when this paper was written, just for the ternary lanthanoid oxotantalates (system: La – Lu, Ta, O) 114 results and for quinary ones with an extra component 118 results were found in the ICSD database. Many of them owe their first discovery the use of uncarefully cleaned tantalum ampoules as reaction containers.

Results and Discussion

The new orthorhombic compounds of the composition $Ln_3F_2Se_2TaO_4$ (Ln = La – Nd) crystallize analogously with $La_3F_2Se_2NbO_4$[2] in the space group *Pnma* with a = 1132.59(6) pm, b = 399.84(2) pm, c = 1811.72(9) pm for Ln = La, a = 1127.43(6) pm, b = 397.36(2) pm, c = 1798.15(2) pm for Ln = Ce, a = 1123.81(6) pm, b = 395.20(2) pm, c = 1787.68(9) pm for Ln = Pr and a = 1120.67(6) pm, b = 393.13(2) pm,

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Table 1. Crystallographic data of the lanthanoid(III) fluoride selenide oxoselenotantalates(V) $Ln_3F_2Se_2TaO_4$ (Ln = La – Nd).

	La$_3$F$_2$Se$_2$TaO$_4$	Ce$_3$F$_2$Se$_2$TaO$_4$	Pr$_3$F$_2$Se$_2$TaO$_4$	Nd$_3$F$_2$Se$_2$TaO$_4$
Crystal system		orthorhombic		
Space group		*Pnma* (no. 62)		
Lattice constants:				
a /pm	1132.59(6)	1127.43(6)	1123.81(6)	1120.67(6)
b /pm	399.84(2)	397.36(2)	395.20(2)	393.13 (2)
c /pm	1811.72(9)	1798.15(9)	1787.68(9)	1778.56(9)
Unit-cell volume, V_{uc} /nm^3	0.82045(7)	0.80556(7)	0.79396(7)	0.78358(7)
Formula units (Z)		4		
Calculated density, D_x /g·cm^{-3}	6.943	7.101	7.225	7.405
Molar volume, V_m /cm^3·mol^{-1}	123.52	121.28	119.52	117.97
Measurement parameters				
Diffractometer	IPDS-I	Kappa-CCD	Kappa-CCD	IPDS-I
Wavelength		Mo-K_α (λ = 71.07 pm)		
$F(000)$	1448	1460	1472	1484
hkl range	$-14 \leq h \leq 14$	$-14 \leq h \leq 14$	$-14 \leq h \leq 14$	$-14 \leq h \leq 14$
	$-5 \leq k \leq 5$	$-5 \leq k \leq 5$	$-5 \leq k \leq 5$	$-5 \leq k \leq 5$
	$-23 \leq l \leq 23$	$-23 \leq l \leq 23$	$-23 \leq l \leq 23$	$-23 \leq l \leq 23$
Θ_{max} / °	27.44	28.19	28.31	27.41
Absorption coefficient, μ /mm^{-1}	37.47	39.20	40.99	42.75
Temperature /K		293(2)		
Data reduction				
Measured reflections	13588	11146	11351	12883
Unique reflections	1064	1129	1129	1003
Absorption correction		X-SHAPE [39]		
R$_{int}$ / R$_\sigma$	0.069 / 0.023	0.098 / 0.060	0.079 / 0.032	0.092 / 0.056
Number of reflections with $|F_o| \geq 4\sigma(F_o)$	1016	871	1003	859
Structure determination and refinement:				
Program		SHELX-97 [40–42]		
R_1 / R_1 with $|F_o| \geq 4\sigma(F_o)$	0.027 / 0.026	0.058 / 0.033	0.032 / 0.024	0.050 / 0.040
wR_2 / GooF	0.062 / 1.090	0.057 / 1.004	0.047 / 1.053	0.068 / 1.061
Extinction coefficient (g)	0.00048(9)	0.00011(4)	0.00021(4)	0.00072(6)
Residual electron density				
$\rho_{max/min}$ /e$^-$·10^{-6}·pm^{-3}	2.13 / –2.18	2.17 / –2.04	1.74 / –1.52	2.17 / –1.95

c = 1778.56(2) pm for Ln = Nd and Z = 4 for all (Table 1). The trend of the unit-cell parameters can be seen in Figure 1 and shows with its steady shrinkage from Ln = La to Ln = Nd the consequences of the lanthanoid contraction. The differences in the unit-cell parameters a, b and c of La$_3$F$_2$Se$_2$TaO$_4$ and La$_3$F$_2$Se$_2$NbO$_4$[2] (a = 1129.0(4) pm, b = 400.1(1) pm, c = 1806.2(4) pm) are smaller than 0.5 %.

For the LnTaO$_4$ series with Ln = La – Nd and Sm – Lu[3] there is a structural change between Ln = Pr and Ln = Nd, but NdTaO$_4$ can be obtained via high-pressure synthesis in the LaTaO$_4$-type structure[27] as well. Such a structural break very often takes place between praseodymium and neodymium or between neodymium and samarium compounds with the same stoichiometry. As mentioned above in the LnTaO$_4$ series with Ln = La – Nd and Sm – Lu,[3] the compounds with Ln = La – Pr crystallize in space group $P2_1/c$ with A-type structure and the compounds of the heavier lanthanoids in $P2/c$ with B-type structure. In the hexagonal Ln_2OF$_2$Se and Ln_6O$_2$F$_8$Se$_3$ series there is also a structural change at the neodymium compounds, which are published with both stoichiometries and structures.[16] For the oxide-poor tetragonal oxide selenides Ln_{10}OSe$_{14}$ only the compounds with Ln = La – Nd seem to exist[28–30] and only the lanthanoids Ln = La – Nd form the nitride tellurides Ln_{13}N$_5$Te$_{12}$[31] or the nitride bismuthides
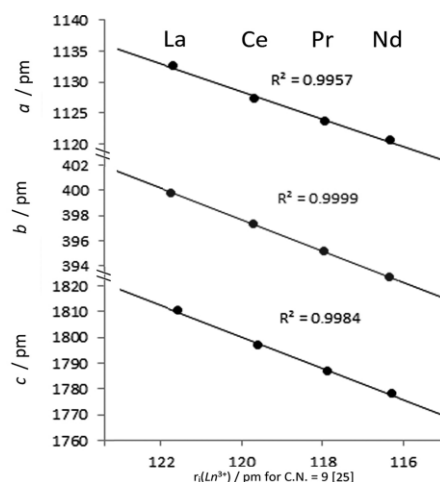
Figure 1. Linear trend of shrinking unit-cell parameters along the Ln_3F$_2$Se$_2$TaO$_4$ series with Ln = La – Nd and coefficients of determination (R^2).

Ln_2NBi.[32] With oxoselenate(IV) anions the Ln_2O[SeO$_3$]$_2$ series starts with the samarium compound as the first one of the lanthanoids[33,34] and has no representative for the bigger ones. While LaCl[SeO$_3$], CeCl[SeO$_3$] and PrCl[SeO$_3$] do not

exist, NdCl[SeO$_3$][35] has a unique structure and the rest of the LnCl[SeO$_3$][35–38] series starts with Ln = Sm again. So the possibility of building a crystal structure is depending among other things much on the size of the respective Ln^{3+} cation. For the bigger ones, a larger coordination number is preferred than for the smaller ones. Lanthanum in A-type LaFS is coordinated as La^{3+} cation by four F$^-$ and five S^{2-} anions, while

Table 2. Fractional atomic coordinates, and equivalent isotropic displacement parameters (U_{eq} /pm^2) for the $Ln_3F_2Se_2TaO_4$ series (Ln = La – Nd). All atoms occupy the *Wyckoff* position 4*c*.

Atom	x/a	y/b	z/c	U_{eq} /pm^2
La$_3$F$_2$Se$_2$TaO$_4$				
La1	0.06964(5)	1/4	0.80060(3)	90(2)
La2	0.00332(5)	1/4	0.39302(3)	93(2)
La3	0.29418(5)	1/4	0.53091(3)	92(2)
F1	0.0636(5)	1/4	0.6686(3)	139(11)
F2	0.0701(5)	1/4	0.5259(3)	113(10)
Se1	0.00796(8)	1/4	0.08046(5)	105(2)
Se2	0.28474(8)	1/4	0.90840(5)	109(2)
Ta	0.19075(3)	1/4	0.19417(2)	74(1)
O1	0.3120(5)	1/4	0.2598(3)	124(13)
O2	0.0530(5)	1/4	0.2533(3)	114(12)
O3	0.2807(5)	1/4	0.0995(3)	85(11)
O4	0.3285(5)	1/4	0.6797(3)	99(12)
Ce$_3$F$_2$Se$_2$TaO$_4$				
Ce1	0.06813(7)	1/4	0.80067(4)	107(2)
Ce2	0.00388(7)	1/4	0.39313(4)	108(2)
Ce3	0.29315(7)	1/4	0.53089(4)	108(2)
F1	0.0617(7)	1/4	0.6687(4)	133(17)
F2	0.0681(7)	1/4	0.5263(4)	114(17)
Se1	0.0082(2)	1/4	0.08017(8)	117(3)
Se2	0.2837(2)	1/4	0.90835(8)	128(3)
Ta	0.19214(5)	1/4	0.19466(3)	91(2)
O1	0.3151(8)	1/4	0.2613(5)	163(23)
O2	0.0535(8)	1/4	0.2564(5)	148(22)
O3	0.2833(8)	1/4	0.0997(5)	113(21)
O4	0.3269(8)	1/4	0.6793(5)	159(23)
Pr$_3$F$_2$Se$_2$TaO$_4$				
Pr1	0.06510(4)	1/4	0.80030(3)	69(1)
Pr2	0.00352(4)	1/4	0.39346(3)	69(1)
Pr3	0.29247(4)	1/4	0.53110(3)	69(1)
F1	0.0615(4)	1/4	0.6681(3)	86(11)
F2	0.0690(4)	1/4	0.5260(3)	83(11)
Se1	0.00906(7)	1/4	0.08007(5)	69(2)
Se2	0.28275(7)	1/4	0.90713(5)	57(2)
Ta	0.19395(3)	1/4	0.19520(2)	47(1)
O1	0.3175(5)	1/4	0.2614(4)	107(14)
O2	0.0554(5)	1/4	0.2570(4)	90(13)
O3	0.2843(5)	1/4	0.0989(4)	78(13)
O4	0.3270(5)	1/4	0.6794(4)	83(13)
Nd$_3$F$_2$Se$_2$TaO$_4$				
Nd1	0.06489(8)	1/4	0.80097(6)	282(2)
Nd2	0.00434(8)	1/4	0.39323(6)	277(2)
Nd3	0.29169(8)	1/4	0.53046(6)	286(2)
F1	0.0594(8)	1/4	0.6708(6)	320(22)
F2	0.0689(8)	1/4	0.5241(6)	444(28)
Se1	0.0092(1)	1/4	0.07951(9)	290(4)
Se2	0.2828(1)	1/4	0.90723(9)	300(4)
Ta	0.19483(6)	1/4	0.19515(4)	262(2)
O1	0.3156(9)	1/4	0.2614(7)	299(27)
O2	0.0561(9)	1/4	0.2561(7)	356(30)
O3	0.2868(9)	1/4	0.0974(7)	341(29)
O4	0.3242(9)	1/4	0.6782(7)	294(27)

lutetium in C-type LuFS is coordinated as Lu^{3+} by only six or eight anions (Lu1: 6 × S^{2-}, Lu2: 2 × S^{2-} *plus* 6 × F$^-$).[4]

In Table 2 the fractional atomic coordinates of the lanthanoid(III) fluoride selenide oxoselenotantalates(V) $Ln_3F_2Se_2TaO_4$ (Ln = La – Nd) and the equivalent isotropic displacement parameters are listed. All atoms occupy the *Wyckoff* position 4*c*.

Four unit cells of the orthorhombic crystal structure of the $Ln_3F_2Se_2TaO_4$ series with Ln = La – Nd are shown in Figure 2 as viewed along [010]. The selenide anion (Se1)$^{2-}$ is surrounded by a square pyramid of Ln^{3+} cations, while (Se2)$^{2-}$ also has a square pyramid of Ln^{3+} cations as neighbors, but exhibits a Ta^{5+} cation as extra cap (Figure 2 and Figure 3). The polyhedra around selenium are edge-linked with distances of 388 and 442 pm between Se1 and Se2, as well as 354 pm between the octahedrally surrounded selenium atoms (Se1) in
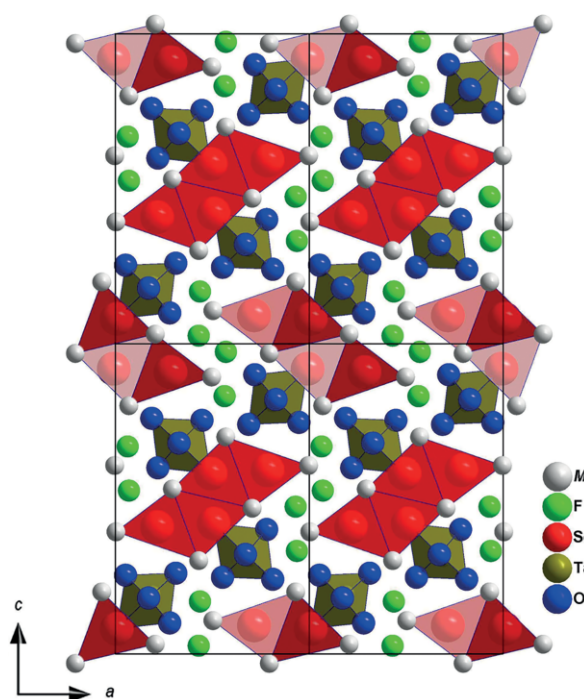

Figure 2. Four unit cells of the crystal structure of the $Ln_3F_2Se_2TaO_4$ series with Ln = La – Nd as viewed along [010]. The coordination polyhedra around tantalum and selenium are emphasized.
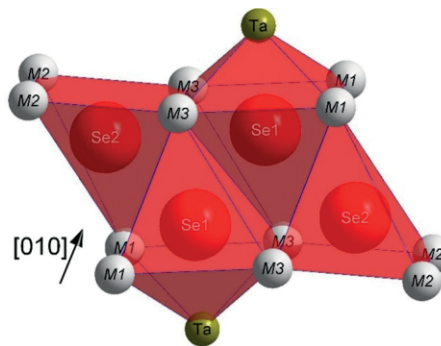

Figure 3. Edge-linked cation polyhedra around the selenide anions building strainds along [010] in the crystal structure of the $Ln_3F_2Se_2TaO_4$ series with Ln = La – Nd.

case of the lanthanum compound $La_3F_2Se_2TaO_4$. Figure 3 shows the connection of the selenium-centered cation polyhedra building a strand along [010] with Se···Se distances of 400 pm ($\equiv b$).

The average $Se^{2-}–La^{3+}$ distance of the $[SeLa_5]^{13-}$-polyhedron is 311 pm, whereas 312 pm occur within the $[(Se2)La_5Ta]^{8-}$ coordination figure. Tantalum is surrounded by a distorted octahedron consisting of five oxygen atoms (d(Ta–O) = 198–203 pm) and one selenide anion (Se1) at a distance of 292 pm. All oxygen atoms in this crystal structure are connected with tantalum and the $[TaO_5Se]^{7-}$ octahedra form a chain $^1_\infty\{[TaO^V_{2/2}O^t_{3/1}Se^t_{1/1}]^{5-}\}$ along [010] by *trans*-vertex oxygen-linkage via O4 with Ta–O4–Ta angles of 160.6° for the lanthanum, 160.0° for the cerium, 158.9° for the praseodymium and 158.7° for the neodymium compound (Figure 4).
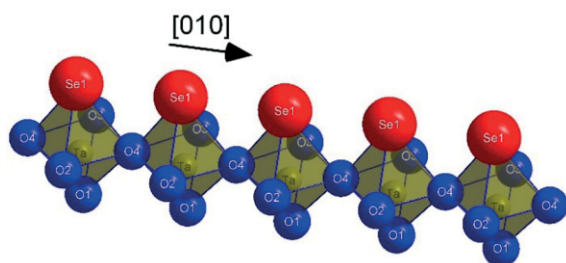

Figure 4. Vertex-linked anion octahedra around tantalum building a chain along [010] via common O4 atoms with isotactical orientation of the Se1 ligands in the crystal structure of the $Ln_3F_2Se_2TaO_4$ series with Ln = La – Nd.

So despite carrying a big selenide anion tantalum shows an octahedral coordination sphere just like in all the different modifications for the composition $LnTaO_4$,[3,21,43–46] where distorted and condensed $[TaO_6]^{7-}$ octahedra are present, which show a very large interval of Ta–O distances (187–220 pm), but never isolated $[TaO_4]^{3-}$ tetrahedra. The Ta–O distances in $La_3F_2Se_2TaO_4$ between 182 and 203 pm are in the range next to them in $LaTaO_4$, while the Ta–Se distance in $La_3F_2Se_2TaO_4$ comes with 292 pm much longer than in $La_2Ta_3Se_2O_8$[24] with values between 255 and 273 pm. But in contrast with 198–233 pm the Ta–O distances in $La_2Ta_3Se_2O_8$[24] markly exceed those of $La_3F_2Se_2TaO_4$.

The three crystallographically different lanthanoid(III) cations are all coordinated by nine anions (Figure 5, top). $(Ln1)^{3+}$ is surrounded by five O^{2-}, one F^- and tree Se^{2-} in the shape of a capped square antiprism just like in the oxide fluoride selenides $Ln_6O_2F_8Se_3$ (Ln = La – Nd).[16] The coordination sphere of the second cation $(Ln2)^{3+}$ has the shape of a tricapped trigonal prism erected by two O^{2-}, five F^- and two Se^{2-} anions as also observed in $Ln_6O_2F_8Se_3$[16] and A-type Ln_2OF_2Se[16,17] (Ln = La – Nd, Sm, Gd – Ho). The third cation $(Ln3)^{3+}$ exhibits the same polyhedral shape as the first one, but it consists of three oxygen atoms and one fluoride anion at the bottom, four selenide anions at the top and one Se^{2-} as the cap. In $La_3F_2Se_2TaO_4$ the distances between Ln^{3+} and its Se^{2-} caps are 312 and 313 pm for $Ln1$ and 315 pm for $Ln3$, hence only just a little longer than the distances from $Ln1$ to Se1 with 307 pm or from $Ln3$ to the not-capping selenide anions

with 312 pm. The environment of $Ln3$ is nearly the same as for Ln^{3+} in A-type LaFSe[8] with the difference of one oxygen ligand instead of a fluoride anion. The $Ln2$ environment can also be described as a distorted capped square antiprism and then the formal tricapped trigonal prisms around all Ln^{3+} cations are sharing triangular faces (Figure 5, bottom). The polyhedral trimer forms a strand along [010], which is in viewing direction of Figure 5 (bottom), where again more triangular faces are shared. The $Ln^{3+}–F^-$ distances range between 239 and 261 pm for Ln = La and the $Ln^{3+}–O^{2-}$ contacts fall into a common interval from 250 to 275 pm.

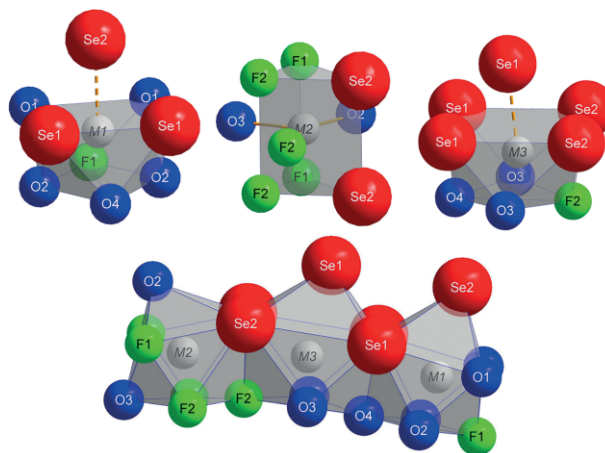**Figure 5.** Coordination polyhedra around $(Ln1)^{3+}$ – $(Ln3)^{3+}$ (top) in the crystal structure of the $Ln_3F_2Se_2TaO_4$ series with Ln = La – Nd and one feature of connection between these polyhedra (bottom).

The first fluoride anion $(F1)^-$ is triangular non-planar surrounded by Ln^{3+} cations at distances of about 240 pm and deflected from the cationic plane by 48 pm, while the second one $(F2)^-$ exhibits a tetrahedral coordination sphere of four Ln^{3+} cations with distances between 252 and 262 pm for $La_3F_2Se_2TaO_4$. $(O1)^{2-}$ is surrounded by tantalum and two Ln^{3+} cations in a triangular non-planar $[(O1)Ta(Ln1)_2]^{7+}$ environment with a distance of 17 pm from the cationic plane. $(O2)^{2-}$ and $(O3)^{2-}$ reside in tetrahedral neighborhood of one Ta^{5+} and three La^{3+} cations, while the cationic tetrahedron $(O4)^{2-}$ around is made of two tantalum and two lanthanum atoms. In all of the oxygen-centered tetrahedra the shortest distances occur to the tantalum atoms with $d(O^{2-}–Ta^{5+})$ = 189–203 pm in case of the lanthanum compound, while the oxygen-to-lanthanum distances in these tetrahedra range between 253 and 276 pm. The cationic polyhedra around the fluoride anions and the oxygen atoms can be seen in Figure 6. The distances between the oxygen atoms and tantalum are much shorter than to the lanthanoids, because of the higher oxidation state of tantalum (+5) as compared to the latter ones (+3).

The sites of the oxygen atoms and the fluoride anions can not be refined unambiguously based on X-ray diffraction data, however. So bond-valence calculations were used to determine the different atoms on their specific *Wyckoff* positions with the help of the bond-valence parameters by *Brese* and *O'Keeffe*.[47] The results of these bond-valence calculations are listed in Table 3. It can be seen that the trigonally coordinated anion at

Table 3. Results of the bond-valence calculations for the $Ln_3F_2Se_2TaO_4$ series (Ln = La – Nd) compared with $La_3F_2Se_2NbO_4$.[2]

Atom		Total bond valence of $Ln_3F_2Se_2TaO_4$ with Ln =				
	$La_3F_2Se_2NbO_4$[2]	La	Ce	Pr	Nd	C.N.
Ln1	2.95	3.17	3.21	3.19	3.17	9
Ln2	3.21	2.88	2.97	2.96	2.92	9
Ln3	3.10	3.05	3.10	3.06	3.08	9
Nb/Ta	4.90	5.04	4.96	5.03	5.17	6
Se1	2.22	2.17	2.25	2.22	2.23	6
Se2	1.76	1.76	1.85	1.77	1.83	5
O1	1.97	2.11	2.08	2.09	2.15	3
O2	2.04	1.99	1.93	1.96	1.97	4
O3	2.08	2.02	2.02	2.02	1.96	4
O4	1.91	1.93	1.97	2.02	2.04	4
F1	1.02	1.00	0.99	1.00	1.00	3
F2	1.16	1.17	1.16	1.16	1.16	4
O at F2 site		1.60	1.58	1.58	1.56	4
F at O1 site		1.76	1.73	1.75	1.82	3

0.31, $^1/_4$, 0.26 should be oxide (B.V. ≈ 2.1) and the tetrahedrally surrounded one at 0.07, $^1/_4$, 0.53 must be fluoride (B.V. ≈ 1.2). The calculated data of the here published compounds $Ln_3F_2Se_2TaO_4$ with Ln = La – Nd are perfectly compatible to those of *Brennan*, *Mansuetto* and *Ibers* for their isotypic niobium analogon $La_3F_2Se_2NbO_4$,[2] since they show that no fluoride ligand enters the coordination sphere of the refractory metal.

The most relevant interatomic distances in the lanthanoid(III) fluoride selenide oxoselenotantalates(V) $Ln_3F_2Se_2TaO_4$ (Ln = La – Nd) are summarized in Table 4 and the motifs of mutual adjunction within the crystal structure of the lanthanoid(III) fluoride selenide oxoselenotantalates(V) $Ln_3F_2Se_2TaO_4$ (Ln = La – Nd) can be seen in Table 5.
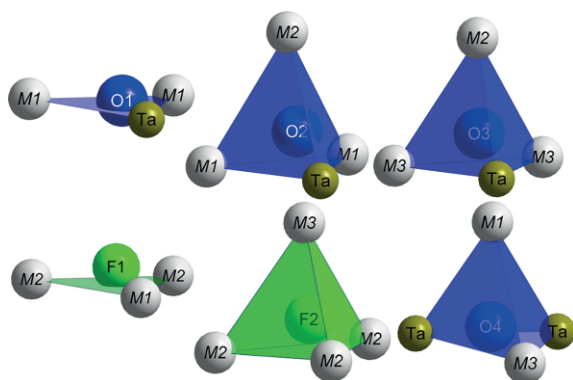
Figure 6. Cationic coordination polyhedra around the oxygen atoms and the fluoride anions in the crystal structure of the $Ln_3F_2Se_2TaO_4$ series with Ln = La – Nd.

Table 4. Selected interatomic distances (d /pm) for the $Ln_3F_2Se_2TaO_4$ series (Ln = La – Nd).

		Ln			
		La	=Ce	Pr	=Nd
Ln1–F1	(1×)	239.3	237.4	236.4	231.6
Ln1–O1	(2×)	251.8	248.6	247.6	248.1
Ln1–O2	(2×)	262.3	262.3	260.6	259.5
Ln1–O4	(1×)	275.5	274.3	270.1	272.2
Ln1–Se1	(2×)	306.8	304.6	302.9	301.2
Ln1–Se2	(1×)	312.2	310.8	310.3	308.9
Ln2–F1	(2×)	241.2	239.4	237.7	238.2
Ln2–F2	(1×)	252.3	250.2	248.2	243.8
Ln2–F2′	(2×)	261.7	259.0	257.7	258.8
Ln2–O2	(1×)	259.3	252.2	250.8	250.6
Ln2–O3	(1×)	252.5	249.0	246.7	244.3
Ln2–Se2	(2×)	313.6	312.4	312.0	310.1
Ln3–F2	(1×)	254.0	253.8	251.4	249.9
Ln3–O3	(2×)	250.2	249.5	247.3	246.1
Ln3–O4	(1×)	272.3	269.5	267.9	265.3
Ln3–Se1	(2×)	313.4	312.2	310.6	309.9
Ln3–Se1′	(1×)	315.2	314.1	314.2	312.6
Ln3–Se2	(2×)	311.8	309.1	308.7	306.0
Ta–O1	(1×)	181.7	183.3	182.4	179.4
Ta–O2	(1×)	189.3	191.7	190.9	189.6
Ta–O3	(1×)	199.6	199.2	199.9	202.1
Ta–O4	(2×)	202.8	201.7	201.0	200.0
Ta–Se1	(1×)	292.1	292.2	292.5	292.5
O1···Δ		17.7	18.0	18.1	19.1
F1···Δ		48.2	46.8	47.4	44.8

The Madelung Part of the Lattice Energy (MAPLE according to *Hoppe*)[48–50] shows a lower value for all $Ln_3F_2Se_2TaO_4$ representatives with Ln = La – Nd than the sum of the formally underlying binaries or ternaries (i.e. $LnTaO_4$ ($P2_1/c$),[3,27]

Table 5. Motifs of mutual adjunction for the $La_3F_2Se_2NbO_4$-type crystal structure of the $Ln_3F_2Se_2TaO_4$ series (Ln = La – Nd).

	F1	F2	Se1	Se2	O1	O2	O3	O4	C.N.
Ln1	1 / 1	0 / 0	2 / 2	1 / 1	2 / 2	2 / 2	0 / 0	1 / 1	9
Ln2	2 / 2	3 / 3	0 / 0	2 / 2	0 / 0	1 / 1	1 / 1	0 / 0	9
Ln3	0 / 0	1 / 1	3 / 3	2 / 2	0 / 0	0 / 0	2 / 2	1 / 1	9
Ta	0 / 0	0 / 0	1 / 1	0 / 0	1 / 1	1 / 1	1 / 1	2 / 2	6
C.N.	3	4	6	5	3	4	4	4	

Table 6. MAPLE for the $Ln_3F_2Se_2TaO_4$ representatives with Ln = La – Nd compared to the MAPLE sum of LnTaO$_4$ ($P2_1/c$), Ln_2Se_3 ($I\bar{4}3d$) and LnF$_3$ ($P\bar{3}c1$).

	MAPLE /kJ·mol^{-1}			
	Ln = La	Ln = Ce	Ln = Pr	Ln = Nd
Ln_2Se_3	14491	14614	14725	14814
LnF$_3$	5360	5408	5447	5482
LnTaO$_4$	26078	26107	26178	25513
Σ(starting materials)$^{a)}$	39312	39456	39626	39044
$Ln_3Se_2F_2TaO_4$	37155	37215	37531	37353
Δ /%	5.80	6.02	5.58	4.53

a) Σ(starting materials) = $^1/_3$ ($3 \times$ MAPLE(LnTaO$_4$) + $2 \times$ MAPLE(Ln_2Se_3) + $2 \times$ MAPLE(LnF$_3$)).

Ln_2Se_3 ($I\bar{4}3d$),[51–53] and LnF$_3$ ($P\bar{3}c1$)[54–57]) by 4.5 to 6.0 %. The MAPLE sum for this comparison was calculated according to $^1/_3$ ($3 \times$ MAPLE(LnTaO$_4$) + $2 \times$ MAPLE(Ln_2Se_3) + $2 \times$ MAPLE(LnF$_3$)) and the respective values can be seen in Table 6.

So it does not surprise too much that the compounds $Ln_3F_2Se_2TaO_4$ (Ln = La – Nd) are only available as by-products during the flux-supported synthesis of lanthanoid(III) oxide fluoride selenides and can not be produced as single-phase products when intended to synthesize them.
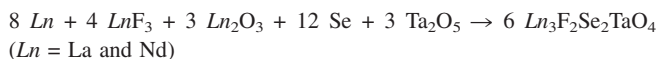
Conclusions

We were able to obtain single crystals of four quinary compounds with the composition $Ln_3F_2Se_2TaO_4$ (Ln = La – Nd) in the orthorhombic system crystallizing analogous to La$_3$F$_2$Se$_2$NbO$_4$[2] as by-products from other syntheses designed to produce (oxide) fluoride selenides of the trivalent lanthanoids successfully (e.g. LnFSe,[7–9] Ln_2F_4Se,[10] Ln_2OF_2Se,[15–17] Ln_2OF_2Se,[15–17] Ln_3OFSe_3,[18] $Ln_3OF_3Se_2$,[18] $Ln_5OF_5Se_4$,[19–21] $Ln_6O_2F_8Se_3$[16] or $Ln_6O_4F_4Se_3$[22] (Ln = La – Lu)) from tantalum capsules. With the same ionic radius of Nb^{5+} and Ta^{5+} this was not really surprising. The needle-shaped crystals of the described compounds were grown in sealed tantalum ampoules at 850 °C for seven days from a sodium-chloride flux. All three crystallographically different Ln^{3+} cations are surrounded by nine anionic ligands, which obviously restricts the range of $Ln_3F_2Se_2TaO_4$ existence to the bigger lanthanoids (Ln = La – Nd). Tantalum is octahedrally coordinated by *trans*-vertex oxygen-connected [TaO$_5$Se]$^{7-}$ octahedra, which build a chain $^1_\infty${[TaO$^V_{2/2}$O$^t_{3/1}$Se$^t_{1/1}$]$^{5-}$} along [010] with isotactically oriented Se^{2-} apices. The fluoride anions are surrounded both tetrahedrally and trigonally non-planar by Ln^{3+} cations. Three of the four oxide anions show tetrahedral coordination spheres, while the other one resides slightly off-center in a triangle of cations. These surroundings were soundly confirmed by bond-valence calculations.

Experimental Section

Synthesis: The four new compounds $Ln_3F_2Se_2TaO_4$ (Ln = La – Nd) were synthesized in a solid-state reaction according the following equations in a sodium-choride melt as fluxing agent as by-products

of syntheses having lanthanoid(III) oxide fluoride selenides as target compounds according to:

$$8\ Ln + 4\ Ln F_3 + 3\ Ln_2O_3 + 12\ Se + 3\ Ta_2O_5 \rightarrow 6\ Ln_3F_2Se_2TaO_4$$
(Ln = La and Nd)

$$9\ Ce + 4\ CeF_3 + 5\ CeO_2 + 12\ Se + 3\ Ta_2O_5 \rightarrow 6\ Ce_3F_2Se_2TaO_4$$

$$8\ Pr + 4\ PrF_3 + Pr_6O_{11} + 12\ Se + 3\ Ta_2O_5 \rightarrow 6\ Pr_3F_2Se_2TaO_4$$

The lanthanoid metals, their fluorides and oxides and sodium chloride were purchased from ChemPur (Karlsruhe, 99.9 %). Tantalum oxide, as mentioned, was not added as Ta$_2$O$_5$, but came from the inner surface of the used tantalum ampoules. Selenium was bought from Alfa-Aesar (Karlsruhe, 99.999 %). These starting materials were mixed in a glove box (MBraun, Garching), put into tantalum capsules, which were welded in an electric arc. The airtightly sealed tantalum ampoules were placed into fused silica secondary tubes to protect them from oxidation in air, and heated for 7 days at 850 °C. After cooling down, the ampoules were opened and some of the needle-shaped single crystals were selected under a polarization microscope for X-ray structure analysis. Attempted reactions according to the mentioned equations to yield the title compounds $Ln_3F_2Se_2TaO_4$ (Ln = La – Nd and Sm) with deliberately added Ta$_2$O$_5$ (ChemPur, 99.9 %) as pure phases were not successful and did not even deliver any crystals of Sm$_3$F$_2$Se$_2$TaO$_4$.

Crystallographic Studies: A selected single crystal of each $Ln_3F_2Se_2TaO_4$ representative with Ln = La – Nd was fixed in a thin-walled glass capillary with a diameter of 0.1 mm. The single-crystal X-ray diffraction measurement was carried out with an IPDS-I diffractometer from STOE and Cie in case of the lanthanum and the neodymium compound or with a κ-CCD diffractometer from Bruker-Nonius in case of the cerium and the praseodymium compound, all driven with Mo-K_α radiation (λ = 71.07 pm). Structure determination and refinement succeeded with the SHELX-97[40–42] program package and for absorption correction the program X-SHAPE[39] was applied. For bond-valence calculations (Table 3) the parameters of *Brese* and *O'Keeffe*[47] were used. MAPLE calculations were carried out with the program of *Hübenthal*[50] based on the ideas of *Hoppe*.[48,49] The crystallographic data are summarized in Table 1, whereas Table 2 shows the atomic coordinates and the displacement parameters. Table 4 offers the most important interatomic distances and Table 5 the motifs of mutual adjunction. Table 3 shows the results of the bond-valence and Table 6 those of the MAPLE calculations.

Further details of the crystal structures investigations may be obtained from the Fachinformationszentrum Karlsruhe, 76344 Eggenstein-Leopoldshafen, Germany (Fax: +49-7247-808-666; E-Mail: crysdata@fiz-karlsruhe.de, http://www.fiz-karlsruhe.de/request for deposited data.html) on quoting the depository numbers CSD-1985037,

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