Article

The Structural Dimorphism of Lanthanum Oxide Fluoride Selenide $\text{La}_2\text{OF}_2\text{Se}$

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Abstract: The new colorless lanthanum oxide fluoride selenide $\text{La}_2\text{OF}_2\text{Se}$ could be synthesized via solid-state reactions in two different structure types. Lamellar crystals of A- $\text{La}_2\text{OF}_2\text{Se}$ were obtained from mixtures of La, LaF_3 , La_2O_3 and Se in molar ratios of 2:2:1:3 with NaCl as flux for seven days in silica-protected sealed tantalum capsules at 850 °C. Needle-shaped crystals of B- $\text{La}_2\text{OF}_2\text{Se}$ emerged from reactions of the same educt mixtures in molar ratios of 6:4:4:9 scheduled to produce $\text{La}_6\text{O}_4\text{F}_4\text{Se}_3$ with CsI as flux for four days in niobium ampoules at 700 °C. The A-type form of $\text{La}_2\text{OF}_2\text{Se}$ crystallizes in the trigonal space group $R\bar{3}m$ with $a = 418.13(3)$ and $c = 4478.2(4)$ pm for $Z = 6$, whereas the B-type form is hexagonal (space group: $P6_3/m$) with $a = 1396.82(9)$ and $c = 401.08(3)$ pm for $Z = 6$. The crystal structure of A- $\text{La}_2\text{OF}_2\text{Se}$ shows a close relationship to the fluoride-free $\text{La}_2\text{O}_2\text{Se}$ and the oxygen-free $\text{La}_2\text{F}_4\text{Se}$. It can even be discussed as 1:1 intergrowth variety, since it contains the $[\text{LaO}_4\text{Se}_3]^{11-}$ and $[\text{LaF}_7\text{Se}_3]^{10-}$ polyhedra typical for the ternaries. B- $\text{La}_2\text{OF}_2\text{Se}$ appears to be structurally very similar to $\text{La}_6\text{O}_2\text{F}_8\text{Se}_3$ in displaying $[\text{LaO}_3\text{FSe}_4]^{12-}$ and $[\text{LaOF}_6\text{Se}_2]^{9-}$ polyhedra. With 6.039 versus 6.036 g/cm³ the B-type form of $\text{La}_2\text{OF}_2\text{Se}$ is slightly denser than the A-type variant.

Keywords: lanthanum oxide fluoride selenides; polymorphism; X-ray diffraction; crystal structure; rare-earth metal compounds

1. Introduction

Rare-earth metal sesquiselenides (RE_2Se_3 , $\text{RE} = \text{Sc}, \text{Y}, \text{La}, \text{Ce-Lu}$) come in three modifications, which offer coordination numbers of eight (C- or Ce_2S_3 -type structure, $\text{RE} = \text{La-Nd}, \text{Sm}, \text{Tb}, \text{Gd}, \text{Ho}, \text{Tm}$; cubic, $I\bar{4}3d$) [1–20], seven (U- or U_2S_3 -type structure, $\text{RE} = \text{Sm-Er}$; orthorhombic, Pnma) [5,16,21–25] and six (Z- or Sc_2S_3 -type structure $\text{RE} = \text{Sc}, \text{Y}, \text{Eu}, \text{Tb}, \text{Ho-Lu}$; orthorhombic, $Fddd$) [3,17,24,26–31] for the RE^{3+} cations, reflecting the consequences of the lanthanoid contraction. They are dark red or black substances and thus not suitable to serve as host materials for luminescent Ln^{3+} cations, such as Eu^{3+} or Tb^{3+} , in order to harvest red or green light. This changes a lot, when one considers their derivatives with hard anions like F^- or O^{2-} . For the rare-earth metal(III) fluoride selenides (REFSe) tetragonal NdFSe with PbFCl -type structure ($P4/nmm$) [32] and hexagonal LaFSe in $P6_3/mmc$ are known [33], both exhibiting $\text{C.N.}(\text{RE}^{3+}) = 9$. With cerium there is a trigonal compound ($R\bar{3}m$) of the composition $\text{Ce}_2\text{F}_4\text{Se}$ in the literature providing a tenfold coordination sphere for Ce^{3+} [34], while HoFSe and ErFSe adopt orthorhombic structures in Pnma with coordination numbers between six and eight for the respective RE^{3+} cations [35–37]. For YFSe , different orthorhombic polymorphs have also been reported, but even monoclinic ones ($P2_1/m$) can be found [37–40]. If oxygen is added to the rare-earth metal(III) selenides, compounds with the compositions $\text{RE}_{10}\text{OSe}_{14}$ ($\text{RE} = \text{La}, \text{Ce-Nd}$; tetragonal, $I4_1/acd$) [41,42], RE_2OSe_2 ($\text{RE} = \text{Pr}$; monoclinic, $P2_1/c$ [42]; $\text{RE} = \text{Gd}$: orthorhombic; Pnma [43]) and $\text{RE}_2\text{O}_2\text{Se}$ ($\text{RE} = \text{La}, \text{Pr}, \text{Nd}, \text{Sm}, \text{Gd}, \text{Ho}, \text{Er}, \text{Yb}$; trigonal, $P2_1/m1$) [42,44] are known. The richer in oxygen these oxide selenides get, the brighter their color becomes, so that $\text{Y}_2\text{O}_2\text{Se}:\text{Ln}^{3+}$ ($\text{Ln} = \text{Ce-Nd}, \text{Sm-Yb}$) even shows luminescence [45]. By adding both oxygen and fluorine as O^{2-} or F^- to the RE/Se systems tetragonal

Ho_3OFSe_3 ($I4/mmm$) [46], orthorhombic $\text{Ho}_3\text{OF}_3\text{Se}_2$ ($Ccce$) [46], orthorhombic $\text{Ce}_6\text{O}_4\text{F}_4\text{Se}_3$ ($Prma$) [47] and tetragonal $\text{Nd}_5\text{OF}_5\text{Se}_4$ ($I4/mmm$) [36] are found as singularities so far, but several members from the series $\text{RE}_6\text{O}_2\text{F}_8\text{Se}_3$ with $\text{RE} = \text{La-Nd}$ and $\text{RE}_2\text{OF}_2\text{Se}$ with $\text{RE} = \text{Nd, Sm, Gd-Ho}$ [48] occur. In the analogous sulfide systems the hexagonal $\text{RE}_6\text{O}_2\text{F}_8\text{S}_3$ series with $\text{RE} = \text{La-Nd, Sm, Gd}$ [49] also exists, but there is an additional one for the formula type $\text{RE}_3\text{OF}_5\text{S}$ with $\text{RE} = \text{Y, Nd, Sm, Gd-Ho}$ [50–52] showing similar structural features. Despite this difference further analogies refer to compounds with the composition $\text{RE}_3\text{OF}_3\text{S}_2$ with $\text{RE} = \text{La, Ce, Er}$ [53,54] and RE_3OFS_3 with $\text{RE} = \text{Er}$ [54]. In our ongoing efforts to elucidate the $\text{REF}_3/\text{RE}_2\text{O}_3/\text{RE}_2\text{Se}_3$ systems, we were now able to synthesize two modifications of a lanthanum oxide fluoride selenide with the formula $\text{La}_2\text{OF}_2\text{Se}$.

2. Materials and Methods

Both forms of $\text{La}_2\text{OF}_2\text{Se}$ were synthesized by mixing lanthanum powder (La: ChemPur, 99.9%, company, city, country), lanthanum trifluoride powder (LaF_3 : ChemPur, 99.9%, company, Karlsruhe, Germany), lanthanum sesquioxide powder (La_2O_3 : ChemPur, 99.9% company, city, country) and selenium powder (Se: Alfa-Aesar, 99.999% company, city, country) (in sum: about 300 mg) in a glove box under argon atmosphere. For A-type $\text{La}_2\text{OF}_2\text{Se}$ the stoichiometric molar ratio 2:2:1:3 was used as well as an excess of about 500 mg sodium chloride powder (NaCl : ChemPur, 99.9% company, city, country) to work as the fluxing agent. After heating this mixture at 850 °C for seven days in a sealed tantalum capsule, protected by an evacuated secondary silica ampoule, colorless platelets with triangular cross-section were obtained. B-type $\text{La}_2\text{OF}_2\text{Se}$ emerged as colorless needles from the same educt mixture in molar ratio of 6:4:4:9, because the target compound was $\text{La}_6\text{O}_4\text{F}_4\text{Se}_3$ in analogy to $\text{Ce}_6\text{O}_4\text{F}_4\text{Se}_3$ [47]. This mixture was charged with 300 mg cesium iodide powder (CsI : ChemPur, 99.9%) as fluxing agent and heated at 700 °C for four days in a sealed niobium tube encapsulated into an evacuated silica ampoule. After cooling down to room temperature directly with 5 K/h in the NaCl -flux case and to 540 °C with 3 K/h and CsI as flux before shutting down the furnace, washing with water, ethanol and ether removed the alkali-metal halides and left the air- and water-stable (but not phase-pure) samples of $\text{La}_2\text{OF}_2\text{Se}$ behind. For B-type $\text{La}_2\text{OF}_2\text{Se}$ the applied stoichiometry leads to $\text{La}_2\text{O}_2\text{Se}$ [44] besides B- $\text{La}_2\text{OF}_2\text{Se}$ according to $6 \text{ La} + 4 \text{ LaF}_3 + 4 \text{ La}_2\text{O}_3 + 9 \text{ Se} \rightarrow 2 \text{ La}_2\text{OF}_2\text{Se} + \text{La}_2\text{O}_2\text{Se}$.

For the data collections enabling X-ray structure analyses a IPDS diffractometer (Stoe and Cie) for A-type $\text{La}_2\text{OF}_2\text{Se}$ and a κ -CCD diffractometer (Bruker–Nonius) for B-type $\text{La}_2\text{OF}_2\text{Se}$ with graphite-monochromatized $\text{Mo-K}\alpha$ radiation ($\lambda = 71.07 \text{ pm}$) was used. The collected data were processed with the program SHELX-97 [55,56] for the structure solutions and refinements. Crystallographic data, atomic positions, equivalent isotropic displacement coefficients, selected interatomic distances and angles can be found in Tables 1–5, while Table 6 displays the motifs of mutual adjunction for both forms of $\text{La}_2\text{OF}_2\text{Se}$. The CIF data sheets of the crystal-structure investigations are available under CSD-1919109 for A- $\text{La}_2\text{OF}_2\text{Se}$ and CSD-1919110 for B- $\text{La}_2\text{OF}_2\text{Se}$ from the Fachinformationszentrum (FIZ) Karlsruhe, D-76344 Eggenstein–Leopoldshafen, Germany (e-mail: crysdata@fiz-karlsruhe.de) (or see Supplementary Materials).

For the determination of the element ratios in B-type $\text{La}_2\text{OF}_2\text{Se}$ an electron-beam microprobe technique has been applied. After performing X-ray diffraction, the single crystal was placed on a conductive carbon pad and vaporized with carbon. This setup entered the electron-beam microprobe (Cameca SX-100), which is equipped with an energy-dispersive X-ray spectrometer (EDXS). The measured energy-dispersive X-ray spectrum with its assigned peaks is shown in later in the running text and the calculated mass content compared to theoretical mass content of each element under consideration can be taken from Table 7.

3. Results

3.1. Structure Description of A-Type $\text{La}_2\text{OF}_2\text{Se}$

The A-type and the B-type form of $\text{La}_2\text{OF}_2\text{Se}$ show markedly different crystal structures. A-type $\text{La}_2\text{OF}_2\text{Se}$ crystallized in the trigonal space group $R\bar{3}m$ with $a = 418.13(3)$ and $c = 4478.2(4)$ pm ($c/a = 10.710$) for $Z = 6$. Its crystal structure (Figure 1) revealed a close relationship to the oxygen-free $\text{La}_2\text{F}_4\text{Se}$ (trigonal, $R\bar{3}m$; $a = 417.86(2)$ pm, $c = 2326.78(9)$ pm, $Z = 3$) [33,57] on the one hand and the fluoride-free $\text{La}_2\text{O}_2\text{Se}$ (trigonal, $P\bar{3}m1$; $a = 408.27(3)$ pm, $c = 717.19(5)$ pm, $Z = 1$) [44,58] on the other. As a consequence two crystallographically different positions for La^{3+} cations exist. The first one (La1) is surrounded by four O^{2-} and three Se^{2-} and anions to build an oxide-capped trigonal antiprism with Se^{2-} on the bottom and O^{2-} on the top (Figure 2a), without participation of any F^- anion. The distance to the capping oxide anion is with 249 pm a little larger than those to the oxygen atoms within the triangular face of the $[(\text{La1})\text{O}_4\text{Se}_3]^{11-}$ polyhedron ($d(\text{La}^{3+}-\text{O}^{2-}) = 247$ pm, $3\times$). The second La^{3+} cation (La2) is coordinated by seven F^- and three Se^{2-} anions, which erect a quadruple-capped trigonal prism $[(\text{La2})(\text{F1})_3(\text{F2})_4\text{Se}_3]^{10-}$ with Se^{2-} at the bottom, $(\text{F2})^-$ as the top cap, $(\text{F2})^-$ in the triangular top face and $(\text{F1})^-$ capping the three side faces (Figure 2b). The distances from $(\text{La2})^{3+}$ to the capping F^- anions range between 242 pm ($3\times$ to F1) and 245 pm ($1\times$ to F2), while the $(\text{La2})^{3+}-(\text{F2})^-$ distance to the top triangular face is 266 pm ($3\times$). The O^{2-} anion is surrounded by a tetrahedron of four $(\text{La1})^{3+}$ cations (Figure 2c) at distances of 247 pm ($3\times$) and 249 pm ($1\times$), whereas the Se^{2-} anions has contact to six La^{3+} cations arranged as triangular antiprism with $3\times$ La1 at 317 pm and $3\times$ La2 at 321 pm distance (Figure 2f). The coordination sphere of $(\text{F1})^-$ appeared triangularly planar by three La^{3+} cations ($d(\text{F1})^--(\text{La2})^{3+} = 242$ pm), while as $(\text{F2})^-$ centers a tetrahedron (Figure 2d,e) of four La^{3+} cations ($d(\text{F2})^--(\text{La2})^{3+} = 245$ pm ($1\times$), 266 pm ($3\times$)). Selected interatomic distances can be seen in detail in Table 4, while the fractional atomic coordinates and the U_{eq} values are summarized in Table 2.

Figure 1. Comparison of the crystal structures of A-type $\text{La}_2\text{OF}_2\text{Se}$ (mid) with $\text{La}_2\text{O}_2\text{Se}$ (left) and $\text{La}_2\text{F}_4\text{Se}$ (right).

Figure 2. Coordination polyhedra in A-type $\text{La}_2\text{OF}_2\text{Se}$.

3.2. Structure Description of B-Type $\text{La}_2\text{OF}_2\text{Se}$

B-type $\text{La}_2\text{OF}_2\text{Se}$ crystallizes isotypically to the structure of the $\text{RE}_2\text{OF}_2\text{Se}$ series with $\text{RE} = \text{Nd}$, Sm , Gd – Ho and similar with the compounds of the $\text{RE}_6\text{O}_2\text{F}_8\text{Se}_3$ series with $\text{RE} = \text{La}$ – Nd [48], both adapting the hexagonal space group $P6_3/m$ with $a = 1396.82(9)$ and $c = 401.08(3)$ pm ($c/a = 0.287$) for $Z = 6$ in the case of B-type $\text{La}_2\text{OF}_2\text{Se}$. Thus the a - and c -axes of B- $\text{La}_2\text{OF}_2\text{Se}$ are larger than for $\text{La}_6\text{O}_2\text{F}_8\text{Se}_3$ with $a = 1394.41(9)$ and $c = 403.97(2)$ pm ($c/a = 0.289$) for $Z = 2$, but show a smaller c/a -ratio. Four unit cells of B-type $\text{La}_2\text{OF}_2\text{Se}$ in comparison to $\text{La}_6\text{O}_2\text{F}_8\text{Se}_3$ are shown in Figure 3. There are two crystallographically different La^{3+} cations present in both structures. The first one (La1 in B- $\text{La}_2\text{OF}_2\text{Se}$) is surrounded by a square antiprism consisting of four Se^{2-} anions in the bottom square, but one (F2) $^-$ and three O^{2-} anions creating the top (Figure 4a). The distances from La1 to the oxide and fluoride anions range between 243 and 251 pm, whereas to the selenide anions four times 318 pm are found. The second one (La2) has a coordination number of nine residing in a tricapped trigonal prism erected by two Se^{2-} , one O^{2-} and six F^- anions (Figure 4b) with distances of 244.5 pm to the oxide anion, between 246 and 261 pm to the fluoride anions and again two times 318 pm to the selenide anions. While the (F1) $^-$ anion in A-type $\text{La}_2\text{OF}_2\text{Se}$ centers the triangular plane of three La^{3+} cations, in B-type $\text{La}_2\text{OF}_2\text{Se}$ the analogous (F1) $^-$ particle is located outside of this triangle with a deflection of about 94 pm (Figure 4d) in a distance of 246.6 pm (2 $\times$) and 260.9 pm to the (La2) $^{3+}$ anions. The (F2) $^-$ and the

O^{2-} anions are in both structures of La_2OF_2Se surrounded by $(La^{3+})_4$ tetrahedra (Figure 4c,e) with distances of about 244 pm in the oxygen and 250 pm in the fluorine case. While the Se^{2-} anions in A-type La_2OF_2Se are surrounded octahedrally, they center trigonal prisms of six La^{3+} cations in B-type La_2OF_2Se (Figure 4f) with six distances of about 318 pm. These $[SeLa_6]^{16+}$ prisms share vertical edges to form a triple and trans-oriented triangular faces to build a chain along the c -axis (Figure 5). The inner channels of these chains remain empty, in B-type La_2OF_2Se , but host F^- -anions in $La_6O_2F_8Se_3$ [48] to increase the coordination number of $(La1)^{3+}$ from eight to nine. Along with this the position of O^{2-} has to be substituted partly with F^- anions to secure the charge balance of $La_6O_2F_8Se_3$ [48]. There is also a not filled tube along the c -axis in B-type La_2OF_2Se and $La_6O_2F_8Se_3$, which can be partly filled with Na^+ cations like in $NaCe_{18}O_9F_{19}Se_9$ [59].

Figure 3. Comparison of the crystal structures of B-type La_2OF_2Se (top) and $La_6O_2F_8Se_3$ (bottom) as viewed along their c -axes.

Figure 4. Coordination polyhedra in B-type $\text{La}_2\text{OF}_2\text{Se}$.

Figure 5. Connected trigonal prisms of La^{3+} cations surrounding the Se^{2-} anions in B- $\text{La}_2\text{OF}_2\text{Se}$, which build a triple chain along the c -axis.

3.3. Single-Crystal Data of A- and B-Type $\text{La}_2\text{OF}_2\text{Se}$

In Table 1 the crystallographic data of A- and B-type $\text{La}_2\text{OF}_2\text{Se}$ as well as their determination can be seen. Tables 2 and 3 show fractional atomic coordinates and U_{eq} values of both structures and

Tables 4 and 5 some selected interatomic distances and angles in the crystal structures. The motifs of mutual adjunction in are summarized in Table 6.

Table 1. Crystallographic data of A- and B-type $\text{La}_2\text{OF}_2\text{Se}$ and their determination.

Compound	A- $\text{La}_2\text{OF}_2\text{Se}$	B- $\text{La}_2\text{OF}_2\text{Se}$
crystal system	trigonal	hexagonal
space group	$R\bar{3}m$ (no. 166)	$P6_3/m$ (no. 172)
lattice parameters,		
a/pm	418.13(3)	1396.82(9)
c/pm	4478.2(4)	401.08(3)
c/a	10.710	0.287
number of formula units (Z)	6	6
unit-cell volume (V_{uc} in nm^3)	0.67804(9)	0.67771(8)
molar volume (V_{m} in cm^3/mol)	68.053	68.020
calculated density (D_{x} in g/cm^3)	6.036	6.039
diffractometer	IPDS (Stoe and Cie)	κ -CCD (Bruker-Nonius)
wavelength (λ in pm)	Mo- $\text{K}\alpha$ ($\lambda = 71.07$ pm)	Mo- $\text{K}\alpha$ ($\lambda = 71.07$ pm)
index range ($\pm h_{\text{max}}, \pm k_{\text{max}}, \pm l_{\text{max}}$)	6/6/67	19/19/5
number of e^- per unit cell ($F(000)$)	1044	1044
absorption coefficient (μ in mm^{-1})	26.59	26.60
number of collected vs. unique reflections	3237/383	13042/749
data-set residuals ($R_{\text{int}}/R_{\sigma}$)	0.070/0.027	0.097/0.052
structure residuals (R_1/wR_2)	0.026/0.088	0.052/0.120
goodness of fit (GooF)	1.072	1.028
residual electron density (max./min. in $e^- 10^{-6} \text{ pm}^{-3}$)	3.12/−2.67	3.57/−1.98
CSD number	1919109	1919110

Table 2. Fractional atomic coordinates and U_{eq} values^a for A- $\text{La}_2\text{OF}_2\text{Se}$.

Atom	Site	x/a	y/b	z/c	$U_{\text{eq}}/\text{pm}^2$
La1	6c	0	0	0.133109(14)	206(3)
La2	6c	0	0	0.293363(14)	111(2)
O	6c	0	0	0.18868(19)	248(18)
F1	6c	0	0	0.03591(17)	178(14)
F2	6c	0	0	0.34832(17)	171(13)
Se	6c	0	0	0.42052(2)	138(3)

$$^a U_{\text{eq}} = 1/3 [U_{33} + 4/3 (U_{11} + U_{22} - U_{12})] \text{ [60]}.$$

Table 3. Fractional atomic coordinates and U_{eq} values^a for B- $\text{La}_2\text{OF}_2\text{Se}$.

Atom	Site	x/a	y/b	z/c	$U_{\text{eq}}/\text{pm}^2$
La1	6h	0.12574(8)	0.51625(8)	1/4	231(3)
La2	6h	0.23351(8)	0.28450(8)	1/4	239(3)
O	6h	0.4323(7)	0.4156(8)	1/4	114(19)
F1	6h	0.1895(9)	0.0901(9)	1/4	335(24)
F2	6h	0.0696(8)	0.3151(8)	1/4	263(21)
Se	6h	0.48066(14)	0.19870(14)	1/4	232(4)

$$^a U_{\text{eq}} = 1/3 [U_{33} + 4/3 (U_{11} + U_{22} - U_{12})] \text{ [60]}.$$

Table 4. Selected interatomic distances (d/pm) and angles ($\angle/^\circ$) in the crystal structure of A-type $\text{La}_2\text{OF}_2\text{Se}$.

Distance			Angle		
		(d/pm)			($\angle/^\circ$)
La1–O	(3×)	246.9	La1–O–La1	(3×)	102.1
La1–O′	(1×)	248.9	La1–O–La1′	(3×)	115.8
La1–Se	(3×)	317.1	La2–F1–La2	(3×)	119.4
La2–F1	(3×)	242.1	La2–F2–La2	(3×)	103.4
La2–F2	(1×)	245.2	La2–F2–La2′	(3×)	115.1
La2–F2′	(3×)	266.5	La1–Se–La1	(3×)	82.5
La2–Se	(3×)	320.9	La1–Se–La2	(6×)	98.1
O–La1	(3×)	246.9	La1–Se–La2′	(3×)	179.2
O–La1′	(1×)	248.9	La2–Se–La2	(3×)	81.3
F1–La2	(3×)	242.1			
F2–La2	(1×)	245.2			
F2–La2′	(3×)	266.5			
Se–La1	(3×)	317.1			
Se–La2	(3×)	320.9			

Table 5. Selected interatomic distances (d/pm) and angles ($\angle/^\circ$) in the crystal structure of B-type $\text{La}_2\text{OF}_2\text{Se}$.

Distance			Angle		
		(d/pm)			($\angle/^\circ$)
La1–O	(1×)	243.0	La1–O–La1	(2×)	105.4
La1–O′	(2×)	243.5	La1–O–La1′	(1×)	110.9
La1–F2	(1×)	251.1	La1–O–La2	(2×)	109.8
La1–Se	(2×)	318.0	La1′–O–La2	(1×)	115.3
La1–Se′	(2×)	318.3	La2–F1–La2′	(2×)	100.4
La2–O	(1×)	244.5	La2–F1–La2	(1×)	110.9
La2–F1	(1×)	246.6	La1–F2–La2	(2×)	105.9
La2–F1′	(2×)	260.9	La1–F2–La2′	(1×)	112.7
La2–F2	(2×)	249.8	La2–F2–La2	(1×)	106.8
La2–F2′	(1×)	253.5	La2–F2–La2′	(2×)	112.5
La2–Se	(2×)	318.3	La1–Se–La1	(2×)	78.1
O–La1	(1×)	243.0	La1–Se–La1′	(2×)	89.8
O–La1′	(2×)	243.5	La1–Se–La2	(2×)	82.5
O–La2	(1×)	244.4	La1′–Se–La2	(2×)	80.6
F1–La2	(1×)	246.6	La2–Se–La2	(2×)	78.1
F1–La2′	(2×)	260.9			
F2–La1	(1×)	251.1			
F2–La2	(2×)	249.8			
F2–La2′	(1×)	253.5			
Se–La1	(2×)	318.0			
Se–La1′	(2×)	318.3			

Table 6. Motifs of mutual adjunction in A- and B-type $\text{La}_2\text{OF}_2\text{Se}$.

A- $\text{La}_2\text{OF}_2\text{Se}$:					
	F1	F2	O	Se	C.N.
La1	0/0	0/0	4/4	3/3	7
La2	3/3	4/4	0/0	3/3	10
C.N.	3	4	4	6	
B- $\text{La}_2\text{OF}_2\text{Se}$:					
	F1	F2	O	Se	C.N.
La1		1/1	3/3	4/4	8
La2		3/3	1/1	2/2	9
C.N.	3	4	4	6	

3.4. Energy-Dispersive X-Ray Spectrum of B-Type $\text{La}_2\text{OF}_2\text{Se}$

Table 7 summarizes the results of an EDXS measurement on a single crystal of B-type $\text{La}_2\text{OF}_2\text{Se}$, which is shown in Figure 6. The content of oxygen was calculated in such a way that there was no change left in the stoichiometric composition $\text{La}_2\text{OF}_2\text{Se}$. For this reason no error margins can be given.

Table 7. Results of an energy-dispersive X-ray spectrometer (EDXS) measurement on a single crystal of B-type $\text{La}_2\text{OF}_2\text{Se}$.

Element	Measured Content [wt-%]	Theoretical Content [wt-%]
La	68.4(5)	67.63
O	4.15	3.90
F	9.66(14)	9.25
Se	17.79(16)	19.22

It can be seen from Table 7, that the measured and the theoretical element content almost coincide. The measured carbon as shown in Figure 6 also was not considered in the calculation, since it originated from the sample preparation.

Figure 6. The energy-dispersive X-Ray spectrum (EDXS) of a single crystal of B-type $\text{La}_2\text{OF}_2\text{Se}$.

4. Discussion

Both crystal structures of $\text{La}_2\text{OF}_2\text{Se}$ show striking resemblance to either $\text{La}_2\text{O}_2\text{Se}$ and $\text{La}_2\text{F}_4\text{Se}$ in the trigonal A-type or $\text{La}_6\text{O}_2\text{F}_8\text{Se}_3$ in the hexagonal B-type case. A- $\text{La}_2\text{OF}_2\text{Se}$ displays the coordination polyhedra with the lowest ($[\text{LaO}_4\text{Se}_3]^{11-}$, C.N. = 7) and the highest coordination numbers ($[\text{LaF}_7\text{Se}_3]^{10-}$, C.N. = 10) for both, while for B- $\text{La}_2\text{OF}_2\text{Se}$ they range in the middle ($[\text{LaO}_3\text{FSe}_4]^{12-}$, C.N. = 8; $[\text{LaOF}_6\text{Se}_2]^{9-}$, C.N. = 9), but carry the more diverse charges. With A- $\text{La}_2\text{OF}_2\text{Se}$ ($a = 418.13(3)$, $c = 4478.2(4)$ pm) being a perfect intergrowth adduct of $\text{La}_2\text{O}_2\text{Se}$ ($a = 408.27(3)$, $c = 717.19(5)$ pm) [58] and $\text{La}_2\text{F}_4\text{Se}$ ($a = 417.86(2)$, $c = 2326.78(9)$ pm) [57] the occurrence of the same polyhedra does not surprise, but the $\text{La}_2\text{O}_2\text{Se}$ compartment of A- $\text{La}_2\text{OF}_2\text{Se}$ appears a little more dilated ($d(\text{La}^{3+}-\text{O}^{2-}) = 3 \times 246.9$ and 1×248.9 pm, $d(\text{La}^{3+}-\text{Se}^{2-}) = 3 \times 317.1$ pm) as compared to the original ternary ($d(\text{La}^{3+}-\text{O}^{2-}) = 1 \times 241.9$ and 3×243.9 pm, $d(\text{La}^{3+}-\text{Se}^{2-}) = 3 \times 313.3$ pm) [58], whereas the $\text{La}_2\text{F}_4\text{Se}$ part ($d(\text{La}^{3+}-\text{F}^-) = 3 \times 242.1$, 1×245.2 plus 3×266.5 pm, $d(\text{La}^{3+}-\text{Se}^{2-}) = 3 \times 320.9$ pm) outstandingly agrees with $\text{La}_2\text{F}_4\text{Se}$ ($d(\text{La}^{3+}-\text{F}^-) = 3 \times 241.9$, 1×242.9 plus 3×266.5 pm, $d(\text{La}^{3+}-\text{Se}^{2-}) = 3 \times 319.7$ pm) [57] itself. Hence the Madelung part of the lattice energy (MAPLE) [61–63] shows a slightly better agreement between the value for A- $\text{La}_2\text{OF}_2\text{Se}$ (12141 kJ/mol) and the sum of the ternaries ($\text{La}_2\text{O}_2\text{Se}$: 13477 kJ/mol, $\text{La}_2\text{F}_4\text{Se}$: 11045 kJ/mol) according to $1/2 \times \text{MAPLE}(\text{La}_2\text{O}_2\text{Se}) + 1/2 \times \text{MAPLE}(\text{La}_2\text{F}_4\text{Se}) =$

6739 + 5523 = 12262 kJ/mol in comparison with B-La₂OFe₂Se (12111 kJ/mol). The latter, B-La₂OFe₂Se ($a = 1396.82(9)$, $c = 401.08(3)$ pm), has a lot more in common with La₆O₂F₈Se₃ ($a = 1394.41(9)$, $c = 402.96(3)$ pm) [48], as the similar interatomic distances ($d(\text{La}^{3+}-\text{O}^{2-}) = 243\text{--}245$ pm, $d(\text{La}^{3+}-\text{F}^-) = 247\text{--}253$ plus 261 pm, $d(\text{La}^{3+}-\text{Se}^{2-}) = 318\text{--}319$ pm versus $d(\text{La}^{3+}-\text{O}^{2-}) = 244\text{--}252$ pm, $d(\text{La}^{3+}-\text{F}^-) = 245\text{--}256$ pm, $d(\text{La}^{3+}-\text{Se}^{2-}) = 316\text{--}318$ pm) prove, in spite of some mixed occupation of O^{2−} and F[−] anions in tetrahedral surrounding of La³⁺ cations in hexagonal La₆O₂F₈Se₃. The slightly higher density of 6.039 g/cm³ for B-La₂OFe₂Se versus 6.036 g/cm³ A-La₂OFe₂Se should predestine the B-type structure of La₂OFe₂Se to be the high-pressure form or the A-type structure to represent the high-temperature modification of La₂OFe₂Se, which needs to become verified as soon as we shall have phase-pure samples in hands.

Supplementary Materials: The CIF of the title compounds are available online at <http://www.mdpi.com/2073-4352/9/9/435/s1>, or in the ICSD with the number 1919109 for A-type or 1919110 for B-type.

Author Contributions: H.G. synthesized the A-type form of La₂OFe₂Se and C.B. the B-type. H.G. and T.S. solved the crystal structure of A-La₂OFe₂Se and C.B. and T.S. of the B-type. T.S. contributed the reagents, the materials, the scientific equipment and the infrastructure. C.B. wrote the paper and T.S. reviewed it.

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