

Structural refinement of the RT LaOF phases by coupling powder X-Ray diffraction, ^{19}F and ^{139}La solid state NMR and DFT calculations of the NMR parameters

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Electronic Supporting Information

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1. Homogeneity ranges of t- and β -LaOF

According to Zachariassen¹ the tetragonal phase has a wide homogeneity range, extending from $\text{LaO}_{0.7}\text{F}_{1.6}$ to LaOF, and is stabilized by the presence of excess fluorine, located in interstitial position, over the ideal composition LaOF. For this ideal composition the tetragonal phase is unstable relative to the rhombohedral phase. The unit-cell dimensions of the tetragonal phases decrease with increasing oxygen content. On the other hand, the chemical composition of the rhombohedral phase is sharply defined and corresponds to the exact formula LaOF. No variation in unit-cell dimensions of this phase is observed. Only Tyagi² suggested that the tetragonal form of stoichiometric LaOF is more stable than the rhombohedral form of LaOF but the reported values of x in $\text{LaO}_{1-x}\text{F}_{1+2x}$ are not consistent with the corresponding compositions (see 2.1.e). The recalculated values of x allow contradicting this suggestion.³ On the other hand, the tetragonal phase has a wider homogeneity range extending from $\text{LaO}_{0.263}\text{F}_{2.474}$ to LaOF (see 2.2.c) and the rhombohedral phase does not correspond only to the exact formula LaOF but presents also an homogeneity range extending from $\text{LaO}_{1.008}\text{F}_{0.984}$ to $\text{LaO}_{1.106}\text{F}_{0.788}$ (see 2.1.e).³ However, as previously outlined by Fergus and Chen,⁴ who determine a maximum value of x equal to 0.43 (see 2.2.d), the maximum value of x for the tetragonal phase was based, by Tyagi,² on the appearance of (diffraction) peaks for LaF_3 which may not be observable in two-phase materials containing small amounts of LaF_3 .

2. Structural data

2.1. β -LaOF (rhomboedral)

2.1.a) ICSD⁵ 30622¹

Space group: R -3 m R (166)

$a = 7.132(1) \text{ \AA}$, $\alpha = 33.01(1)^\circ$, cell volume = 95.82 \AA^3 , $Z = 2$

Fractional atomic coordinates:

Atom	Wyck.	x	y	z
La1	2 c	0.242(1)	0.242(1)	0.242(1)
F1	2 c	0.122	0.122	0.122
O1	2 c	0.37	0.37	0.37

Interatomic distances (\AA):

La1	F1	3x	2.4204
	F1	1x	2.4254
	O1	1x	2.5871
	O1	3x	2.5874

Hexagonal cell: $a = 4.0524 \text{ \AA}$, $c = 20.2120 \text{ \AA}$

Fractional atomic coordinates:

Atom	Wyck.	x	y	z
La1	6c	0	0	0.242
F1	6c	0	0	0.122
O1	6c	0	0	0.37

2.1.b) from ref.⁶

$a = 7.132(1) \text{ \AA}$, $\alpha = 32.99(1)^\circ$

2.1.c) from ref.^{7,8}

Later, the crystal structure of β -LaOF was also refined by Hölsä *et al.*^{7,8} leading to the same conclusions (*i.e.* that the oxygen and fluorine atom positions should be interchanged).

Hexagonal cell: $a = 4.0534(1) \text{ \AA}$, $c = 20.1961(1) \text{ \AA}$ ⁷

Fractional atomic coordinates:

Atom	Wyck.	x	y	z
La1	6c	0	0	0.2425(1)
F1	6c	0	0	0.3707(7)
O1	6c	0	0	0.1190(9)

Interatomic distances (\AA):

La1	O1	3x	2.4084(43)
	O1	1x	2.4942(183)
	F1	3x	2.5773(60)
	F1	1x	2.5891(143)

Hexagonal cell: $a = 4.0534(4) \text{ \AA}$, $c = 20.1961(10) \text{ \AA}$ ⁸

Fractional atomic coordinates:

Atom	Wyck.	x	y	z
La1	6c	0	0	0.24249(1)
F1	6c	0	0	0.37068(6)
O1	6c	0	0	0.11902(7)

Interatomic distances (\AA):

La1	O1	3x	2.4084(4)
	O1	1x	2.4936(14)
	F1	3x	2.5776(6)
	F1	1x	2.5889(12)

2.1.d) from ref.⁹

Hexagonal cell: $a = 4.0505(2) \text{ \AA}$, $c = 20.2115(25) \text{ \AA}$ and $a = 4.051 \text{ \AA}$, $c = 20.22 \text{ \AA}$.

2.1.e) from ref.²

Cell parameters of $\text{LaO}_{1-x}\text{F}_{1+2x}$ with $-0.235 \leq x \leq -0.160$, recalculated as $-0.106 \leq x \leq -0.008$ in ref.³

	$a \text{ (\AA)}$	$\alpha \text{ (}^\circ\text{)}$
$\text{LaO}_{1.008}\text{F}_{0.984}$	7.060(9)	33.48
$\text{LaO}_{1.022}\text{F}_{0.956}$	7.059(9)	33.50
$\text{LaO}_{1.036}\text{F}_{0.928}$	7.057(9)	33.50
$\text{LaO}_{1.106}\text{F}_{0.788}$	7.052(8)	33.67

2.1.f) from ref.¹⁰

Hexagonal cell : $a = 4.056(5) \text{ \AA}$, $c = 20.21(3) \text{ \AA}$.

2.1.g) from ref.⁴

$a = 7.1290 \text{ \AA}$, $\alpha = 33.01^\circ$, same atomic positions as Zachariassen.¹

Hexagonal cell: $a = 4.0512 \text{ \AA}$, $c = 20.2031 \text{ \AA}$.

2.1.h) from ref.¹¹

$\text{LaO}_{1-x}\text{F}_{1+2x}$ with $-0.01 \leq x \leq 0.02$

$a = 7.133 \text{ \AA}$, $\alpha = 33.0^\circ$.

2.1.i) from ref.¹²

Hexagonal cell: $a=4.056(9) \text{ \AA}$, $c=20.227(1) \text{ \AA}$.

2.1.j) from ref.¹³

Hexagonal cell: $a=4.0516(2) \text{ \AA}$, $c=20.177(3) \text{ \AA}$.

2.1.k) from ref.¹⁴

Hexagonal cell: $a=4.044(8) \text{ \AA}$, $c=20.141(8) \text{ \AA}$.

2.2. t-LaOF (tetragonal)

2.2.a) from ref.¹

Space group: P 4/n m m (129)

LaOF (ICSD⁵ 76427)

a = 4.091(1) Å, c = 5.836(1) Å, cell volume = 97.67 Å³, Z = 2

Fractional atomic coordinates:

Atom	Wyck.	x	y	z
La1	2c	0.5	0	0.222(4)
F1	2a	0	0	0
O1	2b	0	0	0.5

Interatomic distances (Å):

La1	F1	4x	2.4213
	O1	4x	2.6108

LaF_{1.6}O_{0.7}

Zachariasen has also reported the positions for the interstitial anions in the tetragonal anion-excess phase LaF_{1.6}O_{0.7}.¹

a = 4.106(2) Å, c = 5.852(4) Å

Fractional atomic coordinates:

Atom	Wyck.	S.O.F.	x	y	z
La1	2c	1	0.5	0	0.235
F1	2a	1	0	0	0
O	2b	0.7	0	0	0.5
F	2b	0.3	0	0	0.5
∅F	2c	0.3	0.5	0	0.75

2.2.b) from ref.⁸

Hölsä *et al.* have also refined the crystal structures of the tetragonal form (with $z_{La} > 0.25$ and then distances La-F > La-O) for various t-LaO_{1-x}F_{1+2x} ($0.05 \leq x \leq 0.30$) but without considering the expected interstitial positions occupied by the excess F⁻ ions. In addition, the evolutions with x of the unit cell parameters are not regular making doubtful the compositions of these non-stoichiometric phases.

Cell parameters a (Å) and c (Å), z_{La} and interatomic distances (Å):

	a	c	z_{La}	La-O distance	La-F distance ^a
LaO _{0.95} F _{1.10}	4.0850(4)	5.8320(7)	0.27592(4)	2.425(4)	2.600(4)
LaO _{0.91} F _{1.18}	4.0906(2)	5.8386(4)	0.27991(3)	2.415(4)	2.618(4)
LaO _{0.89} F _{1.22}	4.0942(2)	5.8423(3)	0.28057(3)	2.415(4)	2.623(4)
LaO _{0.85} F _{1.30}	4.0927(1)	5.8386(2)	0.27887(3)	2.419(4)	2.615(4)
LaO _{0.83} F _{1.34}	4.1202(2)	5.8765(4)	0.27998(4)	2.432(4)	2.637(4)
LaO _{0.72} F _{1.56}	4.1089(1)	5.8593(3)	0.27520(4)	2.440(4)	2.612(4)
LaO _{0.70} F _{1.60}	4.1120(1)	5.8599(4)	0.27255(4)	2.450(4)	2.603(4)

^a One La-F distance since the expected interstitial positions occupied by the excess F⁻ ions were not considered

2.2.c) from ref.²

LaO_{1-x}F_{1+2x} with -0.154 ≤ x ≤ 0.609 recalculated as -0.001 ≤ x ≤ 0.737 in ref.³

The reported a' and c' parameters (Å) are reversed from those determined by Zachariassen¹ and Fergus *et al.*⁴ and are then recalculated below for the sake of clarity.

	a' = c	c' = a√2	c'/√2 = a
LaO _{1.001} F _{0.998}	5.820(3)	5.777(3)	4.085
LaO _{0.965} F _{1.070}	5.821(2)	5.770(2)	4.080
LaO _{0.893} F _{1.214}	5.821(3)	5.769(3)	4.079
LaO _{0.819} F _{1.362}	5.822(2)	5.767(3)	4.078
LaO _{0.744} F _{1.512}	5.827(2)	5.775(2)	4.084
LaO _{0.667} F _{1.666}	5.830(4)	5.783(2)	4.089
LaO _{0.590} F _{1.820}	5.829(2)	5.779(2)	4.086
LaO _{0.510} F _{1.980}	5.837(2)	5.777(2)	4.085
LaO _{0.429} F _{2.142}	5.839(2)	5.793(2)	4.096
LaO _{0.347} F _{2.306}	5.840(5)	5.793(7)	4.096
LaO _{0.263} F _{2.474}	5.842(1)	5.779(2)	4.086

2.2.d) from ref.⁴

LaO_{1-x}F_{1+2x}

Cell parameters a (Å) and c (Å) and δ (zLa = 0.25 - δ/2):

	a (Å)	c (Å)	δ
LaOF	4.0834	5.8300	0.061
LaOF	4.0804	5.8278	0.064
LaO _{0.75} F _{1.5}	4.0916	5.8397	0.056
LaO _{0.57} F _{1.86}	4.0994	5.8451	0.045
LaO _{0.57} F _{1.86}	4.0993	5.8446	0.046

$$a (\text{Å}) = 4.0816 + 0.0044 x \quad (0 < x < 0.43); \quad c (\text{Å}) = 5.8288 + 0.0041 x \quad (0 < x < 0.43)$$

LaOF (x=0)

Fractional atomic coordinates:

Atom	Wyck.	x	y	z
La1	2 c	0.5	0	0.25-δ/2
F1	2 a	0	0	0
O1	2 b	0	0	0.5

x>0

Fergus and Chen⁴ claimed that they follow the analysis of Zachariassen¹ but the occupation rates of the anion sites by oxide and excess fluoride ions differ.

Fractional atomic coordinates:

Atom	Site	S.O.F.	x	y	z
La1	2 c	1	0.5	0	0.25-δ/2
F1	2 a	1	0	0	0
O	2 c	1-2x	0.5	0	0.75
F	2 c	2x	0.5	0	0.75
O	2 b	x	0	0	0.5

2.2.e) from ref.¹²**LaOF**

a = 4.101(1) Å, c = 5.851(8) Å

2.2.f) from ref.¹⁵**LaOF**

a = 4.096586 Å, c = 5.834422 Å

2.2.g) from ref.¹⁴**LaOF**

a = 4.105(7) Å, c = 5.857(1) Å

2.2.h) ICSD⁵ 40371¹⁶

In fact, before the two studies of Hölsa *et al.*⁸ and Fergus and Chen,⁴ the crystal structure of the tetragonal anion-excess phase $\text{LaF}_{1.70}\text{O}_{0.65}$ was investigated by Laval *et al.* by means of neutron diffraction data. They show that O and F have to be reversed (F and O located at 2b and 2a sites, respectively) in both stoichiometric and anion-excess tetragonal phases. They also show that, in $t\text{-LaF}_{1.70}\text{O}_{0.65}$, the O/F order is preserved and that the excess of anions are accommodated by the creation of vacancies within the F-layers, the insertion of F atoms at interstitial site and the partial substitution of F atoms for O ones within the O-layers. The La-O distances (2.46 Å) are shorter than the La-F ones (2.58-2.60 Å).

LaF_{1.7}O_{0.65}

a=4.105(2) Å, c=5.843(3) Å

Fractional atomic coordinates [origin choice 2]:

Atom	Site	S.O.F.	x	y	z
La1	2c	1	1/4	1/4	0.2314(3)
O1	2a	0.65	3/4	1/4	0
F1	2a	0.35	3/4	1/4	0
F2	2b	0.86	3/4	1/4	1/2
F3	8i	0.1225	1/4	0.098(2)	0.663(1)

Interatomic distances (Å):

La1	O1 F1	4x	2.4578
	F3	8x	2.5757
	F2	4x	2.5838
	F3	4x	2.5979

3. Bond valence calculations

The valence, v_{ij} , of a bond between two atoms i and j is defined so that the sum of all the valences from a given atom i with valence V_i obeys: $\sum_j v_{ij} = V_i$. The most commonly adopted empirical expression for the variation of the length d_{ij} of a bond with valence is $v_{ij} = \exp[(R_{ij} - d_{ij})/b]$ with $b=0.37 \text{ \AA}^{-1}$ and $R_{ij} = 2.172 \text{ \AA}$ and 2.057 \AA for La-O and La-F, respectively.^{17,18}

Table S1. Bond valence calculations for tetragonal LaOF¹

Atom i	Atom j	CN	d_{ij} (Å)	v_{ij}	V_i
La1	F1	4	2.4213	0.374	2.72
	O1	4	2.6108	0.305	
F1	La1	4	2.4213	0.374	1.49
O1	La1	4	2.6108	0.305	1.22

Table S2. Bond valence calculations for tetragonal LaOF¹ with oxygen and fluorine atom positions interchanged

Atom i	Atom j	CN	d_{ij} (Å)	v_{ij}	V_i
La1	O1	4	2.4213	0.510	2.93
	F1	4	2.6108	0.224	
O1	La1	4	2.4213	0.510	2.04
F1	La1	4	2.6108	0.224	0.90

Table S3. Bond valence calculations for rhombohedral LaOF¹

Atom i	Atom j	CN	d_{ij} (Å)	v_{ij}	V_i
La1	F1	3	2.4204	0.375	2.79
	F1	1	2.4254	0.369	
	O1	1	2.5871	0.326	
	O1	3	2.5874	0.325	
F1	La1	3	2.4204	0.375	1.49
	La1	1	2.4254	0.369	
O1	La1	1	2.5871	0.326	1.30
	La1	3	2.5874	0.325	

Table S4. Bond valence calculations for rhombohedral LaOF¹ with oxygen and fluorine atom positions interchanged

Atom i	Atom j	CN	d_{ij} (Å)	v_{ij}	V_i
La1	O1	3	2.4204	0.511	2.99
	O1	1	2.4254	0.504	
	F1	1	2.5871	0.239	
	F1	3	2.5874	0.238	
O1	La1	3	2.4204	0.511	2.04
	La1	1	2.4254	0.504	
F1	La1	1	2.5871	0.239	0.95
	La1	3	2.5874	0.238	

4. DFT optimizations of the Zachariasen structures

4.1 β -LaOF

Hexagonal cell: $a = 4.0524 \text{ \AA}$, $c = 20.2120 \text{ \AA}$

Fractional atomic coordinates after optimization:

Atom	Wyck.	x	y	z
La1	6c	0	0	0.2586
F1	6c	0	0	0.1286
O1	6c	0	0	0.3770

4.2 t-LaOF

$a = 4.091(1) \text{ \AA}$, $c = 5.836(1) \text{ \AA}$

Fractional atomic coordinates after optimization:

Atom	Wyck.	x	y	z
La1	2c	0.5	0	0.2854
F1	2a	0	0	0
O1	2b	0	0	0.5

5. Parameters used to generate the OTF USPP pseudopotentials

Details on the string can be found on the Castep website (<http://www.castep.org/>) in the documentation section.

Atom	OTF USPP String
O	2 1.3 16.537 18.375 20.212 20UU:21UU(qc=7.5)[]
F	2 1.4 16.537 18.375 20.212 20UU:21UU(qc=7.5)[]
La	2 2 2 1.4 8 12 13 50N:60NH:51UU:52LGG: 43U1.6+0@0.1672U1.6+0.1@0.1672{5d0.9,4f0.1}{qc=6}[]

6. F-F, F-O and O-O distances for β - and t-LaOF from the Rietveld refinement and after DFT-PBE atomic position optimization

Table S5 F-F, F-O and O-O distances (Å) for β - and t-LaOF from the Rietveld refinement (experimental structure, ES) and after DFT-PBE atomic position optimization (APO). Uncertainties are indicated in brackets. For t-LaOF, the O and F atomic coordinates are fixed by symmetry.

Phase	Distances	ES	APO
β -LaOF	F-F ($\times 3$)	2.768(9)	2.770
	F-O ($\times 3$)	2.912(11)	2.911
	O-O ($\times 3$)	2.949(12)	2.949
t-LaOF	F-F ($\times 4$)	2.8883(1)	2.8883
	O-O ($\times 4$)	2.8883(1)	2.8883
	F-O ($\times 2$)	2.9148(1)	2.9148

7. Eigenvectors of the calculated ^{139}La EFG tensor

Table S9. Eigenvectors of the calculated ^{139}La EFG tensor, expressed in the crystallographic axis, for β -LaOF (APO).

Axis	V_{xx}	V_{yy}	V_{zz}
a	0.01986	-0.28422	0
b	-0.23621	-0.15931	0
c	0	0	0.04946

Table S10. Eigenvectors of the calculated ^{139}La EFG tensor, expressed in the crystallographic axis, for t-LaOF (ES).

Axis	V_{xx}	V_{yy}	V_{zz}
a	0.24227	-0.03516	0
b	0.03516	0.24227	0
c	0	0	0.17154

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