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Supplementary Files

Insights into the Structural Variations in $SmNb_{1-x}Ta_xO_4$ and $HoNb_{1-x}Ta_xO_4$ a combined Experimental and Computational Studies

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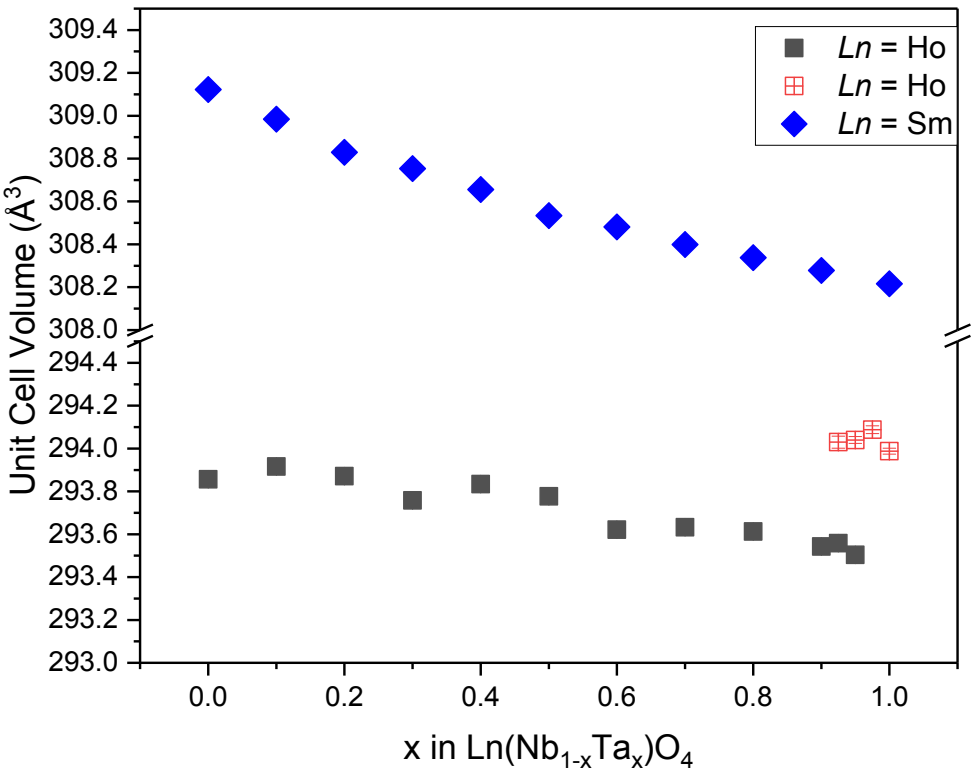


Figure S1. Composition dependence of the unit cell volume for the two series LnNb$_{1-x}$Ta$_x$O$_4$. The values for *Ln* = Sm are from refinements against S-XRD data and those from *Ln* = Ho from PND data. The closed symbols are from refinements in *I*2/*a* and the open symbols are the values for the structure refined in *P*2/*c* multiplied by 2.

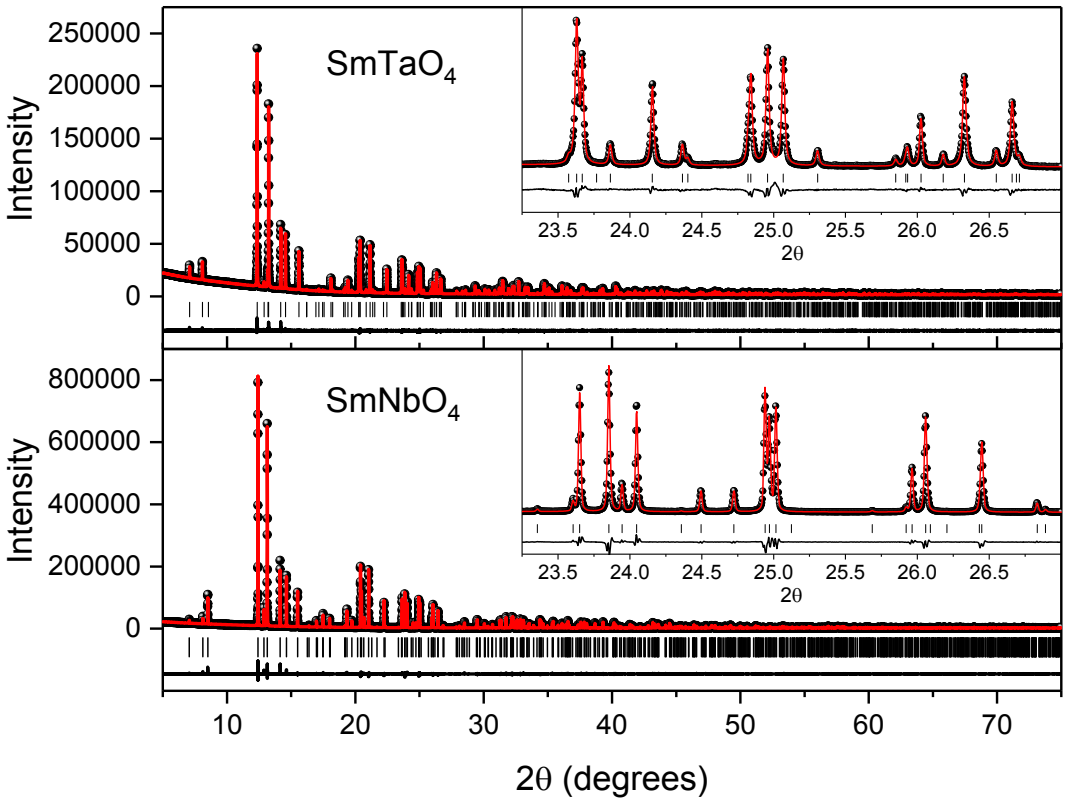


Figure S2. Examples of the Rietveld refinements for $SmTaO_4$ and $SmNbO_4$. The data are represented by the black spheres, the red line is the calculated profile and the lower blue line the difference between the observed and calculated profiles. The short vertical markers show the positions of the space group allowed Bragg reflections. The insets highlight the fits to the regions illustrated in Figure 1.

Table S1. Refined Structural parameters for $SmNbO_4$:

Space group *I*2/*a*

a = 5.420642(6), b = 11.175430(14), c = 5.119937(6) Å, β = 94.67780(10)^0,

Cell volume = 309.1225(6) Å^3

Name	*x*	*y*	*z*	Ui*100 Å^2
Sm1	¼	0.12078(4)	0	0.284(6)
Nb1	¼	0.64619(4)	0	1.219(14)
O1	0.0076(4)	0.71551(20)	0.2029(5)	1.21(6)
O2	0.9039(4)	0.45567(20)	0.2463(4)	0.91(5)

Atomic positions in $SmNbO_4$ obtained from theoretical calculations:

	PBE	PBEsol
Sm1	(¼ 0.1220 0.0)	(¼ 0.1204 0.0)
Nb1	(¼ 0.6414 0.0)	(¼ 0.6466 0.0)
O1	(0.0025 0.7168 0.1957)	(0.0067 0.7190 0.2114)
O2	(0.9060 0.4586 0.2477)	(0.9053 0.4597 0.2458)

Table S2. Refined Structural parameters for $SmTaO_4$:

Space group *I*2/*a*

a = 5.458786(9) b = 11.141779(17) c = 5.093315(9) Å, β = 95.75670(10)^0

Cell volume = 308.2161(9) Å^3

Name	*x*	*y*	*z*	Ui*100 Å^2
Sm1	¼	0.11816(4)	0	0.231(8)
Ta1	¼	0.650607(24)	0	0.171(7)
O1	0.0168(6)	0.71626(24)	0.2161(7)	0.54(7)
O2	0.9011(6)	0.45393(25)	0.2411(7)	0.75(8)

Atomic positions in $SmTaO_4$ obtained from theoretical calculations:

	PBE	PBEsol
Sm1	(¼ 0.1183 0.0)	(¼ 0.1177 0.0)
Ta1	(¼ 0.6504 0.0)	(¼ 0.6517 0.0)
O1	(0.0105 0.7184 0.2167)	(0.0118 0.7195 0.2218)
O2	(0.9022 0.4570 0.2435)	(0.9027 0.4587 0.2435)

Table S3. Refined Structural parameters for $HoNbO_4$:

Space group I2/*a*

a = 5.30221(8), *b* = 10.95710(20), *c* = 5.07411(9) Å, β = 94.5622(13)^0

Cell volume = 293.856(9) Å^3

Name	*x*	*y*	*z*	Ui*100 Å^2
Ho1	¼	0.12099(12)	0	0.042(24)
Nb1	¼	0.64372(13)	0	0.314(35)
O1	0.00398(26)	0.71807(11)	0.20964(25)	0.533(25)
O2	0.90787(26)	0.46015(12)	0.24747(25)	0.623(26)

Atomic positions in $HoNbO_4$ obtained from theoretical calculations:

	PBE	PBEsol
Ho1	(¼ 0.1218 0.0)	(¼ 0.1211 0.0)
Nb1	(¼ 0.6417 0.0)	(¼ 0.6431 0.0)
O1	(0.9990 0.7176 0.2051)	(0.0010 0.7193 0.2120)
O2	(0.9111 0.4608 0.2521)	(0.9130 0.4630 0.2512)

Table S4a. Refined Structural parameters for *P2/c* phase of $HoTaO_4$:

Space Group *P*2/*c*

a = 5.11450(15), *b* = 5.45546(16), *c* = 5.30199(13) Å, β = 96.4704(21)^0

Cell volume = 146.994(7) Å^3

Atom	*x*	*y*	*z*	Ui*100 Å^2
Ho1	½	0.73345(32)	¼	-0.10(4)
Ta1	0	0.1945(4)	¼	0.78(6)
O1	0.2491(4)	0.4171(4)	0.3987(4)	0.72(4)
O2	0.2316(4)	0.0617(4)	0.0041(4)	0.74(4)

Atomic positions in *P2/c* phase of $HoTaO_4$ obtained from theoretical calculations:

	PBE	PBEsol
Ho1	(½ 0.7328 ¼)	(½ 0.7349 ¼)
Ta1	(0.0 0.1943 ¼)	(0.0 0.1964 ¼)
O1	(0.2510 0.4161 0.4008)	(0.2509 0.4223 0.4027)
O2	(0.2326 0.0640 0.0051)	(0.2349 0.0597 0.0097)

Table S4b. Refined Structural parameters for *I2/a* phase of $HoTaO_4$:

Space Group *I*2/*a*

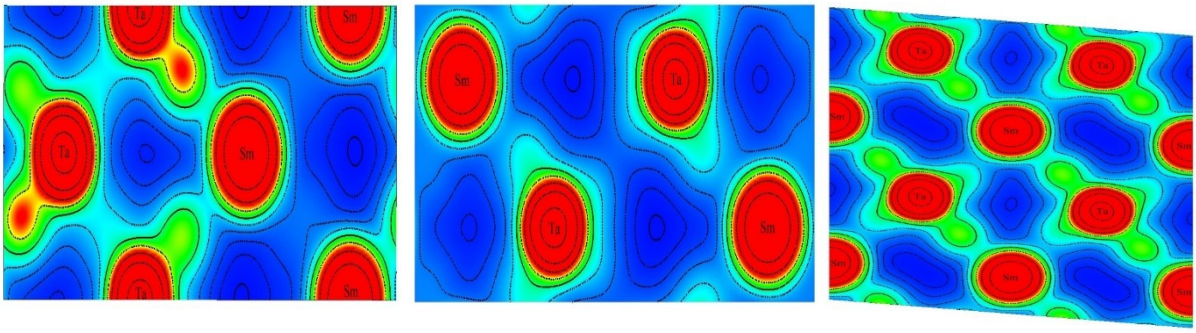
a = 5.33007(6), *b* = 10.93577(16), *c* = 5.05479(8) Å, β = 95.5415(11) ^{0}

Cell volume = 293.259(7) Å^3

Atom	*x*	*y*	*z*	Ui*100 Å^2
Ho1	¼	0.11879(12	0	-0.02(2)
Ta1	¼	0.64805(12)	0	0.21(3)
O1	0.0077(3)	0.71852(10)	0.2205(3)	0.51(3)
O2	0.9078(2)	0.46072(13)	0.2463(3)	0.52(3)

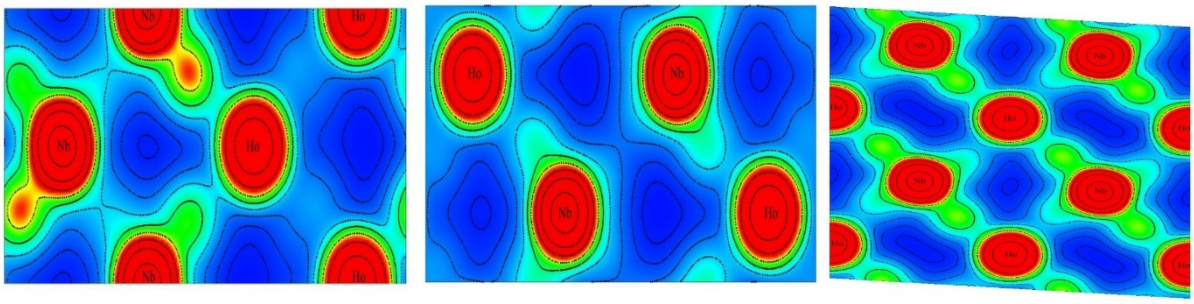
Atomic positions in *I2/a* phase of $HoTaO_4$ obtained from theoretical calculations:

	PBE	PBEsol
Ho1	(¼ 0.1184 0.0)	(¼ 0.1180 0.0)
Ta1	(¼ 0.6483 0.0)	(¼ 0.6490 0.0)
O1	(0.0052 0.7185 0.2200)	(0.0060 0.7198 0.2239)
O2	(0.9081 0.4598 0.2487)	(0.9085 0.4619 0.2488)



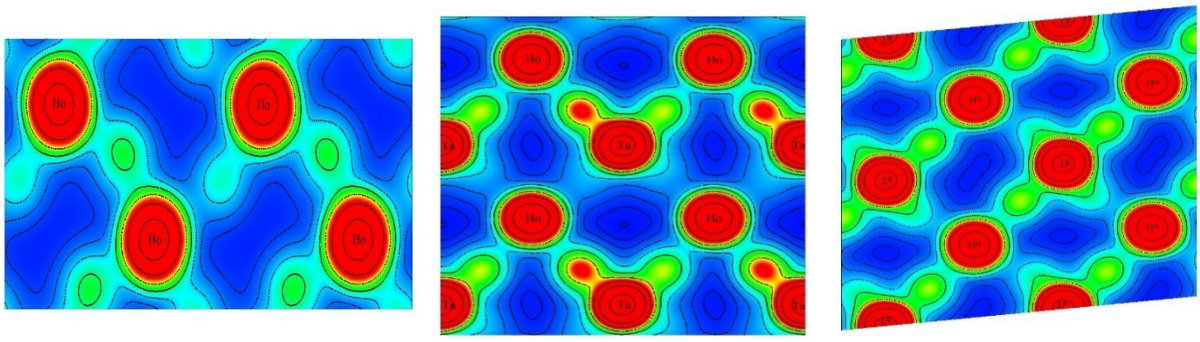
(a) (b) (c)

Figure S3. Electron charge density plot of $SmTaO_4$ in 100 (a), 001 (b) and 010 (c) planes.



(a) (b) (c)

Figure S4. Electron charge density plot of $HoNbO_4$ in 100 (a), 001 (b) and 010 (c) planes.



(a) (b) (c)

Figure S5. Electron charge density plot of *P2/c* phase of $HoTaO_4$ in 100 (a), 001 (b) and 010 (c) planes.

Table S5. Calculated Born effective charge (BEC) of the studied materials.

	Z_{11}	Z_{12}	Z_{13}	Z_{21}	Z_{22}	Z_{23}	Z_{31}	Z_{32}	Z_{33}
$SmNbO_4$									
Sm	4.81	0.00	0.36	0.00	4.04	0.00	-0.19	0.00	4.41
Nb	4.54	0.00	-0.23	0.00	5.32	0.00	0.34	0.00	6.67
O1	-2.70	0.39	0.83	0.43	-2.11	-0.46	0.86	-0.56	-2.67
O2	-1.98	0.34	-0.89	0.26	-2.57	1.16	-0.94	1.12	-2.87
$SmTaO_4$									
Sm	4.74	0.00	0.33	0.00	3.99	0.00	-0.06	0.00	4.19
Ta	4.38	0.00	-0.03	0.00	5.42	0.00	0.39	0.00	6.82
O1	-2.58	0.26	0.68	0.21	-2. 09	-0.47	0.71	-0.56	-2.70
O2	-1.98	0.27	-0.83	0.20	-2.61	1.11	-0.87	1.11	-2.80
$HoNbO_4$									
Ho	4.68	0.00	0.35	0.00	3.94	0.00	-0.22	0.00	4.40
Nb	4.66	0.00	-0.25	0.00	5.39	0.00	0.36	0.00	6.58
O1	-2.65	0.38	0.80	0.44	-2.14	-0.47	0.83	-0.59	-2.64
O2	-2.02	0.37	-0.85	0.28	-2.53	1.10	-0.90	1.00	-2.86
$HoTaO_4$ (*I2/a* #15)									
Ho	4.62	0.00	0.30	0.00	3.89	0.00	-0.07	0.00	4.19
Ta	4.43	0.00	-0.06	0.00	5.30	0.00	0.36	0.00	6.64
O1	-2.55	0.26	0.69	0.24	-2.08	-0.45	0.72	-0.57	-2.65
O2	-1.97	0.30	-0.81	0.24	-2.52	1.05	-0.86	0.98	-2.77
$HoTaO_4$ (*P2/c* #13)									
Ho	4.72	0.00	0.15	0.00	3.88	0.00	0.17	0.00	4.13
Ta	5.49	0.00	0.38	0.00	5.48	0.00	0.47	0.00	5.40
O1	-2.58	-1.07	-0.85	-1.15	-2.59	-0.31	-0.93	-0.28	-2.16
O2	-2.53	0.05	0.58	-0.03	-2.10	-0.51	0.61	-0.51	-2.60

Table S6. Calculated Theoretical IR frequencies (cm^{-1}) of both phases of $HoTaO_4$.

	P2/c (#13)			*I2/a (#15)*		
Mode	Assignment	IR Frequency		Assignment	IR Frequency	
		Calc			Calc	
1	B_u	121.56194		A_u	125.17394	
2	A_u	126.98389		B_u	150.48888	
3	B_u	147.06390		B_u	156.95743	
4	B_u	195.36492		B_u	163.10587	
5	B_u	250.17932		B_u	182.86437	
6	A_u	261.49906		A_u	249.35075	
7	B_u	293.03075		A_u	278.86244	
8	A_u	305.56532		B_u	323.48339	
9	A_u	366.78297		B_u	375.90099	
10	B_u	395.72693		A_u	419.14108	

11	B_u	513.69592		A_u	526.76985	
12	A_u	523.38975		B_u	529.39155	
13	A_u	596.08742		A_u	622.71795	
14	B_u	638.07138		B_u	644.51443	
15	Au	769.40085		A_u	774.41647	

Table S7. Calculated and experimentally obtained atomic positions of $SmNbO_4$, $SmTaO_4$, $HoNbO_4$ and P2/c and I2/a phases of $HoTaO_4$:

$SmNbO_4$:

	Expt.	PBE	PBEsol
Sm	(0.25 0.12078 0.00)	(0.25 0.12199 0.00)	(0.25 0.12041 0.00)
Nb	(0.25 0.64619 0.00)	(0.25 0.64136 0.00)	(0.25 0.6466 0.00)
O1	(0.00760 0.71551 0.20290)	(0.00251 0.71679 0.19574)	(0.00665 0.71901 0.21137)
O2	(0.90390 0.45567 0.24630)	(0.90600 0.45862 0.24770)	(0.90531 0.45972 0.24575)

$SmTaO_4$:

	Expt.	PBE	PBEsol
Sm	(0.25 0.11816 0.00)	(0.25 0.11832 0.00)	(0.25 0.11767 0.00)
Ta	(0.25 0.65061 0.00)	(0.25 0.65043 0.00)	(0.25 0.65165 0.00)
O1	(0.01680 0.71626 0.21610)	(0.01046 0.71842 0.21665)	(0.0118 0.71952 0.2218)
O2	(0.90110 0.45393 0.24110)	(0.90216 0.45701 0.24348)	(0.90265 0.45868 0.24347)

$HoNbO_4$:

	Expt.	PBE	PBEsol
Ho	(0.25 0.12099 0.00)	(0.25 0.12184 0.00)	(0.25 0.12117 0.00)
Nb	(0.25 0.64372 0.00)	(0.25 0.64177 0.00)	(0.25 0.6431 0.00)
O1	(0.00398 0.71807 0.20964)	(0.99897 0.71762 0.20505)	(0.00096 0.7193 0.21201)
O2	(0.90787 0.46015 0.24747)	(0.91111 0.46078 0.25212)	(0.91298 0.46301 0.25119)

$HoTaO_4$ (P2/c):

	Expt.	PBE	PBEsol
Ho	(0.50 0.73345 0.25)	(0.50 0.73282 0.25)	(0.50 0.73487 0.25)
Ta	(0.00 0.19450 0.25)	(0.00 0.19426 0.25)	(0.00 0.19644 0.25)
O1	(0.2491 0.4171 0.3987)	(0.25101 0.41611 0.40080)	(0.2509 0.4223 0.40273)
O2	(0.2316 0.0617 0.0041)	(0.23255 0.06397 0.00513)	(0.23487 0.05969 0.0097)

$HoTaO_4$(I2/a):

	Expt.	PBE	PBEsol
Ho	(0.25 0.11879 0.00)	(0.25 0.11841 0.00)	(0.25 0.11803 0.00)
Ta	(0.25 0.64805 0.00)	(0.25 0.64831 0.00)	(0.25 0.64899 0.00)
O1	(0.0077 0.71852 0.2205)	(0.0052 0.71848 0.21996)	(0.00598 0.71975 0.22393)
O2	(0.9078 0.46072 0.24072)	(0.9081 0.45984 0.24871)	(0.90851 0.46191 0.2488)