ARTICLE

Metal-doped niobate pyrochlores and double-perovskites for glycerol valorization: Structural and electronic properties and DFT calculations

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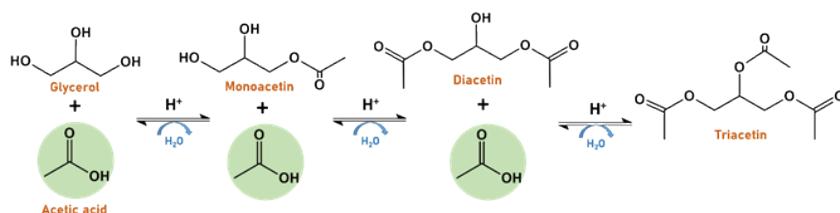
**Fig.S$_1$.** Schematic representation of the esterification of glycerol with acetic acid reaction

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(a)

(b)

(c)
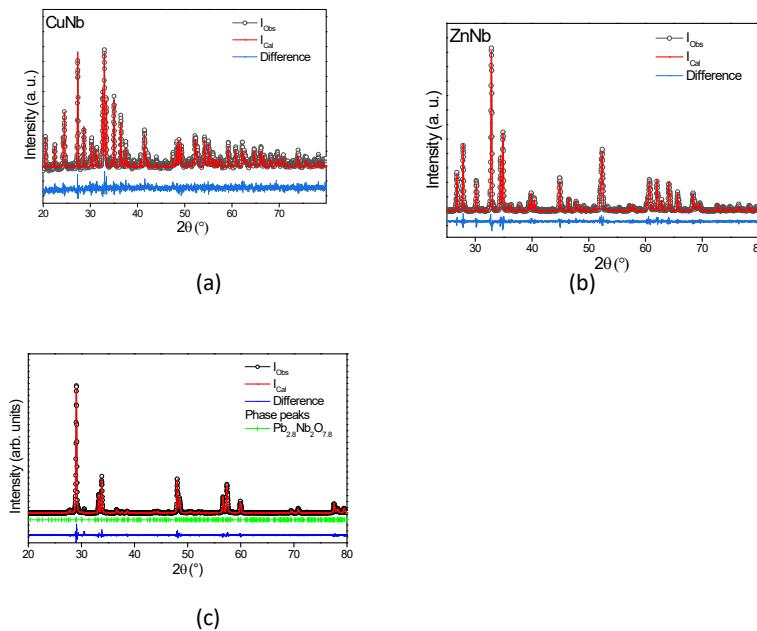
Fig.S₂. Experimental XRD pattern of the (a) CuNb (b) ZnNb and (c) PbNb pyrochlores in black balls. The Rietveld refinement-simulated pattern is in the solid red line.   The difference between experimental and calculated XRD patterns are in blue line at the bottom of the figures.
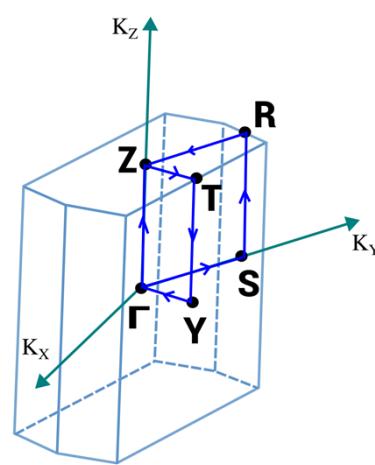
Fig.S$_3$. The first Brillouin zone of the primitive cell with the six high-symmetry points used in this study: G(0,0,0), Z(0,0,1/2), T(1/2,1/2,1/2), Y(1/2,1/2,0), S(0,1/2,0) and R(0,1/2,1/2).

(a)

(b)
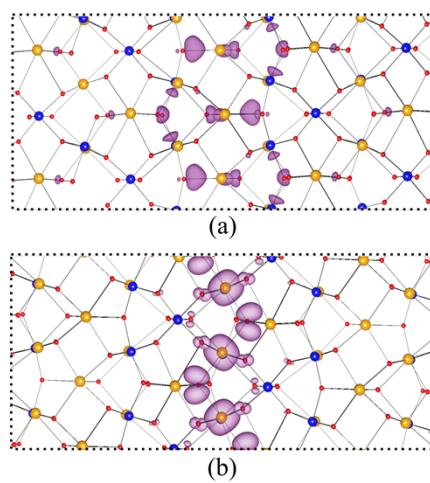
Fig.S$_4$. Wavefunction of the (a) conduction band minimum (CBM) and (b) valence band maximum (VBM) obtained using the PBE functional for the Pb$_{2.8}$Nb$_2$O$_{7.8}$ structure.
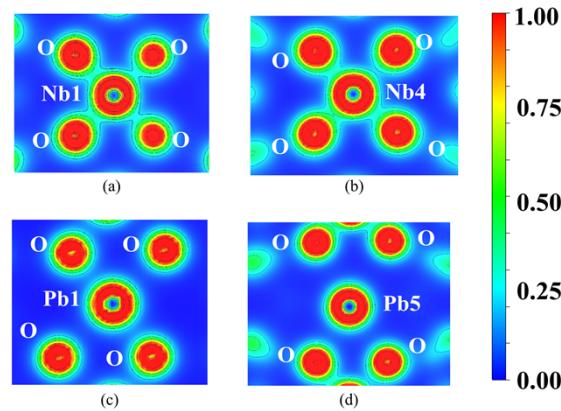
Fig.S₅. The ELF mapping for $Pb_{2.8}Nb_2O_{7.8}$ crystal structure. (a-b) Contours map for the Nb-O bonding's. (d-f) Contours map for the Pb-O bonding's.
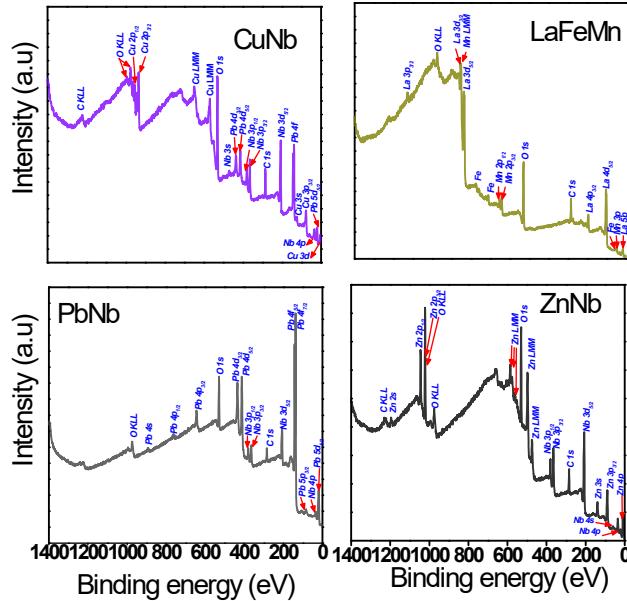
Fig.S₆.XPS survey spectra of all solids.
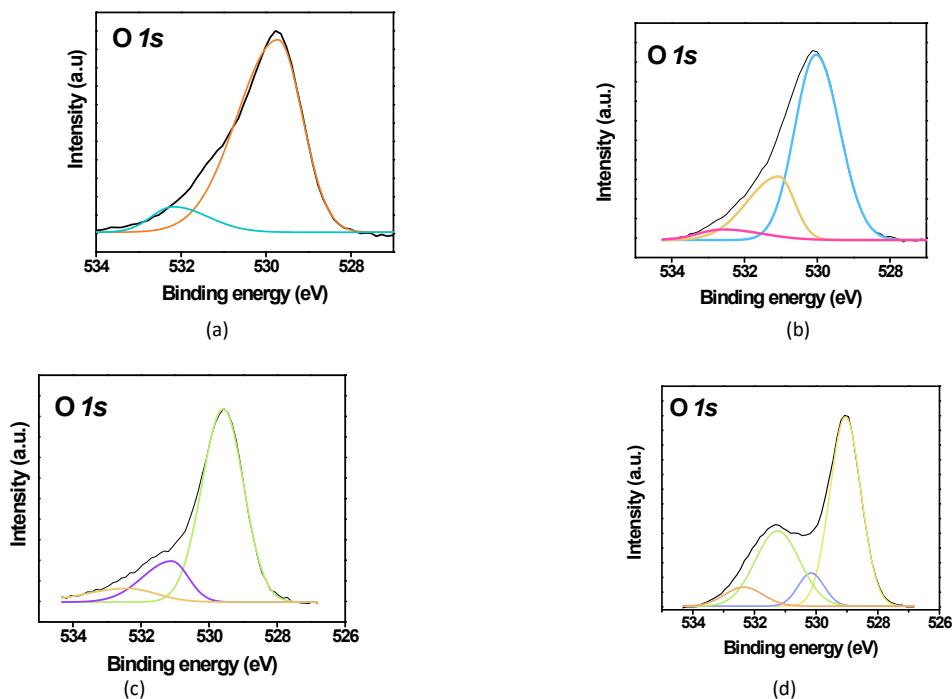
Fig.S$_7$. O 1s core level spectra of the samples: (a) CuNb, (b) ZnNb, (c)PbNb and (d) LaFeMn.
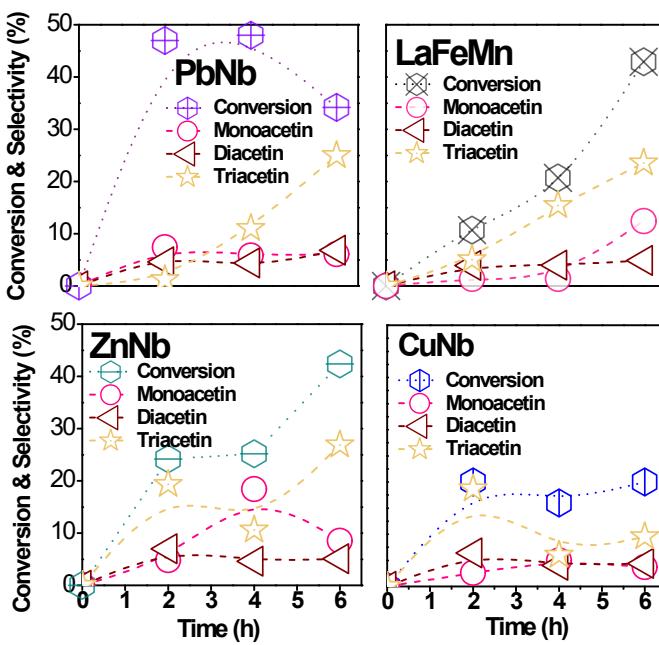
Fig.S$_8$. Conversion and selectivity of the products in function of the time.

The values obtained for the Rietvield refinement quality factors R_{wp}, R_p, and χ^2 are shown in Table S1.

Table S1: Structural parameters and quality factors of PbNb sample obtained by Rietvield refinement

		$Pb_{2.8}Nb_2O_{7.8}$
	a (Å)	7.5200
	b (Å)	32.5130
Lattice parameters	c (Å)	7.5420
	$\alpha(°)$	90.00
	$\beta(°)$	90.00
	$\gamma(°)$	90.00
	χ2	1.40
Quality factors	R_{wp} (%)	23.01

The curve fitting of XRD patterns and the Rietveld refinement lattice parameters are in accordance. The quality factors *i.e.,* Rp and Rwp discrepancy factors are all below 20%. The atomic coordinates are contained in the supplementary material in Table S2.

The crystal structure of $Pb_{2.8}Nb_2O_{7.8}$ is composed of NbO_6 octahedrons, which are interconnected by sharing corners to create an intricate network of intersecting structural channels. This arrangement can be visualized in Fig. 2 (b), which displays the distribution and organization of the niobium octahedrons along the *c* and *a* directions. Those channels are occupied by Pb1 and Pb5 cations, which are bonded to eight oxygen atoms and can also be represented as distorted dodecahedrons. Meanwhile, the Pb4 atoms present irregular coordination with six oxygen atoms due to the displacement of NbO_6 packets from neighboring layers.

Table S2. Refined atomic position parameters of $Pb_{2.8}Nb_2O_{7.8}$ structure.

Atom	Ion	x	y	z	Site
Pb1	Pb2+	0.00000	0.50153	0.00440	4a
Pb2	Pb2+	0.00000	0.16858	0.50510	4a
Pb3	Pb2+	0.00000	0.83030	0.48650	4a
Pb4	Pb2+	0.24980	0.24497	0.25000	8b
Pb5	Pb2+	0.24690	0.41692	0.25430	8b
Nb1	Nb5+	0.00000	0.99827	0.00300	4a
Nb2	Nb5+	0.00000	0.33339	0.49920	4a
Nb3	Nb5+	0.00000	0.66417	0.50410	4a
Nb4	Nb5+	0.24990	0.08283	0.24880	8b
O1	O2-	0.18200	0.04150	0.07000	8b
O2	O2-	0.30800	0.12010	0.06800	8b
O3	O2-	0.18700	0.29820	0.06500	8b
O4	O2-	0.80600	0.96120	0.94700	8b
O5	O2-	0.69100	0.88020	0.94900	8b
O6	O2-	0.81100	0.69980	0.96200	8b
O7	O2-	0.00000	0.10020	0.25600	4a
O8	O2-	0.00000	0.35980	0.25300	4a
O9	O2-	0.00000	0.55900	0.25600	4a
O10	O2-	0.00000	0.68040	0.26100	4a
O11	O2-	0.00000	0.97780	0.26500	4a
O12	O2-	0.00000	0.77820	0.25300	4a
O13	O2-	0.00000	0.46760	0.25100	4a
O14	O2-	0.00000	0.87010	0.25400	4a

The last two lead atoms Pb2 and Pb3 are found inside the pyrochlore stacks, surrounded by seven oxygen atoms; six of them form the typical deformed chair-of-six ring, and one sits at the tip of the polyhedron. This leads to Pb^{2+} and Nb^{5+} ions being in different positions within the unit cell, as shown in Fig. 2 (c). There are three distinct sites for Pb, located at positions 4a (Pb1, Pb2 and Pb3) and two at positions 8b (Pb4 and Pb5). Nb^{5+} ions also occupy distinct

sites, with three at positions 4a (Nb1, Nb2 and Nb3) and one at the 8b site (Nb5).

The PbO impurity phase arises from the incomplete reaction in the formation process, from the $Pb_3Nb_2O_8$, following the following stoichiometric relationship: $Pb_3Nb_2O_8 = Pb_{2.8}Nb_2O_{7.8} + Pb_{0.2}O_{0.2}$. This explains the non-stoichiometric character of $Pb_{2.8}Nb_2O_{7.8}$.

Table S_3 compares the lattice parameters of the PbNb sample. The results show that LDA functional yields lattice parameters on average is 16 % smaller than those observed experimentally. This suggests that the LDA functional may underestimate the crystal's structural dimensions. Meanwhile, the simulation performed with the GGA functional yields lattice parameter values of around 7.54, 32.83, and 7.61 angstroms, for *a*, *b*, and *c*, respectively. These values are, on average, 2.4% higher than the experimental values.

Table S_3: Comparison of lattice parameters obtained from XRD, DFT-LDA and DFT-GGA for the $Pb_{2.8}Nb_2O_{7.8}$ system.

Lattice parameter	XRD	DFT-LDA	DFT-GGA
a (Å)	7.520	7.390	7.547
b (Å)	32.513	32.007	32.830
c (Å)	7.542	7.421	7.613

To further explore the crystal structural properties, the covalent bond lengths and angles are provided in Tables S_5 and S_6, respectively. As one can see, we observed varying values of bond lengths and bond angles for interactions of the same type. In fact, this happens because neighbouring niobium atoms share coordinating oxygen atoms leading to different values on those structural parameters. In general, our calculated structural parameters are in the acceptable range compared with the experimental ones. The greatest deviations were found for the Nb2-O6, Pb1-O13 and Pb4-O6 bond lengths in the ab plane (~ 5 – 13 %) for both GGA and LDA simulations (see Table S_5). The Nb2-O6

interactions stabilize the channels externally in the *ab* plane, while the Pb1-O13 interactions restrict the channel size. Therefore, our simulated structures show a slight increase in the radius of the channels parallel to the *c*-axis since the simulated lengths are, on average, higher than experimental values. On the other hand, Pb4-O6 interactions limit the distances between the NbO_6 octahedrons along the *b*-axis. In this case, the distances are smaller than the experimentally verified ones, indicating that the distances between the layers of niobium octahedrons are slightly smaller in the simulations carried out with both GGA and LDA.

Another important structural aspect are the bond angles formed between the atomic interactions of the crystal. Table S_6 provides a comprehensive comparison of the primary angles observed in the material. Notably, the internal angles of the NbO_6 octahedrons exhibit excellent agreement, with relative deviations below 8%. For example, we observed a reduction of approximately 6% in the equatorial connection angles of the simulated $Nb2O_6$ octahedrons (both LDA and GGA) relative to the experimental data. In particular, the transverse bond angle of $Nb1O_6$ octahedrons exhibits a maximum deviation of 7.9% from the experimental value in GGA simulations. A similar result is observed for the bond angles O-Pb-O and Pb-O-Nb, with maximum deviations around 8.7% and 7%, respectively. The limitations of the LDA and GGA approximations, such as neglecting non-local exchange-correlation effects, can contribute to the observed deviations in the calculated structural parameters. However, based on the comparison between the calculated structural parameters using the LDA and GGA approximations and the corresponding experimental values, it can be inferred that both methods have provided acceptable structural data and can be used to investigate the vibrational and electronic properties of $Pb_{2.8}Nb_2O_{7.8}$ crystal.

Table S₄. Binding and surface atomic ratios determined by XPS analyses.

Sample	Nb 3d	Cu 2p	O 1s	C 1s	Zn 2p	Pb 4f	Mn 2p	La 3d	Fe 2p	Nb/Me ratio	La/Fe ratio	La/Mn ratio
CuNb	206.2 209.1	934.0 936.3 940.6 956.8	529.8 531.4	284.2 286.0 288.7	-	-	-	-	-	1.1	-	-
ZnNb	206.8 209.2	-	530.0 531.0 532.2	284.7 285.8 288.5	1021.6	-	-	-	-	0.89	-	-
PbNb	206.4 209.1	-	529.6 531.1 532.3	284.4 285.7 288.7	-	138.0 143.0	-	-	-	0.47	-	-
LaFeMn	-	-	529.0 530.4 531.5 532.6	284.8 286.0 288.9	-	-	640.9 643.1 652.8 656.3	833.6 837.7 850.5 854.8	709.9 724.1	-	1.9	4.4

Table S$_5$. Comparison of bond lengths obtained from XRD, DFT-LDA and DFT-GGA for the Pb2.8Nb2O7.8 system.

Atoms	XRD Bond lengths (Å)	DFT – LDA Bond lengths (Å)	Δ (%)	DFT – GGA Bond lengths (Å)	Δ (%)	Atoms	XRD Bond lengths (Å)	DFT – LDA Bond lengths (Å)	Δ (%)	DFT – GGA Bond lengths (Å)	Δ (%)
Nb1–O1	2.026	1.963	-3.10	2.013	-0.65	Pb2–O12	2.548	2.456	-3.60	2.541	-0.27
Nb1–O11	2.085	1.980	-5.06	2.189	4.98	Pb2–O14	2.260	2.187	-3.23	2.227	-1.42
Nb1–O11	1.956	1.986	1.49	1.893	-3.24	Pb2–O3	2.629	2.519	-4.18	2.594	-1.32
Nb1–O4	1.939	1.963	1.23	1.970	1.58	Pb2–O5	2.845	2.837	-0.29	2.895	1.77
Nb2–O10	2.025	1.954	-3.48	2.036	0.55	Pb2–O7	2.911	2.967	1.94	2.976	2.23
Nb2–O2	2.154	2.051	-4.80	2.113	-1.93	Pb3–O12	2.444	2.457	0.56	2.525	3.31
Nb2–O6	1.806	1.890	4.63	1.897	5.04	Pb3–O14	2.179	2.186	0.33	2.227	2.17
Nb2–O8	2.046	1.996	-2.42	1.973	-3.55	Pb3–O2	2.888	2.836	-1.81	2.884	-0.15
Nb3–O10	1.908	1.953	2.36	1.910	0.10	Pb3–O6	2.542	2.519	-0.89	2.606	2.50
Nb3–O3	1.920	1.890	-1.55	1.909	-0.54	Pb3–O7	3.039	2.965	-2.45	3.017	-0.72
Nb3–O5	2.078	2.051	-1.30	2.102	1.16	Pb4–O10	2.820	2.762	-2.07	2.937	4.14
Nb3–O8	2.033	1.998	-1.72	2.120	4.28	Pb4–O12	2.170	2.171	0.06	2.197	1.24
Nb4–O1	1.971	2.013	2.11	1.993	1.12	Pb4–O3	2.273	2.303	1.32	2.341	3.01
Nb4–O2	1.876	1.927	2.72	1.915	2.08	Pb4–O3	2.800	2.614	-6.64	2.754	-1.63
Nb4–O4	2.112	2.014	-4.65	2.114	0.08	Pb4–O6	2.662	2.303	-13.49	2.372	-10.90
Nb4–O5	1.980	1.927	-2.68	1.986	0.27	Pb4–O6	2.448	2.614	6.81	2.712	10.79
Nb4–O7	1.963	1.937	-1.34	1.976	0.68	Pb5–O1	2.790	2.732	-2.08	3.030	8.60
Nb4–O9	2.035	1.997	-1.84	2.031	-0.20	Pb5–O11	2.747	2.692	-1.99	2.752	0.18
Pb1–O1	2.766	2.652	-4.15	2.713	-1.94	Pb5–O13	2.483	2.303	-7.25	2.338	-5.81
Pb1–O13	2.162	2.296	6.20	2.348	8.58	Pb5–O14	2.437	2.412	-1.03	2.461	0.96
Pb1–O13	2.159	2.297	6.41	2.354	9.05	Pb5–O2	2.686	2.611	-2.80	2.833	5.44
Pb1–O4	2.684	2.656	-1.05	2.746	2.34	Pb5–O4	2.764	2.723	-1.50	2.633	-4.77
Pb1–O9	2.663	2.638	-0.96	2.682	0.71	Pb5–O5	2.628	2.607	-0.77	2.535	-3.52
Pb1–O9	2.717	2.631	-3.18	2.735	0.67	Pb5–O8	2.626	2.587	-1.50	2.669	1.62

Table S6. Comparison of bond angles obtained from XRD, DFT-LDA and DFT-GGA for the Pb2.8Nb2O7.8 system.

Atoms	XRD Angle(°)	DFT-LDA Angle(°)	Δ(%)	DFT-GGA Angle(°)	Δ(%)	Atoms	XRD Angle(°)	DFT-LDA Angle(°)	Δ(%)	DFT-GGA Angle(°)	Δ(%)
Nb1-O1-Pb1	102.330	105.430	3.03	105.100	2.71	O11-Pb5-O1	59.540	61.360	3.06	58.780	-1.28
Nb1-O1-Pb5	104.640	104.250	-0.37	97.300	-7.01	O11-Pb5-O13	92.310	97.100	5.19	97.230	5.33
Nb1-O11-Nb1	137.950	138.730	0.57	137.530	-0.30	O11-Pb5-O14	84.780	88.690	4.61	87.050	2.68
Nb1-O11-Pb5	101.660	104.980	3.27	100.300	-1.34	O11-Pb5-O2	113.790	117.040	2.86	110.950	-2.50
Nb1-O11-Pb5	108.270	104.980	-3.04	100.300	-7.36	O11-Pb5-O8	178.160	175.880	-1.28	172.450	-3.20
Nb1-O4-Nb4	136.490	139.640	2.31	135.480	-0.74	O12-Pb2-O14	76.600	75.900	-0.91	75.190	-1.84
Nb2-O10-Pb4	97.820	100.580	2.82	99.770	1.99	O12-Pb3-O14	80.310	75.870	-5.53	75.540	-5.94
Nb2-O2-Pb3	95.410	97.130	1.80	96.960	1.62	O12-Pb3-O2	122.710	120.140	-2.09	121.000	-1.39
Nb2-O2-Pb5	101.850	103.960	2.07	99.420	-2.39	O12-Pb3-O6	71.380	68.440	-4.12	68.660	-3.81
Nb2-O6-Pb3	118.860	113.340	-4.64	113.040	-4.90	O12-Pb3-O7	175.860	171.820	-2.30	174.410	-0.82
Nb2-O6-Pb4	133.370	133.371	0.00	134.090	0.54	O12-Pb4-O3	95.370	95.030	-0.36	95.910	0.57
Nb2-O6-Pb4	109.810	107.810	-1.82	111.969	1.971	O12-Pb4-O6	77.870	77.400	-0.60	78.500	0.81
Nb2-O8-Nb3	132.640	131.340	-0.98	134.630	1.50	O13-Pb1-O1	94.920	98.530	3.80	96.290	1.44
Nb2-O8-Pb5	107.060	106.490	-0.53	109.020	1.83	O13-Pb1-O1	86.560	81.510	-5.83	84.978	-1.83
Nb3-O10-Nb2	151.150	150.900	-0.17	152.940	1.18	Nb3-O5-Nb4	136.810	138.950	1.56	136.440	-0.27
Nb3-O10-Pb4	103.540	100.570	-2.87	100.670	-2.77	Nb3-O8-Pb5	105.940	106.420	0.45	102.370	-3.37
Nb3-O3-Pb4	103.930	107.750	3.68	107.260	3.20	Nb4-O1-Nb1	144.950	139.870	-3.50	146.610	1.15
O11-Nb1-O1	87.300	90.780	3.99	84.340	-3.39	Nb4-O1-Pb1	102.630	104.980	2.29	104.580	1.90
O11-Nb1-O11	175.180	180.000	2.75	177.050	1.07	Nb4-O1-Pb5	101.770	101.930	0.16	100.240	-1.50
O11-Nb1-O4	90.460	88.960	-1.66	85.390	-5.60	Nb4-O2-Nb2	141.690	139.030	-1.88	142.950	0.89
O11-Nb1-O4	92.710	88.960	-4.04	85.390	-7.90	Nb4-O2-Pb3	109.180	107.470	-1.57	107.630	-1.42

Table S₆. Cont.

Atoms	XRD	DFT-LDA		DFT-GGA		Atoms	XRD	DFT-LDA		DFT-GGA	
	Angle(°)	Angle(°)	Δ(%)	Angle(°)	Δ(%)		Angle(°)	Angle(°)	Δ(%)	Angle(°)	Δ(%)
Nb4-O2-Pb5	108.360	108.870	0.47	109.420	0.98	O2-Nb2-O2	84.170	86.800	3.12	85.020	1.01
Nb4-O7-Nb4	146.400	147.250	0.58	147.150	0.51	O2-Nb2-O6	169.760	174.660	2.89	171.030	0.75
Nb4-O9-Nb4	135.120	133.770	-1.00	135.260	0.10	O2-Nb4-O4	177.120	176.210	-0.51	179.240	1.20
O1-Nb1-O1	85.000	92.370	8.67	89.680	5.51	O2-Nb4-O5	96.310	96.080	-0.24	95.720	-0.61
O1-Nb1-O4	173.690	179.740	3.48	169.640	-2.33	O2-Nb4-O7	93.280	92.010	-1.36	93.560	0.30
O1-Nb1-O4	88.700	87.645	-1.19	87.910	-0.89	O2-Nb4-O9	92.870	92.480	-0.42	92.570	-0.32
O1-Nb4-O2	90.200	87.720	-2.75	92.720	2.79	O2-Pb3-O2	106.620	107.430	0.76	108.870	2.11
O1-Nb4-O4	88.310	88.630	0.36	87.250	-1.20	O2-Pb3-O6	59.510	61.320	3.04	61.123	2.71
O1-Nb4-O5	173.480	176.040	1.48	171.460	-1.16	O2-Pb3-O6	165.510	168.710	1.93	169.740	2.56
O1-Nb4-O7	88.110	88.940	0.94	89.420	1.49	O1-Pb5-O13	80.230	79.660	-0.71	78.340	-2.36
O1-Nb4-O9	89.890	86.220	-4.08	87.880	-2.24	O1-Pb5-O2	59.660	61.410	2.93	57.580	-3.49
O1-Pb1-O1	119.650	118.490	-0.97	120.440	0.66	O1-Pb5-O8	118.780	117.350	-1.20	113.680	-4.29
O13-Pb1-O13	177.030	180.000	1.68	177.400	0.21	O10-Nb3-O3	93.080	90.460	-2.81	93.140	0.06
O14-Pb3-O2	80.780	79.570	-1.50	82.360	1.96	O10-Nb3-O5	89.990	87.600	-2.66	89.660	-0.37
O14-Pb3-O6	99.790	96.570	-3.23	97.770	-2.02	O10-Nb3-O8	173.510	170.220	-1.90	171.560	-1.12
O14-Pb3-O7	95.550	95.950	0.42	98.870	3.47	O10-Pb4-O12	77.990	76.560	-1.83	78.710	0.92
O14-Pb5-O1	98.850	103.120	4.32	99.620	0.78	O10-Pb4-O3	59.250	60.930	2.84	58.220	-1.74
O14-Pb5-O13	177.000	174.210	-1.58	173.250	-2.12	O10-Pb4-O6	130.660	131.285	0.48	131.530	0.67
O14-Pb5-O2	80.850	80.590	-0.32	79.630	-1.51	O11-Nb1-O1	89.140	90.780	1.84	84.340	-5.38
O14-Pb5-O8	96.340	95.440	-0.93	95.010	-1.38	O3-Pb2-O14	94.930	96.580	1.74	96.460	1.61
O2-Nb2-O10	85.440	87.530	2.45	84.130	-1.53	O3-Pb2-O3	127.110	129.950	2.23	129.420	1.82

Table S₆. Cont.

Atoms	XRD	DFT-LDA		DFT-GGA		Atoms	XRD	DFT-LDA		DFT-GGA	
	Angle(°)	Angle(°)	Δ(%)	Angle(°)	Δ(%)		Angle(°)	Angle(°)	Δ(%)	Angle(°)	Δ(%)
O3-Pb2-O5	61.530	61.320	-0.34	61.200	-0.54	O9-Nb4-O5	90.190	92.490	2.55	90.380	0.21
O3-Pb2-O5	170.370	168.660	-1.00	169.209	-0.68	O9-Nb4-O7	173.540	173.260	-0.16	173.410	-0.07
O3-Pb2-O7	115.130	113.150	-1.72	113.490	-1.42	O9-Pb1-O1	62.800	62.502	-0.47	62.340	-0.73
O3-Pb4-O10	136.350	131.280	-3.72	132.840	-2.57	O9-Pb1-O1	117.620	117.480	-0.12	117.918	0.25
O3-Pb4-O12	78.900	77.400	-1.90	78.810	-0.11	O9-Pb1-O13	75.230	81.410	8.21	81.910	8.88
O3-Pb4-O3	159.700	161.630	1.21	165.030	3.34	O9-Pb1-O13	102.920	98.650	-4.15	96.750	-5.99
O3-Pb4-O6	81.090	81.360	0.33	83.940	3.51	O9-Pb1-O13	107.730	98.650	-8.43	96.750	-10.19
O3-Pb4-O6	87.430	81.360	-6.94	83.940	-3.99	O9-Pb1-O13	74.120	81.410	9.83	81.910	10.51
O3-Pb4-O6	78.670	81.360	3.42	83.940	6.70	O9-Pb1-O4	117.240	117.600	0.31	117.110	-0.11
O4-Nb1-O4	97.600	92.330	-5.40	92.660	-5.06	O4-Nb4-O5	85.210	87.550	2.75	84.290	-1.08
O2-Pb3-O7	56.120	57.210	1.94	57.390	2.26	O4-Nb4-O7	89.130	88.930	-0.22	87.200	-2.17
O2-Pb5-O13	101.030	96.540	-4.44	93.930	-7.03	O4-Pb1-O1	178.470	179.880	0.79	175.902	-1.45
O2-Pb5-O8	65.030	63.730	-2.00	62.450	-3.97	O4-Pb1-O1	61.130	61.623	0.81	60.840	-0.47
O3-Nb3-O3	94.200	96.720	2.68	96.820	2.78	O4-Pb1-O13	83.650	81.430	-2.65	79.630	-4.81
O3-Nb3-O5	89.080	88.202	-0.99	88.660	-0.47	O4-Pb1-O13	94.840	98.525	3.88	99.077	4.47
O3-Nb3-O5	175.380	174.730	-0.37	173.690	-0.96	O4-Pb1-O4	118.070	118.260	0.16	117.590	-0.41
O3-Nb3-O8	91.340	96.020	5.12	92.460	1.23	O4-Pb5-O1	115.620	115.320	-0.26	114.950	-0.58
O3-Pb2-O12	66.100	68.470	3.59	68.300	3.33	O4-Pb5-O11	62.480	61.440	-1.66	63.230	1.20
O8-Nb2-O6	96.300	96.080	-0.23	97.410	1.15	O4-Pb5-O13	76.480	79.870	4.43	82.230	7.52
O8-Pb5-O13	86.590	78.780	-9.02	80.090	-7.51	O4-Pb5-O14	101.480	103.190	1.69	104.400	2.88
O9-Nb4-O4	84.660	86.280	1.91	86.670	2.37	O4-Pb5-O2	175.160	175.710	0.31	172.330	-1.62

Table S₆. Cont.

Atoms	XRD	DFT-LDA		DFT-GGA		Atoms	XRD	DFT-LDA		DFT-GGA	
	Angle(°)	Angle(°)	Δ(%)	Angle(°)	Δ(%)		Angle(°)	Angle(°)	Δ(%)	Angle(°)	Δ(%)
O4-Pb5-O5	61.810	61.500	-0.50	64.340	4.09	O6-Pb4-O12	97.660	95.031	-2.69	96.630	-1.05
O4-Pb5-O8	118.610	117.470	-0.96	122.960	3.67	O6-Pb4-O3	112.730	116.273	3.14	110.710	-1.79
O5-Nb3-O5	87.470	86.820	-0.74	85.700	-2.02	O9-Pb1-O4	62.280	62.418	0.22	62.342	0.10
O5-Nb3-O8	85.330	85.300	-0.04	84.160	-1.37	O9-Pb1-O9	178.150	180.000	1.04	178.660	0.29
O5-Nb4-O7	91.100	92.040	1.03	91.410	0.34	O6-Pb4-O6	165.960	161.630	-2.61	166.510	0.33
O5-Pb2-O12	119.200	120.150	0.80	119.270	0.06	O7-Pb2-O12	172.980	171.830	-0.66	171.020	-1.13
O5-Pb2-O14	79.240	79.530	0.37	79.110	-0.16	O7-Pb2-O14	96.380	95.930	-0.47	95.830	-0.57
O5-Pb2-O5	109.530	107.380	-1.96	108.130	-1.28	O8-Nb2-O10	167.980	170.220	1.33	170.130	1.28
O5-Pb2-O7	58.550	57.200	-2.31	57.750	-1.37	O8-Nb2-O2	85.640	85.370	-0.32	88.610	3.47
O5-Pb5-O1	177.170	175.750	-0.80	177.620	0.25	Pb1-O1-Pb5	84.800	88.820	4.74	84.940	0.17
O5-Pb5-O11	117.640	117.220	-0.36	121.700	3.45	Pb1-O13-Pb1	121.620	107.760	-11.40	108.140	-11.08
O5-Pb5-O13	99.970	96.750	-3.22	99.280	-0.69	Pb1-O13-Pb5	110.320	109.860	-0.42	108.290	-1.84
O5-Pb5-O14	80.810	80.660	-0.19	82.760	2.41	Pb1-O13-Pb5	107.440	109.860	2.25	108.290	0.79
O5-Pb5-O2	122.930	121.590	-1.09	123.040	0.09	Pb1-O4-Nb1	107.840	105.300	-2.36	105.170	-2.48
O5-Pb5-O8	64.040	63.760	-0.44	65.810	2.76	Pb1-O4-Nb4	105.940	105.030	-0.86	104.000	-1.83
O6-Nb2-O10	91.100	90.400	-0.77	89.080	-2.22	Pb1-O9-Nb4	104.370	106.190	1.74	104.540	0.16
O6-Nb2-O2	85.950	88.200	2.62	88.470	2.93	Pb1-O9-Nb4	107.110	106.190	-0.86	104.540	-2.40
O6-Nb2-O6	103.770	96.740	-6.77	97.300	-6.23	Pb1-O9-Pb1	89.030	89.560	0.60	89.300	0.30
O6-Pb3-O6	133.870	129.900	-2.97	128.760	-3.82	Pb2-O12-Pb4	109.300	109.410	0.10	108.710	-0.54
O6-Pb3-O7	109.560	113.180	3.30	112.640	2.81	Pb2-O14-Pb5	110.390	111.360	0.88	108.980	-1.28
O6-Pb4-O10	59.870	60.920	1.75	58.350	-2.54	Pb2-O3-Nb3	110.670	113.360	2.43	113.120	2.21

Table S₆. Cont.

Atoms	XRD Angle(°)	DFT-LDA Angle(°)	Δ(%)	DFT-GGA Angle(°)	Δ(%)	Atoms	XRD Angle(°)	DFT-LDA Angle(°)	Δ(%)	DFT-GGA Angle(°)	Δ(%)
Pb2-O3-Pb4	84.730	85.650	1.09	87.020	2.70	Pb4-O12-Pb4	120.260	120.690	0.36	121.230	0.81
Pb2-O3-Pb4	103.430	103.151	-0.27	103.433	0.00	Pb4-O3-Nb3	141.670	135.860	-4.10	137.460	-2.97
Pb2-O5-Nb3	98.500	97.120	-1.40	96.910	-1.61	Pb4-O3-Pb4	95.960	98.650	2.80	96.600	0.67
Pb2-O5-Nb4	105.570	107.480	1.81	106.100	0.50	Pb4-O6-Pb3	89.660	85.660	-4.46	88.740	-1.03
Pb2-O5-Pb5	89.560	88.440	-1.25	89.100	-0.51	Pb4-O6-Pb4	95.510	98.640	3.28	97.020	1.58
Pb2-O7-Nb4	103.740	102.530	-1.17	103.550	-0.18	Pb5-O11-Pb5	87.710	84.880	-3.23	85.910	-2.05
Pb2-O7-Pb3	82.170	79.230	-3.58	80.560	-1.96	Pb5-O13-Pb5	96.820	109.320	12.91	108.540	12.10
Pb3-O12-Pb2	93.330	95.590	2.42	95.130	1.93	Pb5-O14-Pb5	102.690	97.750	-4.81	99.330	-3.27
Pb3-O12-Pb4	110.650	109.420	-1.11	109.950	-0.63	Pb5-O4-Nb1	102.690	104.570	1.83	110.970	8.06
Pb3-O14-Pb2	109.750	112.640	2.63	114.140	4.00	Pb5-O4-Nb4	102.030	102.040	0.01	101.970	-0.06
Pb3-O14-Pb5	111.720	111.420	-0.27	112.190	0.42	Pb5-O4-Pb1	88.930	88.830	-0.11	89.810	0.99
Pb3-O2-Pb5	86.530	88.410	2.17	85.820	-0.82	Pb5-O5-Nb3	104.530	104.080	-0.43	107.440	2.78
Pb3-O6-Pb4	99.100	103.180	4.12	101.990	2.92	Pb5-O5-Nb4	110.880	108.840	-1.84	109.350	-1.38
Pb3-O7-Nb4	101.270	102.560	1.27	101.220	-0.05	Pb5-O8-Pb5	89.990	93.120	3.48	90.680	0.77
Pb4-O10-Pb4	83.690	86.180	2.98	81.330	-2.82						