Electronic Supplementary Material (ESI) for Journal of Materials Chemistry A.

Interstitial oxide ion migration in scheelite-type electrolytes: a combined neutron diffraction and computational study

Supplementary Information

Table S1 – Interatomic potentials and shell model parameters for $LaNbO_4$ and $NdNbO_4$. A, ρ and C terms refer to the Buckingham from of the potentials expressed by the formula $\varphi_{ij} = A_{ij} \exp\left(-r/\rho_{ij}\right) - C_{ij}/r^6$. The short range pair potentials cutoff was set to 15 Å.

	A /eV	ρ / Å	C /eV	Y / e	k /eVÅ^{-2}
La^{3+} - O^{2-} [a]	1545.21	0.359	0.00	0.00	-
Nd^{3+} - O^{2-} [b]	1379.90	0.36072	22.59	0.00	-
Nb^{5+} - O^{2-} [a]	1286.9583	0.371525	0.00	-4.596	5916.77
W^{6+} - O^{2-} [c]	767.43	0.4386	0.00	5.89	7.69
O^{2-} - O^{2-} [a]	22764.36	0.149	27.89	-2.758	30.211

a - Mather, G. C.; Fisher, C. A. J.; Islam, M. S.; *Chem. Mater.* **2010**, *22*, 5912-5917.
b - Tealdi, C.; Malavasi, L.; Fisher, C. A. J.; Islam, M. S.; *J. Phys. Chem. B* **2006**, *110*, 5395-5402.
c - Islam, M. S.; Lazure, S.; Vannier, R. N.; Nowogrocki, G.; Mairesse, G.; *J. Mater. Chem.* **1998**, 8, 655-660.

Table S2 – Experimental and calculated structural parameter for the scheelite phases $LaNbO_4$ and $NdNbO_4$ structures. Experimental data have been presented in previous studies [La: W.I.F. David, Mat. Res. Bull., 18 (1983) 749-756; Nd: K.A. Gingerich, H.E. Bair, Adv. R-ray Anal., 7 (1963) 22-30]

	Exp a / Å	Calc a/ Å	Δ(exp-calc)	Exp c/ Å	Calc c/ Å	Δ(exp-calc)	Exp V/ Å^3	Calc V/ Å^3	Δ(exp-calc)
$LaNbO_4$	5.4001	5.4347	-0.0346	11.6661	11.6890	-0.0229	340.2	345.3	-5.1
$NdNbO_4$	5.295	5.331	-0.036	11.417	11.421	-0.004	320.1	324.6	-4.5

Table S3 – Rietveld refined structural parameters and agreement factors obtained for NdW08 and NdW16, for the temperature range data set (25°-900°C); atomic positions, thermal factors and Nb-O distances are reported for the NdW016 data at room temperature and 900°C as reference for the monoclinic (space group 15) and tetragonal (space group 88) phases, respectively.

Sample	**a / Å**	**b / Å**	**c/ Å**	**β/ deg**	**χ^2**	**R_p**	**R_{wp}**
NdW08 - RT	5.4542 (2)	11.3117 (3)	5.1482 (1)	94.021 (3)	4.38	3.57	4.57
NdW16 - RT	5.4320 (2)	11.3468 (5)	5.1611 (2)	93.527 (3)	3.64	5.76	7.00
NdW16 - 250°C	5.4159 (3)	11.3879 (6)	5.1942 (3)	92.872 (4)	3.78	5.68	7.03
NdW16 - 500°C	5.3728 (4)	11.4423 (9)	5.2566 (4)	91.468 (6)	4.74	6.33	7.97
NdW16 - 700°C	5.32365 (9)	5.32365 (9)	11.4801 (3)	90	3.02	5.23	6.31
NdW16 - 800°C	5.32814 (8)	5.32814 (8)	11.4972 (2)	90	2.62	4.79	5.82
NdW16 - 900°C	5.33280 (8)	5.33280 (8)	11.5146 (2)	90	2.63	4.71	5.81

NdW16 - RT	***x***	***y***	***z***	**B_{iso}**
Nd	0.00	0.6286 (3)	0.25	0.48 (5)
Nb/W	0.00	0.10977	0.25000	0.94 (6)
O1	0.2395 (5)	0.0334 (2)	0.0555 (5)	1.61 (6)
O2	0.1508 (5)	0.2064 (2)	0.4903 (5)	1.42 (5)
Selected M-O distances	Å			
Nb - O1	1.900 (1)			
Nb - O2	1.813 (2)			

NdW16 – 900°C	***x***	***y***	***z***	**B_{iso}**
Nd	0.50	0.75	0.125	1.89 (4)
Nb/W	0.00	0.25	0.125	2.72 (6)
O	0.1640 (2)	0.4986 (2)	0.2116 (4)	3.78 (4)
Selected M-O distances	Å			
Nb - O	1.875 (2)			

Table S4 –Refined structural parameters and agreement factors obtained for LaW08 and LaW16, for the temperature range data set (25°-900°C). We recall here that, due to the presence of additional peaks ascribed to the presence of a superstructure, these data were analysed according to the profile matching procedure in order to evaluate the temperature dependence of the lattice parameters; agreement factors are affected by the presence of such additional peaks, not taken into account within this simplified description.
Rietveld refined atomic positions, thermal factors and Nb-O distances are reported for the LaW016 data at 900°C as example of the tetragonal (space group 88) phase.

Sample	a / Å	b / Å	c/ Å	β/ deg	χ^2	R_P	R_{wp}
LaW08 - RT	5.4216 (2)	11.6184 (4)	5.2853 (6)	91.77 (3)	5.35	3.64	5.19
LaW16 - RT	5.3510 (8)	11.6890 (1)	5.3135 (1)	90.58 (5)	11.9	6.87	9.45
LaW16 - 250°C	5.3515 (5)	11.7091 (8)	5.3358 (6)	90.26 (7)	12.3	7.55	9.80
LaW16 - 500°C	5.3559 (3)	11.7446 (2)	5.3461(7)	90.19 (6)	12.4	7.74	9.95
LaW16 - 700°C	5.3721 (2)	5.3724 (2)	11.7772 (5)	90	10.4	6.80	9.13
LaW16 - 800°C	5.3812 (1)	5.3812 (1)	11.7894 (4)	90	5.23	5.09	6.41
LaW16 - 900°C	5.3937 (1)	5.3937 (1)	11.8006 (3)	90	3.32	4.12	5.10

LaW16 – 900°C	x	y	z	B_{iso}
La	0.50	0.75	0.125	2.43 (5)
Nb/W	0.00	0.25	0.125	3.24 (7)
O	0.1552 (3)	0.4948 (3)	0.2084 (2)	4.35 (4)
Selected M-O distances	Å			
Nb - O	1.847 (2)			

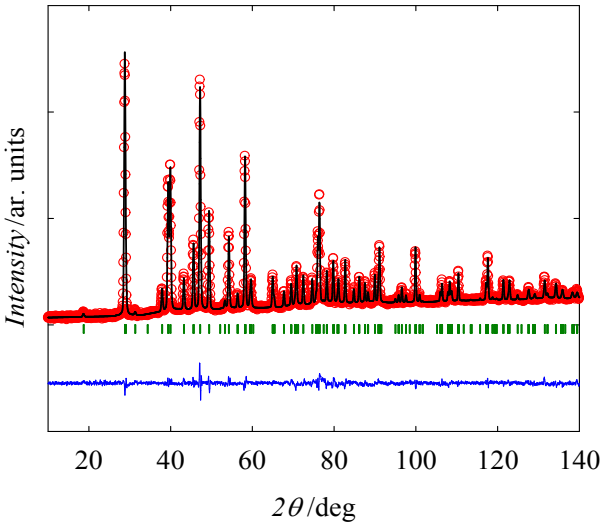

Figure S1- Rietveld refinement results for the tetragonal scheelite-type LaW16 data at 900°C, showing the observed (red circles), calculated (black line) and difference profile (blue line) together with the theoretical Bragg positions (vertical green lines). χ^2 = 3.87, Rp = 4.48, Rwp = 5.50.

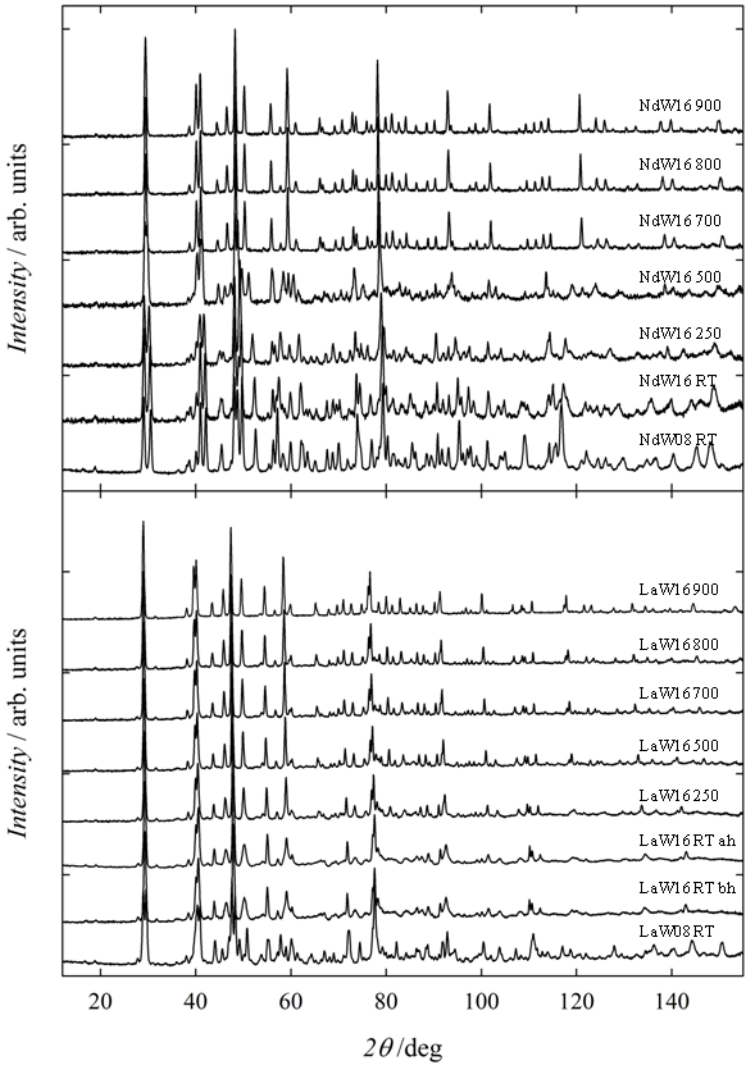

Figure S2 – Neutron diffraction patterns for the NdW08, NdW16, LaW08, LaW16 compositions collected at different temperature in the range 25°-900°C.

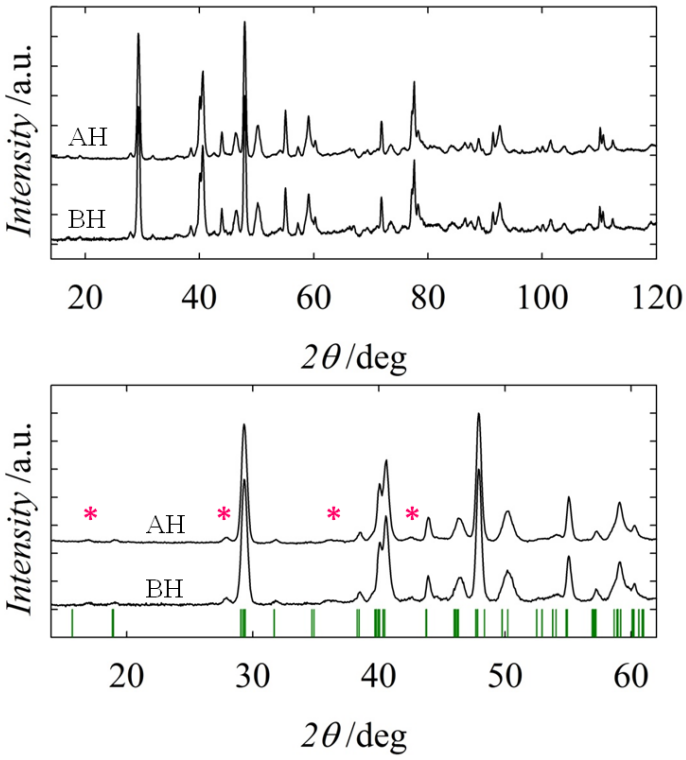

Figure S3 – Neutron diffraction patterns for the LaW16 compositions collected before (BH) and after heating (AH) and Bragg positions (green bars) for the fergusonite structure. Pink stars mark the extra peaks and show the reappearance of the superstructure peaks after the high temperature measurements.

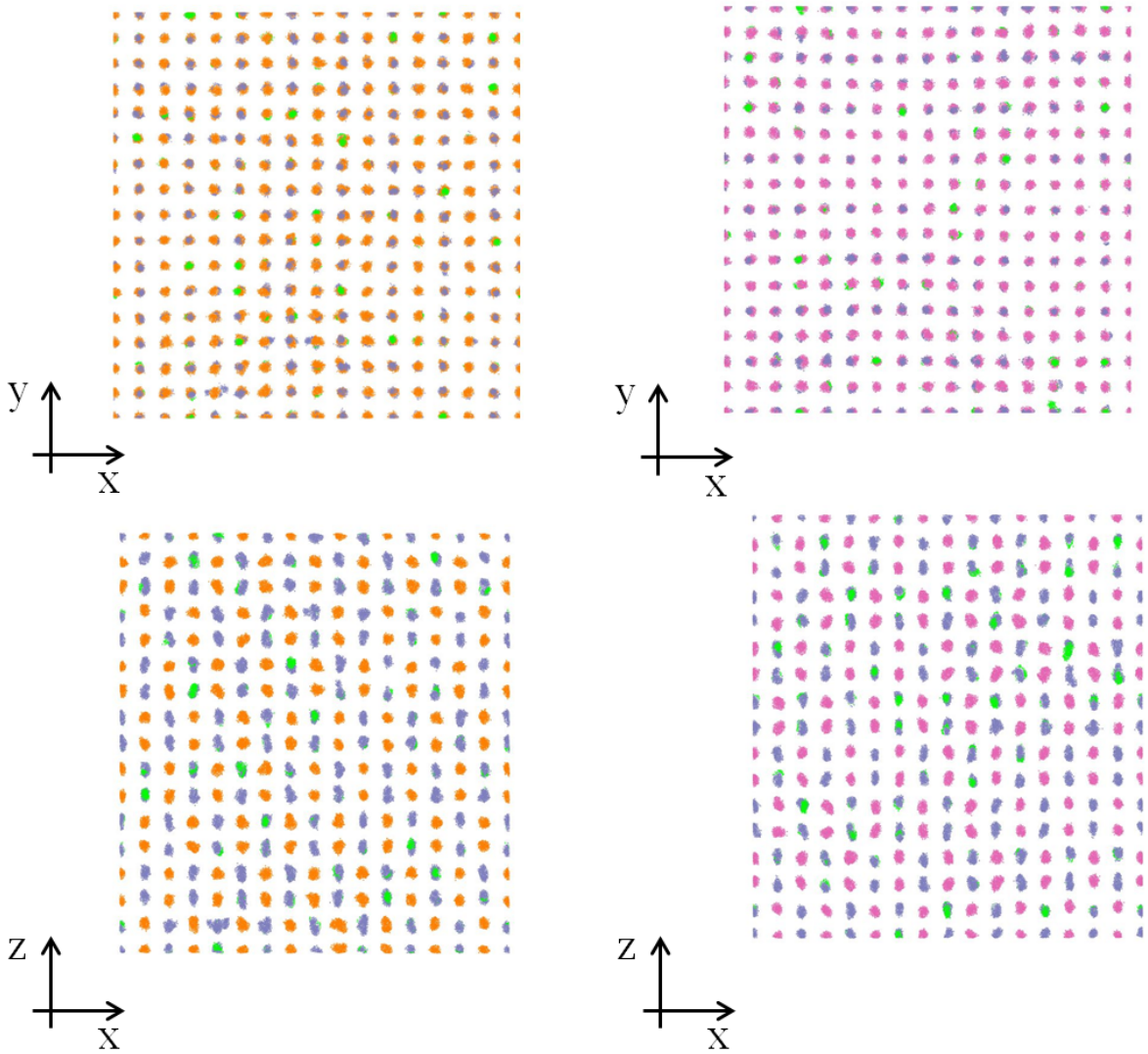

Figure S4 – Cations scatter plots for ion coordinates over the MD simulation at 1200K for La and Nd based supercells. No cations diffusion is observed. La in orange, Nd in pink, Nb in iceblue, W in lime green.