Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics.

Lattice strain effects on doping, hydration and proton transport in scheelite-type electrolytes for solid oxide fuel cells

Chiara Ferrara,[a] Christopher Eames,[b] M. Saiful Islam,[b] Cristina Tealdi[a]

[a]Department of Chemistry, University of Pavia and INSTM, Viale Taramelli 16, 27100 Pavia, Italy.
[b]Department of Chemistry, University of Bath, Bath, BA2 7AY, UK.

Supplementary Information

	A /eV	ς / Å	C /eV	Y / e	k /eVÅ^{-2}
La^{3+} - O^{2-} [1]	1545.2100	0.359000	0.000000	-	-
Nb^{5+} - O^{2-} [1]	1286.9583	0.371525	0.000000	-4.596	5916.77
O^{2-} - O^{2-} [1]	22764.3600	0.149000	27.890000	-2.758	30.211

Table S1 – Buckingham potentials parameters and shell model previously optimized and used for the description of the perfect tetragonal LaNbO$_4$ system; cutoff is set to 15 Å [1].

Morse potential	D /eV	β /Å^{-1}	r$_0$ /Å
O-H [1]	7.0525	2.1986	0.9485
Buckingham potential	A /eV	ρ /Å	C /eV Å^6
O$_H$ – O [1]	311.97	0.25	0

Table S2 – Morse potential parameters relative to the Morse potential form $V_{(r)} = D\{1 - exp[-\beta(r - r_0)]\}$ *and Buckingham parameters for the description of the O-H interaction. The cutoff for the Buckingham potential has been set to 15 Å. The overall charge -1 of the OH group is distributed over the O and H as -1.4263 and 0.4263, respectively. The additional Buckingham potential O$_H$-O is necessary for the description of the interaction between the oxygen of the OH group and the lattice oxygen ions.*

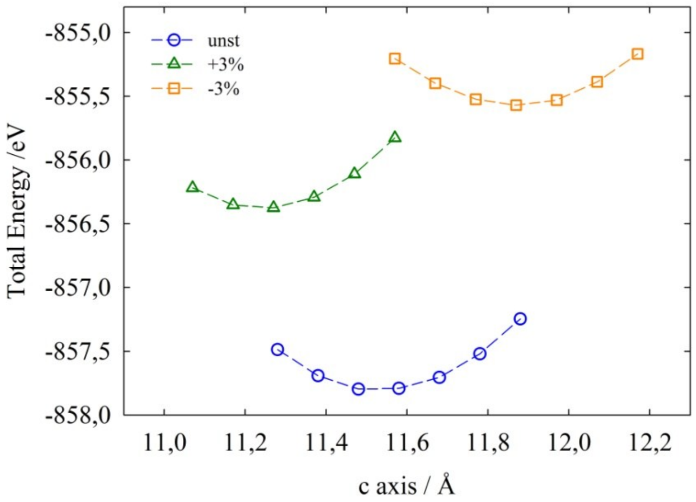

Figure S1 – Total relaxed energy for the unit cell of $LaNbO_4$ as function of the c lattice parameters for the perfect cell (blue circle), biaxial positive strain (green triangle) and negative strain (orange square) applied in the ab- plane. The obtained results indicate that the introduction of positive tensile strain is more favourable compared to compressive strain.

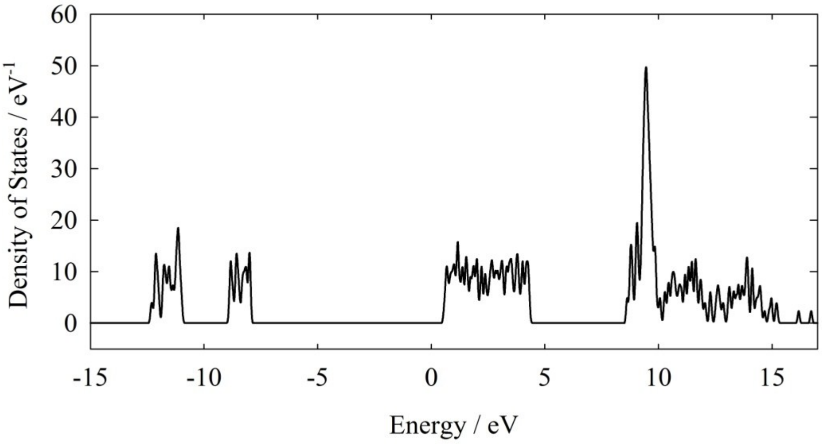

Figure S2 – Total density of states for the perfect unit cell of $LaNbO_4$. The band structure confirms the insulating nature of the considered materials that as expected has a d^0 and f^0 electronic configuration, with a band gap of ~ 3.8 eV. The obtained DOS well reproduce the bands structure already reported for the high temperature phase $LaNbO_4$ system by Kuwabara et al. (see ref. [2]).

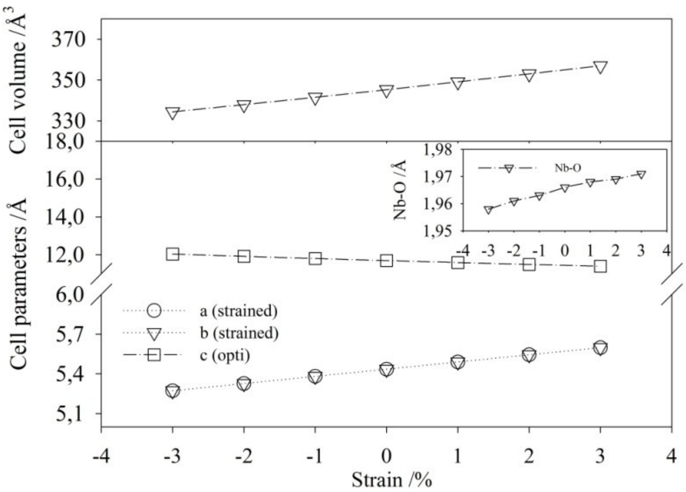

Figure S3 – Constrained and relaxed cell parameters, volume and relaxed Nb-O distances for the strain applied in the ***ab*** *plane as function of the % applied strain. The cell parameters with the imposed strain are reported with the dotted-line graphs while the relaxed parameters as the dash-dotted-line graphs. The introduction of biaxial strain in the ab plane preserves the high symmetry of the system; the NbO4 units remain undistorted and an unique Nb-O distance is observed. The application of the strain at the tetragonal* $LaNbO_4$ *unit cell along* ***ab*** *directions maintains the scheelite structure.*

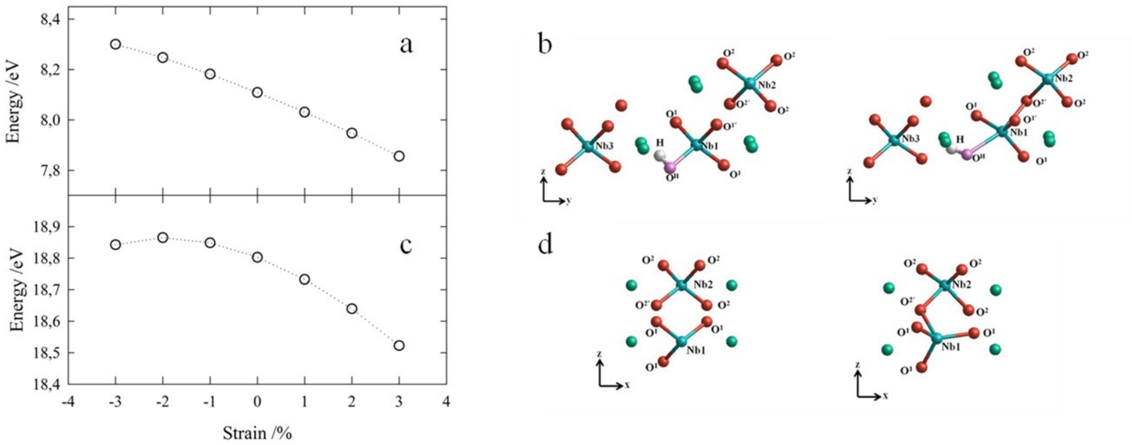

Figure S4 – Calculated energy as function of strain for the introduction of the OH group (a) and the relative schematic representation of the structural relaxation (b), and for the formation of the oxygen vacancy (c) with the corresponding schematic representation of the structural rearrangement (d).

The OH group is accommodated in the structure considering the H ion bonded to an oxygen, O^H, in the coordination sphere of the Nb position, called Nb1 (see panel b). The structure relaxes trough the distortion of the Nb1 tetrahedron and the formation of a cluster $[Nb_2O_8H_1]^{5-}$ as consequence of the formation of a new bond Nb1-$O^{2'}$ where the $O^{2'}$ belongs to the Nb2 coordination sphere. This mechanism has been observed unvaried for all the strain values. The trend found for the $E_{(OH)}$ values (panel a) reflects the behavior of the Nb-O^H bond length as a function of the applied strain in the systems: if the distance Nb-O^H is longer, the energy required for the OH incorporation is lower.

The creation of an oxygen vacancy involves a local rearrangement of the considered NbO_4 unit. The removal of an oxygen ion in the Nb^{5+} coordination sphere would lead to the unstable Nb(III) coordination, the structure rearranges with the formation of a $[Nb_2O_7]^{4-}$ cluster through the creation of a bridging oxygen ion (see panel d) between the Nb1 and Nb2 sites. These condensation mechanism around the oxygen vacancies has been already described for the perfect $LaNbO_4$ system, considering both static lattice and DFT calculations and for other systems based on MO_4 units [1-3]. This mechanism remains unaffected for all the explored values of the strain. The observed trend (see panel c) can be understood considering the combination of two main effects: the strength of the Nb1-O1 broken bond and the strength of the newly formed Nb1-O2' bond. With the increase of the applied strain, the Nb-O bond lengths undergo an elongation, making the formation of an oxygen vacancy in the system more favorable at higher applied strain. At the same time the Nb1-Nb2 distance decreases, making the formation of the new Nb1-O2' bond more favorable for higher value of strain. In addition, in tensile strained systems the formation of the $[Nb_2O_7]^{4-}$ cluster is favored by the reduction in the electrostatic repulsion, between oxygens belonging to nearest-neighbors Nb tetrahedra, in comparison to the unstrained structure. This is due to structural deformations involving mutual tilting of the NbO_4 units participating in the cluster formation, which results in the elongation of the O^1-$O^{2'}$ distance shown in Figure S4-d.

The combination of these two terms according to the following equation:

$$H_2O_{(gas)} + V_O^{\cdot\cdot} + O_O^{\times} \leftrightarrow 2OH^{\cdot}$$

gives origin to the observed trend for the hydration energy as function of the strain discussed in the main text.

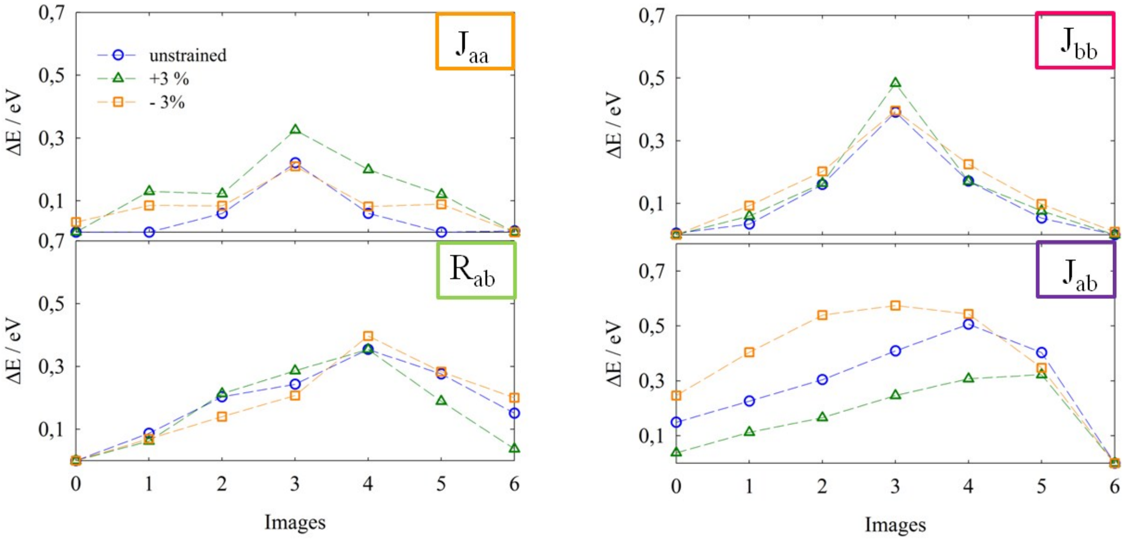

Figure S5 – Energy barriers profile obtained from NEB calculations for the compressive (orange squares), zero (blue circles) and tensile (green triangles) strain for the different jumps and rotations described in Figure 5 of the main text.

[1] G. C. Mather, C. A. J. Fisher, M. S. Islam, *Chem. Mater.*, 2010, **22**, 5912-5917.

[2] A. Kuwabara, R. Haugsrud, S. Stølen, T. Norby, *PCCP*, 2009, **11**, 5550-5553.

[3] E. Kendrick, J. Kendrick, K. S. Knight, M. S. Islam, P. R. Slater, *Nat. Mater.*, 2007, **6**, 871-875