Supplementary Information

Structural transition in orthorhombic $\text{Li}_{5-x}\text{H}_x\text{La}_3\text{Nb}_2\text{O}_{12}$ garnets induced by a concerted lithium and proton diffusion mechanism

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**Fig. S1:** Profile fit of the PXRD pattern of as-prepared Li$_5$La$_3$Nb$_2$O$_{12}$ with S.G. Ia-3d (230), $a=12.7967(3)$ Å.

**Fig. S2:** XRD pattern of as-aged LLNO. The main peaks of possible Li-containing second phases are indicated with $^\wedge$ (LiOH.H$_2$O), $+$ (LiOH) and $^*$ (Li$_2$CO$_3$).
Fig. S3. Raman spectra of aged LLNO after successive preparation steps: (a) as aged; (b) after washing and (c) after 1h homogenization at 200 °C. The non-washed sample presents strong LiOH.H$_2$O and LiOH bands (3575 and 3675 cm$^{-1}$, resp., marked with *), as well as a weak peak from Li$_2$CO$_3$ at 1093 cm$^{-1}$ (marked with a bar). Washing suppresses these secondary phases without affecting the bands from the garnet phase (see section 3.4.1). The short annealing at 200 °C sharpens the bands and increases spectral resolution.

Fig. S4: TG curve of aged Li$_5$La$_3$Nb$_2$O$_{12}$ after washing in distilled water to remove second-phases.
**Fig. S5:** XRD pattern and phase assignment of the TG residue of H-LLNO after 800 °C showing LiLa$_2$NbO$_6$ and LaNbO$_4$ as the main decomposition phases.

**Fig. S6:** DSC curve of H-LLNO between RT and 200 °C, displaying an endothermic event at 165 °C on heating and an exothermic one at 151 °C on cooling.
Fig. S7. Profile fit of the RT XRD pattern (t=3s, above) in the $P2_12_12_1$ (#19) SG and selected regions measured with t=6s showing low intensity reflections (below).
Fig. S8. Profile fit of the XRD pattern at 200 °C in the $I-43d$ (#220) SG. $\chi^2$: 3.60.

Fig. S9: Tree depicting the relation between the SGs of the high and low temperature phases of H-LLNO ($I-43d$ and $P2_12_12_1$, respectively). Adapted from the Bilbao Crystallographic Server (ref. 23 in the main text).
Table S1

Relevant bond-distances in the low-temperature phase of H-LLNO derived from the fit of the RT PND in the $P_{212121}$ SG.

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Nb4 – O14 : 1.87
Nb4 – O15 : 1.97
Li1 – O1 : 1.824
Li1 – O5 : 1.93
Li1 – O13 : 1.90
Li1 – O17 : 2.10
Li2 – O2 : 1.87
Li2 – O4 : 2.19
Li2 – O14 : 2.02
Li2 – O16 : 1.95
Li3 – O3 : 1.94
Li3 – O6 : 1.87
Li3 – O15 : 2.06
Li3 – O18 : 2.06
Li4 – O7 : 2.00
Li4 – O11 : 1.80
Li4 – O19 : 1.96
Li4 – O23 : 1.83
Li5 – O8 : 1.98
Li5 – O10 : 1.80
Li5 – O20 : 2.14
Li5 – O22 : 1.89
Li6 – O9 : 2.01
Li6 – O12 : 1.96
Li6 – O21 : 2.00
Li6 – O24 : 2.19
H1 – O8 : 1.02
H2 – O23 : 0.98
H3 – O10 : 1.03
H4 – O20 : 1.17
H5 – O11 : 1.03
H6 – O22 : 1.10
H7 – O7 : 0.92
H8 – O19 : 0.90
H1 – H3 : 1.51
H1 – H4 : 2.77
H1 – H6 : 2.69
H3 – H4 : 2.30
H3 – H6 : 3.44
H2 – H5 : 2.41
H2 – H7 : 1.88
H2 – H8 : 1.89
H5 – H7 : 1.76
H5 – H8 : 2.04
**Fig. S10.** Unit cell resulting from fitting the RT PND pattern with the $P2_12_12_1$ SG. Atom coordinates and occupancies are given in Table 1 of the main text.

**Table S2.** Relevant distances in the high temperature phase of H-LLNO derived from the fit of the 200 °C PND in the $I-43d$ SG.

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Fig. S11. Unit cell of the high temperature phase (I-43d SG), showing Li1 and Li2 tetrahedra, Nb octahedra and H bonding to Li1 tetrahedra. Large spheres represent octahedral Li ions (Li3).
**Fig. S12.** Profile decomposition of the OH\(^-\) stretching region of the RT Raman spectrum.

**Fig. S13.** Profile decomposition of the \(^1\)H MAS-NMR spectrum (\(\nu_t = 10\) KHz).