

SUPPLEMENTARY INFORMATION

As it is mentioned in the text, different H⁺/Li⁺ exchange states can be reached by treatment in water at reflux for several days. We show in figure SP1 the evolution of the ⁶Li-MAS-NMR spectrum with the degree of proton insertion by treatment at low temperatures. The main change in the ⁶Li-MAS NMR spectra is the decrease of the component assigned to octahedral Li sites.

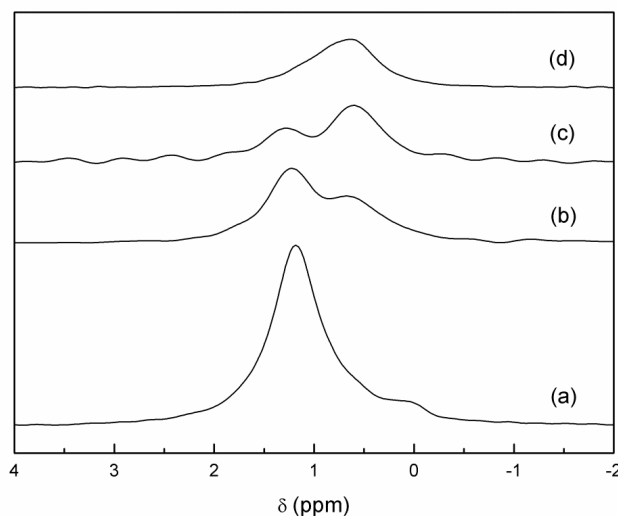


Figure SP1. ⁶Li-MAS NMR spectra of samples with different degree of H⁺/Li⁺ exchange: as prepared ⁶Li₇La₃Zr₂O₁₂ (a), ⁶Li_{3.8}H_{3.2}La₃Zr₂O₁₂ (b), Li_{2.7}H_{4.3}La₃Zr₂O₁₂ (c) and ⁶Li₂H₅La₃Zr₂O₁₂ (d). The four spectra are normalized to the total Li content, as determined by ICP. Note that the sample giving spectrum (c) is not enriched in ⁶Li isotope, which explains the lower signal to noise ratio of that graph.

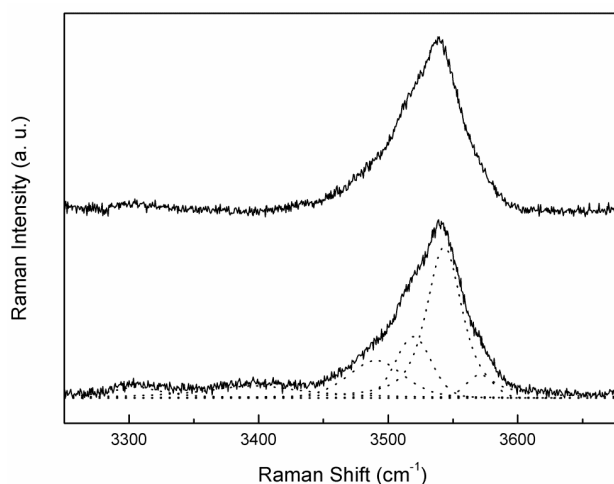


Figure SP2. High frequency Raman spectra of Li_{3.8}H_{3.2}La₃Zr₂O₁₂ (after washing) at RT (bottom) and at 70 °C (top), showing no significant changes in the proton position/bonding. Dotted lines show the components result of the fitting. A background has been subtracted to both spectra.

Dynamic effects:

Following the unexpected observation of thermally activated motional averaging processes in the proton exchanged (aged in air) Li₇La₃Zr₂O₁₂ sample, we decided to carry out a more detailed study of the phenomenon. For that, a new ⁶Li-enriched H⁺/Li⁺ exchanged sample was prepared by treatment of Li₇La₃Zr₂O₁₂ in water for 21h, yielding a stoichiometry of Li₄H₃La₃Zr₂O₁₂, as determined by ICP.

Figure SP3 shows the evolution with increasing temperature of the ⁶Li-MAS NMR spectra of Li₄H₃La₃Zr₂O₁₂. Below 70°C, three components can be resolved (from high to low ppm: “OCT1” less distorted octahedral Li sites, “OCT2”

more distorted octahedral Li sites and “TETR” tetrahedral Li sites). At 70 °C and above only two components are resolved, corresponding to OCT (total octahedral Li sites) and TETR. In Figure SP4 we represent the variation of the chemical shift difference between the OCT2 (or OCT above 70 °C) and tetrahedral Li sites components as a function of temperature, where an onset temperature around 90 °C is calculated for the exchange between both sites. The decrease in the number of NMR components used in the lineshape analysis is not only a matter of resolution: both octahedral sites are in fact located at the same crystallographic cage, their population being determined by the occupancy of two adjacent tetrahedral sites, so upon heating, lithium ions at OCT1 site will shift into OCT2 (and vice versa) due to changes in the neighboring tetrahedral site occupancy more than by a true thermally activated mechanism. Above 90 °C, the averaging is complete and only one component is observed in the ^6Li -MAS NMR spectra, meaning that both octahedral and tetrahedral lithium ions are mobile and exchange sites.

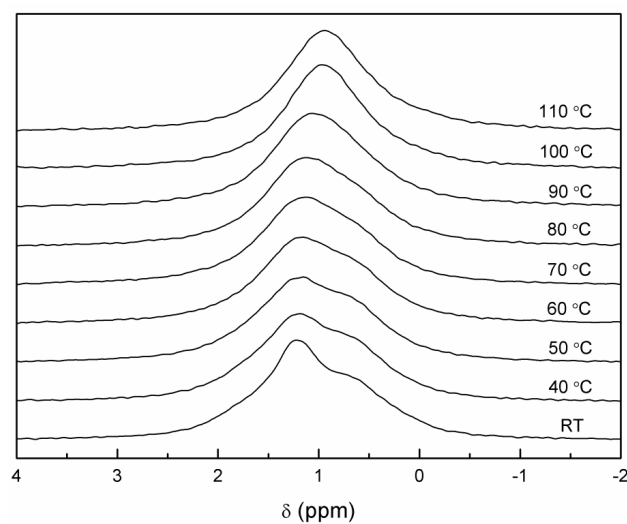


Figure SP3. ^6Li -MAS NMR spectra of $^6\text{Li}_4\text{H}_3\text{La}_3\text{Zr}_2\text{O}_{12}$ as a function of the temperature.

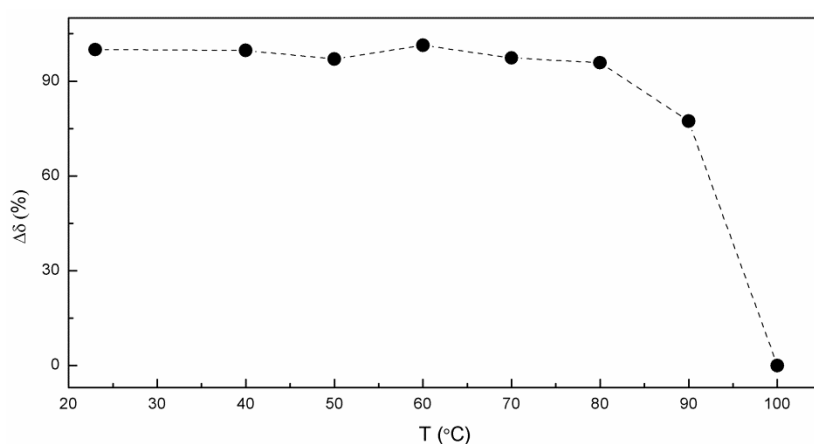


Figure SP4. Chemical shift difference between the octahedral and tetrahedral components (details in the text) of the ^6Li -MAS-NMR spectrum of $\text{Li}_4\text{H}_3\text{La}_3\text{Zr}_2\text{O}_{12}$

An inversion recovery experiment was run for $\text{Li}_4\text{H}_3\text{La}_3\text{Zr}_2\text{O}_{12}$ and T_1 (spin lattice relaxation times) were calculated for the three signals assigned to the garnet. Table SP1 shows the values obtained for the different components at 3 different temperatures. The error associated to T_1 values is mainly due to the overlapping of signals. The lower T_1 values calculated for the two high ppm signals support their assignment to the more mobile octahedral lithium sites.

Table SP1. T_1 (spin lattice relaxation times) calculated from ^6Li -MAS NMR spectra of $^6\text{Li}_4\text{H}_3\text{La}_3\text{Zr}_2\text{O}_{12}$ at different temperatures

Sample	Li site	RT	90 °C	120 °C
$\text{Li}_4\text{H}_3\text{La}_3\text{Zr}_2\text{O}_{12}$	OCT1	$13\text{s} \pm 3$	$6\text{s} \pm 1$	$5\text{s} \pm 1$
	OCT2	$10\text{s} \pm 2$		
	TETR	$17\text{s} \pm 2$	$12\text{s} \pm 2$	