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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Abstract

Proton-exchanged Li-conducting garnets present novel properties compared with their parent compounds, among which proton conductivity may have potential applications. Here we study the structural and dynamical properties of $\text{Li}_{5-x}\text{H}_x\text{La}_3\text{Nb}_2\text{O}_{12}$ garnets with intermediate proton content ($x \approx 2.8$) using neutron and X-ray diffraction, Raman and NMR techniques. At RT the structure is noncentrosymmetric and orthorhombic but transforms reversibly at $\sim 150^\circ\text{C}$ to a cubic, still noncentrosymmetric phase. In the low temperature phase Li is split among six different tetrahedral sites and protons form triplet-wise hydroxyl entities around two of such tetrahedra. In the high temperature phase Li occupies two tetrahedral sites, protons being dynamically disordered around half of the tetrahedra. The occupancy of octahedral Li sites is very low. Spectroscopic techniques evidence that lithium exchange between tetrahedral and octahedral sites and proton reorientation among oxygen sites occur already in the low temperature phase but these processes are restricted at a local scale due to the blocking effect of protons for lithium diffusion and viceversa. We suggest that the phase transition is the consequence of a long range Li and proton redistribution through a concerted hopping mechanism. The relation between the compound stoichiometry, structure and proton mobility is discussed. The occurrence of proton mobility below 200°C for this specific composition may be of practical interest.

KEYWORDS: Li-conducting garnets, $\text{Li}_5\text{La}_3\text{Nb}_2\text{O}_{12}$, exchange, phase transition, neutron diffraction, NMR, Raman, diffusion mechanism

1 INTRODUCTION

Lithium-stuffed garnets are presently studied as possible electrolyte materials in rechargeable all-solid state batteries because of their remarkable ionic conductivity and electrochemical stability, among other properties.¹⁻³ Most efforts in recent years are devoted to optimize Li mobility by appropriate doping strategies. In this context, some concerns regarding the garnet stability when in contact with moisture have led to study the structural and dynamic properties of proton-exchanged materials of $\text{Li}_{n-x}\text{H}_x\text{La}_3\text{M}_2\text{O}_{12}$ type ($\text{M} = \text{Nb}, \text{Ta}, \text{Zr}, \text{Sn}$).⁴⁻¹¹ Though the sensitivity of these materials to moisture might seem a negative issue, it has been proposed that the high structural stability of deeply exchanged garnets makes them suitable candidates for separators between anode and electrolyte in aqueous batteries.¹²⁻¹⁵ Another field of application of proton exchanged compounds arises from their possible proton conductivity.^{8,11} The subject is not easy to elucidate because of the experimental difficulty of sintering water-containing materials.

The structural evolution of proton-exchanged garnets is also of interest because of its implications for conducting properties. Until recently, all non-exchanged $\text{Li}_n\text{La}_3\text{M}_2\text{O}_{12}$ garnets presented either the archetype cubic symmetry with $Ia-3d$ (#230) space group (SG) (for $3 \leq n < 7$) or the tetragonal symmetry with $I4_1/acd$ (#142) SG for $n=7$ (see Ref.1 and references therein). The $I-43d$ (#220) symmetry has been recently reported for Fe or Ga substituted $\text{Li}_7\text{La}_3\text{Zr}_2\text{O}_{12}$ (LLZO).¹⁶

Other symmetries are possible in proton-exchanged garnets: for deeply exchanged $\text{Li}_{7-x}\text{H}_x\text{La}_3\text{Zr}_2\text{O}_{12}$ ($x \approx 4.8$) a noncentrosymmetric $I-43d$ phase was found,⁶ whereas light exchange ($x \leq 1.5$) resulted in a disordered $Ia-3d$ phase.⁴ On the other hand, the also tetragonal $\text{Li}_7\text{La}_3\text{Sn}_2\text{O}_{12}$ transforms to the $Ia-3d$ SG of conventional garnets upon deep exchange ($x = 4.9$).⁹ Regarding $\text{Li}_5\text{La}_3\text{Nb}_2\text{O}_{12}$ (LLNO), there is still some disagreement concerning the symmetry of the hydrated phases and even the maximum achievable degree of exchange. Both the $Ia-3d$ and the non-centrosymmetric $I2_13$ SGs have been reported for proton exchanged LLNO with variable proton content,⁷⁻¹⁰ whereas deeply exchanged $\text{Li}_{6-x}\text{H}_x\text{CaLa}_2\text{Nb}_2\text{O}_{12}$ ($x = 4.9$) crystallizes in the $I-43d$ SG.¹⁷

The tetragonal symmetry of $\text{Li}_7\text{La}_3\text{M}_2\text{O}_{12}$ garnets is a consequence of steric restrictions preventing too-short Li-Li distances. The symmetry evolution of lithium stuffed garnets upon exchange is also a consequence of some exclusion rules: no simultaneous occupancy of an octahedral cavity by two protons or by one proton and one lithium ion can occur. The most important constraint, however, derives from the fact that proton insertion is not random: as proton content increases group around vacant tetrahedral sites tending to form hydrogarnet-like entities $(\text{OH})_4$.^{6,17-19} These entities are detrimental both for proton and lithium mobility, but this behavior may be different for lower proton content. The purpose of this work is to study the structural and dynamical properties of $\text{Li}_{5-x}\text{H}_x\text{La}_3\text{Nb}_2\text{O}_{12}$ garnets with intermediate proton content ($x \approx 2.8$). We show that for this composition the structure is non-centrosymmetric and orthorhombic at RT but transforms reversibly at $T_c \gtrsim 150^\circ\text{C}$ to a cubic, still non-centrosymmetric phase. Results from X-ray and neutron diffraction and from spectroscopic (Raman and NMR) techniques lead us to conclude that the phase transition has a dynamical character and is due to a concerted mechanism of lithium and proton diffusion.

2 EXPERIMENTAL DETAILS

The parent compound $\text{Li}_5\text{La}_3\text{Nb}_2\text{O}_{12}$ was prepared by the conventional solid-state reaction at high-temperature (900°C) using two consecutive heating periods of 24 and 54 hours, with intermediate grinding. High purity ($\geq 99\%$) Li_2CO_3 , La_2O_3 (pretreated at 900°C), and Nb_2O_5 were used as starting chemicals. A 10 wt% excess of Li_2CO_3 was added to the reaction mixture to compensate for Li volatilization on heating. The as-prepared material presented a cubic-like diffractogram (see Fig. S1 of the electronic supplementary information (ESI)) which could be fitted with the usual $Ia-3d$ SG reported for this compound. The lattice parameter ($a = 12.7967(3) \text{ \AA}$) is in agreement with the literature.²⁰

Thermogravimetric analysis (TGA) was carried out in a Q600 thermobalance of TA Instruments, with a heating rate of $10^\circ\text{C}/\text{min}$ under flowing air. Differential scanning calorimetry (DSC) was performed in the same conditions using a TA-Q20 equipment. Lithium content was analyzed by inductively coupled

plasma optical emission spectroscopy (ICP/OES) through microwave assisted digestion of the sample in a 3:1 dilution of HCl and HNO₃.

X-ray diffraction (XRD) experiments were carried out on a Rigaku D/max 2500 diffractometer with Cu K α radiation working at 40 kV and 100 mA. Data were collected between 5 and 120° in a step mode ($\Delta 2\theta = 0.03^\circ$) and a counting time of 3 or 6 s per step. Powder neutron diffraction (PND) experiments were recorded between RT and 200 °C at the Institute Laue-Langevin (Grenoble, France) on a D2B high-resolution neutron diffractometer with $\lambda = 1.5942$ Å. Data were collected between 0 and 160° in a step mode ($\Delta 2\theta = 0.05^\circ$) with ~1h of accumulation time per spectrum. The XRD and PND patterns were analyzed using the FullProf program²¹ and the crystal structures were represented with the VESTA software.²²

Raman scattering measurements were performed using a DILOR XY spectrometer with a CCD detector and 2 cm⁻¹ of spectral resolution. Both the 496.5 and the 514.5 nm lines of an Ar⁺-ion laser were used as excitation sources, the power at the sample surface being ≤ 20 mW. A 50X microscope objective lens was used both for excitation and dispersed light collection. A Linkam TS1500V stage was used for variable temperature measurements.

Single pulse ¹H, ⁷Li and ⁶Li MAS and ⁶Li{¹H}-CP-MAS NMR experiments were conducted on a Bruker Avance-400 NMR spectrometer with a 9.4 T widebore superconducting magnet. The measurements were performed with 4 or 2.5 mm zirconia rotors with Kel-F caps and a spinning rate of 10 or 20 kHz. ⁷Li MAS-NMR spectra were obtained at 155.51 MHz after $\pi/2$ (1.75 ms) pulse irradiation, using a relaxation delay of 10 s, and running 120 scans. The single pulse ⁶Li MAS NMR spectra were recorded at 58.86 MHz after irradiating the samples with a $\pi/8$ (1 ms) pulse, using a relaxation delay of 40 s, and running 80 scans. Chemical shifts refer to an aqueous LiCl (1 M) solution. ¹H MAS NMR spectra were recorded at 400.13 MHz after excitation with a $\pi/2$ pulse length of 3.2 ms and a recycle delay of 90 s. The number of scans was 8. Spectra were referenced to TMS (tetramethylsilane). In high-power proton decoupling (HP-DEC) experiments, ⁶Li nuclei were irradiated with a $\pi/2$ pulse, the relaxation delay used

was 80 s, 32 scans were acquired, and a proton decoupling SPINAL64 sequence was used. ${}^6\text{Li}$ - ${}^1\text{H}$ -CP-MAS-NMR spectra were recorded after a contact time of 7 ms and 64 scans. The relaxation delay was 60 s without acquisition of dummy scans. Hartmann- Hahn polarization transfer from ${}^1\text{H}$ to ${}^6\text{Li}$ was achieved with a nutation frequency of 70 kHz. During acquisition, a proton decoupling SPINAL64 sequence was used.

3 EXPERIMENTAL RESULTS AND DISCUSSION

3.1 Sample preparation

The LLNO powder had been aged at ambient laboratory conditions for several years so it could be expected that garnet hydration through the usual proton for lithium exchange mechanism had occurred. The XRD pattern of the aged sample, shown in Fig. S2 of the ESI, displayed weak peaks at positions that could be indicative of the presence of Li_2CO_3 , LiOH and $\text{LiOH}\cdot\text{H}_2\text{O}$. Due to the low sensitivity of XRD to small amounts of light weight phases, Raman spectroscopy was used to elucidate the presence of lithium hydroxides or carbonate. In fact, the Raman spectrum of the aged sample (Fig. S3, curve (a)), displayed intense bands arising from LiOH (3675 cm^{-1}) and $\text{LiOH}\cdot\text{H}_2\text{O}$ (3575 cm^{-1}), together with a weaker one at 1093 cm^{-1} attributed to Li_2CO_3 . To remove Li containing second-phases phases the aged sample was washed in distilled water and then dried in vacuum. The Raman spectrum after washing is given in curve (b) of Fig. S3. It can be seen that the peaks from Li_2CO_3 , LiOH and $\text{LiOH}\cdot\text{H}_2\text{O}$ have almost completely disappeared, whereas the rest of the spectrum, arising from the garnet phase and to be discussed in section 3.4.1 are not modified.

The most interesting aspect of the diffractogram of the aged sample is that it displays more peaks than expected for the cubic phase of LLNO, either as-grown²⁰ or in hydrated form,^{8,9} which may be indicative of a lower symmetry. However, the pattern presents a broad aspect which is attributed to non homogeneous proton exchange. Following the procedure indicated in Ref. 9, a 1h annealing at $200\text{ }^\circ\text{C}$ was applied to the sample after the washing step before the crystallographic characterization was

attempted. This results in much narrower reflections, as shown in Fig. 1, and in better resolved Raman bands (see spectrum (c) of Fig. S3). In the following, all the experimental results will belong to the washed and homogenized sample, which will be denoted as H-LLNO for short.

3.2 Thermal and chemical analysis

TG analysis of H-LLNO was performed to quantify to what extent proton for lithium exchange had progressed. The TG curve of the washed sample is given in Fig. S4 of the ESI. It shows a ~3% weight loss starting at 400°C, which is ascribed to the garnet deprotonation. In the absence of Li-supplying second phases the deprotonated garnet is unstable and decomposes into $\text{LiLa}_2\text{NbO}_6$ and LaNbO_4 as main phases (see Fig.S5). The weight loss observed in the TG experiment leads to a proton content $x \approx 2.8$ per formula unit, if there are no other sources of weight loss.

The DSC curve of H-LLNO between RT and 200 °C is shown in Fig. S6. It displays two events, at 165 and 152 °C on heating and on cooling, respectively, which strongly suggest the occurrence of a phase transition. It will be the main purpose of this work to analyze the origin of such transition and the structural evolution across it.

To validate the proton content derived from TGA, the lithium composition was analyzed by ICP/OES, which yielded a lithium content per formula $[\text{Li}] = 2.20(8)$ and thus $[\text{H}] = 2.80(8)$, in very good agreement with the TG result.

Fig. 1 XRD pattern of H-LLNO measured at RT. In the inset the regions of the (400) and (402) pseudocubic reflections are expanded to highlight the need of an orthorhombic SG. The red crosses are the experimental points and the black line is the profile fit with the generic orthorhombic *Pmmm* SG that has no reflection conditions.

3.3 Structural characterization

3.3.1 Symmetry at RT

Fig. 1 shows the RT XRD pattern of H-LLNO. The observed peak splitting unambiguously indicates that the symmetry is lower than cubic. In fact, a detailed inspection of the diffractogram evidences that only an orthorhombic approach can explain the peak splitting at high angles. To illustrate such behavior, the regions of the (400) and (402) pseudocubic reflections are expanded in the inset, together with their fit in a generic orthorhombic SG.

Once the crystal system has been determined we have analyzed the (*hkl*) indices of the observed reflections in order to find the SG. We start with the profile fit in the generic orthorhombic SG *Pmmm* and look at the intensities of all possible reflections. We thus see that the great majority of peaks with non-zero intensity fulfill the *I* centering condition $h+k+l=2n$, but some extremely weak peaks that violate the *I*-centering rule cannot be neglected. Examples are (122) at 20.7°, (221) at 20.9°, (140) at 28.9°, (421) at 32.2°, (115) at 35.9°, etc. The presence of such peaks implies a lowering to *P*-like orthorhombic SGs, and there are 30 of them. The appearance of (*h0l*), (*hk0*) and (*0kl*) reflections with

both indices odd excludes 19 SGs of the list. From the rest, the presence of (*h*0*l*), (*hk*0) and (0*kl*) reflections with an even and an odd index excludes 5 more groups. From the remaining 6 groups, the one with the highest symmetry is $P2_12_12_1$ (#19), whose reflection conditions (even indices for *h*00, 0*k*0 and 00*l* reflections) are fulfilled. The profile fit of the RT X-ray diffractogram in the $P2_12_12_1$ SG is shown in Fig. S7 of the ESI, as well as selected regions to highlight some weak diffraction peaks. The fit gives $a = 12.6979(2) \text{ \AA}$, $b = 12.7387(2) \text{ \AA}$, $c = 13.0091(1) \text{ \AA}$ and $V_c = 2104 \text{ \AA}^3$, which is 0.44 % larger than that of the as-prepared compound ($V_c = 2095 \text{ \AA}^3$).

Therefore, we conclude that the exchanged H-LLNO compound, for intermediate proton content $x \approx 2.8$, has orthorhombic symmetry. The SG that best accounts for all observed diffraction peaks is the $P2_12_12_1$ SG.

3.3.2 Thermal evolution of H-LLNO. Orthorhombic to cubic phase transition

Fig. 2 shows the thermal evolution of the XRD patterns of H-LLNO between RT and 200 °C, and back to RT. Having in mind the TG curve, the temperature of 200 °C was chosen so as to be sure that no stoichiometric change is taking place during the heating run. A phase transition to a cubic phase is evident in this figure, as is the reversibility of the process, in agreement with the DSC result. Both the initial and after-heating patterns are consistent with the orthorhombic symmetry previously determined. At 100 °C the pattern looks basically the same as at RT. At 150 °C the peaks are clearly merging but the pattern is not fully cubic yet, indicating that the phase transition is close but slightly above this temperature. At 200 °C the transition is fully accomplished so we have analyzed this diffractogram to elucidate the SG of the high temperature phase.

We follow the same procedure of analysis used for the low temperature phase. We first perform a profile fit in a cubic SG with no reflection conditions such as $Pm\bar{3}m$ and see that all observed peaks fulfill the *I*-centering rule, which limits the search to the 10 *I*-centered cubic groups. Moreover, all (*h*00) peaks fulfill $h=4n$ and this limits the list to groups $Ia\bar{3}d$ (#230), $I\bar{4}3d$ (#220) and $I4_132$ (#214). We

also see that all peaks of type (hhl) fulfill $2h+l=4n$, which are general conditions only for groups $Ia-3d$ and $I-43d$. Finally, we find that there are $(hk0)$ peaks not fulfilling $h, k=2n$ such as (310) at 21.8° , (730) at 54.3° , and so on, which eliminates the $Ia-3d$ SG of conventional garnets. Then we conclude that the SG of the high temperature phase is $I-43d$ (#220), the same as that of H-LLZO and other proton-exchanged garnets. The profile fit of the 200°C diffractogram in the $I-43d$ SG is shown in Fig. S8 of the ESI.

Fig. 2 XRD patterns of H-LLNO as a function of temperature.

The tree depicting the relation between the SGs of the high and low temperature phases is displayed in Fig. S9 of the ESI.²³

3.3.3 Determination of Li and H distribution by PND

Once the SGs of the low and high temperature phases have been assigned, we seek to understand the origin of the low symmetry of H-LLNO at RT and of the phase transition from the properties of the lithium and proton distribution. For that purpose, and because of the weak X-ray scattering ability of Li and H ions, we have measured variable-temperature powder neutron diffraction.

Fig. 3 PND pattern of the aged LLNO at RT. The blue trace is the difference between the experimental data (red points) and the Rietveld fit with the orthorhombic $P2_12_12_1$ space group (black line). Vertical sticks denote the allowed Bragg reflections.

3.3.4 Structure of the low-temperature phase

Fig. 3 shows the PND at RT, together with its fit in the $P2_12_12_1$ space group. To determine the atomic positions we have followed the standard procedure. We first include only La, Nb and O atoms, which in the $P2_12_12_1$ SG occupy 6, 4 and 24 different sites, respectively. In this SG there are no special positions, all atoms occupy generic 4a sites. We then look at the Fourier difference map for peaks with negative scattering length that might arise from lithium or hydrogen ions. We find six occupied tetrahedral positions for lithium, four of them almost fully occupied and two (Li4 and Li5) with partial occupancies. We then search for peaks with negative scattering length inside the octahedral cages limited by two tetrahedra that might belong either to octahedral Li ions or to protons, assuming that protons would be bonded to oxygen atoms at a distance close to 1 Å whereas Li ions in octahedral sites would be bonded to oxygen atoms at distances between ~ 1.8 and 2.8 Å. Applying this criterion we find several possible proton sites but no octahedral lithium, at least to the resolution limit of PND.²⁴ We include step by step the possible proton coordinates and refine their coordinates and occupancies. Lithium coordinates and occupancies are also refined after the introduction of each proton location. We thus

find four proton sites close to oxygen atoms O7, O11, O19 and O23 around Li4 and another set of four proton sites close to O8, O10, O20 and O22 around Li5 which results in a picture of eight different proton sites with variable occupancies in the environments of the two lithium tetrahedra with low occupancy. Further peaks appearing in the Fourier map displayed occupancies below 0.1 protons per site, which is at the limit of the technique resolution. To minimize the correlation between thermal parameters, fractional coordinates and site occupancies, the B_{iso} parameters of similar atoms (La, Nb, O, Li or H) have been constrained to be equal and refined. The neutron wavelength was also refined and yielded $\lambda = 1.59259(2)$.

With these constraints we reach $\chi^2 = 1.21$ and Fourier residuals of ± 0.018 . The parameters derived from the fit are listed in Table 1. Relevant bond distances are given in Table S1 of the ESI. The compound stoichiometry resulting from ND is $\text{Li}_{2.52}\text{H}_{2.77}\text{La}_3\text{Nb}_2\text{O}_{12}$. The proton content is in agreement with that determined from TGA and ICP-OES, within experimental error. The [Li] excess with respect to the nominal value may be ascribed to the correlation between site occupancy factors, thermal parameters and fractional coordinates, especially for the low occupancy sites.

Table 1. Atom sites, fractional coordinates, thermal factors and site occupancy factors of H-LLNO at RT from PND data refined in the orthorhombic $P2_12_12_1$ (#19) space group. All atoms occupy generic 4a Wyckoff sites.

Atom	x	y	z	B_{iso}	Fract. Occ.	Atom content per formula
La1	0.118(1)	-0.002(2)	0.249(2)	0.58(2)	1	0.5
La2	0.252(2)	0.117(1)	0.007(2)	0.58(2)	1	0.5
La3	0.002(2)	0.251(2)	0.124(1)	0.58(2)	1	0.5
La4	0.242(1)	0.370(1)	0.494(2)	0.58(2)	1	0.5

La5	0.366(1)	0.495(2)	0.241(2)	0.58(2)	1	0.5
La6	0.506(2)	0.252(2)	0.373(1)	0.58(2)	1	0.5
Nb1	-0.008(2)	-0.006(2)	-0.019(2)	0.64(3)	1	0.5
Nb2	0.253(2)	0.236(1)	0.240(2)	0.64(3)	1	0.5
Nb3	0.493(2)	0.503(2)	0.488(2)	0.64(3)	1	0.5
Nb4	0.747(2)	0.747(2)	0.737(2)	0.64(3)	1	0.5
O1	0.272(2)	0.101(2)	0.193(2)	0.69(1)	1	0.5
O2	0.199(1)	0.272(1)	0.113(1)	0.69(1)	1	0.5
O3	0.102(1)	0.199(1)	0.272(1)	0.69(1)	1	0.5
O4	0.351(2)	0.527(2)	0.449(2)	0.69(1)	1	0.5
O5	0.524(1)	0.451(2)	0.353(1)	0.69(1)	1	0.5
O6	0.450(1)	0.353(1)	0.527(1)	0.69(1)	1	0.5
O7	0.709(1)	0.893(1)	0.811(1)	0.69(1)	1	0.5
O8	0.802(2)	0.717(1)	0.889(1)	0.69(1)	1	0.5
O9	0.891(2)	0.803(2)	0.727(2)	0.69(1)	1	0.5
O10	0.136(1)	-0.033(1)	0.057(1)	0.69(1)	1	0.5
O11	-0.039(1)	0.053(1)	0.146(1)	0.69(1)	1	0.5
O12	0.049(2)	0.138(2)	-0.027(2)	0.69(1)	1	0.5
O13	0.781(2)	0.605(2)	0.699(2)	0.69(1)	1	0.5
O14	0.698(1)	0.777(1)	0.605(1)	0.69(1)	1	0.5
O15	0.605(1)	0.697(1)	0.774(1)	0.69(1)	1	0.5
O16	0.857(2)	0.022(2)	0.945(2)	0.69(1)	1	0.5
O17	0.027(2)	0.952(2)	0.850(1)	0.69(1)	1	0.5
O18	0.945(1)	0.861(1)	0.027(1)	0.69(1)	1	0.5
O19	0.215(1)	0.393(1)	0.308(1)	0.69(1)	1	0.5
O20	0.301(2)	0.215(2)	0.399(2)	0.69(1)	1	0.5
O21	0.391(2)	0.306(2)	0.226(2)	0.69(1)	1	0.5

O22	0.644(1)	0.469(1)	0.551(1)	0.69(1)	1	0.5
O23	0.457(1)	0.555(1)	0.642(1)	0.69(1)	1	0.5
O24	0.550(2)	0.639(2)	0.481(2)	0.69(1)	1	0.5
Li1	0.365(4)	-0.000(6)	0.237(5)	0.8(1)	0.91(8)	0.45(4)
Li2	0.261(4)	0.364(4)	0.019(5)	0.8(1)	1.02(9)	0.51(4)
Li3	0.003(9)	0.243(6)	0.377(7)	0.8(1)	1.02(6)	0.51(3)
Li4	0.883(6)	-0.00(1)	0.25(1)	0.8(1)	0.62(7)	0.32(4)
Li5	0.25(1)	0.892(7)	0.016(7)	0.8(1)	0.57(8)	0.28(4)
Li6	0.004(9)	0.243(7)	0.871(7)	0.8(1)	0.95(6)	0.47(3)
H1	0.729(3)	0.355(3)	0.406(3)	1.9(2)	0.84(8)	0.42(4)
H2	0.113(3)	0.443(3)	0.174(2)	1.9(2)	1.0(1)	0.49(5)
H3	0.340(3)	0.108(3)	0.575(2)	1.9(2)	0.95(7)	0.47(4)
H4	0.317(8)	0.125(8)	0.401(7)	1.9(2)	0.40(9)	0.20(4)
H5	0.885(3)	0.049(3)	0.173(3)	1.9(2)	0.92(7)	0.46(3)
H6	0.620(7)	0.391(6)	0.579(6)	1.9(2)	0.43(8)	0.22(4)
H7	0.36(1)	0.414(8)	0.70(1)	1.9(2)	0.3(1)	0.15(5)
H8	0.145(6)	0.393(4)	0.307(5)	1.9(2)	0.7(1)	0.37(5)

$a = 12.7065(2) \text{ \AA}$, $b = 12.7328(2) \text{ \AA}$, $c = 13.0081(1) \text{ \AA}$. $R_{\text{Bragg}} = 3.5$, $R_p = 11.3$; $R_{\text{wp}} = 11.0$, $R_{\text{exp}} = 9.96$, $\chi^2 = 1.21$.

The unit cell resulting from this fit is plotted in Fig. S10 of the ESI.

3.3.5 Lithium and proton ordering in the low-temperature phase of H-LLNO

The bonding of protons and of Li tetrahedra around Nb sites in the orthorhombic phase of H-LLNO is extracted in Fig. 4. As already mentioned, only two (Li4 and Li5) out of the six tetrahedral Li sites hold protons in their environment. In turn, the four proton locations around each of these two tetrahedra split into four sites, resulting in H2, H5, H7 and H8 proton sites around Li4 and H1, H3, H4 and H6 sites

around Li4. From the site occupancies given in Table 1 each Li4 and Li5 tetrahedron would hold on the average 2.9 and 2.6 protons, respectively.

Fig. 4 Arrangement of Li tetrahedra around a pair of Nb sites and H bonding around Li4 and Li5 sites in the low temperature phase of H-LLNO. La polyhedra and all atoms except H are omitted for clarity.

It is interesting to compare the Li and H atomic distribution of H-LLNO with that of the parent compound: In contrast with the homogeneous distribution of the octahedral Li ions in LLNO, the exchanged protons are not uniformly distributed in H-LLNO, so that only Li4 and Li5 tetrahedra have protons in their environment. Furthermore, Li4 and Li5 sites are only partially occupied, whereas the other four tetrahedral lithium sites present almost full occupancy. This is a strong evidence (and consequence) of the tendency of protons to cluster around tetrahedral vacancies, as observed in other garnets. It is also interesting that proton-bearing tetrahedra are surrounded by tetrahedra with no protons. This alternating disposition aims to avoid two protons occupying the same octahedral cavity.

All previous works concerning hydration in LLNO reported cubic phases.⁷⁻¹⁰ Cubic phases were also found in other proton-exchanged garnets, even in those with tetragonal symmetry in their parent compounds, such as LLZO and LLSnO.^{4,6,25} The appearance of an as low as orthorhombic symmetry in H-LLNO is likely a consequence of the moderate proton content of the presently studied composition: for higher H content garnets adopt a cubic symmetry with alternating order of lithium tetrahedra with and without bonded protons. PND data suggest that H^+/Li^+ exchange affects mainly octahedral Li ions,

because the occupancy of the tetrahedral cavities remains similar to that of non-exchanged LLNO and no (or very low) occupancy of octahedral cavities by lithium is detected. This conclusion will be supported by ^6Li MAS-NMR data presented in next section.

In deeply hydrated garnets protons tend to form hydrogarnet-like $(\text{OH})_4$ entities around vacant tetrahedral sites.^{6,17} In H-LLNO protons are also located around the less-occupied Li4 and Li5 sites. From the site occupancies given in Table 1 the *average* proton number around a Li4 or Li5 site would be ~ 2.8 . However, at this stage we cannot say whether this statistical value reflects a random proton occupancy, or whether protons cluster in the form of $(\text{OH})_4$ entities around some of the Li4 and Li5 sites, leaving the rest with no protons. This point will be addressed by spectroscopic techniques in next section. We anticipate that the form of the ^1H MAS-NMR spectrum and its thermal evolution favor a three-proton like bonding around a given Li tetrahedron.

3.3.6 Structure of the high-temperature phase

Fig. 5 PND of H-LLNO at 200 °C. The blue trace is the difference between the experimental data (red points) and the Rietveld fit with the cubic $I-43d$ SG (black line). Vertical sticks denote the expected reflections.

Fig. 5 displays the PND diffractogram at 200 °C. To fit this pattern in the *I*-43d SG previously determined for the high temperature phase we have followed the same procedure as for the RT pattern: we first refine the La, Nb and O positions and then identify Li and H population by searching for peaks with negative intensity in the Fourier difference map. In a first step we find two tetrahedral sites for Li and one site for H atoms. In a second step we identify a low-occupancy site which, according to its distances to nearby atoms, might correspond to Li at an octahedral site. Introducing this population into the refinement yields a very good fit with $\chi^2 = 1.15$ (see Fig.5) and $a = 12.8531 \text{ \AA}$. The amount of octahedral Li atoms is of about 0.37 atoms per formula but this value is subject to large error due to the correlation between Li coordinates, thermal factors and site occupancies, especially for the octahedral site. To avoid artifacts we have constrained the $B_{\text{iso}}(\text{Li})$ parameter to be the same for the three Li sites. The Fourier residuals of this structural model are ± 0.017 . The parameters derived from the fit are presented in Table 2. Bond distances are given in Table S2 of the ESI.

Table 2. Wyckoff sites, fractional coordinates, thermal parameters and site occupancy factors of H-LLNO at 200 °C from PND data refined in the *I*-43d SG.

Atom	Wyckoff site	x	y	z	B_{iso}	Fract. Occ.	Atom content per formula
La1	24d	0.1236(5)	0	1/4	1.17(2)	1	3
Nb1	16c	-0.0046(3)	-0.0046(3)	-0.0046(3)	1.89(4)	1	2
O1	48e	0.7152(3)	0.8928(3)	0.8040(4)	1.34(6)	1	6
O2	48e	0.2730(3)	0.1049(3)	0.1983(4)	1.03(5)	1	6
Li1	12b	3/4	5/8	0	2.0(1)	0.54(3)	0.81(2)
Li2	12a	1/4	3/8	0	2.0(1)	1.00(3)	1.50(2)
Li3	48e	0.39(2)	0.32(1)	0.07(2)	2.0(1)	0.06(1)	0.37(7)
H1	48e	0.414(1)	0.304(1)	0.146(1)	5.6(3)	0.47(1)	2.80(5)

$$a = 12.85314(5) \text{ \AA}, R_{\text{Bragg}} = 4.98, R_p = 19.7, R_{\text{wp}} = 14.8, R_{\text{exp}} = 13.8, \chi^2 = 1.15$$

The formula derived from the Rietveld refinement is $\text{Li}_{2.67}\text{H}_{2.80}\text{La}_3\text{Nb}_2\text{O}_{12}$, which is, as it happens at RT, off the charge neutrality. The discrepancy is attributed, as discussed previously, to the high correlation between lithium coordinates, occupancies and thermal factors.

The cubic model deduced for the high temperature phase of H-LLNO resembles that found for the most hydrated LLZO and $\text{Li}_6\text{CaLa}_2\text{Nb}_2\text{O}_{12}$ garnets,^{6,17} despite the lower proton content of H-LLNO. Li ions are divided into two tetrahedral sites, $12a$ and $12b$, but protons are bonded only to the oxygen atoms O1 forming the tetrahedron around the $12b$ site.²⁶ Though there are by symmetry four available positions around each $12b$ tetrahedron, the occupancy of the H1 site is such that only about 50% of O1 atoms will be bonded to a proton. However, as explained when discussing the low temperature phase, we cannot conclude only from diffractometric data whether a pair-like proton distribution occurs, as would be expected from a random occupancy of the H1 sites, or whether protons tend to cluster as $(\text{OH})_4$ entities around half of the $12b$ sites, leaving the rest with no protons. Diffractometric techniques can neither solve the ambiguity about the static or dynamic character of the proton distribution in the high temperature phase. The thermal evolution of spectroscopic results will help in elucidating these aspects.

The same as at RT, in the high temperature phase protons approach the less occupied tetrahedral sites. As expected, the octahedral Li ions also approach the less-occupied tetrahedra. The resulting model is depicted in Fig. S11 of the ESI. The local structure around a pair of Nb octahedra showing the proton and Li distribution is displayed in Fig. 6. The alternating order of $12a$ and $12b$ Li sites warrants the fulfillment of the rule excluding two protons in the same octahedral cage.

The correspondence between the Li and H sites in the low and high temperature phases can be drawn through the transformation relations between the unit cells of both phases. At the phase transition the number of tetrahedral Li sites decreases from 6 to 2. The Li1, Li2 and Li3 sites transform into the Li2 ($12a$) site of the cubic phase, whereas Li4, Li5 and Li6 sites merge into the Li1 ($12b$) site. On

the other hand, the eight H sites surrounding the Li4 and Li5 tetrahedra, together with similar sites around Li6, non-occupied in the low-temperature phase, merge into the single H1 proton site in the high temperature phase. As regards the local proton distribution, in the orthorhombic phase the average number of protons around Li4 and Li5 tetrahedra is 2.8; in the cubic phase the average proton number around Li1 tetrahedra is 1.9.

Fig. 6 Local structure around a pair of Nb-O₆ octahedra in the high-temperature phase of H-LLNO, depicting Li1(12b)-(O1)₄ and Li2(12a)-(O2)₄ tetrahedra, the H bonding around the Li1 site and the octahedral Li3 site between Li1 and Li2 tetrahedra.

The above results give an average picture of the low and high temperature phases, however they do not explain what drives the phase transition at the microscopic level. Uncertainty about the actual proton distribution around Li tetrahedral sites and their static or dynamic character, as discussed, cannot be elucidated only with diffractometric techniques. To get more information about the local atomic distribution and its evolution across the phase transition, we have performed variable-temperature Raman and NMR measurements.

3.4 Spectroscopic characterization of the thermal evolution of H-LLNO

3.4.1 Raman scattering

Fig. 7 shows Raman spectra recorded between RT and 200 °C, and at RT after cooling from 200 °C. The inset shows the spectrum of the parent compound LLNO. Compared to the spectrum of LLNO, the

RT spectrum of H-LLNO presents a higher number of peaks, in agreement with the much lower symmetry. Especially interesting is the splitting of the high frequency band ($\Delta\nu > 700\text{ cm}^{-1}$) in the aged sample. By analogy with LLZO, where the band was attributed to the stretching of Zr-O bonds,⁴ we assign this band in LLNO to Nb-O bond stretching. The splitting of this band in the non-centrosymmetric phase of deeply hydrated LLZO was ascribed to the shift of the transition metal cation to an off-center position within the oxygen octahedron.⁶ Extrapolating this interpretation we also attribute the multi-component aspect of the high frequency band in H-LLNO to the non-centrosymmetric character of its structure, in agreement with the assignment made from diffraction techniques.

Fig. 7 Raman spectra of H-LLNO as a function of temperature between RT and 200 °C and back to RT. The left part of the figure shows the lattice modes and the right part shows the OH⁻ stretching modes. The spectra are vertically shifted for presentation purposes. The inset shows the spectrum of the parent compound Li₅La₃Nb₂O₁₂ at RT.

As Fig. 7 shows, the number of lattice modes decreases as temperature is increased, which is consistent with the evolution toward a cubic symmetry. This figure also shows that the splitting of the 700-800 cm⁻¹ band does not disappear above T_c , thus supporting the non-centrosymmetric character of the high temperature phase. The spectrum recorded after cooling from 200 °C looks basically the same as at RT, in agreement with the reversibility of the phase transition.

To follow changes produced on the amount and location of protons we have measured the temperature dependence of the OH⁻ stretching modes appearing around 3500 cm⁻¹. Spectra in this region recorded at temperatures between RT and 200 °C and after cooling from 200 °C are displayed in Fig. 7. At least four bands are observed at RT between 3400 and 3600 cm⁻¹ (the spectral decomposition is shown in Fig. S12 of the ESI). These bands may be attributed to the existence of non-equivalent proton sites as well as to the coupling between proton vibrations, as occurs in hydrogarnets.²⁷

The temperature evolution of the OH⁻ spectrum suggests that the phase transition occurring at $T_c \gtrsim 150$ °C involves a drastic change in the location and/or dynamic state of protons. Around T_c all the bands suffer a considerable broadening and the multicomponent aspect is lost, which is indicative of an evolution toward a single, disordered site for protons. After cooling from 200 °C the OH⁻ stretching spectrum recovers the same aspect as at RT implying that protons return to their initial sites.

3.4.2 NMR spectra

To support the structural model derived from PND and to reinforce the dynamical origin of the phase transition, we have performed ⁷Li, ⁶Li and ¹H MAS-NMR experiments as a function of temperature.

⁷Li MAS-NMR spectra

Fig. 8 shows the temperature evolution of the ⁷Li MAS-NMR spectra. All spectra are centered at 0.6 ppm and up to 13 spinning sidebands (SSB) are observed at RT. The progressive disappearance of the outer SSB with increasing temperature together with the narrowing of the central band and the broadening of the lateral satellites unambiguously indicate the occurrence of a dynamic process in which dipolar and quadrupolar interactions are being averaged. To gain more insight into the local lithium configuration we have measured ⁶Li spectra, which provide much higher chemical shift resolution than ⁷Li spectra.

Fig. 8 Temperature evolution of the ^7Li MAS-NMR spectra of H-LLNO.

^6Li MAS-NMR spectra

Fig. 9 shows the ^6Li MAS-NMR spectrum, comprising two components at $\delta_1 = 0.5$ and $\delta_2 = 1.1$ ppm with relative intensities around 87 and 13 %, respectively (large errors arise from spectral noise associated with the low amount of ^6Li isotope in non-enriched samples).

Fig. 9 ^6Li Single pulse, HP-DEC and $^6\text{Li}\{^1\text{H}\}$ -CP-MAS spectra of H-LLNO at RT.

According to PND data, in H-LLNO most of the Li ions occupy tetrahedral sites at RT. Then, we may attribute the main band at 0.5 ppm to tetrahedral Li ions. This attribution is also in agreement with results on H-LLZO, where the band arising from tetrahedral sites was allocated at $\delta \approx 0.6$ ppm.⁵ In the orthorhombic phase of H-LLNO there are up to 6 different tetrahedral Li sites. Then, two possibilities can be raised to explain the detection of two bands: i) the separation of tetrahedral ions in two different populations, or ii) the existence of a small amount of octahedral Li ions. As regards the first

possibility, we might envisage that Li ions in tetrahedra with hydroxyls would be different enough from those with no protons. According to PND the Li population in non-H-bonded tetrahedra is higher than in H-bonded ones so that, if the band splitting were due to the presence or absence of OH⁻ at the tetrahedron corners, the most intense band should be ascribed to hydrogen-free tetrahedra, a hypothesis that is ruled out by proton decoupled (HP-DEC) and ⁶Li{¹H}-CP-MAS measurements also shown in Fig. 9. In the HP-DEC spectrum, narrowing of the band at 0.5 ppm is evident, which implies that Li atoms contributing to this band are coupled to protons to a higher extent than those giving the band at 1.1 ppm. Similarly, the band at 1.1 ppm is depleted in the ⁶Li{¹H} CP-MAS spectrum, implying again a weak Li-H interaction for the Li ions contributing to that band.

We conclude that the band at 0.5 ppm arises from all unresolved tetrahedral sites and that the band at 1.1 ppm comes from residual octahedral sites. This attribution is also in agreement with LLZO results, where the octahedral lithium band appeared at $\delta \approx 1.2$ ppm.⁵ From the relative band intensity and assuming a Li content of 2.5 atoms per formula, the Li amount at the octahedral sites would be between 0.2 and 0.3 atoms per formula. The fact that no occupancy of octahedral sites is found by PND can be ascribed to the low amount of octahedral Li ions and their distribution in a high number of non-equivalent sites with very low occupancies.

Fig. 10 shows the temperature evolution of the ⁶Li MAS-NMR spectrum between RT and 160°C, just above the phase transition. Except at RT, all spectra show a single, symmetric band whose position shifts slightly toward higher chemical shift as temperature is increased.

Fig.10 Single-pulse ^6Li MAS-NMR spectra as a function of temperature between RT and 160°C. The inset shows the evolution of the chemical shift and the linewidth of the main band.

The inset of Fig. 10 depicts the chemical shift and the linewidth of the main band as a function of temperature. The temperature evolution of the spectrum between RT and 110 °C can be attributed to a motional narrowing process in which the bands initially at 0.5 and 1.1 ppm coalesce to a single band as a consequence of the lithium exchange between tetrahedral and octahedral sites. This exchange, however, does not affect the long-range orthorhombic symmetry, which points to it being restricted to a short-range character. The position of the band at 110 and 150 °C is close to the weighted average of $\delta 1$ and $\delta 2$, but a downward shift is clearly observed between 150 and 160 °C. The band narrowing may be attributed to the band coalescence as well as to the fast exchange. The narrowing seems to be finished at some temperature between 110 and 150 °C, just at the onset of the phase transition. At 150 and 160 °C the averaged line broadens again. We speculate that this behavior may be due to the superposition of a second dynamical process in which lithium atoms explore further sites beyond their original environment.

^1H MAS-NMR spectra

The temperature evolution of ^1H MAS-NMR spectra between RT and 160 °C has been measured with a spinning frequency $\nu_r = 10$ KHz. The RT spectrum (see Fig.11, upper curve, in blue) is quite complex and can be described as a manifold of up to 9 spinning sidebands (SSB) spanning over 90 KHz with overall center at 4.5 ppm. The general aspect of the spectrum suggests the presence of moderately high dipolar interactions, which is not surprising in view of the hydrogen content per unit cell and the H-H distances (between 1.5 and 3.4 Å) found by PND. A remarkable feature of this spectrum is that each SSB presents a fine structure of at least three components, which is better disclosed in the full profile fit shown in Fig. S13 of the ESI.

Fig. 11 ^1H -MAS-NMR spectra of H-LLNO measured with a spinning frequency of 10 KHz (upper spectrum) and of 20 KHz (lower spectrum). The left and right insets show the fit of the central SSB for spinning at 10 and 20 KHz, respectively.

The central SSB of the $\nu_r = 10$ KHz spectrum is expanded in the left inset of Fig. 11. Together with some weak features coming from the rotor, five bands are required to fit the profile, resulting in a total spread of about 17 ppm (6.8 KHz). Since in first order all anisotropic interactions are averaged by spinning, the appearance of five components in the central SSB points apparently towards the presence of non-equivalent protons with different isotropic chemical shifts. This preliminary approach, however, requires some discussion. If the five components within each band were due to different sites we would expect the pattern of relative intensities to be reproduced at each SSB. Instead of that, the relative intensities present a symmetric disposition around the centre of the spectrum at 4.5 ppm.

At this point, it is interesting to compare the spectrum of H-LLNO with that of the hydro-garnet $\text{Ca}_3\text{Al}_2(\text{OH})_{12}$, a stoichiometric compound with only one proton site and no atomic disorder.²⁸ Both spectra are strikingly similar and, in particular, present the same type of "fine structure" which in Ref. 28 was attributed to "the non-coincidence of the individual proton chemical shift tensor".

In order to elucidate the origin of the SSB fine structure we have recorded the ^1H -MAS-NMR spectrum with a different spinning frequency. If the fine structure were due to sites with different chemical shifts the band splitting in each SSB would be independent of ν_r . Contrary to that, as shown

in the lower curve of Fig. 11, the components within each SSB appear much closer in the spectrum measured with $\nu_r = 20$ KHz compared to that measured with $\nu_r = 10$ KHz. The right inset of Fig. 11 shows the profile decomposition of the central SSB for $\nu_r = 20$ KHz. We conclude that the five components are not due to non-equivalent H sites.

The detailed interpretation of the splitting of the SSBs requires a lengthy discussion of the possible Hamiltonian terms in dipolar-coupled homonuclear but non-equivalent spins, which is out of the scope of this work. The summary of that analysis (to be published elsewhere) is that explaining the relative intensities of the SSB fine structure, and in particular the appearance of a strong central component, requires considering pair-wise dipolar coupling among at least three protons, including second order corrections.²⁹⁻³³ The latter are always proportional to $1/\nu_r$, which explains the dependence of splittings on ν_r .

The configuration with three hydrogen atoms around each of Li4 and Li5 tetrahedra is the most likely one, according to the structural refinements. From the analysis of the relative intensities of the SSB components and the relation between the magnitude of the dipolar coupling and the spin-spin distances we obtain an average proton-proton distance of 2.83 Å, which is within the range of distances resulting from diffractometric techniques.

Temperature evolution of the ^1H MAS-NMR spectrum

The temperature evolution of the ^1H MAS-NMR spectra between RT and 160 °C measured with $\nu_r = 10$ KHz is shown in Fig. 12.

Fig. 12 Temperature evolution of ^1H MAS-NMR spectra ($\nu_r = 10$ KHz). The spectra have been vertically shifted for clarity. The inset shows in ppm units the square root of the second moment as a function of temperature.

It can be seen that as temperature is increased the spectrum simplifies considerably. The overall line width is reduced, implying a decrease of dipolar interactions as evidenced by the evolution of the square root of the second moment shown in the left inset. In parallel with this trend the SSB fine structure disappears progressively. At the highest temperature (160 °C) the spectrum can be assigned to a single proton with greatly reduced first and second order dipolar interactions to other protons. The evolution can be explained by a thermally activated dynamical process in which protons jump randomly among the oxygen atoms forming the tetrahedral cages. Motion averages out all anisotropic interactions, which explains the simultaneous decrease of the second moment and the disappearance of the SSB fine structure. The occurrence of proton dynamics even in the low temperature phase is an argument in favor of the absence of stable hydrogarnet-like $(\text{OH})_4$ entities, which are known to be quite rigid against proton mobility,¹⁹ and support the triangular-like configuration of protons around a given tetrahedron.

We have seen in preceding paragraphs that the ^6Li spectrum reaches the motional narrowing regime already at 70 °C whereas Fig. 13 shows that the ^1H MAS-NMR spectrum is just starting to broaden at this temperature. It is risky to interpret the different evolution of lithium and proton spectra in terms of different kinetics. In fact, the difference may just reflect that lithium diffusion is fast enough to

average the small chemical shift difference (less than 1 ppm) between tetrahedral and octahedral sites already at 70 °C, whereas protons have to average large dipolar splittings which require much higher temperature.

3.5 Relation between cation mobility and structural evolution

Upon heating, a reversible phase transition takes place at $T_c \gtrsim 150$ °C from the orthorhombic phase toward a cubic non-centrosymmetric phase with $I-43d$ SG. Diffractometric and spectroscopic techniques show that the phase transition is driven by proton and Li redistribution and that the high temperature phase has a dynamic character. At the phase transition the number of tetrahedral Li sites decreases from 6 to 2 and the proportion of proton-bearing tetrahedra evolves from one third to half of them. In the high temperature phase the scheme of four equivalent H sites surrounding a single tetrahedron is recovered. The nearly half occupancy of the available H sites in the high temperature phase, however, suggests that the instantaneous proton distribution around each tetrahedron may be mainly pair-like and that the four-site configuration should be understood on a time-average basis. The low Li occupancy of the octahedral sites has to be attributed to the location of the exchanged protons in the octahedral cavities and their role as charge compensators around Li tetrahedral sites.

Variable temperature Raman and NMR measurements show that dynamical effects occur in the Li and H sublattices already in the low T phase. The decrease of the dipolar and quadrupolar interactions in the ^7Li MAS-NMR spectrum and the motional averaging of the ^6Li spectrum with increasing temperature suggest that Li ions jump between tetrahedral and octahedral sites. Similarly, the broadening and structure loss of the OH^- stretching Raman bands as well as the averaging of the anisotropic interactions in ^1H MAS-NMR spectra are attributed to proton reorientation among oxygen atoms surrounding tetrahedral sites. Both dynamical effects, however, must have a local or short-range character below T_c , because the orthorhombic symmetry is not affected. In fact, there is a mutual blocking effect of protons for lithium diffusion and viceversa, as previously reported for other

garnets,^{6,34} which restricts considerably the extent of lithium and proton diffusion paths. Within these assumptions, we propose that the observed phase transition is due to the evolution of the proton and lithium motion character from short to long-range.

NMR experiments point towards a two-step thermally activated process. In the first one Li ions would perform local exchanges between tetrahedral and octahedral sites, accompanied by *intra*-tetrahedral proton reorientation. The broadening of the ⁶Li spectra above 110 °C suggests the onset of another dynamical process, probably due to long-range lithium diffusion. A change in the decreasing trend of the ¹H second moment at T_c also suggests the onset of another dynamic process in the hydrogen sublattice that we ascribe to the development of *inter*-tetrahedral proton motion. The progression of the ¹H spectrum with increasing temperature towards a simple one attributable to a single proton type is also in agreement with the mixing of all possible H sites through long-range diffusion. We note that such extended-range excursions are required to transform the multiple-site and inhomogeneous Li and H distribution of the orthorhombic phase onto the more symmetric distribution of the cubic phase.

At this point it is interesting to discuss on the possible correlation between Li and H jumps at the microscopic level. The heretofore assumed impossibility of having two lithium or two hydrogen atoms or one lithium and one hydrogen within the same octahedral cavity imposes severe restrictions to Li and H mobility. A schematic bi-dimensional picture of the Li and H configuration is drawn in Fig. 13 to help this discussion. In this picture tetrahedra are represented by triangles and octahedra by squares.

Fig. 13 Bidimensional scheme depicting possible lithium and proton exchange events depending on the occupancy of available sites. See text for discussion.

Modeling yields that Li diffusion in Li-stuffed garnets involves jumps between octahedral and tetrahedral Li sites across the tetrahedron face connecting them.^{35,36} In proton-exchanged garnets, Li hopping from a tetrahedral to an octahedral site can only occur if there is no H inside the target cage. Then, move #1 is allowed whereas #1' would not be possible. Similarly, protons can reorient around their own tetrahedron as far as there is no octahedral lithium around (#2) but jumps toward another tetrahedron across the octahedral cage (#4) will be seriously restricted if that site is occupied by a lithium ion. Allowing for these restrictions, the atomic redistribution will be enhanced if lithium and proton move *simultaneously* in a concerted way. For instance, a lithium exchange from a tetrahedral to an octahedral site such as #1 leaves a tetrahedral vacancy behind which may trap a nearby passing proton if this is able to overcome the barrier across the octahedral cavity (#4). Similarly, H reorientation around a tetrahedron (#2) liberates an octahedral cavity which may be occupied by the tetrahedral lithium ion opposite to it (#5). Within this picture, lithium and proton dynamical properties in exchanged garnets rely one on the other and occur through a concerted mechanism. In fact, the occurrence of a concerted mechanism might be inferred from the characteristics of the Li diffusion path through tetrahedral and octahedral cavities, the last ones being shared by Li and H ions. Interestingly, a concerted mechanism was proposed based on molecular dynamics (MD) calculations to explain the Li mobility in tetragonal LLZO, where the high occupancy of octahedral sites hampers the long-range Li diffusion.^{37,38,39} The correlation between the motion of octahedral and tetrahedral lithium ions has also been proposed for $\text{Li}_5\text{La}_3\text{Ta}_2\text{O}_{12}$.⁴⁰

Li mobility is expected to be lower in H-LLNO than in non-exchanged LLNO because of the double deleterious action of protons in occupying nearly half of the octahedral cavities, and also in excluding many tetrahedral sites (those holding protons around) as available sites for Li conduction. In our previous study of H-LLZO we clearly showed the relation between the motional narrowing of the ^6Li MAS-NMR spectrum and the degree of proton-for-lithium exchange, so that only samples with intermediate proton content would show Li dynamical effects.⁵

On the other hand, the occurrence of proton mobility at temperatures as low as 100 °C opens the way to the application of proton-exchanged Li garnets as proton conductors. This possibility depends critically on proton content. In our work on H-LLZO we concluded that the very stable $(\text{OH})_4$ units prevented proton mobility up to 300 °C.⁶ Beyond this temperature protons were progressively lost by dehydroxylation processes eventually leading to garnet decomposition. In the same line, negligible proton conductivity was reported for hydrogarnets.¹⁹ In the H-LLNO composition studied in this work, on the contrary, the low occupancy of proton sites enables proton reorientation first around the tetrahedron center and then to another tetrahedron across the octahedral cavity. We conclude that proton mobility can only occur for moderately exchanged garnets in which $(\text{OH})_4$ entities are not formed yet. In support of the interdependence of the dynamical properties on lithium and proton content in exchanged garnets, Yow et al.¹¹ find by MD calculations that the Li mobility in $\text{Li}_{7-x}\text{H}_x\text{La}_3\text{Zr}_2\text{O}_{12}$ is hardly affected for $x = 0.5$, whereas for composition $\text{Li}_3\text{H}_4\text{La}_3\text{Zr}_2\text{O}_{12}$ Li mobility is greatly reduced and the material behaves essentially as a (bad) proton conductor at RT. Only at very high temperatures it adopts a mixed lithium/proton conductor character.

One final observation supporting the existence of a concerted Li^+ and H^+ diffusion mechanism in H-LLNO: Lithium mobility in Li-stuffed garnets requires the simultaneous presence of both octahedral Li ions *and* octahedral vacancies. If either the number of octahedral vacancies is very low, as in tetragonal LLZO, or if octahedral Li ions have been substituted by low-mobility protons, as in deeply exchanged compounds, the Li conductivity is very low. In that sense, the low proton content in the present H-LLNO composition together with the relatively high concentration of stoichiometric

octahedral vacancies of $\text{Li}_5\text{La}_3\text{Nb}_2\text{O}_{12}$ seem to provide the ideal situation to observe simultaneous lithium and proton mobility.

4 SUMMARY AND CONCLUSION

We have presented, for the first time to our knowledge, evidence of an orthorhombic phase in proton exchanged $\text{Li}_{5-x}\text{H}_x\text{La}_3\text{Nb}_2\text{O}_{12}$ garnets ($x \approx 2.8$). In this phase, lithium is split among six different tetrahedral sites and protons form hydroxyl triplet-wise entities around two of such tetrahedra. The symmetry lowering is attributed to the non-uniform Li distribution in sites with variable occupancy together with proton clustering around the less-occupied Li tetrahedral sites.

A reversible phase transition takes place at $T_c \gtrsim 150^\circ\text{C}$ to a non-centrosymmetric $I-43d$ cubic phase, which is attributed to lithium and proton redistribution. In the cubic phase protons occupy randomly the four available sites around half of the lithium tetrahedral cages, but this has to be understood as a dynamically averaged distribution; the statistical occupancy of proton sites suggests that they are probably forming pairs. Both in the low and in the high temperature phases, the proton preference for oxygen atoms surrounding low-occupancy tetrahedral sites is observed, but less clearly than in deeply exchanged garnets.

The dynamical origin of the phase transition is supported by Raman and ^6Li , ^7Li and ^1H MAS-NMR spectroscopic measurements. A concerted mechanism of lithium and proton diffusion is proposed as the promoter of the phase transition. The relation between the compound stoichiometry, structure and proton mobility has been discussed and compared with other hydrated garnets. The occurrence of proton mobility at temperatures as low as 100°C opens the way to the use of specific H^+ -exchanged garnet compositions as proton-conductors in energy devices.

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Supplementary Information. S1: XRD of as-grown compound; S2: XRD of aged sample; S3: Raman spectra of aged sample before and after washing, and after 1h at 200 °C; S4: TG curve of the aged sample after washing; S5: XRD of decomposition products; S6: DSC curve; S7: profile fit of XRD at RT in the $P2_12_12_1$ SG; S8: profile fit of XRD at 200 °C in the $I-43d$ SG; S9: tree depicting the relation between the SGs of the high and low-temperature phases; Table S1: bond distances at RT; S10: unit cell derived from PND fit at RT in the $P2_12_12_1$ SG; S11 and Table S2: unit cell and bond distances from PND at 200 °C in $I-43d$ SG; S12: decomposition of the Raman spectrum of OH⁻ stretching vibrations; S13: decomposition of the ¹H-MAS-NMR spectrum.

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Table of Contents

$\text{Li}_{5-x}\text{H}_x\text{La}_3\text{Nb}_2\text{O}_{12}$ ($x \approx 2.8$) transforms from orthorhombic to cubic symmetry through a phase transition driven by concerted Li and H diffusion.