Experimental report

06/06/2016

Proposal:	**5-21-1093**	**Council:**	10/2014
Title:	Crystal structures and lithium distribution of proton exchanged Li7-xHxLa3Zr2O12 garnet		
Research area:	Materials		

This proposal is a new proposal

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Samples: Li7-xHxLa3Zr2O12

Instrument	Requested days	Allocated days	From	To
D2B	3	3	13/07/2015	16/07/2015

Abstract:

Lithium-conducting garnets have attracted interest in the last ten years as candidates to be used as electrolytes in lithium batteries. Tetragonal Li7La3Zr2O12 garnet transforms to a cubic phase after partial H+/Li+ exchange. The crystal structure of this cubic phase is different depending on the conditions in which the exchange process is carried out, being indexed in the Ia-3d space group when this exchange is carried out at temperatures above 300ºC and (tentatively) I-43d when at room temperature. The aim of the proposed experiments is the study of the lithium and proton distributions and the dynamic effects involved in the exchange process and space group change.

Motivation

Since the first report by Murugan et al.[1] of a highly conducting cubic polymorph of $Li_7La_3Zr_2O_{12}$ current efforts are now devoted to the stabilization of this cubic form and optimization of its conductivity by appropriate doping. We have previously reported the sensitivity of $Li_7La_3Zr_2O_{12}$ to moisture[2]. Annealing the material in air at temperatures around 300-350 °C resulted in a partial H^+/Li^+ exchange and the transformation of the tetragonal phase (t-LLZO) to a cubic garnet that can be indexed in the same *Ia-3d* s.g. of the conventional cubic garnets (Fig. 1a). However, when H^+/Li^+ exchange takes place at room or low temperature (up to 150 °C) the obtained cubic sample can not be indexed within the aforementioned s.g. Due to the low sensitivity of XRD to light elements as lithium and hydrogen, the aim of using NPD was not only the confirmation of the structural phase transitions (different s.g.) but also the study of Lithium ions distribution (Fig. 2) between the different sites in the crystal[3] and location of the inserted protons in the structure. The aim of our proposal was then to picture a map of the different hydrated phases derived from LLZO and relate them to the proton content as well as with the lithium and proton distribution. For this purpose we submitted $Li_7La_3Zr_2O_{12}$ to air or wet environments at different temperatures during different periods of time. Their thermal evolution was also studied at different temperatures, although is still being analyzed.

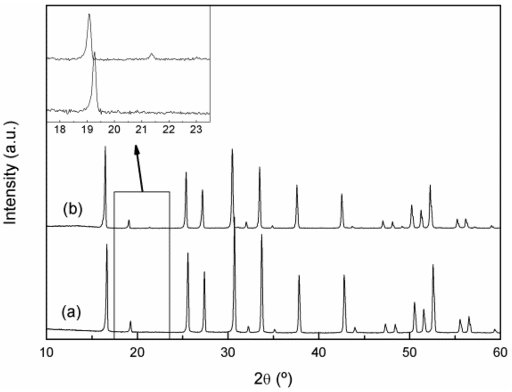

Fig. 1. XRD patterns of $Li_7La_3Zr_2O_{12}$ after aging a) at 300 °C, b) at RT

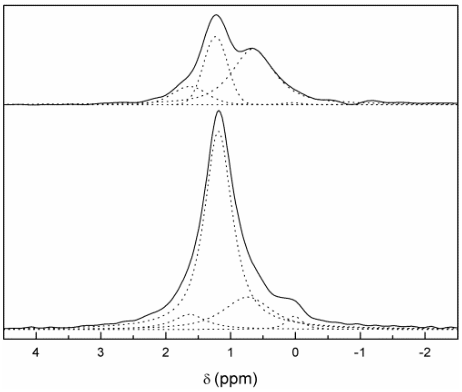

Fig. 2. ^{6}Li-NMR spectrum of $^6Li_7La_3Zr_2O_{12}$ (bottom) and aged at RT.

Results

Annealing in air at 150 °C

The choice of this annealing temperature is based on the observation of a bump in the TG curves of as-grown samples around 150 °C. A 24h treatment of t-LLZO in air at 150°C resulted in a single, cubic garnet phase (c150-LLZO) with stoichiometry $Li_{2.3}H_{4.7}La_3Zr_2O_{12}$ and a XRD pattern similar to that shown in Figure 1b.

The XRD pattern shown in figure 1 can not be fully explained with the $Ia\bar{3}d$ sg usually found for cubic garnets of $Li_xLa_3M_2O_{12}$ type with M a pentavalent or hexavalent cation. Previous work by Galven et al. in hydrated $Li_{5+y-x}H_xLa_{3-y}Ca_yNb_2O_{12}$ garnets had suggested that intense proton exchange may lead to a non-centrosymmetric phase[4] and two different sg were proposed for different compounds: $I2_13$ and $I\bar{4}3d$. In our case, $I\bar{4}3d$ sg is enough to explain the weak additional peaks. As a starting point, and based in our previous NMR results where a preferential exchange of the octahedral Li was observed,[3] a partial refinement of the structure was performed with a structural model including only La, Zr, O and tetrahedral Li atoms. After this first step, a peak with strong negative scattering density and 48 multiplicity was found in the Difference Fourier map (F_{obs}-F_{calc} Fourier synthesis). Due to the distance of this new 48*e* site to the nearest oxygen atom (~1Å), it was attributed to the presence of incorporated protons, and its coordinates added to the final model. It was also observed that Li ions show a clear preference for the 12*b* tetrahedral site, with occupancy three times higher than that of the 12*a* site. The refinement of this model (Figure 3) was very stable with no need of extra constrains, and resulted in a very good agreement with the observed data (R_{Bragg} = 3.58, χ^2 =2.14). As shown in Figure 4, protons are found within the octahedral cages bound to the oxygen atoms (O1) surrounding the less occupied 12*a* Li tetrahedral site. In fact, the count of the number of protons (4.9 per unit formula) and vacant 12*a* sites (1 per unit formula) suggests that protons approach preferably *empty* tetrahedra, forming O_4H_4 entities around the lithium vacancy.

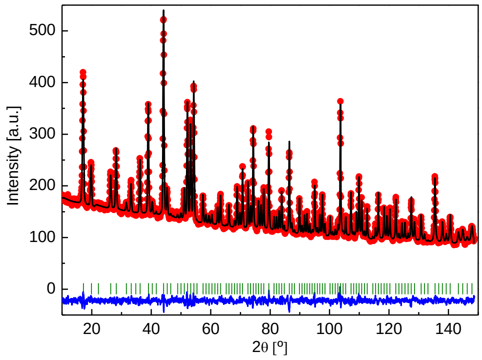

Fig. 3. NDP data of c150-LLZO at 77K. The points are the experimental data and the continuous curve the result of the refinement in the $I\bar{4}3d$ sg. The bottom curve represents the difference between the experimental data and the calculated pattern.

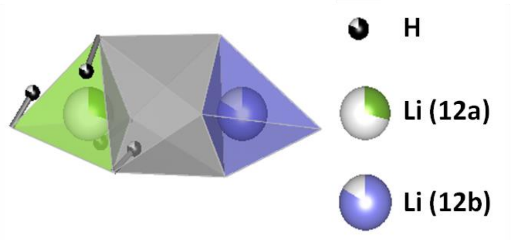

Fig. 4. Schematic representation of the lithium and proton sites resulting from the refinement of the NPD patterns of c150-LLZO within the $I\bar{4}3d$ space group.

Annealing in air at 300-350°C

The diffractogram of the product after 4 days at 350 °C is shown in Figure 1a, and according to ICP determination proton contents of less than 1.5 protons per formula are obtained. Figure 5 shows the result of the Rietveld refinement of the NPD pattern within the $Ia\bar{3}d$ sg when the same procedure as for c150-LLZO was followed (R_{Bragg} = 3.86, χ^2 =1.86). In this case two different sites with negative density were found in the octahedral cavities, with distances to the nearest oxygen atom of around 1.9 and 1.1Å, respectively. From these values, these sites were assigned to remaining octahedral Li and inserted H respectively, each of them occupying a split 96*h* site.

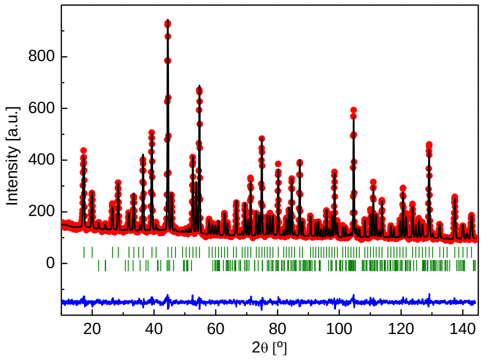

Fig.5. NPD data of c350-LLZO at 77K. The points are the experimental data and the continuous curve the result of the refinement within the $Ia\bar{3}d$ sg. Li_2CO_3 was included in the refinement as second phase.

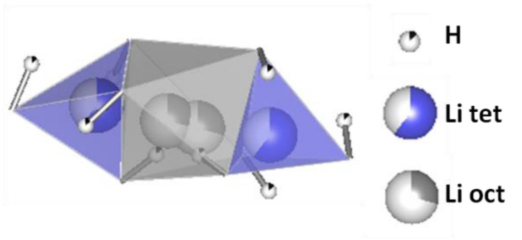

Fig. 6. Schematic representation of the lithium and proton sites resulting from the refinement of the NPD patterns of c350-LLZO within the $Ia\bar{3}d$ space group.

The resolution of the lithium and proton distributions in c150-LLZO and c350-LLZO samples by NPD throws light about the origin of the structural differences found in proton-exchanged LLZO phases. The main difference arises from the separation of tetrahedral lithium ions into two sites with very different occupancies in the ncs phase, a fact which seems to be connected with the preferential binding of protons to the four oxygen atoms around vacant tetrahedral sites. This in turn requires high proton content. The ordering of the tetrahedral lithium ions as well as that of protons results in the loss of inversion symmetry. On the other hand, the high lithium mobility expected at 350°C and a low proton content are probably at the origin of the cs character of samples annealed at this temperature. The disordered occupation of the tetrahedral sites forces octahedral lithium ions and protons to occupy doubly split sites within the octahedral cavity of the $Ia\bar{3}d$ unit cell, as depicted in Figure 6.

The main factors determining whether the centrosymmetric or the non-centrosymmetric structure forms upon protonation are the temperature at which exchange is performed (linked to lithium dynamics) and the total proton content. Unfortunately, it has been shown that both factors are not independent: the high proton content obtained at low temperature favors the ordering of protons around the vacant tetrahedra while low proton content and higher Li (and proton) mobility at 350 °C lead to a disordered configuration of both Li and H ions. The deeply hydrated garnets derived from t-LLZO are stable up to at least 300 °C and also upon ageing at RT, in agreement with the excellent stability found by Ma et al. for proton exchanged c-LLZO[5].

This work has been published in Inorganic Chemistry 2016 (55) 1324-1332 and presented in the 14th International Conference of the European Ceramic Society

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