Experimental report

31/05/2016

Proposal:	**5-21-1087**	**Council:**	10/2014
Title:	Lithium distribution and conduction paths in a new Li conductor tetragonal garnet Li7Sr2LaNb2O12.		
Research area:	Materials		

This proposal is a new proposal

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Samples:
Li5La3Nb2O12
Li7Sr2LaNb2O12
Li6SrLa2Nb2O12

Instrument	Requested days	Allocated days	From	To
D2B	3	3	26/06/2015	29/06/2015

Abstract:

In this proposal we plan to analyze the influence of the Li ion distribution in the three possible crystallographic sites of Li conductors with garnet-type structure. In particular, we will analyze the influence of the carrier number, and their distribution, on the transport properties. For this purpose we will analyze three samples of the Li5+xSrxLa3-xNb2O12 (for x = 0, 1, and 2), in which La3+ is substituted by (Sr2+ and Li+). On the other hand, we will also study the effect of quenching treatment on the Li distribution in order to understand the enhancement of ionic conductivity (more than one order of magnitude) that has been recently found in these materials after this thermal treatment. The analysis of the ND data will allow to correlate the structural data with those data obtained by 6Li and 7Li MAS-NMR and impedances spectroscopies. Furthermore, the analysis of Fourier Map difference of ND data recorded at low temperature (4K) will permit to determine the exact Li location. The analysis of data at different temperatures also will permit to determine diffusion path. In the case of the tetragonal phase, we will analyze the origin of the tetragonal-cubic phase transition.

Title: Lithium distribution and conduction paths in a new Li conductor tetragonal garnet Li7Sr2LaNb2O12.

Lithium garnets of general formula $Li_{3+y}La_3M_2O_{12}$ (M= Nb, Ta, Sb, Zr,…) have been reported as potential solid electrolytes for operation in an all solid-state rechargeable lithium battery [1,2] due to their high ionic conductivity and high chemical stability to reduction process. In order to understand the conduction characteristics of these materials, a detailed evaluation of the structure is required. In particular the amount of Li distributed over tetrahedral and octahedral sites, is important to analyze. To address this challenge, we prepared the $Li_{5+x}Sr_xLa_{3-x}Nb_2O_{12}$ ($0 \leq x \leq 2$) solid solution where La^{3+} is substituted by $Sr^{2+} + Li^+$ in $Li_5La_3Nb_2O_{12}$ increasing the number of charge carriers. On the other hand, the conductivity of different members of this solid solution was increased more than one order of magnitude by quenching heat treatment. The aim of this study was to analyze (a) the influence of Li content on the distribution of lithium in the $Li_{5+x}SrxLa_{3-x}Nb_2O_{12}$ ($0 \leq x \leq 2$) solid solution and (b) the influence of the quenching heat treatment on the population of the Li-sites on three selected samples (x=0, 1 and 2). For that, ^{7}Li-rich samples were prepared in order to reduce absorption problems. We requested three days of neutron beam on the D2B diffractometer to perform variable temperature NDP studies on prepared samples (quenched and slow cooled) at temperatures ranging between 3.5 and 1073 K, in order to determine structural features and analyze occupancy degree of different Li sites. The D2B apparatus (λ= 1.5943 Å), with a step of 0.02º, was used to record ND patterns of prepared samples. XRD demonstrated the single phase character and high crystallinity of the samples x=0 and 1, however, the preparation of 3g of the sample x=2 displayed the presence of some amount of the secondary phase that precluded the proposed structural refinement of the tetragonal $Li_7Sr_2LaNb_2O_1$ phase.

Structural refinements at 3,5K

The Rietveld analysis of NDP of $Li_5La_3Nb_2O_{12}$ and $Li_6SrLa_2Nb_2O_{12}$ samples was successfully performed using the Cussen model [3](Space Group Ia-3d), in which La^{3+} and Sr^{2+}) are 8-fold coordinated (with two different M-O distances) and Nb^{5+} is in the center of regular octahedra, while Li ions are distributed on tetrahedral (Li1;24d site) and distorted octahedral sites (Li2; 96h site). The effect of quenching treatments, which produced a considerably increment in conductivity, was negligible from the structural point of view. In both compositions, NDP were basically the same in quenched and slowly cooled samples. The refinement of the NDP confirmed that unit cell parameters and Li occupancy basically do not change with cooling treatments (Table I). For this reason the experimental work was only performed on quenched samples. A slight expansion in the unit cell parameters was observed by substituting La^{3+} by $Sr^{2+} + Li^+$, which is in agreement with the higher ionic radii of Sr^{2+} (1.44 Å) in comparison with that of La^{3+}(1.32 Å).

The refinement also revealed a different preference of lithium ions for occupation of tetra and octahedral sites with composition. The occupancy of octahedral (96h) Li2 sites increase at expenses of tetrahedral (24d)Li1 sites when Sr increases, confirming the findings of Percival in samples of similar composition [4].

On the other hand the Li-O distances in the tetrahedral sites are larger than in other ionic conductors, suggesting the possible presence of some mobility in prepared samples.

Heating treatments

Evolution of unit cell parameters was determined as a function of temperature (Fig. 2). The dependence observed in unit cell parameters of x= 0 and 1 samples is similar; parameters changing slightly below 200K but increasing considerably above this temperature. Furthermore, the thermal expansion coefficient is also similar in both samples.

In figure 3 we have plotted the temperature dependence of tetrahedral and distorted octahedral sites occupancies for two compositions. The occupancies do not change in the temperature range analyzed; however, a bigger modification was detected with composition.

Finally we have analyzed the evolution with temperature of isotropic thermal factor of atoms. In the case of La, Nb and O, similar evolutions were displayed, while in the case of Li, large differences were found in thermal factors of two structural sites. Although Li1 is located at smaller tetrahedral, its thermal factor increases much more rapidly than that of Li2 sites (distorted octahedral). This suggests again some mobility of lithium in tetrahedral sites. The Li exchange between structural sites does not affect however considerably sites occupancy, indicating important difference on stabilization of lithium in two sites. According to described results, electrostatic interactions between Li ions have a much more effect than temperature on occupation of structural sites.

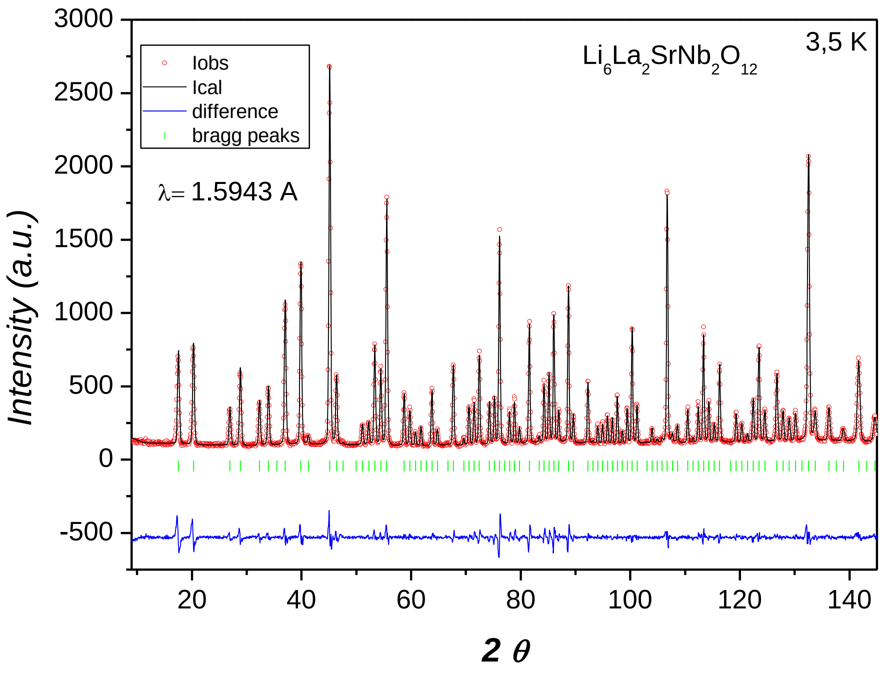

Figure 1. Rietveld refinement of neutron diffraction pattern of the $Li_6SrLa_2Nb_2O_{12}$ quenched sample

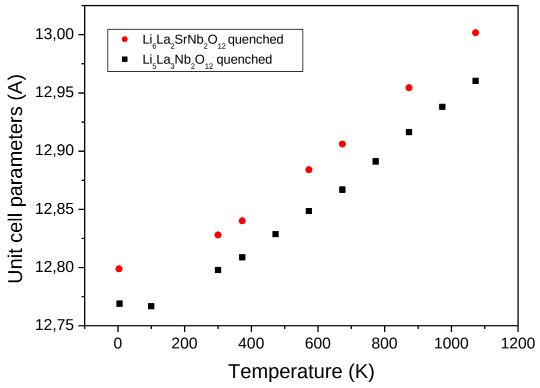

Figure 2.-Temperature dependence of unit cell parameters with temperature in $Li_5La_3Nb_2O_{12}$ and $Li_6SrLa_2Nb_2O_{12}$ samples

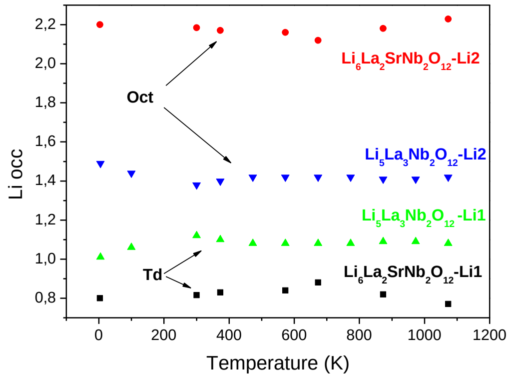

Figure 3.-Temperature dependence of Li sites occupancies

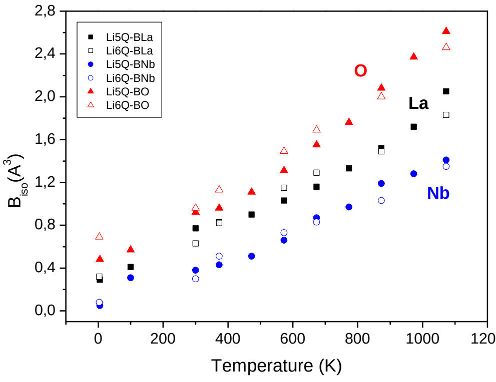

Figure 4.- Temperature dependence of the isotropic thermal factor of La, Nb and O in $Li_5La_3Nb_2O_{12}$ (closed symbols)and $Li_6SrLa_2Nb_2O_{12}$ (open symbols)

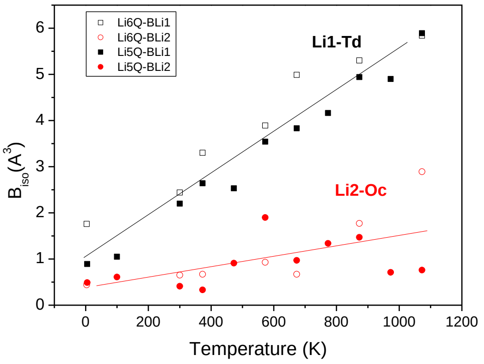

Figure 5.- Temperature dependence of isotropic thermal factors Li1 (black) and Li2(red) for $Li_5La_3Nb_2O_{12}$ (closed symbols)and $Li_6SrLa_2Nb_2O_{12}$ (open symbols)

Table I.- unit cell parameters, isotropic thermal factors and occupancies of slow cooled (SC) and quenched (Q)samples

T (K)		a (A)	Li1			Li2		
			occ	**B**	**%site occ**	**occ**	**B**	**%site occ**
3,5	Li5Q	12.76905(3)	1.92	0.821(2)	63,7	2.96	0.421(2)	49,3
	Li5SC	12.76667(3)	2.13	1.010	70.9	2.87	0.610(2)	47,9
	Li6Q	12.79885(3)	1.61	1.80(2)	53.5	4.39	0.497(8)	73.2
273	Li5Q	12.79780(5)	2.19	1.587	73.1	2.81	0.587	46.8
	Li5SC	12.79316(3)	2.08	1.291	69.2	2.92	0.891	48.7
	Li6Q	12.82803(6)	1.63	2.443	54.3	4.37	0.653	72.9
	Li6SC	12.82825(4)	1.62	1.222	54.1	4.38	0.822	73.0

References

[1] V. Thangadurai, H. Kaack andW. J. F. Weppner, J. Am. Ceram. Soc., 86, (2003), 437.
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[3]E. Cussen, Chem Comm, (2006), 412-413
[4] J. Percival and P.R. Slater, Solid State Communications 142 (2007) 355–357