Experimental report

15/12/2016

Proposal: **5-26-216** **Council:** 4/2015

Title: Neutron Powder Diffraction Study on Bi Doped Li7-xLa3Zr2-xBixO12 Garnet Solid Solutions with x = 0.1-1.0

Research area: Materials

This proposal is a new proposal

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Local contacts: Emmanuelle SUARD

Samples: Li6.8La3Zr1.8Bi0.2O12
Li6.6La3Zr1.6Bi0.4O12
Li6.5La3Zr1.5Bi0.5O12
Li6.4La3Zr1.4Bi0.6O12
Li6.3La3Zr1.3Bi0.7O12
Li6.2La3Zr1.2Bi0.8O12
Li6.1La3Zr1.1Bi0.9O12
Li6.0La3Zr1.0Bi1.0O12
Li6.7La3Zr1.7Bi0.3O12
Li6.9La3Zr1.9Bi0.1O12

Instrument	Requested days	Allocated days	From	To
D2B	2	2	30/11/2015	02/12/2015

Abstract:

The aim of this proposal is to analyze Bi doped Li7-xLa3Zr2-xBixO12 garnet solid solutions with x = 0.1-1.0, which were firstly synthesized in our group (unpublished). Neutron powder diffraction measurements will be coducted to study the Bi- and Li-ion distribution of samples with different Bi content. On the bases of the those data we would be finally able to correlate the crystal chemical with the electrochemical properties of the samples as studied by impedance spectroscopy. This will contribute to a deeper understanding of the structure-property relationship in LLZO garnets, and could be the starting point of the improvement of the electrochemical properties by crystal chemical engineering.

Experimental Report for Proposal 5–26–216

Neutron Powder Diffraction Study on Bi Doped $Li_{7-x}La_3Zr_{2-x}Bi_xO_{12}$ Garnet Solid Solutions with x = 0.1-1.0

College 5A

Instrument: D2B

Council: 2015-04

Allocated days: 2

Date: 30/11/2015 – 02/12/2015

Daniel Rettenwander, Georg Amthauer, Reinhard Wagner, Günther Redhammer

Introduction

Cubic $Li_7La_3Zr_2O_{12}$ (LLZO) garnets are exceptionally well suited to be used as solid electrolytes or protecting layers in novel lithium battery concepts. Unfortunately, the fast ion conducting cubic modification of LLZO is not stable at room temperature (RT) and has to be stabilized by supervalent dopants. In this study we stabilized the cubic phase at RT by the substitution of Zr^{4+} by Bi^{5+}, while at the same time, we achieved an increase of the unit-cell parameter, as the ionic radii of Bi^{5+} is larger compared to the one of Zr^{4+}. The aim of the proposal was to analyze Bi doped $Li_{7-x}La_3Zr_{2-x}Bi_xO_{12}$ garnet solid solutions with x = 0.1-1.0. Neutron powder diffraction measurements were conducted to study the Bi- and Li-ion distribution of samples with different Bi content. On the bases of those data we wanted to link the crystal chemical with the electrochemical properties of the samples as studied by impedance spectroscopy. This will contribute to a deeper understanding of the structure-property relationship in LLZO garnets, and could be the starting point of the improvement of the electrochemical properties by crystal chemical engineering.

Experimental

Neutron powder diffraction measurements were performed at the D2B diffractometer, Institut Laue-Langevin (ILL), Grenoble, France. Powder diffraction data were collected at room temperature in constant wavelength mode with $\lambda = 1.594$ Å, using a step width of 0.04° in the range $5.8° \leq 2\theta \leq 159.7°$. The FULLPROF suite of programs has been used for data treatment and refinement. The atom positions of La, (Zr,Bi), and O were refined using anisotropic atomic displacement parameters. The atomic displacement factor for the Li1 positions was refined isotropically. To avoid large correlations with the occupation factor, the atomic displacement factor of the Li2 site was set to 3.5. Site occupancies of Li sites were then allowed to refine unconstrained, while (Zr+Bi) was fixed to full occupation of this site; however, the relative amounts of Bi and Zr were allowed to refine freely. The results for Bi and Zr occupancies agree well with those obtained from XRPD refinements.

Results

In general, the results of neutron powder diffraction (NPD) confirmed the results obtained by X-ray powder diffraction (XRPD). As the samples used for neutron powder diffraction have been stored under an Ar atmosphere immediately after synthesis, the samples were only slightly affected by protonation and aging. In contrast to this, the samples used for XRPD measurements showed higher amounts of Li_2CO_3 and LiOH, as they were affected by a protonation reaction of the LLZO phase. All LLZBO samples showed about 2% Li_2CO_3; in addition, small contents of LiOH were found as well. As determined by XRPD, the sample with $x = 0.10$ still shows both tetragonal $I4_1/acd$ (resulting from the low substituent concentration) and cubic $Ia\bar{3}d$ garnet modifications. A model with two different cubic (space group $Ia\bar{3}d$) LLZBO phases has been applied for the refinement of NPD data of samples with $x_{int} \geq 0.30$, as the data quality and resolution of data obtained from NPD are better compared to data obtained from XRPD. The model used for the refinement of NPD data consists of an LLZBO phase that is not affected by protonation and a second LLZBO phase which is strongly affected by protonation on the Li2 (96*h*) site, thus showing a larger unit-cell parameter. For this protonated phase only H^+ was assumed to occupy 96*h*. In this case, the fractional atomic coordinates are similar to those reported recently for protonated LLZO (without dopants) with space group $Ia\bar{3}d$. For the unprotonated phase, the Li content decreases with increasing Bi content. This affects both the Li1 and Li2 sites to similar extents; however, the data overlap is large; thus no further detailed structural parameters could be extracted. The unit-cell parameters of both unprotonated and protonated LLZBO phases of different samples obtained by Rietveld refinements of NPD data are shown in Table Figure 1. Unit-cell parameter values for unprotonated LLZBO samples obtained from NPD data are similar to values of as-synthesized samples obtained from XPRD; while the unit-cell parameters of protonated LLZBO phases obtained from NPD refinements are similar to XRPD-derived values of samples that were stored in air for 1 week. A discontinuity of the unit-cell parameter has been observed between samples with $x_{int} = 0.70$ and $x_{int} = 0.80$. This might be related to different alteration stages that could not be resolved. According to Rietveld refinements, the protonated garnet contents are between 22% and 34%.

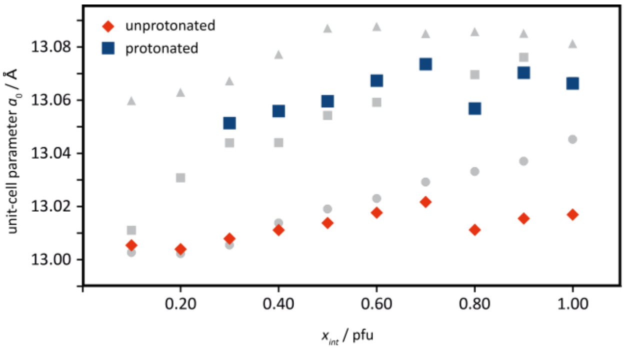

Fig. 1: Unit-cell parameter of $Li_{7-x}La_3Zr_{2-x}Bi_xO_{12}$ obtained from NPD data. Red diamonds represent the unit-cell parameters of unprotonated LLZBO phases; blue squares represent the unit-cell parameter values of protonated LLZBO phases. For comparison, the unit-cell parameter values obtained from XRPD are shown in grey (grey dots: as-synthesized; grey squares: after 1 week exposure to air; grey triangles: after 3 weeks under air). From Wagner et al. (2016)

The results have been published in:

Wagner, R.; Rettenwander, D.; Redhammer, G. J.; Tippelt, G.; Sabathi, G.; Musso, M. E.; Stanje, B.; Wilkening, M.; Suard, E.; Amthauer, G., Synthesis, Crystal Structure, and Stability of Cubic $Li_{7-x}La_3Zr_{2-x}Bi_xO_{12}$. *Inorg Chem* **2016,** 55, 12211-12219. DOI: 10.1021/acs.inorgchem.6b01825