Experimental report

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Proposal: **5-22-755** **Council:** 4/2017

Title: Structural investigation of $Li_{1+x}Cr_x(Ge_{0.2}Ti_{0.8})_{2-x}(PO_4)_3$ glass-ceramics. Correlation with lithium transport

Research area: Materials

This proposal is a new proposal

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Samples: $Li_{1+x}Cr_x(Ge_{0.2}Ti_{0.8})_{2-x}(PO_4)_3$ with $x = 0.2, 0.4, 0.6, 0.8$

Instrument	Requested days	Allocated days	From	To
D2B	2	2	25/04/2018	26/04/2018
			11/06/2018	12/06/2018

Abstract:

Li-based solid electrolytes have been extensively studied in the last decades for their application in batteries. Phosphates with NASICON-like structure have attracted much attention due to their high ionic conductivity and structural versatility. Currently, we have synthesized a new glass-ceramic in the system $Li_{1+x}Cr_x(Ge_yTi_{1-y})_{2-x}(PO_4)_3$ (LCGTP) which presents appreciable glass stability, homogenous nucleation and crystallizes a NASICON-type phase. We have then performed an investigation of the double substitution of Ti by Cr and Ge based on the LCGTP system, pursuing a compromise between the stability of the precursor glass and the electrical properties of the resulting glass-ceramic. A structural investigation by X-ray diffraction helped in finding a correlation between the unit cell volume of the crystalline phase and the ionic conductivity. Unfortunately, similar X-ray scattering factors for Ti and Cr prevented to go further in the information. We now propose to extend the investigation to neutron diffraction, which allows the distinction between Cr and Ti. We expect better insight on the origin of enhancement of conductivity in trivalent-doped NASICON-type compounds.

Experimental Report

EXPERIMENT TITLE

Structural investigation of $Li_{1+x}Cr_xGeTi_{1-x}(PO_4)_3$ glass-ceramics: Correlation with lithium transport.

PROPOSAL NUMBER

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INSTRUMENT D2B

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Introduction

The crystal structure of $LiM_2(PO_4)_3$ (M = Ge, Ti, Zr, Sn or Hf) is based on the NASICON-type rhombohedral structure (space group $R\bar{3}c$) and can be described as formed by infinite ribbons of $[M_2(PO_4)_3]^-$ units composed of alternate corner-sharing $[MO_6]$ octahedra and $[PO_4]$ tetrahedra [1,2] . As reported in the literature, Li^+ ions may occupy different interstitial positions within this network, the most likely M1 site, 6b (0, 0, 0), the M2 sites, 18e (x, 0, 1/4) and the M3, 36f (1/6, 1/3, 1/12) [2-4]. These sites alternate along the channels forming three-dimensional conduction pathways where Li+ ions might move jumping from one site to another. The energy landscape of the conduction channels depends on the skeleton framework, which turns to be governed by the size and electronegativity of the M atoms in the MO_6 octahedra. Among the above-mentioned tetravalent cations, titanium (Ti) and germanium (Ge) tend to lead to the basic NASICON-like compound with the highest lithium conductivity and smallest activation energy. Additionally, the partial substitution of the M cation by a trivalent cation, A^{+3} (Al, Ga, In, Sc, Y, La, Cr or Fe), generates a deficiency in positive charge, which is compensated by additional Li^+ ions, leading to an increase of ionic conductivity in the general $Li_{1+x}A_xM_{2-x}(PO4)_3$ system [1-4]. However, most studies have suggested that the enhancement of ionic conductivity in this system is due to changes in the energy barrier for lithium ion conduction rather than in the increase of Li^+ concentration in the NASICON-type phase [3,5]. Recent works on LATP (A = Al) compounds relying on neutron powder diffraction experiments, starts bringing interesting information on the correlation between structural characteristics of NASICON-type compounds and their electrical properties, such as conduction pathways [2-4]. The goal of the present work is to perform a structural investigation of a new NASICON system $Li_{1+x}Cr_x(Ge_yTi_{1-y})_{2-x}(PO_4)_3$ (LCGTP) which has been proposed by us recently. This system is compatible with glass-ceramic route synthesis when containing considerable amounts of oxide glass formers such as the case of germanium and phosphorus oxides [6]. For this work we choose to use the $Li_{1+x}Cr_xGeTi_{1-x}(PO_4)_3$ formula replacing only Ti by Cr once they have approximately the same crystal radius under octahedral coordination. This strategy avoids considerable changes in the cell parameters as Ti is replaced by Cr, allowing to evaluate the true contribution of the substitution of a tetravalent cation by a trivalent on the energy landscapes of the conduction pathways.

Experimental Details

Seven glass compositions were synthetized varying the value of x (0, 0.2, 0.4, 0.5, 0.6, 0.8 and 1) according to the $Li_{1+x}Cr_xGeTi_{1-x}(PO_4)_3$ (LCGTP) chemical formula. LCGTP precursor glasses were produced (~15 g by batch) by melting a stochiometric mixture of Li_2CO_3 (99.0%, Synth, Brazil), Cr_2O_3 (99.0%, Aldrich, USA), GeO_2 (99.99%, Alpha Aesar, USA), TiO_2 (99.9%, Aldrich, USA) and $NH_4H_2PO_4$ (98%, Aldrich, USA). The reactants were melted in a platinum crucible at 1450 °C for 30 min and the low-viscosity liquid was splat cooled in a brass die to prevent crystallization. Afterwards, the LCGTP glasses were heat-treated as bulk samples at 900 °C for 12 h to obtain fully crystallized glass-ceramics. Elastic coherent neutron scattering experiments were performed at the high-resolution neutron powder diffractometers D2B located at the Institut Laue Langevin. Monochromatic neutrons with wavelengths of 1.594 Å were used for data collection. Measurements were performed in Debye−Scherrer geometry. Powder samples were filled into cylindrical thin-wall vanadium containers (0.15 mm wall thickness). High-resolution neutron powder diffraction data were collected at -73 and 27 °C during about 150min. The collected 2D diffraction patterns were then corrected for geometrical aberrations and curvature of the Debye−Scherrer rings and integrated to have typical diffraction patterns. X-ray diffraction and impedance spectroscopy analysis are also performed but are not presented here although they are used in the discussion.

Results

The main goal of the present work is to find a correlation between structural factors and the ionic conductivity of these electrolytes. The analyses of X-ray and neutron diffraction reveals that single phase electrolytes with rhombohedral NASICON structure (space group $R\bar{3}c$) were obtained only for values of x up to 0.4. The samples with x=0.5 seem to show single phase but not the rhombohedral space group but a triclinic distortion of it (space group $C\bar{1}$). All remaining composition have shown mixed phases suggesting that for the proposed system the substitution limit for x is under 0.5. For compositions containing the rhombohedral phase, the a and b cell parameters oscillate around 8.39±0.02 Å and the cell parameter c around 20.70±0.03 Å, showing that the replacement of Ti by Cr is not associated to considerable volumetric changes of the unity cell. In addition, the impedance spectroscopy analysis allows us to estimate the activation energy for ion conductivity related to the grain contribution (Ea_g). The dependence of Ea_g with the composition shows a minimum activation energy for values of x between 0.2 and 0.4 (around 26% smaller then sample x = 0), which consequently show the highest ionic conductivities related to grain contribution. This activation energy is linked with structural factors such as the position, occupancy and pathways of lithium ions through the structure. Neutron diffraction analyses are helpful to access these parameters because lithium has negative length factors which increase considerably the contrast with the other elements in the structure (except Ti). Based on these ideas, Fourier maps can be generate considering diffraction pattern of the real structure and a particular model. To this end, neutron powder diffraction data were refined using the Rietveld method implemented in the Fullprof software. The three samples (x=0, x=0.2 and x=0.4) where refined using $R\bar{3}c$ space group, starting with a structural model with the atoms that make up the skeleton of the structure, i.e., Ti/Ge/Cr, in 12c (0, 0, 0.14), P in 18e (0.28, 0, 1/4) and O1 and O2 in 36f (0.19, 0.99, 0.19 and 0.19, 0.16, 0.08) sites. At this point Li is not added to the model because the resulting Fourier maps should reveal its positions. Structural parameters, atomic coordinates and isotropic atomic displacement were refined while the profile parameters were kept constant according the D2B equipment specification files. The resulting Fourier maps were calculated considering the scattering density difference between the real structure and the model. Ideally, the positions of Li atoms missing in the starting model can be correlate to the remaining negative density. Fig. 1 shows the used structural model and isosurfaces for neutron scattering negative density corresponding to the compositions x = 0 ($LiGeTi(PO_4)_3$) and x = 0.4 ($Li_{1.4}Cr_{0.4}GeTi_{0.6}(PO_4)_3$), as well as, their respective Fourier maps at the lattice plan (0 1 −4). For the glass-ceramic sample $LiGeTi(PO_4)_3$ the negative density isosurface reveals immediately the preferential occupancy of Li in the 6b (0, 0, 0) position (Fig. 1 a). On the other hand, the negative density isosurface of the $Li_{1.4}Cr_{0.4}GeTi_{0.6}(PO_4)_3$ sample shows several residuals negative density around the samples, mainly around the 12c (0, 0, 0.14) sites because of titanium but also around oxygen and phosphorus sites (Fig. 1 b), probably due to misfit linked to the increase of the anisotropic displacement of these species. Even though, negative densities are also spotted around the 6b (0, 0, 0) and the 36f (1/6, 1/3, 1/12) positions. The Fourier maps at the lattice plan (0 1 −4) display these results in a clearer way (Fig. 1 c and Fig. 1 d). The most intense negative density peaks at this lattice plan are located around the 6b site for the $LiGeTi(PO_4)_3$ sample and besides 6b also 36f for the $Li_{1.4}Cr_{0.4}GeTi_{0.6}(PO_4)_3$ sample. The Fourier maps for $Li_{1.2}Cr_{0.2}GeTi_{0.8}(PO_4)_3$ sample (x=0.2) is not shown here but they present similar features of the Fourrier maps from the $Li_{1.4}Cr_{0.4}GeTi_{0.6}(PO_4)_3$ sample. The negative densities at this lattice plan around the 6b and 36f sites in those samples gives rise to a zig-zag trajectory through the structure, in accordance with previously reported results for LATP [2-3]. On contrary, $LiGeTi(PO_4)_3$ sample shows practically no negative density in the 36f position. Indeed, the further refinement of the neutron pattern of this sample considering Li in the 36f position additionally to the Li in 6b position, gives occupancy factors of 0.1/36 and 5.9/6, respectively. When the same procedure is done for samples $Li_{1.2}Cr_{0.2}GeTi_{0.8}(PO_4)_3$ and $Li_{1.4}Cr_{0.4}GeTi_{0.6}(PO_4)_3$, the occupancy of 36f increases to 2.8/36 and 4.8/36 while the occupancy of 6b decreases to 4.4/6 and 3.6/6, respectively. Therefore, the most probable cause for the drop in Ea_g for the chromium-doped samples with respect to the $LiGeTi(PO_4)_3$ sample is the partial occupancy of the site 36f in detriment of the total occupancy of the 6b site. Additionally, bond valance energy landscape maps are being constructed to help us understand the impact of the aforementioned features in the activation energy for ionic conductivity. Yet, this part of the study is still under investigation but should be presented combined with the discussed results in a scientific publication as soon as possible.

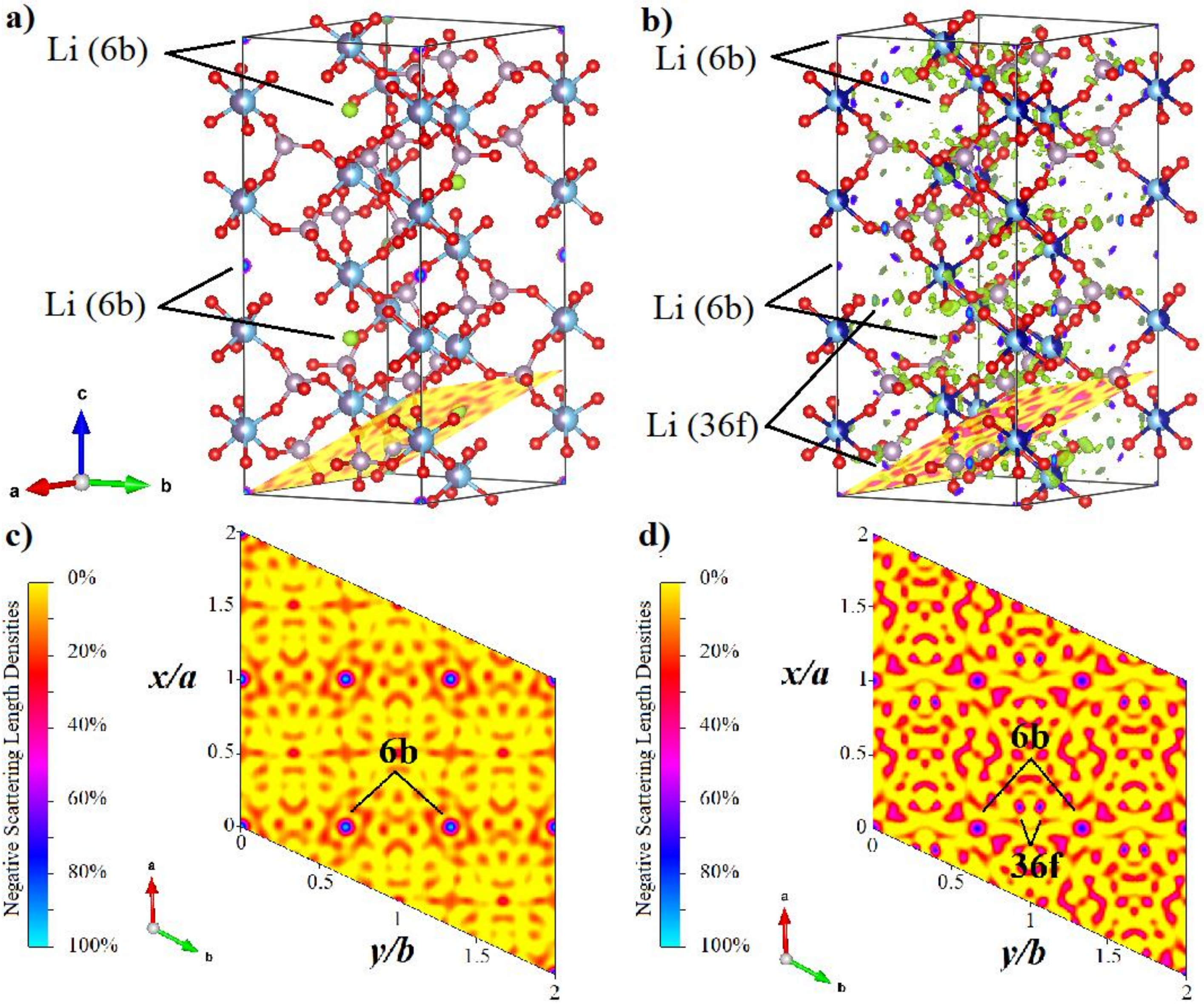

Fig. 1 - Structural model based on space group R$\bar{3}$c for $Li_{1+x}Cr_xGeTi_{1-x}(PO_4)_3$ glass-ceramics with composition range $0 \leq x \leq 0.4$. Light and dark blue spheres represent Ti/Ge/Cr (12c), light purple spheres represent P (18e) and red spheres represent O (36f). Isosurfaces of neutron scattering negative density are represent by light green color for the glass-ceramic composition $LiGeTi(PO_4)_3$ (a) and $Li_{1.4}Cr_{0.4}GeTi_{0.6}(PO_4)_3$ (b). The Fourier maps calculated based on scattering density differences between the real structure and the model at the lattice plan (0 1 −4) is also shown for $LiGeTi(PO_4)_3$ (c) and $Li_{1.4}Cr_{0.4}GeTi_{0.6}(PO_4)_3$ (d) compositions. The 6b and 36f sites are indicate in the maps making up a zig-zag trajectory through the structure.

References

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