



## **Disorder and mobility of lithium ions in NASICON phosphates for energy applications**

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NASICON materials are crystalline phosphates of transition metals Me and alkali atoms A (Li or Na), according to the formula  $A_x\text{Me}_2(\text{PO}_4)_3$ , which display a high mobility of the  $A^+$  ion, and are thus promising materials for applications in rechargeable lithium batteries. They may be used as solid state electrolytes or as electrodes, according to the value of the redox standard potential of the transition metal cation. The structural characterization of the mobile alkali ion environment, and of its bonding interactions with the neighbouring atoms, is essential to understand the mechanisms of ionic conduction in these phases. Owing to the poor X-ray scattering power of lithium, neutron scattering is a particularly suitable technique for such studies. We have been investigating a number of lithium NASICON compounds by high-resolution neutron powder diffraction at variable temperature (HRPD time-of-flight diffractometer at the ISIS Facility, Rutherford Appleton Laboratory, U.K.; resolution  $\Delta d/d \approx 4 \times 10^{-4}$ ). By use of Rietveld refinements coupled with difference Fourier maps, multiple disorder effects involving the alkali ions in the large M1 and M2 cavities of the NASICON framework can be detected [1-5].

The standard NASICON structure is rhombohedral  $R\bar{3}c$ , and may be derived from the corundum ( $\text{Al}_2\text{O}_3$ ) structure by the Al/Me substitution and by replacing every O atom with a  $\text{PO}_4$  group. There is thus a framework of  $\text{MeO}_6$  octahedra and  $\text{PO}_4$  tetrahedra linked to one another, where two large cavities are observed, surrounding the M1 (at 0,0,0 with  $\bar{3}$  symmetry) and M2 (at 2/3,0,1/4 with 2 symmetry) sites, respectively. The alkali ions are therein located with variable degree of order/disorder, and the channels connecting such cavities provide the mobility paths for ionic transport under an applied electric field. Structural distortions involving a symmetry lowering

to orthorhombic, monoclinic or triclinic are possible, and they may affect the disorder state and mobility of lithium substantially.

The most important systems examined were  $\text{LiZr}_2(\text{PO}_4)_3$ ,  $\text{Li}_{1+x}\text{Fe}_x\text{Ti}_{2-x}(\text{PO}_4)_3$  (with  $0.5 < x < 1.2$ ),  $(\text{Li,Na})_2\text{FeTi}(\text{PO}_4)_3$ , and  $(\text{Li,Na})_2\text{FeZr}(\text{PO}_4)_3$ . They correspond to different variants of the basic NASICON structure, with space groups  $\text{R}\bar{3}\text{c}$ ,  $\text{R}\bar{3}$ ,  $\text{Pbna}$ ,  $\text{Pbca}$ ,  $\text{C}\bar{1}$ . The lithium atoms appear to be distributed over different sites located in the M1 and/or M2 main hollows, with a variable extent of disorder. A detailed analysis of such sites allowed us to identify the pathways of ion transport inside the NASICON framework, and then to propose atomistic mechanisms to explain the macroscopic properties of ionic conductivity in these systems.

[1] M. Catti and S. Stramare, *Solid State Ionics* 136-137, 489 (2000)

[2] M. Catti, N. Morgante and R.M. Ibberson, *J. Solid State Chem.* 152, 340 (2000)

[3] M. Catti, *J. Solid State Chem.* 156, 305-312 (2001)

[4] M. Catti, A. Comotti and S. Di Blas, *Chem. Materials* 15, 1628 (2003)

[5] M. Catti, A. Comotti, S. Di Blas and R.M. Ibberson, *J. Mater. Chem.* 14, 835 (2004)