Local and long-range structure in LLTO perovskites with Li⁺ superionic mobility

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LLTO (Li$_{1/4}$La$_{23/4}$TiO$_3$) is an excellent Li⁺ ion conductor at room temperature ($10^{-2}$ S cm⁻¹ for x=0.3), of interest as solid electrolyte in electrochemical devices. Structural studies by neutron powder diffraction showed perovskite superstructures with $2^{1/2}a_p \times 2^{1/2}a_p \times 2a_o$, tetragonal ($x$>0.24) and $2a_p$×$2a_p$×$2a_o$ orthorhombic ($x$<0.24) unit-cells, and $P4/nbm$ and $Cmnm$ symmetries. A partial La-Li ordering according to (001) layers is coupled to anti-phase octahedral tilts $a'dc'$ and $a'bdc'$ for the tetragonal and orthorhombic cases. Li is heavily disordered within the A-type cage, accounting for the high ionic mobility. The local Li environment was studied by ab initio periodic quantum-mechanical simulations of selected ordered structural models. The phases Li$_{1/8}$La$_{5/8}$TiO$_3$ ($2a_p$×$2a_p$×$2a_o$, $Z$=8) and Li$_{3/8}$La$_{15/8}$TiO$_3$ ($2a_p$×$2a_p$×$4a_o$, $Z$=16) were considered, with $Pm$ or $P1$ symmetry, to represent the Li-poor and Li-rich compositions. Several different La-Li-vacancy ordering patterns within the (001) layers of A cages were devised. The structures were optimized by energy minimization, so as to localize the preferred lithium sites for each ordering scheme. It was found that the Rietveld-refined most populated Li site, close to the O₆ windows separating adjacent A cavities in the layer, corresponds to La-poor local configurations, and is actively involved in the ion migration process. The second populated site is related to La-rich local environments, and is a trapping location less favourable to ionic transport. By combining NPD results (long-range Li disorder) and ab initio simulations (local Li order), one- and two-dimensional atomistic pathways are proposed for Li⁺ ion diffusion within the perovskite framework, including the prediction of activation energy barriers for ionic hopping.

Keywords: solid electrolytes, ab-initio calculations, neutron powder diffraction

Size and strain effects in nanostructured relaxor and morphotropic compounds

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The field of morphotropic systems with giant dielectric and piezoelectric properties is very active, and many interesting results have been obtained, in particular in lead-based systems. However up to now, only very few papers have addressed the question of grain size reduction and its effect on the physical and structural properties of these materials. We will report results obtained in nanocrystalline powders and ceramics with controlled grain size from 15nm up to micrometric sizes, as well in thin films with several thicknesses from 40nm and different substrates, in PbMg₁₋ₓNₓB₂O₆-PbTiO₃, PbSc₁₋ₓNb₂O₆-PbTiO₃, and BiScO₃-PbTiO₃ systems. The consequences on the dielectric properties and on the rotation of polarization will be discussed and compared with the situation in bulk materials. In particular it will be shown that changing the grain sizes provides an easy way to tailor the direction of the polarization...