	Experiment title: Local environment and dynamics around gallium in proton-conducting LaBaGaO4 ceramics	Experiment number: MA-669
Beamline: BM8	Date of experiment: from: 25/9/2009 to: 29/9/2009	Date of report: 4/7/2010
Shifts: 12	Local contact(s): Francesco D’Acapito	<i>Received at ESRF:</i>
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Report:

Powders of nominal composition $\text{La}_{1-x}\text{Ba}_{1+x}\text{GaO}_4$ (LBG), with x up to 20%, were synthesized by solid-state route, performing two calcinations at 1300 °C with intermediate grinding. Protonation was subsequently achieved by equilibration with water vapour at 300 °C, and confirmed by thermogravimetric analysis. Single-phase formation and purity was checked with a Bruker D500 diffractometer.

X-ray absorption spectra (XAS) on the Ga K-edge (10.4 keV) were collected at 77 K in transmission mode. The extended X-ray absorption fine structure (EXAFS) spectra were analyzed with Feff 8.4 and Viper. The Ga-O distances and disorder factors in both LBG and NBG do not vary with the self-doping level: remaining almost unchanged in all samples, the GaO₄ tetrahedra react like rigid bodies to the changes caused by Ba/La substitution. The disorder factors of the Ga-O first shell are 0.0043 Å² in LBG₀, and 0.0048 Å² in LBG₂₀, with an almost negligible increase. Therefore, we did not observe a significant enhancement in oxygen ion vibrations induced by hydrogen bonding. On the contrary, in all the proton-conducting perovskites we have analyzed, the MO₆ octahedra were always found to be very sensitive to the doping level, the disorder increasing dramatically with the concentration of defects in the lattice. The reason of this difference is likely to reside in the network structure of the polyhedra, that can be summarized as follows. In perovskites, the MO₆ octahedra share all corners, so that the dynamics of one octahedron is coupled in all directions to the octahedra nearby: large oxygen vibrations enhanced by thermal motion bring the O-O distance to lower values, and favour the formation of transient hydrogen bonds that enhance the proton hopping. In LBG, each GaO₄ unit behaves like a rigid body in a softer environment (the larger La³⁺ and Ba²⁺ cations), and then its dynamics is largely independent from the surroundings (given that the above observations hold at both liquid N₂ and room temperatures). The structural relaxation taking place upon Ba²⁺/La³⁺ self-doping has influence on the Ga-M distances (M=La, Ba), whose bond length and disorder slightly increase with self-doping level, always maintaining the GaO₄ groups almost unchanged. There results are in course of publication in reference [1].

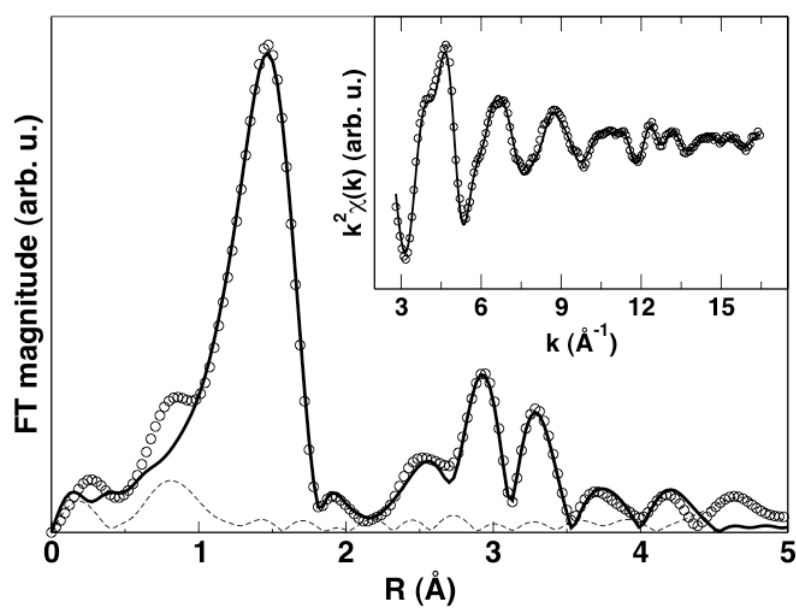


Figure 1: EXAFS data and model of LBG20: (a) Fourier transform of experimental (circles), fit (line) and residual (dashes); (b) k-weighted EXAFS experimental data (circles) and fit (line).

[1] F. Giannici, D. Messina, A. Longo, A. Martorana, submitted to *J. Phys. Chem. C*