

# DOPANTS AND DEFECTS IN PROTON-CONDUCTING PEROVSKITES

F. Giannici<sup>1</sup>, A. Longo<sup>2</sup>, A. Balerna<sup>3</sup>, K.-D. Kreuer<sup>4</sup>, A. Martorana<sup>1</sup>.

<sup>1</sup>Dip. di Chimica Inorganica e Analitica “Stanislao Cannizzaro”, Università di Palermo (I).  
(giannici\_nospam@pa.ismn.cnr.it)

<sup>2</sup>ISMN-CNR, Palermo (I).

<sup>3</sup>LNF-INFN, Frascati (I).

<sup>4</sup>Max-Planck-Institut für Festkörperforschung, Stuttgart (D)

Many doped perovskites show high proton conductivity at intermediate to high temperatures (500-900 °C), which has opened possibilities for many prospected applications in energy conversion (fuel cells), and electrochemical devices. In a doped perovskite, e.g.  $\text{BaCe}_{1-x}\text{Y}_x\text{O}_{3-y}$ , oxygen vacancies are created by charge compensation, and can eventually react with air moisture to form structural protonic defects. The sluggish nature of the proton, which is practically invisible to most structural analyses, and poses enormous problems to quantum chemistry, has surely contributed to slow down the progress in the understanding of these materials: in fact, the conduction dynamics and its interplay with structure are still matter of debate. The kind of trivalent dopant and its size, and the doping level, have all been found to critically influence the conductivity: to date, however, no comprehensive model was developed, and no clear explanations exist between the chemical and dynamical properties.

**Here we present results collected in several EXAFS experiments on doped  $\text{BaCeO}_3$  and  $\text{BaZrO}_3$  spanning three years, on the Ba site, Ce site, and the dopant (yttrium, gadolinium, indium: the ionic sizes of these are respectively equal, larger and smaller than  $\text{Ce}^{4+}$ ) site. The local structures up to about 6 Å around each site are solved with state-of-the-art techniques employing both the GNXAS and FEFF approaches, revealing unique features and demonstrating that in this case the conventional diffraction techniques are not suited to unravel the complexity of doped crystals. In particular, the attention will be drawn on the local deviations from Vegard’s law, the local expansion/contraction as a function of hydration degree, the interplay between dopant and defects, and the chemical compatibility (Pearson absolute hardness) instead of ionic size matching. The EXAFS results are correlated with complementary information about the dynamics of protons and other defects (IR and neutron vibrational spectroscopy, QENS, ionic and electronic conductivity measurements).**