Highlights

Oxides - 2016

A-Site Cation Substitutions in Strained Y-Doped $BaZrO_3$ Multilayer Films Leading to Fast Proton Transport Pathways

C. Aruta[1],C. Han[2], S. Zhou[3], C. Cantoni[4], N. Yang[1], A. Tebano[1] , T.L. Lee[5], C. Schlueter[5] and A. Bongiorno[6]

[1]National Research Council CNR-SPIN and Department DICII, University of Roma «Tor Vergata», Italy
[2]School of Chemistry & Biochemistry, Georgia Institute of Technology, Atlanta, United States
[3]College of Advances Science and Technology, Dalian University of Technology, China
[4]Materials Science and Technology Division, Oak Ridge National Laboratory, Oak Ridge, United States
[5]Diamond Light Source Ltd., Harwell Science and Innovation Campus, Didcot, United Kingdom
[6]Department of Chemistry, College of Staten Island, Staten Island, New York 10314, United States

THE JOURNAL OF PHYSICAL CHEMISTRY C 120, 8387 (2016)

Proton-conducting perovskite oxides form a class of solid electrolytes for novel electrochemical devices operating at moderate temperatures. Our nanometer-thick epitaxial $BaZr_{0.8}Y_{0.2}O_3$ (BZY) films on $NdGaO_3$(110) substrates have been shown to possess high values of the proton conductivity at temperatures of 550−600 °C. Here we elucidate the atomistic origin of the fast proton transport properties of strained ultrathin BZY films by hard X-ray photoelectron spectroscopy (HAXPES), scanning transmission electron microscopy (STEM) and density functional theory (DFT) calculations. HAXPES measurements demonstrate that our BZY films incorporate a significant amount of Y dopants substituting for Ba^{2+} and STEM shows that these substitutional defects agglomerate forming columnar regions crossing vertically from the surface to the interface the entire film. DFT calculations also show that, in regions rich in Y substitutions for both Zr and Ba, the proton transfer process involves nearly zero-energy barriers, indicating that A-site cation substitutions by Y lead to fast transport pathways and hence are responsible for the previously observed enhanced values of the proton conductivity of these perovskite oxide films.

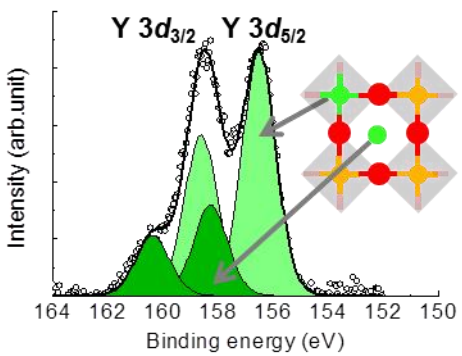

Figure 1. Y 3d HAXPES peaks together with the result of the fitting. The inset shows a ball and stick illustration of the chemical species in the strained BZY film assigned to the peaks.

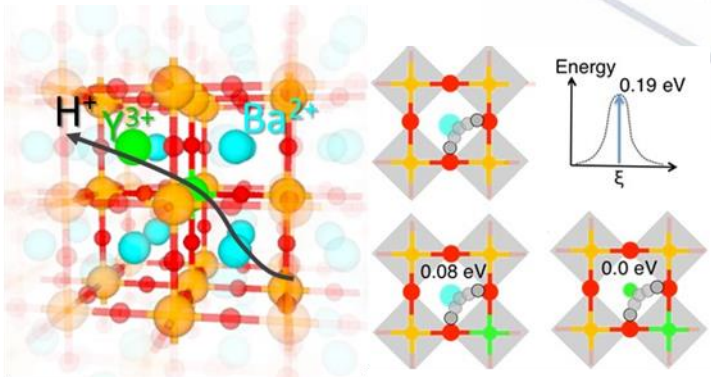

Figure 2. (Left) BZY lattice with the relaxed atomic positions as obtained from a DFT calculation. (Right) Proton transfer between two nearest neighbor O2− ions coordinated or in close proximity of substitutional Y dopants, together with a schematics of the energy profile visited during the proton transfer process. The energy barrier values calculated by DFT are also shown in each panel.