

Investigating CO₂ Stability in Donor Doped BaCe_{1-(x+y)}Zr_xNb_yO₃ Proton Conductors Using X-Ray Photoelectron Spectroscopy

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Barium cerate doped with acceptors such as Y³⁺ or Gd³⁺ has been widely studied for its high proton conductivity that makes it useful for high temperature proton conductors (HTPCs) [1-3]. A primary shortcoming of these materials is that they are incompatible with CO₂ containing gas streams since formation of BaCO₃ is thermodynamically favored below 1040°C. This prevents the materials from being used in devices that utilize practical carbon-containing fuels or feedstocks including hydrocarbons and alcohols. Zr substitution on the Ce site enhances the chemical stability due to its higher electronegativity than Ce, but diminishes the conductivity and sinterability of the material [4]. Donor doped barium cerate-zirconates have been considered less frequently. Bhella et al recently reported proton conduction in Zr and Nb -codoped BaCe_{0.9-x}Zr_xNb_{0.1}O_{3±δ} (BCZN) which was found to be chemically stable in CO₂ at elevated temperature, at which highly conductive Y-doped BaCeO₃ is known to be chemically unstable [5]. The proton conduction was assumed to be due to a similar mechanism to that of acceptor-doped perovskites where the reduction of B-site cations is likely. BCZN demonstrated a bulk conductivity of ~ 10⁻³ Scm⁻¹ in wet H₂ at 500 °C with an activation energy of 0.69 - 0.73 eV which is comparable to Y-doped BaCeO₃.

The necessary co-sintering of electrolyte and electrodes for HTPC fabrication motivates an understanding of how to control porosity in the electrodes while maintaining a dense electrolyte. We have performed a systematic investigation to understand the role of sintering temperature and composition on microstructure, porosity and electrical transport properties of BaCe_{1-x-y}Zr_xNb_yO₃. Furthermore, the oxidation state of the B site constituents is investigated to relate to possible proton conduction mechanisms.

X-ray photoelectron spectroscopy (XPS), energy dispersive X-ray spectroscopy (EDS), powder X-ray diffraction (PXRD), and AC impedance methods were employed to investigate the phases, composition, and electronic properties of the donor-doped perovskites. Scanning electron microscopy (SEM) and Archimedes measurements were used to determine sample porosity. In addition, in-situ monitoring of carbonate formation was performed employing thermo-gravimetric analysis from RT to 1100 °C in a 30% CO₂ atmosphere.

SEM imaging revealed that negligible porosity existed in samples sintered at 1600 °C (Fig. 1), which is corroborated by Archimedes porosity measurements. The grain size and sinterability decreased with increasing Zr content, as expected, but the Nb content increased grain sizes and sinterability, which is useful since barium cerates tend to have large grain boundary resistance. In-situ chemical stability by TGA confirmed that samples with x ≥ 0.1 and y ≥ 0.1 are stable in CO₂ (Fig. 2). The surface

analysis by XPS revealed that there is no Ba loss at 1450 °C, but there is at 1600 °C. Furthermore, evidence of Nb enrichment at the surface or grain boundaries of the samples is observed and may correlate to CO₂ stability. The resulting oxidation state of the multivalent elements Ce and Nb are also revealed.

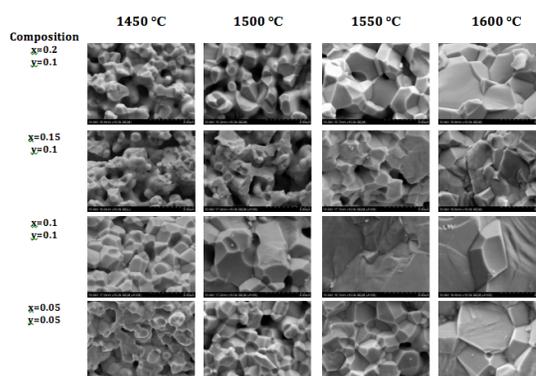


Figure 1: Microstructure versus sintering temperature and composition of BaCe_{1-x-y}Zr_xNb_yO₃.

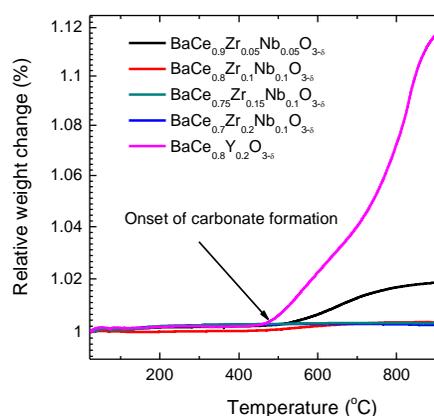


Figure 2: Mass gain due to carbonate formation by TGA in 30% CO₂ atmosphere showing chemical stability with dopant levels x=0.1, y=0.1 and above.

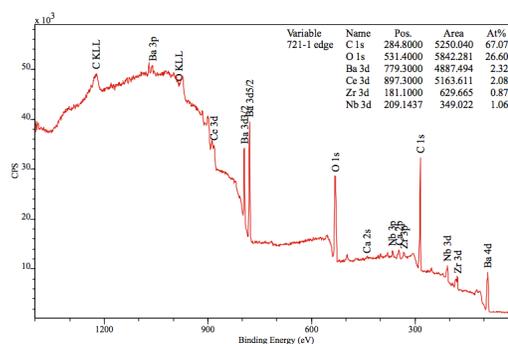


Figure 3: XPS survey spectra of BaCe_{0.7}Zr_{0.2}Nb_{0.1}O₃ surface after sintering at 1600 °C for 4h.

References:

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