

Insight into Solid Oxide Proton Conductors with Dopants by Use of Positron Annihilation Spectroscopy

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There is a big effort to improve the proton conductivity of barium-zirconate based ceramics used as the electrolyte for fuel cells, electrolyzers, and membrane reactors. Understanding and controlling proton migration through lattice in the electrolyte materials is important especially when dopants are incorporated into their system for better structure stability. Some dopants cause stoichiometric violations and ionic radius mismatch thus perturb proton migration through the crystal structure [1,2].

In this work the proton trapping effect in BaZrO₃ electrolytes (BZO) without/with 20% (Sc-20) and 40% (Sc-40) of dopant by use of Positron Lifetime Spectroscopy (PAL) is discussed. The electrolytes were prepared by the solid-state reaction method and calcinated at 1200 °C. Samples were pressed at 296 MPa and sintered at 1600 °C for 5 hours. Three solid samples of each type were prepared, with polished and unpolished site for surface effects analysis. PAL measurements were carried on by use of TechnoAP [3] spectrometer, analysed by use of Kansy LT10 program [4].

The PAL spectrum was deconvoluted into three lifetimes due to bulk, trapping and a positronium formation (<1%). There was a significant difference in the positron trapping between BZO specimens without dopant, versus with dopant indicated by the changes in trapping lifetime and intensity. But the differences between “Sc-20” vs “Sc-40” were not significant as the T-test showed. For BZO the lifetime, $\tau_2 = 0.251 \pm 0.003$ ns, vs 0.239 ± 0.006 (Sc-20) ns and 0.237 ± 0.003 (Sc-40). Trapping intensity was higher for BZO: $I_2 = 34.77\% \pm 0.37$ vs I_2 (Sc-20) = $44.40\% \pm 4.21$ and I_2 (Sc-40) = $44.03\% \pm 1.31$ respectively (Fig.1). The decrease in the trapping value with simultaneous increase in its probability suggest a change in the characteristics of the electron configuration of the trapping sites, with Sc-3 (three valence electrons) replacing Zr-4.

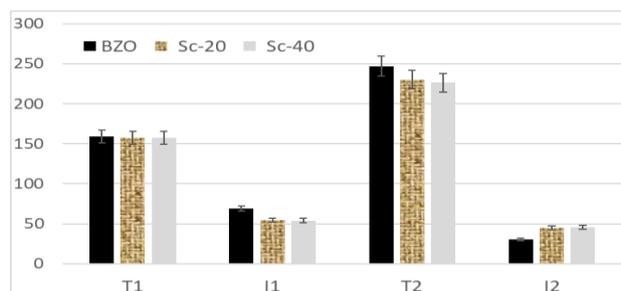


Fig.1. PAL Average Lifetime [ps] and Intensity [%] Values

This is a work in progress. The analysis capabilities include multi-variate analysis approach to extract relevant information due to different effects. The PAS measurements would be extended into other capabilities (CDB) and more extensive analysis of BZO with more Sc loadings and different dopant materials. The measurements will be carried out for protonated samples (loaded with more protons) compared to “dry” samples that were measured so far.

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