Proton-conducting Properties of Rare Earth Substituted non-Stoichiometric $Ba_3Ca_{1+x}Nb_{2-x}O_{9-\delta}$ Ceramics

L. H. Francisco[1,*,#], J. E. F. S. Rodrigues[1], A. C. Hernandes[1]

[1]Crystal Grouth and Ceramic Materials Group, São Carlos Institute of Physics, University of São Paulo, São Carlos, Brazil.

[#]Corresponding author: lucas.francisco@usp.br

Proton conduction is a physical phenomenon observed in a variety of crystalline non-crystalline materials. An important class of proton-conducting materials is formed by ceramic electrolytes, applied on solid oxide fuel cells (SOFC), alternative sources of clean and renewable energy. [1] Being the composition $Ba_3Ca_{1.18}Nb_{1.52}Y_{0.3}O_{9-\delta}$ (perovskite structure) a material that combines high intermediate temperature (<600°C) proton conductivity and chemical stability under typical working SOFC conditions, [2] this project objectives studying yttrium site rare earth substitution effects on the final material's conductive properties. The elements neodymium, samarium and gadolinium where chosen for having ionic radii similar to yttrium but different polarizabilities, making possible the observation of the atomic environment effect on the conductivity of protonic defects. For this project, powders of the different compositions were synthetized using solid-state reactions. The synthesis parameters were varied and their effect on final material structure was observed by x-ray diffraction. Sintered ceramic pallets were used for electrical characterization using impedance spectroscopy on frequency range 100mHz-10MHz. Structural characterization revealed initial formation of 1:1 type cation ordering during the synthesis, followed by a disordered state, which plays an important role on proton-conducting properties of the material. [3] Impedance spectra showed conductive properties were altered by the rare earth substitution, demonstrating atomic environment influence on proton conduction. Temperature dependence on the conductivity revealed the thermal nature of the conductive process and allowed activation energy determination. A high grain boundary resistivity was observed, in agreement with space-charge formation theory. [4] This high grain boundary resistivity is a challenge for the application of this class of ceramics, justifying the necessity of a deeper understanding of its relation to the basic properties of the material.

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