

INDIUM DOPING OF PROTON-CONDUCTING SOLID OXIDES

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Solid oxides protonic conductors are prepared by doping the pure matrix compounds with cationic species. Barium cerate and barium zirconate are perovskite-like compounds, characterized by a network of corner-sharing MeO_6 octahedra ($\text{Me}=\text{Ce}, \text{Zr}$). Barium lies in the cavities between octahedra. Insertion of trivalent species in the octahedral site involves the formation of charge-compensating oxygen vacancies, that can be filled by hydroxyls coming from dissociative water absorption. Then, proton delocalization among structural oxygens ensures conductivity. The most effective conductors are obtained by yttrium doping that, on the other hand, enters only in limited amounts in both BaZrO_3 and BaCeO_3 , thus involving limited carrier concentration. Perovskites are affected by different drawbacks: barium cerate compounds are very sensitive to the acidic components present in the environment and in particular to CO_2 that induces decomposition in barium carbonate and cerium oxide; barium zirconate, notwithstanding a very high bulk conductivity, is biased by high grain boundary resistivity.

A possible alternative to perovskite-like compounds is constituted by fergusonite-type lanthanum niobate and lanthanum tantalate compounds, characterized by a tetrahedral coordination of Nb and Ta. These oxides present a very high chemical stability but very low carrier concentration, usually induced by Ca-doping the lanthanum site [1].

Among the different trivalent dopants, it was demonstrated by X-ray absorption spectroscopy that indium is able to enter in any composition in the perovskite network, thus providing a very high carrier concentration, even if with lower proton mobility. This property of indium was ascribed to its electronic structure and in particular to the low Pearson hardness, allowing this cation to fit in a hosting matrix with the least structural strain [2]. A preliminar attempt of exploiting indium for enhancing the carrier concentration of lanthanum niobate was carried out. The solid state synthesis involved amounts of the reactant simple oxides suitable to force indium doping of the niobium site. X-ray diffraction do not show significant amounts of secondary oxide phases.

References

[1] R. Haugsrud, T. Norby. *Nature Mater.* 5 (2006) 193-196.

[2] F. Giannici, A. Longo, A. Balerna, K.-D. Kreuer, A. Martorana. *Chem. Mater.* 19 (2007) 5714-5720.