

Role of Sc, Y and In dopants on structures and lattice dynamics of protonconducting BaZrO₃

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Acceptor-doped zirconates are among the promising low-temperature electrolytes in the proton conducting fuel cells. The proton transferability of those oxides was established to depend strongly on the nature of the dopant ions. Here we will present our theoretical results concerning the effect of lower valence dopants at Zr-sites in BaZrO₃ crystals on the local and long range structures, and lattice vibrations. The computations were carried out with Density Functional Theory based periodic approach. Structural details and lattice dynamics in $BaZr_{1-x}M_xH_xO_3$ (M = Y, Sc and In, and x = 0.125, 0.25 and 0.375) with protonic defects in three different oxygen configurations were compared in order to investigate the role of dopant chemical nature and concentration on hydroxide ion formations and its relation to the proton conductivity. Our results showed that the oxide symmetry and the short and long range structural arrangements in the M-rich and Zr-rich regions are nearly independent on the dopant chemical nature, concentration and arrangement in the cell. The O-H bond formation is however strongly influenced by the dopant, which is associated with the differences in dopant-oxygen bond character. Whereas only ionic In-O and Sc-O bonds are established, the yttrium ions are covalently bound to the lattice oxygens. This causes a strong decrease of the negative charge at oxygen sites in Y-O-Y configurations, which hinders the creation of protonic defect. As a result, a lower concentration of hydroxide ions in Y-doped zirconates was predicted in comparison to Sc- and In-doped crystals.

The oxide-lattice dynamics, studied from the computed vibrational frequencies of $BaM_xZr_{1-x}H_xO_3$ will be also presented and discussed. These theoretical results have been further related and used to explain the observed differences of proton transfer capacities in the doped zirconates.

Keywords: BaZrO₃, dopants, protonic defects, DFT