Effect of oxygen vacancies in yttrium doped barium zirconate on proton conductivity

Alice VanBokkelen, Maria A Gomez

Department of Chemistry, Mount Holyoke College, South Hadley, MA, USA

A recent experimental study [1] suggested that oxygen vacancies within a perovskite structure can enhance proton conduction. In the absence of the oxygen vacancy in a 12.5% Y-doped $BaZrO_3$, the average limiting barrier of direct periodic paths traversing the simulation box found via graph theory is 0.30-0.33 eV in the temperature range of 900-1300K [2]. Taking account of meandering pathways, kinetic Monte Carlo (kMC) simulations for the same system at 1000 K show an average limiting barrier of 0.39 eV [3]. Preliminary studies using conjugate gradient optimization on the Vienna *Ab initio* Simulations Package (VASP)[4] implementation of the Density Functional Theory (DFT) using the Perdew Burke Ernzerhof (PBE) functional with a generalized gradient approximation and the Projector Augment Wave (PAW) method show the energy of the proton binding site next to the yttrium dopant is highly dependant on the location of the oxygen vacancy, with the lowest energies found near or adjacent to the vacancy. A preliminary Nudged Elastic Band (NEB) [5,6] calculation shows a very low barrier of 0.05 eV for a proton move away from the dopant in the presence of an adjacent oxygen vacancy. While this is substantially lower than both graph theory and kinetic Monte Carlo estimates of the limiting barrier to conduction in the absence of the vacancy, many proton binding sites and transitions near the dopant and the oxygen vacancy need be considered to obtain a fuller picture.

[1] I. Oikawa and H. Takamura, "Correlation among oxygen vacancies, protonic defects and the acceptor dopant in Sc-Doped BaZrO3 studied by 45Sc nuclear magnetic resonance," Chemistry of Materials, **27**, 6660 (2015).
[2] M. A. Gomez, M. Chunduru, L. Chigweshe, L Foster, S. J. Fensin, K. M. Fletcher, and L. E. Fernandez, "The effect of yttrium dopant on the proton conduction pathways of BaZrO3, a cubic perovskite," J. Chem. Phys. **132**, 214709 (2010).
[3] R. A. Krueger, F. G. Haibach, D. L. Fry, and M. A. Gomez, "Centrality measures highlight proton traps and access points to proton highways in kinetic Monte Carlo trajectories," J. Chem. Phys. **142**, 154110 (2015).
[4]G. Kresse and J. Hafner. "Ab initio molecular dynamics for liquid metals." Phys. Rev. B, 47, 558, (1993); G. Kresse and J. Hafner. "Ab initio molecular-dynamics simulation of the liquid- metal-amorphous-semiconductor transition in germanium." Phys. Rev. B, **49**, 14251 (1994); G. Kresse and J. Furthmüller. "Efficiency of ab-initio total energy calculations for metals and semiconductors using a plane-wave basis set." Comput. Mat. Sci., 6, 15 (1996); G. Kresse and J. Furthmüller. "Efficient iterative schemes for ab initio total-energy calculations using a plane- wave basis set." Phys. Rev. B, **54**, 11169 (1996).
[5]G. Henkelman, B.P. Uberuaga, and H. Jónsson, A climbing image nudged elastic band method for finding saddle points and minimum energy paths, J. Chem. Phys. **113**, 9901 (2000).
[6]H. Jónsson, G. Mills, K. W. Jacobsen, Nudged Elastic Band Method for Finding Minimum Energy Paths of Transitions, in Classical and Quantum Dynamics in Condensed Phase Simulations, Ed. B. J. Berne, G. Ciccotti and D. F. Coker (World Scientific, 1998), page 385.