

FIRST PRINCIPLES CALCULATIONS OF DEFECT CLUSTERING IN ACCEPTOR-DOPED BaZrO₃

Akihide Kuwabara, Japan Fine Ceramics Center
kuwabara@jfcc.or.jp

Craig A. J. Fisher, Japan Fine Ceramics Center
Yuji Okuyama, University of Miyazaki
Yoshihiro Yamazaki, Kyushu University

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Acceptor-doped BaZrO₃ shows high proton conductivity under wet atmosphere conditions and is a promising material used for a proton conductive electrolyte. Similar to other kinds of ionic conductors, however, carrier trapping by dopant occurs and suppresses conductivity of the acceptor-doped BaZrO₃ [1]. The carrier trapping is an unavoidable phenomenon for ionic conductors because formation of charge carriers for ionic conduction is attributed to dopants with opposite charge states to the carriers. We have to understand and to control the carrier trapping behavior to optimize properties of ionic conductors.

In this work, we calculate association energies between acceptors and protons in BaZrO₃ using first principles calculations. Several types of cations, Sc, In, Lu, Y, Er, Gd and Eu, are adopted as acceptors for comparison. Total energy calculations were performed using the VASP code. At first, a unit cell of BaZrO₃ was fully optimized, and then supercells of 5 × 5 × 5 unit cells containing 625 atoms was constructed for calculations of defective systems. Distances between a dopant and a proton are systematically changed and dependence of association energies on the distance is investigated.

From the series of our calculations, it is revealed that dopants can be categorized into two types. In the cases of dopants with smaller ionic size such as Sc, In and Lu, protons prefer to be located at the first nearest neighbor from the dopants. Cations with larger ionic size like Y, Er, Gd and Eu capture protons at the next nearest neighbor sites. It is also found that association energies are well correlated to the state of hydrogen bonding. The stronger hydrogen bond is, the more stable protons are trapped. Hydrogen bonding strength changes according to local distortion nearby dopant and proton.

[1] Y. Yamazaki et al., Nature Mater., 12 (2013) 647-651.

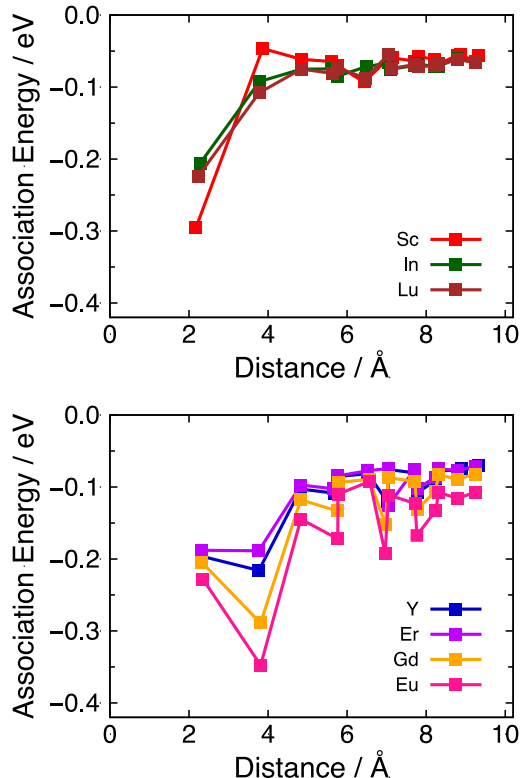


Fig.1 Dependence of association energy on dopant-proton distance in R₂O₃-doped BaZrO₃ (R= Sc, In, Lu, Y, Er, Gd and Eu).