

# First Principles Calculations of Point Defects in Acceptor-doped BaZrO<sub>3</sub>

Akihide Kuwabara<sup>1</sup>, Kazuaki Toyoura<sup>2</sup>, Yukinori Koyama<sup>3</sup>, Craig A. J. Fisher<sup>1</sup>,  
Fumiyasu Oba<sup>3</sup>, Katsuyuki Matsunaga<sup>2</sup>, Hiroki Moriwake<sup>1</sup>, Isao Tanaka<sup>1,3</sup>

<sup>1</sup>Nanostructures Research Laboratory, Japan Fine Ceramics Center, Nagoya, 456-8587, Japan

<sup>2</sup>Department of Materials Science and Engineering, Nagoya University, Nagoya, 464-8603, Japan

<sup>3</sup>Department of Materials Science, Kyoto University, Kyoto, 594-8587, Japan

Acceptor-doped BaZrO<sub>3</sub> exhibits high proton conductivity at elevated temperatures in wet atmospheres [1]. It is a candidate for an electrolyte in a proton-conducting solid oxide fuel cell. Acceptor doping of BaZrO<sub>3</sub> forms oxide ion vacancies in order to maintain electrical neutrality. In wet atmospheres, the vacancies react with water vapor, whereby the vacancies are filled and protons are introduced into lattices. Theoretical calculations based on density functional theory have been systematically performed to evaluate the defect energetics of BaZrO<sub>3</sub> [2-3]. However, defect equilibria involving cation defects are not yet well understood. The aim of the present study is to clarify defect formation behaviors in the acceptor-doped BaZrO<sub>3</sub>.

Total energy calculations were carried out using the VASP code [4]. Electron-ion interactions were represented by the projector augmented wave method, and the generalized gradient approximation was chosen for the exchange-correlation functional. Plane waves up to an energy cut-off of 400 eV were used as the basis set for wave functions. First, a unit cell of BaZrO<sub>3</sub> was fully optimized, and then supercells containing 320 atoms, 4 × 4 × 4 unit cells, was constructed for the calculations of defective systems. In this study, we calculated all kinds of point defects such as vacancy, interstitial, anti-site type. Only the  $\Gamma$  point was adopted in the  $k$ -point sampling for the supercells. All atomic positions in defective systems were fully relaxed until all residual forces were less than 0.02 eV/Å. Details of the calculation methodologies of point defect formation energy are available elsewhere [5].

Figure 1 shows dependence of calculated defect formation energies on Fermi levels in a band gap under Ba- and Zr-rich condition at  $T = 1900$  K,  $p(\text{O}_2) = 0.1$  atm and  $p(\text{H}_2\text{O}) = 0.02$  atm in Y-doped BaZrO<sub>3</sub>. In these plots, positive and negative gradients correspond to donor- and acceptor-type defects, respectively. Under the Ba-rich condition, oxygen vacancies ( $V_{\text{O}}^{\bullet\bullet}$ ) and substituted Y ions at Zr sites ( $Y'_{\text{Zr}}$ ) have the lowest formation energies among donor- and acceptor-type defects, respectively. Charge neutrality is mainly controlled by equilibrium between these two defects. When a temperature goes down,  $V_{\text{O}}^{\bullet\bullet}$  are hydrated and then protons ( $\text{OH}_{\text{O}}^{\bullet}$ ) are introduced. In case of the Zr-rich condition, defect equilibrium is different. In addition to  $V_{\text{O}}^{\bullet\bullet}$  and  $Y'_{\text{Zr}}$ , Y ions at Ba sites ( $Y^{\bullet}_{\text{Ba}}$ ) and Ba vacancies ( $V_{\text{Ba}}^{\bullet\bullet}$ ) have lower energy as shown in Fig. 1(b). Self-charge compensation of dopants by  $Y'_{\text{Zr}}$  and  $Y^{\bullet}_{\text{Ba}}$  deteriorates ionic conductivity because amount of charge carrier is reduced. Chemical equilibrium needs to be carefully controlled in order to optimize protonic conductivity of BaZrO<sub>3</sub>.

Reference

1. S. Imashuku, T. Uda, Y. Nose, G. Taniguchi, Y. Ito, and Y. Awakura, *J. Electrochem. Soc.*, **156** (2009) B1.
2. M. E. Björketun, P. G. Sundell and G. Wahnström, *Phys. Rev. B*, **76** (2007) 054307.
3. M. E. Björketun, P. G. Sundell and G. Wahnström, *Faraday Discussions*, **134** (2007) 247.
4. G. Kresse and J. Furthmüller, *Phys. Rev. B*, **54** (1996) 11169.
5. A. Kuwabara, R. Haugsrud, S Stølen and T. Norby, *PCCP*, **11** (2009) 5550.
6. G. Łupina *et al.*, *Appl. Phys. Lett.*, **94** (2009) 152903.

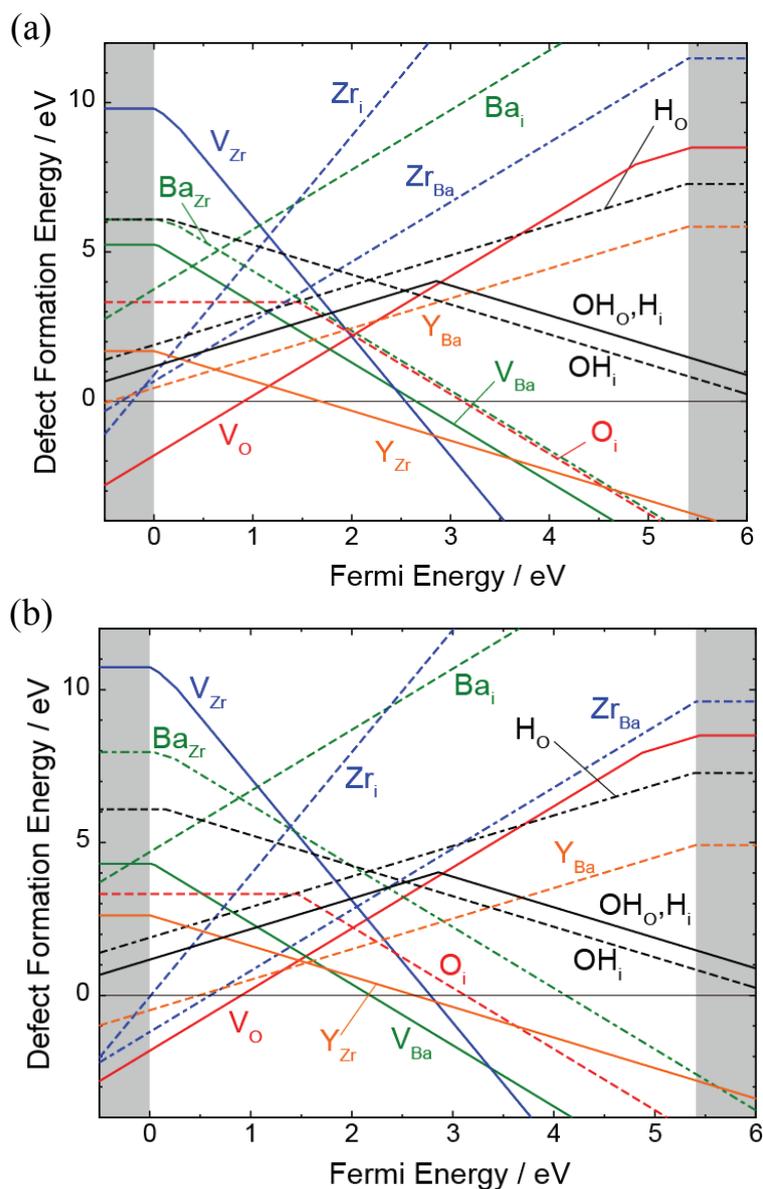


Figure 1. Dependence of calculated defect formation energy on Fermi level positions in a band gap under (a) Ba-rich and (b) Zr-rich conditions at  $T = 1900$  K,  $pO_2 = 0.1$  atm and  $pH_2O = 0.02$  atm. In the horizontal axis, the valence band top is set to be 0 eV. The conduction band bottom is 5.4 eV [6].