Analysis of proton creation mechanism of trivalent cations doped BaZrO$_3$ by first principles calculations

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BaZrO$_3$ is a prime candidate for an eletrolyte of solid oxide fuel cells (SOFC). It is reported that Y^{3+} doped BaZrO$_3$ has the highest proton conductivity so far[1)]. However, it is still unclear how we can further improve proton conductivity of these trivalent cations-doped BaZrO$_3$. The mechanism of proton conduction can be partitioned following parts: First, when trivalent cations are doped to BaZrO$_3$, oxygen vacancies are formed if trivalent cations is substituted for Zr ions to maintain charge neutrality. Second, protons are created by absorbing water molecules to the oxygen vacancies. Finally, protons conduct in BaZrO$_3$ under chemical potential gradient for the protons. These three steps are necessary to realize proton conductivity, although they are mixed up in experiments. Theoretical calculations enable to separately evaluate these three steps. An aim of this study is to reveal influence of trivalent cations at the three steps by first principles calculations. Especially this paper focuses on proton creation mechanism of trivalent cations-doped BaZrO$_3$.

Figure 1 shows creation probabilities of oxygen vacancies as a function of ionic radius of doped cation (Al^{3+}, Sc^{3+}, Y^{3+}, La^{3+}) obtained in our previous study[2)]. It is found that the concentrations of oxygen vacancies were almost unity for ions smaller than Y^{3+} and almost zero for larger ions. Furthermore, it implied that oxygen vacancies can be more easily introduced by substitution of trivalent cations for Zr atoms in BaZrO$_3$ when they accompany less local strain to the matrix. In this study, we focused on the second step, that is, creation of protons by absorption of water molecules. The aims of this are to reveal mechanisms governing creation of protons dependent on trivalent cation species and to obtain strategies to improve the proton conductivity.

The creation probabilities of a neutral defect complex that accompanies formation of oxygen vacancies were examined based on formation energy with configurational entropy term for all the possible configurations in cubic perovskite supercells containing 320 atoms. The energetically most favorable configuration that accompanies formation of oxygen vacancies is employed a representative for the Y^{3+}-doped BaZrO$_3$. In this configuration an oxygen vacancy is positioned at the center of linearly-aligned two Y^{3+}. In order to shed light only on the difference in the trivalent species, this configuration was used for all trivalent cations species. To quantitatively examine creation of protons, water-absorption energies in that configuration were calculated according to this equation.

$$\Delta E_{absorb} = E_{T,after} - (E_{T,before} + E_{T,H_2O} + \Delta\mu_{H_2O}(T,p))$$

where $E_{T,\text{after}}$ and $E_{T,\text{before}}$ are total energies of a supercell after and before absorption of water, E_{T,H_2O} is a total energy of water, $\Delta\mu_{H_2O}(T,p)$ denotes a chemical potential of water. All the values, except for the chemical potensial of water, were computed by first principles calculations using generalized gradient approximation for exchange-correlation term, with sufficient number of plane waves, k-point mesh, and mesh for fast Fourier transformation. All calculations were carried out using VASP

code[3]. Calculation of the chemical potential of water is based on NIST-JANAF thermochemical tables[4]. The following equation was used to obtain $\Delta\mu_{H_2O}$:

$$\Delta\mu_{H_2O}(T,p)=H^0(T)-H^0(0)-TS^0(T)+k_B\ln p_{H_2O}\big/p^0_{H_2O}$$

where $H^0(T)$ and $S^0(T)$ are the enthalpy and absolute entropy per gas molecule at the reference partial pressure $p^0_{H_2O}$, respectively.

The absorption energies are plotted as a function of ionic radius of doped trivalent cations (Al^{3+}, Sc^{3+}, Y^{3+}, La^{3+}) in Figure 2, where the absorption energies became lower with the decrease in ionic radius. This result indicates that water molecules were more easily absorbed at oxygen vacancies when local strain imposed upon creation of oxygen vacancies was more relieved. It is found that ionic size of doped traivalent cations is an important factor to optimize proton concentration.

In summary, correlation between ionic radii of doped trivalent cations and the absorption energies in turn proton concentration was quantitatively revealed. This result indicates that water molecules were more easily absorbed at oxygen vacancies when local strain imposed upon creation of oxygen vacancies was more relieved. Further analysis for other configurations and correlation between an oxygen vacancy and two trivalent cations, which is now in progress, would quantify the correlation with better accuracy and would enable to optimize the doping to maximize the proton concentration.

References
[1] S. Imashuku et al., *J. Electrochem. Soc.,* **156** (2009) B1-B8.
[2] K. Nakano et al., *AMTC Letters*, **2** (2010) 176-177.
[3] G. Kresse et al., *Phys. Rev. B.,* **54** (1996) 11169-11186.
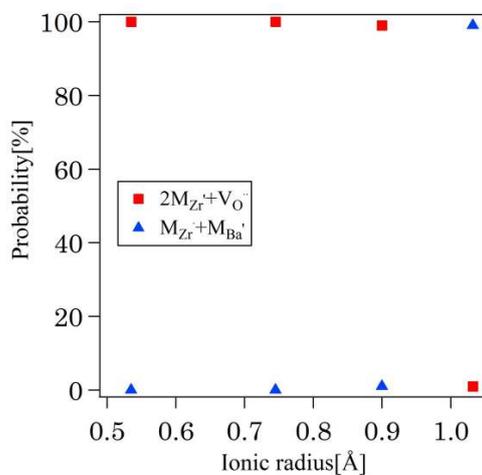[4] M. W. Chase Jr, *NIST-JANAF Thermochemical*, 4th ed, 1998.

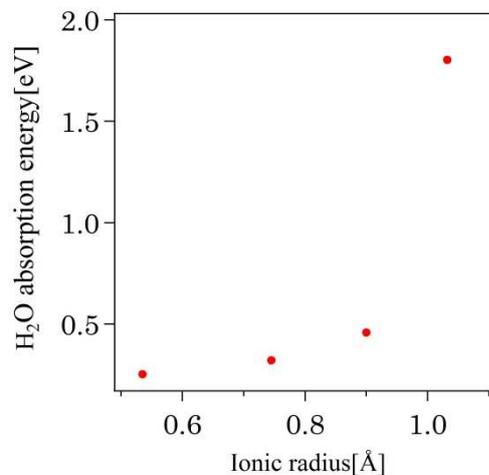Fig. 1. Probabilities of oxygen vacancies are plotted as a function of ionic radius of doped trivalent cation (Al^{3+}, Sc^{3+}, Y^{3+}, La^{3+})[2]

Fig. 2. The absorption energies are plotted as a function of ionic radius of doped trivalent cations (Al^{3+}, Sc^{3+}, Y^{3+}, La^{3+}).