

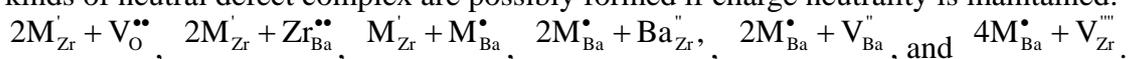
Defect complex of trivalent dopant and resultant proton in BaZrO₃ by first principles calculations with an aid of force-field calculations

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BaZrO₃ is a prime candidate for a protonic conductor which can be used as an electrolyte for the low-temperature solid oxide fuel cell [1,2]. The BaZrO₃ has perovskite structure (ABO₃), in which A site and B site are occupied by divalent Ba and tetravalent Zr, respectively. When two trivalent cations (M³⁺) were doped to BaZrO₃, six kinds of neutral defect complex are possibly formed if charge neutrality is maintained:



Here, Kröger–Vink notation is used to describe defect species. In order to produce protons, oxygen vacancies in BaZrO₃ are essentially needed at first, and then H₂O molecules are decomposed to substitute OH for an oxygen vacancy and H⁺ loosely adhere to nearby oxygen under wet condition. However, as specified above, not all the defect complexes accompany formation of oxygen vacancies and substitution of M³⁺ for Zr is prerequisite for the formation of oxygen vacancies. Although whether M³⁺ substitutes for either Ba or Zr has been predicted only by its ionic radius for simplicity thus far, whether it is closer to that of either Ba or Zr, it is plausible to assume M³⁺ substitutes for both ones with some probabilities instead of substitution for either one, depending on interatomic bonding. In this study, to reveal correlation between trivalent dopant (Sc³⁺, Y³⁺, La³⁺ and so on) and the probability to form oxygen vacancies, first principles calculations as well as calculations by static lattice energy minimization technique have been carried out.

Cubic perovskite supercells containing 320 atoms, repeated four times along each axis, were used and each defect complex with all the possible configurations of the complex was substituted. Although it is more appropriate to evaluate all the energies and structures by first principles calculation, a quantum mechanics (QM) calculation, it is, in fact, many orders of magnitude more computationally expensive than static lattice energy minimization calculation with pairwise interatomic potentials, a classical mechanics (CM) calculation. Therefore, structural optimization with respect to lattice constants and atomic coordinates in the defect complex-containing supercells was carried out at first by CM calculations using GULP code [3], to roughly estimate the formation energies of the defect complexes. Then, QM calculations using generalized gradient approximation (GGA) for exchange–correlation term with sufficient number of plane waves, k-point mesh, and mesh for fast Fourier transformation, to guarantee convergence in total energy with errors smaller than a few eV per atom, were carried out using VASP code [4], for selected configurations of defect complexes that show lower formation energies by CM calculations.

In statistical mechanics, the probability of existence of a defect complex species, *s*, with a configuration, *c*, can be determined from the formation energy of the defect complex, $E_{formation}(s, c)$ as

$$P(s, c) = n(s, c) \exp(-E_{formation}(s, c)/k_B T) / \sum_i \sum_j n(i, j) \exp(-E_{formation}(i, j)/k_B T)$$

where $n(s, c)$ is the number of identical configuration for configuration *c* and defect complex *s* and k_B and *T* are Boltzmann constant and temperature, respectively. In this study, formation energy of a neutral defect complex, $E_{formation}$, was defined as

$$E_{\text{formation}} = E_{\text{T,defective}} + \mu_A + \mu_B - E_{\text{T,perfect}} - \mu_M$$

where $E_{\text{T,perfect}}$ and $E_{\text{T,defective}}$ are total energies of a supercell without any defect complex and of a supercell with a defect complex, respectively, μ_A and μ_B denote chemical potentials of substituted atoms and μ_M denotes chemical potential of a trivalent cation that substitute A-site and/or B-site atoms.

The formation energies for selected configuration of various defect complexes obtained by QM calculations were compared with the formation energies obtained by CM calculations in Fig. 1, which shows that their relationship is almost liner with downward deviation, in some cases, due to the use of formal charges in CM calculations. Here, upward deviation does not matter since those configurations were not screened out due to lower energy by CM calculation and then were evaluated again by QM calculation. Thus, it was possible to narrow down the likely configurations of defect complexes with CM calculations.

Figure 2 shows that probabilities of the two-likely defect complexes, selected by CM calculations, are plotted as a function of ionic radius of doped trivalent cation (Sc^{3+} , Y^{3+} , La^{3+}). It is found that the probability of the defect complex that generates oxygen vacancy increases with decreasing ionic radius. Furthermore, it is found that the defect complexes that exhibit greater probabilities accompany less change in volume of the supercells, implying that the defect complexes can be more easily formed when they introduce less local strain to the matrix.

In summary, correlation between ionic radii of doped trivalent cations and concentration of oxygen vacancy, and, in turn, concentration of protons was quantitatively revealed. Further analysis for other 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.

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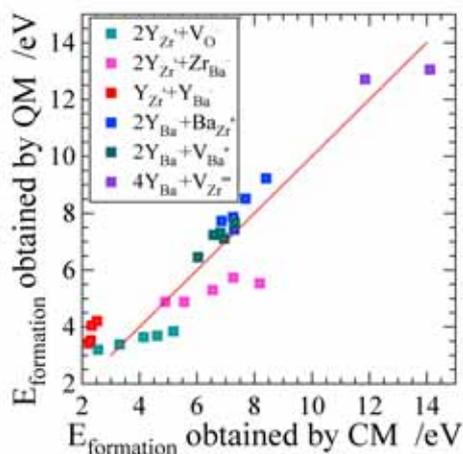


Fig. 1 Formation energy obtained by QM calculations and CM calculations, respectively.

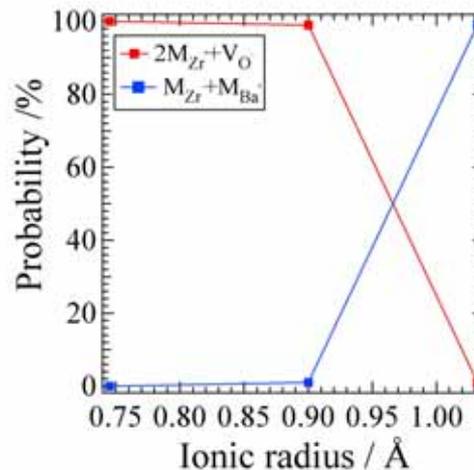


Fig. 2 Probabilities of the two-likely defect complexes plotted as a function of ionic radius of doped trivalent cations (Sc^{3+} , Y^{3+} , La^{3+}).