

## DFT-based *ab initio* MD Simulation of the Ionic Conduction in N/F-Doped ZrO<sub>2</sub> under Epitaxial Strain

Mayuko Oka<sup>1</sup>, Hideyuki Kamisaka<sup>1</sup>, Tomoteru Fukumura<sup>2</sup>, Tetsuya Hasegawa<sup>1,3</sup>

<sup>1</sup> Department of Chemistry, The University of Tokyo  
7-3-1 Hongo, Bunkyo-ku, Tokyo 113-0033, Japan

Phone: +81-3-5841-4354 E-mail: moka@chem.s.u-tokyo.ac.jp

<sup>2</sup> Department of Chemistry, Tohoku University  
6-3 Azaaoba, Aramaki, Aoba, Sendai 980-8578, Japan

<sup>3</sup> Kanagawa Academy of Science and Technology  
Sakado, Takatsu-ku, Kanagawa 213-0012, Japan

### Abstract

The conduction of oxygen ions in N/F-doped ZrO<sub>2</sub> systems under tensile epitaxial strain was investigated by conducting *ab initio* molecular dynamics (MD) calculations. In our preceding study, we have discussed three factors, lattice strain, oxygen vacancies, and dopants, as the essential factors in the enhancement of ionic conduction observed in the Y<sub>2</sub>O<sub>3</sub>-stabilized ZrO<sub>2</sub>/SrTiO<sub>3</sub> heterostructure. In this subsequent report, we show that N/F-doping also contributes to the ionic conduction. We observed flipping motion of zigzag structure of oxygen sublattice under strain, and that the motion was affected by oxygen vacancies or anion dopants. This flipping motion seemingly promotes the ionic conduction.

### 1. Introduction

Oxygen ion conductors are widely used in ionic sensors or as electrolytes for solid oxide fuel cells. Among the possible structural configurations, multilayer thin films have been intensively studied recently, due to their potential ability to realize higher ionic conductivity [1]. In particular, heteroepitaxial structure consisting of 8% Y<sub>2</sub>O<sub>3</sub>-stabilized ZrO<sub>2</sub> (8YSZ) and SrTiO<sub>3</sub> has been attracting much attention because of its anomalous enhancement of oxygen ion conductivity [2]. Several theoretical studies have investigated the origin of the increase in ionic conduction in terms of strain imposed at the interface [3][4]. In our recent paper, using density functional theory (DFT)-based *ab initio* MD calculations, we suggested that formation of the new oxygen sublattice caused by tensile epitaxial strain at the interface and its distortion by oxygen vacancies play an important role for increasing the oxygen ion conductivity in ZrO<sub>2</sub> systems [5]. In the light of this observation, doping of anions, such as nitrogen and fluorine, could also affect the ionic conductivity as these dopants are directly incorporated into the mobile sublattice rather than the cation counterpart. In the present study, we performed the *ab initio* MD simulations on N/F-doped ZrO<sub>2</sub> systems under epitaxial strain. The effect of N/F doping was analyzed not only from the magnitude of ionic conduction but also from the dynamical motion of anion sublattice.

### 2. Calculation method

First, the most stable structure of undoped ZrO<sub>2</sub> under tensile epitaxial strain was determined using density functional perturbation theory (DFPT)-based phonon calculations using Quantum ESPRESSO software package. The primitive unit cell was expanded along the *a*- and *b*-axes to match the lattice constant to SrTiO<sub>3</sub> with a 45° rotation (5.5225 Å), and thus to reproduce the epitaxial strain in the YSZ/SrTiO<sub>3</sub> multilayer. Phonon dispersion curves were drawn connecting the high symmetry *k*-points in the conventional cell. Several negative frequencies were found in the curves. In such a case, the positions of the atoms were displaced along the eigenvector for the dynamical matrices with the largest negative frequency. The resulting structure was optimized using Vienna *ab initio* Simulation Package. This procedure was repeated until no imaginary phonons appeared, i.e., dynamic instability was completely eliminated [5].

Second, we constructed 3×3×2 supercell of the unit cell above as a starting model for the tensile-strained undoped ZrO<sub>2</sub>. The following models were constructed as doped models; (1) 1 oxygen vacancy (*V<sub>o</sub>*) and 3 N/F doping (Zr<sub>72</sub>O<sub>140</sub>N<sub>3</sub>□ and Zr<sub>72</sub>O<sub>140</sub>F<sub>3</sub>□, where □ denotes *V<sub>o</sub>*); (2) 3*V<sub>o</sub>* and 3 N/F doping (Zr<sub>72</sub>O<sub>138</sub>N<sub>3</sub>□<sub>3</sub> and Zr<sub>72</sub>O<sub>138</sub>F<sub>3</sub>□<sub>3</sub>); (3) 6*V<sub>o</sub>* and 3 N/F doping (Zr<sub>72</sub>O<sub>135</sub>N<sub>3</sub>□<sub>6</sub> and Zr<sub>72</sub>O<sub>135</sub>F<sub>3</sub>□<sub>6</sub>). The oxygen vacancy concentration of 6*V<sub>o</sub>* corresponds to the 9% Y<sub>2</sub>O<sub>3</sub> doped ZrO<sub>2</sub>, which is close to the experimental data of 8YSZ [2]. The results of anion-doped samples were compared against the ZrO<sub>2</sub> samples without anion dopants (Zr<sub>72</sub>O<sub>143</sub>□, Zr<sub>72</sub>O<sub>141</sub>□<sub>3</sub>, and Zr<sub>72</sub>O<sub>138</sub>□<sub>6</sub>). The initial structures for MD calculations were prepared *via* normal structure optimization. The *c*-axis length was optimized under the fixed *a*- and *b*-axes.

Finally, the finite-temperature DFT-based *ab initio* MD calculations were performed. The lattice constants were fixed throughout the duration of the entire simulation. The temperature was gradually increased from 500 to 2000 K during the first 1000 steps (*t* = 0–2 ps) and then held constant at *T* = 2000 K for the successive 4000 steps (*t* = 2–10 ps). A Nôse–Hoover thermostat was used to control the temperature. This gradual heating procedure worked effectively to attain the relevant structural relaxation from the initials, which are potentially thermodynamically-unstable.

The ionic conductivity was evaluated as the MSD given

by the following equation:

$$MSD = \frac{1}{n} \sum_i |r_i(t) - r_i(0)|^2 \quad (1)$$

where  $n$  is the number of particles, and  $r_i(t)$  is the position of ion  $i$  at time  $t$ . The MSD was then smoothed by averaging  $MSD(t, t_0)$  over the time origin  $t_0$  in order to estimate the diffusion coefficient:

$$MSD(t, t_0) = \frac{1}{n} \sum_i |r_i(t + t_0) - r_i(t_0)|^2 \quad (2)$$

The results of eq. (1) and (2) should coincide at the thermodynamic limit ( $n \rightarrow \infty, t \rightarrow \infty$ ).

In the present study, the MSD was calculated from eq. (2) using the data in the constant temperature region at  $T = 2000$  K ( $t = 2\text{--}10$  ps). The diffusion coefficient  $D$  can be estimated by linear fitting to  $MSD = 6Dt + \text{constant}$ . The diffusion coefficient gives the ionic conductivity  $\sigma$  through the Nernst–Einstein relation  $\sigma = Nq^2D/k_B T$ , where  $N$  and  $q$  are the density and charge of the mobile ions, respectively.

## 2. Results and discussion

Figure 1 shows the MSDs of oxygen ions in  $1V_o$ ,  $3V_o$ ,  $6V_o$  and 3 N/F doped  $ZrO_2$  systems (black lines;  $1V_o$ ,  $3V_o$ ,  $6V_o$ , purple lines;  $1V_o+3F$ ,  $3V_o+3F$ ,  $6V_o+3F$ , blue lines;  $1V_o+3N$ ,  $3V_o+3N$ ,  $6V_o+3N$ ,  $a, b$ -axes tensile strain was applied except for the red lines; unstrained  $1V_o$ ,  $3V_o$ ,  $6V_o$ ). Several lines with the same color in the same composition represent other sample of the MD calculation.

Phonon calculation revealed the emergence of structural change of  $ZrO_2$  under tensile strain. However, this structural change does not straightforwardly induce the increase in

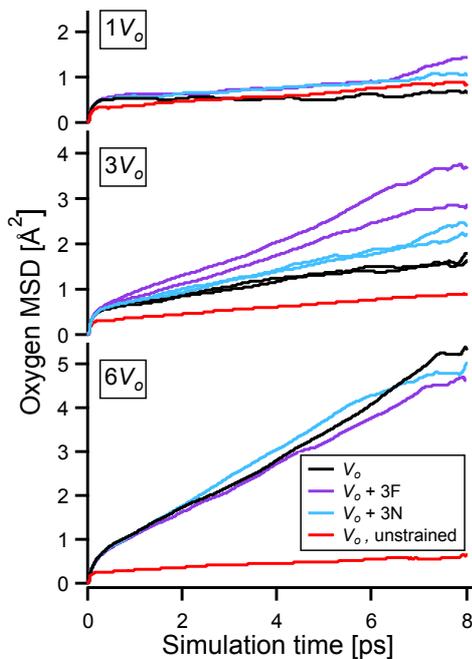


Fig. 1 MSDs of oxygen ions in  $1V_o$ ,  $3V_o$ ,  $6V_o$  and 3 N/F doped  $ZrO_2$  systems. Tensile strain was applied to the system except for red lines. Several lines with the same color represent different sample of the MD calculation.

ionic conductivity (Fig. 1, red and black lines in  $1V_o$ ). One would expect that the introduction of tensile strain enlarge the Zr–O distances, i.e., weaken the bonds, and thus enhance oxygen diffusion. In fact, under the tensile strain, the Zr–O distance was not increased, but a new oxygen sublattice was formed. This behavior was confirmed by examining the radial distribution functions (RDFs) between the Zr and O ions. The ionic conductivity was increased only when the tensile strain and several oxygen vacancies were introduced simultaneously (Fig. 1, red line and others in  $6V_o$ ). These results explain that the enhancement of ionic conductivity observed in  $YSZ/SrTiO_3$  is related to the structural change of anion sublattice by epitaxial strain and its displacement by several vacancies.

Though the effect of N/F doping was not clear in  $1V_o$  and  $6V_o$ , the addition of N/F to  $3V_o$  show prominent enhancement of the oxygen ion conductivity. By taking a

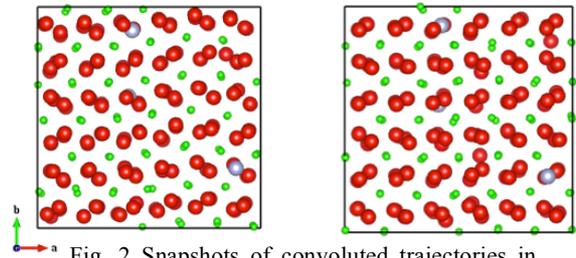


Fig. 2 Snapshots of convoluted trajectories in  $Zr_{72}O_{138}N_3\Box_3$ .

convolution with a Gaussian function over time in trajectory of ions, we noticed flipping motion of the zigzag structure of anion sublattice, which appeared to have some relationship with the ionic conduction (Fig. 2). Doping of anion or oxygen vacancies seems to facilitate the flipping. In particular, for the case with intermediate concentration of  $V_o$ , most strongly in  $3V_o$  systems, the N/F dopants enabled more frequent flipping of the zigzag structure, and thus promoted the ionic conduction.

## 3. Conclusions

In this study, we performed DFT-based *ab initio* MD calculations for N/F-doped  $ZrO_2$  systems. The results indicate that a new oxygen sublattice was formed under tensile strain and that their flipping motions can be enhanced by oxygen vacancies or anion dopants, which may have resulted in the higher ionic conductivity.

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