

Segregation of Trivalent Impurities and Resultant Ionic Conductivity at $\Sigma 5$ (310)/[001] Symmetric Tilt Grain Boundary of ZrO_2

Yuya YOSHIKAWA¹⁾, Masato YOSHIYA^{1,2)}, and Hideyuki YASUDA¹⁾

¹⁾Department of Adaptive Machine Systems, Osaka University, Osaka 565-0871, Japan.

²⁾Nanostructure Research Laboratory, Japan Fine Ceramics Center, 2-4-1 Mutsuno, Atsuta, Nagoya 456-8587, Japan.

Lattice discontinuity at grain boundary (GB) or surface brings about potential change for impurities or point defects not only at a boundary plane but also in its vicinity. This results in GB segregation or surface segregation, i.e., enrichment of the impurities or point defects. Thus, it might be possible to dissolve the foreign species in the region in the vicinity of GB to the amount that exceeds solubility limit of bulk phase, which provides greater degrees of freedom to control materials properties. In addition, controlling chemical composition at surfaces or interfaces becomes more and more crucial especially in polycrystals [1]. The cubic stabilized ZrO_2 is widely used as solid state electrolytes for fuel cells and oxygen sensors, due to its high ionic conductivity. We focused on the effect of GB segregation of various trivalent impurities (Y^{3+} , Al^{3+} , Sc^{3+} , Yb^{3+} , Gd^{3+} , Ce^{3+} , and La^{3+}) and accompanied oxygen vacancies on ionic conductivity across the GB plane of ZrO_2 . Aims of this study are to analyze segregation behavior of various trivalent impurities at the $\Sigma 5(310)/[001]$ symmetric tilt grain boundary of cubic ZrO_2 (Fig. 1) and to obtain a guideline for improvement of ionic conductivity across the GB using atomistic calculations.

As a first step, we calculated the segregation energies of just one cation defect (M_{Zr}') and a pair of defects (M_{Zr}' and V_{O}'') for each trivalent impurities in the vicinity of grain boundary as a function of the distance from GB plane, in order to compare the segregation behavior in the simplest cases. Segregation energy, calculated from static lattice energy minimization technique using GULP code with pairwise interatomic potentials, is defined as the difference in substitution energies of defect between the averaged value at grain interior (GI), E_{GI} , and a value at given cation site, E_x :

$$E_{\text{segregation}} = E_x - E_{\text{GI}}$$

In order to obtain configurations of defects, which is hereafter referred to as segregation structure, we carried out Monte Carlo simulations of site interchange of impurities and vacancies. During these simulations, the lattice energies of super cells with various defect configurations were calculated by above mentioned static lattice energy minimization technique [2]. By a combination of these two techniques, the most stable segregation structure was obtained as a function of amount of dopants. Then, molecular dynamics simulations have carried out with those segregation structures to obtain coordinates of atoms as a function of time, from which diffusivity or ionic conductivity was calculated using Einstein and Nernst equation, respectively, through calculations of mean square displacement (MSD).

Figure 2 shows segregation energy of sole cation defect (M_{Zr}') model as a function of distance from GB plane, x . When an Y^{3+} ion approaches to a grain boundary, segregation energy increased with some scattering as shown by blue circles. In the case of a Sc^{3+} ion (green circle), segregation energy monotonically increased. In contrast, an Al^{3+} ion (red circle) showed monotonically decrease, indicating that Al^{3+} ions can be segregated to the GB without oxygen vacancies. It is found that substitution energies for

impurities showed different trend respectively approaching toward GB plane, whereas they were decreased by co-segregation of oxygen vacancy for every impurity studied, as shown in Fig. 3. In other words, GB segregation of impurities was often accompanied by oxygen vacancy, with different magnitude. The difference in the magnitude would influence local concentration of the oxygen vacancies, which significantly affect ionic conduction across GB. Furthermore, binding energies between each impurity and oxygen vacancy pair showed different trend one by one in spite of the same relative positions, when they changed their positions from GI to the vicinity of GB. These segregation trends were correlated with the difference in the binding energy for each impurity.

In summary, atomistic calculations have been carried out to investigate the segregation behavior and configurations of trivalent impurities and oxygen vacancy. It is found that the segregation configurations of defects are resulted from the difference in binding energies between impurity and oxygen vacancy over impurity species. We assume these results indicate each impurity modify the ionic conductivity across the GB with segregation.

References

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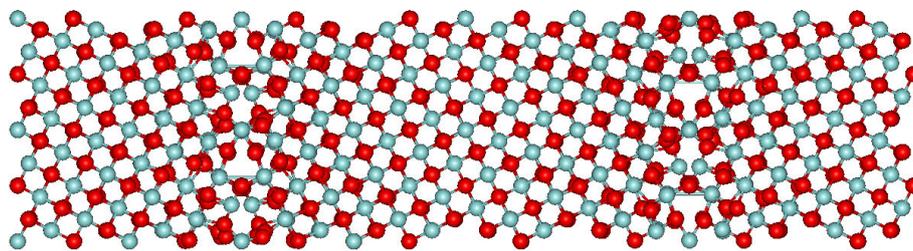


FIG. 1. $\text{ZrO}_2 \Sigma 5(310)/[001]$ symmetric tilt grain boundary model.

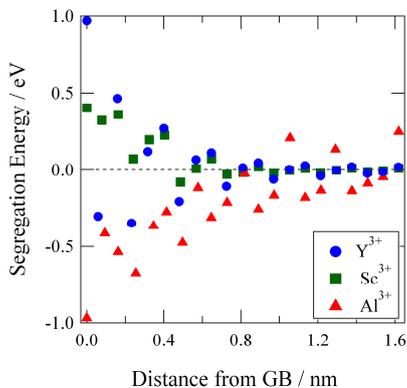


FIG. 2. Segregation energy of M_{Zr}' ($M = \text{Y}, \text{Al}, \text{Sc}$).

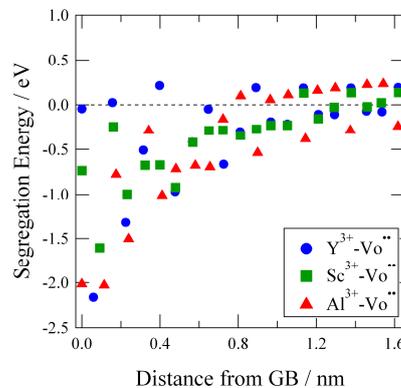


FIG. 3. Segregation energy of $M_{\text{Zr}}' - \text{V}_\text{o}^{\bullet\bullet}$ ($M = \text{Y}, \text{Al}, \text{Sc}$).