



On modeling of grain boundary segregation in aliovalent cation doped ZrO_2 : Critical factors in site-selective point defect occupancy

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Correlation between the bond strain and stabilization of point defects near a symmetric grain boundary in ZrO_2 materials is examined to reveal essential factors for grain boundary segregation of dopants and O^{2-} vacancies. Even at dilute dopant concentrations the segregation sites cannot be predicted from bond strain alone. Rather, long-range Coulombic interactions which prevail more in grain interior play a dominant role to determine local modifications at grain boundaries, i.e., enrichment and site-selective occupation of point defects with varying magnitude.

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Segregation of point defects at interfaces including surfaces [1], grain boundaries (GBs) [2] and hetero-interfaces [3] determines various macroscopic materials properties even though the effects of individual defects are normally confined to at most a few nanometers either side of the interface. Many transmission electron microscopy (TEM) and scanning TEM (STEM) studies have revealed atomic-level distributions of point defects near interfaces in various types of materials, such as metals [4], intermetallics [5] and oxides [6]. In order to understand, control and ultimately utilize point defect segregation, which is a complex phenomenon, it is necessary to create an atomistic model with minimal complications for describing segregation phenomena in various materials. Once a suitable model is established, it can be applied to various segregation-related problems, ideally by carrying out first-principles calculations.

Both macroscopic and microscopic theories have been proposed to describe segregation phenomena [7,8]. One well-known atomistic model for segregation is based on the bond distortion arising in the vicinity of interfaces and the resultant size mismatch between point defects and matrix elements [10,16]. In addition, attempts to correlate “free volume” and “excess volume” near interfaces have been successful to some extent [11,17]. So far, however, successful descriptions of GBS phenomena by these models

and agreement with experimental results have been confined to dilute defect concentrations [6,11].

In order to understand the mechanism of GBS which brings about enrichment of point defects at GBs, the influence of size mismatch of constituent ions on GBS is extensively discussed [10,22–25]. Furthermore, the space theory has been proposed for oxide systems to explain segregation of charged point defects to GBs [19]. Guo [20] applied the theory to Y_2O_3 -doped ZrO_2 systems. However, our previous study suggests that enrichment alone is inadequate to minimize the total energy of a system that contains GBs [21]: In addition to the enrichment, point defects must occupy specific sites near a GB plane and exhibit a nonrandom distribution to minimize the total energy of a system. At present, critical factors of the site-selective occupation and nonrandom distribution remain unclear. Taking into account all possible factors influencing GBS is not an efficient way to solve GBS-related problems. Therefore, firstly, it is necessary to determine the critical factors.

In this study, we focus on GBS of M^{3+} ions, where $\text{M} = \text{Al}, \text{Sc}, \text{Y}, \text{Gd}$ and La , and O^{2-} vacancies to a symmetrical GB in M -doped ZrO_2 , which is an important system with practical applications [9] and an appropriate model material for addressing GBS modeling. In this fluorite-structured material, 8-fold coordinated Zr^{4+} and 4-fold coordinated O^{2-} ions form face-centered-cubic (fcc) and simple cubic sublattices, respectively, and point defects with different effective charges are introduced by doping with aliovalent cations, for example, yttria-stabilized cubic zirconia (YSZ). These structural and defect features, at

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least in part, are common to a wide range of materials from metals to oxides, and thus the knowledge obtained for this material can be applied to a wide range of systems.

In this study, we first examine an undoped GB model to verify the validity of conventional schemes for modeling a segregated GB, i.e., to determine the segregation sites near the GB at dilute dopant concentrations. Then, in order to clarify whether the results at dilute concentrations can be applied to those at high concentrations, we compare the bond strain as well as energetics of GBS at various concentrations.

To model GBS of Y^{3+} ions and O^{2-} vacancies, a $\Sigma 5(310)/[001]$ symmetrical tilt GB was used because of the relatively high GB energy [13], which leads to substantial GBS. The cell size was $96 \text{ \AA} \times 8 \text{ \AA} \times 10 \text{ \AA}$, with the undoped system containing 236 Zr^{4+} and 472 O^{2-} ions. The energy of each system was calculated by the static lattice method implemented in the GULP code [18]. Buckingham-type empirical potentials were used to calculate short-range interaction energies. The total lattice energy, E^{total} , is represented by the sum of the short-range, E^{short} , and long-range Coulombic interactions, E^{Coulomb} . For the Buckingham-type potentials of all trivalent cations, the well-tested empirical parameter set reported in literature [14,15] was used to calculate E^{short} . The definition of the driving force for GBS at dilute defect concentrations, $\Delta E_{\text{dilute}}^{\text{GBS}}$, is given by

$$\Delta E_{\text{dilute}}^{\text{GBS}} = E(r) - E(\infty) \quad (1)$$

where r is the distance between a dopant and the GB plane, and $E(\infty)$ represents the reference state where a point defect is infinitely far from the GB plane. It is assumed that there is only one M^{3+} ion and one O^{2-} vacancy located on a second-nearest-neighbor site relative to the M^{3+} ion, hereafter denoted by $(M'_{Zr} - V_{O}^{\bullet\bullet})^{\bullet}$ using Kröger–Vink notation. When a combination of point defects breaks charge neutrality in a supercell, in order to calculate the Coulombic interaction energy, an extra component is added to the lattice energy in the form of jellium-like spatially-uniform background charges to cancel the excess charge. This treatment is employed in all calculations and thus the influence of background charges is canceled out. In addition, the interaction between the jellium-like background charges and point defects is site- or even space-independent. Thus, use of this technique does not modify the results obtained and conclusions drawn whether the charge neutrality is broken or not.

In this study, we evaluated the bond strain, which is a measure of the magnitude of bond distortion between nearest-neighbor (NN) species, in order to examine the correlation between bond strain and the energetics of GBS. We defined the total bond strain, ϵ^{total} , as

$$\epsilon^{\text{total}} = \sum_{i=1}^N 1/CN_i \sum_{j=1}^{CN_i} (l_{ij} - l_{\text{eq}})/l_{\text{eq}} \quad (2)$$

where CN_i is the number of NN ions bonded to ion i , N is the total number of atoms in the computational cell, and l_{ij} and l_{eq} represent the bond length between i and j and their equilibrium bond length in a perfect crystal, respectively. Atoms within the median distance between the closest NN and the closest next-nearest-neighbor are assumed to be NN atoms. Although this definition is somewhat arbitrary, we have checked that the observed trends do not change significantly when the cutoff radius is changed

slightly. In this study, Zr–Zr, Zr–O and O–O bond strains were calculated. In addition, the bond strains on Zr and O sites, $\epsilon_{Zr}^{\text{total}}$ and $\epsilon_{O}^{\text{total}}$, are separated into the bond strains at individual cation and anion sites in an attempt to differentiate their effect on GBS.

In our previous studies of dilute dopant concentrations, where one M^{3+} ion and one O^{2-} vacancy are introduced, it was found that the A sites (Fig. 1) are energetically preferential sites for point defect segregation [12,13]. Nevertheless, the A sites do not correspond to the largest bond strain. Instead, the B sites correspond to the largest magnitude of $\epsilon_{Zr}^{\text{total}}$ for all cation sites. The highest bond strain sites (B sites) thus do not correspond to the lowest energy sites (A sites). The magnitude of the bond strain is qualitatively correlated with that of $\Delta E_{\text{dilute}}^{\text{GBS}}$ but these two quantities do not follow precisely in the same way as each other.

To examine more directly the correlation between the bond strain and lattice energy at each cation site using a pure GB model, we evaluated the magnitudes of the lattice energies of individual Zr sites, as shown in Figure 1b–d. Comparison between Figure 1a and b indicates that the magnitude of $\epsilon_{Zr}^{\text{total}}$ is not necessarily consistent with that of E_{Zr}^{total} near the GB plane. For example, the A and B sites (Fig. 1a) exhibit higher bond strains, but they do not provide energetically stable atomic sites for dopants (Fig. 1b). This difference in the two trends stems from the irregular contribution of the long-range Coulombic interactions, E_{Zr}^{Coulomb} , as shown in Figure 1d, while the magnitude of short-range interactions (Fig. 1c), E_{Zr}^{short} , correlates reasonably well with $\epsilon_{Zr}^{\text{total}}$. The contribution of E_{Zr}^{Coulomb} to E_{Zr}^{total} results from the abrupt disruption of crystal periodicity at the GB.

For O^{2-} ions, the lack of correlation between the magnitude of the bond strain, $\epsilon_{O}^{\text{total}}$, and total lattice energy, E_{O}^{total} , is much more remarkable, as seen in Figure 2. The A sites correspond to the largest magnitude of $\epsilon_{O}^{\text{total}}$ while the B sites exhibit the highest lattice energy. Our previous study

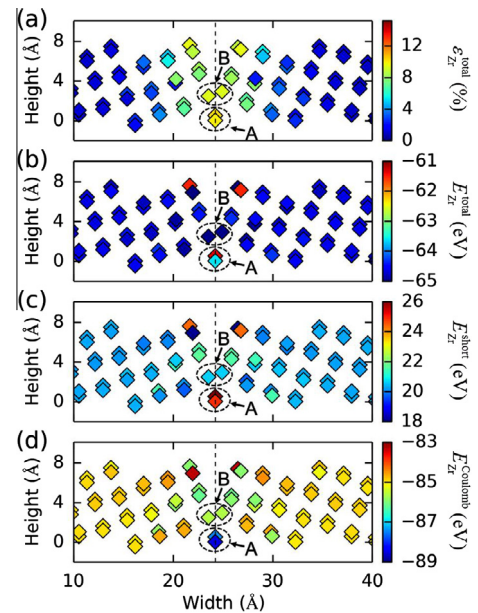


Figure 1. Magnitude of (a) $\epsilon_{Zr}^{\text{total}}$ and (b) E_{Zr}^{total} at each Zr site. The total energy is separated into two terms, namely (c) the short-range interaction, E_{Zr}^{short} , and (d) the long-range Coulomb interaction, E_{Zr}^{Coulomb} . The dashed line corresponds to the GB plane.

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