Relationship between grain boundary segregation of extrinsic point defects and local diffusion of O^{2-} in M_2O_3 doped ZrO_2

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Microscopic structural changes triggered by lattice defects often modify various materials' properties such as mechanical, diffusional and electrical property and so on. Such modification is sometimes beneficial and sometimes harmful for synthesizing advanced materials. Thus it is necessary to understand microscopic physics of lattice defects and to control lattice defects for obtaining beneficial properties. Grain Boundaries (GB), which is one of planar defects, also often play a key role of macroscopic materials' properties although GBs bring about only microscopic structural changes within a few nm from GB plane.

Polycrystallines of impurity doped ZrO_2 have been widely investigated as high ionic conductor and an appropriate model system for understanding diffusional property of O^{2-} ions. The experimental studies have reported that GBs also modify macroscopic diffusional property and suggested that its modification is caused by GB structure itself and/or GB segregation (GBS) of extrinsic point defects, namely dopants and O^{2-} vacancies [1, 2]. Therefore, to improve O^{2-} ionic conductivity in polycrystallines, at first, it is necessary to understand the structural change triggered by GB/GBS and its contribution to O^{2-} diffusion near the GB plane on microscopic scale. However, it is difficult to understand the relationship between GB/GBS and materials' properties only with experiment, because GBs bring about simultaneous complex phenomena: for example discontinuity of lattices, unbalance of charges and GBS of elements. To overcome this difficulty, we utilize atomistic computational techniques, namely lattice static method (LSM) and molecular dynamics (MD). The purposes of this study are (1) to specify the microscopic structures of GB/GBS with focuses on the spatial distribution of the extrinsic point defects, (2) to understand the driving force for GBS and (3) to understand the relationship between GB/GBS and O^{2-} diffusion near the GB plane which would depend on the spatial configuration of extrinsic point defects.

To understand essentials of GB/GBS, we construct the Σ5 (310) / [001] symmetric tilt GB model. To decide energetically stable configurations of extrinsic point defects, we use LSM with the Metropolis algorithm of atomistic Monte Carlo simulation. To understand the driving force for GBS, we construct the three different GB models for comparisons: (1) The GB overall random (GBOR) model, where the extrinsic point defects are randomly distributed through the GB model, (2) the GB random (GBR) model, where the extrinsic point defects are segregated near GB plane with random spatial distribution, and (3) the GBS model, where the extrinsic point defects segregate near the GB plane, and they occupy the specific sites to minimize lattice energy. In the evaluation of O^{2-} diffusional property near the GB model, we calculate O^{2-} self-diffusion coefficient by using MD. To reveal the effect of spatial configuration of the extrinsic point defects, we compare the results of the GBR and the GBS model.

In Fig. 1, we show the spatial configuration of the each dopant species near GB plane. The spatial configuration of the Y^{3+} ions (Fig. 1 (a)) is agreement with the result of direct observation by transmission electron microscopy with atomic resolution [3, 4].

All the dopant species occupy the specific cation site instead of random distribution to minimize the total lattice energy. But the cation sites occupied by the dopants are different between dopant species as shown in fig. 1(a) and (b). We also obtained the spatial distribution of the O^{2-} ions near the GB plane. The O^{2-} ions also occupy the specific anion sites. This tendency of the O^{2-} ions is seen for all the dopant species.

Figure 2 shows the driving force for GBS as a function of the number of defect complexes for Y_2O_3 doped ZrO_2. The result (Fig. 2 (b)) indicates that the lattice energy of the GBR model is nearly the same as that of the GBOR model, suggesting that only GBS is insufficient to minimize lattice energy and that the occupation of specific sites by the extrinsic point defects is necessary to minimize lattice energy. Regarding the component of the driving force, Coulombic repulsion in the GBS model is smaller than that in the GBR model. Thus, the relief of Coulombic repulsion is one of the key factors to decrease the total lattice energy in the GBS model (Fig.2 (a)).

Figure 3 shows O^{2-} self-diffusion coefficient D_{oxy} near GB plane as a function of absolute temperature in the GBR and the GBS model evaluated by MD simulations. It is obvious that the temperature-dependence of diffusional behavior is different between the GBR and the GBS model; the quantitative value of D_{oxy} and the activation energy given by the gradient of the lines are different between the two GB models. These analyses clarified that the spatial configuration of the extrinsic point defects can affect O^{2-} diffusional property near the GB plane. The same trend is also observed for Sc_2O_3 doped ZrO_2, as shown in Fig. 3 (b). Although the only two cases, Y_2O_3 and Sc_2O_3 doped ZrO_2 system, are shown in this study, it is highly likely that the spatial configuration of extrinsic point defects also affects D_{oxy} in the case of other dopant species.
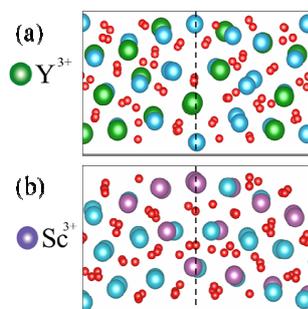
FIG. 1.spatial configuration of the dopants near GB plane in the case of (a) Y_2O_3 and (b) Sc_2O_3 doped ZrO_2
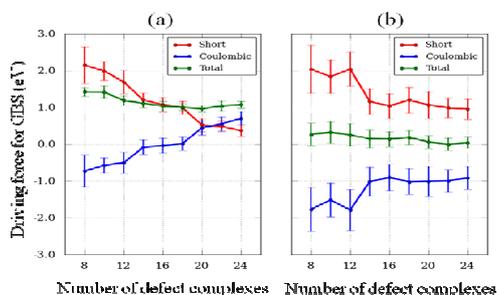

FIG. 2. driving force for GBS as a function of number of defect complexes in the case of (a) the GBS and (b) the GBR model.
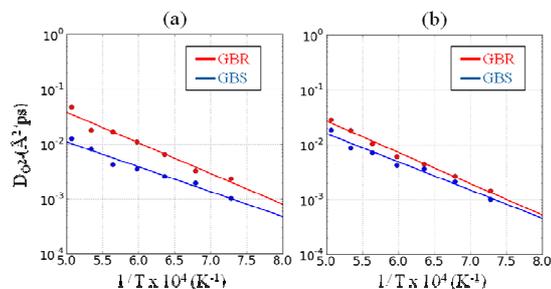

FIG. 3. O^{2-} self-diffusion coefficient as a function of inverse of absolute temperature in the case of (a) Sc_2O_3 and (b) Y_2O_3oped ZrO_2.

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