Oxide Ion Conduction at Grain Boundary of M_2O_3 doped ZrO_2 by Molecular Dynamics: A Challenge to Reduce Grain Boundary Resistance

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Lattice discontinuity at grain boundary (GB) brings about potential change for foreign atoms and defect species not only at GB plane but also in the vicinity of GB. This results in GB segregation, enrichment (or depletion) of the foreign atoms or defect species. It is noteworthy that the change in chemistry in the vicinity of GB (hereafter, it is referred to as GB region) often deviate compositional range available for bulk region since larger amount of foreign species can be settled in the GB region if it relieves the local strain in the GB region generated by the lattice discontinuity upon accommodation in the GB region. Overall amount of the foreign species in the GB region is determined by balance of chemical potential between bulk and the GB region [1]. Thus, it is possible to dissolve the foreign species in the GB region to the amount that exceeds solubility limit of bulk phase, which provides greater degree of freedom to control materials properties: If an overall property of a material were governed by characteristics of the GB, it might by able to greatly modify bulk properties through controlling GB chemistry.

ZrO_2-based ceramics has high electrical conductivity at high temperature due to oxide ion diffusion. Because of its property, ZrO_2-based ceramics is one of the candidates for a solid electrolyte in Solid Oxide Fuel Cell [2]. Numerous experiments have been made to improve ionic conductivity of ZrO_2-based ceramics with trivalent dopants since the aliovalency creates oxide ion vacancies to maintain local charge neutrality. Experimental studies showed that, when dopant was changed from Y_2O_3 which is widely used dopant to stabilize cubic structure of zirconia, ionic conductivity also changed. However, changing dopant species alters density of sintered body, grain size, GB character and so on, and thus, it is difficult to tell what the real effect of the dopant on the ionic conductivity is. Furthermore, it is difficult to distinguish and evaluate ionic conductivity of the GB region and grain interior independently by experiments, which rationalize investigating ionic conductivity in the GB region by atomistic simulation in order to evaluate so-called GB resistance, a decrease in ionic conduction in the GB region [3].

We have calculated local ionic conductivity of various M_2O_3-doped ZrO_2 (M = Al, Sc, Yb, Y, Gd, Ce, La) in bulk and in the GB region, aiming at finding correlation between characteristics of dopant and resulting ionic conductivity. In order to evaluate the effects of (1) dopant species, (2) lattice discontinuity, and (3) GB segregation, we have carried out atomistic simulations using the three models, (a) the bulk model, (b) the GB model with random M_2O_3 substitution, and (c) the GB model with segregation. The atomic configuration of the segregation model reported for Y_2O_3-doped ZrO_2 [1] was used for all the dopant species for simplicity. Then, molecular dynamics simulation have carried out to obtain coordinates of atoms as a function of time, from which diffusivity or ionic conductivity was calculated using Einstein or Nernst equation, respectively, through calculations of mean square displacement.

Figure 1 shows ionic conductivity of bulk phases with various dopant species. As seen in the figure, when Sc^{3+} is doped, the diffusivity was the highest among them. One of the reasons is that ionic radius of Sc^{3+} is the closest to that of Zr^{4+} [4] and, thus, doping of Sc^{3+} does not distort ZrO_2 cell or obstruct diffusion of the oxide ion conduction. With the deviation of ionic radius from that of Zr^{4+}, diffusivity decreased. This is the general trend found in bulk phases. However, local diffusivity in the GB region showed a slightly different trend: Although those values were much smaller due to GB resistance, they were not proportional to the bulk ionic conductivities. The changes in ionic conductivity for three selected dopants are shown in Figure 2, which shows the decrease due to GB for two cases: (b) random substitution and (c) segregation. As for Sc^{3+} doped one, the decrease relative to the bulk value is almost the same as others when dopant is randomly substituted, meaning that absolute decrease, i.e., GB resistance, is the greatest for Sc^{3+}. On the other hand, the bulk ionic conductivity of Al^{3+} doped one was the lowest. This disadvantageous behavior is unchanged for GB with random substitution. However, the ionic conductivity was much increased when Al^{3+} is segregated as shown in Fig. 2, showing minimal GB resistance relative

to bulk one. This is clearly explained by local oxide vacancy concentration in the GB region as shown in Fig. 3. According to our accompanying study [3], excess amount of oxide ion vacancy impedes oxide ion conduction. As shown in the figure, segregation of Al^{3+} in GB region expelled oxide ion vacancies from the GB region, which is the reason why Al^{3+} segregation to improve GB resistance.

In summary, GB ionic conductivity showed different trend from bulk one especially when dopant segregation is realized due to change in local oxide ion concentration at GB. Although Al^{3+} is not a good candidate for bulk doping since the bulk conductivity is low, doping small amount of Al^{3+} to other M_2O_3-doped ZrO_2 would expel excess oxide ion vacancies from GB, thereby improving GB resistance.

References
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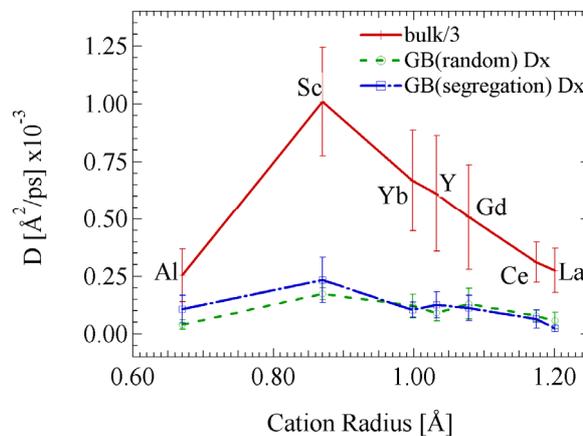[4] R.D.Shannon, C.T.Prewitt Acta Cryst, **B25** (1969) 925.

FIG. 1. Bulk diffusivities for various M_2O_3-doped ZrO_2 and those for randomly substituted GBs and GBs with segregation.
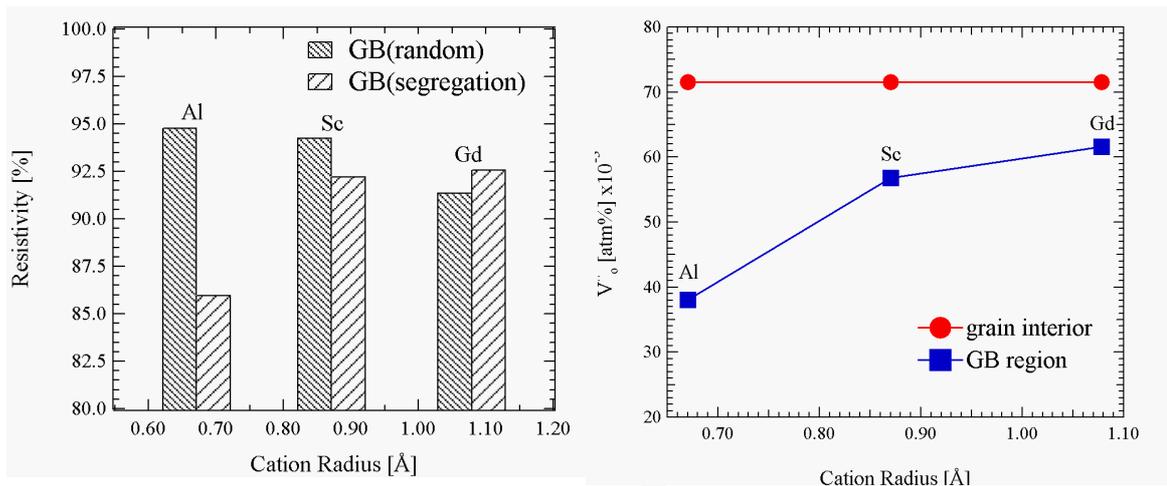

FIG. 2 Ratio of decrease in local diffusivity at GB: for GB with random substitution and GB with segregation for selected M_2O_3-doped ZrO_2.

FIG. 3 Local oxide vacancy content at GB with segregation for selected M_2O_3-doped ZrO_2.