Atomistic analysis of dopant and oxygen vacancy segregation to grain boundary and its contribution to ionic conductivity in M_2O_3-doped ZrO_2

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M_xO_{2x-1}(x =1, 2)-doped ZrO_2 has been widely investigated as high ionic conductor for last decades. Usually di- or trivalent cations are selected as a stabilizer of cubic crystal structure and vacancies are created for charge neutrality. For practical use, polycrytalline materials instead of single crystals are used, and therefore grain boundaries (GBs) in M_xO_{2x-1}-doped ZrO_2. It has been reported that ionic conductivity near GBs was lowered by a factor of ~10^3 compared with that in bulk even if impurity such as Si or Al did not exist [1]. On the other hand, though they are controversial, recently many reports have revealed that nanocystalline material of M_xO_{2x-1}-doped ZrO_2 shows different behavior compared with bulk materials. It is argued that such singularity is related to existence of GBs indicating that it is important to control the GB in order to improve overall conductivity. However, it is difficult to understand phenomena in the vinicity of GB and specify the factor that affects ionic conductivity since if GBs exist many kind of phenomena simultaneously such as, the distortion of crystal lattice, local unbalance of charges and segregation of dopants and oxygen vacancies.

In order to understand phenomena in the GB region, we have investigated the influence of GB on ionic conductivity and the mechanism behind it with atomistic analyses. In our study, we paid attention to the GB segregation of trivalent cation (M_{Zr}') and oxygen vacancy ($V_O^{\bullet\bullet}$). As a first step to specify the factor that influences GB segregation behavior, we investigated the relation between ionic radius in trivalent cations and GB segregation behavior. As result, it is shown that there is possibility that the GB segregation structures varies with dopant species. Beside, the distributions of dopant and oxygen vacancy are different in each case. However, it is not still clear how GB segregation contributes ionic conductivity. One of objectives of this study is to obtain the knowledge about the relationship between GB segregation and ionic conductivity. In addition, we discuss a concrete guideline to improve ionic conductivity by applying the knowledge obtained from our study.

We constructed following four models in order to clarify what influences ionic conductivity if GB exists and M_{Zr}' and $V_O^{\bullet\bullet}$ segregation to GB can occur, as shown in Figs.1-4. Here we forcused on Σ5(310)/[001] symmetry tilt GB.

- Model_SC: the single crystal cubic ZrO_2 model, in which M_{Zr}' and $V_O^{\bullet\bullet}$ are distributed randomly throughout the model.
- Model_RD: a GB model, in which M_{Zr}' and $V_O^{\bullet\bullet}$ are distributed randomly throughout the model.
- Model_GBR: the GB model, the deviation of M_{Zr}' and $V_O^{\bullet\bullet}$ in GB region from that in bulk occur. The local concentrations of M_{Zr}' and $V_O^{\bullet\bullet}$ in GB region are random.
- Model_GBS: the GB model, in which the segregation of dopant and oxygen vacancy takes place resulting in the deviation of M_{Zr}' and $V_O^{\bullet\bullet}$ concentration mentioned above.

Firstly, we compared the ionic conductivity in Model_SC with that in Model_RD. Secondly, we evaluated the contribution of the deviation of dopant concentration in GB region. It can be considered that dopant and oxygen vacancy concentration in GB region

is different from that in bulk due to dopant and oxygen vacancy segregation to GB region. Thirdly, in the Model_GBS, we consider M_{Zr}' and $V_O^{\cdot\cdot}$ segregation including the difference of M_{Zr}' and $V_O^{\cdot\cdot}$ in GB region and bulk mentioned above. We used the results in previous research as segregation models, which were obtained by combination of lattice static method and Monte Carlo simulation. In Model_GBR and Model_GBS, we defined the ionic conductivity in the range of 0.8 from GB core as GB ionic conductivity.

From this study, it was found that GB conductivity was lower than bulk ionic conductivity. It can be considered that this degradation results from combination between deviation of M_{Zr}' and $V_O^{\cdot\cdot}$ from those of bulk and GB structure, which are different from single crystal structure. GB conductivity in Model_GBS is different from that in Model_GBR. This indicates that the contribution of GB segregation to ionic conductivity was important when GBs are present. Therefore, we must consider GB segregation of M_{Zr}' and $V_O^{\cdot\cdot}$ to control and improve ionic conductivity in polycrystalline materials.

In summary of our study, we quantitatively examined the contribution of GB segregation to ionic conduction. In order to control GB conductivity, it is important to consider the M_{Zr}' and $V_O^{\cdot\cdot}$ segregation behavior, which varies depending on dopant.

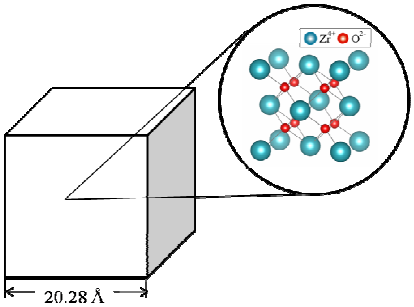

FIG.1. Model_SC: Single crystal

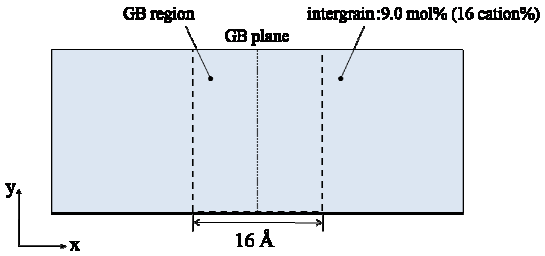

FIG.2. Model_RD: GB model; Overall radom

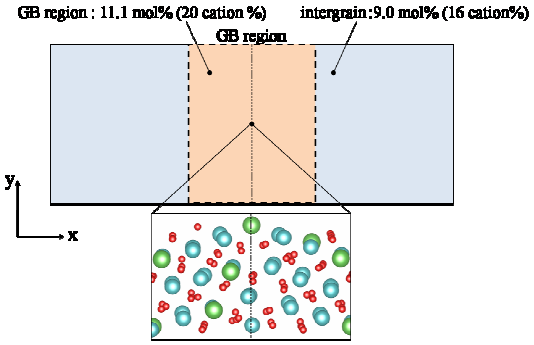

FIG.3. Model_GBR; GB region random model

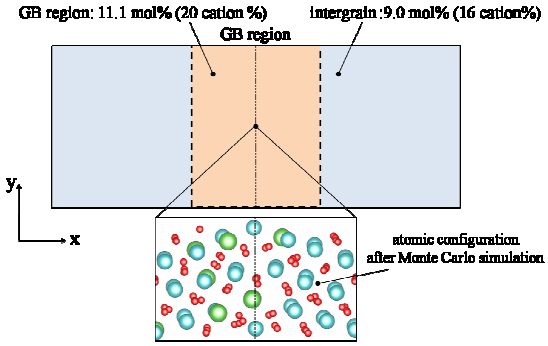

FIG.4. Model_GBS; GB segregation model

Reference

[1] M. Aoki et. al., *J. Am. Ceram. Soc.*, **79** [5] 1169-80 (1996)