Grain Boundary Structure Transformation and Reconstruction in Oxide Ceramics

Y. Ikuhara[1,2,3], Y.Sato[1,] and N.Shibata[1,]

[1]Institute of Engineering Innovation, The University of Tokyo, Tokyo, 113-8656, Japan
[2]Nanostructures Research Laboratory, Japan Fine Ceramics Center, Nagoya, 456-8587, Japan
[3]WPI-AIMR Research Center, Tohoku University, Sendai, 980-8577, Japan

Grain boundary (GB) atomic structures are dependent on the GB characters such as misorientation angle and GB planes. In addition, GB structures are also influenced by the segregated dopants and vacancies to form relaxed structure. It is therefore needed to investigate the distribution and the sites of vacancies and dopants segregated at GB, depending on the GB characters, to fully understand GB atomic structures, which are related to the material's properties. It has been also expected that GB structure transformation and reconstruction occur as a function of misorientation angle, but the detailed mechanism has not been well understand because there have been few systematic investigations to clarify the GB phenomena. In this study, GBs of CeO_2 were studied to clarify the role of oxygen vacancies to form stoichiometric and non-stoichiometric GBs [1,2], and GBs of ZnO were investigated to understand the GB transformation mechanism due to praseodymium (Pr) segregation [3].

It has been reported that GBs play an important role in the oxygen transport properties in CeO_2, which must be influenced by the vacancies introduced in GBs. Concerning ZnO, a small amount of Pr dopant is known to be effective to improve the varistic properties. We fabricated well-defined GB structures of CeO_2 and ZnO by bicrystal techniques as the model samples [1-3], and the behavior of the GB structure reconstruction due to vacancies and dopants are systematically investigated by combining aberration-corrected STEM, EELS and theoretical calculations. STEM observations were performed using JEM-2100F and ARM-200F (JEOL) equipped with CEOS Cs-corrector. EELS spectra were acquired in STEM mode by an Enfina spectrometer (Gatan Inc). For theoretical approach, static lattice and density functional theory (DFT) calculations were used complementary.

Fig.1(a) shows HAADF STEM image of Σ5(210)/[001] GB [1], in which the periodic structural units are shown. In the figure, (c) the most stable stoichiometric GB structure and (b) simulated STEM images based on the model (c) are shown. As can be seen, the experimental image is not consistent with the theoretical image. But, both images are found to be consistent, comparing (f) the theoretically obtained most stable non-stoichiometric GB structure, which includes oxygen vacancies, and (e) the corresponding simulated STEM images. It is therefore concluded that nonstoichiometric GB core structure with oxygen vacancies is considered to be the most suitable model for the experimentally observed Σ5 GB. On the other hand, Σ3 GB has the stoichiometric GB core structure [2], which was confirmed by comparing the STEM images and theoretically calculated atomic structures. These results indicates that Σ3 GB structure is stable without oxygen vacancies, and the GB reconstruction behavior strongly depends on the GB characters.

Fig.2 (a) shows (a) HAADF STEM image of the Pr-doped ZnO Σ13 GB, indicating that GB plane is parallel to (25$\bar{7}$0), and the zig-zag alignment of structural units (SUs) are formed. This SU is named as γ SU , comparing to the α and β SUs appeared in another GBs [3]. As can be seen in the figure, the Pr segregation sites form trimmer-like configuration. The dotted lines show a structural period, and set of circles denote the atomic arrangement in a single period. Fig.2 (b) shows the most stable atomic configuration obtained by the first-principles calculation. The structure contains zigzag-aligned two SUs per a single period. These SUs are categorized into SU γ, where three columns are occupied with Pr. The trimmer-like structure directs inversely for the neighboring SUs, resulting in the zigzag feature. Location of Pr is consistent with the location observed in the STEM image. It will be discussed that the structure of Pr-doped GBs has different structural sequence with the increase of θ. For smaller θ, Pr simply substitutes particular columns in SUs α and/or β without causing transition to SU γ. For higher θ, structure changes into SU γ. It can be said that GB structural transition occurs at proper θ degree for the [0001] symmetrical tilt GBs in ZnO..

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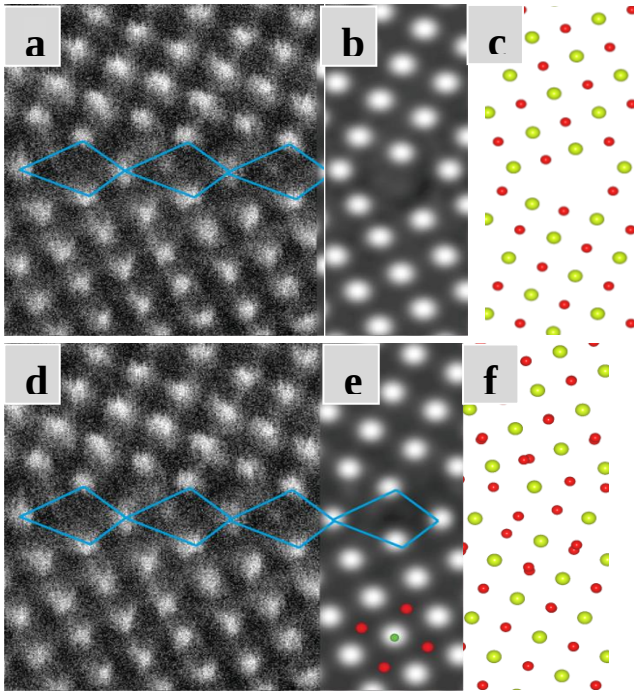

Fig.1: (a,d) HAADF STEM image for CeO_2 Σ5(210)/[001] GB.. (c, f) Most stable GB atomic structures calculated for stoichiometric and non-stoichiometric models, respectively. (b,e) Simulated STEM images for the corresponding theoretical models.

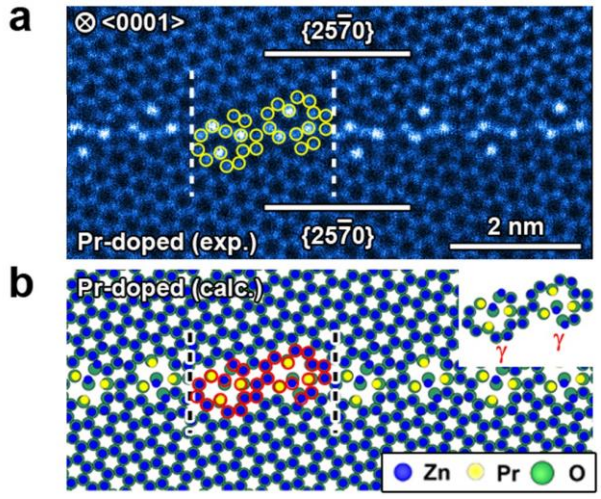

Fig.2: (a) HAADF STEM image of Pr-doped ZnO Σ13 GB and (b) the most stable atomic configuration obtained by the first-principles calculations. The dotted lines show a structural period, and set of circles denote the atomic arrangement in a single period. SUs (γ γ) are shown in the inset.