Properties of ceramics are strongly dependent on the grain boundaries (GBs) which have different atomic structures due to the disorder in periodicity. The grain boundary structures are also influenced by dopants and vacancies segregated at GBs, providing various functional properties, which cannot be observed in a perfect crystal. In order to control GB structures to improve the properties, we need to understand the relationships between GB characters, atomic structures and chemistry. It is considered that the formation of vacancies reconstructs the GB atomic structures, depending on the GB characters such as misorientation angle and GB plane. In addition, the segregated dopants also should play an crucial role to change the GB atomic structures, which is related to the GB structural transition.

In this study, well-defined GBs structures of CeO$_2$ and co-doped MgO and Al$_2$O$_3$, which are fabricated by the bicrystal techniques, are used as the model samples, and the behavior of the GB structure reconstruction due to vacancies and co-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.

CeO$_2$ has attracted much attention as electrolyte materials for solid oxide fuel cells. 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. Various types of GBs of CeO$_2$ were characterized by STEM, in which the periodic structural units are formed. In the case of $\Sigma 5$ GB, nonstoichiometric GB core structure with oxygen vacancies is considered to be the most suitable model for the experimentally observed $\Sigma 5$ GB. On the other hand, the $\Sigma 3$ GB has the stoichiometric GB core structure. According to the DFT calculations, the structural distortions at the $\Sigma 3$ GB are not as clear as those at the $\Sigma 5$ stoichiometric GB. These results suggest that the oxygen stoichiometry at the GBs does not only depend on the atmosphere but also on the GB atomic structure, which is closely related to the GB energies, dangling bonds and strain. Co-dopant systems with aliovalent dopants were also investigated by the same method. For the model GB with the co-dopants, Ca and Si doped Al$_2$O$_3$ and Ca and Ti doped MgO were are selected for the present investigation. It was found that the two different dopants form the periodic structures along the respective GBs to compensate the charge neutrality at the GBs to relax their atomic structures.

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