

Atomic Structure and the Oxygen Vacancy Formation in CeO₂ [100](210)Σ5 Grain Boundary

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A variety of macroscopic properties of ceramic materials are often affected by the characters of grain boundaries (GBs). Therefore, an understanding of the GB structures and related properties is of critical importance for materials developments and applications.

CeO₂ is a mixed ionic and electronic conductor and shows high oxygen ion conductivity when doped with lower valent cations, which makes this material a promising candidate for electrolyte in solid oxide fuel cells. It is well known that both oxygen ion and electronic conductivity are strongly influenced by the impurity segregation at the GBs [1] and the grain sizes [2], indicating that the GBs play an important role on the transport properties. To understand the properties due to the GBs, it is essential to clarify the atomic structures of the individual GBs. In this study, high-angle annular dark-field (HAADF) scanning transmission electron microscopy (STEM) observations, electron energy loss spectroscopy (EELS) measurements, and theoretical calculations were combined to reveal the atomic structures and defect formations at the GB of CeO₂.

We selected a (210)Σ5 GB with a common tilt axis of [100] as a model GB. Due to the difficulty in obtaining CeO₂ bicrystals, CeO₂ thin films were grown on cubic zirconia bicrystal substrates by a pulsed laser deposition technique. The cubic zirconia bicrystal containing a [100](210)Σ5 GB was fabricated by diffusion bonding of two single crystals at 1600 °C for 15h. Then, a CeO₂ thin film was deposited on the cubic zirconia bicrystal at 900 °C substrate temperature in oxygen partial pressure of 3.0×10^{-3} Pa. Out-of-plane and in-plane x-ray diffraction measurements confirmed that the thin film was epitaxially grown on the cubic zirconia bicrystal. Specimens for STEM observations were prepared by back thinning from the substrate side, including mechanical polishing, dimple gliding, and ion thinning. These specimens were observed using a JEM-2100F TEM/STEM microscope (JEOL Co. Ltd.) equipped with Cs-corrector (CEOS Co. Ltd.) and an Enfina EELS spectrometer (Gatan Inc.).

The atomic structures were modeled by the static lattice calculation with the GULP program code [3]. Buckingham-type two-body ionic potentials were employed with the potential parameters reported by Minervini et al. [4]. It was confirmed that the potential parameters can reproduce the experimental lattice constants, elastic modulus, and dielectric constants of CeO₂. In the simulations of CeO₂ GBs, we used a rectangular cell that contained two identical GBs. Here, we studied two kinds of GBs. One is stoichiometric GB, and the other is non-stoichiometric GB where two oxygen

vacancies are introduced at each GB in the supercell. To find the stable structure, three dimensional rigid body translations were systematically considered.

It is found that no amorphous layers or secondary phase are present at the GB of CeO₂ thin film on the YSZ bicrystal. In HAADF-STEM images, atomic columns of Ce are clearly observed even in the GB core region. Figure 1 compares stable stoichiometric (Fig. 1(a)) and non-stoichiometric (Fig. 1(b)) GB structures obtained by the theoretical calculations. The stable GB structures including the translation states strongly depend on the stoichiometry at the GBs. Comparing the Ce sublattices of the stable GB structures for the stoichiometric and non-stoichiometric models with the HAADF-STEM image, we found that the non-stoichiometric GB structure show better agreement with the experimental image. This indicates that oxygen vacancies are present at the CeO₂ GBs, and play an important role for the stable atomic GB structures.

References

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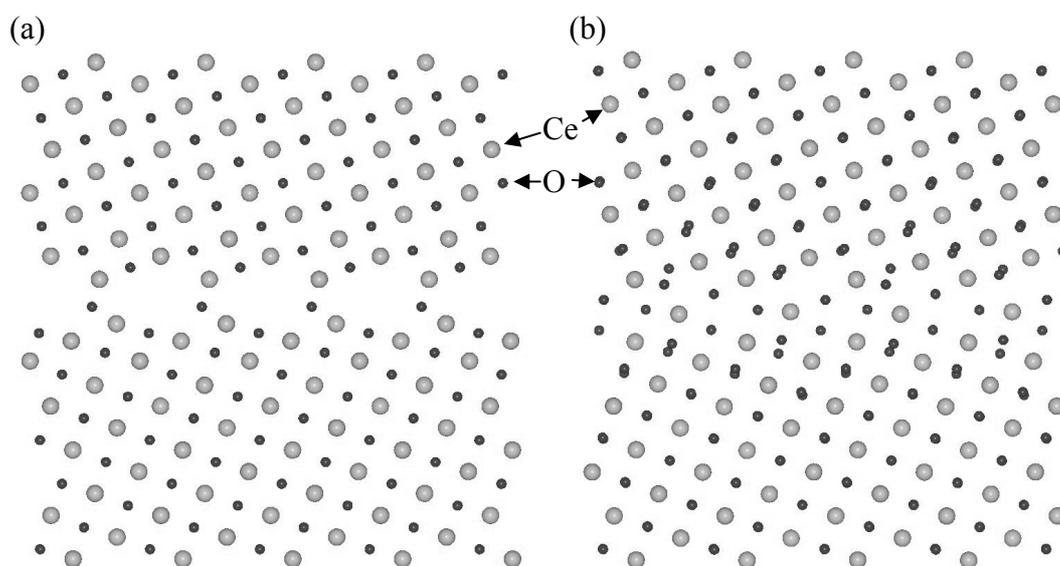


FIG. 1. Stable atomic structures of (a) stoichiometric and (b) non-stoichiometric $\Sigma 5$ CeO₂ GBs.