Investigation of cation migration in Gd-doped ceria

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The study of electronic ceramics has always been an important topic for decades. Fluorite-type AO_2 oxides are highly relevant material for energy conversion as a result of their mixed ionic-electronic conductivity, which is caused by doping. In contrast to the enthusiastic study of oxygen-ion transport, much less attention has been paid to cation diffusion in these materials, despite its importance for degradation phenomena.[1] Previous computational studies have shown that cations in nominally undoped and doped ceria tend to migrate along the <110> directions by means of vacancy migration.[2] Time-of-flight secondary ion mass spectrometry (ToF-SIMS) has been used to identify bulk and grain boundary diffusion of Hf in Gd-doped polycrystalline ceria and the corresponding activation enthalpies have been calculated.[3] However, the observation of the cation diffusion paths is still required, in order to explain the diffusion process in detail. In this contribution, we aim to study the cation diffusion in ceria and ceria-based materials. Transmission electron microscopy (TEM) and spectroscopy with high spatial resolution was employed to study the Hf diffusion in Gd doped ceria both ex situ and in situ. The influence of an external electric fields on the diffusion behavior is also studied.

Crystallized $(Hf, Zr)O_2$ (HZO) thin films of thickness between 10 nm and 30 nm were deposited onto the $Gd_{0.005}Ce_{1-n}O_{2-n/2}$ polycrystalline. Half of each sample was annealed in air at 1270 °C and 1325 °C for approximately 70 hours in air, while the other half remained un-annealed as a reference. Focused ion beam (FIB) milling was used to prepare TEM specimens with minimal surface damage and a uniform thickness, while conventional grinding and polishing were used to perform statistical measurements. An FEI Titan G^2 60-200 ChemiSTEM equipped with a spherical aberration corrector for the probe forming system was used to perform elemental mapping to identify the Hf distribution in the annealed samples. High-angle annular dark-field (HAADF) scanning TEM (STEM) images were also recorded, in order to provide information about the sample morphology and crystallinity. An average grain size of 7 μm was determined for both the reference and the annealed samples. After annealing, the HZO deposition layer fully degraded, and no phase transition of ceria was observed. With regard to bulk diffusion (Fig. 1a), the diffusion depth was observed to increase with annealing temperature that is related to the activation enthalpy and is irrelevant to the deposition thickness that is related to the diffusant concentration. Fast grain boundary diffusion along grain boundaries (Fig. 1b) to a depth of several μm was found to be much more probable for the samples that had been annealed at 1325°C. On-going in-situ experiments are focused on the observation of the emergence of Hf enrichment in different areas, particularly next to grain boundaries and on the grain surfaces.

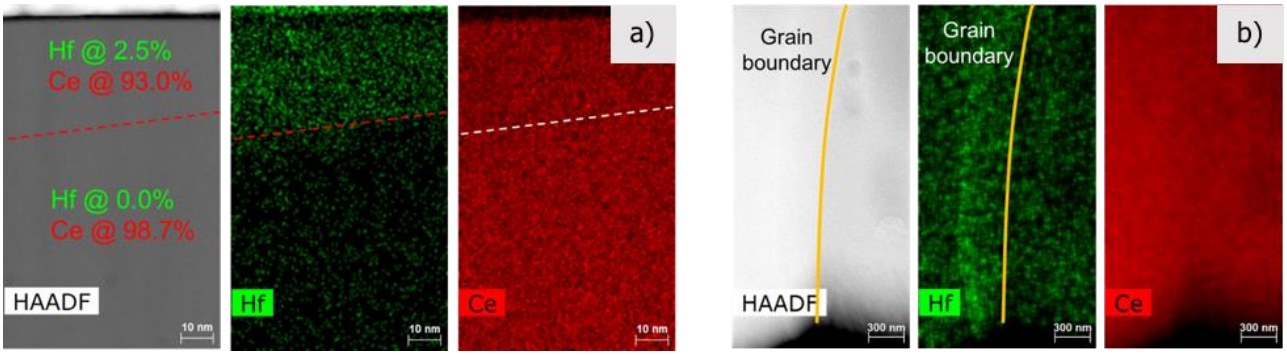

Figure 1(a) HAADF image corresponding elemental maps showing grain surface diffusion.(b) HAADF image and corresponding elemental maps showing diffusion along grain boundary.

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References

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