

## Cation transport studies by dopant (Sm, Gd) diffusion in polycrystalline CeO<sub>2</sub> substrates

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Doped ceria is a promising electrolyte material for solid oxide fuel cells (SOFC). Due to its good chemical stability regarding the reaction with (La,Sr)CoO<sub>3-δ</sub> cathode materials compared to ZrO<sub>2</sub>-based electrolytes, doped CeO<sub>2</sub> is used as buffer layer between ZrO<sub>2</sub> electrolytes and the cathode to enhance long-term SOFC stability. Nevertheless, cations in common cathodes (e.g. Sr) tend to penetrate polycrystalline CeO<sub>2</sub> diffusion barriers resulting in the formation of phases like strontium zirconate at the zirconia-ceria interface [1].

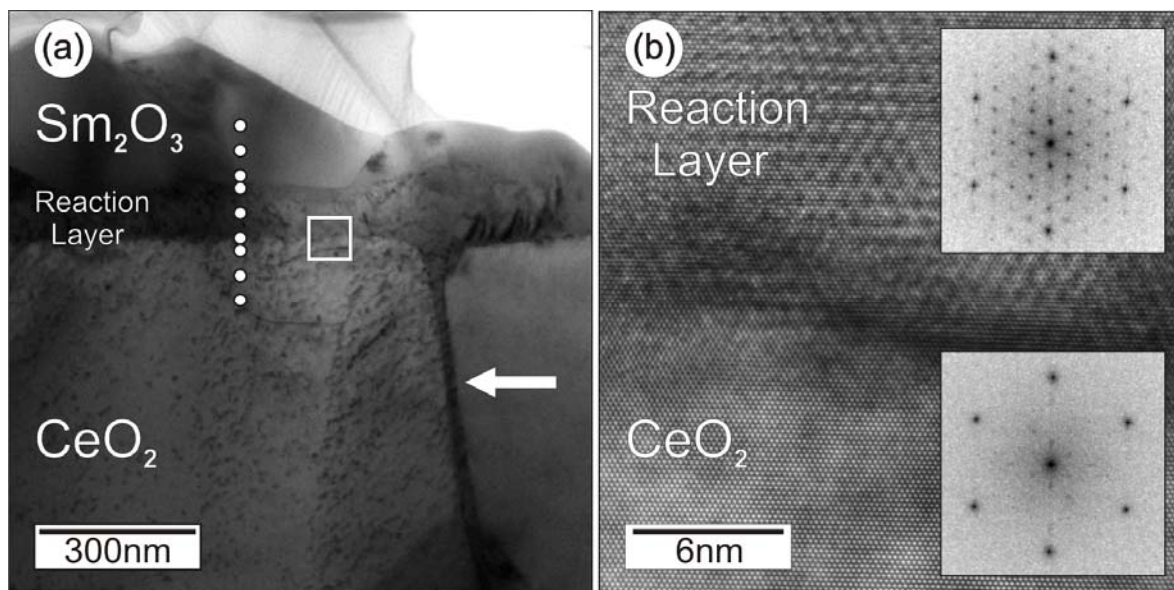
To systematically investigate a) cation bulk and grain-boundary diffusion in pure CeO<sub>2</sub> and b) the phase formation, donor thin films were deposited on polycrystalline CeO<sub>2</sub>. In the present study the diffusion of Sm and Gd from a dopant layer (Sm<sub>2</sub>O<sub>3</sub>, Gd<sub>2</sub>O<sub>3</sub>) was examined. The source layers with an initial thickness of about 150 nm were deposited by pulsed laser deposition (PLD). The specimens were annealed at temperatures in the range of 1000-1300 °C for 100 h under oxidizing Ar(0.8)/O<sub>2</sub>(0.2) atmosphere. To study solubility and diffusivity of the different cations, cross-section samples were investigated by means of high-resolution TEM (HRTEM) combined with energy-dispersive x-ray spectroscopy (EDXS).

The TEM bright-field image Fig. 1a shows an overview cross-section view of a specimen with a Sm<sub>2</sub>O<sub>3</sub> film, heat treated at 1170 °C for 100 h denoted as sample Sm1170. A grain boundary is marked by an arrow. The cap layer corresponds to the residue of the deposited Sm<sub>2</sub>O<sub>3</sub> dopant layer. The intermediate reaction layer (RL) of uniform thickness (~100 nm), which is independent of the local crystalline orientation of the substrate, can be clearly recognized below the dopant layer. It is also observed that the RL extends deeply into the substrate along the grain boundary.

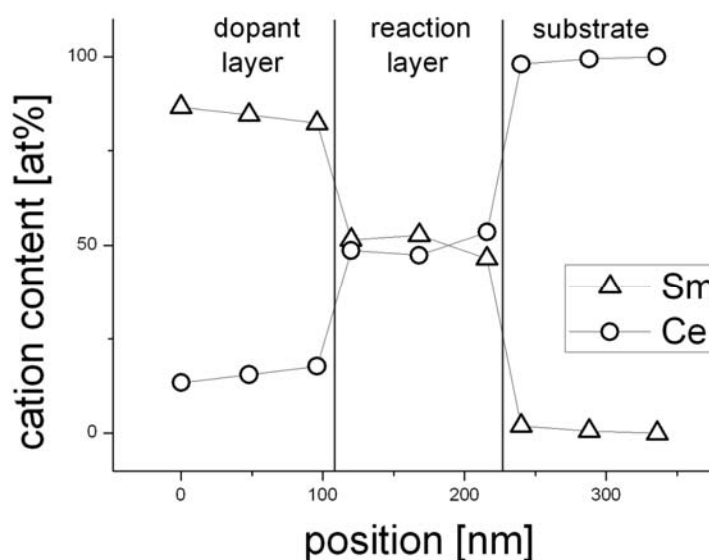
EDX spectra were taken across the RL (marked in Fig. 1a). The quantification of the Ce and Sm concentrations yielded a constant high Sm content of about 50 at% on the cationic sublattice in the RL (Fig. 2). A sharp concentration gradient was observed at both interfaces (donor film/RL, RL/CeO<sub>2</sub> substrate). The same holds for examinations at the grain-boundary RLs. HRTEM imaging of the interface between CeO<sub>2</sub> substrate and RL, as depicted in Fig. 1b, revealed the coherence between the substrate grain (oriented in [111]-zone axis) and the RL. The FFT of the lower region (pure CeO<sub>2</sub>) resulted in a pattern that exclusively shows reflections of the expected fluorite (F-type) structure, whereas the FFT of the RL exhibited additional reflections. Both FFTs are given in the insets of Fig. 1b. To analyze the structure of the RL, simulations were carried out on the basis of the cubic rare earth oxide (C-type) structure proposed by Grover et al. [2] for the Gd<sub>2</sub>O<sub>3</sub>-CeO<sub>2</sub> system. The simulations and experimental FFT agree well along several different zone axes suggesting that the RL layer consists of Sm<sub>0.5</sub>Ce<sub>0.5</sub>O<sub>2-δ</sub>.

Fig. 2 yields information on the phases at 1170 °C in the  $\text{CeO}_2\text{-Sm}_2\text{O}_3$  phase diagram. The constant composition of the  $\text{Sm}_{0.5}\text{Ce}_{0.5}\text{O}_{2-\delta}$  phase in the RL and steep concentration gradients indicate that the phase field of the  $\text{Sm}_{0.5}\text{Ce}_{0.5}\text{O}_{2-\delta}$  phase is rather narrow. Tentatively, we postulate a low solubility of Sm in  $\text{CeO}_2$  and vice versa although the effect of diffusivities has to be studied by carrying out annealing treatments at different temperatures. Fast diffusion occurs along the grain boundaries which also leads to the  $\text{Sm}_{0.5}\text{Ce}_{0.5}\text{O}_{2-\delta}$  phase.

1. N. Jordan et al., *Solid State Ionics* **179** (2008) p919.
2. V. Grover et al., *J. Appl. Crystallogr.* **36** (2003) p1082.
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**Figure 1.** (a) Bright-field image of Sm1170 with a grain boundary (arrow). The EDXS line scan is marked by white dots. The white square illustrates the position of the HRTEM image shown in (b) with calculated FFTs of the corresponding regions.



**Figure 2.** Cation concentrations across the reaction layer (position of line scan marked in Fig. 1a).