

Introduction

Ceria and ceria-based materials are used as technical ceramics in different technological fields due to their favorable material properties. Examples are the use as catalyst or carrier for metallic catalyst particles due to their catalytic interactions with small molecules (H, CO, O, NO) or as Mixed Ionic-Electronic Conductor (MIEC) in oxygen sensors. CeO_2 is also investigated for application in electrochromic thin-film applications, medicine, as inert matrix fuel in reactors, as well as in Solid Oxide Fuel Cells (SOFCs).

Doping ceria with different Rare Earth (RE) atoms, especially Gd and Sm, strongly influences the oxygen-ion conductivity. This allows to control the (generally high) oxygen-ion conductivity of GDC and SDC. The high oxygen-ion conductivity facilitates the application of GDC and SDC in SOFCs as anode, electrolyte, and as diffusion barrier between the commonly used Y_2O_3 -doped ZrO_2 (YDZ) electrolyte and Co-containing cathode layers.

Despite the high application potential of GDC and SDC, some basic materials properties are not well known. Oxygen-ion conductivities have been in detail studied in these materials, but few data are available on cation interdiffusion. Cation-interdiffusion coefficients and activation enthalpies for interdiffusion were up to now only derived from grain-growth experiments which can be strongly influenced by the formation of grain boundary phases or impurity segregation. The determined activation enthalpies range from 0.143 eV/atom to 9 eV/atom dependent on the used model. These findings motivate cation-interdiffusion studies on the basis of $\text{Gd}_2\text{O}_3/\text{CeO}_2$ and $\text{Sm}_2\text{O}_3/\text{CeO}_2$ diffusion couples which were performed for the first time in this work. The diffusion-couple geometry yields a well-established solution of the diffusion equation and allows straightforward evaluation of interdiffusion profiles.

Another aspect concerns the phase diagrams of GDC and SDC which are not well known for application-relevant temperatures below 1200 °C. $\text{Gd}_x\text{Ce}_{1-x}\text{O}_{2-x/2}$ and $\text{Sm}_x\text{Ce}_{1-x}\text{O}_{2-x/2}$ occur in different crystalline structures across the complete concentration range. GDC and SDC occur in the cubic fluorite phase at low and intermediate RE concentrations. The cubic bixbyite phase follows with increasing RE concentrations. Depending on the temperature the bixbyite structure or the monoclinic structure is stable at high RE concentrations. Possible miscibility gaps and a metastable cubic phase are still under debate, even at temperatures above 1200 °C. Hence, the investigation

of the phase formation at lower application-relevant temperatures is interesting from a basic-science and application-relevant point of view.

Electron microscopy is a viable tool to study phase evolution and interdiffusion processes on the nanoscale. TEM allows to determine the local crystalline structure in the samples by high-resolution imaging and electron diffraction. Using STEM combined with analytical techniques, different phases in the samples can be characterized in detail. The nm-scale resolution of the analytical measurements additionally enables the quantitative determination of interdiffusion coefficients from interdiffusion profiles obtained from diffusion couples.

The present work is divided into four main parts. In Chapter 1 some basic material properties of GDC and SDC are presented. Then the different crystal structures and phase stability in the $\text{Gd}_x\text{Ce}_{1-x}\text{O}_{2-x/2}$ and $\text{Sm}_x\text{Ce}_{1-x}\text{O}_{2-x/2}$ systems are reviewed in detail. This is followed by an introduction to binary diffusion couples and temperature dependence of diffusion coefficients. Chapter 2 gives an overview of the electron microscopical techniques used in this work and presents the employed instrumentation. Chapter 3 contains the results on the $\text{Gd}_x\text{Ce}_{1-x}\text{O}_{2-x/2}$ system which was studied in the temperature range from 986 °C to 1270 °C. The results of microstructural characterization and the measured concentration profiles for the $\text{Gd}_x\text{Ce}_{1-x}\text{O}_{2-x/2}$ system allow conclusions on the phase evolution and facilitates the determination of interdiffusion coefficients. Analogous results for the more complex $\text{Sm}_x\text{Ce}_{1-x}\text{O}_{2-x/2}$ system are presented in Chapter 4. This system was investigated in the temperature range between 987 °C to 1266 °C.

Electron Microscopical Investigation of Interdiffusion
and Phase Formation at Gd₂O₃/CeO₂- and
Sm₂O₃/CeO₂-Interfaces

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