

2 Experimental Techniques and Instrumentation

Methods and instruments used in this work are described in this chapter. Regarding TEM there are numerous techniques in addition to the basic functionality of imaging. The analytical techniques EDXS and EELS were used in combination with STEM to acquire interdiffusion profiles for evaluation. The two techniques are described in detail in the subsequent sections especially considering quantification of the experimental data. A basic overview of TEM is, for example, given in the books of Williams & Carter [133] and Reimer & Kohl [134]. SEM was used during the preparation process of the samples. The textbook by Reimer [135] explains SEM in detail.

2.1 Electron Microscopical Instrumentation

Microstructural characterization and HRTEM were conducted using two different transmission electron microscopes. The Philips CM200 FEG/ST microscope (now: FEI company, Hillsboro, Oregon, United States of America (USA)) was operated at 200 kV and is equipped with a Field Emission Gun (FEG) and a 4k×4k TemCam-F416 CMOS camera from TVIPS (Tietz Viedeo and Imaging Processing systems, Munich, Germany). The FEI Titan³ 80-300 microscope (FEI company) was operated at 300 kV and is equipped with an aberration corrector, for short C_s -corrector (CEOS – Corrected Electron Optical Systems GmbH, Heidelberg, Germany), in the imaging lens system. Single energy-dispersive X-ray spectra were collected using the NORAN Vantage system (Noran Instruments Inc., now: Thermo Fisher Scientific, Waltham, Massachusetts, USA) of the Philips CM200 FEG/ST microscope with a Ge X-ray detector and a probe diameter of about 2 nm. EDXS line scans were acquired utilizing the 30 mm EDAX Si(Li) X-ray detector with an ultra-thin window and an energy resolution of 136 eV (EDAX Inc., Mahwah, New Jersey, USA) in the FEI Titan³ 80-300 microscope. EELS was performed with the post-column Tridien 865 HR Gatan Imaging Filter (GIF) (Gatan Inc., Pleasanton, California, USA) of the FEI Titan³ 80-300 microscope. EELS spectra can be with an energy resolution of 0.7 eV and a total channel count of 2048. The GIF was

operated at a dispersion of 0.5 eV/channel for elemental quantification. SAED was performed on the Philips CM 200 FEG/ST microscope and the diffraction patterns were recorded on imaging plates from DITABIS (Digital Biomedical Imaging Systems AG, Pforzheim, Germany).

A LEO 1530 microscope (LEO Electron Microscopy Inc., now: Carl Zeiss NTS GmbH, Oberkochen, Germany) equipped with a FEG and a GEMINI® column was used for SEM.

Diffraction patterns were simulated with the software package Java Electron Microscopy Simulations (JEMS) version 3.3826U2009 by Stadelmann [136].

2.2 Transmission Electron Microscopy (TEM)

In TEM the sample is illuminated by a defocused electron beam which is transmitted through the sample and then used for imaging. The first transmission electron microscope of this type was built by Knoll and Ruska in 1932 [137]. It uses condensor lenses to produce the illuminating beam. A lens system below the sample is used to form the image with at least three lenses, i.e., an objective lens, an intermediate lens, and a projector lens. This arrangement can be used in two different modes – the imaging or the diffraction mode. They are selected by the excitation of the intermediate lens. It is either used to magnify the first intermediate image (imaging mode) or the diffraction pattern (diffraction mode) formed by the objective lens. The first intermediate image or the diffraction pattern is then further magnified by the projector lens onto an electron-sensitive scintillator and Charge-Coupled Device (CCD) camera which is used for detection.

The contrast in the final TEM image arises because of the scattering of the incident electrons by the specimen. Amplitude and phase of the electron wave can both be changed during its transit through the specimen and, thus, both can contribute to the image contrast. Hence, the fundamental distinction in TEM is between amplitude contrast and phase contrast. Both contrast types are normally involved in the image formation process. Usually, the imaging conditions are selected in a way that one contrast type dominates to be able to interpret the image accordingly.

Three different techniques used in this work are described in more detail. BFTEM and HRTEM are imaging techniques, whereas the diffraction mode is used for SAED. In-depth descriptions of these techniques are given in textbooks for TEM, e.g. [133, 134].

2.2.1 Bright-Field Transmission Electron Microscopy (BFTEM)

BFTEM is a method which is used to generate mass-thickness contrast or Bragg contrast. An aperture in the back focal plane is used to select only the un-diffracted electrons and exclude Bragg reflections from the image formation process. Mass-thickness contrast dominates the contrast in amorphous samples and crystalline samples only under kinematic excitation conditions. Bragg contrast dominates the contrast in crystalline materials. If mass-thickness contrast prevails, thicker sample areas or sample areas with higher mass (higher density or atomic number) scatter more electrons. Since scattered electrons do not contribute to the image, these sample areas appear darker than the surrounding area. If the imaging intensity is governed by Bragg contrast, the local intensity is determined by the excitation of Bragg reflections and the local sample thickness.

2.2.2 High-Resolution Transmission Electron Microscopy (HRTEM)

Phase contrast contributes significantly to image formation in HRTEM. The contrast arises due to coherent interference of contributions from at least two Bragg reflections. The interference pattern acquired by HRTEM reflects the periodicity of the crystal lattice (and is not a direct image of the crystal lattice). The resolution of transmission electron microscopes was limited by the spherical aberration of the lenses until the late 1990s. The groundbreaking development of a novel hexapole corrector by Rose and Haider for commercial microscopes made microscopes available with sub-Ångstrom resolution [138].

HRTEM requires the (crystalline) specimen to be oriented into a highly symmetrical (low-index) zone axis. Diffraction occurs and the atoms are arranged in columns parallel to the electron beam. A large objective aperture is used to select several Bragg beams which interfere and produce an interference pattern. This interference pattern is not a direct image of the atom positions and, therefore, cannot be readily interpreted. Intuitive interpretation in terms of atom positions is prevented by dynamic electron diffraction in the sample and the imaging process in the electron microscope. The influence of the microscope on the object wave function can be described by the contrast-transfer function. The contrast transfer function includes the phase distortion function

$$\chi(u) = \frac{2\pi}{\lambda_e} \left(C_s \frac{\lambda_e^4 u^4}{4} + \Delta f \frac{\lambda_e^2 u^2}{2} \right).$$

It depends on defocus Δf , spatial frequency u , the electron wavelength λ_e , and the spherical aberration coefficient of the objective lens C_s . The spherical aberration can be corrected in aberration-corrected transmission electron microscopes.

HRTEM imaging requires thin samples because inelastic electron scattering has to be avoided. If atomic structure determination is intended, the experimental HRTEM images must be compared to simulations taking into account the local sample thickness and objective lens defocus. It is also possible to calculate the Fourier-transform from the image (or parts of it) which are called diffractograms. Diffractograms are used in this work for structure determination by comparison with simulated diffraction patterns. However, it must be taken into account, that additional Bragg reflections may appear in diffractograms due to dynamic electron diffraction and nonlinear image formation.

2.2.3 Selected Area Electron Diffraction (SAED)

The crystal structure can be determined from diffraction patterns using SAED. SAED allows to select a sample area from which a diffraction pattern is acquired by inserting an aperture in the first intermediate image plane. The sample is illuminated by a parallel beam and the microscope is operated in diffraction mode. The diffraction pattern is acquired by the CCD camera or imaging plates with a higher dynamical range. The diffraction pattern depends on the crystal structure and the orientation of the specimen.

The information contained in a SAED pattern is interpreted on the basis of the Bragg condition

$$2d\sin\theta_b = n\lambda_e$$

which allows to extract the lattice plane distances. Size and symmetry of the unit cell determine the position of the Bragg reflections in the SAED pattern. The intensity of the reflections in the diffraction pattern depends on the structure factor and the lattice amplitude. Size and symmetry of the unit cell determines the position of the reflections in the diffraction pattern. The structure factor determines the occurrence and intensity of reflections in kinematical diffraction which only applies if the intensity of the Bragg reflections is low in comparison to the undiffracted beam. The crystal structure is determined by orienting the specimen in different low-index zone axes, indexing the observed reflections, and comparing the result to simulated diffraction patterns.

Usually, dynamic electron diffraction has to be taken into consideration. Multiple scattering occurs with increasing sample thickness which leads to the appearance of kinematically forbidden reflections. In addition to dynamical

effects, the number of inelastically scattered electrons increases with thickness. A reasonable method to reduce these effects is the selection of thin sample areas.

2.3 Scanning Transmission Electron Microscopy (STEM) and Beam Broadening

In STEM the sample is not illuminated by a broad beam as in conventional TEM. Instead a small probe is formed by focusing the electron beam to a small diameter and the sample is scanned sequentially. The signal of the scattered electrons transmitted through the sample is detected at every position. In a subsequent step the detected electron intensity from the scanned positions are assembled to an image of the sample where the local electron intensity determines the brightness of the corresponding pixel. The electrons are detected by different detectors depending on their scattering angle. The first scanning transmission electron microscope based on this functional principle was constructed by von Ardenne in 1938 [139, 140]. Usually, nowadays three different classes of detectors are distinguished. A bright-field detector is used for small scattering angles. Electrons scattered in larger angles are collected by annular dark-field detectors, where the largest scattering angles are covered by the High-Angle Annular Dark-Field (HAADF) detector. Due to the strong dependence of the total cross section for the scattering of electrons on the atomic number of the scatterer (here: the sample), imaging with strong material contrast is possible in the HAADF STEM mode where contribution of coherent Bragg diffraction can be neglected. Further detail on STEM imaging are given by Pennycook and Nellist [141].

In this work the contrast of STEM images was not evaluated directly. STEM imaging was mainly used to locate the interface between the thin film and the substrate. This allowed to acquire EDXS and EELS line scans across the interface using an electron probe with a diameter < 1 nm (spot size 6 in the FEI Titan³ 80-300 microscope [142]). However, beam broadening due to the electrons interacting with the specimen has to be taken into consideration in addition to the probe size itself which limits the spatial resolution of the composition analysis. The amount that the beam spreads on its way through the specimen can be approximated by the following formula [143] under the assumption that the electron undergoes only one elastic scattering event:

$$b = 8 \cdot 10^{-12} \frac{Z}{E_0} (N_V)^{\frac{1}{2}} t_S^{\frac{3}{2}} \quad (2.1)$$

Here b is the beam spread in nm, Z the atomic number, E_0 the primary electron energy in keV, N_V the number of atoms/m³, and t_S the sample thick-

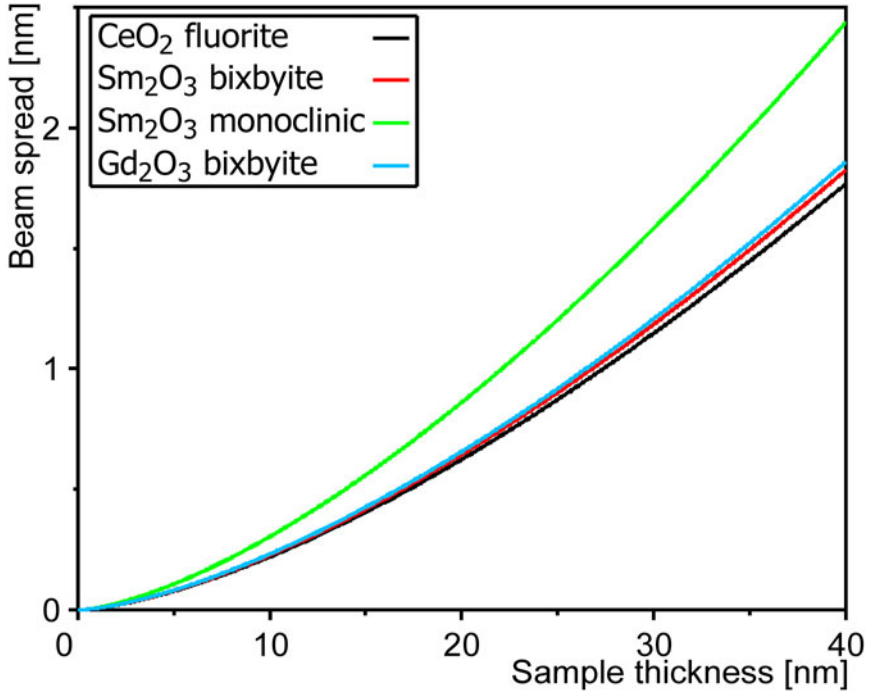


Figure 2.1: Beamsread calculated according to Eq. 2.1 for CeO_2 , Gd_2O_3 , and Sm_2O_3 with material parameters listed in Tab. 2.1.

ness. The mean atomic numbers $\bar{Z}$ of the different investigated materials were used to calculate the beam spread. The primary electron energy is 300 keV. The constant parameters $\bar{Z}$ and N_V of Eq. 2.1 are listed for CeO_2 , Gd_2O_3 , and Sm_2O_3 (with different crystalline structures) in Tab. 2.1.

A plot of the beam spread up to a sample thickness of 40 nm is shown in Fig. 2.1. The maximum beam spread is clearly expected for monoclinic Sm_2O_3 . The beam spread of the mixed systems $\text{Gd}_x\text{Ce}_{1-x}\text{O}_{2-x/2}$ and $\text{Sm}_x\text{Ce}_{1-x}\text{O}_{2-x/2}$ with bixbyite structure correspond approximately to the beam spread of the pure materials (CeO_2 , Gd_2O_3 and Sm_2O_3) with fluorite and bixbyite structure. A maximum local sample thickness of 38 nm is determined in Chapter 2.5.1 for all investigations which lead to quantitative evaluations of interdiffusion coefficients. This thickness yields a beam spread of 2.25 nm for monoclinic Sm_2O_3 and about 1.65 nm for the other structures.

2.4 Quantitative Energy-Dispersive X-ray Spectroscopy (EDXS)

The idea of using X-rays for elemental analysis in electron-beam instruments was first described by Hillier and Baker in 1944 [144]. The outstanding dissertation by Castaing [145] was devoted to the construction of the required instrumentation. In this work the Cliff-Lorimer method was used for quantification of the EDXS spectra [146]. This ratio technique developed by Cliff and Lorimer in 1975 relates the elemental concentrations of different elements and the element characteristic X-ray intensity by the following equation:

$$\frac{C_A}{C_B} = k_{A,B} \frac{I_A}{I_B} \quad (2.2)$$

Here C_A and C_B are the concentrations of element A and element B and I_A and I_B the peak intensities of the chosen characteristic X-ray line of element A and element B. Additionally the sum of the concentrations of the elements is assumed to constitute 100 % of the sample, meaning

$$C_A + C_B = 100\% \quad (2.3)$$

The Cliff-Lorimer factor $k_{A,B}$ is a sensitivity factor which depends on the characteristic X-ray lines considered for the investigation, the experimental setup, and the elements involved. The FEI TEM Imaging and Analysis (TIA) software suite (version 4.3 build 904) used for EDXS quantification supplies a database of $k_{A,B}$ factors for quantitative investigations. A consistency check of the available $k_{A,B}$ factors was made in this thesis which involves EELS as described in the respective Chapter 2.5.

The L_α – and L_β – X-ray-emission lines of Ce, Gd and Sm, which were used for quantification, are tabulated in Tab. 2.2. The values of the X-ray energies are from Bearden [147]. The emission lines of Ce and Gd do not overlap, and the $L_{\alpha 1}$ and $L_{\alpha 2}$ lines of Ce and Sm are also clearly separated. However, there

Table 2.1: Constant parameters $\bar{Z}$, N_V , and crystal structures of different materials.

material	crystal structure	space group	$\bar{Z}$	N_V [atoms/m ³]
CeO ₂	fluorite	Fm $\bar{3}$ m	30	$7.62078951379363 \cdot 10^{28}$
Sm ₂ O ₃	bixbyite	Ia $\bar{3}$	34.4	$6.17746784048851 \cdot 10^{28}$
Sm ₂ O ₃	monoclinic	C2/m	34.4	$1.10154090324473 \cdot 10^{29}$
Gd ₂ O ₃	bixbyite	Ia $\bar{3}$	35.2	$6.12001911107205 \cdot 10^{28}$

Table 2.2: X-ray emission lines of Ce, Gd, and Sm used for EDXS quantification

X-ray energy [keV]	Ce	Gd	Sm
4.8230	$L_{\alpha 2}$		
4.8402	$L_{\alpha 1}$		
5.2622	$L_{\beta 1}$		
5.2765	$L_{\beta 4}$		
5.3651	$L_{\beta 3}$		
5.6090			$L_{\alpha 2}$
5.6134	$L_{\beta 2}$		
5.6361			$L_{\alpha 1}$
6.0250		$L_{\alpha 2}$	
6.0572		$L_{\alpha 1}$	
6.1960			$L_{\beta 4}$
6.2051			$L_{\beta 1}$
6.6871		$L_{\beta 4}$	
6.7132		$L_{\beta 1}$	

is an overlap between the Sm- L_{α} emission lines and the Ce- $L_{\beta 2}$ emission line. This can be corrected for because the known relative intensity of the Ce- $L_{\beta 2}$ is 21 % [148].

Absorption and secondary fluorescence of X-rays in the samples may affect quantification. Photon mass absorption was first investigated by Bouguer [149] and in more depth by Lambert [150]. The phenomenological Beer-Lambert law is shown here in the form which is used when discussing material-specific mass attenuation coefficients (for example by Hubbell [151]):

$$\frac{I_{att}}{I_{inc}} = \exp\left(-\frac{\mu}{\rho}l\right) \quad (2.4)$$

The incident intensity of photons I_{inc} is attenuated to the intensity I_{att} in passing through a layer with mass-per-unit area or area density $l = \rho t_l$. t_l is the layer thickness and ρ the density of the layer material. The process of attenuation is dependent on the material- and energy-dependent attenuation coefficient μ . The mass attenuation coefficient is given by $\frac{\mu}{\rho}$. The mass attenuation coefficient is the weighted sum of the atomic constituents or homogeneous mixtures and compounds with

$$\frac{\mu}{\rho} = \sum_i w_i \left(\frac{\mu}{\rho} \right)_i, \quad (2.5)$$

where w_i is the fraction by weight of the i th atomic constituent [152]. Eq. 2.5 means that the compound with the maximum mass attenuation coefficient in the relevant X-ray energy range between 4.8 kV and 6.8 kV (as listed in Tab. 2.2) limits the thickness of the sample regarding absorption and secondary fluorescence. The database specialized on crystallography and XRD by Chantler [153, 154] provides the maximum value of $\left(\frac{\mu}{\rho} \right)_{Ce,max} = 504 \text{ cm}^2\text{g}^{-1}$ for CeO_2 in the given energy range. The database is also available online in convenient form [155]. The mass attenuation coefficients of Gd_2O_3 and Sm_2O_3 are lower in this energy range and, thus, also of the compound systems $\text{Gd}_x\text{Ce}_{1-x}\text{O}_{2-x/2}$ and $\text{Sm}_x\text{Ce}_{1-x}\text{O}_{2-x/2}$. $\left(\frac{\mu}{\rho} \right)_{Ce,max}$ allows to calculate the thickness for an absorption of 1 % of the X-ray intensity. This occurs at a TEM sample thickness of about 60 nm. The thickness of the investigated samples is estimated to be lower than 38 nm (c.f. Chapter 2.5). Hence, absorption can be neglected for quantitative EDXS analyses.

Quantitative composition analysis was performed with the TIA software. To remove the background from the EDXS spectra a 5th order polynomial was fitted to the signal in chosen energy windows between the X-ray lines. This polynomial was used to extrapolate the background signal under the characteristic X-ray peaks and to subtract the background from the signal. Gaussian curves were fitted standard-less to the characteristic peaks of the L_{α} - and L_{β} -lines of the background corrected data to obtain the intensity (counts) of the X-ray lines. This fit was reiterated until the fit parameters converged to the same values for subsequent iterations. The cation concentrations were evaluated from the determined intensities using the $k_{A,B}$ factors implemented in the TIA software. Since these factors yield compositions in weight percent, all determined concentrations were converted to atomic percent (at%).

The complete concentration data presented in this study refers to cation concentration normalized to 100 at% as given in Eq. 2.3. The concentration of O-atoms on the anion sublattice is not evaluated as quantification of light elements is prone to introduce large errors owing to the low X-ray yield of light elements. The systematic error of the cation concentrations stems from inaccuracies in peak fitting and background subtraction as well as absorption effects. Also the preparation process including Ar^+ -ion milling may introduce measurement artifacts. In general the total systematic error of the cation concentrations is estimated to be ± 3 at% for the complete data shown in this work. The statistic error is assessed by multiple measurements of diffusion profiles at different

sample positions and calculation of the standard deviation of the determined values. The total error is given together with the corresponding data in the following.

2.5 Electron Energy Loss Spectroscopy (EELS)

EELS is a technique which can be used for analysis of several different material properties in TEM. To this purpose the energy distribution of electrons transmitted through the sample is measured by a magnetic-prism spectrometer. These electrons may have undergone inelastic scattering (losing energy). The energy-loss events yield detailed information about the chemical composition of the specimen, the sample thickness, and the electronic structure of the specimen atoms including, amongst others, the valence state, the dielectric response, and the free-electron density. First measurements of the kinetic energy of electron utilizing a magnetic spectrometer were performed with reflected electrons by Rudberg [156]. Ruthemann [157] later used electrons transmitted through a thin film to measure low-loss spectra. The first instrument to achieve elemental analysis was constructed by Hillier and Baker [144]. An introduction to EELS can be found in the book by Williams and Carter [133]. Methods for thickness determination and composition analysis are presented in detail by Egerton [158] and Brydson [159]. A fine overview on instrumentation and reference spectra is found in the textbook edited by Ahn [160].

The basic component in all EELS and energy-filtering systems is the magnetic prism. It produces the spatial separation of the electrons according to their energy. The magnetic spectrometer in modern transmission electron microscopes is implemented in two different ways – either as an in-column filter or as a post-column spectrometer. Both allow operation in spectroscopic mode with parallel acquisition of the complete energy-loss spectra (Parallel-Collection Electron Energy Loss Spectroscopy (PEELS)) or in imaging mode which allows the acquisition of energy-filtered images. An in-column filter is passed by all electrons during microscope operation, because it is incorporated in the microscope column in the optical path. Aberrations may be introduced in the imaging system by the lens properties of this kind of spectrometer and image artifacts will also be present for unfiltered applications. The main advantages of in-column filters are high count rates for energy-filtered imaging and the possibility of filtered images and diffraction patterns in all imaging planes of the microscope. Post-column spectrometers are attached as an additional piece of equipment after the viewing screen and/or CCD camera. No aberrations are created in the beam path before entry into the GIF. In this work a post-column spectrometer was used to acquire electron energy-loss spectra.

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

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