Complex Oxide Thin Films: Pyrochlore, Defect Fluorite and Perovskite

Model Systems for Structural, Spectroscopic and Catalytic Studies

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Abstract

Well-ordered thin films of different defect fluorite and perovskite materials, namely lanthanum zirconate ($\text{La}_2\text{Zr}_2\text{O}_7$), cerium zirconate ($\text{Ce}_2\text{Zr}_2\text{O}_7$), lanthanum cerate ($\text{La}_2\text{Ce}_2\text{O}_7$) and lanthanum strontium ferrite ($\text{La}_{0.4}\text{Sr}_{0.6}\text{FeO}_3$), have been prepared by sputtering the respective powder targets onto vacuum-cleaved $\text{NaCl}(001)$ single crystal facets. Characterization specifically also includes the sophisticated preparation of the initial target materials. For the defect fluorite materials, the target materials are the respective pyrochlore compounds, which reproducibly transform to the respective defect fluorite structures upon sputtering. At template temperatures of around 573 K, well-crystallized epitaxial thin films of the defect fluorite compounds $\text{La}_2\text{Zr}_2\text{O}_7$ and $\text{Ce}_2\text{Zr}_2\text{O}_7$ result, whereas for the perovskite compound post-annealing procedures at 973 K in air are necessary to obtain epitaxial ordering of orthorhombic structures. Epitaxial relations for the well-ordered defect fluorite thin films are determined to be $\text{La}_2\text{Zr}_2\text{O}_7(001)//\text{NaCl}(001)$ and $\text{Ce}_2\text{Zr}_2\text{O}_7(001)//\text{NaCl}(001)$, respectively. Structural and spectroscopic characterization of the films by (high-resolution) electron microscopy (HR-TEM), selected-area electron diffraction (SAED) and depth-profiling X-ray photoelectron spectroscopy (XPS) reveal that the structures and compositions of the initial target materials are well-preserved during the sputtering process. Following this preparation routine, access to well-ordered thin films of complex oxide materials with defined stoichiometry is therefore granted, which can subsequently be used as model systems for studies of their material's or catalytic properties, as presented for simpler systems earlier. As a primary example, we show that for the defect fluorite thin films of $\text{Ce}_2\text{Zr}_2\text{O}_7$ the defect fluorite-pyrochlore phase transformation can be observed at around 1123 K as detected by *in situ* electron diffraction.

1. Introduction

Complex oxide materials have evoked recent interest in a number of research fields, especially in catalytic applications. As for the latter, usage in solid oxide fuel cell technology is widespread, owing to their generally beneficial physicochemical properties, such as high thermal stability, resistance against sintering or pronounced catalytic activity through a vital oxide redox chemistry. Many systems are employed, including, but not being limited to, fluorite, perovskite, spinel or pyrochlore phases. [1-27]

Prominent examples of fluorite structures are cubic ZrO_2 or CeO_2 . If these species are doped with trivalent ions, they tend to exhibit a high ionic conductivity of oxygen anions because of oxygen vacancies formed as a result of the charge deficiency caused by the substitution. Because of the presence of vacancies, these structures are often referred to as defect fluorites (even though they do not differ in structure from fluorites) and comprise a large class of technically relevant oxides, such as yttria-stabilized zirconia (YSZ). The latter is one of the most-used solid electrolytes with applications in solid oxide fuel cells (SOFCs) or chemical sensors. Structurally, these defect fluorites (space group Fm-3m , corresponding to the CaF_2 structure) can be regarded as a solid solution of the stabilizing oxide in the fluorite species. For instance, YSZ is a solid solution of Y_2O_3 in ZrO_2 , and gadolinia-doped ceria is a solution of Gd_2O_3 in CeO_2 . These structures can comprise a large range of compositions.

In the doped fluorite phase diagrams, various ordered structures exist, depending on the ionic radii of the constituents, such as the δ -phase ($\text{A}_3\text{B}_4\text{O}_7$) or pyrochlores ($\text{A}_2\text{B}_2\text{O}_7$). The latter can be viewed as a $2 \times 2 \times 2$ supercell of the defect fluorite structure (space group Fd-3m), with the A- and B-ions, as well as the oxygen vacancies, being ordered (in contrast to the stochastic distribution in the defect fluorite case). In this ternary oxide compound, which crystallographically can be denoted as $\text{A}_2\text{B}_2\text{O}_6\text{O}'$, A (a trivalent ion) is 8-fold coordinated (in edge-sharing $[\text{AO}_6\text{O}'_2]$ scalenohedra), while B (being in the +IV oxidation state) forms

trigonal antiprisms $[\text{BO}_6]$. These $[\text{BO}_6]$ polyhedra are connected via corner-sharing networks, in-between which $[\text{O}'\text{A}_4]$ tetrahedra are intercalated.[1]

Pyrochlores encompass a particular broad range of physico-chemical and electronic applications, ranging from catalysis,[2–5] ionic conductivity,[6–8] metallic oxides,[9] thermal barrier coatings,[10] superconductors,[11] to spin glasses and spin ices.[12] The reason for this behavior can be tracked down to the wide range of compositions and dopant materials that can be accommodated by the structure. The properties of the materials are largely determined by the smaller ion B, which exhibits the stronger metal-oxygen bond (because of the lower B-O distance as compared to A-O).[1]

Like defect fluorites, pyrochlores can be ionic conductors.[13] Different oxide ion diffusion capabilities between those two structures can occur because of their different ordering. Hence, also differences in *e.g.* the catalytic behavior of defect fluorite and pyrochlore compounds result.[4] This is of importance as the two phases can undergo phase transformations: phase transitions from defect fluorites of suitable composition can occur at elevated temperatures to allow for the re-arrangement of the ions,[14] and pyrochlores have a limited thermal stability and tend to undergo an order-disorder transition.

A similar discussion also holds for the respective perovskite compounds, a materials class with the general sum formula ABX_3 (A=large cation, B=small cation, X=oxide or halogenide anion). These ternary oxides usually crystallize in a cubic structure,[15] but symmetry reduction to orthorhombic,[16] rhombohedral,[17] or tetragonal structures readily occurs.[18] Of the vast amount of possible compounds and structures, iron-containing systems, such as *e.g.* lanthanum strontium ferrite ($\text{La}_{0.6}\text{Sr}_{0.4}\text{FeO}_3$, LSF), are particularly promising for applications in solid oxide fuel cells due to their high electric and ionic conductivity, as well as pronounced redox chemistry.[19-23]

While the bulk physico-chemical properties of these classes of materials are already well-understood, the characterization as thin films is by far less developed. This is a particular pity, as *e.g.* the solid oxide fuel cell technology aims at reducing the size dimensions of the cells by formation of μm -thick entities to lower operating temperatures and increase both the technological and cost efficiency.[24–27] Preparation on NaCl (001) single crystal facets would then also allow to gain access to model systems of the aforementioned class of materials. Such model systems are an indispensable tool in catalysis and material science, as the usually at least well-defined, but often epitaxially grown self-supported films allow to infer mechanistic details or study the principles of relevant processes (*e.g.* phase transformations in materials) much more sophisticated than by using less-defined entities.[27–29]

The aim of the presented study, hence, is to discuss the preparation and subsequent characterization of such complex oxide model thin film systems using exemplary structures from three important material classes: pyrochlore, defect fluorite and perovskite. The choice of materials is mainly fueled by their technological and catalytic importance. As examples for pyrochlores and defect-fluorites, lanthanum and cerium zirconate, $\text{La}_2\text{Zr}_2\text{O}_7$, $\text{Ce}_2\text{Zr}_2\text{O}_7$, as well as lanthanum cerate, $\text{La}_2\text{Ce}_2\text{O}_7$, [30] and the perovskite material lanthanum strontium ferrite, $\text{La}_{0.6}\text{Sr}_{0.4}\text{O}_3$, have been selected. $\text{La}_2\text{Zr}_2\text{O}_7$ is thermally extraordinarily stable, sinter-resistant and exhibits a low thermal conductivity, high thermal expansion coefficients, ionic conductivity and promising catalytic and fluorescence properties. It is, however, also formed as intermediate layer between the electrolyte and perovskite electrodes in solid oxide fuel cells, where it degrades the cell performance.[31,32] $\text{Ce}_2\text{Zr}_2\text{O}_7$, on the other hand, is a catalyst support for, *e.g.*, steam reforming of methane (when loaded with Ni).[4] Defect fluorite $\text{La}_2\text{Ce}_2\text{O}_7$, not crystallizing in a pyrochlore structure due to the unfavourable ratio of the ionic radii, exhibits interesting proton conducting properties and can also be employed in solid

oxide fuel cells.[33] Bulk $\text{La}_{0.6}\text{Sr}_{0.4}\text{FeO}_3$ is an already intensively studied material,[34,35] and therefore serves as a particularly worthwhile material for comparison of thin film and bulk properties. For preparation, DC sputtering from respective powder target materials has been employed. This pathway for the pyrochlore thin films specifically also included the preparation of suitable target materials following glycine-nitrate auto-combustion or co-precipitation pathways, with glycine as both fuel and chelating agent in the former case. For ease of preparation, we take the advantage from starting from pyrochlore target materials, which already have the desired composition.

2. Experimental

2.1. Target materials preparation

For the LSF thin films, commercially available LSF powder (Sigma Aldrich) was employed, which was pressed into a pellet at a force of 20 kN and was subsequently mounted in our self-built direct-current ion beam sputter source, as described in [28]. This source consists of a thoriated tungsten filament, which is used to emit electrons. These are subsequently accelerated towards a conical cage (kept at about +250 V), within which the Ar (in the pressure range of 10^{-5} to 10^{-4} mbar) is ionized. The target itself is kept at -2000 V and the Ar^+ ions are accelerated towards it.

For $\text{La}_2\text{Zr}_2\text{O}_7$, equimolar amounts (3.5 mmol) of $\text{ZrOCl}_2 \cdot 8\text{H}_2\text{O}$ and $\text{La}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ were dissolved in HNO_3 conc. and mixed under gentle stirring. A more-than-five-fold molar excess of glycine was added directly as solid and subsequently stirred for 15 min. at 333 K. The resulting solution was gently dried overnight (12 h) to induce the complexation process. Afterwards, the resulting mass was rapidly heated above its ignition temperature of approximately 523 K. The combustion remnants were collected, ground, homogenized and heated in an Al_2O_3 crucible in air at 1273 K.

To prepare $\text{Ce}_2\text{Zr}_2\text{O}_7$, a slightly modified variant of the synthesis route as used for lanthanum zirconate was followed, incorporating a final reduction step described by Tada *et al.* for their co-precipitation synthesis.[4] CeO_2 was dissolved in a mixture of HNO_3 conc. and H_2O_2 under heating. An equimolar amount of $\text{ZrOCl}_2 \cdot 8\text{H}_2\text{O}$ (dissolved in HNO_3 and pre-heated to remove HCl) is added to the cerium-containing solution. To this mixture, glycine is added again (with the same molar ratio as in the lanthanum zirconate synthesis). After combustion, the product is calcined in air at 1273 K, which results in a yellowish powder. Reduction in flowing CO at 1273 K (1 ml s^{-1}) for 12 hours yields the black-coloured pyrochlore product.

$\text{La}_2\text{Ce}_2\text{O}_7$ is prepared by a different protocol, namely co-precipitation: CeO_2 is dissolved as described above, and an equimolar solution of $\text{La}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$, which was further acidified by nitric acid, is added to that solution under heating to 333 K. Subsequently, ammonia was added drop-wise to this solution until a pH of 10–11 is reached. The white precipitate is again filtrated and calcined at 1273 K, resulting in a white-coloured powder.

The resulting structures were verified by X-ray diffraction (XRD) and were assigned to the respective pyrochlore structures due to the presence of their characteristic reflexes (*e.g.* (111) or (311), see Figure 1 for $\text{La}_2\text{Zr}_2\text{O}_7$ and $\text{Ce}_2\text{Zr}_2\text{O}_7$) or to the fluorite structure due to the lack thereof (Figure 1 - $\text{La}_2\text{Ce}_2\text{O}_7$). Chemical composition analyses by X-ray photoelectron spectroscopy (XPS) reveals only the expected elements for both the powder and the thin film, with all other impurity elements (apart from adventitious carbon) well below the detection limit of the spectrometer.

2.2. Thin Film Deposition

Thin film preparation has been carried out using an already well-described dedicated modular high-vacuum apparatus (with a base pressure of 6×10^{-7} mbar). The sputter deposition is carried out using a home-built direct current ion beam sputter gun discussed in detail

elsewhere.[28,36] This source has the advantage of producing more nanoparticulate thin films as compared to the columnar growth usually obtained with magnetron sputtering, where higher pressures are used.[28,29] This more layered growth is desirable for modelling SOFC electrodes that require a large degree of porosity. Furthermore, the low Ar pressures used with this source (in the 10^{-5} mbar range, see below) cause a low deposition rate (approximately 2 nm h^{-1}) facilitates a large degree of ordering in the films. To prepare the targets (10 mm in diameter and 1 mm in thickness), the respective powder materials are pressed onto a 0.3 mm diameter tantalum spiral wire support (using a press force of around 20 kN) to partly overcome the low electronic conductivity of the powder materials, which is subsequently mounted in the sputter source (at the other end of the wire, approximately 5 mm away from the target).[28] The deposition is carried out in an Ar background pressure of 8×10^{-5} mbar using Ar ions of 2 keV. As substrates, NaCl(001) single crystals are employed, which are heated to 573 K. The resulting films are floated off in distilled water and collected using TEM gold grids. For the XPS measurements, Si(111) wafers are used as substrates (573 K).

2.3. Structural characterization

X-ray diffraction measurements are carried out on a Stadi P (STOE & Cie GmbH) spectrometer in transmission geometry, including a MYTHEN2 DCS4 detector system using Mo $K_{\alpha 1}$ radiation ($0.7093 \text{ \AA}$) and a curved Ge(111) monochromator crystal. Diffractograms are acquired in a 2θ range between $2-50^\circ$ using a step size of 0.6° . Analysis of the data was performed using the WinX^{POW} software. Phase analysis was based on references from the ICDD database.

Transmission electron microscopy (TEM) images and selected area electron diffraction patterns were collected on a ZEISS EM 10 C electron microscope at an acceleration voltage

of 100 kV. Furthermore, a Tecnai F20 S-TWIN analytical (high-resolution) transmission electron microscope (200 kV), equipped with an Apollo XLTW SDD X-ray detector, was utilized. A TEM heating holder, enabling *in situ* experiments up to 1273 K, was used in this instrument to detect the eventual phase transformations.

2.4. Spectroscopic characterization

In order to investigate the surface-near chemistry, representative samples were analyzed by X-ray photoelectron spectroscopy (XPS) using a Thermo Scientific MultiLab 2000 spectrometer with a base pressure in the low 10^{-10} mbar range. The instrument is equipped with a monochromated Al-K $_{\alpha}$ X-ray source, an Alpha 110 hemispherical sector analyzer, as well as a flood gun for charge compensation, providing electrons with a kinetic energy of 6 eV. Also, the system was fitted with an ion source for sputter depth profiling (for which 3 keV Ar ions were used that were continuously scanned across a 1.5 mm $\times$ 1.5 mm square on the sample with an ion current of 1.0 μ A). The etching rates are estimates that were calibrated for a MgF $_2$ /ZnS band pass filter (with 16 layers in total).

All high-resolution spectra were acquired using a pass energy of 25 eV and energy steps of 0.1 eV. Separate tests using the Fermi edge of a palladium foil revealed the (combined apparatus) resolution at these settings to be approximately 0.2 eV, which is very close to the line width of the monochromated X-ray source (0.2 eV). Thus, the broadening resulting from the analyzer is negligible. The energy axis shift due to charging was calibrated relative to the C-C component of the C 1s peak (set to 284.8 eV), which is due to adventitious carbon.

In order to determine the oxidation states of Ce (3d region) and Fe (2p region), reference spectra of CeO $_2$ /Ce $_2$ O $_3$ and FeO/Fe $_2$ O $_3$, [35] respectively, were fitted to these complex signals (with the same background subtraction methods). In the case of the Ce 3d regions, the

background was a spline Shirley background (to account for the difficulties of the software in fitting a proper Shirley background to the complex spectral region), and, for Fe 2p, a Shirley background was used.

3. Results and Discussion

3.1. $\text{La}_2\text{Zr}_2\text{O}_7$, $\text{Ce}_2\text{Zr}_2\text{O}_7$ and $\text{La}_2\text{Ce}_2\text{O}_7$

Figure 1: X-ray diffractograms of the pyrochlore $\text{La}_2\text{Zr}_2\text{O}_7$ (a) and $\text{Ce}_2\text{Zr}_2\text{O}_7$ (b), as well as the defect fluorite $\text{La}_2\text{Ce}_2\text{O}_7$ (c) as-synthesized target materials. The blue reference lines denote pyrochlore reflexes, while the red lines denote the fluorite lattice. Intensity axis is shown as linear scale.

As a preliminary structural check on the synthesized target materials, Figure 1 shows the X-ray powder diffractograms of the target materials. The diffractograms correspond to the pyrochlore ($\text{La}_2\text{Zr}_2\text{O}_7$ and $\text{Ce}_2\text{Zr}_2\text{O}_7$) and defect fluorite structures ($\text{La}_2\text{Ce}_2\text{O}_7$). Calcination of $\text{La}_2\text{Zr}_2\text{O}_7$ and $\text{Ce}_2\text{Zr}_2\text{O}_7$ in both cases yields nm-sized polycrystalline materials (determined on the basis of the Scherrer equation). The crystallite size determination by the Scherrer equation shows bigger crystallites (30 nm) for $\text{Ce}_2\text{Zr}_2\text{O}_7$ than for $\text{La}_2\text{Zr}_2\text{O}_7$ (10 nm), which is consistent with the higher preparation temperatures. In contrast, $\text{La}_2\text{Ce}_2\text{O}_7$ only exhibits a defect fluorite structure, where the characteristic pyrochlore reflexes, such as those from the (111) or (311) planes, are absent. Rietveld refinement allows to determine the cell parameter to be 5.5088 Å, which is somewhat in agreement with neutron diffraction data (5.5657 Å). [37]. Hence, a slightly smaller unit cell with a mass density of 5.82 g cm⁻³ is obtained, which can in principle be explained by small variations of the composition, as Ce is expected to be in its Ce⁴⁺ oxidation state in a defect fluorite, which has a significantly lower ionic radius compared to La³⁺. Slight deviations from the ideal atom concentrations also change the vacancy density, which will also affect the unit cell volume.

Figure 2: X-ray photoelectron spectra of a) the pyrochlore/defect fluorite target powder materials and b) the corresponding sputtered thin films.

In Figure 2, the XP spectra of the powders (a) and the thin films (b) of the two pyrochlore compounds as well as the lanthanum cerate defect fluorite are compared. In both cases, the top panels correspond to the spectra of $\text{Ce}_2\text{Zr}_2\text{O}_7$. Fitting the Ce 3d spectrum (left panel) of the powder sample with reference spectra of CeO_2 and Ce_2O_3 reveals that, in the depth regions accessible via this method, cerium is not purely present as Ce^{3+} , but in fact is a mixture of 30 % Ce^{3+} and 70 % Ce^{4+} . Since, in a pyrochlore with the formula $\text{A}_2\text{B}_2\text{O}_7$, the A site (*i.e.* Ce in this case) generally is occupied by a trivalent ion, this suggests that the surfaces of this pyrochlore are actually terminated by a thin CeO_2 layer. The Zr 3d region (second column), on the other hand, exhibits only a single oxidation state, corresponding to Zr^{4+} (with the $3d_{5/2}$ component being located at a binding energy of 182.5 eV), which is in agreement with the expected valency of this species. The quantification results in a composition of 23.7 at.-% Ce, 13.9 at.-% Zr as well as 62.4 at.-% O (with an uncertainty of approximately 1 at.-%). This corresponds to a sum formula of approximately $\text{Ce}_2\text{Zr}_{1.2}\text{O}_{5.3}$. The abundance of cerium is due to the CeO_2 termination of the crystallites. The cerium zirconate thin film (upper panels in (b)) exhibit slightly different electronic structures: whereas the cerium again is a mixture of Ce^{4+} and Ce^{3+} (80 % and 20 %, respectively), the zirconium is present in multiple states as well: apart from Zr^{4+} at a $3d_{5/2}$ binding energy of 182.7 eV, comprising the majority with 53%, there is another signal (about 28%) from a second state at 181.6 eV, corresponding to Zr^{3+} . Furthermore, the binding energy of the third component would correlate with Zr^{2+} (at 180.7 eV),[37] making up 19 % of the total zirconium signal. This indicates the presence of reduced oxidic zirconium compounds,[28,38] the introduction of which is conceivable during the sputter-deposition process at these low pressures. The O 1s spectra (right-most panels) of powder and thin film are very similar, with the thin film exhibiting an additional component in form of the shoulder at the low binding energy side, which most likely results from the reduced zirconium species. Integration over these regions

yields a composition of 16.8 at.-% Ce, 17.7 at.-% Zr and 65.5 at.-% O, which results in a sum formula of $\text{Ce}_2\text{Zr}_{2.1}\text{O}_{7.8}$, which is very close to that of the ideal pyrochlore structure.

As a comparison, the spectra of $\text{La}_2\text{Ce}_2\text{O}_7$ (defect fluorite) are shown in the middle rows for the powder (a) and the thin films (b), respectively. In the powder, there are 30.6 at.-% La, 8.6 at.-% Ce and 60.8 at.-% of oxygen in the sampled region. This corresponds to a sum formula of $\text{La}_2\text{Ce}_{0.6}\text{O}_4$, which deviates even more from the pyrochlore-like composition of the target than was the case for the cerium zirconate samples. However, this specimen also exhibits an enrichment in A on the surface. This is most likely in the form of La_2O_3 , as the La 3d panel in Figure 2 (a) does not feature the multiplet splitting characteristic of lanthanum,[39] which is possible when multiple components are present, such as the La^{3+} in the solid solution and lanthanum oxide at the surface. For the thin film sample, the La segregation is not as prominent, with 21.0 at.-% La, 10.6 at.-% Ce and 68.4 at.-% O in the spectrum. This is corroborated by the La 3d region, where the discussed multiplet splitting is more pronounced, hinting at a smaller fraction of the second, La-rich component. The cerium regions in both sample types contain signals stemming from Ce^{3+} (20% in the case of the powder and 17% for the thin film), even though Ce is expected to be present as Ce^{4+} in the defect fluorite lattice. However, as Ce^{3+} and La^{3+} have very similar radii, it is feasible that Ce^{3+} is partly dissolved in La_2O_3 due to the similarities in required space, accounting for the noticeable second Ce component in the spectra.

The lower panels in Figure 2 (a) and (b) show the spectra for $\text{La}_2\text{Zr}_2\text{O}_7$. Like for lanthanum cerate, there is an abundance of La at the surface, with the composition of the powder being 25.1 at.-% La, 13.6 at.-% Zr and 61.3 at.-% O (corresponding to $\text{La}_2\text{Zr}_{1.1}\text{O}_{4.9}$), and that of the thin film 17.9 at.-% La, 14.5 at.-% Zr and 67.6 at.-% O ($\text{La}_2\text{Zr}_{1.6}\text{O}_{7.6}$). Similar to lanthanum cerate, the La segregation in the thin film is not as prominent as in the powder, with the La/Zr ratio being approximately 1.2. Also, the surface state of La seems to appear in larger

concentrations in the powder than the thin film. In contrast to the cerium zirconate specimens, the Zr here is strongly reduced in the powder, with 34 % being in the form of Zr^{3+} and 25 % present as Zr^{2+} , which is surprising considering the calcination treatment. However, these lower oxidation states could have the same origin as for the cerium, *i.e.* dissolved Zr oxides in the La-enriched phase. This is corroborated by the fact that, in the thin film, the amount of reduced zirconium states is lower (23.1 % Zr^{3+} , 9.4 % Zr^{2+}), correlating with the decreased intensity of the second lanthanum component.

In order to highlight the compositional homogeneity of the thin films throughout their thickness, two exemplary sputter depth profiles of one pyrochlore ($\text{Ce}_2\text{Zr}_2\text{O}_7$, a) and the defect fluorite ($\text{La}_2\text{Ce}_2\text{O}_7$, b) specimen are shown in Figure 3. In a), the surface-terminating CeO_2 layer is only visible in the Ce 3d spectrum corresponding to the surface, but diminishing rapidly upon sputtering. At a depth of 2 nm, 78 % of the Ce accessible by this method is already in the state of Ce^{3+} , which increases to 100% at 7 nm. For Zr, in contrast, the sub-oxides disappear during the depth profiling process, which indicates that these species are related to the Ce^{4+} overlayer. While, usually, Zr is expected to be reduced during bombardment with Ar ions due to preferential sputtering of oxygen, [27,28] this is not the case here, because Ce^{4+} is present which is more easily reduced compared to Zr^{4+} , and hence, acts as a kind of chemical and structural buffer. In fact, starting from 7 nm, when all Ce is fully reduced to Ce^{3+} , the Zr sub-oxides appear again. At the largest depth, the Zr signal is indistinguishable from the baseline noise, whereas the Ce peaks can still be discerned. This is due to the significantly larger relative sensitivity factor of Ce 3d (51.6) as compared to the same transition for Zr (7.04).[40] The oxygen present at this depth originates from the underlying Si substrate, containing an oxidic passivation layer at its surface.

Figure 3: Sputter depth profiles of a) cerium zirconate and b) lanthanum cerate thin films, with the concentration profiles shown in c). The shaded areas in c) represent the estimated error bars of the concentrations, indicating that the uncertainties become relatively large at high depths due to the low intensities of the signals.

For lanthanum cerate (b), the second La-component is lost as soon as the sputter process is started too, resulting in a better apparent resolution of the multiplet-split La 3d peaks and the lack of a low-binding-energy-side shoulder. Moreover, the apparent multiplet splitting is reduced from approximately 4.6 eV to 4.2 eV, indicating a loss of an oxidic component (which has a splitting of 4.6 eV).[39] Furthermore, this loss of the surface species, as was the case for $\text{Ce}_2\text{Zr}_2\text{O}_7$, is accompanied by the removal of low-binding-energy-side components in the O 1s region. The cerium is reduced to Ce^{3+} , as expected due to the preferential sputtering of O from the lattice. Furthermore, the intensity of the Ce 3d signal is decreasing more rapidly than that of La with increasing sputter depth.

Figure 3 (c) displays the results of the quantification of the depth profiles from the other panels. In both cases, there is an apparent O enrichment at the surface, which results from the already mentioned preferential sputtering. [27,28] In the case of cerium zirconate (upper panel), the Ce and Zr concentrations at the surface are approximately equal, as expected for a pyrochlore (although the discussed CeO_2 surface layer has to be taken into account). However, during the sputtering process, this changes to slightly more cerium. While this could result from deviations in the actual composition, it could also stem from preferential sputtering as well, since Zr is significantly lighter than Ce. The concentration profile appears very homogeneous, with negligible differences in the Ce/Zr ratio.

For $\text{La}_2\text{Ce}_2\text{O}_7$ (lower panel), the loss of oxygen due to sputtering is more pronounced (dropping from 68 at.-% to 48 at.-%). Also, the Ce concentration, which is lower than that of La at the surface, remains lower than La throughout the whole sample depth. Thus, the

different surface composition does not originate from segregation effects, but rather from a change in composition during the thin film deposition itself, which is expected since the defect fluorite structure can accommodate a wide range of compositions. The La concentration remains pretty constant, whereas the Ce concentration actually drops noticeably between 7 nm and 26 nm. Since the masses of La and Ce are very close together, no preferential sputtering is expected here.

To examine the morphology and microstructure of the thin film pyrochlores, $\text{La}_2\text{Zr}_2\text{O}_7$ and $\text{Ce}_2\text{Zr}_2\text{O}_7$, TEM images were recorded and an *in situ* TEM heating experiment was conducted up to temperatures of 1273 K. In Figure 4, bright field (BF) overview images of $\text{La}_2\text{Zr}_2\text{O}_7$ and $\text{Ce}_2\text{Zr}_2\text{O}_7$ thin films are presented, as well as their respective selected area electron diffraction patterns (SAED, as insets) and high resolution TEM (HRTEM) micrographs. The BF image of $\text{La}_2\text{Zr}_2\text{O}_7$ (a) reveals multiple layers of particles, where the top-most layer appears to be torn, as visible by the prominent cracks (bright contrast). No pinholes are formed during the deposition, as the layer-by-layer growth characteristic of the used DC sputter source makes these less likely to occur.[28,29] Smaller roundish crystallites with an approximate diameter of 10 nm are also observable. The bright field image of $\text{Ce}_2\text{Zr}_2\text{O}_7$ (c) exhibits less pronounced contrast differences, with the morphology appearing similar to amorphous materials. However, some dark crystallites (with diameters of approximately 10 nm), originating from Bragg contrast, are also observed.

Figure 4: Overview bright-field images, HRTEM (with FFTs displayed as insets) and SAED patterns of the as grown defect fluorite thin films of $\text{La}_2\text{Zr}_2\text{O}_7$ (a–b) and $\text{Ce}_2\text{Zr}_2\text{O}_7$ (c–d).

Both SAED patterns in Figure 4 (the insets in panels a) and c) reveal the defect fluorite (df) structure of each thin film [41–43] by the presence of the defect fluorite (111) (with a measured lattice spacing of 0.31 nm as compared to a theoretical one of 0.305 nm), (200) (0.27 nm, theoretically 0.264 nm) and $df(220)$ reflexes (0.19 nm as measured, which is in good agreement to the theoretical value of 0.187 nm).[43] This suggests that the crystal structure of the target (pyrochlores in both cases) could not be retained during the sputtering

process, with the thin films becoming structurally disordered during the deposition process. However, from the diffraction patterns, a large degree of ordering/texturing can be deduced as distinct spots are present instead of Debye-Scherrer-like rings, owing to the quasi-epitaxial growth of these defect fluorites on NaCl(001). The polycrystalline film consists of crystallites with an average size of approximately 5 nm, which is smaller than the powder precursor which can be reasoned by the lower substrate temperature of 400 °C.

The HRTEM images of b) $\text{La}_2\text{Zr}_2\text{O}_7$ and d) $\text{Ce}_2\text{Zr}_2\text{O}_7$ are also displayed in Figure 4. In both cases, the visible lattice fringes mainly correspond to the set of $\{111\}$ planes of the defect fluorite structures. The FFT (inset) for $\text{La}_2\text{Zr}_2\text{O}_7$ (b) reveals the presence of some Moiré patterns (with larger apparent spacings), again confirming the layered growth of the thin films during deposition, whereas the FFT of $\text{Ce}_2\text{Zr}_2\text{O}_7$ (d) also indicates the presence of (200) reflexes from the defect fluorite lattice.

Figure 5: HAADF images (top panels) and respective EDX mappings (bottom panels) of the as grown defect fluorite thin films (a) $\text{La}_2\text{Zr}_2\text{O}_7$, (b) $\text{Ce}_2\text{Zr}_2\text{O}_7$. For the panel in (a), EDX spectrum imaging refers to the entire image, for panel (b) it is referred to the area of the white square.

To gain information about composition and spatial homogeneity of the thin films, EDX spectrum imaging was employed. The results are shown in Figure 5. Each panel contains the HAADF image as well as the respective EDX maps for (a) $\text{La}_2\text{Zr}_2\text{O}_7$ and (b) $\text{Ce}_2\text{Zr}_2\text{O}_7$. Both thin films are very homogeneous, with no accumulation of either elements, as can be gathered from the lower panels depicting the elemental distributions. For the cerium zirconate specimen, the composition across the whole area can be determined to be 23.6 at.-% Ce, 27.0 at.-% Zr and 49.4 at.-% O. That less oxygen is detected than would be expected can be explained by the fact that the quantification of O is more difficult in EDX due to the low energy of the O K transition. That more zirconium than cerium is detected is in excellent agreement with the XPS results for the surface spectra. During the XPS depth profiling, however, the Ce concentration started to increase rapidly, which was ascribed to preferential sputtering of Zr. This is corroborated by the fact that EDX, which measures the composition in projection through the whole sample thickness, detects a sum excess of zirconium ($\text{Ce}/\text{Zr} = 0.88$, while integrating over the whole depth using XPS would yield a Ce/Zr ratio of about 1.5). For $\text{La}_2\text{Zr}_2\text{O}_7$, the agreement with the target composition is even better, as 25.7 at.-% La, 25.2 at.-% Zr and 49.1 at.-% O are detected, leading to a La/Zr ratio of 0.97. The surface-sensitive XP spectra yielded a slight La-enrichment ($\text{La}/\text{Zr} = 1.2$), which is due to the additional surface compound.

In order to reveal information about the thermal stability of defect fluorite thin films, as well as to try to trigger the eventual phase transformation to the pyrochlore structure, SAED patterns were captured while simultaneously heating to a maximum temperature of 1163 K. This phase transition can be observed for $\text{La}_2\text{Zr}_2\text{O}_7$ at about 1073 K in Figure 6 (diffraction patterns between 373 K and 1023 K are not shown because no changes occur in that temperature range). The results are in agreement with the temperatures reported by Paul *et al.*[44] The diffraction patterns generally show a high number of reflexes that persist over the

heating process, as they are found for both, the pyrochlore, as well as the defect fluorite structures. Some amorphous rings (for instance those in proximity to the (111) reflexes) seem to transform into a more distinct reflex pattern at 1163 K, owing to the crystallization of amorphous regions at these high temperatures.

Starting at 1073 K, additional reflexes start to appear in the diffraction patterns that can be attributed to the pyrochlore lattice: close to the direct beam, faint spots appear with measured lattice spacings of 0.63 nm, that can be clearly related to the pyrochlore (111) planes (at 0.62 nm). These are highlighted in the insets for the SAED patterns recorded at 1073 K and 1123 K. Furthermore, the region where the $df(111)$ and spots were located for the defect fluorite structure shows additional splitting due to the pyrochlore (311) reflexes (see bottom inset in the 1123 K pattern). Since the pyrochlore lattice is a $2\times 2\times 2$ superstructure of the defect fluorite, the defect fluorite reflexes are present as well (with doubled miller indices). For example, the $df(111)$ reflex has the same spacing as the $pyr(222)$ lattice planes.[44,45]

The phase transition could not be observed for the $Ce_2Zr_2O_7$ thin film under the same experimental conditions. This most likely results from the fact that the vacuum inside the TEM was not reducing enough to form enough Ce^{3+} , which is required for the ordering to the pyrochlore lattice (see the experimental part on the synthesis, where the powder had to be reduced in CO at 1273 K to achieve substantial cerium reduction).[4] In lanthanum zirconate, both ions were already in the correct oxidation state prior to the *in situ* heating experiment, making the recrystallization possible at the sampled temperatures.

Figure 6: SAED patterns of the defect fluorite/pyrochlore thin film La₂Zr₂O₇ observed *in situ* at temperatures between 373 K and 1163 K. The table in the lower right panel contains the corresponding planes and lattice distances. The insets in the higher temperature diffraction patterns highlight the changes due to the defect fluorite-to-pyrochlore transition.

3.2. La_{0.6}Sr_{0.4}FeO₃

In a separate approach, a thin film sample of a sputter-prepared lanthanum strontium ferrite (LSF) phase of the nominal target composition La_{0.6}Sr_{0.4}FeO₃ was prepared. The choice of this particular perovskite was mainly fueled by the vast amount of powder bulk data and the relative simplicity of the material. The main anticipated obstacles are the structural stability of the thin film perovskite phases and the direct influence of the oxygen stoichiometry on the structure. Several stable bulk structures (including orthorhombic, rhombohedral and cubic) are observed, both as a function of temperature and oxygen sub-stoichiometry.[46,47] The anticipated structure as derived from a bulk phase diagram is a rhombohedral phase, but

additional factors such as epitaxial stabilization by the single-crystalline NaCl(001) template might lead to particular stabilization of other structures. In addition, the oxygen substoichiometry due to eventual preferential sputtering is notoriously difficult to control and *a priori* predictions of obtaining a particular phase by sputtering are very difficult.

However, Figure 7 directly reveals (in combination with Figure 8 highlighting the depth profiling) that the surface composition of the thin film samples is very close to that of the powder target materials. Thus, the thin film exhibits an approximate composition of 15 at.-% Fe, 60 at.-% O, 8 at.-% Sr and 17 at.-% La, in comparison to 14 at.-% Fe, 60 at.-% O, 8 at.-% Sr and 18 at.-% La for the powder target material, the difference being within the error margin of the analysis.

Figure 7: Comparison of the XP spectra of a DC-sputtered LSF thin film on a Si-wafer at 843 K (top panel) with a pure powder LSF sample (bottom panel). For comparison, the most relevant LSF regions of the XP spectra, namely Fe 2p (red), La 3d (green), O 1s (blue) and Sr 3d (orange) are shown.

Figure 8: XPS sputter-depth profile of an LSF thin film deposited by DC-sputtering on a Si-wafer at 843 K. The concentration of the four different components are given in atomic percent (data derived from quantitative XPS of the single regions), highlighted with different colors, and imaged for each sputter depth.

Figure 8 also reveals that the surface and bulk chemical composition is very homogeneous within the film, at least down to sputtering depths of approximately 60 nm. The composition at etch depths at about 3 nanometers, especially the increase of La 3d and the decrease of the O 1s signal could be explained by preferential sputtering (because of the large mass differences between the elements). Close inspection of the individual XP regions of Fe 2p, La 3d, O 1s and Sr 3d peaks of both powder target material and resulting thin film revealed no substantial differences. The BE of the Fe 2p_{3/2} peak is found at around 712.0 eV, which indicates the presence of Fe²⁺ and Fe³⁺. Shake-up satellites (at 9.0 eV higher BE), present for both samples, point to Fe³⁺. Fitting these peaks (Fe 2p_{3/2} peaks) with reference spectra, as seen in Figure 9, reveals the chemical states of surface iron species. The reference spectra were obtained from pure FeO and Fe₂O₃ (powder) samples, with the former being formed *in situ* from an iron(II) oxalate precursor (*via* thermal decomposition slightly above 573 K) to prevent disproportionation to Fe and Fe₃O₄. [35] In contrast to the powder material, which shows a composition of 75% Fe³⁺ and 25% Fe²⁺, the surface of the thin film sample contains

no detectable amounts of Fe^{2+} . The La 3d region shows the characteristic spin-orbit coupled complex shape of a single La component, which is confirmed by the BE of the La $3d_{5/2}$ peak at 834.7 eV and the energy difference of the f^1 and f^0 states of 4.1 eV as that of a perovskite species. Both O 1s and Sr 3d peaks show broadened signals due the presence of at least two different components, which can be assigned to bulk lattice/surface-segregated components (O 1s region between 528.5 and 529.7 eV, Sr $3d_{5/2}$ peak at 132.4 eV) and surface/adsorbed species (O 1s region between 531.0 – 532.5 eV, Sr $3d_{5/2}$ component at 133.2 eV).[48]

Figure 9: XP spectra of the Fe $2p_{3/2}$ region of a dc-sputtered LSF thin film (panel) on a Si-wafer at 843 K and a pure powder LSF sample (bottom). The Fe(III) components are displayed with red colors and the Fe(II) with green ones. For fitting, reference samples of Fe(III) and Fe(II) are used.

Transmission electron microscopic analysis subsequently further revealed the structure and morphology of the thin films. After deposition (Figure 10 a), the perovskite films exhibit no distinct crystallite features, but rather, a porous, but homogeneous structure is observed. In SAED, the film clearly appears amorphous (*cf.* inset). Crystalline films are only obtained by post-annealing in air at temperatures above 973 K (Figure 10 b). In this case, small nanometer-sized crystallites with strong Bragg contrast appear, increasing the observed porosity even further. These crystallites give rise to a well-ordered SAED pattern. In fact,

even an almost epitaxial ordering is observed, which is remarkable insofar as the thin film is removed from the NaCl crystal prior to annealing, suggesting some memory effect of the deposition substrate in the amorphous as grown film, which causes this texturing to appear after annealing. The SAED pattern can be attributed to an orthorhombic lattice (space group $Pmma$),[49] as it explains all the measured reflexes, some of which are marked in the inset in Fig. 10 (b): the innermost spots at measured lattice spacings of 0.39 nm correspond to the (101) planes of orthorhombic LSF (that have a theoretical spacing of 0.39 nm). Moreover, the ring at 0.33 nm is due to the (121) lattice planes (0.33 nm according to the crystal structure), the (040) reflexes (0.30 nm) are found at 0.30 nm, and the (131) planes yield a signal at 0.28 nm, which is in excellent agreement with the expected value (0.28 nm). Additional reflexes found in the diffraction pattern originate from the (022) planes (0.25 nm), the (230) lattice planes (0.23 nm) and the (202) planes (0.20 nm), the measured spacings of all agree perfectly with the expected values.[49] The presence of the orthorhombic structure is further backed by HRTEM images (Figure 10 c), which feature lattice fringes of this particular structure (*e.g.* the (101) lattice planes measured at 0.55 nm).[49]

Figure 10: Bright field images of (a) the as grown LSF thin film sample and (b) after post-deposition annealing at 973 K. The insets show the respective SAED patterns. c) HRTEM image of a single orthorhombic LSF grain displaying (011) lattice fringes.

4. Conclusions

We have shown the capabilities of the thin film model approach for the synthesis and characterization of complex ternary oxide materials. The latter, especially also in nm and μm -thick films, gain increasing importance in various technological areas such as solid-oxide fuel cells. Clarifying the structural, morphological and chemical properties of such films is therefore imperative. Following the concept of sputter-deposition on single-crystalline NaCl(001) cleavage faces, the chosen preparation routine has been proven to yield precisely controlled films in terms of structure, morphology, stoichiometry, chemical composition and electronic structure. This, in turn, is a prerequisite for sophisticated experimental characterization approaches such as the highlighted *in situ* electron diffraction, which consequently allowed us to monitor the defect fluorite-to-pyrochlore phase transition using well-structured and well-defined materials. This is just one example of complex properties inherent to oxidic materials beyond simple binary oxides, which can be especially well-tackled following the outlined approach. We envision extension of these studies to other pending problems in oxide research, such as the construction of thin film phase diagrams, clarifying exsolution phenomena or the stabilization (and subsequent characterization) of unusual crystallographic structures by epitaxial mediation of the underlying NaCl template. A preliminary example of the latter is given in the second part of the discussed work by formation of an orthorhombic perovskite structure, but the concepts can be generalized to various classes of complex materials.

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Graphical Abstract