Facile and General Synthesis of Thermally Stable Ordered Mesoporous Rare-Earth Oxide Ceramic Thin Films with Uniform Mid- to Large-Size Pores and Strong Crystalline Texture

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Abstract

We describe the general synthesis of sub-micron-thick rare-earth/lanthanide sesquioxide (RE_2O_3) films with tailorable pore and grain sizes by polymer templating of hydrated chloride salt precursors. Mesoporous RE_2O_3 ($\text{RE} = \text{Sm}, \text{Tb-Lu}$) ceramics with cubic pore symmetry and high surface area ($S_{\text{BET}} \geq 50 \text{ m}^2\cdot\text{g}^{-1}$) were prepared using different diblock copolymer structure-directing agents and were characterized by a combination of electron microscopy, *in situ* and *ex situ* grazing incidence small-angle X-ray scattering, N_2 -physisorption, X-ray photoelectron spectroscopy, X-ray diffraction including Rietveld refinement, and UV-vis spectroscopy. In the present work, we specifically focus on Dy_2O_3 and Yb_2O_3 and use both of these materials as model systems to study, among other things, the film formation and microstructure. Our research data collectively demonstrate that (1) record pore sizes of up to 42 nm in diameter can be achieved without the need for swelling agents, (2) the nanostructure can be preserved up to 1000 °C for the heavier oxides, (3) the sizes of the optical band gaps (4.9-5.6 eV) are comparable to those reported for single crystals, (4) the sol-gel derived materials are single phase and adopt the *C*-type crystal structure, and that (5) the grain growth is virtually linear with domain sizes ranging from approx. 3 nm to 16 nm. We also show that, except for Yb_2O_3 , all samples have fiber texture and that the preferred orientation is significant in Sm_2O_3 and Lu_2O_3 films (March G_2 parameters of under 0.1). Overall, the synthesis parameters described in this work provide a blueprint for the preparation of thermally stable rare-earth oxide ceramics with both a mesoporous morphology and iso-oriented nanocrystalline walls.

Keywords

Rare-earth oxides, ceramics, films, self-assembly, mesoporous, crystalline texture

Introduction

Oxide ceramics of the lanthanide group, along with scandium and yttrium, are collectively known as the rare-earth oxides. Most of these materials are technologically important and have many uses: as phosphors/activators/host materials,^[1,2] heterogeneous catalysts,^[3] high dielectric constant gate oxides,^[4] and as corrosion-resistant coatings^[5] to mention a few.

Apart from non-stoichiometric phases, rare-earth oxides are typically found in three compositions, namely monoxide (REO), dioxide (REO₂), and sesquioxide (RE₂O₃). Of these, sesquioxides are both the most stable and the most important oxide ceramics of the lanthanide group and have been shown to have three distinct polymorphs over a wide temperature range: *A*-type (hexagonal), *B*-type (monoclinic), and *C*-type (cubic).^[3,6] For the heavier oxides, the *C*-type polymorph is known to be stable (in the bulk) under ambient conditions. It adopts a cubic structure with the space group $Ia\bar{3}$ (T_h^{24}) and the unit-cell comprises 80 atoms equivalent to 16 formula units RE₂O₃. In this fluorite-derived structure, which is isomorphous to the naturally occurring mineral Bixbyite [(Mn³⁺, Fe³⁺)₂O₃], the rare-earth atoms occupy two crystallographically non-equivalent six-fold positions to oxygen – *8b* and *24d* Wyckoff sites with *S*₈ and *C*₂ symmetry, respectively – and the oxygens are located on *48e* sites.^[7,8]

Here, we describe a facile and general method for the synthesis of mesostructured *C*-type rare-earth sesquioxide thin films with cubic pore symmetry by swelling agent-free polymer templating using an evaporation-induced self-assembly (EISA)^[9,10] process. This process was introduced by Brinker and others some years ago and relies on the coassembly of inorganic building blocks with an amphiphilic polymer (or surfactant) – with the latter acting as structure-directing agent (SDA).^[11] The fundamental principles of templating and self-assembly have been described in detail in excellent reviews elsewhere.^[12-21] We do not focus on particular

applications of these sol-gel derived materials. Instead, the synthesis parameters described in this work provide a blueprint for the preparation of rare-earth oxide ceramics with (1) an ordered mesoporous morphology, (2) nanocrystalline walls with sub-20 nm grains, (3) high thermal stability, and with (4) a crystalline texture. All these features combined make the polymer-templated RE₂O₃ films presented below certainly interesting for a variety of applications (e.g., in microelectronics, catalysis, optics, and other fields).

It should be noted that, in particular, literature reports on mesoporous thin films with iso-oriented nanocrystalline wall structures are scarce.^[22] This is due, in part, to the fact that the synthesis of non-silicate oxides with both a well defined pore-solid architecture and highly crystalline walls itself is still challenging. One of the reasons for this is the lack of appropriate polymer SDAs. The vast majority of those described over the last decade have been shown to produce materials with small repeat distances – in other words – with wall structures that are not sufficiently thick to allow for uniform crystallization with retention of porosity. Advances in soft-templating and processing of sol-gel derived coatings have, nevertheless, enabled the preparation of a range of metal oxides.^[15,18,20-26] However, to our knowledge, only few crystalline rare-earth sesquioxides with an ordered mesoporous structure have been reported so far.^[27-30]

Castro *et al.* reported the synthesis and optical properties of Eu₂O₃ and Y₂O₃.^[28,29] They showed that both materials can be templated to produce mesoporous thin films, but the synthesis involved several different steps and was rather complicated and time-consuming. However, as described, these steps were crucial to prevent the recrystallization of rare-earth chloride species and to advance the stability of the as-made films, which apparently came at cost to the overall pore ordering. Also, both these sesquioxides scarcely exhibited any crystalline texture, the reason for this remaining unclear. A more promising approach was recently developed by Xiao *et al.*

using an ionic block copolymer (polystyrene-*block*-poly(acrylic acid), PS₆₀-*b*-PAA₁₀₀) as SDA.^[30] They successfully prepared La₂O₃, Eu₂O₃, Tb₂O₃, and Yb₂O₃ thin films with reasonable pore ordering by spin-coating. A drawback, however, is the requirement of a mixed solvent of dimethylformamide and dichloromethane in the synthesis, which at first glance does not seem to be compatible with the dip-coating technique. Furthermore, the fact that the particular polymer SDA used produced materials with rather small repeat distances is not beneficial as it strongly limits the thermal stability of the materials. Nevertheless, this approach is the only one in the literature that tends to be of a more general nature.

In this work, we describe the polymer templating of hydrated chloride salt precursors for making large-pore mesoporous RE₂O₃ thin films and demonstrate that the synthesis procedure is applicable to a multitude of (if not all) rare-earth oxides. In particular, we take advantage of the superior templating properties of poly(ethylene-*co*-butylene)-*block*-poly(ethylene oxide) – referred to as KLE^[22,25,27,31] – and polyisobutylene-*block*-poly(ethylene oxide) – referred to as PIB_{*x*}-*b*-PEO_{*y*}^[32] – diblock copolymers to achieve thermally stable, high quality nanomaterials with tailorable pore and grain sizes. Overall, it seems that the unique combination of nanoscale porosity with crystalline texture might offer the possibility to broaden the scope of application for these oxide ceramics.

Experimental Section

Materials. SmCl₃·6H₂O (99.9%), TbCl₃·6H₂O (99.9%), DyCl₃·6H₂O (99.9%), HoCl₃·6H₂O (99.9%), ErCl₃·6H₂O (99.9%), TmCl₃·6H₂O (99.9%), and LuCl₃·6H₂O (99.9%) were purchased from ABCR. Glacial acetic acid (99.99%), absolute ethanol, 2-methoxyethanol, and YbCl₃·6H₂O (99.9%) were purchased from Sigma-Aldrich. Both

$\text{H}[(\text{CH}_2\text{CH}_2)_{0.67}(\text{CH}_2\text{CHCH}_2\text{CH}_3)_{0.33}]_{89}(\text{OCH}_2\text{CH}_2)_{79}\text{OH}$, referred to as KLE,^[31] and $\text{H}[\text{C}(\text{CH}_3)_2\text{CH}_2]_x\text{C}_6\text{H}_4(\text{OCH}_2\text{CH}_2)_y\text{OH}$, referred to as $\text{PIB}_x\text{-}b\text{-PEO}_y$,^[32] were obtained from BASF SE and were used as polymer SDAs in this work. The synthesis of these block copolymers is described elsewhere.

Synthesis. First, a 50 mg portion of the polymer SDA is dissolved in a mixed solvent of ethanol (0.95 mL), 2-methoxyethanol (0.95 mL), and glacial acetic acid (0.25 mL). This solution is then combined with the hydrated rare-earth chloride salt. Table 1 summarizes reagent masses for each type of film prepared in the present work. Once the solution is clear, sub-micron-thick films can be produced *via* (multiple) dip-coating on polar substrates. Optimal conditions include relative humidities of 10-15% and constant withdrawal rates of $1\text{-}10\text{ mm}\cdot\text{s}^{-1}$. After drying the as-made films for 2-3 min at room temperature, the samples are directly transferred to an oven at $150\text{ }^\circ\text{C}$ for 1 h and then heated to $300\text{ }^\circ\text{C}$ using a ramp of $1\text{ }^\circ\text{C}\cdot\text{min}^{-1}$ followed by aging for 12 h. Lastly, the films are heated to temperatures up to $1000\text{ }^\circ\text{C}$ in air using a ramp of $10\text{ }^\circ\text{C}\cdot\text{min}^{-1}$ to remove the polymer SDA and to induce crystallization.

Table 1. Recipes for the synthesis of polymer-templated mesoporous RE_2O_3 thin films.

	$\text{SmCl}_3\cdot 6\text{H}_2\text{O}$ (mg)	$\text{TbCl}_3\cdot 6\text{H}_2\text{O}$ (mg)	$\text{DyCl}_3\cdot 6\text{H}_2\text{O}$ (mg)	$\text{HoCl}_3\cdot 6\text{H}_2\text{O}$ (mg)	$\text{ErCl}_3\cdot 6\text{H}_2\text{O}$ (mg)	$\text{TmCl}_3\cdot 6\text{H}_2\text{O}$ (mg)	$\text{YbCl}_3\cdot 6\text{H}_2\text{O}$ (mg)	$\text{LuCl}_3\cdot 6\text{H}_2\text{O}$ (mg)
Sm_2O_3	235.1	—	—	—	—	—	—	—
Tb_2O_3	—	229.6	—	—	—	—	—	—
Dy_2O_3	—	—	227.4	—	—	—	—	—
Ho_2O_3	—	—	—	225.9	—	—	—	—
Er_2O_3	—	—	—	—	224.5	—	—	—

Tm ₂ O ₃	–	–	–	–	–	223.6	–	–
Yb ₂ O ₃	–	–	–	–	–	–	221.2	–
Lu ₂ O ₃	–	–	–	–	–	–	–	220.2

Methods. Transmission electron microscopy (TEM) and scanning electron microscopy (SEM) images were taken with a CM30-ST from Philips at an accelerating voltage of 300 kV and a MERLIN from Carl Zeiss at an accelerating voltage of 5 kV and sample current of 120 pA, respectively. X-ray diffraction (XRD) measurements were carried out on an X’Pert PRO diffractometer from PANalytical instruments (wavelength: 0.15418 nm) using an X’Celerator RTMS detector (sample-detector distance: 24 cm). *Ex situ* and *in situ* grazing incidence small-angle X-ray scattering (GISAXS) patterns were collected at the German synchrotron radiation facility HASYLAB at DESY on beamline BW4 (wavelength: 0.1381 nm, beam size: 23 μ m (vertical) $\times$ 30 μ m (horizontal), sample-detector distance: 1808 mm, incident angle: 0.2°) using a MarCCD area detector (pixel size: 79 μ m, resolution: $1.99 \cdot 10^{-3}$ nm⁻¹ px⁻¹, counting time: 2 $\times$ 150 s) and a Pilatus 300k (pixel size: 172 μ m, resolution: $4.33 \cdot 10^{-3}$ nm⁻¹ px⁻¹, counting time: 5 s), respectively. X-ray photoelectron spectroscopy (XPS) data were acquired on a VersaProbe PHI 5000 Scanning ESCA Microprobe from Physical Electronics with monochromatic Al-K α X-ray source and a hemispherical electron energy analyzer at 50° electron takeoff angle. The C 1s signal from adventitious hydrocarbon at 284.8 eV was used as energy reference to correct for charging. Optical absorption measurements were carried out on a Perkin Elmer Lambda 900 UV-vis-NIR spectrophotometer (pinhole slit: 1 mm in diameter, step size: 1 nm step⁻¹, integration time: 0.5 sec step⁻¹, scan speed: 2 nm sec⁻¹). A substrate made from quartz glass and an aluminum mirror served as a reference for transmission and reflection measurements, respectively. N₂-physisorption measurements were conducted at 77 K using the Autosorb-6

automated gas adsorption station from Quantachrome Corporation. The film thickness was determined with an Alpha Step IQ Surface Profiler from KLA Tencor. For Rietveld refinement, the software FullProf was used. In the refinement, the half-width parameters V , W , and X were kept constant at instrumental values determined using LaB₆.

Results and Discussion

As mentioned above, in the present work we describe a facile and general synthesis of ordered mesoporous rare-earth sesquioxide thin films. In short, in a typical synthesis both the sol-gel precursor and the polymer SDA are dissolved in a mixed solvent of ethanol, 2-methoxyethanol, and glacial acetic acid. The latter is found to be important in achieving well defined mesostructured films. It seems that glacial acetic acid is capable of suppressing the recrystallization of chloride species perhaps by some sort of complexation. If no glacial acetic acid is used, the otherwise optically clear films become turbid during the drying process. Furthermore, we find that the best results in terms of periodicity and overall structural homogeneity are achieved at low relative humidities (here 10-15%). This finding also provides an explanation for understanding why the same synthesis using such polymer SDAs as Pluronic P123 or F127 failed. These triblock copolymers have been shown to typically require room temperature humidities of 20% or more and often also (time-consuming) post-treatments to form self-assembled inorganic-organic composite films with good structural ordering.^[24,33,34] After stirring the resulting solution for a couple of minutes, films with thicknesses in the sub-micrometer range can be produced *via* dip-coating on polar substrates, including quartz glass slides and polished Si(100) wafers. A multistep thermal treatment is then necessary to (1) stabilize the mesostructured composite architecture by driving condensation, (2) combust the

polymer SDA to make the material porous, and to (3) crystallize the inorganic wall structure. As is evident from the data below, this synthesis procedure is not only straightforward but is also applicable to a wide variety of rare-earth oxides.

Here, we incorporated both the well-known KLE and various $\text{PIB}_x\text{-}b\text{-PEO}_y$ diblock copolymers with different block lengths as SDAs to produce highly crystalline sesquioxides with exceptional thermal stability and in-plane pore sizes averaging 17, 19, 25, and 42 nm in diameter. The latter dimension corresponds to a record pore size, far exceeding those of conventional polymer-templated mesoporous metal oxides produced from sol-gel precursors without using any swelling agents. Although both types of diblock copolymers are known to be very efficient for making non-silicate films with large pores,^[22,25,27,32,35,36] we believe that any amphiphilic polymer can be used in the synthesis as long as it shows a strong tendency to form robust nanostructures at relative humidities below 15% and further produces materials with sufficiently thick walls (i.e., large repeat distances) that can be fully crystallized with retention of porosity.

The pore structure of the KLE-templated thin films heated to 800 °C in air both at the top surface and in the interior was analyzed by a combination of scanning electron microscopy (SEM), transmission electron microscopy (TEM), *in situ* and *ex situ* grazing incidence small-angle X-ray scattering (GISAXS), and conventional small-angle X-ray scattering (SAXS). **Figure 1** shows structural data from SEM and TEM imaging (see also **Figures S1** and **S2** in the Supporting Information (SI) for additional data) for dysprosium (Dy_2O_3) and ytterbium sesquioxide (Yb_2O_3). In the following, we specifically focus on both of these materials and use them as model systems. Nevertheless, we show data for each type of film prepared in this work. From cross-sectional SEM, it can be clearly seen that (1) both materials are mesostructured with cubic pore symmetry, (2) the nanoscale structure persists throughout the bulk of the films, (3) the

top surface is flat and crack-free (see also **Figure S1** in the SI), (4) the pores at the top surface are open, and that (5) the pore cavities are anisotropic in shape due to unidirectional lattice contraction during thermal annealing. TEM results show that the pores have an average in-plane diameter of 19 nm and further indicate that the inorganic walls consist of sub-12 nm crystallites. Selected-area electron diffraction (SAED) and high-resolution TEM (HRTEM) studies demonstrate the crystallinity of these oxide ceramics and show that both adopt a cubic structure with the space group $Ia\bar{3} (T_h^7)$, as expected for *C*-type RE_2O_3 compounds.

Figure 1. Microstructure of KLE-templated Yb_2O_3 (a–c) and Dy_2O_3 (d–f) thin films heated to 800 °C. (a, d) Cross-sectional SEM images showing that the pore structure persists throughout

the bulk. (b, e) Bright-field TEM images. (c) HRTEM image and (f) SAED pattern demonstrating the nanocrystalline nature of both oxides. The d -values are in agreement with those obtained from the Joint Committee on Powder Diffraction Standards (JCPDS) reference cards no. 22-0612 and 41-1106 for bulk Dy_2O_3 and Yb_2O_3 , respectively.

Comparable microstructure data are obtained for samarium (Sm_2O_3), terbium (Tb_2O_3), holmium (Ho_2O_3), erbium (Er_2O_3), thulium (Tm_2O_3), and lutetium sesquioxide (Lu_2O_3) thin films templated by the large diblock copolymer KLE. **Figure 2** shows bright-field TEM images at different magnifications and results from HRTEM imaging and SAED which provide ample evidence that the synthesis method employed here is in fact applicable to a broad range of rare-earth sesquioxides. These sol-gel derived materials also exhibit cubic mesostructures with 18-20 nm diameter pores, very similar to that of Dy_2O_3 and Yb_2O_3 . SAED and HRTEM further establish that the different samples are both highly crystalline and single phase – the presence of mesopores does not seem to interfere with the crystallization. All SAED patterns show several rings and the corresponding d -values match those reported for C-type RE_2O_3 compounds (see also JCPDS reference cards no. 15-0813, 23-1418, 44-1268, 8-0050, 41-1090, and 12-0728 for bulk Sm_2O_3 , Tb_2O_3 , Ho_2O_3 , Er_2O_3 , Tm_2O_3 , and Lu_2O_3 , respectively).

In summary, the electron microscopy results lead us to conclude that the network of pores is well developed after thermal treatment at 800 °C in air and that the pore cavities are uniform in size and shape. In addition, the data indicate that the KLE-templated thin films are both thermally very stable and free from major structural defects – such features are prerequisites for many applications.

Figure 2. Microstructure of KLE-templated Ho_2O_3 (a, f), Tm_2O_3 (b, c, h), Er_2O_3 (d, g), Lu_2O_3 (e, i), Tb_2O_3 (j, k), and Sm_2O_3 (l) thin films heated to 800 °C. (a) HRTEM image. (b–e, j–l) Bright-field TEM images at different magnifications showing open pores averaging 19 nm in diameter.

(f–i, inset in panels j and l) SAED patterns with Debye-Scherrer rings characteristic of nanocrystalline C-type rare-earth sesquioxides.

As mentioned above, the nanoscale structure – particularly the film formation as a function of drying time after dip-coating and structural changes during the course of framework condensation and crystallization – was also analyzed by various *in situ* and *ex situ* scattering techniques. The GISAXS experiments were conducted at an angle of incidence $\beta = 0.2^\circ$ (between the beam and the film surface). **Figure 3** shows synchrotron-based *in situ* GISAXS patterns obtained on KLE-templated Dy₂O₃ and Yb₂O₃ thin films. As expected, the mesophase forms quite slowly because 2-methoxyethanol was used as a co-solvent in the synthesis. It should be noted, however, that 2-methoxyethanol is not vital for a successful synthesis. Instead, it helps obtain more homogeneous films with a higher degree of pore ordering. At $t = 90$ s the patterns display a faint intensity ring for both materials. This is the beginning of the formation of an ordered powder-like superstructure.^[37] By $t = 120$ s the mesophase seems fully developed with scattering maxima that can be indexed to a face-centered cubic (fcc) structure with (111) orientation relative to the plane of the substrate. The same data also show that the KLE-templated Yb₂O₃ films exhibit a higher degree of preferred orientation – the intensity ring is much less distinct. These results indicate that a powder-like mesophase is formed first, and that the individual domains begin to align at a later stage of the drying process. The fact that the degree of preferred orientation is different among both materials might be related to the different sol-gel behavior. After a drying time of approx. 120 s at ambient temperature, the films can be directly transferred to an oven at 150 °C to stabilize the composite architecture. At $t \geq 150$ s the scattering maxima begin to smear into a diffuse ring, and by approx. 420 s they have virtually

completely disappeared (see **Figure S3** in the SI). The latter effect is most likely due to X-ray induced damage.^[38]

Figure 3. *In situ* GISAXS at an angle of incidence $\beta = 0.2^\circ$ on KLE-templated Yb₂O₃ (left) and Dy₂O₃ (right) thin films as a function of drying time. Scattering vector $\mathbf{q}$ components are given in nm⁻¹.

To gain insights into how thermal annealing affects the pore-solid architecture of the KLE-templated thin films and to probe their thermal stability, *ex situ* GISAXS measurements were carried out. **Figure 4** shows synchrotron-based GISAXS patterns of Yb₂O₃ and Dy₂O₃ films heated at 300 °C for 12 h, and 600 °C and 900 °C for 10 s, respectively. Scattering data for Ho₂O₃, Er₂O₃, Tm₂O₃, and Lu₂O₃ can be found in **Figure S4** in the SI. All patterns show characteristic intensity maxima consistent with the results from *in situ* GISAXS. The fact that

both fundamental and higher order maxima can be clearly observed emphasizes the ordered nature of the porosity. In agreement, SAXS patterns in Bragg-Brentano geometry obtained on the same samples heated at 300 °C show distinct peaks (see **Figure 5a**). Although such measurements only provide information about the periodicity in the out-of-plane direction, i.e., perpendicular to the plane of the substrate, they indicate good structural ordering with pores of uniform size and shape. Furthermore, it can be seen from the GISAXS patterns that the scattering maxima appear as lines rather than spots, which we believe is due to the fact that the films undergo lattice contraction in the out-of-plane direction during thermal annealing. This volume change can be as large as 65% by 600 °C, as is evident for Yb₂O₃, and is associated with pore transformation from spherical to oblate. In addition, GISAXS shows that the crystallization ($T_{\text{onset}} \geq 550$ °C) of the initially amorphous (glassy) wall structures comes at little cost to the overall ordering of the fcc mesostructures – loss of order is typically observed at the onset of crystallization. The lack of out-of-plane scattering after heating the oxide ceramics to 900 °C can be explained by the morphological anisotropy of the films with significantly fewer repeat units in this direction and by small changes in nanoscale structure throughout crystallization and grain growth. However, we note that the heavier rare-earth sesquioxides can withstand annealing temperatures of 1000 °C for a short time, which is unique for polymer-templated mesoporous metal oxides. To our knowledge, similar thermal stability has only been reported for alumina-based systems.^[39,40] This observed trend that the heavier oxides are thermally more stable can also be seen in the GISAXS data. For example, in contrast to Dy₂O₃, KLE-templated Yb₂O₃ shows no signs of partial restructuring after heating at 900 °C – indicated by the appearance of scattering at lower q -values. Nonetheless, each type of film shown here can be annealed at 600 °C for several hours without any notable change in nanoscale structure. In this regard, it should

be noted that a temperature of 600 °C is regarded as sufficient for most application purposes of thin film materials.

Taken together, *in situ* GISAXS strongly suggests that a film drying time of 2 min or more after dip-coating is key to ensuring formation of mesostructured inorganic-organic composite materials with a well defined morphology (no further aging steps are needed). Moreover, the results with both *ex situ* GISAXS and conventional SAXS corroborate the microscopy data and confirm the high quality of the KLE-templated films. In addition, they show that the cubic pore structure of the different rare-earth sesquioxides can be preserved up to annealing temperatures of 900 °C and higher.

Figure 4. *Ex situ* GISAXS patterns at an angle of incidence $\beta = 0.2^\circ$ obtained on KLE-templated Yb_2O_3 (a–c) and Dy_2O_3 (d–f) thin films heated at 300 °C for 12 h, and 600 °C and 900 °C for 10 s, respectively. Scattering vector $\mathbf{q}$ components are given in nm^{-1} .

Lastly, the porous properties were also analyzed by nitrogen physisorption at 77 K. For these measurements, films were deposited on 300 micron-thick, double side polished silicon wafers, cut into small pieces, and were then transferred to a sorption cell. The measured Brunauer-Emmett-Teller (BET) surface areas were in the range 0.5-0.6 m², which should be sufficient to make the results reliable. **Figure 5b** shows adsorption/desorption isotherms obtained on approx. 550 nm thick Yb₂O₃ films with a total area of 50 cm² heated to 900 °C. Results for KLE-templated Dy₂O₃ thin films can be found in **Figure S5** in the SI. All these data show isotherms of type IV, which implies that the mesopore cavities are accessible to nitrogen gas and interconnected through smaller necks. For Yb₂O₃, data analysis provides a total pore volume of 1.82·10⁻³ cm³ (~62% porosity) and a BET surface area of 192 m²·cm⁻³. Assuming a density of 9.206 g·cm⁻³ (from Rietveld refinement of X-ray diffraction data in **Figure 8a**), the latter value corresponds to 55 m²·g⁻¹. We estimate the error margin as being ±10%. Similar results are obtained for Dy₂O₃ after heating the films to 800 °C, while the same material heated to 900 °C was found to have a significantly lower BET surface area. This finding can be explained by the fact that the framework is thermally less stable and undergoes more severe structural changes at such a high temperature, as indicated by GISAXS. The pore size distribution shown in the inset of **Figure 5b** was calculated using a non-local density functional theory (NLDF) equilibrium model for silica (NLDF adsorption branch model gave very similar results). From these data, it is apparent that the distribution is rather narrow with a maximum at 12.5 nm. At first glance, this dimension seems to be underestimated when compared to TEM data. However, the anisotropic pore shape has to be considered and, in so doing, the value of 12.5 nm is reasonable.

Figure 5. (a) SAXS in Bragg-Brentano geometry on KLE-templated Yb_2O_3 (blue) and Dy_2O_3 (black) thin films heated at 300 °C for 12 h. (b) Nitrogen adsorption/desorption isotherms for approx. $550 \text{ nm} \times 50 \text{ cm}^2$ KLE-templated Yb_2O_3 films heated to 900 °C. The corresponding pore size distribution shown in the inset was calculated using a NLDFT equilibrium model for silica.

In addition to KLE, $\text{PIB}_x\text{-}b\text{-PEO}_y$ diblock copolymers with different block lengths were also probed as SDAs to determine whether and if so, to what extent, the pore size can be tailored. In particular, we incorporated three such polymers, namely $\text{PIB}_{357}\text{-}b\text{-PEO}_{454}$, $\text{PIB}_{107}\text{-}b\text{-PEO}_{150}$, and $\text{PIB}_{53}\text{-}b\text{-PEO}_{45}$.^[32] We note that films were prepared under identical conditions – the polymer

weight fraction was kept constant at 31% in the synthesis (based on the total weight of the composite, i.e., SDA and RE_2O_3). Only for $\text{PIB}_{357}\text{-}b\text{-PEO}_{454}$, ethanol was replaced by tetrahydrofuran due to solubility issues.

Figure 6 shows electron microscopy data for $\text{PIB}_x\text{-}b\text{-PEO}_y$ -templated Yb_2O_3 thin films heated to 800 °C. The TEM and SEM images collectively demonstrate that all materials have a cubic mesostructure and that the in-plane pore size and, therefore, also the wall thickness can be readily tailored over a wide range. Films formed with $\text{PIB}_{53}\text{-}b\text{-PEO}_{45}$ seem to be similar to those produced using the diblock copolymer KLE, but the nanoscale architecture is less ordered – the pore cavities have an average in-plane diameter of 17 nm. By contrast, $\text{PIB}_{107}\text{-}b\text{-PEO}_{150}$ -templated samples exhibit 25 nm diameter pores, which is comparably large for sol-gel derived non-silicate materials. The data in **Figure 6** demonstrate further that it is possible to synthesize mesoporous Yb_2O_3 with pores averaging 42 nm in diameter when using $\text{PIB}_{357}\text{-}b\text{-PEO}_{454}$ as polymer SDA. This dimension is remarkable considering that the sample was produced from molecular precursors without the need for swelling agents. However, the TEM images also indicate that the structural ordering is less pronounced and that the pore size distribution is broader than that of the KLE-templated Yb_2O_3 films. Nevertheless, the increased wall thickness should improve the thermal stability even further. The nanocrystalline nature of Yb_2O_3 is confirmed by SAED. Because the calculated d -values are in good agreement with those for bulk material, we conclude that the films are single phase, polycrystalline C-type Yb_2O_3 .

Figure 6. Microstructure of PIB₃₅₇-*b*-PEO₄₅₄-templated (a–c), PIB₁₀₇-*b*-PEO₁₅₀-templated (d, e), and PIB₅₃-*b*-PEO₄₅-templated (f) Yb₂O₃ thin films heated to 800 °C. (a, d–f) Bright-field TEM images at different magnifications showing that the in-plane pore size can be effectively tailored from approx. 17 nm to 42 nm in diameter. (b) Top view SEM image. (c) SAED pattern indicating the nanocrystalline nature of Yb₂O₃.

GISAXS was also used to characterize the different PIB_{*x*}-*b*-PEO_{*y*}-templated Yb₂O₃ thin films. **Figure 7** shows synchrotron-based GISAXS patterns obtained after heating the samples at 300

°C for 12 h, and 600 °C and 900 °C for 10 s, respectively, thus enabling a direct comparison with the data in **Figure 4**. It is apparent that the pore ordering is in fact less pronounced compared to the KLE-templated films. However, both amorphous and crystalline films produce patterns with distinct maxima that can be indexed to “distorted” cubic mesostructures with medium to large repeat distances (d_y ~19 nm for PIB₅₃-*b*-PEO₄₅, ~29 nm for PIB₁₀₇-*b*-PEO₁₅₀, and ~45 nm for PIB₃₅₇-*b*-PEO₄₅₄). In addition, conventional SAXS data (see **Figure S6** in the SI) show higher order peaks for both PIB₅₃-*b*-PEO₄₅-templated and PIB₁₀₇-*b*-PEO₁₅₀-templated films heated at 300 °C. The elliptical shape of the GISAXS patterns is again indicative of out-of-plane lattice contraction; the in-plane contraction is negligible. As mentioned above, this volume change is a direct result of hydrolysis, condensation, and combustion reactions during thermal annealing. Furthermore, it can be seen that also for the PIB_{*x*}-*b*-PEO_{*y*}-templated films the out-of-plane scattering is lost upon heating to 900 °C and that the overall thermal stability with regard to structure preservation is increased for the samples with larger repeat distances – the maxima are less smeared out.

In summary, the data in **Figures 6** and **7** establish that Yb₂O₃ can be templated using PIB_{*x*}-*b*-PEO_{*y*} diblock copolymers to produce cubic mesoporous films with in-plane pore sizes ranging from 17 nm to 42 nm and up to 20 nm thick walls.

Figure 7. *Ex situ* GISAXS patterns at an angle of incidence $\beta = 0.2^\circ$ obtained on PIB₅₃-*b*-PEO₄₅-templated (a–c), PIB₁₀₇-*b*-PEO₁₅₀-templated (d–f), and PIB₃₅₇-*b*-PEO₄₅₄-templated (g–i) Yb₂O₃ thin films heated at 300 °C for 12 h, and 600 °C and 900 °C for 10 s, respectively. Scattering vector $\mathbf{q}$ components are given in nm^{−1}.

To better understand why (except for Sm₂O₃ and Tb₂O₃) the nanoscale structure of the different rare-earth sesquioxides can be preserved up to annealing temperatures of 900 °C and higher and to gain insight into the crystallization behavior, a series of X-ray diffraction (XRD)

measurements was conducted on the KLE-templated thin films. **Figure 8a** shows XRD patterns of Yb_2O_3 heated to 600 °C, 700 °C, 800 °C, 900 °C, and 1000 °C. Temperature-dependent data for all materials presented in this work can be found in **Figure S7** in the SI. For Yb_2O_3 , the crystallization begins at $T_{\text{onset}} \geq 550$ °C and the peaks are indicative of the *C*-type crystal structure. The XRD data were also analyzed using Rietveld analysis to extract microstructural information such as unit-cell parameter, average crystallite size, crystallographic orientation, and so forth. The refinement was carried out using a modified Thompson-Cox-Hastings pseudo-Voigt profile function and the background profile was modeled using a cubic interpolation of predetermined background points with refinable heights. From this analysis, we find that the mesoporous Yb_2O_3 films are in fact single phase and polycrystalline with lattice parameter $a = 10.438(1)$ Å. Furthermore, we find that the crystallites in the walls gradually grow with increasing annealing temperature (~ 2.9 nm per 100 °C; see **Figure S8** in the SI). This means that the *C*-type domain sizes can be tailored very finely, which should allow tuning of the material properties. The average size of the crystallites after heating the films to 600 °C and 1000 °C is 3.3 nm and 14.6 nm, respectively. The former dimension is assumed to be the stable crystallite size and the latter is in fair agreement with the wall thickness determined from TEM, thereby providing a clear explanation as to why no significant loss of order is observed up to 1000 °C (see also section on GISAXS above). Similar data are obtained for Dy_2O_3 . This material is also single phase with lattice parameter $a = 10.632(1)$ Å, but shows a preferred crystallographic orientation in [400], as is evident from **Figure 8b**. The average crystallite size can be tailored over a range of 5.2 nm at 600 °C to 15.2 nm at 900 °C (~ 3.4 nm per 100 °C; see **Figure S8** in the SI). The value of 15.2 nm shows that the nanocrystalline *C*-type domains are already larger than

those in Yb_2O_3 heated to 1000 °C and, therefore, helps explain why KLE-templated Dy_2O_3 films are thermally less stable – the growth rate is faster.

The finding that the stable crystallite size is well below 10 nm suggests that basically any amphiphilic block copolymer should be suited for preparing such mesoporous rare-earth sesquioxide films as long as it is compatible with the synthesis conditions described above. However, the vast majority of polymer SDAs have been shown to produce materials with walls that are thinner than 10 nm, which is quite often not sufficient to allow for uniform nucleation and growth of the crystalline phase with retention of porosity. In other words, there is a mismatch between the stable crystallite size and the wall thickness. However, for the sol-gel derived RE_2O_3 films, such a mismatch is unlikely due to the favorable crystallization behavior with very small initial domain sizes.

Figure 8. (a) XRD patterns for KLE-templated Yb_2O_3 thin films heated to 600 °C, 700 °C, 800 °C, 900 °C, and 1000 °C. (b) XRD patterns for KLE-templated Dy_2O_3 thin films heated to 600 °C, 700 °C, 800 °C, and 900 °C. The solid-line curves are simulated patterns by Rietveld refinement. The region between $2\Theta = 32.8^\circ$ and 33.2° (containing a strong Si(100) substrate peak) was excluded in the refinement.

The apparent crystallographic orientation was analyzed in more detail by Rietveld refinement using the modified March's function.^[41,42] Although such refinement is known to work only to a

limited extent with films with strong preferred orientation (works much better for powder-like samples), it provides semiquantitative information about both the crystalline texture and the degree of orientation. **Figure 9a** shows XRD data for KLE-templated Dy₂O₃, Ho₂O₃, Er₂O₃, Tm₂O₃, Yb₂O₃, and Lu₂O₃ thin films heated to 800 °C along with simulated patterns. We note that the (400) peak intensity was normalized to the same value in all the patterns to better illustrate the differences in crystallographic orientation. **Figure 9b** shows an XRD pattern obtained on a KLE-templated Sm₂O₃ thin film heated to 800 °C. From these data and the patterns in **Figure S7** in the SI, it can be clearly seen that Sm₂O₃ displays a strong preferred orientation in [400] and that the degree of crystallographic alignment decreases continuously with increasing atomic number, with one exception, namely Lu₂O₃. From Rietveld analysis, we find that Sm₂O₃ has indeed the strongest preferred orientation with $G_1 = 14.07(1)$ and $G_2 = 0.05(1)$. Both G_1 and G_2 are refinable orientation parameters – G_2 is a measure of the fraction of the sample that is not textured and can take values between 0 and 1 (random orientation would have a parameter of 1), and when $G_1 > 1$ the texture is fiber-like. As mentioned before, the preferred orientation decreases when going to the heavier oxides. For example, for Tm₂O₃, we find values of 1.51(1) and 0.421(1) for G_1 and G_2 , respectively, and Yb₂O₃ displays virtually no preferred orientation (i.e., nearly perfectly random crystallite orientation). In contrast, Lu₂O₃ shows a strong preferred orientation in [222] with $G_1 = 3.0(2)$ and $G_2 = 0.06(1)$. The same trend is apparent, in part, from SAED. Unlike Sm₂O₃, Lu₂O₃ shows a very intense diffraction ring corresponding to the (222) peak in agreement with the XRD results.

Overall, the data in **Figure 9** and **S7** in the SI demonstrate that the materials studied in this work are not only mesoporous but also have iso-oriented nanocrystalline walls, which is unique for polymer-templated oxide ceramic films. However, we note that we have not yet fully

understood the basis for the preferred orientation. Nevertheless, in contrast to layered crystalline α -MoO₃, T -Nb₂O₅, and L -Ta₂O₅ thin films which can also be produced with a high degree of crystallographic alignment by soft-templating strategies, the basic requirement for preferred orientation cannot be explained by the concept of “soft epitaxy” and the highly anisotropic bonding within the unit cell.^[22]

Figure 9. (a) XRD patterns for KLE-templated Dy₂O₃ (black), Ho₂O₃ (green), Er₂O₃ (red), Tm₂O₃ (yellow), Yb₂O₃ (blue), and Lu₂O₃ (cyan) thin films heated to 800 °C. The (400) peak intensity was normalized to the same value in all the patterns. The colored solid-line curves are simulated patterns by Rietveld refinement which include corrections for preferred orientation. The region between $2\Theta = 32.8^\circ$ and 33.2° (containing a strong Si(100) substrate peak) was excluded in the refinement. (b) XRD pattern of a KLE-templated Sm₂O₃ thin film heated to 800 °C showing a high degree of crystallographic alignment in [400].

Both the chemical composition and bonding configuration of KLE-templated Yb₂O₃ and Dy₂O₃ thin films heated to 800 °C were examined using X-ray photoelectron spectroscopy (XPS). **Figure 10** shows a survey spectrum as well as detail spectra of the Yb 4*d* and O 1*s* levels

for Yb_2O_3 . XPS data obtained on mesoporous Dy_2O_3 can be found in **Figure S9** in the SI. The survey spectrum in **Figure 10a** shows that carbon contamination is negligible – only ytterbium and oxygen peaks can be clearly observed. The Yb 4*d* spectrum in **Figure 10b** is rather complex and cannot be fitted using standard spin-orbit splitting parameters. We note that the Dy 4*d* spectrum is even more complex and, therefore, also cannot be readily deconvoluted. The complexity of these spectra results from plasmon loss structures.^[43] Nevertheless, the most intense peaks at (198.47 ± 0.05) eV and (184.18 ± 0.05) eV are due to emissions from the 4*d*_{3/2} and 4*d*_{5/2} levels of the Yb atoms, respectively, and those 6-7 eV higher in binding energy than the main peaks are shake-up lines.^[44] The O 1*s* spectrum in **Figure 10c** reveals two different oxygen bonding states. The main peak centered at (529.00 ± 0.05) eV can be attributed to lattice oxygen whilst the minor one at (531.16 ± 0.05) eV can likely be associated with hydroxyl groups. Similar data are obtained for the KLE-templated Dy_2O_3 thin films.^[45] Taken together, the results with XPS demonstrate that the mesoporous rare-earth sesquioxides are also well defined at the atomic level, which emphasizes the quality of these oxide ceramics.

Figure 10. (a) XPS surface spectrum of KLE-templated Yb_2O_3 thin films heated to 800 °C in air. Plasmon loss peaks are indicated by asterisks. (b, c) XPS detail spectra of the Yb 4d and O 1s levels, respectively. The solid-line curves in panel (c) are fits to the data assuming linear background.

Lastly, in order to obtain a more complete picture of the KLE-templated RE_2O_3 thin films, we also investigated their optical properties. As mentioned above, many of these materials are technologically important and show promise for use in optical coatings and as high- k gate dielectrics (to replace SiO_2). For such applications, knowledge of the band gap energy (E_g) is

crucial. **Figure 11** shows results from optical absorption measurements on Dy_2O_3 , Ho_2O_3 , Er_2O_3 , Tm_2O_3 , Yb_2O_3 , and Lu_2O_3 . These data reveal (indirect) E_g values at room temperature ranging from 4.9 eV to 5.6 eV in agreement with those of single crystals.^[46,47] The slight blue shift likely arises because of finite size effects associated with the nanocrystalline nature of the mesoporous films. From the data in **Figure 11**, it can be clearly seen that the size of the band gap – between oxygen $2p$ states (valence band) and lanthanide $5d(6s)$ states (conduction band) – increases with increasing atomic number, with one exception, namely Yb_2O_3 .^[48] Literature reports attribute the dip observed for Yb_2O_3 to either a minimum in the conduction band energy or to empty $4f$ states entering the forbidden gap.^[46,49]

Figure 11. Optical properties of KLE-templated Yb_2O_3 (blue) and Dy_2O_3 (black) thin films heated to 800 °C. Inset: plot showing the band gap energy at room temperature for KLE-templated films (black circles) and single crystals (red circles) of Dy_2O_3 , Ho_2O_3 , Er_2O_3 , Tm_2O_3 , Yb_2O_3 , and Lu_2O_3 .

Overall, the results demonstrate that many desirable features can be combined in oxide ceramics of the lanthanide group, which makes the polymer-templated RE_2O_3 thin films

interesting for applications in catalysis (e.g., as support or catalyst), electronics (e.g., as gate dielectric), optics (e.g., as light emitter), and in other fields. In addition, they might find applicability as advanced water-repellent coatings that are robust to harsh environments, as shown recently by Azimi *et al.*^[50] Future work will be dedicated to (1) testing all the different materials for particular applications, (2) finding out if the unique combination of thermal stability, high specific surface area, tailorable pore and grain sizes, and crystalline texture is beneficial to broaden the scope of these oxide ceramics, and to (3) seeing if the synthesis method employed here can be extended to nanopowders as well as to ternary or even quaternary oxides containing rare-earth elements such as multiferroic orthoferrites ($h\text{-REFeO}_3$) with the space group $P6_3cm$ (C_{6v}^3) and/or magnetostrictive lanthanum strontium manganese oxide (LSMO). The latter would open up the possibility for exploring the physical properties of new and exciting classes of interface-controlled nanomaterials.

Conclusion

A series of sub-micron-thick mesoporous films of the rare-earth sesquioxide family has been prepared by solution-phase coassembly of hydrated chloride salt precursors with different amphiphilic diblock copolymers and has been characterized in detail. Materials with good structural ordering can be readily achieved at low relative humidity when using both 2-methoxyethanol and glacial acetic acid in the synthesis. The former acts as a co-solvent and slows down the drying process of the deposited inorganic/organic composite films while the latter actively prevents recrystallization of chloride species by some sort of complexation. Under these conditions sufficient film drying time is found to be key to ensuring formation of well defined mesostructured materials with cubic pore symmetry.

Morphology and microstructure studies using various state-of-the-art techniques show that (1) the pore size can be tailored over a wide range, from approx. 17 nm to 42 nm in diameter, through the choice of polymer SDA, (2) the nanoscale structure can be retained up to temperatures of 800 °C and higher (1000 °C for the heavier oxides), (3) the optical properties are similar to those of single crystals, and that (4) the presence of larger amounts of defects on the nano- and microscale as well as on the atomic level can be ruled out. We also find that all the different oxide ceramics presented in this work are single phase in the temperature range investigated and that, in particular, Sm₂O₃ and Lu₂O₃ films exhibit a strong crystalline texture, which is unique for such polymer-templated mesoporous thin films. In summary, our research data demonstrate that the synthesis procedure is not only straightforward but also yields high quality nanomaterials, and is further applicable to a multitude of (if not all) rare-earth oxides.

ASSOCIATED CONTENT

Supporting Information. Additional data from TEM and SEM imaging, *in situ* and *ex situ* GISAXS, N₂-physisorption, SAXS, XRD, and XPS. This information is available free of charge via the Internet at <http://pubs.acs.org/>.

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Notes

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