General Synthesis of Ordered Mesoporous Rare-Earth Orthovanadate Thin Films and Their Use as Photocatalysts and Phosphors for Lighting Applications

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Abstract

Herein, the block copolymer templating sol-gel synthesis of a novel class of ternary oxide nanomaterials is reported. NdVO_4 , EuVO_4 , GdVO_4 , DyVO_4 , YVO_4 , and TmVO_4 have been prepared as open mesoporous films by the dip-coating method using hydrated rare-earth nitrate salt precursors along with vanadium oxytrichloride. All materials crystallize in the tetragonal ZrSiO_4 -type structure with space-group $I4_1/amd$. Short-term treatment at 550 °C is found sufficient to initiate crystallization. Characterization via X-ray and electron diffraction, Raman and X-ray photoelectron spectroscopy, and time-of-flight secondary ion mass spectrometry confirms the single-phase nature and uniformity of the different orthovanadates with tailorable crystallite sizes. The integrated results from electron and atomic force microscopy, Kr-physisorption as well as *in-situ* and *ex-situ* synchrotron-based small-angle X-ray scattering reveal that the porosity persists throughout the thickness of films and the mesoscopic ordering is retained even after heating in air at 700 °C. Photobleaching experiments indicate that the sol-gel derived materials, showing an indirect band gap transition at (3.8 ± 0.1) eV, exhibit good photocatalytic properties—the activity is highly superior to that of bulk films of the same nominal composition. Moreover, when doping GdVO_4 , YVO_4 , and solid solution GdVO_4 - YVO_4 with trivalent rare-earth ions such as Eu^{3+} , Dy^{3+} , Er^{3+} , or Tm^{3+} ions, the films hold promise as phosphors for lighting applications, which might pave the way toward development of (3-dimensional) intricate nanocomposites with unprecedented functionalities.

Introduction

Nanoscale oxides and nonoxides with their size- and shape-dependent properties have been attracting a great deal of attention, among others, because of potential applications in various sectors such as healthcare, electronics, and energy. Rare-earth orthovanadates, REVO_4 (RE = trivalent rare-earth ion), are one such class of materials, showing promise, for example, as catalysts, especially when produced with nanoscale dimensions.^{1–3} In addition, they are widely used as substrates for phosphor and laser materials.^{4–7} However, there are also studies on the magnetic, electronic, and other properties of nanocrystalline rare-earth orthovanadates available in the literature.^{7–9}

Rare-earth orthovanadates are known to have two polymorphs, the tetragonal zircon (ZrSiO_4) and the monoclinic monazite (LnPO_4) forms.^{10,11} The type of polymorph formed depends, for the most part, on the ionic radius, and typically, the larger RE^{3+} ions prefer the monoclinic structure type.¹¹ Although rare-earth orthovanadates have been prepared in various forms and shapes and with different nanostructures, we are unaware of reports on ZrSiO_4 -type ordered mesoporous films. It should be noted, however, that for most applications in the electronic and optical industries, high-quality (structured and unstructured) materials in the form of films are required.

In this work, we report, to our knowledge for the first time, the evaporation-induced self-assembly (EISA) synthesis of a series of nanocrystalline rare-earth orthovanadate films of thickness ≤ 500 nm and primarily focus on the characterization of this novel class of mesostructured materials. Specifically, films of NdVO_4 , EuVO_4 , RE^{3+} -doped and undoped GdVO_4 , DyVO_4 , RE^{3+} -doped and undoped YVO_4 , and TmVO_4 were produced (as model systems) by the dip-coating method via coassembly of hydrolyzing nitrate and chloride salt precursors and an amphiphilic KLE-type diblock copolymer [KLE = KRATON LIQUID-*b*-poly(ethylene oxide)].¹² Similar to poly(ethylene oxide)-*b*-poly(propylene oxide)-*b*-poly(ethylene oxide), poly(ethylene oxide)-*b*-polybutadiene-*b*-poly(ethylene oxide), and poly(ethylene oxide)-*b*-polystyrene, to name a few,^{13–17} such amphiphilic polymers have proven in the past to be promising and effective structure-directing agents for the preparation of mesoporous metal oxides (especially nanocrystalline ones), including ternary phases.^{18–24} This is due in part to the formation of composite mesostructures with relatively large repeat distances. Of note, the EISA process was already introduced in the late 1990's, and soft-templating approaches, in general, are still those that are most widely used along with sol-gel/molecular precursors or nanocrystal building blocks when targeting large- and small-size mesoporous materials as not only thin films but also powders.^{25–38}

Apart from the general synthesis and structural/compositional characterization, we also briefly address the use of block copolymer-templated mesostructured rare-earth orthovanadate films as photocatalysts and phosphors. Yet, their (real) application potential should be further explored. Nevertheless, we demonstrate that especially GdVO_4 shows superior UV-light photocatalytic activity, which appears to be due in part to the large number of active sites and favorable recombination rates of free charge carriers. Moreover, we show that the bulk photoluminescence can be tailored by making use of the precise control the sol-gel synthesis offers over the materials' composition and stoichiometry. This could enable development of novel optical devices.

Experimental Section

Materials

$\text{Eu}(\text{NO}_3)_3 \cdot 5\text{H}_2\text{O}$, $\text{Gd}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$, $\text{Nd}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$, $\text{Tm}(\text{NO}_3)_3 \cdot 5\text{H}_2\text{O}$, $\text{Y}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$, VOCl_3 , EtOH, and 2-methoxyethanol were purchased in the highest available purity from Sigma-Aldrich. $\text{Dy}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ was obtained from ABCR. $\text{H}[(\text{CH}_2\text{CH}_2)_{0.67}(\text{CH}_2\text{CHCH}_2\text{CH}_3)_{0.33}]_{89}(\text{OCH}_2\text{CH}_2)_{79}\text{OH}$ (KLE) served as the structure-directing agent in the coassembly synthesis.¹⁸ Polished Si substrates of (001) orientation were purchased from Si-Mat.

Thin-Film Preparation

Dry EtOH (1 mL) was added to a flask under argon with the hydrated rare-earth nitrate salt and VOCl_3 precursors (1:1 molar ratio; e.g., 232.1 mg of $\text{Gd}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ and 89.1 mg of VOCl_3 for the preparation of GdVO_4). After stirring the reaction mixture for 1 h,

it was combined with 70 mg of KLE diblock copolymer dissolved in 1 mL of dry EtOH and 0.5 mL of 2-methoxyethanol to give a transparent yellow/red-colored solution. Films of different thicknesses were produced by the dip-coating method at withdrawal rates of 5-15 mm/s using both Si wafer and quartz glass substrates. During the film formation process, the relative humidity was controlled at 13-16%. For best results, the as-made films were transferred to an oven for drying at 150 °C for 2 h before heating to 300 °C at 5 °C/min, with 12 h dwell time to stabilize the mesostructure by driving condensation and combustion reactions.³⁹ Crystallization was achieved by heating in air to temperatures ≥ 500 °C at 10 °C/min. A scheme illustrating both the fabrication and system is shown in **Figure 1**.

Characterization of Materials

Transmission electron microscopy (TEM), field-emission scanning electron microscopy (SEM), and atomic force microscopy (AFM) images were collected on a CM30-ST from Philips, a MERLIN from Carl Zeiss, and a multimode atomic force microscope from Veeco Instruments using OLYMPUS micro cantilevers (300 kHz, 42 N/m), respectively. X-ray diffraction (XRD) was performed using an X'Pert PRO diffractometer from PANalytical instruments. For crystal structure visualization, Crystal Impact Diamond software version 3.2g was used. Raman spectra were collected on a SENTERRA dispersive Raman microscope from Bruker Optics, equipped with an objective from Olympus (MPlan N 20x/0.40/FN22) and a Nd:YAG laser (532 nm, 10 mW). Time-of-flight secondary ion mass spectrometry (ToF-SIMS) was performed on a TOF.SIMS 5 instrument from IONTOF GmbH using 25 keV Bi₃⁺ as the primary ion species. Sputter etching was done by means of 1 keV O₂⁺. The film thickness was determined with an Alpha Step IQ Surface Profiler from KLA-Tencor. X-ray photoelectron spectroscopy (XPS) was performed on a setup from VG Instruments, consisting of a custom ultra-high vacuum chamber and a Mark II dual anode (Al- and Mg-K_{alpha}) X-ray source. The spot size at the sample surface was 8x8 mm². Spectra were analyzed via the software package UNIFIT 2005. *Ex-situ* grazing incidence small-angle X-ray scattering (GISAXS) and *in-situ* SAXS measurements were performed at the German synchrotron radiation facility HASYLAB at DESY on beamline BW4 using a MarCCD area detector and a Pilatus 300k, respectively. The sample-detector distance was around 1820 mm. Krypton physisorption at 87.4 K was conducted on ≈ 180 nm thick films of total area (40 $\pm$ 4) cm² using an Autosorb-1-MP automated gas adsorption station from Quantachrome Corporation, equipped with a cryostat from Oxford Instruments. Optical absorption measurements were performed using a PerkinElmer Lambda 900 UV-Vis-NIR spectrophotometer. A fused silica substrate and an aluminum mirror served as the reference for transmission and reflection measurements, respectively. Photobleaching experiments were performed using methylene blue as the model pollutant. To this end, 8 mL of an aqueous solution of 10 μ mol/L methylene blue was illuminated with 254 nm light (8 W) in the absence or presence of ≈ 180 nm thick films of total area (4.0 $\pm$ 0.2) cm². Photoluminescence (light emission) was dispersed by an Oriel MS257 1/4 m monochromator and detected using a standard photomultiplier system, connected to a lock-in amplifier.

Results and Discussion

Figure 1. Fabrication scheme for mesoporous rare-earth orthovanadate thin films and the corresponding crystal structure of tetragonal REVO_4 with space-group $I4_1/amd$. V^{5+} is in black, RE^{3+} in dark gray, and O^{2-} in light gray. $[\text{VO}_4]^{3-}$ units are highlighted.

Since the different rare-earth orthovanadates are fairly similar in terms of nanoscale structure and porosity, in the following section, we focus primarily on both GdVO_4 and TmVO_4 . The film structure/morphology before and after crystallization and the mesophase formation were analyzed via a combination of electron and atomic force microscopy and small-angle X-ray scattering. Top-view and cross-sectional SEM and tapping mode AFM images of ≤ 500 nm thick films heated in air to 700°C are shown in **Figure 2** (see also **Figure S1** for electron microscopy of block copolymer-templated mesostructured EuVO_4 and DyVO_4 films). Evidently, the porosity persists throughout the bulk and the mesoscopic ordering is well retained after high-temperature treatment. The latter can also be seen from the top-view SEM images in **Figure S2**. These were obtained on individual films heated at different temperatures of 300 , 550 , and 700°C and reveal that both the in-plane pore ordering and the average repeat distances are hardly affected by the crystallization of the initially amorphous materials. Yet, some of the pores at the top surface seem to be closed, at least to some degree, the reason of which is unclear. The hexagonal pore arrangement further hints at a face-centered cubic (fcc) structure with (111) orientation relative to the substrate plane. In addition, SEM and AFM analysis demonstrates that the films are relatively smooth and more importantly, that they are of good quality without major structural defects at the nanometer and micrometer length scales.

Figure 2. Electron and atomic force microscopy of block copolymer-templated mesostructured GdVO₄ (a, b) and TmVO₄ thin films (c, d) heated in air to 700 °C. (a, c) Top-view SEM images at different magnifications, (b) tapping mode AFM phase image, and (d) cross-sectional SEM image.

Figure 3 shows the corresponding TEM images at different magnifications along with selected-area electron diffraction (SAED) patterns. Bright-field TEM indicates an in-plane pore size of ≤ 16 nm, in accordance with the SEM imaging results, and further reveals the nanoparticulate nature of wall structures. High-resolution TEM confirms the bulk crystallinity. According to SAED, the materials adopt a tetragonal ZrSiO₄-type crystal structure with space-group $I4_1/amd$ (D_{4h}^{19}) and consist of randomly oriented crystallites. In summary, electron and atomic force microscopy provides profound evidence that the rare-earth orthovanadate films can be crystallized with minimum losses in mesoscopic ordering. Both the thermal stability and structural uniformity are notable, especially for ternary metal oxides.

Figure 3. Electron microscopy of block copolymer-templated mesostructured GdVO₄ (a, b, d) and TmVO₄ thin films (c, e) heated in air to 700 °C. (a, c) Bright-field TEM images, (b) high-resolution TEM image showing the (200) lattice planes of tetragonal GdVO₄, and (d, e) SAED patterns revealing the single-phase nature of the sol-gel derived materials. The 200 reflection is denoted by a dashed red circle in parts (d) and (e).

In order to gain insight into the mesophase formation, synchrotron-based SAXS measurements were conducted *in-situ* on the GdVO₄ and TmVO₄ films during the drying process after dip-coating onto ultrathin Si substrates. Patterns were collected in 1 min intervals over a 3 min period (**Figure 4**). The mesophase formation proceeds rather slowly. The reason is that 2-methoxyethanol, which served as a cosolvent in the reaction mixture, slows down the drying of films significantly. However, its use may be beneficial, as it can help prevent immediate recrystallization of precursor species. Initially (1 min), the SAXS patterns reveal a diffuse ring with some faint scattering spots, indicative of primarily powder-like structures. After 2 min of drying, the mesophase formation seems largely completed. Consistent with the SEM observations, the scattering maxima can be indexed to a distorted [111] oriented fcc lattice, with TmVO₄ exhibiting a much more preferred orientation of the mesostructure to the substrate than GdVO₄. This result also suggests that domain alignment occurs somewhat later in the drying process. In addition, it can be seen that there is some shrinkage of the mesostructure as drying proceeds. Since the films in the as-made state are quite loosely bound to the substrate, such shrinkage is virtually isotropic in nature.

Figure 4. *In-situ* SAXS at 5° incidence angle of block copolymer-templated mesostructured GdVO₄ (a-d) and TmVO₄ thin films (e-h). The patterns were recorded at room temperature in 1 min intervals over a 3 min period and reveal the formation of fcc structures with large repeat distances and varying degrees of preferred orientation to the substrate. Both q_z and q_y are given in units of nm⁻¹.

The bulk porosity/nanoscale structure was probed *ex-situ* by synchrotron-based GISAXS. Patterns obtained on the GdVO₄ and TmVO₄ films heated in air at 300 and 700 °C for 12 h and 1 min, respectively, are shown in **Figure 5**. As expected, samples with an amorphous wall structure produce distinct scattering maxima in the q_z and q_y directions, and even higher order maxima are clearly visible, despite the linear intensity scaling. However, only the in-plane periodicity is retained in the crystalline samples, which is due to the morphological anisotropy of films. The average in-plane d -spacing is 23 nm, which is characteristic of KLE-templated mesoporous materials.²¹⁻²⁴ It can also be seen that the films experience $\geq 75\%$ lattice contraction normal to the substrate plane during processing (determined from the position of the in- and out-of-plane scattering maxima after heating at 300 °C) due to an increase in the degree of condensation of the inorganic phase. Conversely, the in-plane contraction is negligible. The reason is that the films after heating are bonded to the substrate surface. Taken together, the integrated results from *in-situ* SAXS and *ex-situ* GISAXS lead us to conclude that the rare-earth orthovanadate films form stable fcc structures with similar repeat distances, which can be fully retained at temperatures as high as 700 °C; there are no apparent signs of restructuring or collapse of the cubic pore networks. However, we note that extended annealing at ≥ 700 °C causes significant reduction in pore ordering due to grain growth, among others.

Figure 5. *Ex-situ* GISAXS patterns at 0.2° incidence angle of block copolymer-templated mesostructured GdVO₄ (a, b) and TmVO₄ thin films (c, d) heated in air at 300 °C for 12 h (a, c) and then at 700 °C for 1 min (b, d). The heating rate was 10 °C/min. Both q_z and q_y are given in units of nm⁻¹.

Finally, Kr-physisorption at 87.4 K was conducted on the GdVO₄ and TmVO₄ films heated in air to 700 °C to determine both the (BET) surface area and pore volume. The measured adsorption-desorption isotherms are shown in **Figure S3**. Their characteristic type IV shape is typical of mesostructured materials with an open porosity, where the pore cavities are connected through smaller necks. Using a Kr saturation pressure of 13 mmHg (17.3 hPa) and assuming a cross-sectional area of 20.5 Å, the volume-specific surface area and total pore volume were calculated as ≈ 140 m²/cm³ and $\approx 2.8 \times 10^{-4}$ cm³, respectively. The latter value corresponds to $\approx 40\%$ porosity, which is in fair agreement with the surface porosity from SEM image processing when using Otsu's method.⁴⁰ The error margin is estimated as being $\pm 10\%$.

The crystal structure of ZrSiO₄-type REVO₄ materials is depicted in **Figure 1**. The isolated [VO₄]³⁻ units are the Raman active species, with the V-O and O-V-O bonds undergoing specific stretching and bending vibrations.⁴¹⁻⁴³ Our data indicate the presence of either 5 or 6 Raman bands. The internal modes of [VO₄]³⁻ tetrahedra can be assigned as follows: (ν_1) symmetric stretching, (ν_2) symmetric bending, (ν_3) asymmetric stretching, and (ν_4) asymmetric bending.⁴¹⁻⁴³ External modes cannot be detected because of their low intensities and superposition of the spectrum from the substrate. Representative Raman spectra of the NdVO₄, EuVO₄, GdVO₄, DyVO₄, YVO₄, and TmVO₄ films heated in air to 700 °C are shown in **Figure 6**, and **Table 1** lists the measured Raman shifts of the respective modes. The experimental Raman shifts agree well with that reported in the literature. The spectra reveal a distinct shift of the high-frequency modes B_{1g} , E_g , and A_{1g} depending on the size of the trivalent

rare-earth ion. Note that stretching vibrations (ν_1 and ν_3) are more strongly affected than are bending vibrations (ν_2 and ν_4). A similar observation was made by Barth *et al.* and explained by the altered force constant of the V-O bond for different RE³⁺ ions in rare-earth orthovanadates.⁴⁴

Figure 6. Raman spectra in the wavenumber range between 150 and 1250 cm⁻¹ of block copolymer-templated mesostructured NdVO₄ (A), EuVO₄ (B), GdVO₄ (C), DyVO₄ (D), YVO₄ (E), and TmVO₄ thin films (F) on Si substrate heated in air to 700 °C (left). Detailed spectra showing the B_{1g}, E_g, and A_{1g} modes (right).

Table 1. Experimental Raman shifts and mode assignments.

Sample	A _{1g} ν_1 (cm ⁻¹)	E _g ν_3 (cm ⁻¹)	B _{1g} ν_3 (cm ⁻¹)	B _{2g} ν_4 (cm ⁻¹)	A _{1g} ν_2 (cm ⁻¹)	B _{1g} ν_2 (cm ⁻¹)
NdVO ₄	870	808	792	471	379	259
EuVO ₄	877	819	795	*	380	259
GdVO ₄	883	825	806	*	380	259
DyVO ₄	888	831	812	*	382	259
YVO ₄	891	838	815	*	382	259
TmVO ₄	895	842	820	*	384	259

*too weak in intensity.

The crystallization behavior and phase composition were also studied by XRD. Patterns in the 2 θ range of the 101 and 200 reflections of the NdVO₄, EuVO₄, GdVO₄, DyVO₄, YVO₄, and TmVO₄ films heated in air to 550 and 700 °C are shown in **Figure 7**. The patterns are normalized to the intensity of the most intense reflection for ZrSiO₄-type REVO₄ compounds, the 200 reflection at 24.4-25.4°. They reveal the expected shift in reflection locations and confirm that the materials crystallize in the space group *I4₁/amd*, in agreement with the ICSD reference codes 78077 (PDF no. 15-769) for NdVO₄, 81702 (PDF no. 15-809) for EuVO₄, 81703 (PDF no. 17-260) for GdVO₄, 81704 (PDF no. 16-870) for DyVO₄, 78074 (PDF no. 17-341) for YVO₄, and 78081

(PDF no. 18-1379) for TmVO_4 . Except for NdVO_4 , the average crystallite size calculated from the line broadening of the 200 reflection varies from 10-16 nm at 550 °C to 14-17 nm at 700 °C, which is in the range of the pore wall thicknesses (see SEM imaging data in **Figures 2, S1, and S2**). NdVO_4 apparently exhibits larger crystallite sizes of 20 nm (550 °C) and 24 nm (700 °C) for unknown reason. In summary, structural characterization via electron and X-ray diffraction and Raman spectroscopy demonstrates the single-phase nature of the rare-earth orthovanadates, which are already in a crystalline state after short-term treatment at 550 °C (≤ 1 min). Severe grain growth or coarsening during subsequent heating to 700 °C can be ruled out.

Figure 7. Normalized XRD patterns in the 2θ range between 16 and 28° of block copolymer-templated mesostructured NdVO_4 (A), EuVO_4 (B), GdVO_4 (C), DyVO_4 (D), YVO_4 (E), and TmVO_4 thin films (F) heated in air to 550 (top) and 700 °C (bottom).

As mentioned earlier, the rare-earth orthovanadate films were also tested as photocatalysts. Because there is conflicting information in the literature, the optical properties of the sol-gel derived materials were examined first. The Tauc plots shown in the top panel of **Figure 8** and **Figure S4** argue for an indirect band gap transition at (3.8 ± 0.1) eV. The direct band gap value was estimated by extrapolating the linear part of curve to the x-axis and found to be slightly larger at (4.1 ± 0.1) eV. Overall, these

data suggest that the different thin-film materials have a similar band gap energy, which is not too far off from that of anatase nano-TiO₂, for example.⁴⁵ Consequently, high-surface-area rare-earth orthovanadates might show promise for UV-light applications.³

The catalytic activity of the rare-earth orthovanadates was evaluated in room temperature photobleaching experiments of methylene blue (MB). The bottom panel of **Figure 8** and **Figure S5** depict semi-logarithmic plots, indicating that the degradation reaction follows pseudo first-order kinetics. The shift in absorption maxima, which is characteristic of only partial chromophore cleavage of the model pollutant, was found to be negligible. Likewise, the self-degradation of MB over the entire time period of the experiment was negligible. The degradation rate for the different materials tested was determined by linear regression analysis of data. Note that the apparently faster kinetics within the first 15 min is probably due in part to adsorption effects. For better comparison between the samples, the turnover frequency, defined as $TOF = k'/n_{\text{photocatalyst}}$, was calculated from the degradation rate and the amount of photocatalyst (assuming 60% of the solid-state density of the different REVO₄ phases for the mesoporous films). TOF values ranging from 60 to 180 mol⁻¹ s⁻¹ were thus obtained, with GdVO₄ showing the highest activity, even exceeding that of anatase TiO₂ films (≈130 mol⁻¹ s⁻¹) made using the same diblock copolymer structure-directing agent. The beneficial effect of nanoscale porosity on the activity is clearly evident from the control experiment with unstructured (bulk) GdVO₄ as the photocatalyst—there is a factor of about 6 difference in TOF between the block copolymer-templated and nontemplated material. Taken together, these preliminary results suggest that especially GdVO₄ exhibits promising properties for the photocatalytic degradation/mineralization of organic pollutants.

Figure 8. Room temperature optical and photocatalytic properties of block copolymer-templated mesostructured GdVO_4 and TmVO_4 thin films heated in air to 700 °C. Direct and indirect optical transitions (top). Photobleaching of methylene blue achieved in the absence and presence of ≈ 180 nm thick films of total area (4.0 ± 0.2) cm^2 (bottom). Dashed lines are linear fits to the experimental data.

Lastly, we looked at the performance of RE^{3+} -doped GdVO_4 , YVO_4 , and solid solution GdVO_4 - YVO_4 films as phosphors. The dopant concentration was controlled at 0.83 at.% (e.g., $\text{Gd}_{1-x}\text{Eu}_x\text{VO}_4$, with $x = 0.05$). The top panel of **Figure 9** and **Figure S6** show XRD patterns of the different samples. The temperature-dependent study conducted on the $\text{YVO}_4:\text{Eu}^{3+}$ system (**Figure S6**) establishes that the dopant incorporation does not affect the overall crystallization behavior. Likewise, the crystallite size after heating in air to 700 °C remains unaffected—within the experimental error—and the samples are free of impurity phases, as can be seen from the patterns obtained on the $\text{GdVO}_4:\text{RE}^{3+}$ films (with $\text{RE} = \text{Eu}, \text{Dy}, \text{Er}, \text{and Tm}$) in **Figure S6**, among others. In addition, the 200 reflection is found to gradually shift toward lower 2θ values with increasing Gd content (top panel of **Figure 9**), thus clearly indicating solid solution behavior in the case of GdVO_4 - $\text{YVO}_4:\text{Eu}^{3+}$ ($\text{Gd}_{0.475}\text{Y}_{0.475}\text{Eu}_{0.05}\text{VO}_4$). This result is also confirmed by Raman spectroscopy. As denoted by vertical dashed lines in the middle

panel of **Figure 9**, the high-frequency A_{1g} band maximum is right between that observed for $YVO_4:Eu^{3+}$ and $GdVO_4:Eu^{3+}$.

Even though XRD and Raman spectroscopy already demonstrate that the RE^{3+} -doped rare-earth orthovanadates employed in this work are well defined, too, both XPS and ToF-SIMS depth profiling analysis of the element distribution were performed on the $GdVO_4:Eu^{3+}$, $YVO_4:Eu^{3+}$, and $GdVO_4-YVO_4:Eu^{3+}$ films heated in air to 700 °C. Their chemical composition was studied by XPS. Since the materials are porous throughout and the wall thickness is in the lower nm range, the information from XPS can be considered to reflect the bulk. Both survey spectra for all samples and detailed spectra of the Gd3d, O1s, V2p, and Eu3d_{5/2} core level regions for $GdVO_4:Eu^{3+}$ are shown in **Figure S7**. Apart from adventitious C, only Gd, Y, Eu, V, and O core levels are observed, with the symmetric V2p and Eu3d peaks being characteristic of the 5+ and 3+ oxidation state, respectively. Besides, quantitative XPS analysis (**Table S1**) indicates that there are only minor deviations from the expected stoichiometries.

ToF-SIMS depth profiling results obtained on a ≈ 180 nm thick $GdVO_4:Eu^{3+}$ film are shown in the bottom panel of **Figure 9** (see **Figure S8** for ToF-SIMS of the $YVO_4:Eu^{3+}$ and $GdVO_4-YVO_4:Eu^{3+}$ systems). From the V^+ , Gd^+ , and Eu^+ signals, and taking into the account the XPS findings, we conclude a uniform element distribution throughout the layer thickness. The increase in Gd^+ and Eu^+ intensities at the film/substrate interface does not necessarily imply enrichment, but rather is due to changes in chemical environment. This hypothesis is corroborated by the fact that other species showed the same behavior. Moreover, the C^+ signal evidences that the diblock copolymer structure-directing agent is fully removed after heating, thus indirectly confirming that the 3D pore network is open.

Figure 9. Normalized XRD patterns in the 2θ range of the 101 and 200 reflections (top) and Raman spectra (middle) of block copolymer-templated mesostructured $\text{YVO}_4\text{:Eu}^{3+}$ (A), $\text{GdVO}_4\text{-YVO}_4\text{:Eu}^{3+}$ (B), and $\text{GdVO}_4\text{:Eu}^{3+}$ thin films (C) on Si substrate heated in air to 700 °C. Shift in reflection and band locations is denoted by vertical dashed lines. ToF-SIMS depth profiling of $\text{GdVO}_4\text{:Eu}^{3+}$ (bottom). Signal intensities from individual ions are divided by the total ion count.

Room temperature emission spectra of the $\text{YVO}_4\text{:Eu}^{3+}$, $\text{GdVO}_4\text{-YVO}_4\text{:Eu}^{3+}$, and $\text{GdVO}_4\text{:Eu}^{3+}$ films heated in air to 700 °C are shown in **Figure 10**. The excitation wavelength was controlled at 266 nm using a Nd:YAG solid-state laser, i.e., only the static host material environment was altered. According to selection rules, the photoluminescence emission of Eu^{3+} dopant should produce distinct lines around 590 and 620 nm for the magnetic-dipole-allowed $^5\text{D}_0\text{-}^7\text{F}_1$ and electric-dipole-allowed $^5\text{D}_0\text{-}^7\text{F}_2$ transitions, respectively.^{4,6,7,11,46} These transitions are clearly visible for the different samples. Evidently, the $^5\text{D}_0\text{-}^7\text{F}_2$ lines at 615 and 619 nm, giving rise to strong (hypersensitive) red emission (see **Figure S9** for photographs of the $\text{GdVO}_4\text{:Eu}^{3+}$, $\text{GdVO}_4\text{:Dy}^{3+}$, $\text{GdVO}_4\text{:Er}^{3+}$, and $\text{GdVO}_4\text{:Tm}^{3+}$ films after excitation with light of wavelength 254 nm), are narrow and well defined and there is no wavelength shift.^{46,47} Their relative intensities are obviously higher for the solid solution $\text{GdVO}_4\text{-YVO}_4\text{:Eu}^{3+}$ film due to either more favorable charge transfer or differences in symmetry of the host lattice compared to both the YVO_4 and GdVO_4 systems. The latter is also reflected in the fact that the $^5\text{D}_0\text{-}^7\text{F}_1$ emission centered at 594 nm reveals clear line splitting in the case of $\text{YVO}_4\text{:Eu}^{3+}$ and no splitting in the case of $\text{GdVO}_4\text{:Eu}^{3+}$. $\text{GdVO}_4\text{-YVO}_4\text{:Eu}^{3+}$ shows an intermediate state with partial splitting of the $^5\text{D}_0\text{-}^7\text{F}_1$ line. However, we note that slight differences in the degree of crystallinity between the mesoporous films cannot be ruled out. Moreover, there are also minor emission lines at 585, 587, 589, 609, and 613 nm, which can be associated with other $^5\text{D}_0\text{-}^7\text{F}_J$ transitions.

Figure 10. Room temperature emission spectra in the wavelength range between 580 and 630 nm of block copolymer-templated mesostructured $\text{YVO}_4\text{:Eu}^{3+}$ (A), $\text{GdVO}_4\text{-YVO}_4\text{:Eu}^{3+}$ (B), and $\text{GdVO}_4\text{:Eu}^{3+}$ thin films (C) heated in air to 700 °C.

Conclusions

Single-phase ZrSiO_4 -type rare-earth orthovanadates were prepared in the form of ordered mesoporous films by the dip-coating method using a soft-templating process via coassembly of hydrolyzing nitrate and chloride salt precursors and an amphiphilic diblock copolymer. Thermal treatment at 550 °C led to crystallization, and there were no signs of restructuring or collapse of the cubic pore-solid architectures up to

temperatures of at least 700 °C due to lack of significant grain growth during heating in air. Structural characterization confirmed the tetragonal lattice structures and further revealed that the pore networks are open and continuous. Moreover, trivalent rare-earth ion-doped orthovanadates and solid solution phases were successfully prepared. As somewhat expected, dopant incorporation did neither affect the structuring nor the film crystallization behavior. Spectroscopic and spectrometric analysis demonstrated both the high compositional homogeneity of the nanocrystalline materials and the uniform element distribution throughout the films, emphasizing the precise control the templating sol-gel synthesis offers over the materials' stoichiometry and porosity at the nanometer level.

Although the scope of the present work was limited, for the most part, to the preparation and characterization of this novel class of ternary oxide nanomaterials, preliminary photobleaching and photoluminescent measurements were conducted on the mesoporous films to assess their potential as catalysts and phosphors, respectively. In particular, GdVO_4 , NdVO_4 , and EuVO_4 were found to exhibit favorable properties for the photocatalytic mineralization of methylene blue. Besides, GdVO_4 , YVO_4 , and solid solution $\text{GdVO}_4\text{-YVO}_4$ turned out to be promising host materials for optical applications (e.g., as stand-alone nanophosphors with tailorable emission or conceivable as a novel platform for upconversion nanostructures). We believe that especially the integration of open mesoporosity with robust catalytic and/or photoluminescence activity paves the way toward development of interpenetrating phase composites as thin films with unprecedented functionalities and properties—by filling the pore cavities with other materials or functionalizing the pore walls.

Associated Content

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website. Additional SEM/TEM images and SAED patterns; Kr adsorption-desorption isotherms; Tauc plots; photocatalytic activity data; XRD patterns; XPS spectra and quantitative analysis; ToF-SIMS depth profiles; and photographs of films after light excitation.

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