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Synthesis and characterization of rod-like Y_2O_3 and $Y_2O_3:Eu^{3+}$

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Y_2O_3 rods 100 to 200 nm in diameter and 10 to 20 μm in length are accessible via polyol-mediated synthesis of a precursor material with similar shape. By heating of $Y(CH_3COO)_3 \cdot xH_2O$ and a defined amount of water at 190°C in diethylene glycol, the rod-like precursor material is formed. Infrared spectroscopy (IR), differential thermal analysis (DTA) and thermal gravimetry (TG) evidence that this precursor material still contains acetate. However, the precursor material can be transformed to Y_2O_3 by sintering at 600°C without destruction of the rod-like shape. According to X-ray powder diffraction analysis, the rods are well crystallized. They can be assumed to be with [100] orientation. By doping with Eu^{3+} (5 mol%), red emitting phosphor rods can be realized. With optical spectroscopy the typical line emission of Eu^{3+} is observed. Diffuse reflectance of $Y_2O_3:Eu^{3+}$ rods is determined to be higher than 95% in the visible. While exciting at 254 nm (Hg-discharge), a quantum efficiency of 38.5% is proven for the prepared $Y_2O_3:Eu^{3+}$ rods.
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1. Introduction

The preparation of anisotropically shaped materials on the micron-scale is a rapidly growing field of materials science and preparative chemistry. Especially tubes [1, 2], but also other anisotropic shapes such as wires, rods, plates or cubes become more and more interesting [3–5]. This is due to the potentially anisotropic properties of such matter. Possible areas of application are, for instance, microscopic probes, field emission sources or light emitting devices [6, 7]. Although, several methods to prepare anisotropically shaped materials are known, synthesis still suffers from a lack of preparative knowledge. In order to establish conditions leading to an anisotropic grain growth at low temperatures, liquid-based synthesis normally requires suited templates such as long-chained amines or phosphines, tensides or lyotropic phases [8–11]. However, these additives which cover the materials surface can be disadvantageous with concern to later application. For instance, electrical or optical properties of the anisotropic matter can be strongly influenced by the additives themselves or their thermal decomposition products. An alternative strategy can be a preparation of an anisotropically shaped precursor material in a first step which is then transformed to the target compound. To do so, the conditions of decomposition have to be well-controlled in order to keep the anisotropic shape. Such a measure in principle is well-known, for instance, for the transition of needle-type FeOOH into magnetic γ-Fe_2O_3 or Fe_3O_4 [12].

Here, the preparation of micron-size Y_2O_3 rods and red emitting micron-size $Y_2O_3:Eu^{3+}$ rods via a precursor route is described. The rod-like precursor itself is prepared based on the so-called polyol method. With the underlying experimental conditions normally submicron size and spherical particles of elemental noble metals [13] as well as of metal salts such as oxides, sulfides and phosphates are yielded [14, 15]. The relevant experimental conditions and the characterisation of Y_2O_3 rods and $Y_2O_3:Eu^{3+}$(5 mol%) rods with regard to particle size and shape, crystallinity and luminescent properties are presented.

2. Experimental

2.1. Synthesis

Y_2O_3 rods were prepared by heating of 8.40 mmol $Y(CH_3COO)_3 \cdot xH_2O$ (99.9%, Aldrich) and 1 ml demineralised water in 50 ml diethylene glycol (DEG, 99%, Merck). Firstly, this mixture was heated to 140°C in order to get a homogeneous solution with all the salt dissolved. When the solution had become clear, it was heated to 190°C and kept at that temperature for 2 h. After the reaction, the solid material was separated from the liquid by centrifugation. In order to remove all DEG, the solid was trice resuspended in ethanol and centrifuged again. Finally, the solid was heated in a tube furnace for 30 min at 600°C. To get red emitting $Y_2O_3:Eu^{3+}$ (5 mol%), 0.42 mmol

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$Eu(CH_3COO)_3 \cdot xH_2O$ (99.9%, Aldrich) were added to the DEG mixture.

2.2. Scanning electron microscopy (SEM)

A PHILIPS SEM XL30 equipped with a tungsten field emission gun was used for scanning electron microscopy (SEM). Samples were sputtered with carbon (300 Å). The investigations were carried out at room temperature applying a voltage of 15 to 25 kV. The spot size was 20 nm and the free working distance (FWD) 9 to 12 mm.

2.3. X-ray powder diffraction (XRD)

Diffractograms were performed with a PHILIPS vertical goniometer PW1050 with Bragg-Brentano-geometry. The diffractometer was equipped with a fixed divergence slit and a proportional counter. Cu K_α radiation was used and monochromatised by a secondary graphite monochromator.

2.4. Infrared spectroscopy (IR)

Spectra were recorded with a BIO-RAD FTS40 FT-IR spectrometer. Samples were diluted in KBr pellets.

2.5. Optical characterisation

Excitation and emission spectra were recorded at room temperature on a home-built spectrofluorimeter. The spectrometer was equipped with a Xe-lamp, a double monochromator (ISA1680b) in the excitation as well as in the emission beam line and a Peltier-cooled photon counter. Diffuse reflection was measured in an Ulbricht-sphere (double monochromator, semi-infinite layer of samples). Spectra were recorded at room temperature, using home-built equipment. $BaSO_4$ was used as reference material.

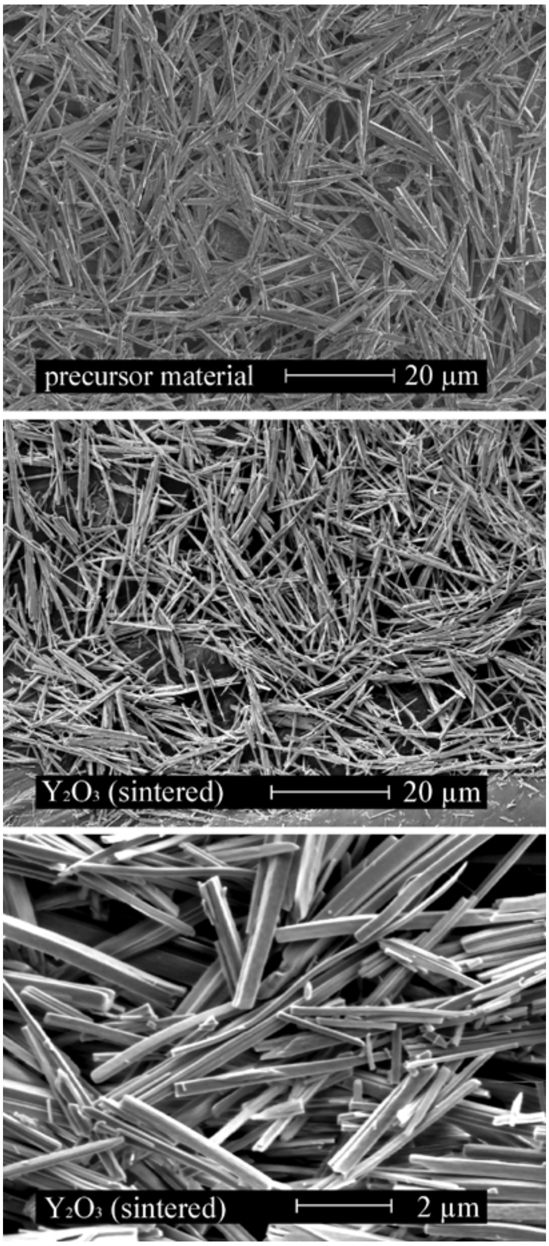


Figure 1 SEM images of precursor material and sintered Y_2O_3 rods.

3. Results and discussion

By heating of $Y(CH_3COO)_3 \cdot xH_2O$ in diethylene glycol, a rod-like solid is formed. SEM analysis indicates that rods 100 to 200 nm in diameter and 10 to 20 μm in length are realised (Fig. 1). According to the results of X-ray powder diffraction (Fig. 2), the preparation at 190°C in the polyol medium does not directly yield Y_2O_3. The prepared precursor material is crystalline and with d-values being much larger than for Y_2O_3. Based on the ICDD reference database [16], a compound showing such a diffraction pattern till now is unknown. Based on the measured diffraction data, the unit cell must be assumed to be with monoclinic cell symmetry and comparably large lattice parameters (Fig. 2). Infrared spectra allow more insights into the chemical composition of the precursor (Fig. 3). Stretching modes such as ν(C—H), ν(C=O), ν(C—O) and δ(C—H) are clearly visible [17]. The occurrence of a broad ν(O—H) band is attributed to residual traces of water in the sample. Based on the IR spectra, the precursor material must be assumed to contain acetate. Differential thermal analysis (DTA) and thermal gravimetry (TG) evidence an exothermal decomposition of the precursor in one step between 300°C and 550°C (36% weight loss). Altogether, the findings can be valued as a strong hint for a composition such as $YO(CH_3COO)$. X-ray single crystal structure analysis is aiming to clarify composition and structure of the precursor compound [18].

In order to guarantee complete decomposition of the precursor, heating for 30 min at 600°C in air was performed. With this sintering process, the precursor material is transformed to Y_2O_3. Most remarkably, size and shape of the rods remain unaffected (Fig. 1). SEM photos show rods still about 100 to 200 nm in diameter and 10 to 20 μm in length. X-ray powder diffraction patterns prove the presence of pure Y_2O_3 and the crystallinity of the rods (Fig. 2). IR spectra of sintered Y_2O_3 do not exhibit the characteristic stretching modes related to acetate any longer. The crystal orientation of the Y_2O_3 rods can be deduced based on the powder diffraction patterns. Comparing rod-like Y_2O_3 with an Y_2O_3 powder that consists of almost spherical particles

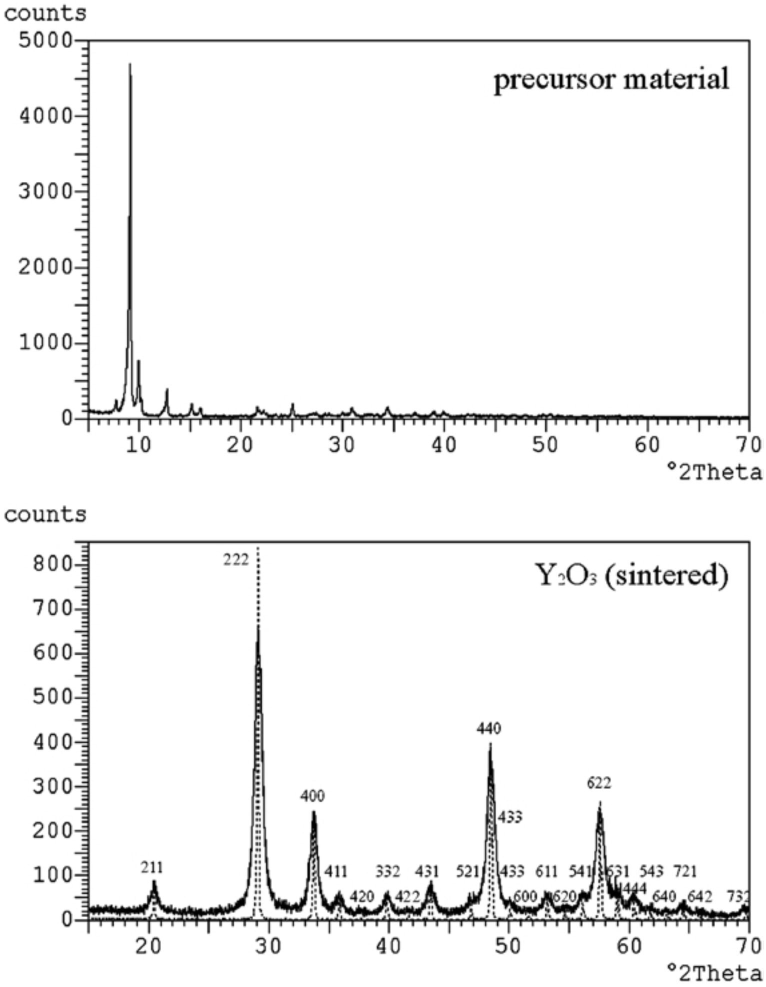


Figure 2 XRD patterns of precursor material (strongest reflections: 9.657/100; 8.880/13.5; 6.955/12.7; 5.829/8.0; 3.549/6.5; *d*[Å]/I[%]) and sintered Y_2O_3 rods (reference: Y_2O_3:Eu^{3+} standard lamp phosphor, spherical particles, 4 to 6 μm in diameter, dotted line).

4 to 6 μm in diameter (Y_2O_3:Eu^{3+}, standard lamp phosphor, Philips), the significantly increased intensity of the [222] reflection tends to the conclusion that [100] is the preferred orientation of the Y_2O_3 rods (Fig. 2).

While doping Y_2O_3 rods with 5 mol% Eu^{3+}, a luminescent material showing red emission can be realised. In fact, Y_2O_3:Eu^{3+} is a well-known phosphor with major technical relevance, especially for tri-colour fluorescent lamps [19]. The optical properties of sintered Y_2O_3:Eu^{3+} rods and of the doped precursor material are studied based on reflection, excitation and emission spectra (Fig. 4). Diffuse reflectance of precursor

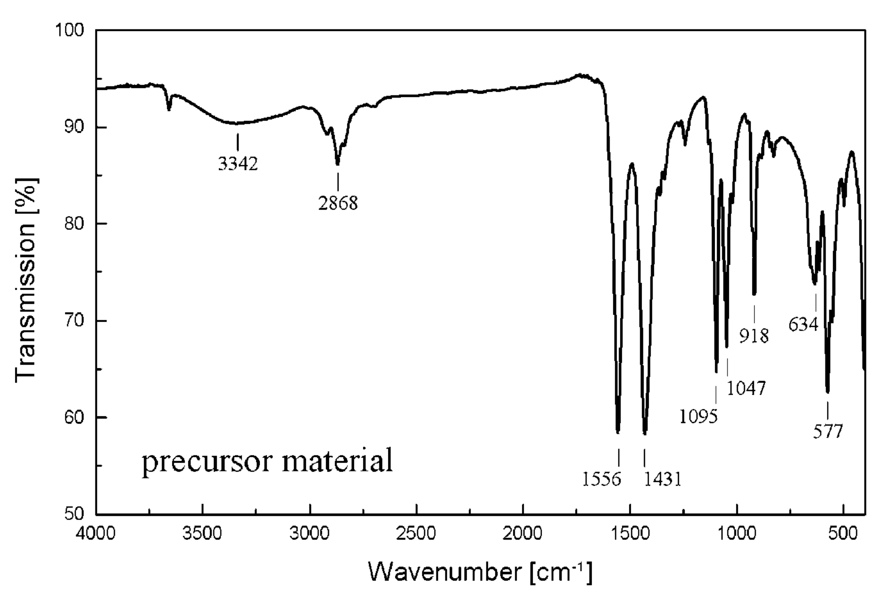
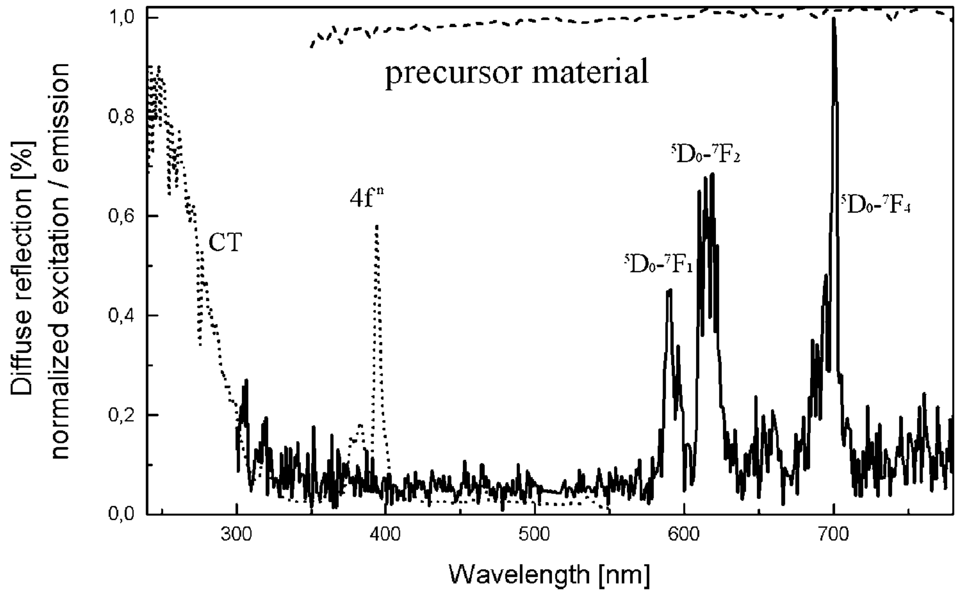


Figure 3 IR spectrum of precursor material (3342 cm^{-1}: ν(O—H); 2868 cm^{-1}: ν(C—H); 1556/1431 cm^{-1}: ν(C═O); 1095/1047 cm^{-1}: ν(C—O); 918 cm^{-1}: δ(C—H) [17].



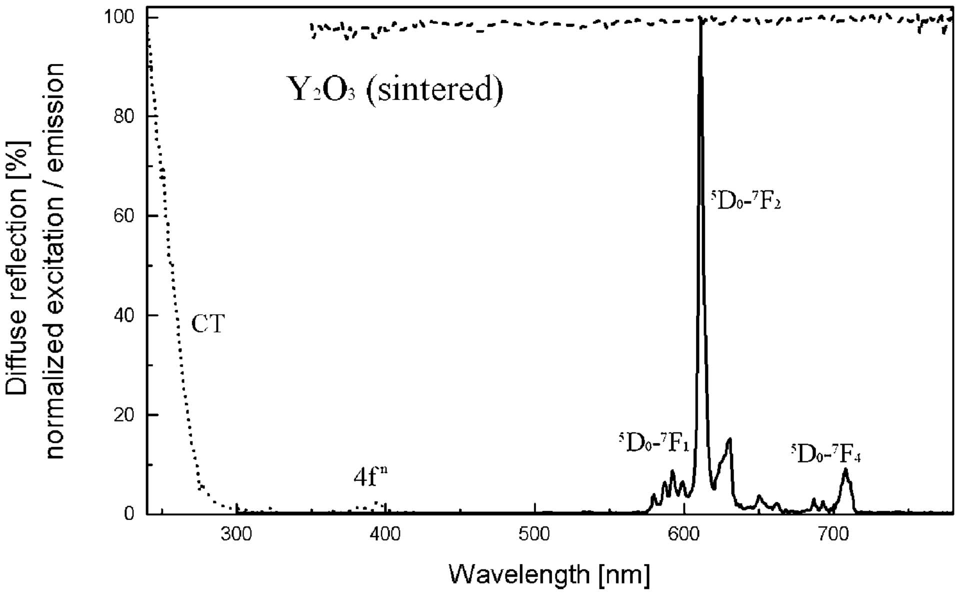


Figure 4 Optical properties of Eu^{3+}-doped precursor material and sintered Y_2O_3:Eu^{3+} rods: excitation spectrum (dotted, monitored at 661 nm); emission spectrum (solid, excited at 254 nm); diffuse reflectance (dashed).

material as well as sintered Y_2O_3:Eu^{3+} is high (>95%) over the whole measured spectral range. This evidences in both cases quite a low defect concentration. In case of sintered Y_2O_3:Eu^{3+} also the absence of carbon impurities due to decomposition of acetate or residual diethylene glycol is proven. Excitation spectra of precursor material and sintered Y_2O_3:Eu^{3+}, in principal, are identical. Of course, 4f^n absorption on Eu^{3+} seems to be strongly increased compared to $O^{2-} \rightarrow Eu^{3+}$ charge transfer absorption in case of the precursor material. Taking the energetically high lying vibration modes into account, this situation must be ascribed to the fact that the charge transfer absorption mainly leads to nonradiative transition which does not occur in the excitation spectra while monitoring 661 nm emission of Eu^{3+} [19]. Emission spectra exhibiting $^5D_0 \rightarrow {}^7F_1$, $^5D_0 \rightarrow {}^7F_2$ and $^5D_0 \rightarrow {}^7F_4$ transition on Eu^{3+} are also very similar. In case of the precursor material, again due to dominating nonradiative decay, emission is very weak resulting in a quantum efficiency of only 1.7%. Emission spectra of sintered Y_2O_3:Eu^{3+} are identical to conventional phosphor material as applied in fluorescent lamps. With 38.5%, the quantum efficiency is significantly increased compared to the precursor material. Taking the very unfavourable surface to volume ratio into account, it can not surprise that the quantum efficiency is still relatively low compared to standard bulk phosphor material (viz. 95%). Nevertheless, in comparison to the quantum efficiencies reported for Y_2O_3:Eu^{3+} particles on the micron-scale, the observed values are remarkable.

4. Conclusions

With polyol-mediated synthesis for the first time Y_2O_3 and Y_2O_3:Eu^{3+} (5 mol%) rods are prepared. The rods are 100 to 200 nm in diameter and 10 to 20 μm in length. The acetate containing precursor compound gained directly after the reaction can be transformed to crystalline Y_2O_3 by sintering at 600°C. This sintering is without any significant shrinkage of the rods. After heating at 600°C, the rods are crystalline and oriented along [100]. While doping the Y_2O_3 rods with 5 mol% Eu^{3+}, well-known red emission can be realised. The quantum efficiency of the luminescent material with 38.5% is remarkably high when excited with 254 nm (Hg discharge).

Acknowledgements

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