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# Eu<sup>3+</sup> doped yttrium oxide nano-luminophores from laser synthesis

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## ABSTRACT

Nano-sized Y<sub>2</sub>O<sub>3</sub>:Eu phosphors were obtained from laser synthesis at a production rate of 25 g/h, the initial product consisting of purely monoclinic material, of primary particle sizes of 20–30 nm as could be shown by powder X-ray diffraction, TEM and BET. Despite a large amount of surface adsorbed water and O–H groups, and peculiarly, nitrous oxide species, as shown by mass spectrometer coupled thermo-analysis/thermogravimetry and FTIR, the luminescence efficiency still amounted to approximately 19% relative to bulk Y<sub>2</sub>O<sub>3</sub>:Eu. On thermal conversion at 900 °C, the transformation to cubic Y<sub>2</sub>O<sub>3</sub>:Eu, now yielding particles of approximately 60 nm appeared to be complete and had an efficiency of about 68%, however, an efficiency of 93%, approaching that of bulk Y<sub>2</sub>O<sub>3</sub>:Eu, was obtained on annealing at 1200 °C. Significantly, a rapid re-formation of carbonates takes place on the calcined samples also.

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## 1. Introduction

The Y<sub>2</sub>O<sub>3</sub> lattice is in many respects a present by nature as it has some unique and readily exploitable optical, chemical and thermal properties, ease of access and stability not being the least of them. Setting the focus on optical applications, the band to band absorption just below 250 nm and its capability to imbed various trivalent rare earth ions, Eu<sup>3+</sup> in particular, have made it probably the most widespread phosphor, among others applied in fluorescent lighting and thus still providing the majority of artificially generated red photons [1–3].

In Y<sub>2</sub>O<sub>3</sub>:Eu, the allocation of the O→Eu charge transfer band (O–Eu–CT) coincides with the 254 nm emission of the mercury plasma, thus giving an efficient excitation channel, eventually yielding an efficiency in excess of 90%. In the last decade or so, an ever increasing interest in nano-scaled Y<sub>2</sub>O<sub>3</sub>:Eu and other sesquioxides for many applications (biophotonics [4–7], (radio-) imaging [8], displays [9], anticounterfeit markers [10], or the fabrication of transparent ceramics [11,12]) has born a demand for suitable synthetic pathways.

In the meanwhile, a multitude of preparative approaches to yield nano-Y<sub>2</sub>O<sub>3</sub> have been reported, a complete review of which would by far exceed the scope of this paper, therefore, we will restrict the list to a few general methodological examples. To be mentioned are gas-phase methods like chemical vapor synthesis

[13] and flame pyrolysis [14], and solution methods such as sol–gel and Pechini [15,16], microemulsion [17], homogeneous precipitation [18], combustion [19], and hydro- and solvothermal [7–20] techniques; in addition to these laser ablation has been used to deposit thin films of Y<sub>2</sub>O<sub>3</sub>:Eu on various substrates as well, see e.g. Ref. [21]. In the present article we would like to present a readily scalable method, which enables the preparation of nano-sized Y<sub>2</sub>O<sub>3</sub>:Eu particles via laser synthesis and report on structural and optical properties of the resulting materials. Detailed knowledge of these properties is indispensable for subsequent ceramic conversions, as well as for the application of the powders as such. This holds particularly true for both, high performance optical ceramics, where details of the surface composition and surface driven sintering processes are mandatory for absolute control of the stoichiometry, ultimately at the ppm level. For nanoparticles in biophotonic applications on the other hand, the surface properties are decisive for their subsequent functionalization and conjugation to target substrates. In this sense, we believe that our results substantially add to the present knowledge on the uttermost importance of the powder history and the need to clarify accompanying surface properties.

## 2. Experimental

### 2.1. Y<sub>2</sub>O<sub>3</sub>:Eu nanopowder synthesis

The europium doped Y<sub>2</sub>O<sub>3</sub> (5 mol% Eu<sup>3+</sup>:Y<sub>2</sub>O<sub>3</sub>) nanopowders were synthesized by material evaporation with an ytterbium fiber

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laser. The material to evaporate was a mixture of 5 mol%  $\text{Eu}_2\text{O}_3$  (99.99% REO, Treibacher Industrie AG) and 95 mol%  $\text{Y}_2\text{O}_3$  (99.99% REO, ITO-lum, JSC "URALREDMET") commercially available powders. The evaporation technique is described in detail in Ref. [24]. The ytterbium fiber laser used (YLR-1000, IPG Photonics) was operated in pulse laser radiation mode, repetition rate 5 kHz, pulse duration 100  $\mu\text{s}$ , average laser power 500 W. The intensity of laser radiation in the focal spot was about  $10^6 \text{ W/cm}^2$ , distribution-close to Gaussian. The air pressure in the evaporation chamber was 1 atm, at a gas flow rate through the evaporation chamber of 65 l/min. The average output rate of the nanopowder production was about 25 g/h. The initial metastable monoclinic nanopowders were converted to the cubic phase in a chamber furnace LHT 02/18 (Nabertherm) at various temperatures.

## 2.2. Characterization

Transmission electron microscopy (TEM) was made with JEM 2100 (JEOL Ltd., Japan). Phase structure and composition of the nanopowders were characterized using X-ray powder diffraction (D8 DISCOVER, BrukerAXS) with copper radiation ( $\text{Cu K}_{\alpha 1,2}$   $\lambda=1.542 \text{ \AA}$ ) with a carbon monochromator. The XRD data were treated by aid of the TOPAS 3 software (BRUKERAXS) with Rietveld's algorithm to specify structure parameters by Scherrer's method with regard to diffraction line broadening (compensation factor  $k=0.89$ ).

The specific surface area ( $S_{\text{BET}}$ ) of the nanopowders was measured by nitrogen adsorption according to the BET method (TriStar 3000, Micromeritics). Adsorbates content, and exo/endothelial reactions that take place during heating up to 1400  $^{\circ}\text{C}$ , were analyzed by simultaneous thermo analysis (TG-DSC, NETZSCH-STA409PC).

IR spectra were recorded on Perkin-Elmer Spectrum One FTIR spectrometer as KBr disks in the range between 4000  $\text{cm}^{-1}$  and 450  $\text{cm}^{-1}$ .

Emission, excitation and reflectance spectra of the powderous products were measured at room temperature on an ARC spectrometer (monochromators of 300 mm focal length, a 450 W Xe lamp as light source, photomultiplier tube P2, the resolution of the spectrometer was 0.1 nm) equipped with optical fibers. The quantum yields were obtained by measuring relative to a Lumogen Red F300 doped (50 ppm) PMMA powder standard, for which a quantum yield of 42% was assumed. Reflectance spectra were taken in synchronous scan through a 10 cm spectralon coated integrating sphere.

## 3. Results and discussion

The morphology of the laser-synthesized  $\text{Y}_2\text{O}_3:\text{Eu}$  (5 mol% of europium) nanopowder is shown in Fig. 1. The mean diameter of "primary" particles is 20–30 nm, some of the particles are agglomerated and form secondary particles with a diameter of about 100 nm. The specific surface area ( $S_{\text{BET}}$ ) of the initial (as-obtained) nanopowders was 66.2  $\text{m}^2/\text{g}$ . A TG-DSC analysis of the nanopowder revealed a very weak exothermal reaction due to the phase transformation (from monoclinic to cubic) at 900–950  $^{\circ}\text{C}$ . The powders additionally contained an unexpectedly high content of adsorbates, which amounted to 7.3 wt%. The main constituents of the adsorbates desorbed during heating up to 800  $^{\circ}\text{C}$  and were identified in a coupled mass spectrometer to be water and  $\text{CO}_2$ , while at temperatures between 200 and 350  $^{\circ}\text{C}$  as well as 550 and 700  $^{\circ}\text{C}$ , the TG/DSC additionally revealed two small peaks of NO desorption.

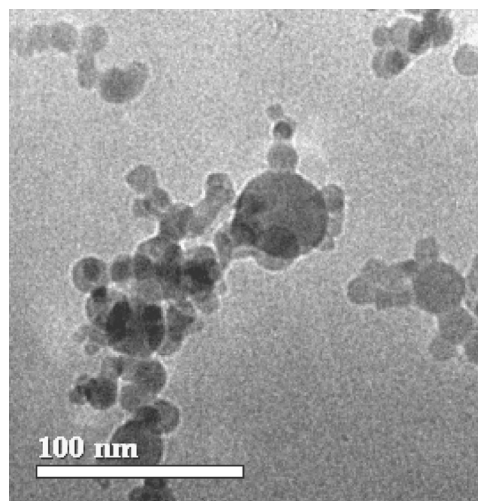


Fig. 1. SEM image of the  $\text{Y}_2\text{O}_3:\text{Eu}$  nanopowder obtained from laser synthesis.

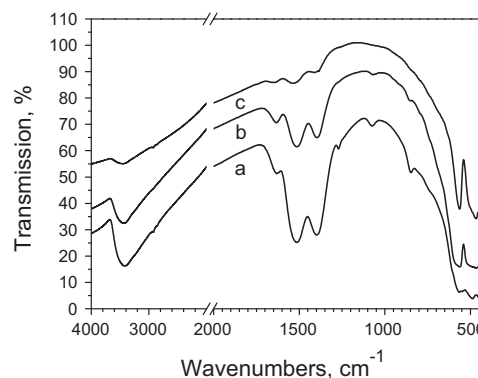


Fig. 2. FTIR spectra (KBr disks) of  $\text{Y}_2\text{O}_3:\text{Eu}$  nanopowder obtained from laser synthesis: as obtained (a), after calcination at 900  $^{\circ}\text{C}$  (b), and after calcination at 1200  $^{\circ}\text{C}$  (c). The spectra were recorded using the same amounts of nanopowder; (b) and (c) were plotted with an offset for better visibility.

Table 1  
FT-IR analysis of the  $\text{Y}_2\text{O}_3:\text{Eu}$  nanopowder.

Maximum of absorption band $\text{cm}^{-1}$	Assignment <sup>a</sup>
3500–3000	$\text{OH}^-$ stretch ( $\text{H}_2\text{O}$ , $\text{YCO}_3\text{OH}$ )
1635	H–O–H bend
1515	$\text{CO}_3^{2-}$ ; $\nu_3$ asymmetric stretch <sup>b</sup>
1398	$\text{CO}_3^{2-}$ ; $\nu_3$ symmetric stretch <sup>b</sup>
1384 (narrow)	$\text{NO}_3^-$ ; asymmetric stretch
1270 (narrow)	$\text{NO}_2^-$ ; asymmetric stretch ( $\text{C}_{2v}$ ; $\text{B}_2$ )
1077	$\text{CO}_3^{2-}$ ; $\nu_1$ symmetric stretch <sup>b</sup>
841	$\text{CO}_3^{2-}$ ; $\delta$ , out-of-plane bend
650	$\text{CO}_3^{2-}$ ; $\delta$ , OCO in-plane bend
567	Y–O lattice vibrations

<sup>a</sup> J. Weidlein, U. Müller, K. Dehnicke, *Schwingungsfrequenzen I. Hauptgruppennelemente*, Georg ThiemeVerlag Stuttgart, New York, 1981.

<sup>b</sup> The appearance of 3 C–O stretching modes confirm coordination to Y ( $\text{C}_{2v}$  symmetry).

The presence of  $\text{OH}^-$ ,  $\text{CO}_3^{2-}$ ,  $\text{NO}_2^-$  and  $\text{NO}_3^-$  could also be confirmed by FT-IR analysis (Fig. 2 and Table 1). The origin of some of the species is quite obvious: since the nanopowder has a large specific surface (66  $\text{m}^2/\text{g}$ ), it adsorbs an appreciable amount of water. The water molecules from atmospheric moisture interact strongly with the surface of  $\text{Y}_2\text{O}_3$ , become progressively incorporated into the surface layer and step by step form a "bulk hydroxide layer" at room temperature, as has previously been shown for

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