Optical Materials 76 (2018) 48–55

Contents lists available at ScienceDirect

Optical Materials

journal homepage: www.elsevier.com/locate/optmat

Nanostructured $CeO_2:Eu^{3+}$ luminophore obtained by low temperature benzenetricarboxylate method

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ARTICLE INFO

Article history:
Received 18 October 2017
Received in revised form
23 November 2017
Accepted 8 December 2017

Keywords:
Benzenetricarboxylate
Trimesic acid
Europium doping
Cerium
Photoluminescence

ABSTRACT

Nanostructured $CeO_2:Eu^{3+}$ was synthesized by low temperature thermolysis (500 °C, 1 h) of RE^{3+}-benzenetricarboxylate precursors (RE: Rare Earth). This preparation method is shown to produce easily dispersible highly crystalline nanoparticles with sharp crystallite size distribution, presenting large advantage over widespread available processes. The resulting nanomaterial (Ø 7–48 nm obtained from TEM and PXRD analysis) presents exclusively Ce^{IV} oxidation state according to XANES measurements. The doping process provides a solid solution with Eu^{3+} occupying the octahedral Ce^{IV} site, indicated by the photoluminescent characterization of the nanoparticles. The use of aqueous solvent, simple experimental apparatus, low energy input and easily accessible precursors make the benzenetricarboxylate method attractive for low cost nanoparticle synthesis.

1. Introduction

In the last decades, a great number of techniques have been developed or adapted for the preparation of nanostructured materials, *e.g.* the ceramic, precipitation, Sol-Gel, combustion and Pechini methods [1–5]. Mainly, these techniques seek reactions that occur preferentially at reduced temperatures, produce improved structural and morphological properties and dopant homogeneity.

The ceramic method is the oldest solid state reaction used to prepare inorganic materials. It consists of the physical mixing of the reactants in powder form, grinding and sintering for long periods (12–72 h) at high temperatures (1000–1700 °C) due to the refractory nature of the oxide precursors, which makes the method slow, laborious and costly, presenting high average crystallite sizes. Additional drawbacks are the difficulty in monitoring reaction progress and poor control of product homogeneity [1–5]. Most alternative methods proposed to bypass these difficulties have disadvantages: complex experimental procedures, high cost, use of highly reactive/hazardous precursors or high annealing temperature.

The recent use of complexes as precursors in the synthesis of nanomaterials has been revealed to provide high homogeneity, a large range of possibilities of final products, morphologies and applications [6–8]. In this way, the search for suitable complexes with easy synthesis and low decomposition temperature is the key to the facile fabrication of nanomaterials.

The benzenetricarboxylate method is based on the thermolysis of 1,3,5-benzenetricarboxylate (trimesate, TMA) metal complexes in air. TMA complexes can be easily synthesized by a one-pot reaction in aqueous solution, not requiring complicated experimental apparatus. The benzenetricarboxylate method is a simple, low cost and fast way for the synthesis of nanostructured single-phase materials at temperatures as low as 500 °C, well below those used in the ceramic method. This low energy input results from both the low decomposition temperature [7,9] of TMA complexes and its initial homogeneity, which decreases the need for high diffusion speeds. The low temperatures used allow to obtain small particle and crystallite, avoiding the sintering of the particles commonly observed at higher temperatures [10–13].

This report demonstrates the synthesis of nanostructured $CeO_2:Eu^{3+}$ materials obtained by low temperature thermolysis of $Ce(TMA):Eu^{3+}$ complexes formed in water [6,14]. Increasing the

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https://doi.org/10.1016/j.optmat.2017.12.019
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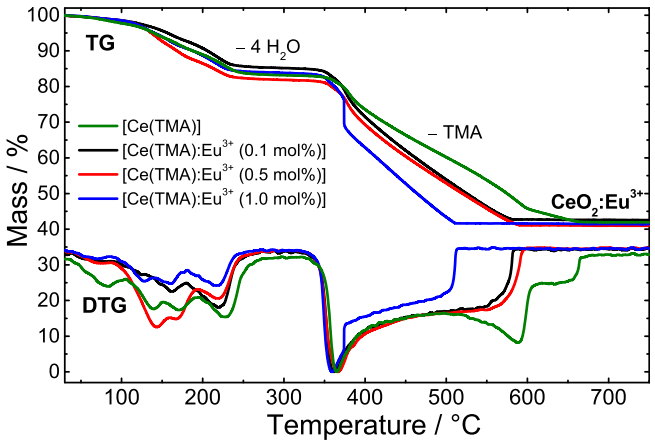

Fig. 1. TG and DTG curves and of [CeTMA:Eu^{3+} (x mol%)] (x = 0, 0.1, 0.5 and 1.0) complexes in synthetic air atmosphere.

annealing temperature, different crystallite sizes can be obtained, as shown by powder X-ray diffraction (PXRD) and transmission electron microscopy (TEM). The optical properties of the nanoparticles were demonstrated to be size dependent. This dependence can be attributed to the combination of phonon confinement phenomena and dielectric energy gap effects on the $O^{2-} \rightarrow Ce^{IV}$ energy transfer band. The photoluminescence properties of the doped materials were studied based on their excitation and emission spectra and luminescence decay curves of the $(Eu^{3+})^5D_0$ excited level [8,15,16]. The $(Eu^{3+})^5D_0 \rightarrow {}^7F_J$ (J = 0–4) intraconfigurational transitions are used as local probes for the local symmetry around the dopant sites, while X-ray absorption near-edge structure (XANES) is used to characterize the oxidation state of Cerium.

2. Experimental section

The H_3TMA ligand (97% purity) was obtained from Sigma-Aldrich. $RECl_3 \cdot (H_2O)_6$ salts (RE^{3+}: Eu and Ce) were prepared via aqueous suspension of the respective oxides (Eu_2O_3 - CSTARM, 99,99% and CeO_2 - Rhodia, 99,99%), with addition of concentrated hydrochloric acid. To prepare $CeCl_3 \cdot (H_2O)_6$, H_2O_2 was used to convert Ce^{IV} to Ce^{3+} [9].

Elemental analysis of the hydrogen and carbon contents was performed in a Perkin-Elmer CHN 2400 elemental analyzer. The infrared absorption spectra (Fourier transform infrared spectroscopy, FTIR) were recorded from 400 to 4000 cm^{-1} using the KBr pellet technique in a Bomem MB100 FTIR spectrometer. PXRD patterns were recorded in a Rigaku Miniflex II ($CuK_{\alpha 1}$, 1.5406 Å) from 4 to 70° (2θ). Thermogravimetric analyses (TG and DTG) were carried out from 30 to 900 °C (heating rate of 5 °C min^{-1}) in dynamic synthetic air with a flow rate of 50 cm^3 min^{-1} using a TA Instruments HI-RES TGA 2850 equipment. Transmission electron microscopy was set in a JEOL JEM-2100 microscope with LaB_6 filament operating at 200 kV. For specimen preparation, powder samples were diluted in ethanol and sonicated for 15 min. 3 μL were then dropped in the formvar side of a formvar/Carbon 200 mesh copper TEM grid (Electron

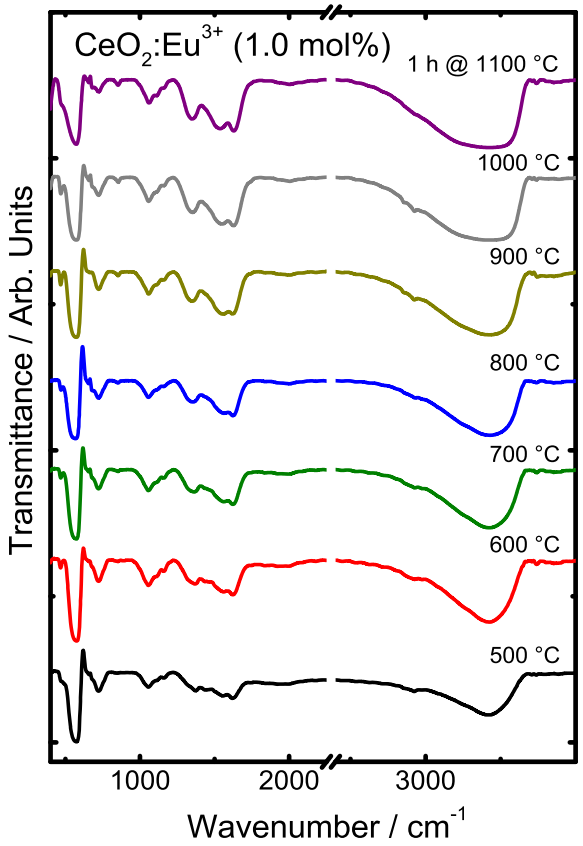

Fig. 2. Infrared transmission spectra of CeO_2:Eu^{3+} (1.0 mol%) for different preparation temperatures.

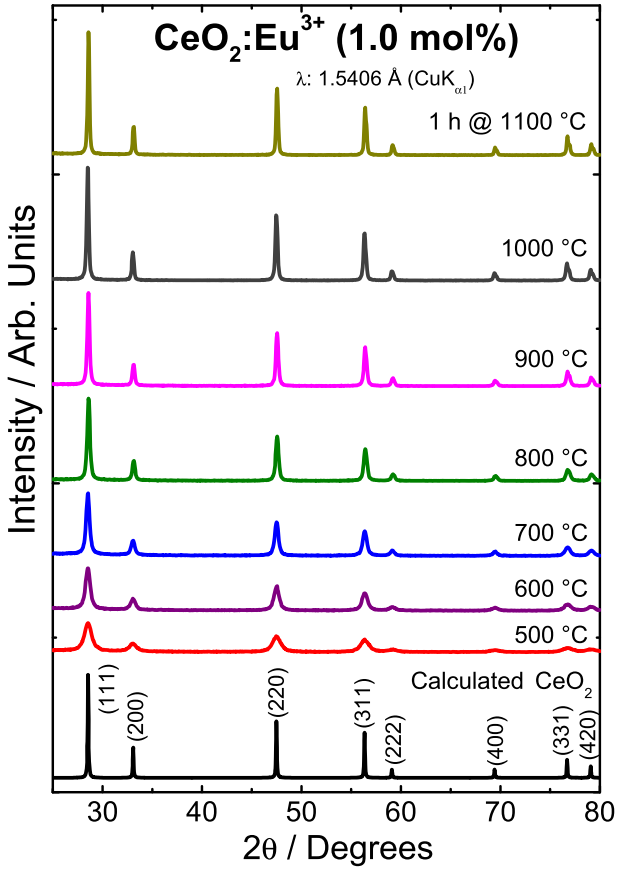

Fig. 3. Powder X-ray diffraction patterns of CeO_2:Eu^{3+} (1.0 mol%) for different annealing temperatures and the simulated data.