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Fabrication and luminescent properties of $(Y_{0.99}Eu_{0.01})_2O_3$ transparent nanostructured ceramics

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ABSTRACT

$(Y_{0.99}Eu_{0.01})_2O_3$ nanoceramics have been produced by sintering of stable cubic nanopowders under 8 GPa at temperature in the range of 25–500 °C with the use of Low Temperature High Pressure (LTHP) technique. During consolidation step irreversible phase transition from cubic to monoclinic yttria occurs resulting in two-phase nanoceramics with a grain size in the 10–40 nm range. It has been demonstrated that composite nanoceramics possess a high transmittance in the visible and mid IR ranges due to small light scattering on the nanoscale pores and low birefringence due to extremely small grain size.

It has been shown that Eu^{3+} ions act as a luminescent probe in composite $(Y_{0.99}Eu_{0.01})_2O_3$ nanoceramics since their 4f–4f luminescence strongly depends on the crystallographic environment. The luminescence spectra excited in the charge transfer band (CTB) are presented by superposition of emission from europium ions in cubic and monoclinic yttria. A new wide emission band of $(Y_{0.99}Eu_{0.01})_2O_3$ ceramics in the $\lambda = 500–650$ nm wavelengths range ($\lambda_{ex.} = 307$ nm) were attributed to luminescence of Eu^{3+} ions located in perturbed sites at grain boundaries or interfaces.

1. Introduction

Dense bulk nanoceramics combine excellent mechanical characteristics with unprecedented optical and luminescent properties owing to extremely low grain size (below 100 nm) and negligible light scattering on nanosized pores. For this reason nanoceramics retain reasonable transparency even for non-cubic materials like Al_2O_3 [1] and composite materials like Y_2O_3-MgO [2]. Rare-earth doped yttria is considered as an excellent optical material for IR window, phosphors and solid-state lasers due to high melting point, hardness, chemical stability and good optical properties. Recently we have proposed an approach to fabricate $(Y_{1-x}Eu_x)_2O_3$ optical nanoceramics by the transformation-assisted consolidation of nanospheres under 8 GPa pressure [3,4]. The nanoceramics were prepared by low-temperature high-pressure sintering (~0.04–0.2T_m, where T_m is the melting temperature) accompanied by the irreversible cubic-to-monoclinic phase transition. It has been shown that $(Y_{0.99}Eu_{0.01})_2O_3$ nanostructured ceramics consisting of individual (cubic or monoclinic) phases or their mixture can be obtained by variation of the sintering temperature during consolidation of nanopowders at 8 GPa. The use of transformation-assisted consolidation makes it possible to prepare $(Y_{0.99}Eu_{0.01})_2O_3$ nanoceramics with average grain size up to three times smaller (12 nm) than that of the starting nanopowders (37 nm), which corresponds to extremely low grain growth factor of 0.3 [4].

Luminescence properties of cubic, monoclinic or mixed nanopowders and thin films are widely studied in the scientific literature [see, for example, 5–7]. Luminescence of $(Y_{1-x}Eu_x)_2O_3$ under high pressure is reported in Refs. [8–10]. Despite this fact there is lack of information on luminescence and optical properties of transparent nanostructured yttria ceramics under ambient pressure. In this work we present luminescent properties of two-phase $(Y_{0.99}Eu_{0.01})_2O_3$ nanoceramics using europium ions as a fluorescent probe.

2. Experimental

$(Y_{0.99}Eu_{0.01})_2O_3$ transparent nanoceramics were obtained by transformation-assisted consolidation of nanopowders by using

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Low Temperature High Pressure (LTHP) technique [11]. Briefly, $(Y_{0.99}Eu_{0.01})_2O_3$ nanospheres were obtained by homogeneous chemical co-precipitation method using yttrium and europium nitrates as starting materials, and urea as a precipitant [3,4]. Consolidation of nanopowders was carried out by sintering under 8 GPa pressure in the 25–500°C temperature range for 30–180 s using a toroid type high pressure (HP) apparatus. Before placing in the HP cell, the initial nanopowders were uniaxially compacted under 250 MPa pressure into pellets.

Phase identification was performed via X-ray diffraction (XRD) method on a SIEMENS D-500 X-ray diffractometer (CuKα radiation, graphite monochromator) on the powdered ceramics samples. The phases were identified using JCPDS PDF-1 card file and EVA retrieval system included in the diffractometer software. The Rietveld refinement was performed with FullProf program [12]. The average apparent size of the crystallites was calculated with FullProf using a powder pattern of LaB_6 to obtain the instrumental profile function. The microstructure of the ceramics was studied by high-resolution analytical transmission electron microscopy (HR TEM) using a JEM-2100F (JEOL) microscope; the samples for HR TEM were prepared by ion thinning.

The in-line optical transmittance of the samples was determined using a Varian Cary 5E UV-VIS-NIR Spectrophotometer in 200–2000 nm wavelength range. Emission and excitation spectra were measured using the FLS980 Fluorescence Spectrometer from Edinburgh Instruments equipped with 450 W Xenon lamp. Both the excitation and emission 300 mm focal length monochromators were in Czerny Turner configuration. Excitation arm was supplied with holographic grating of 1800 lines/mm, blazed at 250 nm, while the emission spectra was supplied with ruled grating, 1800 lines/mm blazed at 500 nm. The spectral resolution was 0.1 nm. The R928P side window photomultiplier tube from Hamamatsu was used as a detector.

3. Results and discussion

3.1. Structural-phase state of $(Y_{0.99}Eu_{0.01})_2O_3$ nanoceramics

It is known that the sintering temperature of $(Y_{0.99}Eu_{0.01})_2O_3$ nanoceramics at a pressure of 8 GPa greatly affects its phase composition and average grain size [4]. Fig. 1 shows the diffraction patterns of $(Y_{0.99}Eu_{0.01})_2O_3$ nanopowders and nanoceramics consolidated at P = 8GPa and different temperatures for 30 s. Consolidation of $(Y_{0.99}Eu_{0.01})_2O_3$ nanospheres at room temperature does not cause a phase transition, whereas the temperature increase up to 100 °C initiates the phase transformation of the cubic yttria into a metastable monoclinic modification ($C \rightarrow B$). The phase transition terminates completely at 500 °C. Consolidation at the temperature of 200 °C for 30 s results in transition of approximately 60% of the starting cubic yttrium oxide into the monoclinic phase (Table 1). Since the cubic-to-monoclinic phase transition is reconstructive transformation accompanied by large changes in crystalline structure, the monoclinic modification survives after decompression to ambient pressure. Increase the internal pressure for the nanopowders with a particle size below 22 nm is also responsible for stabilization of monoclinic structure [10]. Under normal conditions, monoclinic modification is metastable, so the reverse transition at room temperature is suppressed.

Table 1 shows phase composition of $(Y_{0.99}Eu_{0.01})_2O_3$ nanopowders and nanoceramics subjected to consolidation at 8GPa and different temperatures. The ceramics sintered at P = 8GPa and T = 25 °C were characterized by 100% content of cubic yttrium oxide, and the lattice constants were: a = 10.6184(4) Å, V = 1197.23(8) Å^3. The obtained parameters are slightly higher than those for the initial nanopowders due to the elastic deformation of

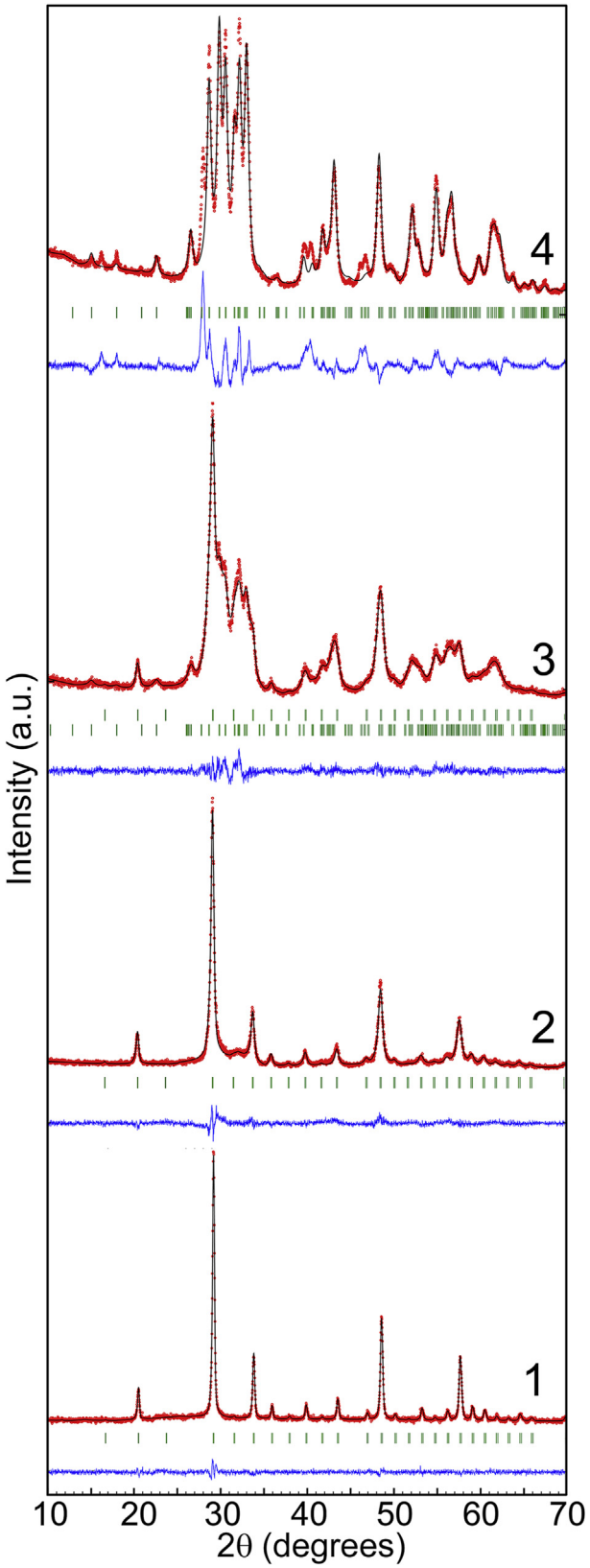

Fig. 1. X-ray diffraction patterns of starting nanopowders (1) and $(Y_{0.99}Eu_{0.01})_2O_3$ nanoceramics synthesized at 8 GPa and T = 25 (2), 300 (3) and 500 °C (4) for 30 s. Upper and lower rows of vertical bars show the Bragg position of reflections for cubic and monoclinic phases, respectively.