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Spectroscopic properties of Eu-doped Y-stabilized ZrO_2 microtubes

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ABSTRACT

Hereby we report a new microstructured luminescent material – Eu-doped yttria-stabilized zirconia (YSZ) microtube – prepared by a special sol–gel route. Transparent, crack-free and brightly luminescent microtubes were obtained after thermal treatment at temperatures as high as 1100 °C. The implications of time-resolved and site-selective studies of Eu^{3+} luminescence are discussed. The decay kinetics of Eu^{3+} luminescence is modeled following the Judd–Ofelt theory and matched to the experimental data.

1. Introduction

Functional optical materials are often required in specific geometry. For example, a microtubular geometry could have an advantage in applications such as miniature fuel cells [1], gas sensors [2], microfluidics [3], *etc*. The sol–gel method appears to be particularly versatile in the preparation of metal oxides with desired microscale geometrical shapes. While nanopowders and thin films are the most common products of sol–gel processing, fibers and especially tubular structures are very rare [4]. Since the sol–gel method is flexible also in the doping of oxide matrices, functionalization of the resulting structures for optical or electrical applications is of particular interest.

Yttria-stabilized tetragonal or cubic ZrO_2 (YSZ) is an important refractory, optical and electroceramic material which combines outstanding optical properties with excellent hardness and durability in harsh environment. In particular, the deleterious tetragonal-to-monoclinic phase transition of pure ZrO_2 is hindered in YSZ permitting device operation up to very high temperatures. The high ionic conductivity of YSZ is the basis for its use in ion conducting membrane applications such as gas sensors and fuel cells. Trivalent rare earth (RE^{3+}) activators are natural dopants for YSZ contributing to the phase stabilization similarly to yttrium [6] and their solubility in the stabilized phase is considerably higher. RE doping of YSZ has already allowed multifunctional use of the material as thermal barrier coating/thermographic phosphor [5]. In the microtubular geometry the range of potential applications also include miniature solid oxide fuel cells, spray nozzles for liquid metals, miniature plasma systems *etc*.

Hereby we focus on the optical spectroscopy of sol–gel-derived Eu^{3+}-doped YSZ microtubes. Using a combination of site-selective and time-resolved spectroscopy, existence of three Eu^{3+} centers in tetragonal YSZ with characteristic emission patterns and lifetimes is demonstrated for the first time.

2. Samples and experimental

To prepare YSZ microtubes, first a sol with shear thinning viscoelastic properties was obtained from $Zr(OBu)_4$ solution in butanol as a result of hydrolysis (initiated by drop-wise addition of 0.7 mol of water per 1 mol of alkoxide as 5% solution in butanol) and final evacuation of the excess solvent. 8 mol% yttrium and 1 mol% europium were incorporated by dissolving respective nitrate in the sol. By using a glass rod, the sol was pulled into jets which were first kept in air with 80–90% relative humidity at 20–22 °C for 1 min and then in air with 3–5% relative humidity at 20 °C for 15 min. The microtubes self-formed during the period due to solidification of the outer layer and formation of a hollow core. The tubes had lengths 10–15 mm, typical outer diameters 30–50 μm and wall thicknesses 10–15 μm (Fig. 1a). The tubes were annealed up to 1100 °C in air to crystallize and densify the material, remove organic residues and optimize the RE fluorescence. For some measurements (XRD, spectrofluorometry), powders were prepared from the same sol under identical conditions and were assumed to have identical structural and spectroscopic properties.

Photoluminescence (PL) emission spectra were collected from single free-standing microtubes excited with a focused beam of a diode-pumped solid state laser (355 or 266 nm), laser diode (405 nm) or tunable pulsed optical parametric oscillator (pulse duration 3 ns,

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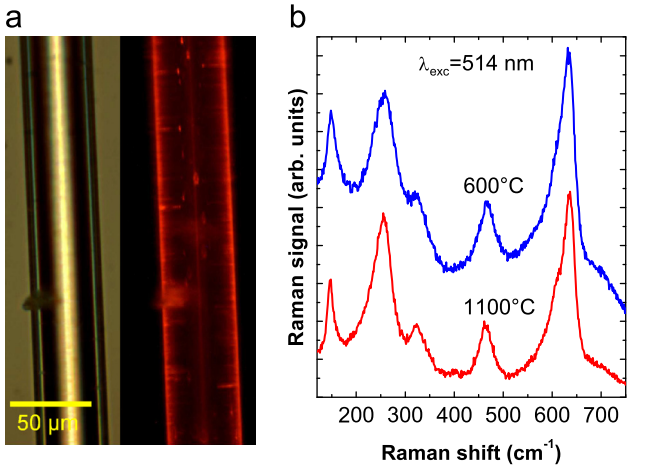

Fig. 1. (a) Optical micrographs of a YSZ:Eu^{3+} microtube annealed at 700 °C. Left: illumination with white light. Right: fluorescence of Eu^{3+} excited by 405 nm laser (focused at a point slightly above the field of view) and observed through 550 nm high-pass filter. (b) Raman spectrum of YSZ:Eu^{3+} microtubes depending on annealing temperature (indicated).

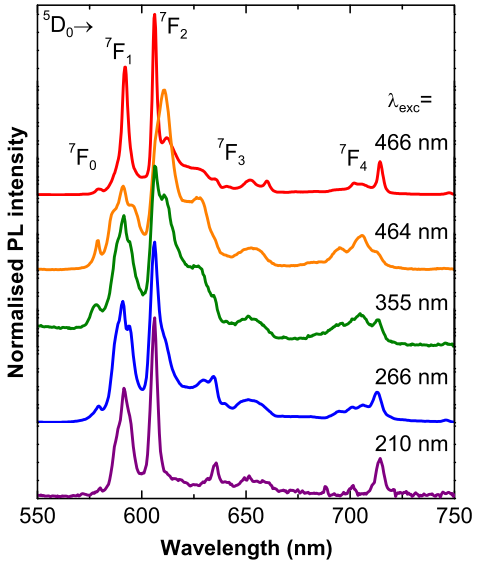

Fig. 2. PL spectra of YSZ:Eu^{3+} microtubes annealed at 1100 °C depending on the excitation wavelength (indicated).

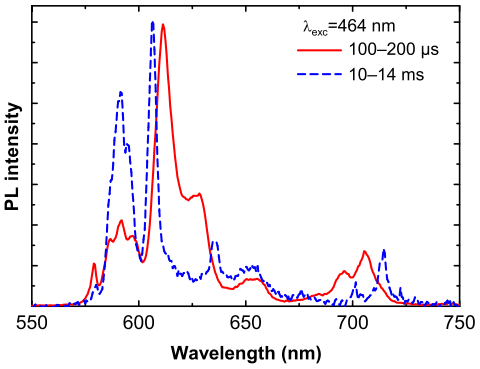

Fig. 3. Time-resolved PL spectra of YSZ:Eu^{3+} microtubes annealed at 1100 °C excited at 464 nm. The detection time window with respect to the laser pulse is indicated.

pulse energy ~20 μJ, repetition rate 20 Hz). The spectra were recorded by using a spectrograph (Andor SR-303i, spectral resolution 1 nm) equipped with an image-intensified CCD (Andor DH-501). PL spectra were corrected to instrumental response. PL decay kinetics was recorded with a Hamamatsu photomultiplier tube (H8259-01) operating in photon counting mode.

3. Results and discussion

The crystal structure of the microtubes was evaluated from Raman spectra recorded with a Renishaw inVia micro-Raman spectrometer (Fig. 1b). The Raman pattern is easily assigned to tetragonal YSZ; there are no peaks due to monoclinic phase. The cubic phase should be identified by a relatively broad band centered at 617 cm^{-1} which unfortunately has an overlap with the 611 and 641 cm^{-1} peaks due to the tetragonal phase [7]. Moreover, it is argued that Raman-scattering is relatively less sensitive to the cubic phase [8]. An increase of annealing temperature (from 600–1100 °C) preserves the Raman pattern but leads to the removal of the broad background and a slight narrowing of Raman peaks. Rietveld refinement of XRD pattern (not shown) also confirmed that the tetragonal phase is prevalent.

Under focused blue or UV laser beam, the Eu-doped microtubes emitted bright red luminescence easily seen by naked eye. Optical quality of the microtubes was characterized by inspecting the propagation of light in the microtube under a microscope (Fig. 1a). To inject light into a microtube, a bright luminescent spot was created inside the microtube by focusing a UV laser beam on its side area. In general, the microtubes remained transparent even after annealing at 1100 °C. Practically no attenuation of light was detected over distances of a few mm. The fluorescence image reveals that in addition to the weak uniform glow caused by scattering from inhomogeneities on the nano scale, some brighter spots are observed which indicate extended defects inside the microtubes not easily seen with white light illumination. The defects probably result from deficiencies in the preparation.

A survey of PL spectra at several excitation wavelengths is shown in Fig. 2. The observed crystal-field-split spectral lines are markedly broadened, even after thermal treatment at 1100 °C. In YSZ the contribution of inhomogeneous broadening is expected to be quite strong since each oxygen vacancy produces a large number of differently distorted cationic sites due to lattice relaxation towards oxygen vacancies although the number of differently coordinated sites remains small [9]. Jang and Meltzer [10] have used spectral hole burning to show that both the inhomogeneous and homogeneous linewidths of Eu^{3+} are dramatically increased in YSZ relative to ordinary crystals.

Yet, the correlations between different peaks (with changing excitation wavelength) suggest at least three distinguishable Eu^{3+} sites in the YSZ microtubes. A distinct emission pattern is obtained by site-selective excitation at 466 nm (in resonant with the $^7F_0 \rightarrow {}^5D_2$ transition of Eu^{3+}). Corresponding Eu center is labeled as Eu I. Only a slight variation of excitation wavelength (464 nm) leads to completely different spectrum. However, this spectrum turns out to be a mixture of two Eu centers as revealed by time-resolved spectroscopy (Fig. 3). The longer-living Eu^{3+} site is labeled as Eu II and the shorter-living one as Eu III. The Eu II center is also separately observed under excitation with 210 nm, which presumably leads to host-mediated excitation.

A common feature of all emission spectra is the presence of a weak line due to the $^5D_0 \rightarrow {}^7F_0$ transition. It is known that this emission is generally obtained only from noncentrosymmetric sites [11,12]. At least for Eu II and Eu III centers, also a threefold splitting of the $^5D_0 \rightarrow {}^7F_1$ band is clearly observed. Although for Eu I emission we observe only single line at $^5D_0 \rightarrow {}^7F_1$ transition, some works on tetragonal YSZ:Eu have reported similar emission