Short communication

Red light from ZrO$_2$:Eu$^{3+}$ nanostructures


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Zirconia nanocrystals doped with europium ions were developed envisaging optical applications. The nanostructures were produced using zirconyl nitrate (ZrO(NO$_3$)$_2$·H$_2$O) and europium nitrate (Eu(NO$_3$)$_3$·5H$_2$O) as cation precursors, and urea (C$_2$H$_5$NO$_2$) as the fuel, by the combustion synthesis process. The lanthanide-doped nanostructures were characterized by X-ray diffraction, transmission electron microscopy, Raman spectroscopy and photoluminescence. X-ray diffraction revealed the presence of tetragonal and monoclinic crystalline ZrO$_2$ phases. The latter was found to be a minority phase as identified by Raman and corroborated by the observed europium luminescence when compared to the intraionic emission in crystalline tetragonal fibres grown by the laser floating zone technique. Bright red europium luminescence is observed at room temperature when the combustion synthesized zirconia powders are excited with ultraviolet radiation. The spectroscopic properties of the europium ions in the powders are ascertained by comparing combined excitation–emission measurements with those from crystalline fibres.

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1. Introduction

The increasing market demand for efficient visible light sources is motivating the worldwide research in phosphors activated with lanthanide ions [1,2]. Nowadays, the technological issues for illumination and displays are focused on the production of efficient white light to compete with traditional sources. One way of achieving white light emission is the tri-color scheme in which red, green and blue phosphors allowing for a RGB-type emission. These LEDs can have excellent whiteness and paved the way for new mercury-less solid-state light sources. However, the luminous efficiency, lifetime and stability of the different color phosphors are often different, resulting in a complex device structure and a possible unbalanced white hue as a function of time [3]. Therefore, more efficient and chemical phosphors combined with an easy/low-cost industrial scale-up are needed. In ultraviolet excited red, green and blue – RGB phosphors, the red component optimization requires efficient narrowband red emission attainable by the transitions between distinct multiplets of the europium ions. For this purpose, wide band gap materials are advantageous as they allow the incorporation of several subgap energy levels from rare earth ions. Additionally, in materials with low phonon cutoff energy, nonradiative loss is expected to be reduced leading to higher luminescence efficiency at room temperature [4,5]. Due to their high transparency and low phonon cutoff energy, zirconia hosts are among the promising materials for the mentioned applications [6–11]. The location of 4$f$ electron energy levels from the lanthanide ions in several host materials has been extensively reported [12–18] and for the case of Eu$^{3+}$ ions the characteristic orange/red sharp line structures are mostly due to the transitions between the $^2$D$_{0,1}$ and $^7$F$_{J=0,1,2,3}$ multiplets [16–18].

The study of the europium spectroscopic properties in zirconia-based hosts was earlier reported by Dexpert-Ghys et al. [19]. In their work, the optical properties of europium doped yttria-stabilized zirconia with different compositions and crystalline domains (tetragonal, cubic and monoclinic) were investigated at 77 K. Since then, the emission of the trivalent europium ion in zirconia samples processed by different routes (powders, films and nanocrystals) has been reported [4,10,20–30]. Nanocrystalline zirconia activated with rare earth ions has recently enjoyed great developments to outcome the requirements needed for applications in solid state lighting nanophosphors [31,32]. Combustion synthesis method provides an attractive alternative to the other techniques usually used for nanopowders preparation, since it offers advantages in terms of process simplicity and energy and time saving [33]. Additionally, the high temperature process allows an easy doping route and lattice stabilization, in short time periods. In order to improve their efficiency for optical application purposes, it is important to compare the luminescence results with those from bulk samples, which are scarcely reported in the literature. Recently, we showed that the activation with rare earth ions give rise to bright luminescence at room temperature in bulk tetragonal zirconia fibres grown by laser floating zone (LFZ) [34,35], a simple
and economic method. A comparison between the spectroscopic properties of europium ions in LFZ grown bulk zirconia and in nanocrystalline zirconia powder samples prepared by combustion synthesis is reported.

2. Experimental details

Zirconyl nitrate (Zr(NO$_3$)$_2$·H$_2$O) plus europium nitrate (Eu(NO$_3$)$_3$·5H$_2$O) oxidizers, and urea (C$_2$H$_6$N$_2$O$_2$) fuel, were used to produce 3 mol% Eu$^{3+}$ doped zirconia nanopowders, by a combustion synthesis (CS). Based on this approach [36], in order to release the maximum energy from the reaction [37], the molar proportion of (Zr(NO$_3$)$_2$·H$_2$O), (Eu(NO$_3$)$_3$·5H$_2$O) and (C$_2$H$_6$N$_2$O$_2$) used in this work was 0.97:0.03:1.69, respectively. The redox mixture was put in a hot plate heated to $-180^\circ$C under stirring, resulting in a homogeneous solution. Afterwards, the mixture was transferred to a pre-heated furnace, at 450 $^\circ$C, where the combustion was self-initiated after few minutes. The single crystal zirconia fibres used as reference samples were grown by LFZ as described elsewhere [34]. Contrary to the precursors used for the CS samples, the LFZ growth europium doped fibres were prepared by cold extrusion by mixing the initial powders, zirconia with 8 mol% of Y$_2$O$_3$ (yttria stabilized zirconia) and 3 mol% Eu$^{3+}$. In order to compare the optical properties of the CS samples with those of the single crystalline reference fibres the same europium amount was used.

The structural characterization of the white powder obtained from the combustion synthesis was performed by X-ray powder diffraction (XRD) analysis using a Panalytical X’Pert Pro system and room temperature (RT) Raman spectroscopy. The latter was performed under backscattering geometry, using the Jobin Yvon T64000 ($\lambda = 532$ nm) and the Horiba Jobin Yvon HR800 ($\lambda = 325$ nm) instruments. The powders morphology and grain size were analysed by transmission electron microscopy (TEM) on a Hitachi T64000 ($\phi = 532$ nm) and the Horiba Jobin Yvon H-9000.

Steady state PL data were acquired between 14 K and RT using a 1000 W Xe arc lamp coupled to a monochromator or the 325 nm He–Cd laser line as excitation sources. The luminescence was dispersed by a Spex 1704 monochromator (1 m, 1200 mm$^{-1}$) and detected by a cooled Hamamatsu R928 photomultiplier. Photoluminescence excitation (PLE) measurements were further carried out at RT, the emission monochromator being set at the Eu$^{3+}$ luminescence excitation (PLE) measurements. Spectrum (a and c) stands for the ZrO$_2$:Eu$^{3+}$ crystalline fibres grown by LFZ, (b, d and e) for the ZrO$_2$:Eu$^{3+}$ powders produced by combustion synthesis method. $T$ and $m$ indicate the diffracting planes of the tetragonal and monoclinic ZrO$_2$, respectively.

3. Results and discussion

The XRD spectra of 3 mol% ZrO$_2$:Eu$^{3+}$ powders obtained by the combustion synthesis (CS) method are shown in Fig. 1. In contrast with the fibres grown by laser floating zone (LFZ), for which only the tetragonal phase was detected [34], the powders doped with europium ions exhibit both the tetragonal and monoclinic ZrO$_2$ crystalline phases. The tetragonal structure belongs to the P4$_{2}$/mcm space group (D$_{4h}$ point group) and crystallizes with the lattice parameters $a = 3.61$ Å, $b = 3.61$ Å and $c = 5.19$ Å. The monoclinic structure crystallizes in the P2$_1$/c space group (C$_{2h}$ point group) with lattice parameters $a = 5.17$ Å, $b = 5.23$ Å, $c = 5.34$ Å, $\alpha = 90$, $\beta = 99.25$, and $\gamma = 90$. The coexistence of the two crystalline phases in the CS powders is due to the reduced amount of stabilizer in the CS precursors. Although rare earth elements including Eu$^{3+}$ were reported to stabilize zirconia, 3 mol% Eu$^{3+}$ are not enough to stabilize the tetragonal phase in the whole mixture. Conversely, the powder mix precursors used in the LFZ grown fibres included 3 mol% Eu$^{3+}$ + 8 mol% Y$_2$O$_3$, the latter known for its efficiency on stabilizing the high temperature crystalline phases of zirconia [38], thus attaining tetragonal single phase [34].

Fig. 2 shows the RT Raman spectra of the ZrO$_2$:Eu$^{3+}$ powders obtained by CS. For comparison, a Raman spectrum of the LFZ reference fibre is also shown (Fig. 2a and c). Either under ultraviolet (Fig. 2a and b) and visible excitation (Fig. 2c and d), the A$_{1g}$, B$_{1g}$ and E$_{g}$ symmetry vibrational modes of tetragonal zirconia are clearly observed in both LFZ and CS samples, in line with previous reports [34,35,39,40]. Under visible excitation, the vibrational modes assigned to the monoclinic zirconia are also observed in the powders (Fig. 2e) [39,40]. However, the Raman spectra assigned to the monoclinic phase are detected only in some specific and minority regions of the powders, suggesting that this phase is present in very low content in the CS powders (or not uniformly distributed) as also is inferred from the X-ray diffraction patterns (Fig. 1). Two
additional peaks (marked with asterisk) can be observed in Fig. 2c and d for the europium doped zirconia powders and fibre, when the 532 nm laser line is used as excitation source. These additional lines can be explained in the frame of the intraionic luminescence as indicated hereafter.

The morphology and RT spectroscopic properties of the ZrO$_2$:Eu$^{3+}$ powders prepared by combustion synthesis are shown in Fig. 3. After preparing, the powders exhibit a white color (Fig. 3a) as expected for a wide band gap material. The bright red luminescence of the europium ions in the matrix is observed with naked eye at room temperature under ultraviolet excitation (Fig. 3b). TEM images of the doped nanopowders (Fig. 3c) reveal that they exhibit a large grain size distribution and high agglomeration degree, resulting from the high temperature achieved in the combustion synthesis. The powders have an average grain size of ~50 nm. The RT PL/PLE spectra of the ZrO$_2$:Eu$^{3+}$ powders are shown in Fig. 3d and e. Under ultraviolet excitation, besides the Eu$^{3+}$ 5D$_0$ $\rightarrow$ 7F$_J$ transitions, the RT luminescence also exhibits a broad emission band centred at ~490 nm. Broad emission bands are usually observed in zirconia polymorphs being assigned to native defects and their complexes [41–43]. For pure zirconia in monoclinic phase, a broad emission band at ~490 nm has been reported [44]. Considering this, it is reasonable to assume that the band observed at ~490 nm in our CS powders comes from native defects in grains with monoclinic crystalline structure.

Concerning the intra-4$^f$ lines, it is worth mentioning that the peak position and spectral shape of the detected transitions match well with those found from the tetragonal LFZ grown crystalline fibres [34], meaning that the same Eu-centres are present in the CS produced nanopowders. The PLE spectrum performed at the strongest intensity Eu$^{3+}$ emission lines shows that the ions emission could be achieved by excitation in the broad charge transfer (CT) ultraviolet bands (with local maxima at about 270, 280 and 320 nm) and by exciting the samples in the 5D, 5L and 5G excited states of the Eu$^{3+}$ ions as shown in Figs. 3 and 4. Among these, the 5D$_1$ excited state is seen to be located at ~532 nm, which means that the two additional lines detected in the Raman spectra of Fig. 2 are likely to be due to the emission from the 1D$_{v}$ state for the 7F$_1$ multiplet when the samples are excited resonantly in the Eu$^{3+}$ excited state.

Combined excitation–emission spectroscopy (CEES) has proven to be a powerful technique to identify different optical centres associated with the europium ions in a given host [45]. Fig. 4(a) shows RT CEES contour plots for the ZrO$_2$:Eu$^{3+}$ powders in the region of the highest intensity emission lines for excitation wavelengths between 250 and 500 nm. As mentioned above, it is evident that the red RT Eu$^{3+}$ luminescence can be obtained either by exciting the CS samples in the ultraviolet CT excitation bands as well as in the high-energy multiplets of the lanthanide ion. In fact, exciting the samples between 250 and 325 nm gives rise to a dominant 5D$_0$ $\rightarrow$ 7F$_2$ transition centred at 606 nm, identified in Fig. 3e. Moreover, this transition is the strongest one under excitation in the 5L$_6$ (~396 nm) and 5D$_2$ (~470 nm) multiplets, as shown in Fig. 4b. On the high wavelength side of the 606 nm transition, in the spectral region of the 5D$_0$ $\rightarrow$ 7F$_2$ transitions, a peak at 613 nm is identified. This emission is always present when the excitation is performed on the CT bands, but in a lesser extent for shorter wavelengths, as shown by the CEES plot.

Slight variations on the excitation wavelength give rise to distinct relative intensity strengths of the 5D$_0$ $\rightarrow$ 7F$_J$ Eu$^{3+}$ transitions, meaning that different ion environments and/or site location are responsible for the overall emission. This behaviour was previously found in the LFZ grown fibres [34]. Low temperature PL spectra obtained with different excitation wavelengths are shown in Fig. 4b, where the differences in relative intensity of the Eu-lines are highlighted indicating the presence of multiple Eu$^{3+}$ optical centres in CS powders. Changes on the relative intensity strength of the 606 nm 5D$_0$ $\rightarrow$ 7F$_2$ line (and 5D$_0$ $\rightarrow$ 7F$_4$) occur for non-resonant excitation pathways, as shown in upper spectra of Fig. 4b. Under these circumstances, vibronic assisted transitions supporting the observed luminescence must also be considered. As shown by the CEES and PLE spectra the detected CT excitation bands indicate the existence of different Eu–O distances [46,47]. As the europium ions usually substitute the Zr$^{4+}$ with charge compensation provided by the generation of oxygen vacancies rather than multiple sites, it is likely to assume the ion in lower local site symmetry than the tetragonal one. The different Eu–O bond lengths are responsible for the distinct ion environments leading to the observed multiple optical centres.

The europium doped CS powder luminescence was further investigated as a function of temperature, between 14 K and the room temperature, by exciting the samples in the CT excitation band (Fig. 5). Despite the fact that a bright intraionic luminescence is observed at RT, thermal quenching of the overall luminescence is seen when the temperature increases from 14 K to RT. Indeed, an overall low temperature to room temperature PL intensity ratio (1/14K)/(RT) of ~2.3 was found, indicating additional non-radiative processes competing with the intraionic emission. A similar behaviour was also detected for the intraionic luminescence in the LFZ grown fibres [34].

In summary, the europium doped CS prepared samples exhibit bright red luminescence at RT, when excited not only in the ultraviolet CT bands (like in most samples grown by other methods [4,28]) but also in the bandwidth emission of commercial InGaN-based LEDs.
dependent normalized PL spectra.

Fig. 5. Temperature-dependent (between 14 K and the room temperature) PL spectrum for the ZrO$_2$:Eu$^{3+}$ CS powders obtained upon 325 nm excitation.

4. Conclusions

The spectroscopic properties of the ZrO$_2$:Eu$^{3+}$ powders prepared by the combustion synthesis method have been analysed and compared with those of europium ions in crystalline fibres grown by the laser floating zone technique. The europium emission, observed with naked eye at room temperature, was found to be due to multiple europium optical centres in the zirconia host. Despite the fact that XRD measurements indicate that the presence, observed with naked eye at room temperature, was found to be due to multiple europium optical centres in the zirconia host. Despite the fact that XRD measurements indicate that the presence of both the monoclinic and tetragonal crystalline phases in the combustion synthesis prepared powders, the monoclinic phase must be considered a minority phase as indicated by both XRD and Raman spectroscopy. This interpretation is also corroborated by the photoluminescence measurements, as the measured intratracation transitions are the same previously detected for the tetragonal crystalline fibres.

Fig. 4. (a) RT combined excitation–emission spectroscopy contour plots for the ZrO$_2$:Eu$^{3+}$ powders produced by combustion synthesis. (b) 14 K wavelength-dependent normalized PL spectra.

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