Novel method to control initial crystallization of Eu$^{3+}$ doped ZrO$_2$ nanophosphors derived from a Sol–Gel route based on HNO$_3$ and their site-selective photoluminescence

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In this study, Eu$^{3+}$-doped ZrO$_2$ nanophosphors were obtained by a sol–gel method with HNO$_3$ as a catalyst, which led to white powders of small ZrO$_2$ nanocrystals after low temperature calcination. However, exothermic reactions of NO$_3^-$ were observed during the heat-treatment leading to ZrO$_2$ crystallization. To avoid such reactions and to understand the initial crystallization of ZrO$_2$ doped with Eu$^{3+}$ ions, we developed an original route in which the xerogel powders were pre-washed in ethanol before immersing them in Eu$^{3+}$ solution to remove NO$_3^-$. The effects of heat-treatment on the Eu$^{3+}$ photoluminescence (PL), crystallization of ZrO$_2$ xerogels, and Eu$^{3+}$ localization were studied with PL spectroscopy, thermogravimetric analysis and powder X-ray diffraction. It was found that the amorphous ZrO$_2$ xerogels crystallized in a tetragonal structure, with a small amount of monoclinic ZrO$_2$ also being precipitated after longer calcination periods. Finally, the Eu$^{3+}$ ions on the surface of the ZrO$_2$ xerogels were found to diffuse into higher symmetric Zr substitutional sites in the tetragonal ZrO$_2$ matrix after heat-treatment.

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1. Introduction

Recently, high-efficiency light-energy conversion has become a key research area, and studying new nanophosphors has received considerable attention with the aim of developing high-efficiency white light emitting diodes (w-LEDs).$^{1,2}$ Zirconia (ZrO$_2$) is one of ideal host materials for various phosphors because ZrO$_2$ has a wide bandgap and possesses low phonon energy.$^{3–5}$ Moreover, luminescent rare earth ions, which are widely used as optical activators, can easily be distributed in zirconia. Europium (III) (Eu$^{3+}$) ion is well-known as a red luminescent center. The luminescence properties of Eu$^{3+}$ ions are assigned to $^5D_{0–}^7F_J$ electronic transitions.$^2$ The photoluminescence (PL) spectra and lifetimes depend on the local environment around Eu$^{3+}$ ions, allowing the ions to be used as structural probes.$^6$ The objectives of this study are to prepare Eu$^{3+}$ doped ZrO$_2$ nanophosphors by a sol–gel method, and to investigate the effects of heat-treatment on the crystallization of ZrO$_2$ xerogels and the localization of Eu$^{3+}$ ions. Better understanding of the localization of rare earth ions in such nanophosphors is important in order to control their PL properties.

By using a sol–gel method, the microstructure of the final product can be controlled by suitable selection of the synthesis parameters.$^{7–10}$ The resultant xerogels have porous and very fine structures, and thus enable themselves to be thermally evolved to nanocrystals. In a previous study, Eu$^{3+}$ doped ZrO$_2$ nanocrystals were produced using a sol–gel route based on HNO$_3$.$^{11}$ This route leads to white powders after calcination, in contrast to black powders not suitable as luminescent materials, that are obtained using other agents (acetylacetone, H$_2$SO$_4$).$^{12,13}$ However, even the HNO$_3$ route is still problematic. During heat-treatment, even at temperatures lower than 200°C, explosion of the powders was observed, which makes it difficult to control sizes of ZrO$_2$:Eu$^{3+}$ nanophosphors. In
order to solve this issue, we’ve developed an original route which consists of pre-washing the raw powders in ethanol overnight to remove a portion of \( \text{NO}_3^- \). The final \( \text{ZrO}_2 \) xerogel powders do not have explosive properties. This paper also reports the results of PL spectroscopy, thermogravimetric analysis (TG), and X-ray diffraction (XRD) studies of \( \text{Eu}^{3+} \)-doped \( \text{ZrO}_2 \) xerogels produced via the new route.

2. Materials and methods

2.1 Synthesis

The materials used for the gel synthesis were zirconium n-propoxide (70 weight\% \( \text{Zr}[\text{O}((\text{CH}_3)_2\text{CH}_3]_4 \) n-propanol solution), water, and nitric acid (68 weight\% \( \text{HNO}_3 \) aqueous solution). The solvent was 2-propanol \( ([\text{CH}_3]_2\text{CHOH}] \). All sols were synthesized in a dry atmosphere at room temperature to avoid uncontrolled hydrolysis of the precursors. First, zirconium n-propoxide was dissolved in 2-propanol under mechanical stirring. Next, \( \text{HNO}_3 \) was slowly added as an acidic catalyst. The resulting mixture was then slowly hydrolyzed with the required quantity of water, followed by 5 min. of stirring. The sol parameters are as follows: dilution ratio of zirconium n-propoxide \( [\text{Zr}] = 0.5 \text{ mol L}^{-1} \), hydrolysis ratio \( h = [\text{H}_2\text{O}]/[\text{Zr}] = 3.45 \), acidic catalyst ratio \( m = [\text{HNO}_3]/[\text{Zr}] = 0.88 \). The sols gelled after 1–2 h at room temperature, resulting in a transparent wet gel, as seen in Fig. 1.

2.2 Drying and washing step

The wet gels were dried at 80°C for 48 h to form xerogels, which causes the gels to break into small pieces which were then ground. Thermal analyses of the raw xerogel powders were carried out by TG. In order to remove a good proportion of \( \text{NO}_3^- \) as well as residual organics, the raw xerogel powders were washed in ethanol overnight under mechanical stirring. The solid phase was then separated from the liquid phase by centrifugation. Next, \( \text{EuCl}_3 \) salts were dissolved in ethanol and mixed with the xerogel powders under stirring. The solution was dried by stirring and heating at 60°C (See Fig. 2). The doping ratio \( x = [\text{Eu}]/[\text{ZrO}_2] \) was 1 mol\%. Thermal analyses of the washed xerogel powders were also carried out by TG.

2.3 Thermal treatment

The washed xerogel powders were pre-heated at 170°C for 10 min to remove completely residual \( \text{NO}_3^- \) and organics. The raw xerogel powders were heated in the same way to assess the effect of the washing step. The pre-heated powders were characterized by XRD. Finally, the pre-heated and washed xerogel powders were heated from room temperature up to 400°C, and kept at that temperature for 24 h. Thereafter, the samples were analyzed by PL and XRD.

2.4 Characterizations

XRD patterns of \( \text{ZrO}_2: \text{Eu}^{3+} \) xerogels were obtained by X-ray diffractometer (Bruker, D8 ADVANCE), and TG curves were examined with Thermogravimetric apparatus (NETZSCH STA 409 CD). Nitrogen contents in xerogels were evaluated by an O/N/H combustion analyzer (HORIBA, EMGA-930). PL spectra of \( \text{ZrO}_2: \text{Eu}^{3+} \) xerogels at wavelength resolution of 2.5 nm (\( \Delta \nu_{\text{PL}} \approx 69 \text{ cm}^{-1} \) at 600 nm) were acquired by Varian Cary Eclipse Fluorescence Spectrophotometer with a Xe flash lamp. High resolutional PLE/PL experiments were conducted using site-selective laser excitation by a wavelength-tunable dye laser [Type 599, Coherent; Rhodamine6G(R6G)] pumped by a green diode pumped solid state (DPSS) laser (Verdi, Coherent; linewidth \( \Delta \nu_{\text{ex}} \approx 8 \text{ cm}^{-1} \)) for PL detection at \( \Delta \nu_{\text{PL}} \approx 30 \text{ cm}^{-1} \) resolution by HR-320 monochromator (Jobin Yvon) and a R955 photomultiplier (Hamamatsu).

3. Results and discussion

Figure 3 shows TG curves of the raw \( \text{ZrO}_2 \) xerogels (a) and washed xerogels (b). Explosion of the powders was observed in the TG curves of the raw \( \text{ZrO}_2 \) xerogels that were not subjected to washing [Fig. 3(a)]. Such explosions are a result of the exothermic reaction of \( \text{NO}_3^- \) ions, and make it difficult to control nucleation and growth of \( \text{ZrO}_2 \) nanocrystals. On the other hand, the washed xerogels were free from explosions [Fig. 3(b)] while \( \approx 25\% \) weight decrease in TG curve was seen due to dispelling adsorbed water, hydroxyl groups, residual organics and so on.
As a result of O/N/H elementary analysis, it was found that the raw (unwashed) xerogel contained 4.98% (m/m) nitrogen, 40.5% (m/m) oxygen and 2.44% (m/m) hydrogen (See Table 1). The nitrogen content decreased to 4.78% after ethanol washing and further down to 4.32% after double ethanol washing. For Eu³⁺-coating on ZrO₂ xerogels, the xerogel (once washed) was immersed to EuCl₃ solution. Even after the immersion process, the nitrogen was removed and the amount of nitrogen became 3.43%. Correspondingly, the oxygen was also decreased from 40.5 to 30.8%, which mean that NO₃⁻ ions could be removed via the washing and immersion processes though it was still by ~30% decrease. Nevertheless, the subjected xerogels had no experience of explosive combustion around 150°C. From the results, it is seen that porous structures of ZrO₂ xerogels became much opener by the washing and immersion processes so that NO₃⁻ ions in ZrO₂ xerogels could be released together with residual organics by heat-treatment, otherwise NO₃⁻ ions and organics in unwashed xerogel were still encapsulated in closed pores and exhibited explosive exothermic reactions in a small volume of closed pores.

Table 1. Results of elemental analysis (nitrogen, oxygen and hydrogen) for ZrO₂ xerogels unwashed, washed in ethanol (once and twice) and subsequently immersed in EuCl₃ solution

|                | Raw (unwashed) | Washed, once | Washed, twice | After subsequent immersion to EuCl₃ solution |
|----------------|---------------|--------------|--------------|---------------------------------------------|
| N% (m/m)       | 4.98 ± 0.06   | 4.78 ± 0.01  | 4.32 ± 0.03  | 3.43 ± 0.04                                 |
| O% (m/m)       | 40.5 ± 1.7    | 39.1 ± 0.4   | 35.9 ± 0.5   | 30.8 ± 0.8                                  |
| H% (m/m)       | 2.44 ± 0.10   | 3.40 ± 1.14  | 2.32 ± 0.03  | 2.10 ± 0.02                                 |

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Figure 4 shows the powder XRD patterns of the raw (unwashed) (a) and washed xerogels (b) after pre-heating at 170°C. The XRD patterns indicate that the former had already crystallized due to the exothermic reactions of NO₃⁻. A small peak centered at 30.27° (101) is observed. The peak positions are in good agreement with PDF card No. 79-1768, indicating that the ZrO₂ xerogels have a tetragonal structure. On the other hand, the pre-heated samples of the washed xerogel were still amorphous.

Figure 5 shows room temperature PL spectra of the Eu³⁺-coated ZrO₂ xerogels under excitation at the wavelength corresponding to the charge-transfer band (CTB)
of the Eu\(^{3+}\) ions (\(\lambda_{ex} = 240\,\text{nm}\)).\(^{15}\) These xerogels were obtained after ethanol washing, followed by immersion in a Eu\(^{3+}\) solution and dry process at 60°C (See Section 2.2 Drying and washing step). The PL spectra contain four groups of emission bands at approximately 576–582, 584–602, 604–638, and 640–662 nm, which are due to the electronic transitions from \(^{5}D_{0} \rightarrow ^{7}F_{J}\) (\(J = 0, 1, 2, 3\)). Before the heat-treatment at 400°C for 24 h, the xerogel was amorphous and the PL spectrum peaked at 616 nm was typical for Eu\(^{3+}\) ions in amorphous state, which can be confirmed to be much strong \(^{5}D_{0} \rightarrow ^{7}F_{2}\) intensity in comparison with \(^{5}D_{0} \rightarrow ^{7}F_{1}\). On the other hand, the heat-treated xerogel had a varied PL spectrum with comparable \(^{5}D_{0} \rightarrow ^{7}F_{2}\) and \(^{7}F_{2}\) emission and moreover the peak position of \(^{5}D_{0} \rightarrow ^{7}F_{2}\) was shifted to 606 nm. \(^{5}D_{0} \rightarrow ^{7}F_{1}\) is a magnetic dipole transition and its intensity is only slightly affected by the ligand environment surrounding the Eu\(^{3+}\) ions. \(^{5}D_{0} \rightarrow ^{7}F_{2}\) is an electric dipole transition in nature, which is hypersensitive to the coordination environment of the Eu\(^{3+}\) ions. The intensity ratio (\(R\)) of \(^{5}D_{0} \rightarrow ^{7}F_{2}\) to \(^{5}D_{0} \rightarrow ^{7}F_{1}\), called “Asymmetry Ratio” (\(R\)), can thus be used to estimate the degree of the site symmetries of the Eu\(^{3+}\) ions.\(^{4,15}\) The \(R\) value of Eu\(^{3+}\)-coated ZrO\(_2\) xerogels before the heat-treatment was 4.01, whereas it was reduced to 2.01 after the heat-treatment. This change indicates that the Eu\(^{3+}\) ions occupy higher symmetry sites (substitutional Zr site) after the heat treatment. In addition, the emission peak at 606 nm, originating from the \(^{5}D_{0} \rightarrow ^{7}F_{2}\) transition, is characteristic of Eu\(^{3+}\) ions in the tetragonal structure of ZrO\(_2\).\(^{16}\) Therefore, it can be concluded that the heat-treatment (400°C, 24 h) allowed the Eu\(^{3+}\) ions coated on washed ZrO\(_2\) xerogels to diffuse into tetragonal ZrO\(_2\) phase.

Figure 4(c) shows the powder XRD pattern of the Eu\(^{3+}\)-coated ZrO\(_2\) xerogels heated at 400°C for 24 h. The XRD pattern clarifies that the well-heated ZrO\(_2\) xerogels mainly have a tetragonal structure, which is in good agreement with the results of the PL analysis. Moreover, a small amount of the monoclinic structure was also observed. However, PL peaks characteristic of Eu\(^{3+}\) ions in the monoclinic structure of ZrO\(_2\) are too weak to be identified in Fig. 5. The average crystallite size \(D\) was estimated from the diffraction data using Scherrer’s equation.\(^{17}\) The calculated \(D\) value of the tetragonal ZrO\(_2\):Eu\(^{3+}\) was 27.4 nm. It is clear that this method can be applied to the synthesis of very small ZrO\(_2\) crystals with respect of varied heat-treatment period. Thus, it can prospectively be mentioned that this synthesis route provides a way to understand the initiation of crystallization of ZrO\(_2\) from amorphous ZrO\(_2\) gels, and to determine which phase of ZrO\(_2\) (tetragonal/monoclinic) triggers the initial crystallization of ZrO\(_2\) from its amorphous state.

To show a prospective way to distinguish each contribution of tetragonal and monoclinic ZrO\(_2\):Eu\(^{3+}\) phases to the red Eu\(^{3+}\) PL, we here report a high resolutional PLE/PL technique using site-selective laser excitation,\(^{14}\) applied to a ZrO\(_2\):Eu\(^{3+}\) xerogel with an ultra-small size of \(\sim 2\,\text{nm}\) previously reported by SPCTS lab. in Limoges university.\(^{18}\) By the direct excitation of Eu\(^{3+}\) ions to degenerative \(^{5}D_{0}\) level in the range of 574–586 nm, the respective contribution to the PL could individually be separated in the following: Figure 6(a) shows a PLE

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**Fig. 6.** (a) PL excitation spectrum monitored at 592.50 nm (\(\sim 16,877\,\text{cm}^{-1}\)) for Eu\(^{3+}\) doped ZrO\(_2\) xerogel and PL spectra of Eu\(^{3+}\) doped ZrO\(_2\) xerogel excited at (b) 581.22 nm (\(\sim 17,205\,\text{cm}^{-1}\)) (tetragonal phase) (c) 583.37 nm (\(\sim 17,141\,\text{cm}^{-1}\)) (monoclinic phase).
spectrum monitoring the 592 nm PL in correspondence to $^{5}\text{D}_{0} - ^{5}\text{F}_{1}$ transition. One can see a quite strong, sharp peak with a small plateau around at 581.22 nm (17,205.26 cm$^{-1}$) (bold black arrow), which was used as an excitation to take a PL spectrum [See Fig. 6(b)]. The obtained spectrum has well defined PL lines attributed to tetragonal ZrO$_2$:Eu$^{3+}$ which are the $^{5}\text{D}_{0} - ^{5}\text{F}_{j}$ (J = 0, 1, 2, 3) transitions, 581.2 nm ($^{5}\text{D}_{0} - ^{5}\text{F}_{3}$), 592.3 nm ($^{5}\text{D}_{0} - ^{5}\text{F}_{1}$), 606.2, 613.3 nm ($^{5}\text{D}_{0} - ^{5}\text{F}_{2}$) and 623.5 nm ($^{5}\text{D}_{0} - ^{5}\text{F}_{3}$). The PLE spectrum has several small sharp peaks (white arrows) on a broad band in the range from 17,200 to 17,360 cm$^{-1}$, indicating the presence of disordered structures around Eu$^{3+}$ ions as well as more complex crystalline states which might be related with surfaces of ZrO$_2$:Eu$^{3+}$ nanocrystals. In the lower energy side, there are two clear peaks at 17,139.96 and 17,113.59 cm$^{-1}$ (thin black arrows), which is a contribution of monoclinic ZrO$_2$:Eu$^{3+}$ because the corresponding PL spectrum as shown in Fig. 6(c) exhibits a characteristic spectral pattern of monoclinic phase of ZrO$_2$:Eu$^{3+}$.\textsuperscript{19} Bearing in mind that the normal PL experiment whose data was given in Fig. 5 could not separate the contribution of monoclinic ZrO$_2$:Eu$^{3+}$ but the site-selective spectroscopy clarifies the presence of the monoclinic ZrO$_2$:Eu$^{3+}$. The estimation of the respective band areas would be used to quantitatively know the fractional numbers of Eu$^{3+}$ ions in the respective ZrO$_2$ phases by use of Eu$^{3+}$ spectroscopic probe, which was obtained to be 4.08:1:0.13 for amorphous(A), tetragonal(T) and monoclinic(M) ZrO$_2$.

However, since amorphous phases can enhance optical transition probability of $^{5}\text{D}_{0} - ^{5}\text{F}_{2}$ of Eu$^{3+}$, as evidenced for the comparison with PL spectra given in Fig. 5 in this study as well, it is to be carefully taken into consideration. Asymmetry ratio of Eu$^{3+}$ $^{5}\text{D}_{0} - ^{5}\text{F}_{1,2}$ emission intensity, $R = I_{0,2}/I_{0,1}$ = $W_{0,2}/W_{0,1}$ can provide a knowledge of the emission probability of $^{5}\text{D}_{0}$ level of Eu$^{3+}$ ions in amorphous and tetragonal monoclinic crysalline phases because $I_{0,1}$ or $W_{0,1}$ is in magnetic dipole nature and almost independent of the local structures, as mentioned above, and the obtained band areas should be considered to be obtained so as to be weighted with the transition probability against total $^{5}\text{D}_{0}$ transition probability $\sim W_{0,1}/\sum J W_{0-J}$ for the respective phases.

\[
I_{0,1} \propto \frac{W_{0,1}}{\sum J W_{0-J}} N_{c} \left(\frac{1}{1 + R + R_3(N \times W_{abs})}\right)
\]

The PL intensity $I_{0,1}$ is also proportional to the number of Eu$^{3+}$ ions in excited state of $^{5}\text{D}_{0}$ $N_{c}$, which is given by the total number $N$ of Eu$^{3+}$ in a site times the absorption probability $W_{abs}$ from the ground state $^{7}\text{F}_{0}$ [See Eq. (1)]. The 0–0 transition ($^{5}\text{D}_{0} - ^{5}\text{F}_{0}$) is not allowed both in electric and magnetic dipole transitions but is possible by J-mixing effect, called “Wybourne-Downer mechanism.”\textsuperscript{19} Here we are not going to show theoretical prediction of the $W_{abs}$ transition probability for each of the phases but fortunately exponential estimation can be conducted from the intensity ratio of $^{5}\text{D}_{0} - ^{5}\text{F}_{0}$ transition against $^{5}\text{D}_{0} - ^{5}\text{F}_{1}$ transition in PL spectra [Figs. 5, 6(b) and 6(c)]. The value $W_{abs}/W_{0,1} \propto I_{0,0}/I_{0,1}$ is 0.196, 0.077, and 0.238 for amorphous, tetragonal and monoclinic ZrO$_2$ phases. From the same spectra, the $R$ value of Eu$^{3+}$ ions in A, T and M phase was calculated to be 3.95, 1.69, and 2.72, respectively. Assuming that $W_{0,1}$ (J = 3–6) is negligible for the amorphous and tetragonal phases (actually the intensities $I_{0,3,4,5}$ were sufficiently small in comparison with $I_{0,1}$ and $I_{0,3}$), and $I_{0,3}/I_{0,1}$ ($=R_3$) = 1.26 for the monoclinic phase is taken into account, the fractional number of Eu$^{3+}$ ions obtained from such consideration $N(\propto [1 + R(+R_3)]I_{0,1}/W_{abs})$ is 73.2, 24.8, 1.9% for A, T and M phases. The number of Eu$^{3+}$ ions in monoclinic ZrO$_2$ phase is confirmed to be small. It is amazing that even after the crystallization to tetragonal structure the majority of Eu$^{3+}$ distributions are still amorphous states, which may be related with even the small size of ~2 nm and surface states of ZrO$_2$:Eu$^{3+}$ nanoparticles. Nevertheless, there appears a discrepancy between the result obtained via the site selective excitation and the previous one shown in Fig. 5. However, this can be easily understood by the excitation wavelength dependency of Eu$^{3+}$ PL spectra. The PL spectra in Fig. 5 were obtained via 240 nm excitation in CTB, which is a preferable route to excite Eu$^{3+}$ ions in ZrO$_2$ crystals if they are present. On the other hand, amorphous local structures around Eu$^{3+}$ provide lower excitation energy in CTB around 250 nm due to longer Eu–O bonding length.\textsuperscript{20}

4. Conclusion

Samples of 1 mol% Eu$^{3+}$-doped ZrO$_2$ nanophosphors were synthesized by a sol–gel method based on HNO$_3$. The pre-washing process allowed to remove a large portion of the NO$_3$ from raw ZrO$_2$ xerogels, and the final ZrO$_2$ xerogel powders were devoid of explosions during calcination, providing an advantage for controlling the nucleation and growth of ZrO$_2$ crystals. The amorphous ZrO$_2$ xerogels crystallized in a tetragonal structure with a small amount of the monoclinic phase, unveiled by XRD and high resolution PL spectroscopy. The average crystallite size of the tetragonal ZrO$_2$ was found to be 27.4 nm after a 24 h heat treatment at 400°C. From PL investigations, it could be seen that the Eu$^{3+}$ ions coated on the surface of the ZrO$_2$ xerogels diffused into higher symmetry sites in tetragonal ZrO$_2$ upon heat treatment. This paper also reported the high resolution PL technique to distinguish contributions of amorphous, tetragonal and even monoclinic ZrO$_2$ phases to the red Eu$^{3+}$ PL.

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