

SiO₂–GeO₂ Soot Preform as a Core for Eu₂O₃ Nanocoating: Synthesis and Photophysical Study

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Abstract Nowadays solid state chemists have the possibility of work with low temperature strategies to obtain solid state materials with appropriate physical and chemical properties for useful technological applications. Photonic core shell materials having a core and shell domains composed by a variety of compounds have been synthesized by different methods. In this work we used silica-germania soot prepared by vapor-phase axial deposition as a core where a nanoshell of Eu₂O₃ was deposited. A new sol-gel like method was used to obtain the Eu₂O₃ nanoshell coating the SiO₂–GeO₂ particles, which was prepared by the polymeric precursor method. The photophysical properties of Eu³⁺ were used to obtain information about the rare earth surrounding in the SiO₂–GeO₂@Eu₂O₃ material during the sintering process. The sintering process was followed by the luminescence spectra of Eu³⁺ and all the samples present the characteristic emission related to the ⁵D₀→⁷F_J (J=0, 1, 2, 3 and 4). The ratios of the ⁵D₀→⁷F₂/⁵D₀→⁷F₁ emission intensity for the SiO₂–GeO₂@Eu₂O₃ systems were calculated and it was observed an increase in its values, indicating a low symmetry around the Eu³⁺ as the temperature increases.

Keywords Europium · Luminescence · SiO₂–GeO₂ · Core shell · Nanocoating

Introduction

Nowadays solid state chemists have the possibility of work with low temperature strategies to obtain solid state materials with appropriate physical and chemical properties for useful technological applications. Silica-germania glasses are being widely used for passive devices for optical communication like optical fibers, couplers, and wavelength division multiplexers, being one of the most promising materials for the development of integrated optics. In SiO₂:GeO₂ glass the second-order optical non-linearity, which provides the potential use of this material in devices like optical switches, electro-optic modulators, and paramagnetic frequency converters, is linked to the presence of germanium oxygen deficient centers induced by the manufacturing process. In the case of glass prepared by vapor-phase axial deposition (VAD) method, the type and content of Ge-related defects would be strongly dependent on processing conditions. In the specific case of the SiO₂/GeO₂ used here it was concluded that the enhancement of the second-order non-linearity is observed for the material preform with low H₂/O₂ ratio and higher GeO₂ content [1]. The inclusion of rare earth elements in these materials could provide a rout to the simple fabrication of integrated optics amplifiers and lasers [2, 3]. The results obtained from molecular dynamics simulation of Eu³⁺ doped germanosilicate glass reveals an homogeneous distribution of SiO₂ and GeO₂ units, a decrease of defects compared to SiO₂ and GeO₂ glasses, and a trend to clustering of the doping ions [4]. In another work Eu-doped GeO₂-SiO₂ glass heated under an H₂ atmosphere was prepared using a

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sol gel method and its optical absorption and fluorescence properties were studied. The data showed that the sample heated at 1,000 °C presented Eu^{3+} ions cluster and an optical absorption band associated with the oxygen-deficient defects is significantly enhanced in the presence of Eu^{3+} . Since the electron released from the Ge–O bonds are captured to the Eu^{3+} ions, no fluorescence from this ion is observed [5].

The design and controlled fabrication of nanostructured composites like core-shell structured materials have attracted much interest of researchers due to its ability to fine-tune their properties. Core-shell materials consist of a core structural domain covered by a shell domain, where both of them may be composed of polymers, inorganic solids, and metals [4]. Photonic core shell materials having core and shell domains of a great variety of compounds have been synthesized by different methods [6–8].

In this work we used silica-germania soot ($\text{SiO}_2\text{-GeO}_2$) prepared by vapor-phase axial deposition (VAD) [9] as a core where a single nanoshell of Eu_2O_3 was deposited. A new sol-gel like method [7] was used to obtain the Eu_2O_3 nanoshell coating the $\text{SiO}_2\text{-GeO}_2$ particles. The photo-physical properties of Eu^{3+} were used to get information about the rare earth environment in the $\text{SiO}_2\text{-GeO}_2\text{@Eu}_2\text{O}_3$ material during the sintering process.

Experimental section

The resin used for coating $\text{SiO}_2\text{-GeO}_2$ glass was synthesized by the polymeric precursor modified method using an aqueous Eu^{3+} citrate solution prepared from europium nitrate (europium oxide in nitric acid) and citric acid with citric acid/metals ratio of 3:1(mol%). Ethylene glycol was added to the citric solution at a mass ratio of 40:60 in relation to the citric acid to produce a polymerizing reaction. The Eu^{3+} polymeric coating (molar ration of 9:1) on the $\text{SiO}_2\text{-GeO}_2$ surface was prepared by a wet, soft chemical method. An amount of 0.81 g of $\text{SiO}_2\text{-GeO}_2$ was dispersed in 25 ml of deionized water and sonicated for 10 min. The resin containing Eu^{3+} previously prepared was then added. This mixture was sonicated for 1 h more for stabilization and was evaporated to give the $\text{SiO}_2\text{-GeO}_2\text{@Eu}_2\text{O}_3$ powder sample. This material was then heat treated at 100, 300, 400, 500, 800 and 1,000 °C for 2 h under a heating rate of 5 °C/min in an EDGCON 3P furnace.

The surface morphology and microstructure of the $\text{SiO}_2\text{-GeO}_2$ matrix and $\text{SiO}_2\text{-GeO}_2\text{@Eu}_2\text{O}_3$ samples were analyzed using a Philips CM 200 microscope operating at an acceleration voltage of 200 kV. The TEM/HRTEM samples were prepared by dispersing the powder suspensions (powder heat-treated at several temperatures) deposited on carbon-covered Cu grids. X-ray diffraction (XRD) studies

were carried out on a Rigaku Dmax 2500PC diffractometer, using a $\text{CuK}\alpha$ radiation. Emission and excitation spectra were obtained under a 450 W xenon lamp in a SPEX-Fluorolog II spectrofluorometer at room temperature. Luminescence lifetime measurements were carried out as well using a 1934D model spectrophosphorometer coupled to the SPEX.

Results and discussion

The XRD patterns for the $\text{SiO}_2\text{-GeO}_2$ VAD soot (a) and for the $\text{SiO}_2\text{-GeO}_2\text{@Eu}_2\text{O}_3$ samples annealed at 100 °C (b), 800 °C (c) and 1,000 °C (d), are respectively presented at Fig. 1a–d, where it is seen the diffraction profiles ascribed to a crystalline phase of hexagonal GeO_2 [10]. It was observed the decrease in the intensity of all peaks as the temperature increases. The sample heat treated at 1,000 °C did not present any crystallographic pattern (Fig. 1d). The diffraction profiles ascribed to the crystalline phase of hexagonal GeO_2 disappear, indicating the incorporation of germanium by the amorphous SiO_2 matrix.

The disordered inorganic phase, which characterizes the non-periodic structure of the nanocoating shell containing the Eu^{3+} around $\text{SiO}_2\text{-GeO}_2$ VAD soot matrix is impossible to be detected by RXD analysis, so the luminescence study of the Eu^{3+} was used to show the no long-range order structure belonging to these materials.

The high resolution transmission electron microscopy image (HRTEM) of $\text{SiO}_2\text{-GeO}_2$ matrix and Eu_2O_3 coated $\text{SiO}_2\text{-GeO}_2$ VAD soot sample ($\text{SiO}_2\text{-GeO}_2\text{@Eu}_2\text{O}_3$ samples) heat treated at 1000 °C are presented at Fig. 2a–c, respectively. In Fig. 2a and b, a heterogeneous distribution of nanoparticles was observed, and in the Fig. 2c, it was observed a thin layer which was ascribed to the Eu_2O_3 nanocoating. Despite the energy dispersive x-ray data (EDX) from this sample did not confirm the presence of

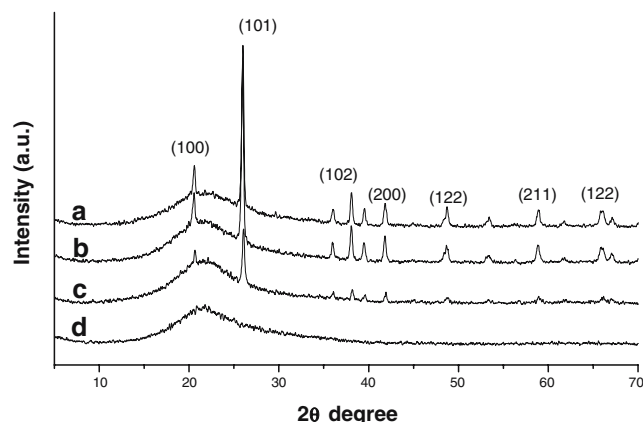
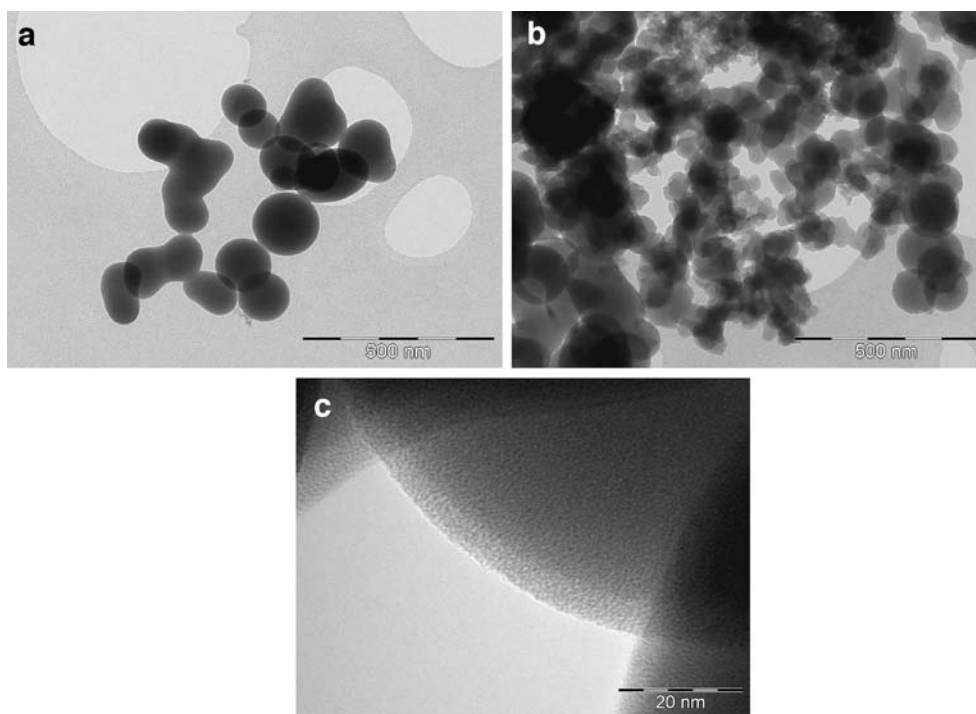


Fig. 1 XRD spectra of the $\text{SiO}_2\text{-GeO}_2$ VAD soot (a) and for the $\text{SiO}_2\text{-GeO}_2\text{@Eu}_2\text{O}_3$ samples annealed at 100 (b), 800 (c) and 1,000 °C (d)

Fig. 2 TEM/HRTEM of SiO₂–GeO₂@Eu₂O₃ annealed at 1,000 °C for 2 h **a** particles distribution, **b** Eu₂O₃ coated SiO₂–GeO₂ VAD soot sample



europium, it can be seen the gray color thin layer of around 5 nm around it. The results of TEM for the other samples did not present long order patterns like it was observed for this one. The lack of detection of this element could be ascribed to the very low concentration of europium in a unique thin layer and to its diffusion through the SiO₂–GeO₂ matrix. This is in accordance with RXD data which indicated the absence of the Eu₂O₃ crystallographic phase, and that the crystalline phase of hexagonal GeO₂ present in the samples

became amorphous as the temperature is increased. The temperature range used here probably could not detect the crystallographic phase of Eu₂O₃ when the samples were heat treated from 100 to 500 °C. Above 800 °C the sample became amorphous as it was observed by RXD data. So it was impossible to see crystallographic phase of Eu₂O₃ or GeO₂ through these techniques.

The sintering process of the samples was then followed by the luminescence spectra of the Eu³⁺ in the samples obtained at room temperature. This technique allows us to see the short-range order interactions around the Eu³⁺ ions. The particularities of the luminescence of rare earth ions like long decay time and narrow-band emission spectra makes then important for a great variety of applications. These properties are due to the fact that these ions have the 4*f* electronic configuration whose 4*f* electrons are shielded by the outer *s* and *p* electrons, which protect them from the external surrounding [11]. Eu³⁺ is one of the most studied by luminescence spectroscopy among the rare earth ions owing

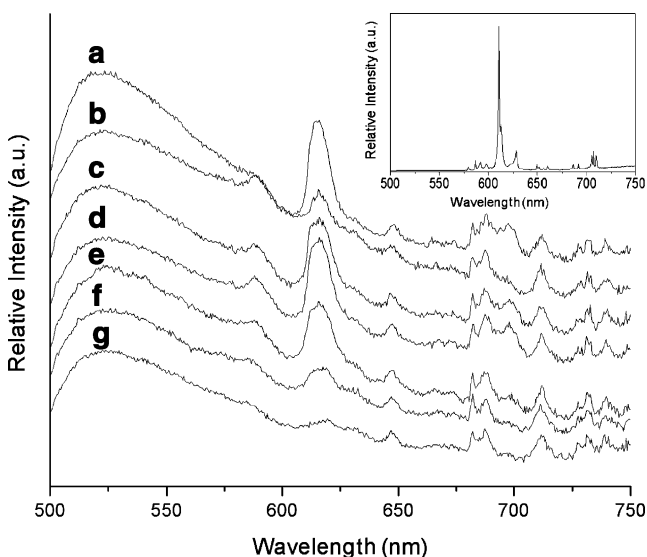


Fig. 3 Emission spectra of the SiO₂–GeO₂@Eu₂O₃ annealed at 100 (a), 300 (b), 400 (c), 500 (d), 800 (e) and 1,000 °C (f), and SiO₂–GeO₂ matrix (g), recorded at room temperature λ_{exc}=394 nm. The emission spectrum of the Eu₂O₃ powder at the same conditions is presented at the insert

Table 1 Lifetimes of the ⁵D₀ → ⁷F₂ transition of the Eu³⁺ ion for the SiO₂–GeO₂@Eu₂O₃ samples heat treated at 100, 300, 400, 500, 800 and 1,000 °C

Heating temperatures (°C)	Lifetime/ms
100	0.18
300	0.40
400	0.47
500	0.49
800	0.60
1,000	0.61

to the simplicity of its spectra and because of its great application as red phosphor in TV screen. Figure 3 presents the emission spectra of the $\text{SiO}_2\text{-GeO}_2\text{@Eu}_2\text{O}_3$ annealed at 100 (a), 300 (b), 400(c), 500 (d), 800 (e), 1000 °C (f), and $\text{SiO}_2\text{-GeO}_2$ matrix (g), recorded at room temperature using the excitation source at 394 nm. The emission spectrum of the Eu_2O_3 powder at the same conditions is presented at the insert.

Normally, in inorganic systems when the Eu^{3+} is excited by the 394 nm light ($^5\text{L}_6$ level) it decays to the ^5D levels, mainly to the $^5\text{D}_0$ one, from which the ground state is reached which emission of radiation to the fundamental term $^7\text{F}_J$ (where $J=0,1,2,3,4,5$ and 6) [12]. The initial sample presents the Eu^{3+} ions surrounded by the organic compounds in a thin layer around the $\text{SiO}_2\text{-GeO}_2$ VAD soot matrix. At this stage the sample was heated at 100 °C (Fig. 3a) and presented in its emission spectrum some of the characteristic Eu^{3+} transitions. It was observed specifically the $^5\text{D}_0 \rightarrow ^7\text{F}_2$, $^5\text{D}_0 \rightarrow ^7\text{F}_3$ and $^5\text{D}_0 \rightarrow ^7\text{F}_4$ transitions, which maximum intensities were observed at, respectively, 615, 647 and 688 nm. The $^5\text{D}_0 \rightarrow ^7\text{F}_0$ and $^5\text{D}_0 \rightarrow ^7\text{F}_1$ transitions were not observed for this sample, probably due to the overlay with the broad band at around 520 nm. As the temperature increases, it was noticed in the emission spectra of the $\text{SiO}_2\text{-GeO}_2\text{@Eu}_2\text{O}_3$ samples heat treated at 300, 400 and 500 °C (Fig. 3b–d) the presence of the $^5\text{D}_0 \rightarrow ^7\text{F}_0$ and $^5\text{D}_0 \rightarrow ^7\text{F}_1$ transitions, which bands are located at around 577 and 590 nm, respectively, as well as the $^5\text{D}_0 \rightarrow ^7\text{F}_2$, $^5\text{D}_0 \rightarrow ^7\text{F}_3$ and $^5\text{D}_0 \rightarrow ^7\text{F}_4$ transitions of the Eu^{3+} at, respectively, 615, 647 and 688 nm. The inhomogeneously broadened $^5\text{D}_0 \rightarrow ^7\text{F}_0$ band at around 577 nm suggests that the Eu^{3+} ions are associated with C_{2v} or lower symmetry [5]. As the temperature was increased it was also noticed a decrease in the intensity of the broad band located at around 520 nm, ascribed to the $\text{SiO}_2\text{-GeO}_2$ VAD soot matrix. The samples heat treated at 800 and 1,000 °C (Fig. 3e and f) did not present in their photoluminescent spectra the band ascribed to the $^5\text{D}_0 \rightarrow ^7\text{F}_0$ transition of Eu^{3+} . It is believed that this change in the Eu^{3+} emission spectrum when the sample is heat treated at higher temperatures is due to the interactions between the Eu_2O_3 thin layer and the $\text{SiO}_2\text{-GeO}_2$ VAD soot matrix. The intensities of the Eu^{3+} emission for the sample heat treated at 800 °C decrease when compared to the emission intensity of the sample heat treated at 500 °C. When the sample was treated at 1,000 °C (Fig. 3e) it was noticed an even more pronounced decrease of the Eu^{3+} emission intensities, indicating a stronger interaction from the Eu_2O_3 coating with the $\text{SiO}_2\text{-GeO}_2$ VAD soot matrix, which is responsible for the Eu^{3+} emissions quenching. This behavior is consistent with the presence of Eu^{3+} ions cluster and with the interaction of these clusters with Ge–O bonds, which are present in the $\text{SiO}_2\text{-GeO}_2$ VAD soot matrix [5].

The photoluminescence spectra of the $\text{SiO}_2\text{-GeO}_2$ matrix and Eu_2O_3 powder was presented for comparison.

The hypersensitive transition $^5\text{D}_0 \rightarrow ^7\text{F}_2$ is strongly dependent on the Eu^{3+} surrounding due to its electric dipole character, while the intensity of the $^5\text{D}_0 \rightarrow ^7\text{F}_1$, a magnetic dipole transition, is almost independent of the environment around the Eu^{3+} . The ratio of the $^5\text{D}_0 \rightarrow ^7\text{F}_2/{}^5\text{D}_0 \rightarrow ^7\text{F}_1$ emission intensity gave us valuable information about the environmental changes around the rare earth ion and can be used as a dimension of the degree of distortion from the inversion symmetry of the Eu^{3+} site in the lattice [7]. The ratios of the $^5\text{D}_0 \rightarrow ^7\text{F}_2/{}^5\text{D}_0 \rightarrow ^7\text{F}_1$ emission intensity for the $\text{SiO}_2\text{-GeO}_2\text{@Eu}_2\text{O}_3$ samples heat treated at 100, 300, 400, 500, 800 and 1,000 °C were calculated providing the values of, respectively, 2.9, 5.7, 6.2, 5.6, 4.9 and 6.2. The pronounced increase in these values as the temperature increases from 100 to 1,000 °C is indicative of a structural change of the Eu^{3+} to a lower symmetry around it.

The lifetimes of the $^5\text{D}_0 \rightarrow ^7\text{F}_2$ transition of the Eu^{3+} for the $\text{SiO}_2\text{-GeO}_2\text{@Eu}_2\text{O}_3$ samples treated at 100, 300, 400, 500, 800, and 1,000 °C were evaluated from the decay curves, which showed a monoexponential feature. These data are presented at Table 1.

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