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Synthesis of Gd$_2$O$_3$:Eu$^{3+}$ nanocrystallites emmbeded in SiO$_2$ using polyvinylpyrrolidone (pvp) by sol-gel process

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Europium doped gadolinium oxide were synthesized by sol-gel method. SiO$_2$ matrix was prepared by sol-gel method using TEOS, ammonium hydroxide and water as precursors. Both sols were mixed in different molar ratio in order to obtain Gd$_2$O$_3$:Eu$^{3+}$/SiO$_2$ stable sol. We report the structure and morphology of Gd$_2$O$_3$:Eu$^{3+}$ (2.5% mol)/SiO$_2$ with PVP (average molecular weight 1300 000) analyzed using DRX and SEM. The XRD pattern of Gd$_2$O$_3$:Eu$^{3+}$/SiO$_2$ powders heat treated at 700°C for 10 min revealed crystalline cubic phase. SEM analysis showed significant changes in the morphology which depends on the concentration ratio Gd$_2$O$_3$/SiO$_2$. Luminescent properties of glass ceramics (Gd:Si=8:1) showed intense emission bands in comparison with bare Gd$_2$O$_3$:Eu$^{3+}$ powders. This result is promising to the elaboration of thick films with optical properties.

Keywords: Gadolinium oxide; europium; silica; PVP; sol-gel.

1. Introduction

Rare earth doped core-shell systems are promising alternatives for practical applications involving the production of different visible fluorescent color, such as cathode rays tubes, trichromatic lamps, high-definition television screen, X ray imaging, etc. [1-3]. Composites systems have extended boundaries of materials science applications as explained above. These materials have shown superior characteristics that overcome the limits of the individual component [4]. Among the rare earth oxides as an individual component, europium doped Gd$_2$O$_3$ has attractive features for optical applications [5]. The production of luminescent materials for technology films applications requires strict control over their powder characteristics, which include chemical homogeneity, low-impurity levels and sub-micrometer particle size with a narrow distribution. The requirements for films, relies in thickness of 1–10 µm [6]. Theoretically, optical properties measurements in thickness film less than 1 µm are very difficult because the energy is absorbed by the substrate exhibiting its own emission [7]. The thickness required for films have been obtaining via repetitive cycles producing cracked films. Xiaolin Liu et al. [8] have demonstrated that the addition of polyvinylpyrrolidone (PVP) in alkoxide solutions allows crack-free films after 15 cycles deposition with 1.5 µm of the Gd$_2$O$_3$:Eu system. García Hernández et al. [9,10] have incorporated PVP in alkoxides solution obtaining crack-free films with ~800 nm in thickness created via single-step deposition of BaTiO$_3$:Er$^{3+}$ and BaTiO$_3$:Eu$^{3+}$. An important factor in the preparation of these films is the reduction of cost production, the strategy followed by different authors was the addition of SiO$_2$ in the synthesis process, recombining the
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Figure 1. X-ray diffraction patterns of Gd$_2$O$_3$:Eu$^{3+}$@SiO$_2$ composites with different Gd:Si molar ratios and heat-treated at 700°C for 20 min. Gd$_2$O$_3$ cubic phase (JCPDS 43-1014).

fluorescence properties of rare earth oxide with SiO$_2$ particles for the cost efficient phosphor [11,12]. To our knowledge, the synthesis of Gd$_2$O$_3$:Eu$^{3+}$@SiO$_2$ powders using PVP establishing the influence of the presence of PVP in the phosphor matrix never has been reported. In the present paper, Gd$_2$O$_3$:Eu@SiO$_2$ composites were prepared by sol-gel method using PVP as viscosity modifier agent. Gd$_2$O$_3$:Eu@SiO$_2$ composites were analyzed by X-ray diffraction and SEM in order to study their structural and morphological characteristics. The luminescent properties of the systems were investigated using photoluminescence.

2. Experimental

2.1. Synthesis of SiO$_2$

SiO$_2$ were prepared by the sol-gel method using tetraethoxysilane (Si(OC$_2$H$_5$)$_4$, ≥99.0 %, Fluka), ethylic alcohol (C$_2$H$_5$O, Fermont), distilled water and ammonium hydroxide (NH$_4$OH, 28 volume % in H$_2$O, ≥99.99%, Sigma Aldrich) as a catalyst. The molar ratio of ethylic alcohol/TEOS and TEOS/water was kept at 4:1 according to Klein’s diagram [13]. TEOS was dissolved in ethylic alcohol for one hour under vigorous stirring. Distilled water and NH$_4$OH were added in appropriate quantities to the solution in order to adjust the pH at 6.

2.2. Synthesis of Gd$_2$O$_3$:Eu$^{3+}$

Gd$_2$O$_3$:Eu$^{3+}$ was prepared using gadolinium acetate [GdO(Ac)·xH$_2$O] (99.5 % Alfa Aesar), glacial acetic acid anhydrous (C$_2$H$_4$O$_2$), 99.8%, Fermont), methanol [CH$_3$OH] (99.8%, Fermont), europium (III) nitrate [Eu(NO$_3$)$_3$] (99.9 % Alfa Aesar) and PVP [1 300000 g mol$^{-1}$]. The molar composition of the sol was Gd:Eu:PVP:CH$_3$OH:H$_2$O:C$_2$H$_4$O$_2$ = 1:0.05:1:240:100:17, where the molar ratio for PVP was defined for the monomer. Gadolinium acetate was dissolved in a mixture of acetic acid, distilled water and europium nitrate for 6 hours. The PVP was dissolved in methyl alcohol for 2 hours. Both solutions were prepared at room temperature. Then, gadolinium solution was added drop by drop into PVP solutions under vigorous stirring at room temperature for 2 hours. An appropriate quantity of europium nitrate was added to gadolinium solution to get the defined concentrations (5 % mol Eu$^{3+}$).

2.3. Gd$_2$O$_3$:Eu$^{3+}$@SiO$_2$ sols

The preparation of composite consisted of dissolving Gd$_2$O$_3$:Eu$^{3+}$ sol into the SiO$_2$ sol in different molar ratio Gd:Si, 4:1, 5:1, 6:1, 8:1, 10:1 and 25:1. Thereafter, these solutions were ultrasonically dispersed for 1 h at 65°C. Additionally, Gd$_2$O$_3$:Eu$^{3+}$@SiO$_2$ composites were dried at 100°C for 24 h and thereafter thermally treated 450°C and 700°C for 20 min. at each temperature in order to yield the glass ceramic powders.

3. Results and Discussion

3.1. Structural and morphological characterization

The X-Ray diffraction patterns of the Gd$_2$O$_3$:Eu$^{3+}$@SiO$_2$ (4:1, 5:1, 6:1, 8:1, 10:1 and 25:1 molar ratios) samples heated at 700°C are depicts in Fig. 1.

The sample corresponding to Gd:Si=4:1 molar ratio exhibits very weak intensity of the peaks assigned as (2 2 2) and (4 4 0) reflection lines characteristic of cubic phase of gadolinium oxide. This suggests that local crystalline Gd$_2$O$_3$ has been formed on the surface of silica. After increasing the Gd:Si molar ratio, the diffraction peaks becomes sharpened. Owing to short thermal treatment, the peaks of gadolinium oxide in the Gd$_2$O$_3$:Eu$^{3+}$@SiO$_2$ (10:1, 25:1) powders presented lowest peaks intensity than that observed for Gd:Si=8:1.
SYNTHESIS OF Gd$_2$O$_3$:Eu$^{3+}$ NANOCRYSTALLITES EMMEBDED IN SiO$_2$ USING POLYVINYL PYRROLIDONE (PVP).

This effect could be related to the short time of the heat treatment due to the increased presence of Gd$_2$O$_3$ in the systems. Previous reports have revealed that well defined crystalline structure is obtained after 700$^\circ$C for 1 h [14].

The powders crystallite sizes $D$ (nm) were estimated by the Debye–Scherer equation $D = (0.9\lambda)/(\beta \cos \theta)$, where $\lambda = 1.5406$ Å is the X-ray wavelength, $\theta$ is the diffraction angle and $\beta$ is the corrected half-width of the strongest diffraction peak [15]. The crystallite size of the Gd$_2$O$_3$:Eu$^{3+}$@SiO$_2$ powders is presented inside Fig. 1. This value was found to increase when the increasing gadolinium ratio, corresponding the biggest crystallite size to Gd:Si=8:1, after this molar ratios, the crystallite size decreases.

The best Gd:Si molar ratio observed by XRD corresponded to 6:1, 8:1 and 10:1. At Gd:Si<8:1 molar ratio, the crystalline Gd$_2$O$_3$ is surrounded by amorphous phase of SiO$_2$. From this result SEM analyses were performed and are presented in Fig. 2(a–c). The SEM images for Gd:Si=6:1 (Fig. 2a) revealed big particles associated to the amorphous phase from SiO$_2$, some ceramic oxide particles of Gd$_2$O$_3$ can be observed inside the SiO$_2$. In Fig. 2b is presented the Gd$_2$O$_3$:Eu$^{3+}$@SiO$_2$ composites with Gd:Si=8:1, the image shows particles with stars-like shape associated to gadolinium oxide and some big amorphous SiO$_2$ particles. In the Fig. 2c, homogeneous particles are observed attributed to ceramic Gd$_2$O$_3$. The amorphous phase was not observed in this molar ratio (Gd:Si=10:1) because of the high concentration of gadolinium oxide in the system. From SEM and XRD result was possible determine that molar ratio Gd:Si=8:1 for Gd$_2$O$_3$:Eu$^{3+}$@SiO$_2$ powders revealed the most homogeneous morphology and best crystallinity. For this reason, the luminescent properties were studied by this system.

4. Luminescent properties

In order to compare the luminescence properties of Gd$_2$O$_3$:Eu$^{3+}$@SiO$_2$ with that of the bulk Gd$_2$O$_3$:Eu$^{3+}$, we prepare the europium doped gadolinium oxide ceramic system by sol-gel process as previously indicated.

The emission spectra of Gd$_2$O$_3$:Eu$^{3+}$@SiO$_2$ composites corresponding to 6:1, 8:1 and 10:1 with 260 nm excitation is presented in Fig. 3. The positions and intensities of Gd$_2$O$_3$:Eu$^{3+}$@SiO$_2$ composites are very similar to bare particles. In this emission spectra, the strongest emission peaks at 610 nm correspond to forced electron dipole transition of...
Eu\textsuperscript{3+} ($^5\text{D}_0 \rightarrow ^7\text{F}_2$) for all studied samples. Additional emission bands at 590 nm, 630 nm and 650 nm corresponds to ($^5\text{D}_0 \rightarrow ^7\text{F}_J$) transitions ($J=0-3$).

The absence of new emission bands or shift of the peaks position arising from energy level of Eu\textsuperscript{3+} in the three coated silica coating do not alter the crystalline field of Gd\textsubscript{2}O\textsubscript{3}. It is observed that the largest signal emitted correspond to the samples prepared at Gd:Si=8:1 molar ratio, see Fig. 3, and correspond to the characteristic transition $^5\text{D}_0 \rightarrow ^7\text{F}_2$ of Eu\textsuperscript{3+}.

5. Conclusions

The Gd\textsubscript{2}O\textsubscript{3}:Eu\textsuperscript{3+}\@SiO\textsubscript{2} composites in presence of PVP were obtained by sol-gel method. The silica glass coated Gd\textsubscript{2}O\textsubscript{3}:Eu\textsuperscript{3+} systems were studied by means of XRD and SEM. The crystallite size of cubic Gd\textsubscript{2}O\textsubscript{3}:Eu\textsuperscript{3+} ceramics were determined to be in the range 17-25 nm depending of Gd:Si molar ratio. Emission spectra showed that the amount of silica does not diminish the luminescent properties of the Gd\textsubscript{2}O\textsubscript{3}:Eu\textsuperscript{3+}. We conclude that the glass ceramic systems with different silica molar ratios prepared by this route demonstrated the possibility to elaborate Gd\textsubscript{2}O\textsubscript{3}:Eu\textsuperscript{3+} thick films with promising red emission properties.

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