Sonochemical Preparation and Characterization of Eu$_2$O$_3$ and Tb$_2$O$_3$ Doped in and Coated on Silica and Alumina Nanoparticles

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Submicron size spheres of silica and alumina prepared by well-known methods were coated sonochemically by nanoparticles of oxides of europium and terbium using the same concentration of ions. We have also used sonochemistry to prepare nanoparticles of silica and alumina doped by the same rare-earth ions for comparison. The highest luminescence intensities were observed for europium and terbium doped in nanoparticles of alumina of dimension 20−30 nm. The intensities are comparative or higher than in commercial phosphors.

Introduction

The optical properties of rare-earth ions trapped in host lattices continue to be a research attraction in terms of both their fundamental and technological importance.[1,2] Sol−gel is the most widely used technique for the preparation of these composites. A few papers have recently reported on doping rare-earth ions in silica[3] or alumina[4,5] or in their mixture,[6] which is the topic of this manuscript. They find wide-ranging applications such as optical amplifiers, micro lasers, catalysts, photocatalysts, and luminescent labels.[5,7,8] However, their effective use in optical materials has been limited by the quenching of the rare-earth ionic excited state by high-energy oscillators such as O−H and N−H most often resulting from water or the solvent employed in their synthesis.[9] Efforts to overcome this problem by the complexation of the rare-earth ion with polydendate ligands have a long record and are still an active area of research.[10] Nanoparticles on the other hand have recently been recognized to hold tremendous potential in the area of optics, heterogeneous catalysis, and magnetics.[11] Combining the promising optical properties of rare-earth ions and nanoparticles in the form of coatings or thin films is important in the fabrication of optical devices such as optical amplifiers and microlasers in a submicron dimension.[12] This requires that the rare-earth-based nanoparticles be synthesized and integrated with functionally interesting substrates such as single crystals, ceramic microspheres, or nanofibers. Stober's silica microbeads[13] obtained by the sol−gel process serve as potential substrates for the deposition of a variety of nanoparticles due to their wide-ranging surface reactivity. Similar to the Stober method, we have reported recently on a similar hydrolytic process leading to the formation of submicron alumina spheres.[14] Also, isotropic interaction exhibited by the substrate microspheres in a suspension [15] is an important property in forming an ordered array of the substrates by self-assembly or Langmuir−Blodgett techniques for the deposition of a variety of metal and metal oxide nanoparticles.

In earlier experiments we have investigated the ultrasound-driven deposition and adhesion of nanophasic nickel, iron, and iron oxides on the surface of submicrospherical silica.[16−18] The ability of the power ultrasound to effect chemical changes arise from the cavitation phenomena involving the formation, growth, and collapse of bubbles.[19] In this manuscript we report the ultrasound-driven synthesis, morphological characterization, and optical properties of amorphous europium oxide and terbium oxide nanoparticles of size ∼5 nm immobilized on the surface of submicrospherical silica and on submicrospherical alumina. We also report on the preparation and optical properties of silica and alumina nanoparticles doped with europium oxide and terbium oxide. The paper presents also a general method for the preparation of rare-earth oxide nanoparticles, a method by which we have also prepared Er$_2$O$_3$ and Nd$_2$O$_3$. It is worth mentioning that only a few investigations have dealt so far with nanoparticles of the rare-earth oxides. The methods by which they were prepared, prior to this project, are sol−gel techniques[21] and gas-phase condensation with cw-CO$_2$ laser heating.[22,23]

Experimental: Synthetic Methods

(a) Coating and Doping Silica. Amorphous submicrospheres of silica in the size range 200−250 nm were synthesized by the hydrolysis of tetraethyl orthosilicate (TEOS) following the method described by Stober et al.[13] In the present manuscript we present the synthesis, characterization, and optical properties of three Eu$_2$O$_3$−silica composites. The first samples were prepared by depositing nanophased europium oxide on the outer surface of submicron spherical silica particles. In the second, the silica sample was doped with Eu$_2$O$_3$, and the third sample was prepared by the co-deposition of silica with Eu$_2$O$_3$ and Al$_2$O$_3$. A detailed description of the sonochemical deposition technique applied for the coating of (99.0 SiO$_2$−1.0 Eu$_2$O$_3$ mol %) amorphous europium oxide nanoparticles on the silica microspheres is described elsewhere;[20] we will repeat it briefly. First, europium oxide was dissolved in a minimum amount of nitric acid and evaporated to dryness. The dry nitrate was dissolved in 5 mL of water. The required amount of silica microspheres was taken in a beaker with 30 mL of water adding

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the europium nitrate solution to it. The sonication was carried out for 1 h employing a direct immersion titanium horn (Vibracell, 20 kHz, 100 W/cm^2) in an open beaker kept in an ice bath. Five milliliters of 25% aqueous ammonia was added in drops during the sonication. The resulting product after sonication was washed extensively with water, centrifuged, and dried under vacuum. The above samples were heated to 700 °C in air for 24 h.

The preparation of the europium oxide-doped silica nanoparticles (99.0 SiO$_2$−1.0 Eu$_2$O$_3$ mol %) was different. It was also carried out by the hydrolysis of tetraethyl orthosilicate (TEOS) in the presence of H$_2$O, ethanol, and europium nitrate solution. First, europium oxide was dissolved in a minimum amount of nitric acid and evaporated to dryness. It was dissolved in 5 mL of water, and transferred to the required amount of TEOS solution. The mixture was sonicated for 30 min employing a direct immersion titanium horn (Vibracell, 20 kHz, 100 W/cm^2) in the solution beaker which was kept in an ice bath. Five milliliters of 25% aqueous ammonia was added in drops during the sonication. In this way, europium oxide incorporated into silica particles was obtained. The resulting product after sonication was washed extensively with water in a centrifuge and dried under vacuum. The above sample was heated to 700 °C in air.

We have also experimented with codoping the silica particles with Eu$_2$O$_3$ and Al$_2$O$_3$. For Al$_2$O$_3$-codoped nanoparticles (2.0 mol % Al$_2$O$_3$), aluminum triisopropoxide was added into the mixture of the TEOS and europium nitrate solution. The sonication was carried out for 30 min employing a direct immersion titanium horn (Vibracell, 20 kHz, 100 W/cm^2) in the solution beaker which was kept in an ice bath. Five milliliters of 25% aqueous ammonia was added in drops during the sonication. The resulting product after sonication was washed extensively with water in a centrifuge and dried under vacuum. The above sample was heated to 700 °C in air. The deposition of the Tb$_2$O$_3$ on the surface of the silica spheres and its doping in the silica nanoparticles were carried out in exactly the same way.

(b) Coating and Doping Alumina. The preparation of alumina submicron spheres has been described alsewhere.[14] In short, it was prepared by the hydrolysis of aluminum *sec*-butoxide (ABS) in a dilute solution of 1-octanol, 1-butanol, and acetonitrile. In the process, hydroxypropylcellulose (HPC) was added as a dispersant. First, the ABS was dissolved at 60 °C, then two solutions were prepared: the first, by dissolving a small amount of HPC (0.1 mg/cm^3) in acetonitrile and the second by mixing 1-octanol and 1-butanol. The two solutions were mixed for 30 s at 25 °C using a magnetic stirrer, and were left to age for 30 min. The composition of the solution at this stage expressed in vol % is 1-octanol:1-butanol:acetonitrile = 59:1:40. The aluminum alkoxide and water concentrations were 0.05 and 0.01, respectively. The precipitate was washed thoroughly with acetone, dried in a vacuum, and heated in air at 400 °C for 3 h and at 700 °C for 4 h. This process yielded alumina spheres of approximately 200 nm diameter. The deposition process of the Eu$_2$O$_3$ and Tb$_2$O$_3$ on its surface is exactly as described above for the silica spheres.

The XRD diffraction pattern of the product did not reveal any peaks confirming its amorphous structure. Structure was detected neither for the alumina[14] nor for the rare-earth oxide, the reason being the fast cooling rates exceeding 10^{10} K/s obtained when the sonochemical bubble collapses.[19] The doping process was similar to the doping of the silica, the only difference being the precursor, aluminum triisopropoxide,

replacing the TEOS and that its aqueous solution was formed with the addition of formic acid. The precipitate was washed with distilled water twice and with acetone three times. The washing was followed by drying in a vacuum overnight. The dried sample was heated at 400 °C for 2 h, and at 700 °C for 4 h.

Elemental composition was measured employing an EDXA JEOL-JSM 840 scanning electron microscope. The morphology of the silica and alumina substrates, the rare-earth-coated samples, and the doped samples were investigated by transmission electron microscopy (JEOL-JEM 100SX). The samples were examined by XRD (Rigaku) and FTIR spectroscopy employing a Nicolet impact 410 instrument. The excitation and emission spectra of Eu^{3+} and Tb^{3+} ions deposited and doped in silica and alumina were measured using a JASCO FP 750 spectrometer and the absorption of the species on a Milton Roy Spectronic 3000 array spectrometer. Samples for excitation and emission spectroscopic measurements were prepared by spreading a paste of the solid material in acetone over a glass plate, and spectra were recorded on a JASCO FP-750 spectrofluorimeter. All mesurements were done at room temperature. All Eu samples were excited at 244 nm (bandwidth (Ex) = 5 nm, bandwidth (Em) = 5 nm, sensitivity = low). All the Tb samples were excited at 246 nm (bandwidth (Ex) = 5 nm, and bandwidth (Em) = 5 nm).

Results and Discussion

The FT-IR spectra of the bare substrate spheres, as-prepared europium oxide-coated silica, and the sample heated to 700 °C are shown in Figure 1. The infrared absorptions in the range of 3000−3800 cm^{-1} are due to various types of surface and internal silanols. The absorptions at 800 cm^{-1} and at 1200 cm^{-1} have been assigned to the bulk modes of silica.[24,25] A significant change in the spectra, as observed in Figure 1, is the elimination of surface silanols and adsorbed water in the case of the heated samples (Figure 1c). Also the band at 960 cm^{-1} (Si−OH) diminished in intensity in the case of the as-prepared sample and was completely absent in the case of the heated samples. The reduced relative intensity of this band in the case of the as-prepared sample arises from the self-condensation among the interparticle surface silanols as well as the cross condensation of the surface silanols with the rare-earth hydroxyls on the surface of Eu(OH)$_3$ nanoparticles. We have shown in an earlier investigation that power ultrasound can disrupt the hydrogen-bonded network of silanols on silica microspheres and initiate the condensation of interparticle silanols.[15]

In Figures 2 and 3 we present the TEM pictures of the Eu$_2$O$_3$ coated on the surface of the silica spheres (Figure 2) and of the Eu$_2$O$_3$-doped silica (Figure 3). Figure 2 shows the 200 nm silica spheres coated by a thin layer of 5−10 nm size. Figure 3, which depicts the image of the doped material, shows a highly aggregated compound consisting of 20−40 nm spheres. The same TEM picture, as Figure 3, was obtained for the europium oxide−alumina codoped material. The difference between the resulting particles has to do with their preparation methods. While for the coated Eu$_2$O$_3$, sonochemistry is involved only in the deposition process, whereas the silica is prepared by the wet-chemical method reported by Stober. The doped material, on the other hand, is prepared only sonochemically. It is well-known from previous work of Suslick[19] and others that the sonochemistry is yielding nanoparticles, independently of whether the reaction takes place inside the collapsing bubble or in the outside ring. The TEM pictures of the corresponding coated and doped alumina particles are very similar to the silica images.
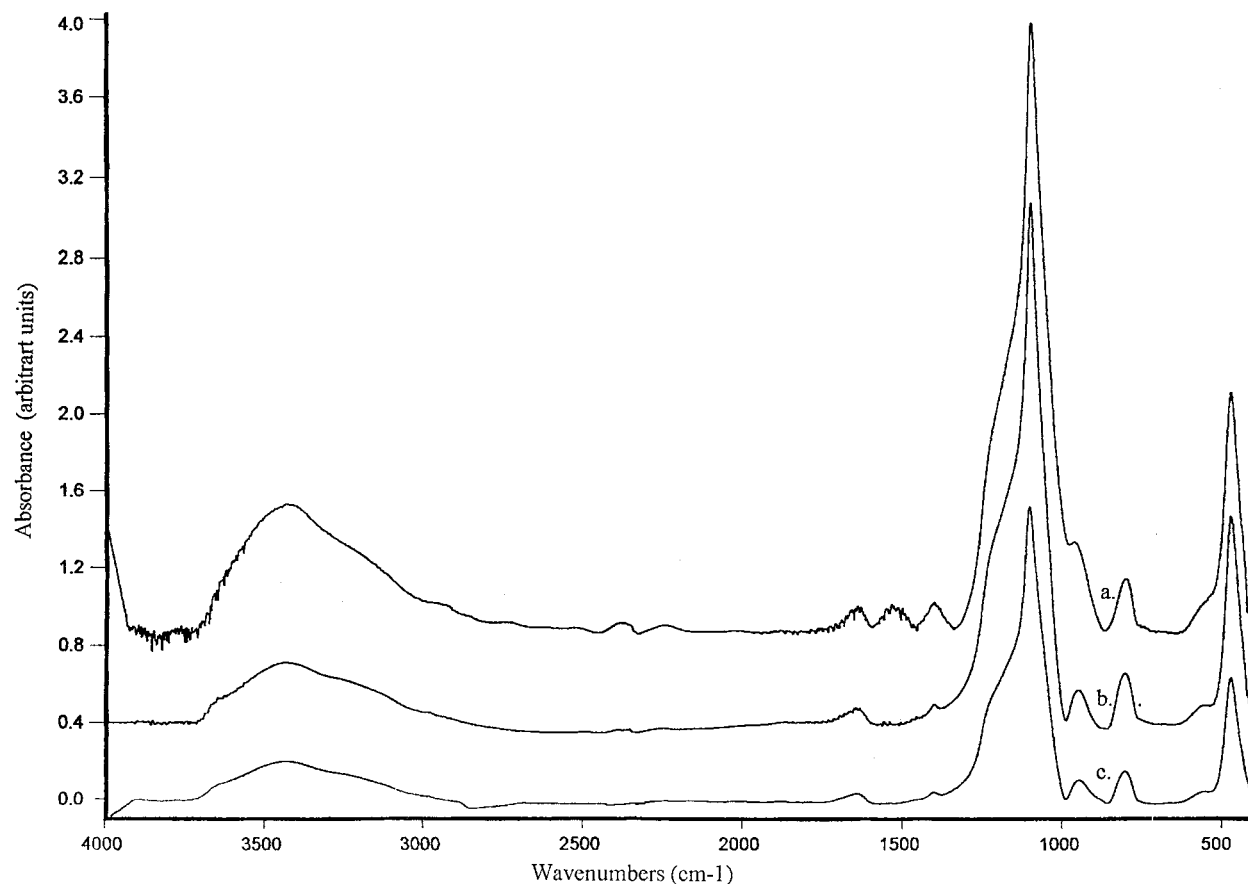
Figure 1. FTIR spectra of (a) bare silica particles, (b) as-prepared Eu$_2$O$_3$ coated on the silica submicron spheres, (c) sample b heated to 700° C. In all three samples pellets of KBr were measured. The ratio of nanoparticles to KBr is 1:20.
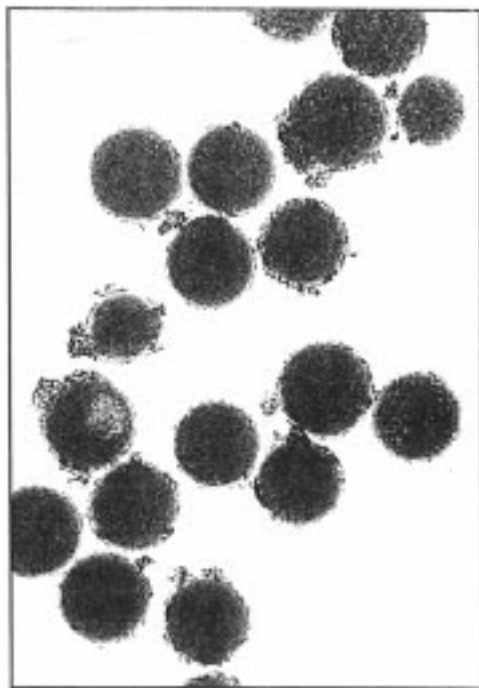

Figure 2. TEM image of the Eu$_2$O$_3$ deposited on Stober silica submicron spheres.

Figure 3. TEM image of Eu$_2$O$_3$ doped in silica nanoparticles.

The existence of the rare-earth ion in the coated or doped materials was examined by EDAX measurements. The EDAX spectrum serves also as a rough estimate for the quantitative determination of the rare-earth atom. A typical spectrum of the Tb$_2$O$_3$-coated silica particles is presented in Figure 4. It shows that the concentration of terbium on the silica surface is approximately 1% (mole percent).

Figure 5 provides a representative spectrum of europium in alumina and Figure 6 of terbium in alumina. The assignments of the transitions are given in Table 1. The wavelengths of the main transitions as well as their intensities are assembled in Table 2 (measured at the same experimental conditions). The most striking result is the dramatic increase of the emission intensities of europium and terbium doped in the nanoparticles
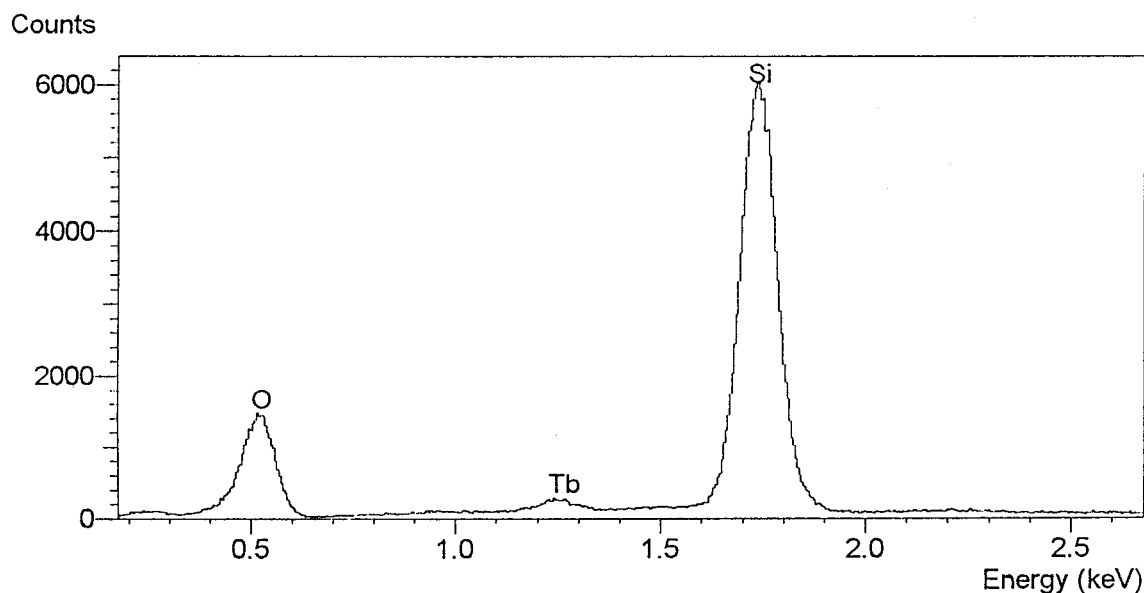
Counts

Figure 4. EDAX spectrum of Tb$_2$O$_3$ doped in silica nanoparticles.

Europium + Aluminium: 2.7 mol% Eu$_2$O$_3$
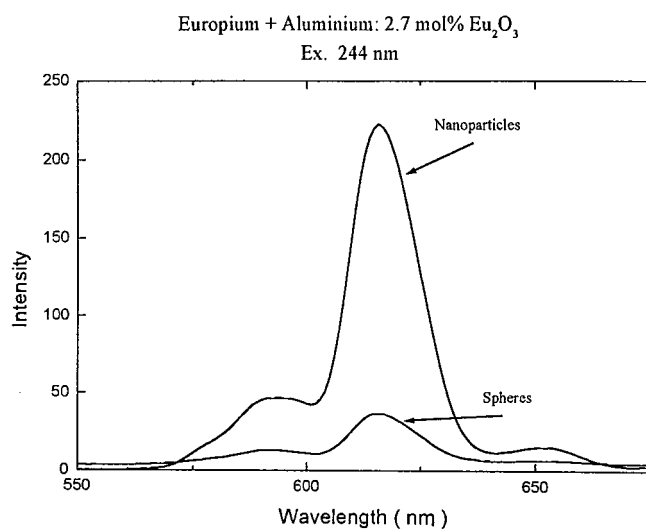Ex. 244 nm

Figure 5. Luminescence spectrum of Eu$_2$O$_3$ doped in alumina nanoparticles and deposited on submicron silica spheres. The excitation wavelength is 244 nm.

of alumina as compared to the coated submicrospheres, and the increase of intensities in alumina as compared to silica. In europium the $^5D_0 \rightarrow {^7F_1}$ transition is mainly magnetically allowed and is not dependent on the site symmetry at which europium is situated. The $^5D_0 \rightarrow {^7F_2}$ is a forced electric dipole transition being allowed only at low symmetries with no inversion center[1]. The ratio between the electric dipole and the magnetic dipole is a measure of the site symmetry in which europium is situated. The higher the ratio, the lower the site symmetry at which the rare-earth ion situated. Europium ion is therefore used very often as the probe of site symmetry.

From the ratio of the intensities it is clear that the site symmetry of the europium is higher in silica particles and the luminescent intensities are much lower in this matrix, such behavior was also observed earlier in silicated glasses.[24] It should be remembered that the f $\rightarrow$ f transitions arising from forced electric dipole are parity forbidden and become partially allowed when the ion is situated at the low symmetry site. Such situation allows intermixing of the ^{4}f states with the higher electronic configuration.[1]

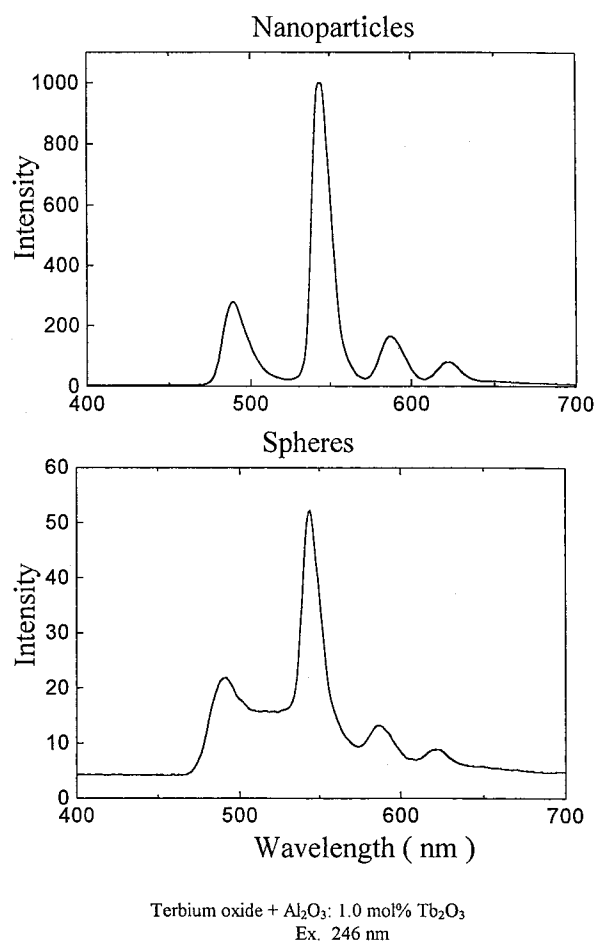From our results it is clear that europium in alumina has much

Nanoparticles

Spheres

Terbium oxide + Al$_2$O$_3$: 1.0 mol% Tb$_2$O$_3$
Ex. 246 nm

Figure 6. Luminescence spectrum of Tb$_2$O$_3$ doped in alumina nanoparticles and deposited on submicron silica spheres. The excitation wavelength is 246 nm.

higher luminescent intensities than in silica. In addition in the nanoparticles (the doped particles), where the dispersion of europium is much better than in microspheres (coated particles), the intensities of the luminescence increase dramatically. The same situation is also evident for terbium where the intensities of terbium doped in nanoparticles of alumina are higher by the factor of 20 to 100 than the intensity of the coated particles.

TABLE 1: Optical Transitions and Their Assignments

europium transitions	wavelength (nm)	terbium transitions	wavelength (nm)
5D$_0$ − 5F$_2$	614	5D$_4$ − 7F$_6$	489
5D$_0$ − 7F$_1$	590	5D$_0$ − 7F$_5$	546
5D$_0$ − 7F$_3$	650	5D$_0$ − 7F$_4$	580
		5D$_0$ − 7F$_3$	620

TABLE 2: Comparison of Emission Intensities of Rare Earths in Nanoparticles of SiO$_2$ and Al$_2$O$_3$ and Deposited on Microspheres^a

Europium

materials^b	microspheres Ex	microspheres Em (614)/(590)		nanoparticles Ex	nanoparticles Em (614)/(590)	
Eu + Si	(391)	(590) 0.35		(390)	(590) 0.43	
		(615) 0.64	1.8		(614) 0.55	1.3
Eu + Al + Si				(391)	(590) 0.57	
					(614) 0.60	1.1
Eu + Al (1)				(244)	(594) 46	
					(616) 212	4.6
				(393)	(594) 3	
					(616) 14	4.6
(2)	(244)	(594) 11				
		(616) 40	3.6			
	(393)	(593) 3				
		(616) 12	3.7			
(3)				(244)	(594) 61	
					(616) 294	4.8
				(393)	(594) 8	
					(616) 39	4.7
(4)	(244)	(594) 19				
		(616) 35	3.6			
	(393)	(594) 3				
		(616) 9	3.6			
(5)	(244)	(594) 7				
		(616) 31	4.4			
	(393)	(594) 2				
		(616) 7	4.4			

Terbium

substances^c	microspheres Ex	microspheres Em	nanoparticles Ex	nanoparticles Em
Tb + Al	(246)	(543) 53	(246)	(546) 1000
		(491) 22		(489) 278
Tb + Si			(243)	(546) 142
				(490) 51

^{a} The numbers in parentheses are the wavelengths of the main transitions. ^{b} Eu + Si: 1.0% Eu$_2$O$_3$; Eu + Al + Si: + 2 mol % Al$_2$O$_3$; Eu + Al (1): 2.7 mol % Eu$_2$O$_3$, (2): 2.7 mol % Eu$_2$O$_3$, (3): 4.2 mol % Eu$_2$O$_3$, (4): 2.7 mol % Eu$_2$O$_3$, (5): 1.0 mol % Eu$_2$O$_3$. ^{c} Tb + Al:1.0 mol % Tb$_2$O$_3$; Tb + Si: + 1.0 mol % SiO$_2$.

The ratio of emission of terbium in nanoparticles of alumina to that of silica is larger by a factor of 5 to 7. Optical transitions assignments are presented in Table 1 and the corresponding intensities in Table 2.

Recently we observed a similar situation of increase of intensities of luminescence of Sm^{3+} and Pr^{3+} in aluminum silica glasses as compared to silica glasses. The glasses were prepared by the sol−gel method.[26,27]

Similarly to the situation described in this paper the addition or replacement of silica atoms by alumina prevents the aggregation of the rare-earth ions and also decreases the site symmetry at which the rare earth is situated.

We have compared the luminescent efficiencies of the nanoparticle of alumina doped by europium and terbium with those of commercial phosphors and found the intensities to be higher in the doped nanoparticles. The described results open a new synthetic route to highly luminescent materials.

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