Functions of Eu^{3+} ions in materials
with CdS nanoparticles and oxide matrices

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CdS semiconductor nanoparticles are used to improve the luminescence properties of europium(III) -doped matrices such as silica xerogel and silica nanoparticles, both prepared by a sol-gel method as well as zeolite NaY. The impregnation of CdS nanosized clusters on an Eu^{3+}-doped matrix enhances the luminescence of both dopants. Additionally, the luminescence of the materials can be improved by thermal treatment and by changing the Eu^{3+}/CdS molar ratio. Eu^{3+} emission spectra show changes in the intensities of the bands at 595 and 612 nm, depending on the structural order of the oxide matrices.

Key words: luminescent materials; nanoparticles; Eu^{3+} ions; oxide matrices; structural order

1. Introduction

Nanoparticles small enough have a very significant portion of their total atoms on the surface. Therefore, intrinsically different surface chemistry due to unusual surface defects and unusual electronic states affecting surface chemistry might be expected. Due to the range of dimensions involved in nanostructures, the surface-to-volume ratio is high and a significant proportion of the molecules in such systems lie in or close to the region of inhomogeneity associated with particle–medium interfaces. These molecules will have properties (e.g. energy) different from those in the bulk phase. A significant and often dominating contribution comes from molecules in the interfacial region. This is why surface chemistry plays such an important role in

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nanoparticles and why surface properties become evident when particle size falls below 100 nm [1].

The II–VI semiconductor nanocrystals offer an attractive application. Their emission spectra are very narrow (spectrally pure) and the emission colour is simply tuned by changing their size. As nanocrystal size increases, the energy of the first excited state decreases, qualitatively following a particle-in-a-box behaviour.

This size dependence and the emergence of a discrete electronic structure from a continuum of levels in the valence and conduction bands of the bulk semiconductor result from quantum confinement; hence, semiconducting nanocrystals are referred to as "quantum dots" [2].

In the case of Eu^{3+} ions, the main emission lines occur between the $^5D_0$ level and ^7F_J multiplets. Their narrow emission lines have low intensity, because they are parity and spin forbidden. The oscillator strengths of absorption to the excited states of Eu^{3+} ions, as for other rare earth ions, are of the order of magnitude 10^{-5}–10^{-6} [3].

The $^5D_0 \rightarrow {}^7F_J$ emission is very suitable for surveying the transition probabilities of sharp spectral features in rare earths. If a rare-earth ion occupies a site with inversion symmetry in a crystal lattice, the optical transitions between $4f^n$ levels are strictly forbidden as electric-dipole transitions (due to the parity selection rule). They can only occur as magnetic-dipole transitions, which obey the selection rule $\Delta J = 0, \pm 1$ ($J = 0$ to $J = 0$ being forbidden), or as vibronic electric dipole transitions.

If there is no inversion symmetry at the site of a rare-earth ion, the odd crystal field components can mix opposite-parity states into $4f^n$-configurational levels. Electric-dipole transitions are now no longer strictly forbidden and appear as weak lines in the spectra, the so-called forced electric-dipole transitions. Some transitions, viz. those with $\Delta J = 0, \pm 2$, are hypersensitive to this effect. Even for small deviations from inversion symmetry, they appear dominantly in the spectrum [4].

Hayakawa et al. discussed the interaction between CdS nanoparticles and Eu^{3+} ions in silica xerogel as observed by photoluminescence spectroscopy [5–7]. The authors observed that CdS nanocrystals deposited on the surface of Eu^{3+}-doped silica xerogel greatly enhanced the luminescence from Eu(II) ions. Reisfeld et al. formed CdS quantum dots in ZrO_2 films together with Eu(III) and Tb(III) ions [3]. The increased emission intensity of the lanthanide ions was explained by energy transfer resulting from electron-hole recombination in the CdS to the lanthanide.

The matrices in our samples were prepared by a conventional sol-gel method and then immersed in Eu^{3+} aqueous solution and a CdS sol. The deposition of CdS nanocrystals on the surface of Eu^{3+}-doped SiO_2 xerogel greatly enhanced the luminescence emission not only from Eu^{3+} ions, but also from the CdS nanoparticles themselves. Here we report the enhanced luminescence of both these components, incorporated in such oxide matrices as silica xerogel, silica nanoparticles, and zeolite NaY. Moreover, changes are observed in the relative intensities of emission bands attributed to $^5D_0 \rightarrow {}^7F_1$ and $^5D_0 \rightarrow {}^7F_2$ hypersensitive transitions, which are related to structural order changes in the matrices.

2. Experimental

2.1. Sample preparation

Silica xerogel was prepared by a sol-gel process using Si(OCH$_3$)$_4$ (TMOS, Aldrich), distilled water, and methanol (POCh, Poland) [7]. The obtained alcogel was dried at room temperature and then at 120 °C for 3 h. The xerogel was immersed for 1 day in an aqueous solution of EuCl$_3$. After that, the material was rinsed with water and dried at 100 °C for 5 h. CdS sol was prepared according to thea method described elsewhere [8], viz. 1 cm^3 concentrated (0.1 M) Na$_2$S (P.O.Ch, Poland) was injected rapidly into 50 cm^3 stirred 10^{-2} M Cd(NO$_3$)$_2$ (POCh, Poland) containing 10^{-2} M (NaPO$_3$)$_3$ (POCh, Poland). After immersion in the CdS sol for 1 day, the Eu^{3+}-containing silica xerogel with adsorbed CdS particles was washed with water and dried at 100 °C for 5 h [9].

Monodispersed silica nanoparticles were synthesized at 25 °C from the solution containing 0.25 M Si(OC$_2$H$_5$)$_4$ (TEOS, Aldrich), 0.5 M NH$_3$, and 7.7 M deionized H$_2$O in ethanol [10]. The obtained silica particles, with an average size of 392 nm, were (as above) immersed in EuCl$_3$ solution and then CdS sol. The same impregnation procedure was followed for zeolite NaY (Aldrich), which was also treated as a matrix for Eu^{3+} ions and CdS nanoparticles.

To compare the difference in the emission intensities between the samples with and without CdS, and the structural orders in matrices, the same procedure was done for silica xerogel containing only Eu^{3+} or CdS, which were designated as control samples. In each case, the Eu^{3+} concentration in the impregnation solution was 5×10^{-5} mole per gram of matrix. The luminescence spectra of the samples consisting of Eu^{3+} ions and CdS nanoparticles immobilized in solid matrices were recorded with a Perkin-Elmer LS-50 spectrofluorimeter equipped with a reflection spectra attachment.

3. Results

Figure 1 shows the luminescence spectra of silica xerogels doped with Eu^{3+} ions (emission spectrum (a)), CdS nanoparticles (emission spectrum (b)), as well as with both Eu^{3+} and CdS (two emission spectra (c) and (d), and excitation spectrum (e)). The emission spectrum (a) consists of two bands at 595 and 612 nm, which are attributed to the $^5D_0 \rightarrow {}^7F_1$ and $^5D_0 \rightarrow {}^7F_2$ transitions in the Eu^{3+} ion, respectively [4]. The emission spectrum (b), with a band at 620 nm, is characteristic of CdS. The three-component material comprising the silica xerogel doped with both Eu^{3+} and CdS exhibits manifold higher intensity in both the cases simultaneously, viz. Eu^{3+} and CdS (see Fig. 1c and d). In the Eu^{3+} emission spectrum (Fig. 1c), the ratio of the $^5D_0 \rightarrow {}^7F_2/{}^5D_0 \rightarrow {}^7F_1$ band intensities is lower than for the two-component material with Eu^{3+} (Fig. 1a). The excitation spectrum of the three-component material consists of two distinct bands: at 394 nm, related to Eu^{3+}
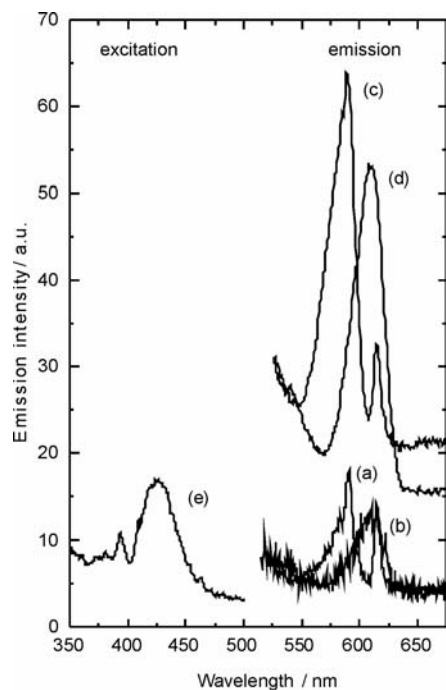
Fig. 1. Emission spectra of: SiO$_2$ xerogel impregnated with Eu^{3+}, λ_{exc} = 394 nm (a), SiO$_2$ impregnated with CdS sol, λ_{exc} = 420 nm (b) and (d), SiO$_2$ impregnated with Eu^{3+} and CdS, λ_{exc} = 394 and 420 nm (c), excitation spectrum of SiO$_2$ impregnated with Eu^{3+} and CdS, λ_{em} = 615 nm (e)
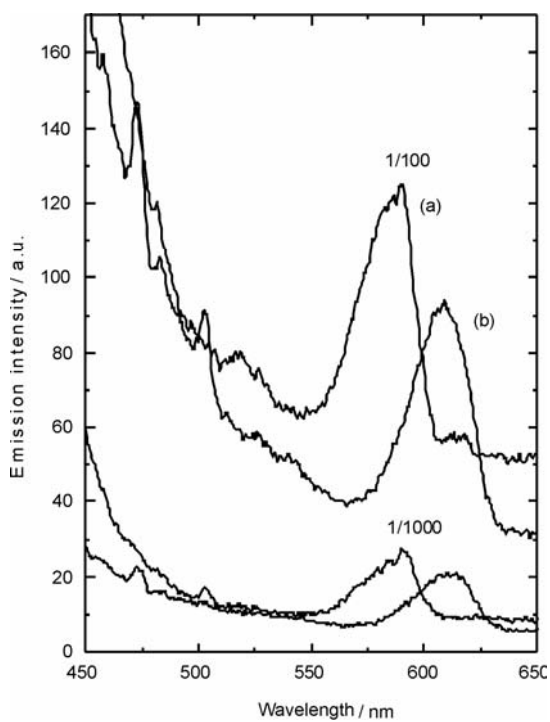

Fig. 2. Emission intensity changes with the Eu^{3+}/CdS molar ratio in SiO$_2$ nanoparticles impregnated with Eu^{3+} and CdS: a) λ_{exc} = 394 nm, b) λ_{exc} = 420 nm
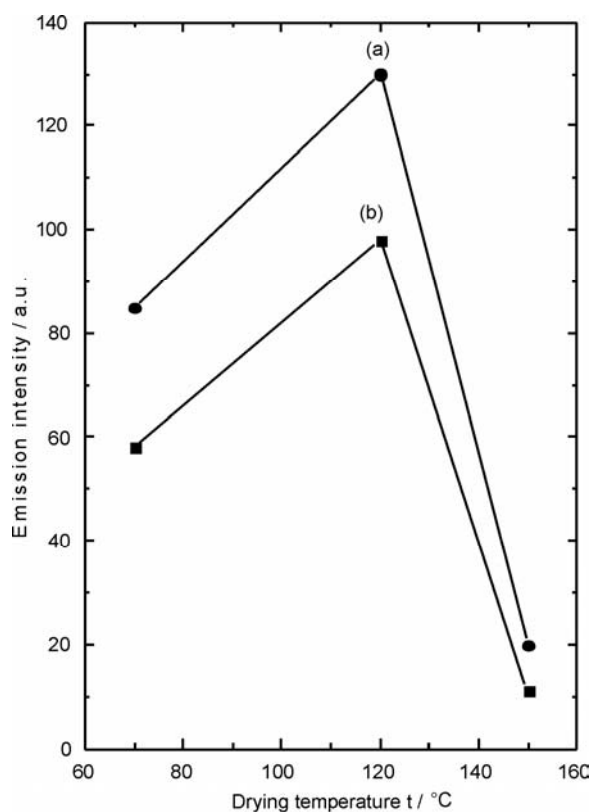
Fig. 3. Emission intensity vs. the drying temperature of SiO$_2$ xerogel
impregnated with Eu^{3+} and CdS: a) $\lambda_{exc} = 394$ nm, b) $\lambda_{exc} = 420$ nm.
The lines are drawn as guides for the eye

ions, and at 420 nm, related to CdS nanoparticles (Fig. 1e). In the three-component
material (e.g. with SiO$_2$ nanoparticles as a matrix), the emission intensities of Eu^{3+}
and CdS depend on the Eu^{3+}/CdS molar ratio, i.e. for higher value of this ratio (in the
range 1/1000–1/100), the intensities of both spectra increase (Fig. 2). Changes in the
emission intensities with the drying temperature of the material are shown in Fig. 3.
The intensity reaches a maximum in both cases at 120 °C. In the material dried at
a higher temperature (150 °C), the emission intensity dramatically decreases. In Fig-
ure 4, the emission spectra of three-component materials with various matrices are
compared. Thus, the emission spectra in Fig. 2 are related to the zeolite NaY, silica
nanoparticles, and silica xerogel, respectively. In each case, relatively high intensities
of both the CdS and Eu^{3+} emission spectra are observed, but especially high values are
reached for silica nanoparticles. In Fig. 2a, practically only the $^5D_0 \rightarrow {}^7F_1$ band is seen
in the Eu^{3+} spectrum, while in Fig. 2b, besides the $^5D_0 \rightarrow {}^7F_1$ band there is also the $^5D_0$
$\rightarrow {}^7F_2$ band with very low intensity. Finally, in Fig. 2c both the bands are present,
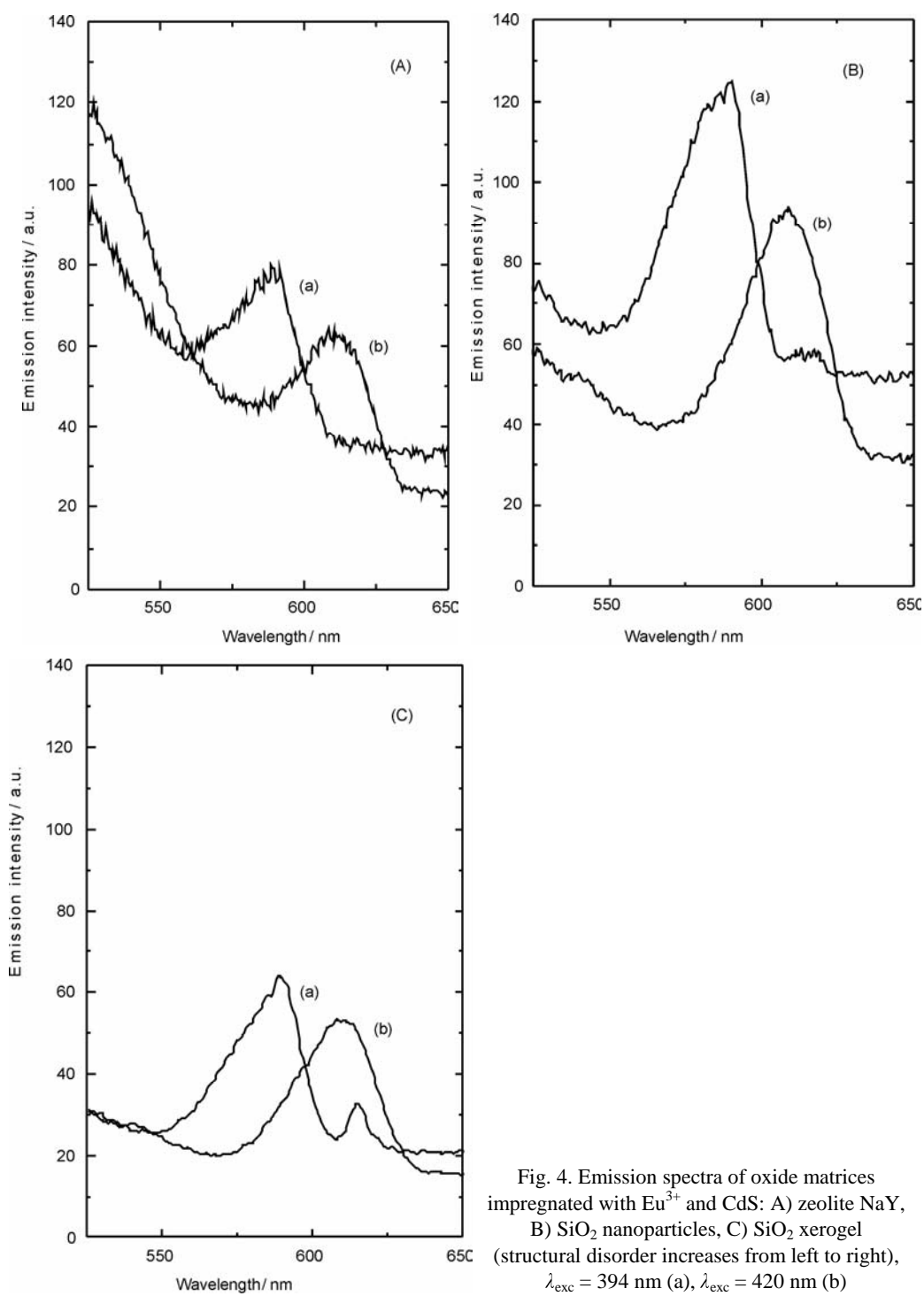however the one at a lower wavelength distinctly dominates.

Fig. 4. Emission spectra of oxide matrices impregnated with Eu^{3+} and CdS: A) zeolite NaY, B) SiO$_2$ nanoparticles, C) SiO$_2$ xerogel (structural disorder increases from left to right), λ_{exc} = 394 nm (a), λ_{exc} = 420 nm (b)

4. Discussion

CdS nanocrystals have been widely studied because they find several applications in optoelectronics. The most striking feature of these nanosized materials is that their chemical and physical properties differ from those of bulk solids. The reasons explaining this behaviour can be determined by the quantum size effect in nanometer scale materials [11]. Nonradiative energy transfer from a surface level on the CdS particle to the Eu^{3+} ion has been thoroughly discussed by Hayakawa, Selvan and Nogami [5].

According to our experimental results, the emission of f-f transitions is enhanced when CdS is present in the Eu^{3+}-doped silica xerogel as a II–VI semiconductor and vice versa, the emission of the semiconductor increases in the presence of Eu^{3+} ions in the matrix (compare spectra (a) and (c), and (b) and (d) in Fig. 1). It is noteworthy that in both emission actions no CdS $\rightarrow$ Eu^{3+} or Eu^{3+} $\rightarrow$ CdS energy transfer is observed, because Eu^{3+} ions and CdS nanoparticles are excited by a λ_{exc} typical of these particles (394 and 420 nm, respectively). The positions of the CdS spectra (b) and (d) at 620 nm are typical of the bulk semiconductor.

In Eu^{3+} spectra, the intensity ratio of the hypersensitive bands ($^5D_0 \rightarrow {}^7F_2/{}^5D_0 \rightarrow {}^7F_1$) decreases when CdS is present (cf. Figs. 1a, c). This means that the presence of nanocrystalline CdS increases the domination of the band characteristic for Eu^{3+} ions, which occupy the crystal lattice sites with inversion symmetry, in comparison to the case only Eu^{3+} ions exist in the amorphous silica matrix.

When the Eu^{3+}/CdS molar ratio increases, luminescent centres of Eu^{3+} are formed, and more electrons and holes in CdS nanoparticles can be excited, and consequently radiative recombination in both cases is enhanced (Fig. 2). The simultaneous enhancement of Eu^{3+} and CdS emissions reaches a maximum if the sample is dried at 120 °C, as illustrated in Fig. 3. For Eu^{3+}, this effect is caused by removing water as a quencher. A higher concentration of active Eu^{3+} emission centres probably improves CdS emission intensity. At temperatures above 120 °C, both emission centres are partly deactivated.

Among the studied oxide matrices, the highest luminescence improvement for Eu^{3+} and CdS is noted for silica nanoparticles (Fig. 4). Matrices in the materials are ordered according to their structural order: crystalline zeolite (A) > silica nanoparticles (crystallites) (B) > amorphous silica xerogel (C). With increasing disorder, the band intensity attributed to the $^5D_0 \rightarrow 7F_2$ transition increases. Thus, the Eu^{3+} ion might be used as a probe and the intensity ratio of its bands ($^5D_0 \rightarrow {}^7F_2/{}^5D_0 \rightarrow {}^7F_1$) could serve as a measure of the structural order in materials with oxide matrices.

5. Conclusions

Luminescent materials with Eu^{3+} ions and CdS nanostructures, immobilized on such oxide matrices as silica xerogel, silica nanoparticles, and zeolite NaY by im-

pregnation, exhibit an enhanced emission intensity of both components (Eu^{3+} and CdS) when excited by the wavelengths characteristic for the species (394 and 420 nm, respectively).

The emission intensity of both components can be improved by changing the Eu^{3+}/CdS molar ratio in the range 1/1000–1/100 and drying at an elevated temperature (not higher than 120 °C).

The luminescence emission spectra of the Eu^{3+} probe ion allow the intensity ratio of the bands $^5D_0 \rightarrow {}^7F_2$ and $^5D_0 \rightarrow {}^7F_1$ to be treated as a measure of the structural order in doped materials.

References

[1] EVERETT D.H., *Basic Principles of Colloid Science*, Royal Society of Chemistry, London, 1992, p. 8.

[2] KIPPENY T., SWAFFORD L.A., ROSENTHAL S.J., J. Chem. Educ., 79 (2002), 1094.

[3] REISFELD R., GAFT M., SARIDAROV T., PANCZER G., ZELNER M., Mater. Lett., 45 (2000), 154.

[4] BLASSE G., GRABMAIER B.C., *Luminescent Materials*, Springer-Verlag, Berlin, 1994, p. 41ff.

[5] HAKAYAMA T., TAMIL SELVAN S., NOGAMI M., J. Sol-Gel Sci. Tech., 19 (2000), 779.

[6] HAKAYAMA T., TAMIL SELVAN S., NOGAMI M., J. Luminesc., 87–89 (2000), 532.

[7] BRINKER C.J., SCHERER G.W., *Sol-Gel Science, The Physics and Chemistry of Sol-Gel Processing*, Academic Press, London, 1990.

[8] TAMIL SELVAN S., HAKAYAMA T., NOGAMI M., J. Non-Cryst. Solids, 291 (2001), 137.

[9] TAMIL SELVAN S., HAYAKAWA T., NOGAMI M., J. Phys. Chem. B, 103 (1999), 7064.

[10] BOGUSH G.H., TRACY M.A., ZUKOSKI C.F. IV, J. Non-Cryst. Solids, 104 (1988), 95.

[11] KLABUNDE K.J., MOHS C., [in:] *Chemistry of Advanced Materials. An Overview*, L.V. Interrante, M.J. Hampden-Smith (Eds.), Wiley, New York 1998, Chap. 7.