Room temperature synthesis of hybrid organic–inorganic nanocomposites containing Eu^{2+}

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For the first time, the room temperature synthesis of new Eu^{2+} doped hybrid materials together with their absorption and emission properties are reported. These hybrids containing Eu^{2+} and a small amount of Eu^{3+} are obtained through the hydrolysis and condensation of diethoxymethylsilane, methyltriethoxysilane and zirconium tetrapropoxide precursors in the presence of europium trichloride. These Eu^{2+} doped materials exhibit a strong host dependent Eu^{2+} luminescence, the intensity of which does not change upon air storage, confirming that Eu^{2+} ions are efficiently trapped inside these hybrid matrices.

The Eu^{2+} ion is particularly unique because its broad band luminescence $4f^65d^1 \rightarrow 4f^7$ is strongly host dependent with emission wavelengths extending from the UV to the red range of the electromagnetic spectrum.[1] Therefore, the luminescent properties of Eu^{2+} doped solids have been intensively studied during the past three decades. Theses studies have led to use of these compounds as phosphors, notably blue-emitting Eu^{2+}:BaMgAl$_{10}$O$_{17}$ in lamp and plasma display panels and UV-emitting Eu^{2+}:SrB$_4$O$_7$ for medical applications and skin tanning. Crystalline or glassy Eu^{2+} doped materials are usually processed at relatively high temperatures.[1–4] Moreover, the synthesis and stabilization of europium in the divalent state under mild synthetic conditions are not easy tasks. To the best of our knowledge no work has been reported on the synthesis and optical properties of room temperature processed Eu^{2+} doped matrices.

The mild conditions provided by the sol–gel process allow the synthesis of new hybrid organic–inorganic materials.[5–10] The formation of the hybrid macromolecular network involves hydrolysis and condensation of organically functionalized metal alkoxide precursors such as alkoxysilanes R$_x$Si(OR′)$_{4-x}$ (R=methyl, H or any organic function). The nature of the R group allows the tailoring of materials which exhibit a wide range of optical, mechanical, electrochemical and catalytic properties.[5–14]

Organic hydrosilanes HSi(OR)$_3$ are precursors which are particularly versatile for the synthesis of new hybrid materials.[15–18] It has been recently demonstrated that hybrid matrices synthesized from HSi(OEt)$_3$ and HSi(CH$_3$)(OEt)$_2$ precursors are high performance host matrices for spirooxazine photochromic dyes.[19] These dyes embedded within such matrices exhibit photochromic kinetics much faster than those reported for spirooxazine in any other solid matrix.[19,20]

On the other hand, dehydrocondensation of organic hydrosilanes with silanols is one of the common methods for the synthesis of the siloxane linkage.[21] This reaction occurs with the evolution of hydrogen gas. In this sense, alkoxide precursors containing Si—H groups demonstrate the possibility of using the Si—H group as an *in situ* reducing agent which allows the formation of metal–silica nanocomposites.[15]

In the present work, the *in situ* formation of hydrogen provided by the cleavage of the Si—H bonds is used to generate, during the first step of hydrolysis and condensation reactions, europium in the divalent state. This communication addresses the room temperature synthesis of two new Eu^{2+} hybrid materials. Absorption and emission properties of these Eu^{2+} doped hybrid matrices, which can be processed as bulks or coatings, are also presented.

The first matrix (system A) is obtained through the hydrolysis–condensation of diethoxymethylsilane [HSi(CH$_3$)(OCH$_2$CH$_3$)$_2$, MDES] and methyltriethoxysilane [(CH$_3$)Si(OCH$_2$CH$_3$)$_3$, MTEOS] precursors in the presence of a europium(III) salt and zirconium tetrapropoxide (ZrP). MDES and MTEOS were first hydrolyzed with neutral water in ethanol. The molar ratio MDES:MTEOS:H$_2$O:ethanol was 1:1:2:2. An ethanolic solution of ZrP and europium trichloride in the presence of acetylacetone was then added to the siloxane based sol. The final molar Zr:Eu:Si ratio was 1:0.01:9. The ZrP precursor plays a double role: it is used as a Lewis acid catalyst to assist the cleavage of the Si—H bonds,[21] and it can help to host Eu ions which usually demand high coordination numbers.

The second matrix (system B) was synthesized as follows. europium(III) chloride was first cohydrolyzed with MDES and triethoxysilane [HSi(OCH$_2$CH$_3$)$_3$, TREOS]. The molar ratio MDES:TREOS:Eu:H$_2$O:ethanol was 1.4:0.6:0.02:2:1. This siloxane based sol containing europium was then added dropwise to a solution of ZrP in propanol. The Zr:Si molar ratio was 2:10.

For both A and B, the mixing between the zirconium propoxide solution and the siloxane sol leads to the evolution of hydrogen gas which was used as a reducing agent to decrease the valence of europium cations from III to II. The resulting clear sols (A and B) were magnetically stirred for 30 min in an argon atmosphere. In order to obtain transparent monolithic gels and coatings a few microns thick, an appropriate amount of the sol (A or B) was poured into a plastic cuvette or deposited onto previously cleaned glass sheets.

The IR spectra of the xerogels A and B show the presence of a weak broad band located at 3500 cm^{-1} (v_{O-H}) which corresponds to some residual hydroxyl groups, and absorption bands located at about 2200 cm^{-1} assigned to stretching vibrations of residual Si—H bonds. Several bands are also observed at 1145–1025 cm^{-1}, due to Si—O—Si bond vibrations and indicate that the siloxane network is partly homocondensed. Moreover, the presence of an IR band located at 960 cm^{-1} assigned to Si—O—Zr linkages[22] shows that the siloxane species are linked to zirconium oxopolymers. This kind of hybrid network made from hydrolysis and condensation of alkoxysilane precursors and zirconium alkoxides can be described as nanocomposites built from siloxane polymers cross-linked by zirconium oxo species.[1,23] A more complete characterization of these new hybrid matrices by MAS NMR and SAXS is under investigation.

The absorption spectra have been recorded at room temperature for sols and xerogels (A and B) on a Cary 5 (Varian) spectrophotometer using as reference undoped sols and xerogels. For a given system (A or B) the spectra are similar in the sol and in the xerogel states. Absorption spectra are constituted of a broad absorption band in the UV range (200–400 nm) attributed to the $4f^75d^0 \rightarrow 4f^65d^1$ (Eu^{2+}) transition. As an example Fig. 1 shows the Eu^{2+} absorption spectra of coatings processed from hybrid systems A and B. In samples A, small peaks attributed to Eu^{3+} at 536 nm, 465.9 nm and 394.3 nm are also present in the visible range corresponding to transitions from the fundamental $^7F_0$ level to the excited $^5D_{0,1,2,3}$ and $^5L_6$ levels. Strong differences are observed between the two systems: absorption maxima are located at 365 nm (*ca.* 27400 cm^{-1}) and 310 nm (*ca.* 32250 cm^{-1}) respectively for A and B. The areas of the absorption curves are two order of magnitude larger for divalent than for trivalent europium as expected according to the nature of the electronic transition.

The emission spectra of the two systems under excitation at 355 nm show a broad emission corresponding to the interconfigurational $4f^65d^1 \rightarrow 4f^75d^0$ transition centered at 460 nm (*ca.* 21800 cm^{-1}) and 430 nm (*ca.* 23250 cm^{-1}) for the A and B systems respectively and an intraconfigurational 4f–4f Eu^{3+} emission at longer wavelengths. Several bands are obtained corresponding to the $^5D_0 \rightarrow {}^7F_{0,1,2,3}$ transitions. The more intense is the allowed dipolar electric $^5D_0 \rightarrow {}^7F_2$ transition at 610 nm (see Fig. 2). A Stokes shift value of the Eu^{2+} luminescence around 5600 cm^{-1} is obtained for the hybrid coatings processed from system A while the Stokes shift value increases
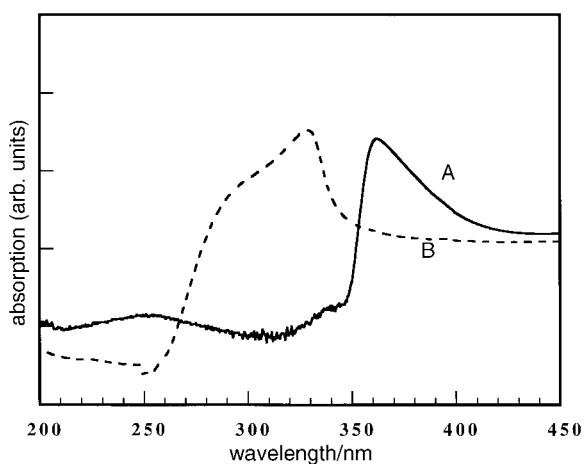

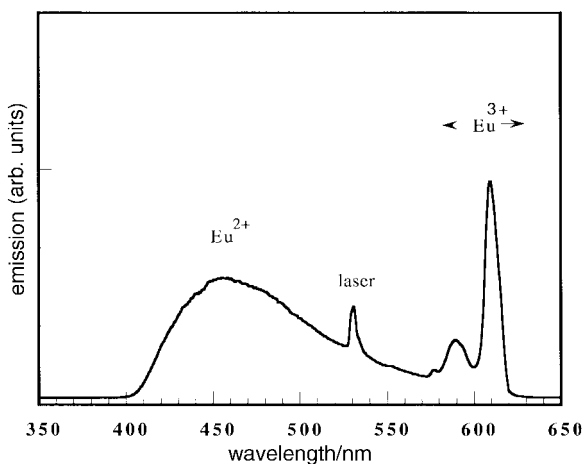Fig. 1 Absorption spectra of europium doped hybrid xerogels: systems A and B

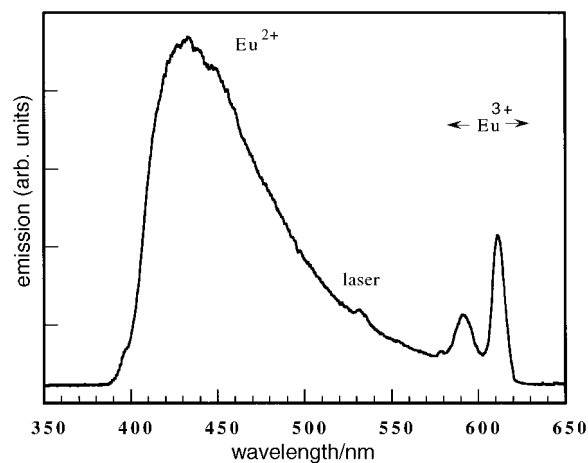Fig. 2 Emission spectrum of europium doped hybrid xerogel of system A ($\lambda_{exc} = 355$ nm)

Fig. 3 Emission spectrum of europium doped hybrid xerogel of system B ($\lambda_{exc} = 355$ nm)

to about 9000 cm^{-1} for the hybrid films obtained from system B. The shift between the absorption and emission energies of Eu^{2+} located in an oxygen ligand field has been assigned to a combination of crystal field and nephelauxetic effects.[1] Structures containing oxygen atoms in higher coordination number environments (highly coordinated by metal atoms) produce Eu^{2+} emissions at longer wavelengths, and distortion of the oxygen polyhedra from ideal coordination geometry results in a larger Stokes shift. Large Stokes shifts have also been associated with a more asymmetric dopant geometry.[2,3] The differences observed in the optical responses between A and B are probably related to differences in the processing of the hybrid materials which lead to a modification of its coordination sphere.

For system A, europium is first reacted with zirconium propoxide and then cocondensed with siloxane precursors. As a consequence, in system A europium should be efficiently sequestered in the zirconium–oxo domains. Its coordination polyhedra should be mainly made of Eu—O—Zr bonds and therefore should be quite homogeneous.

For system B, europium is first reacted with the siloxane precursors and then with zirconium propoxide. Thus the sequestering of europium by zirconium is probably less efficient. The second neighbors of the europium ion should be, not only zirconium atoms, but also silicon atoms (Eu—O—Zr and Eu—O—Si). The Eu^{2+} coordination sphere in system B should be consequently more distorted. Moreover, because Eu—O—Si bonds are made with μ_2-oxo bridges while Eu—O—Zr bonds are built with μ_3-oxo and μ_4-oxo bridges, for system B the europium coordination polyhedron should contain less oxygen atoms in higher coordination number environments. As a consequence, for system B, the absorption and emission bands are blue shifted and moreover this system also exhibits a larger Stokes shift.

Lifetime measurements have been performed at different wavelengths in A and B xerogels. At 610 nm, the $^5D_0$ (Eu^{3+}) emitting level presents an exponential decay profile with a lifetime value around 670 µs while the Eu^{2+} lifetime measured at the maximum of the broad emission band is estimated to be about 0.5 µs. With our intensified optical multichannel analyzer detector, it is also possible to observe the $^5D_1$ emission around 550 nm. This emitting level presents a short lifetime value of 2 µs as this lifetime is shortened by the non-radiative $^5D_1 \rightarrow {}^5D_0$ multiphonon relaxation mechanism. First measurements indicate a larger $Eu^{2+} : Eu^{3+}$ concentration ratio in xerogel B than in system A. A qualitative approach based on the measured absorption and emission coefficients of the divalent and trivalent europium species indicate that the $Eu^{2+} : Eu^{3+}$ ratios are about 1:1 and 5:1 respectively for

samples A and B.[24] The higher Eu^{2+} content of sample B is probably related to the more efficient reducing medium provided by the initial mixture of the europium trichloride with the MDES and TREOS silane precursors. Moreover, the intensity of the Eu^{2+} luminescence did not change when the xerogels (A and B systems) were stored in air for several months, showing that Eu^{2+} ions are efficiently trapped inside the hybrid matrix.

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24 The concentration ratio between Eu^{2+} and Eu^{3+} cations has been evaluated through the areas of the absorption bands and taking into account the probability of transition which is different for each cation. These probabilities have been estimated from the measured lifetimes.