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Divalent europium in silica gels

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Abstract

Eu $^{2+}$ has electronic transitions between the $4f^7$ ground state and the $4f^6d^1$ first excited state. These transitions are very sensitive to the surroundings in which the ion is embedded. Due to this characteristic, divalent europium has been employed as a sensitive optical probe. For this work we prepared silica gels doped with Eu^{2+} ions. The doping was achieved in two different ways, as explained in the text. Excitation and emission spectra were taken, and from the excitation data a very small splitting between the T_{2g} and E_g levels was calculated. This splitting implies that the impurity ions are located in a weak crystalline electric field as can be expected for this kind of amorphous materials.

Keywords: Gels; Luminescence; Divalent europium

1. Introduction

The sol–gel synthesis of inorganic glasses gives a procedure to obtain good quality optical materials that can be prepared at room temperature. By means of this technique it is possible to encapsulate both organic and inorganic impurities. It has been very well established that the optical properties of the materials depend mainly on the impurities they have. This optical activity has been exploited in the study of sol–gel materials, by doping them with optically active species. Thus, rare earth and transition metal ions have been utilized to characterize glasses [1,2]. Eu^{3+} has been incorporated as a probe to study the gel-to-glass transition in silica-based gels [3,4]. For this work Eu^{2+} ions were introduced into silica gels, in order to take advantage of the fact that its optical response is strongly dependent on the crystalline electric field around it. That is, as Eu^{2+} has a $4f^7$ ground state, optical transitions occur between the ground state and the 5-fold degenerate $4f^65d^1$ state, giving rise to two broad bands. The separation between these two bands gives the parameter $10Dq$, whose magnitude is indicative of the strength of the surrounding crystalline electric field. So, the determination of this parameter will give an estimation of the electric field surrounding the ion in these materials.

2. Experimental

Silica gels were prepared by stirring TEOS (39%), distilled water (9%), ethanol (51%), and HCl (0.9%). The doping was first achieved by dissolving 1 mol.% of $EuCl_2$ in the acid.

As another way to incorporate Eu^{2+} in the gel, $EuCl_3$ was added to the solution at 1 mol.% and later reduced. That is, when the gel had solidified, it was heated at 500°C in a hydrogen atmosphere. To verify the presence of Eu^{2+} in the reduced sample, the gel was illuminated with a UV lamp, so a strong blue-green fluorescence was observed. This sample is named as Eu^{2+} reduced from now on. Excitation and emission spectra for pure, Eu^{2+}-doped and Eu^{2+}-reduced samples were obtained using a Perkin-Elmer 650-10S Spectrofluorimeter. Corrections were done considering the lamp emission and detector response.

3. Results and discussion

Fig. 1 shows the excitation spectra of the silica gels. As can be observed for curves A and B, the spectra show an excitation band around 260 nm. There is a second band peaking around 360 nm that is more intense in the specimens doped with Eu^{2+}. From these data we can observe that, for the doped samples, the 360 nm band has increased with respect to the pure one. This increment is bigger for the reduced sample, indicating that the Eu^{2+} concentration is greater in this case, although the amount

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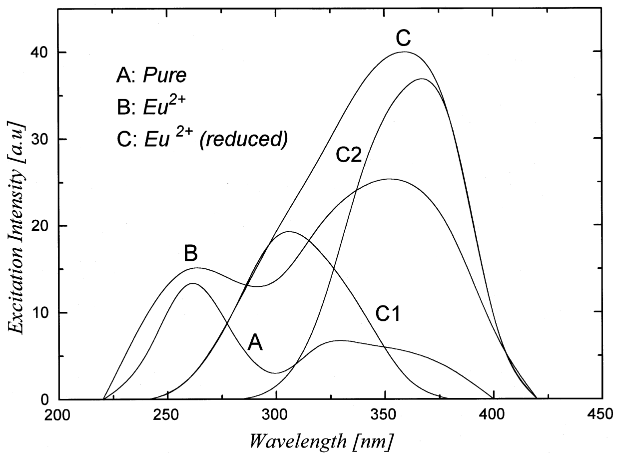

Fig. 1. Excitation spectra for the SiO_2 gels by detecting the emission at 480 nm.

of the corresponding europium chloride was the same for the two doping procedures. For the reduced sample, the excitation curve was deconvoluted in two bands, C1 and C2 peaking at 307 and 367 nm, respectively. From these, a $10Dq$ value of 5293 cm^{-1} was obtained. For Eu^{2+} in NaCl (in octahedral symmetry), $10Dq=12\,849$ cm^{-1} [5], thus in a tetrahedral environment the splitting would be $4/9\times 10Dq(\mathrm{NaCl})\approx 5700$ cm^{-1} which is close to the actual splitting found in our case. So it is reasonable to assume that the Eu^{2+} ions are in a weak crystalline field of tetrahedral symmetry. The emission curves for the three samples are presented in Fig. 2. They were obtained by exciting at 355 nm. For the pure sample, curve A, the blue emission at 436 nm intrinsic to this type of materials is observed [6,7]. The sample doped with Eu^{2+}, curve B, peaking at 450 nm, shows an enhancement of the emission and also a shifting to longer wavelengths. In the case of the reduced sample, it is observed that the emission has been considerably increased and shifted to 489 nm. This shift to longer wavelengths is considerably bigger for the reduced sample than for the Eu^{2+}-doped one. In Fig. 2, subtracting curve A from curve B, the dashed curve D was obtained. This curve overlaps well with curve C, so this should represent the luminescence of Eu^{2+} ions in the sample doped with Eu^{2+}. No evidence of the presence of Eu^{3+} was detected by exciting the $^5L_7$ level at 394 nm. Even more, the sample doped with Eu^{2+} was subjected to the same reduction process as the Eu^{2+}-reduced sample. Subsequently, a 70% loss of the total emission was observed for curve B. This result confirms the presence of Eu^{2+} in curve B and the absence of Eu^{3+}. The intrinsic blue emission of the gel has been previously reported and has been related to organic remnants of the chemical reactions that take place during the gelation process, and it is considerably reduced when the gels are heated over 500°C [6,7]. So the decrease of the luminescence of curve B after the reduction is due to the pyrolysis of the remaining organic components.

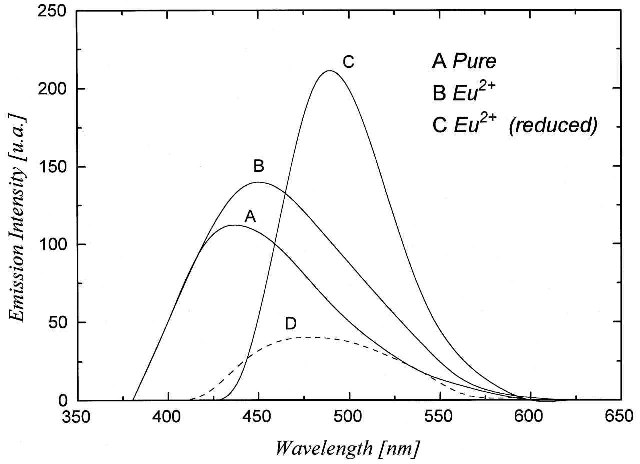

Fig. 2. Emission spectra of the SiO_2 gels.

It is known that the Eu^{2+} emission shifts to longer wavelengths when there is covalency, so the shifting observed for the Eu^{2+}-reduced sample is indicative of some degree of covalency. An overlap between the matrix emission and the Eu^{2+} excitation is clearly present

4. Conclusions

Eu^{2+} was successfully incorporated in silica gels by reducing the gel previously obtained by mixing $EuCl_3$ to the solution. The reduced gel showed a greater concentration of Eu^{2+} ions as evidenced from the excitation and emission spectra. A value for $10Dq$ was obtained from the excitation data, indicating that the impurity is located in a weak crystalline electric field of tetrahedral symmetry. Upon Eu^{2+} doping, silica gels become good UV-blue converters.

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