

Intermolecular energy transfer from coumarin-120 to rare earth ions (Eu^{3+} , Tb^{3+}) in silica xerogels

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Received 16 January 1998; accepted 7 April 1998

Abstract

Co-doped with coumarin-120 (C120) and rare earth ions (Eu^{3+} and Tb^{3+}) in silica xerogels via sol–gel technique, the fluorescence properties of rare earth ions and the energy transfer process between C120 and rare earth ions were studied. The characteristic fluorescence intensities of Eu^{3+} and Tb^{3+} ions can be increased by a factor of 35 and 8, respectively, as a result of the sensitization of C120 absorption at about 344 nm. The sensitized emission of rare earth ions is through intermolecularly resonant exchange interaction. Because of fluorescence enhancement accompanied by concentration quenching of C120, the fluorescence intensities of Eu^{3+} and Tb^{3+} increase to maximum when the C120 doping concentration is of 0.1 mol%. © 1998 Elsevier Science S.A. All rights reserved.

Keywords: Intermolecular energy transfer; Fluorescence property; Silica xerogel; Coumarin-120; Rare earth ions

1. Introduction

The photophysical processes of energy transfer among rare earth ions in oxide glasses and intramolecular energy transfer from the ligand to the central metal ion in rare earth chelates have been the subject of extensive research [1–4]. The intermolecular energy transfer between rare earth ions and organic molecules in liquid solutions has also been widely investigated [5,6]. However, it seems that few studies have been done on the energy transfer from organic molecules to rare earth ions in an inorganic transparent solid. In the present paper, we co-doped with coumarin-120 (C120) and rare earth ions (Eu^{3+} and Tb^{3+}) in silica xerogels via sol–gel technique, and studied the energy transfer process between C120 and rare earth ions.

2. Experimental details

The doped silica xerogels were prepared by the acidic (HCl) hydrolysis of tetrathoxysilane (TEOS) in

ethanol. Ethanol, C120, TEOS and hydrochloric acid were of analytical grade. EuCl_3 and TbCl_3 solutions were prepared from Eu_2O_3 and Tb_2O_3 (both 99.99% purity), respectively, by dissolution in hydrochloric. The starting solutions contained 10 mmol TEOS, 40 mmol ethanol and 40 mmol deionized water. Lanthanide(III) chlorides and/or C120, in deionized water and ethanol, respectively, were introduced into these solutions. The mixed solutions were adjusted to a pH of about 2 by the addition of HCl and stirred vigorously for 1 h at room temperature and were then placed in sealed plastic containers at 40°C. The precursor solutions converted to wet gels after several days. The wet gels were further allowed to remain at ambient temperature in the containers having a perforation at the top, and continuously dried to obtain doped silica xerogels at room temperature.

The fluorescence spectra were measured with a Hitachi 850 spectrofluorometer. The fluorescence decay curves were measured with HRG 9-5-90 N_2 laser using SPEX 1403 double grating monochromter, and the average lifetimes were calculated by the exponential equation.

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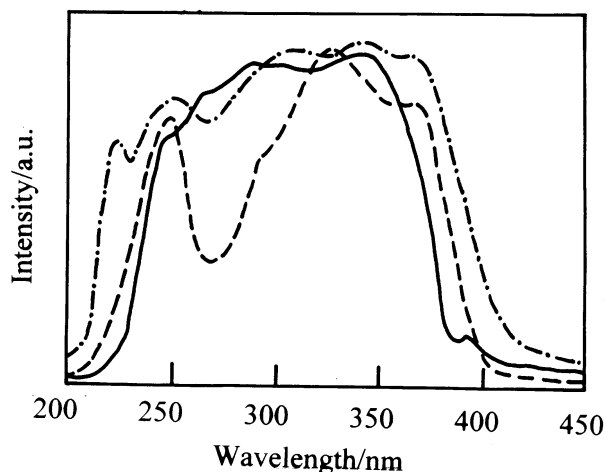


Fig. 1. Excitation spectra of doped silica xerogels measured at room temperature. —: co-doped with Eu^{3+} (2 mol%) and C120 (0.1 mol%), $\text{Em} = 616$ nm, ---: co doped with Tb^{3+} (4 mol%) and C120 (0.1 mol%), $\text{Em} = 544$ nm, -.-: doped only with C120, $\text{Em} = 438$ nm.

3. Results and discussion

3.1. Sensitized fluorescence emission of rare earth ions by C120

Fig. 1 shows the excitation spectra for 616 nm (or 544 nm) emission of Eu^{3+} ions (or Tb^{3+} ions) and for 438 nm emission of C120 in the doped silica xerogels measured at room temperature. The excitation spectra of the xerogels co-doped with C120 and Eu^{3+} ions (or Tb^{3+} ions) exhibit broad band with less vibrational structure, which are similar to that of the xerogel doped only with C120. It has been observed that the lanthanide ions absorb very little in the wavelength range

of 200 and 300 nm, and exhibit sharp bands between 300 and 450 nm in the excitation spectra which represent the $f-f^*$ transitions of lanthanide ions. It can be suggested that the broad band between 200 and 450 nm of the xerogels co-doped with C120 and Eu^{3+} ions (or Tb^{3+} ions) correspond to the absorption of C120, which also indicates an energy transfer process from C120 to Eu^{3+} ions (or Tb^{3+} ions). The emission spectra of doped xerogels show similar results, as shown in Fig. 2. Excited at 344 nm, the xerogels co-doped with C120 and Eu^{3+} ions (or Tb^{3+} ions) give rise to not only the broad band emission centered at 438 nm of C120, but also the sharp bands due to $f-f^*$ transitions of Eu^{3+} ions (or Tb^{3+} ions). The fluorescence intensity of Eu^{3+} ions (or Tb^{3+} ions) in co-doped xerogels increases by a factor of 35 (or 8) compared to that of the xerogels doped only with Eu^{3+} ions (or Tb^{3+} ions). Energy transfer between C120 and Eu^{3+} ions is more efficient.

Fig. 3 shows the fluorescence intensity of Eu^{3+} ions (or Tb^{3+} ions) versus the C120 doping concentration in co-doped xerogels, where Eu^{3+} and Tb^{3+} ion concentrations are constant of 2 and 4 mol% (mol% refer to SiO_2 in silica xerogel), respectively. The fluorescence intensity of Eu^{3+} ions (or Tb^{3+} ions) increases with the increase in the C120 concentration, and reaches a maximum when the C120 concentration is about 0.1 mol%.

3.2. Mechanism of energy transfer between C120 and Eu^{3+} ions (or Tb^{3+} ions)

In general, there are two mechanisms of energy transfer between rare earth ions and organic molecules, known as intramolecular and intermolecular energy transfer. The former usually occurs in rare earth

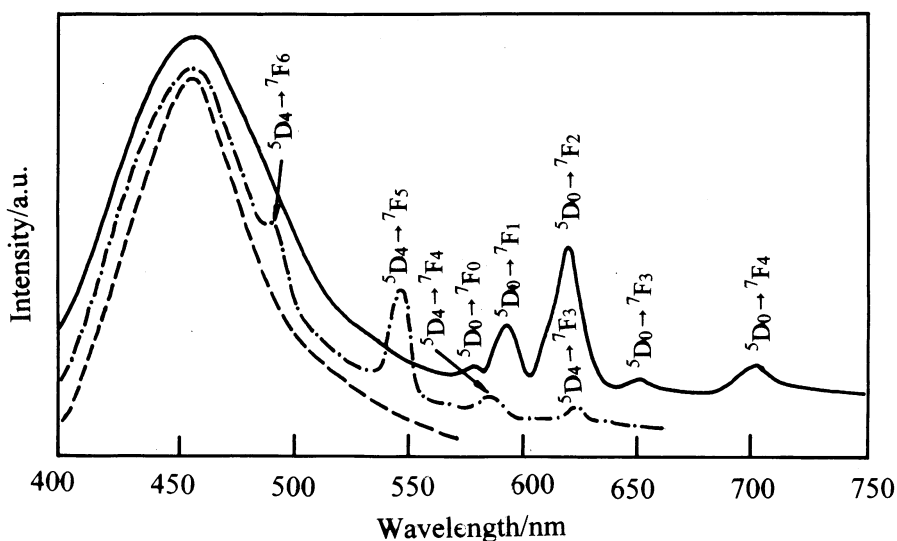


Fig. 2. Emission spectra of doped silica xerogels measured at room temperature. —: co-doped with Eu^{3+} (2 mol%) and C120 (0.1 mol%), $\text{Ex} = 344$ nm, ---: co-doped with Tb^{3+} (4 mol%) and C120 (0.1 mol%), $\text{Ex} = 344$ nm, -.-: doped only with C120, $\text{Ex} = 344$ nm.

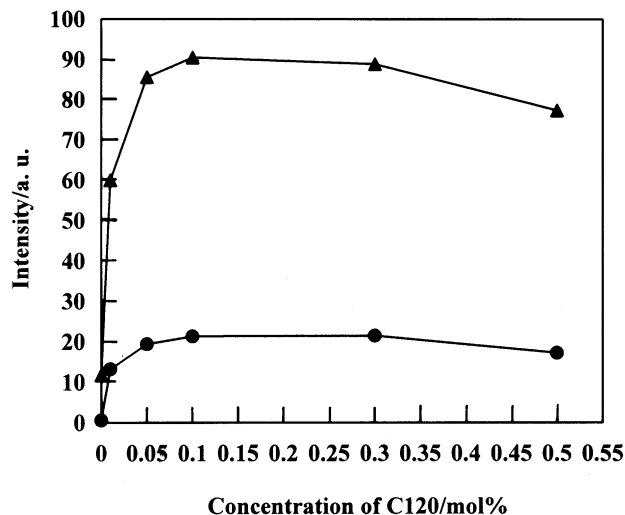


Fig. 3. C120 doping concentration dependence fluorescence intensities of Eu^{3+} and Tb^{3+} in co-doped silica gel glasses. (▲) co-doped with Tb^{3+} (4 mol%) and C120, (●) co-doped with Eu^{3+} (2 mol%) and C120.

chelates, and the fluorescence lifetime of the central metal ion increases compared to free metal ion as a result of the shielding of the organic ligand [7]. The latter can occur between separate rare earth ions and organic molecules. The intermolecular energy transfer from organics to rare earth ions in liquid solutions has been widely investigated, and an intermolecular diffusion controlled energy transfer has been suggested [5,6].

To study the energy transfer mechanism between C120 and Eu^{3+} ions (or Tb^{3+} ions), the fluorescence decay curves of Eu^{3+} and Tb^{3+} ions in the doped xerogels are measured. The decay times calculated by the exponential equation are given in Table 1. The lifetimes of Eu^{3+} ions (or Tb^{3+} ions) show no changes whether C120 is co-doped or not. So it can be suggested that no any complex species between C120 and rare earth ions form in silica xerogels, and intermolecular energy transfer occurs between C120 and Eu^{3+} ions (or Tb^{3+} ions) [7].

It has previously been indicated that organic molecules and rare earth ions doped in silica xerogels are isolated and adsorbed in the pore walls of the silica network steadily [8], and limited in diffusion and collision each other which are likely in liquid solutions. According to the results mentioned above, the intermolecular diffusion controlled energy transfer cannot

meet the case, and a resonance exchange energy transfer from C120 to rare earth ions in silica xerogels can be suggested. It is stated that the resonance transfer mechanism is dependent upon a long-range donor–acceptor interaction (often dipole–dipole), so energy transfer may occur over distances as great as 50–100 Å, e.g. in solid solutions under conditions such that molecular diffusion is impossible [9]. Förster has been able to develop a quantitative expression for the rate of energy transfer due to dipole–dipole interactions in terms of experimental parameters. The probability that energy will be transferred from one chromophore to another is inversely proportional to the sixth power of the distance between the two oscillators as follows:

$$K_{D^* \rightarrow A} \propto \frac{1}{R^6}$$

where $K_{D^* \rightarrow A}$ is the rate constant of energy transfer, R is the donor–acceptor separation, D^* and A are donor and acceptor respectively, corresponding to C120 and Eu^{3+} ions (or Tb^{3+} ions) respectively, in this paper.

The rate constant should increase exponentially with the decrease in the separation (R) between the donor and acceptor. In the work, the fluorescence intensity of Eu^{3+} ions (or Tb^{3+} ions) in C120 and Eu^{3+} ions (or Tb^{3+} ions) co-doped xerogels increases with the increase in C120 doping concentration as a result of the decrease in the separation between C120 and Eu^{3+} ions (or Tb^{3+} ions). When C120 doping concentration is over 0.1 mol%, the concentration quenching effect of C120 becomes dominant, which makes the fluorescence intensities of Eu^{3+} and Tb^{3+} ions decrease gradually Fig. 3.

Moreover, the transition probability for the nonradiative energy transfer is proportional to the overlap between the emission of the donor and the absorption of the acceptor [10]. The emission spectrum of C120 is a broad band centered at 438 nm (Fig. 2). The $^7\text{F}_0 \rightarrow ^5\text{D}_2$ and $^7\text{F}_0 \rightarrow ^5\text{D}_3$ transitions of Eu^{3+} ion are located in this wavelength range, and their oscillator strengths are 1.248×10^{-7} and 0.547×10^{-7} , respectively. The $^7\text{F}_6 \rightarrow ^5\text{D}_4$ transition of Tb^{3+} ion is in this range and its oscillator strength is 0.633×10^{-7} [11]. It is obvious that the overlap degree between the absorption of Eu^{3+} ions and the emission spectrum of C120 is higher than that between Tb^{3+} ions and C120. This is in agreement with the higher luminescence enhancement for Eu^{3+} ions with respect to Tb^{3+} ions in co-doped xerogels.

Table 1
Fluorescence lifetime of Eu^{3+} and Tb^{3+}

Sample	Eu^{3+} and C120 co-doped	Tb^{3+} and C120 co-doped	Eu^{3+} -doped	Tb^{3+} -doped
τ (μs)	207	486	216	495

4. Conclusions

Co-doped with C120 and Eu^{3+} ions (or Tb^{3+} ions) in silica xerogel via sol–gel technique, the characteristic fluorescence intensities of Eu^{3+} and Tb^{3+} ions can be increased by a factor of 35 and 8, respectively, as a result of the sensitization of C120 absorption at about 344 nm. The results show that no complex species between C120 and rare earth ions form in co-doped xerogels. The sensitized emission of rare earth ions is through intermolecularly resonant exchange interaction. Because of fluorescence enhancement accompanied by concentration quenching of C120, the fluorescence intensities of Eu^{3+} and Tb^{3+} increase to maximum when the C120 doping concentration is of 0.1 mol% (mole percent referred to SiO_2).

Acknowledgements

This work is supported by the grant from Natio-

nal Natural Science Foundation of China (No. 69890230).

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