

Journal of Physics and Chemistry of Solids 64 (2003) 1333-1337

JOURNAL OF PHYSICS AND CHEMISTRY OF SOLIDS

www.elsevier.com/locate/jpcs

Photoacoustic spectroscopy study on the co-fluorescence effect of $Eu^{3+}-La^{3+}$ -Hba solid complexes

Yue-tao Yang*, Shu-yi Zhang

State Key Laboratory of Modern Acoustics and Institute of Acoustics, Nanjing University, Nanjing 210093, People's Republic of China

Received 29 July 2002; accepted 4 March 2003

Abstract

The photoacoustic (PA) spectra of $Eu^{3+}-La^{3+}$ -Hba complexes are reported (Hba: benzoic acid). It is found that the PA intensity of the ligand bears a relation to the energy transfer processes. For $Eu^{3+}-La^{3+}$ -Hba coprecipitates, with increasing the concentration of La^{3+} , the PA intensity in the region of the ligand absorption decreases firstly, then increases. It is indicated that the addition of the second rare earth ion La^{3+} -changes the relaxation processes of the complexes. The changes of fluorescence spectra turn out to be complementary to the PA spectra. The intramolecular energy transfer and intermolecular energy transfer processes in the coprecipitates are discussed.

© 2003 Elsevier Science Ltd. All rights reserved.

1. Introduction

Rare earth complexes have received great interest because of their important roles in the study of luminescent materials, NMR shift reagents and biological systems. Increasingly more attention has been paid on rare earth complexes in solid states [1-2]. The addition of Y^{3+} or certain lanthanide ions can considerably enhance the fluorescence intensities of the chelates of Eu³⁺, Sm³⁺ and Tb³⁺ in solution. This type of fluorescence actually is an intrinsic fluorescence phenomenon called 'co-fluorescence' effect [3]. The cofluorescence can be found in chelate suspensions and in a micellar environment. While in an actual solution, there is no co-fluorescence enhancement because the long distance between the chelates makes intermolecular energy transfer impossible [4]. In solids, especially in coprecipitates, the distance between chelates could be

short enough to take intermolecular energy transfer. The fluorescence enhancement and quenching phenomena have been found for the coprecipitates of rare earth β -diketone complexes [5]. Similarly to the β -diketone complexes, rare earth complexes with aromatic carboxylic acids exhibit excellent luminescence properties. It is necessary to study the co-fluorescence effect of those compounds in solid states. Such study can be helpful in better understanding regarding the co-fluorescence mechanism.

The photoacoustic (PA) technique has been widely used to investigate the chemical and physical properties of many samples [6]. The PA technique enables to obtain spectra on any type of solids whether it be crystalline, powder or gel. It can be a direct monitor of the energy gap and nonradiative relaxation channels, and the complement of absorption and photoluminescence spectroscopic techniques [7]. In this paper, $Eu^{3+}-La^{3+}$ –Hba (Hba: benzoic acid) complexes are prepared. Using PA and fluorescence spectroscopy, the luminescence properties of Eu^{3+} influenced by La^{3+} , and the relaxation processes in $Eu^{3+}-La^{3+}$ –Hba coprecipitates are studied in depth from two aspects: nonradiative process and radiative process.

^{*} Corresponding author. Tel.: +86-25-3594066; fax: +86-25-3313690.

E-mail address: yyang@nju.edu.cn (Y. Yang).

1334

2. Experimental

3. Results and discussion

3.1. Photoacoustic spectra

Eu_{1-x}La_x(Hba)₃ (x = 0.0,0.15,0.35,0.65,0.75,0.85,0.95, 1.0) complexes were prepared by mixing the solution of ammonium benzoate, europium chloride and lanthanum chloride in proportion (pH 5–6). Each mixture was digested for 4 h in a water bath, cooled to room temperature, then filtered. The solids were washed free of Cl^{-1} and NH_4^+ and sucked dry. The anhydrous compounds were obtained after drying at 85 °C. Eu_{1-x}Nd_x(Hba)₃ complexes were prepared according to the procedures described above. Their elemental and thermal analyses were performed and were consistent with the expected formulae.

2.1. Preparation of $Eu_{1-x}La_x(Hba)_3$ complexes

2.2. Spectroscopic measurements

The PA spectra containing both amplitude and phase information were measured on a single-beam spectrometer constructed in our laboratory [8]. Excitation source was a 500 W xenon lamp. The optical system was a monochromator and a variable speed mechanical chopper at a frequency of 30 Hz, which was used to modulate the light source intensity. The acoustic signal was monitored with the sample placed in an indigenous photoacoustic cell fitted with an electret microphone. The output signal from the microphone was amplified by a preamplifier and then fed to a lock-in-amplifier with a reference signal imputed from the chopper. The final signal was normalized for the changes in lamp intensity using a reference by carbon black. The PA spectra of all the complexes were recorded in the region of $300 \sim 700$ nm.

The infrared spectra were measured with pellets using KBr on Magna IR-750 spectrometer. The infrared spectra of $Eu_{1-x}La_x(Hba)_3$ were identical with that of $Eu(Hba)_3$, which indicated the nature of metal-ligand bonding was similar for the two types of complexes. For the complexes, the absorption bands of characteristic asymmetric (v_{as}) and symmetric (v_s) stretching vibrations of carboxyl group shifted to lower frequencies compared with those of sodium benzoate. Both of the absorption bands (ν_{as} and ν_{s}) showed splitting. The difference ($\Delta \nu$) between v_{as} and v_s ranged from 118 to 123 cm⁻¹ for the complexes, which was less than that of sodium benzoate $(\Delta \nu = 137 \ cm^{-1})$. According to the IR spectral results, it was suggested that the carboxyl groups coordinated with Ln^{3+} in both chelating and bridging ways [9–10], and $Eu_{1-x}La_x(Hba)_3$ had the structure of a polynuclear form.

The fluorescence spectra were taken with a Hitachi 850 fluorescence spectrophotometer.

The PA signal is obtained by detecting the heat generated through the nonradiative transitions by the sample after absorbing a periodically varying incident light [11]. The PA spectrum of Eu_{0.85}La_{0.15}(Hba)₃ is shown in Fig. 1. The broad PA band around 304 nm is assigned to the $\pi - \pi^*$ transition of the complex [12]. For the central Eu³⁺ ion of the complex, only f-f transitions are observed from 300 to 700 nm in Fig. 1 [13–14]. Since the $\pi - \pi^*$ transition of the ligand is far more stronger than the parity forbidden f-f transitions [15], the f-f transitions of Eu³⁺ in the region of 300 ~ 400 nm are lost in the strong $\pi - \pi^*$ transition.

It is known that after excitation there are two kinds of relaxation processes: radiative and nonradiative processes. As the PA spectrum only corresponds to the nonradiative relaxation process, the PA signals of energy levels of Eu^{3+} , which have fluorescence properties, are quite weak or vanished [16]. For Eu^{3+} , the relaxation of ${}^{5}D_{0}$ can not be monitored by PA spectroscopy, and the PA signals of ${}^{5}D_{1}$, ${}^{5}D_{2}$ at 469 and 540 nm are also quite weak. It can be interpreted by the relaxation model according to the previous paper [17].

With the change of La^{3+} (mole fraction) in the complexes, the PA band location of the ligand hardly changes, and the PA intensity changes correspondently. These changes are recorded in Fig. 2. With increasing the concentration of La^{3+} , the PA absorbency of Eu_{1-x} . La_x (Hba)₃ decreases. When seventy five percent of Eu^{3+} in Eu(Hba)₃ are substituted by La^{3+} , the PA intensity becomes the weakest (at 304 nm). Then the PA intensity increases rapidly. When all Eu^{3+} in Eu(Hba)₃ are replaced by La^{3+} , the PA intensity becomes the strongest. As we know, PA intensity of the ligand is the sum of the nonradiative relaxation of the ligand, the energy transfer and the following nonradiative relaxations of the central Ln^{3+} ion [17,18]. For $Eu_{1-x}La_x$ (Hba)₃, the PA signal of the ligand changes with the addition of La^{3+} , which indicates



Fig. 1. PA spectrum of Eu_{0.85}La_{0.15}(Hba)₃.



Fig. 2. Variation of the PA intensity as a function of the mole fraction of La^{3+} .

the relaxation processes of the complexes change correspondingly. The changes can be reflected in their fluorescence spectra.

3.2. Fluorescence spectra

The shapes of fluorescence spectra of $Eu_{1-x}La_x(Hba)_3$ are almost the same. The fluorescence spectra of $Eu_{0.85}$ - $La_{0.15}(Hba)_3$ are shown in Fig. 3. In the emission spectrum, the four characteristic emissions of Eu^{3+} at 582 nm $({}^5D_0 \rightarrow {}^7F_0)$, 595 nm $({}^5D_0 \rightarrow {}^7F_1)$, 619 nm $({}^5D_0 \rightarrow {}^7F_2)$, 703 nm $({}^5D_0 \rightarrow {}^7F_4)$ have been clearly observed. Among them, the emission at 619 nm is the strongest.

The emission intensities of $Eu_{1-x}La_x(Hba)_3$ versus the concentration of La^{3+} are shown in Fig. 4. With the increase of La^{3+} mole fraction, the fluorescence intensity increases remarkably. When seventy five percent of Eu^{3+} in $Eu(Hba)_3$ are replaced by La^{3+} , the fluorescence intensity becomes the strongest. Then the fluorescence intensity decreases quickly. Figs 2 and 4 are mutually complementary. As the probability of radiative transition increases, the PA intensity exhibits a corresponding decrease [16].



Fig. 3. Fluorescence spectra of Eu_{0.85}La_{0.15}(Hba)₃. (a) Excitation spectrum ($\lambda_{em} = 619 \text{ nm}$); (b) emission spectrum ($\lambda_{ex} = 304 \text{ nm}$).



Fig. 4. Variation of the emission intensity as a function of the mole fraction of La^{3+} .

3.3. Energy transfer processes

3.3.1. Intramolecular energy transfer

The PA signal is selectively sensitive only to the nonradiative relaxation process, according to Adams et al. [19] the PA signal (P) can be written as,

$$P = KA_{\rm abs}\gamma\tag{1}$$

where A_{abs} is the absorbency of the sample, γ is the probability of nonradiative transitions after excitation, and *K* is a coefficient which is determined by the thermal properties of the sample and by the spectrometer.

The fluorescence signal (E), which is proportional to the probability of radiative transitions after excitation, can be expressed similarly as [20],

$$E = K' A_{\rm abs} (1 - \gamma) \tag{2}$$

So Eq. (3) is obtained after combining Eqs. (1) and (2),

$$\frac{1}{R} = c \left(\frac{1}{\gamma} - 1\right) \tag{3}$$

where R = P/E, and c = K'/K. For the thermal properties of the title complexes are almost the same and the experimental condition does not change, we can take *c* as a constant. It can be inferred from Eq. (3) that as the probability of nonradiative transition γ increases, *R* exhibits a corresponding increase. The PA and emission intensities are listed in Table 1 with the values of *R* for comparison.

Table 1

PA ($\lambda=304~\text{nm})$ and emission intensities ($\lambda_{ex}=304~\text{nm})$ of the title compounds

	PA relative intensity (P)	Emission relative intensity (E)	R = P/E
Eu(Hba)3	1.00	1.00	1.00
Eu _{0.85} La _{0.15} (Hba) ₃	0.81	1.31	0.62
Eu _{0.25} La _{0.75} (Hba) ₃	0.56	1.70	0.33
Eu _{0.05} La _{0.95} (Hba) ₃	1.15	0.71	1.62

It can be seen from Fig. 3(a) that the excitation spectrum is a broad band due to the absorption of the ligand Hba, which means that there is an efficient energy transfer process between Hba and Eu^{3+} . This is also confirmed by the emission spectra of Fig. 3(b). Since the excitation wavelength is fixed in the region of the ligand absorption, the existence of characteristic emissions of Eu^{3+} demonstrates the energy transfer process from the ligand to Eu^{3+} .

According to the Dexter's theory [21], the energy transfer probability (T) is proportional to the overlap integral:

$$T = \left(\frac{2\pi Z^2}{h}\right) \int F_s(E)\varepsilon_a(E)dE \tag{4}$$

where $F_s(E)$ represents the observed shape of the emission band of the energy donor and the $\varepsilon_a(E)$ is the shape of the absorption band of acceptor.

It has been proposed that there should be a matching energy difference between the triplet state of the ligand and the resonance energy level of the central ion for rare earth complexes that exhibit efficient intramolecular energy transfer [22]. If the energy gap is too large, the energy transfer rate will decrease due to the diminution in the overlap between the donor and acceptor. If the energy gap is too small, the efficiency of energy transfer will decrease because of the thermal deexcitation process [23]. The resonance energy level (${}^{5}D_{0}$) of Eu³⁺ is at 17300 cm⁻¹, and the triplet state (T_{I}) of Hba is at 24800 cm⁻¹. The energy gap between Hba (T_{1}) and Eu³⁺ (${}^{5}D_{0}$) is suitable. So the excited energy on T_{I} is transferred to the fluorescent ion Eu³⁺, which results the characteristic line-type emissions of Eu³⁺.

3.3.2. Intermolecular energy transfer

For $Eu_{1-x}La_x(Hba)_3$ complexes, the intramolecular energy transfer can explain the characteristic emissions of Eu^{3+} , but it cannot explain the changes of fluorescence intensity of Eu^{3+} with the addition of La^{3+} . Considering the Foster [24] and Dexter's theories, energy can be transferred to molecules in short distance by an intermolecular energy transfer. The efficiency of intermolecular energy transfer is dependent on close approach or contact between the donor and acceptor. For the system studied, $Eu_{1-x}La_x(Hba)_3$ are prepared by coprecipitation. The short distance between molecules in the coprecipitates makes the intermolecular energy transfer possible.

 La^{3+} has no low-lying energy levels, the energy absorbed by La(Hba)₃ molecule cannot be dissipated through the central La^{3+} ion. The excited energy on the ligand triplet state would be gathered. So La(Hba)₃ molecules can be energy donors and become the enhancing chelates. The stabilized triplet state of La(Hba)₃ transfers the energy to the nearby molecules Eu(Hba)₃ (acceptor) in the aggregated particles. The excited energy of La(Hba)₃ may also be transferred to the neighbor Eu(Hba)₃ through



Fig. 5. Energy transfer and relaxation processes of Eu_{1-x}La_x(Hba)₃.

the bridging carboxyl groups in $Eu_{1-x}La_x(Hba)_3$ coprecipitates, according to the IR spectral results. Thus the fluorescence intensity of Eu^{3+} is enhanced considerably by the addition of La^{3+} through the intermolecular energy transfer processes.

The energy transfer processes of $Eu_{1-x}La_x(Hba)_3$ are illustrated in Fig. 5.

After seventy five percent of Eu^{3+} in $Eu(Hba)_3$ are substituted by La^{3+} , however, the fluorescence intensity of Eu^{3+} begins to decrease quickly because of over replacing the fluorescent ion Eu^{3+} by La^{3+} , which results in the excessive decrease of the acceptor.

As can be seen in Table 1, for $Eu_{1-x}La_x(Hba)_3$ (x: 0.15 or 0.75) complex, the addition of La^{3+} enhances the fluorescence intensity of Eu^{3+} . As the probability of radiative transition increases, the value of *R* exhibits a conrespondent decrease. While for $Eu_{0.05}La_{0.95}(Hba)_3$, the addition of La^{3+} weakens the fluorescence intensity of Eu^{3+} due to the excessive decrease of the acceptor in the complex. The value of *R* for $Eu_{0.05}La_{0.95}(Hba)_3$ increases remarkably, because the probability of nonradiative transition increases.

For Eu³⁺–Nd³⁺–Hba systems, the result is different. The fluorescence intensity of Eu³⁺ is quenched remarkably with the addition of the second rare earth ion Nd³⁺ at any concentration. This is because that the numerous closely packed excited states of Nd³⁺ provide paths for efficient quenching of the excited states of the complex, and Nd³⁺ ion acts as a competitive energy acceptor with Eu³⁺ ion. A large part of the excited energy of Eu(Hba)₃ molecules is transferred to Nd³⁺ ion through an intermolecular energy transfer process, dominantly following by nonradiative transitions to the ground state which results in weakening the luminescence intensity of Eu³⁺.

Experimental results show that the fluorescence enhancement and quenching phenomena cannot be found in the mixtures of $Eu(Hba)_3$ and $Ln(Hba)_3$ (Ln^{3+} : La^{3+} or Nd^{3+}) in any proportion. As the mixture is obtained in a mechanical way, the distance between the molecules is too far to incur an intermolecular energy transfer.

1336

4. Conclusions

The PA and fluorescence spectra of Eu³⁺-La³⁺-Hba complexes are measured and interpreted. With the increase of La^{3+} mole fraction, the fluorescence intensity of Eu^{3+} increases correspondently, and reaches it maximum for $Eu_{0.25}La_{0.75}(Hba)_3$, then decreases quickly. The ratio (R) of PA to fluorescence signals is used to interpret the cofluorescence effect of the complexes. For $Eu_{1-x}La_x(Hba)_3$ (x: 0.15, 0.75) complexes, the additions of La³⁺ enhance the fluorescence intensity of Eu^{3+} considerably. The values of R decrease as the probability of radiative transition increases for the complexes. While for Eu_{0.05}La_{0.95}(Hba)₃, the addition of La3+ weakens the fluorescence intensity of Eu^{3+} . The value of R for $Eu_{0.05}La_{0.95}$ (Hba)₃ increases, for the probability of nonradiative transition increases. The energy transfer processes of the coprecipitates are interpreted in depth from two aspects: nonradiative process and radiative process.

Acknowledgements

We thank the National Natural Science Foundation of People's Republic of China for supporting this program.

References

- [1] J.C.G. Bunzli, E. Moret, V. Foiret, Structure and photophysical properties of europium (III) mixed complexes with β -diketonates and o-phenanthroline, J. Alloys Compd. 207/208 (1994) 107–111.
- [2] G. Qian, M. Wang, Preparation and fluorescence properties of nanocomposites of amorphous silica glasses doped with lanthanide (III) benzoates, J. Phys. Chem. Sol. 58 (1997) 375–378.
- [3] J. Yang, G. Zhu, H. Wang, Enhanced luminescence of the Eu/ Tb/TTA/Phen/surfactant system, and its analytical application, Anal. Chim. Acta. 198 (1987) 287–291.
- [4] G. Zhu, J. Yang, Z. Shi, Study on the mechanism of the columinescence effect of rare earths, J. Chin. Rare Earth Soc. 7 (1989) 73–78.
- [5] Y. Yang, Q. Su, G. Zhao, Photoacousitc study of the cofluorescence effect of lanthanide ternary complexes in solid states, J. Mol. Struct. 525 (2000) 47–52.
- [6] C.S. Sunadana, Physical applications of photoacoustic spectroscopy, Phys. Stat. Sol. 105 (1988) 11–43.

- [7] T. Ikarl, H. Yokoyama, S. Shigetomi, Near band edge photoacoustic spectra of p-Si single crystals, Japan, J. Appl. Phys. 29 (1990) 887–890.
- [8] S. Qiu, S. Zhang, C. Hu, Single beam photoacoustic spectroscope system, J. Appl. Sci. 4 (3) (1986) 207–212.
- [9] G.B. Deacon, R.J. Philips, Relationships between the carbonoxygen stretching frequencies of carboxylato complexes and the type of carboxylate coordination, Coord. Chem. Rev. 33 (1980) 227–250.
- [10] J. Ma, J. Ni, The structures of rare earth carboxylates, Prog. Chem. 8 (1996) 259–276.
- [11] A. Rosencwaig, A. Gersho, Theory of the photoacosutic effect with solids, J. Appl. Phys. 47 (1976) 64–69.
- [12] X. Lian, S. Ma, Study of the fluorescence spectra of europiumbenzoate complexes, Chinese Rare Earths. 20 (5) (1999) 7–11.
- [13] D.H. Dieke, H.M. Crosswhite, The spectra of the doubly and triply ionized rare earths, Appl. Opt. 2 (7) (1963) 675–686.
- [14] J.C. Krupa, M. Queffelec, UV and VUV optical excitations in wide band gap materials doped with rare earth ions: 4f-5d transitions, J. Alloys Comps. 250 (1997) 287–292.
- [15] N. Sabbatini, M. Guardigli, Luminescent lanthanide complexes as photochemical supramolecular devices, Coord. Chem. Rev. 123 (1993) 201–228.
- [16] A. Rosencwaig, Photoacoustic spectroscopy: a new tool for investigation of solids, Anal. Chem. 47 (1975) 592A–593A.
- [17] Y. Yang, Q. Su, H. Zhao, G. Zhao, Photoacoustic spectra of complexes of tryptophan with Sm(III) Tb(III) and Dy(III), Spectrochim. Acta. 54 (1999) 645.
- [18] A. Sikorska, A. Sliwinski, S. Zachara, Photoacoustic signal analysis for the relaxation study of dibenzoilmethane, Spectrosc. Lett. 28 (1995) 547–555.
- [19] M.J. Adams, J.G. Highfield, G.F. Kirkbright, Determination of the absolute quantum efficiency of luminescence of solid material employing photoacoustic spectroscopy, Anal. Chem. 52 (1980) 1260–1264.
- [20] Q. Su, K. Gao, Y. Tao, G. Zhao, Photoacoustic and fluorescence studies of rare earth β-diketone complexes doped in silica gel, Chem. J. Chinese Universities. 4 (1998) 526–529.
- [21] D.L. Dexter, A theory of sensitized luminescence in solid, J. Chem. Phys. 21 (1953) 836–850.
- [22] Y.S. Yang, M.L. Gong, Y.Y. Lei, S.L. Wu, Effects of the structure of ligands and their Ln³⁺ complexes on the luminescence of the central Ln³⁺ ions, J. Alloys Compd. 207/208 (1994) 112–114.
- [23] S. Sato, M. Wada, Relation between intramolecular energy transfer efficiencies and triplet state energies in rare earth βdiketone chelates, Japan. J. Appl. Phys. 43 (1970) 1955–1962.
- [24] T. Forster, Intermolecular energy transference and fluorescence, Ann. Physik. 2 (1948) 55–75.