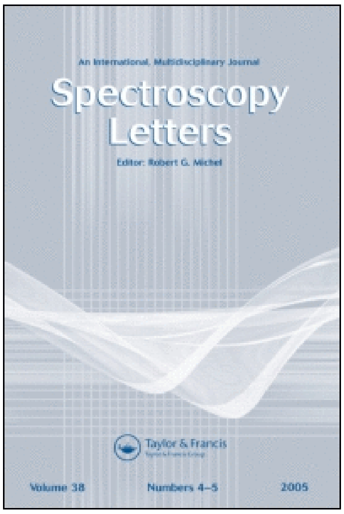

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Photoacoustic Spectroscopy Study on the Luminescence Properties of SM^3 Complexes

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PHOTOACOUSTIC SPECTROSCOPY STUDY ON THE LUMINESCENCE PROPERTIES OF SM^{3+} COMPLEXES

Key words: PA spectroscopy, rare earth, salicylic acid, dibenzoylmethide, intramolecular energy transfer.

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ABSTRACT

The luminescence properties, energy transfer processes and energy levels of solid state Sm^{3+} complexes with salicylic acid (SAL) and dibenzoylmethide (DBM) are studied by using photoacoustic (PA) spectroscopy at room temperature. The different energy transfer paths and the efficiency of intramolecular energy transfer between the ligands and the central ion are discussed according to Dexter's theory.

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* the corresponding author

INTRODUCTION

With their characteristic f-f and f-d transitions, the rare earth compounds have been widely used as luminescence and laser materials[1-3]. It is known that there are 1693 energy levels in the $4f^n$ state of lanthanide ions(Ln^{3+}), and the number of possible transitions, especially the middle lanthanide ions, Sm^{3+},Eu^{3+},Tb^{3+},Dy^{3+}, is about 199177. Thus the rare earth is a tremendous luminescence material's deposit, from which many new kinds of luminescence and laser materials will be discovered.

Because of the narrow absorption band of f-f transitions, the luminescence efficiency of Ln^{3+} is rather low[4]. In order to enhance the luminescence efficiency, several organic ligands (such as hydroxyl acid and β-diketone) are used[5-7]. These ligands have strong and wide absorption bands in the UV-Visible region. When Ln^{3+} was combined with the organic ligand, the absorbed energy can be transferred from the ligand to Ln^{3+}, which contribute to the sensitized luminescence of Ln^{3+}. So the efficiency of energy transfer from the ligand to Ln^{3+} (which means there is enough energy converts into the luminescence of Ln^{3+}) becomes an important factor in the study on the luminescence properties of rare earth materials.

Photoacoustic(PA) spectroscopy is a recently developed technique for detecting the luminescence properties of opaque or light-scattering samples at room temperature. It is a direct monitor of solid state samples after excitation[8-10]. If any of the energy transferred from the ligand to the central ion converts into the luminescence of the central ion, the nonradiative part of the relaxation process will be diminished, with the result of a decrease of the PA signal. Thus, the change of PA intensity can indicate if there is efficient energy transfers from the ligand to the central ion. Furthermore, since the ligand-to-central ion energy transfer is decided by the energy level structure of the ligand and the central ion, the study on PA signal can also reveal the energy structure of samples.

In this paper, the salicylic acid(SAL) and dibenzoylmethide(DBM) are selected to be the ligand. Based on the PA spectra of Sm(SAL)$_3$ and Sm(DBM)$_3$ complexes, the efficiency of ligand-to-Ln^{3+} energy transfer is discussed, and the model of relaxation and energy transfer processes is established.

EXPERIMENTAL

1. Preparation of the complexes.

The rare earth oxide Ln_2O_3 was converted to the chloride $LnCl_3 \cdot 6H_2O$ by treatment with concentrated HCl. Then the chloride was added to a solution of DBM (or SAL) in absolute ethanol. The precipitation of Ln(DBM)$_3$ was accomplished by the addition of piperidine. The microcrystalline products were recrystallized and air dried. The elemental analyses and infrared spectra of Ln(DBM)$_3$ and Ln(SAL)$_3$ were performed and were consistent with the expected formulae.

2. Spectroscopic Measurements

The photoacoustic (PA) spectra were measured on a single-beam spectrometer constructed in our lab[11]. A 500w xenon lamp, a CT-30F monochromator and a PA cell fitted with an ERM 10 electret microphone were used. The chopper frequency was 12 HZ. The output signal of the microphone was amplified by a preamplifier and fed to a lock-in-amplifier(LI-547A) with a reference signal inputted from the chopper. The signal was normalized for the changes in lamp intensity using a reference by carbon-black. The PA spectra of Ln(DBM)$_3$ and Ln(SAL)$_3$ microcrystalline samples were recorded at room temperature in the range of 300-800nm.

The emission spectra of Sm(DBM)$_3$ and Sm(SAL)$_3$ microcrystalline samples were taken with a PE LS-50 spectrophotometer.

RESULTS AND DISCUSSION

1. The fluorescence properties of Sm^{3+}

The photoacoustic (PA) spectra of $LnCl_3 \cdot 6H_2O$ microcrystalline samples can reveal the absorption and relaxation processes of Ln^{3+}. The PA intensity spectrum of $SmCl_3 \cdot 6H_2O$ at room temperature is shown in Fig. 1. It is distinguished by sharply defined and almost line-like absorption bands. Compared with the absorption spectrum in solution, the PA spectrum is more complex and more intense.

In Fig1., the strongest PA band appears in the region of 410nm which is attributed to the transition from the ground state $^6H_{5/2}$ to excited state $^4P_{3/2}$[12]. This indicates that the superior relaxation process of $^4P_{3/2}$ is nonradiative relaxation. The PA bands in the region of 563nm ,532nm and 508nm are attributed to the transition from ground state to the excited state $^4G_{5/2}$, $^4F_{3/2}$ and $^4G_{7/2}$, respectively. The $^4G_{5/2}$ level is the first excited state of Sm^{3+}, which means the radiative relaxation of $^4G_{5/2}$ is its prominent process. Since the $^4F_{3/2}$ and $^4G_{7/2}$ level have many similarities with the $^4G_{5/2}$ level, the energy transferred to these two levels is easy to be transferred to the $^4G_{5/2}$ level. So $^4G_{5/2}$, $^4F_{3/2}$ and $^4G_{7/2}$ are the three radiative levels of Sm^{3+}. As it indicates in Fig. 1. The PA intensity correspond to these three levels is fairly weak.

2. The fluorescence properties of $Sm(SAL)_3$ and $Sm(DBM)_3$ complexes

As is known, lanthanide ions show very small absorption coefficients in the visible and UV-Visible region. This drawback can be overcomed by using organic ligand which shows strong and wide absorption band in the UV-Visible region. The energy transfer between triplet state of the ligand and excited states of Ln^{3+} is the main way in sensitizing the luminescence of Ln^{3+}. An important aspect of this method consists in the efficiency of energy convertion to optimize the luminescence properties of Ln^{3+} by choosing suitable ligands.

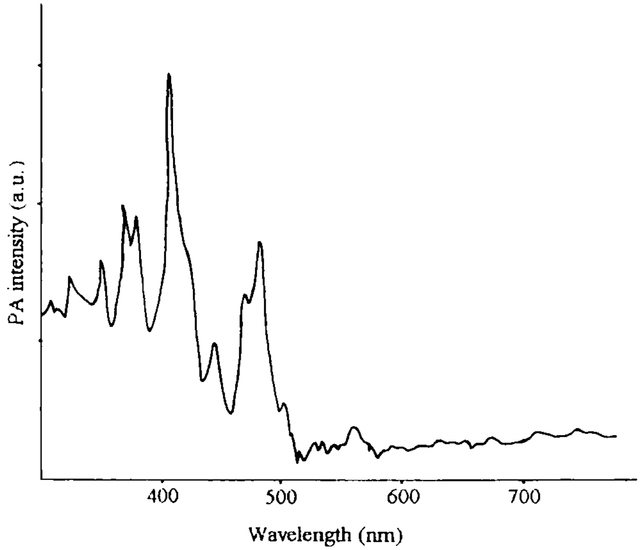

FIG. 1. PA Spectrum of $SmCl_3·6H_2O$

It was observed that the ligand-sensitized fluorescence of Ln^{3+} in complex may occur if the lowest triplet level of the ligand lies above the emissive level of the Ln^{3+}[5]. The emissive level of Sm^{3+} ($^4G_{5/2}$, λ =562nm) is below the lowest triplet level of the organic ligands salicylic acid (SAL)and dibenzoylmethide(DBM) (λ =403,476nm,respectively),and the $Sm(SAL)_3$ and $Sm(DBM)_3$ complexes show predominant absorption bands in the region of 300-400nm. So it can be predicted that both SAL and DBM can sensitize the luminescence properties of Sm^{3+}.

Fig2a,b are the emission spectra of $Sm(DBM)_3$ and $Sm(DBM)_3$ which is fixed in the region of the ligand absorption. In the emission spectrum of $Sm(DBM)_3$ (Fig2a), the three characteristic emissions of Sm^{3+} (λ =563,605 and 635nm), which are attributed to the transition from $^4G_{5/2}$ to $^6H_{5/2}$, $^6H_{7/2}$ and $^6H_{9/2}$, can be clearly observed. But in the emission spectrum of $Sm(SAL)_3$ (Fig2b), the emissions of Sm^{3+} can not be observed, which is not coincident with the prediction.

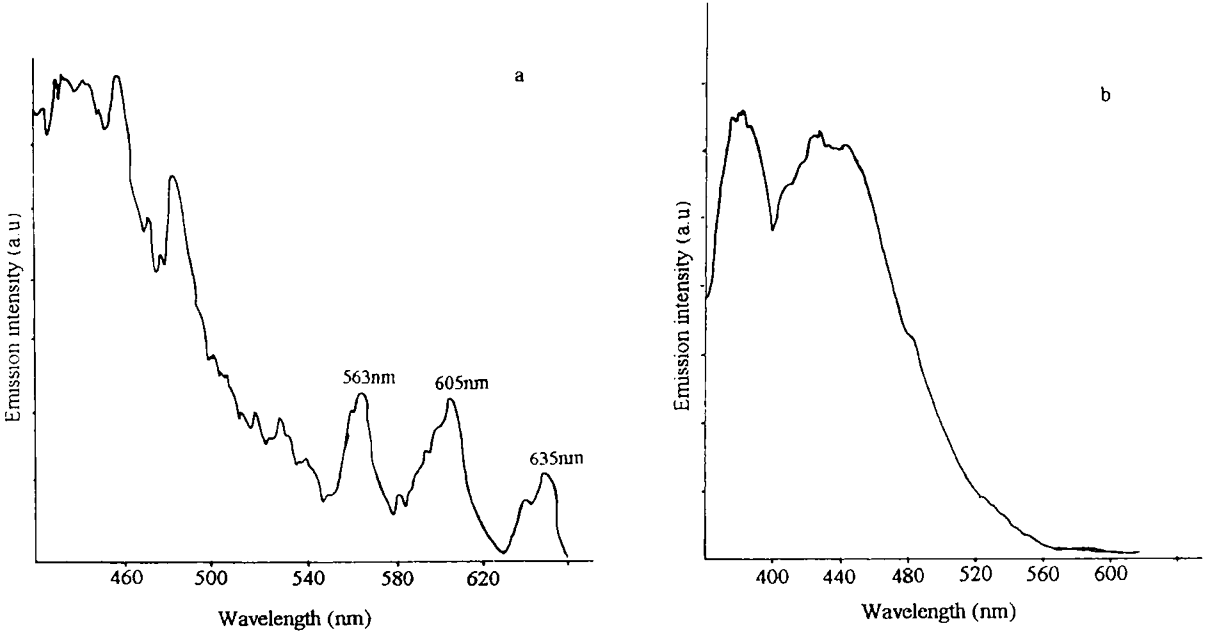

FIG.2 .a. Emission Spectrum of $Sm(DBM)_3$ (λ_{ex} =410nm)

b. Emission Spectrum of $Sm(SAL)_3$ (λ_{ex} =340nm)

3. The PAS studies on the energy transfer processes of Sm complexes

3-1. The PA spectra of Sm complexes

In this section, we will use the PA spectra of those complexes, through the detection of nonradiative processes, to discover the relationship between the energy level of the ligand and the central ion, and to interpret the above phenomenon.

Fig3a,b are the PA spectra of Sm,Nd(DBM)$_3$ and Sm,Nd(SAL)$_3$ microcrystalline samples at room temperature. The energy levels of Nd^{3+} are often intermixed and the relaxation of Nd^{3+} is always known as a nonradiative process. Since the absorption and relaxation of ligand depend slightly on the central ion, with the comparison of PA intensity spectrum of Sm complex to that of Nd complex in the region of the same ligand, we can get the information of relaxation of Sm^{3+} and the energy transfer between the ligand and Sm^{3+}. (As we know, the PA intensity signal in the ligand absorption region is the sum of the signal of nonradiative relaxation of the ligand, the intramolecular energy transfer, and the nonradiative relaxation of Ln^{3+}.)

As it shows in Fig3a, in the region of DBM absorption, the PA intensity of Sm(DBM)$_3$ is weaker than that of Nd(DBM)$_3$. In room temperature, the only relaxation of triplet state is nonradiative. So part of the energy transferred from DBM to Sm^{3+} must be converted into the fluorescence of Sm^{3+}. That is, the efficient energy transfer occurs. In Fig3b, the PA intensity of Sm(SAL)$_3$ and Nd(SAL)$_3$ is the same. This indicates that the energy transferred from SAL to Sm^{3+} are all converted into nonradiative process, which is the reason that there is no SAL sensitized luminescence of Sm^{3+}.

3-2. The model of relaxation and energy transfer processes of Sm complexes

The above results show that the lowest triplet level of ligand lying above the emission levels of Ln^{3+} does not necessarily cause the ligand sensitized luminescence of Ln^{3+}.

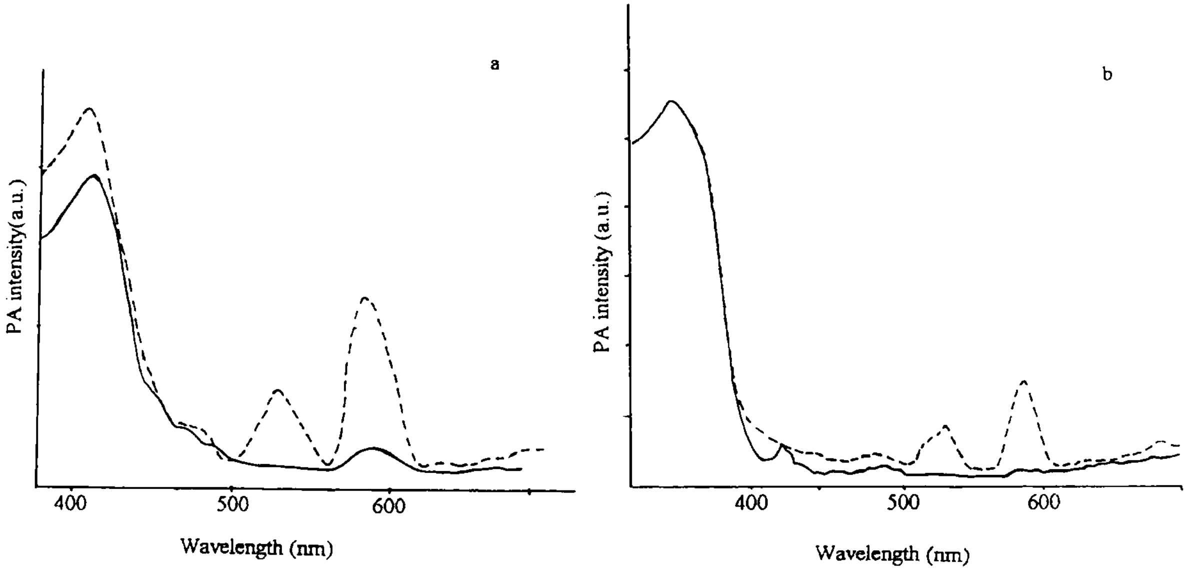

FIG.3. a. PA Spectra of Sm(DBM)$_3$ (solid line) and Nd(DBM)$_3$ (dotted line)

b.PA Spectra of Sm(SAL)$_3$ (solid line) and Nd(SAL)$_3$ (dotted line)

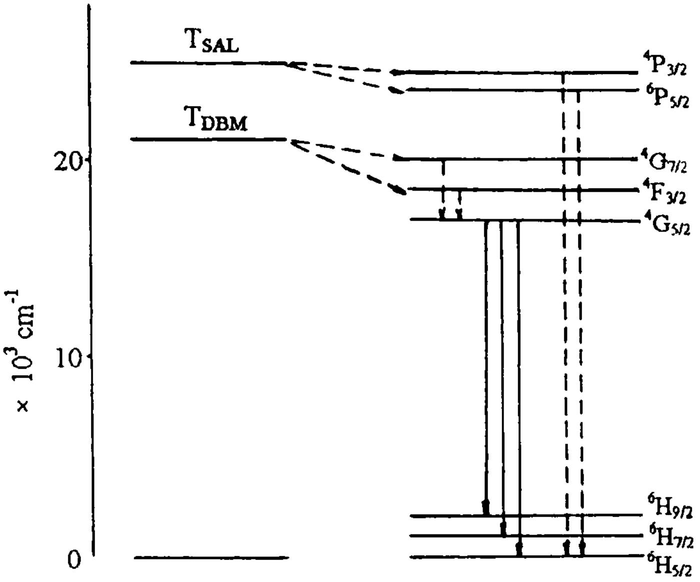

FIG.4. Model of Relaxation and Energy Transfer Processes of Sm(DBM)$_3$ and Sm(SAL)$_3$ at room temperature.

——— Radiative ------- Nonradiative

According to Dexter's theoty[13], the energy transfer probability(η) is proportional to the overlap integral:

$$\eta \propto \int f_d(E)F_a(E)dE \qquad (1)$$

where f_d *(E)* represents the observed shape of the emission band of the energy donor (the triplet state of ligand)and *Fa(E)* is the shape of the absorption band of acceptor(the excited state of central ion). Both functions are normalized. It is calculated that if the energy gap between these two levels is within about 2 × 10^{-3} cm^{-1} ($\Delta \bar{\nu} = 2 \times 10^{-3}$ cm^{-1}), the energy transfer should occur in a time of the order of 10^{-10}-10^{-11} sec. Since the lifetime of emission level is generally

10^{-4}-10^{-8} sec, then the nonradiative energy transfer between the two levels is the main relaxation process.

We know that: $$\Delta\,\bar{\nu} = \Delta\left(\frac{1}{\lambda}\right) = -\frac{1}{\lambda^2}\Delta\lambda \qquad (2)$$

the lowest triplet level of DBM is located in 476nm (λ =476nm), so that Δ λ =45nm. Thus, the energy is easy to be transferred from the triplet level to $^4F_{3/2}$ and $^4G_{7/2}$ level of Sm^{3+} (Δ λ =56nm and 32nm). And as we discussed in section 1, this energy can contribute to the emission of Sm^{3+}.

The lowest triplet level of SAL is located in 403nm. So that Δ λ =32nm. Since the energy gap between the triplet level and the $^4F_{3/2}$, $^4G_{7/2}$ and $^4G_{5/2}$ level is 123, 105 and 160nm respectively, the energy transfer possibility between these levels is almost zero. The energy acceptor is these nonradiative $^4P_{3/2}$(Δ λ =7nm) and $^6P_{5/2}$(Δ λ =21nm) levels of Sm^{3+}.

Thus, the model of relaxation and energy transfer processes is shown in Fig 4.

In conclusion, the PA spectrum can provide great information of relaxation and energy transfer of rare earth complexes and it will be an imperative technique in the investigation of luminescence properties of solid state Ln^{3+} complex materials.

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REFERENCES

1. Buono-Core GE., Li H. And Marciniak B. Quenching of Excited States by Lanthanide Ions and Chelates in Solution. Coord. Chem. Rev. 1990; 99:55

2. Yang YS., Gong ML and Li YY. Effects of the Structure of Ligands and Their Ln^{3+} Complexes on the Luminescence of the Central Ln^{3+} Ions. J. Alloys and Compounds. 1994; 207/208:112

3. Li W. New Advances on the study of Luminescence properties of Rare Earth-Organic Complexes. Chemistry(in Chinese) 1991; 8:1

4. Gschneider KA and Eying L. *Handbook on The Physics and Chemistry of Rare Earths.* Amsterdam : North-Holland 1979: 171

5. Whan RE and Crosby GA. Luminescence Studies of Rare Earth Complexes: Benzoylacetonate and Dibenzoylmethide Chelates. J. Mol. Spectro. 1962; 8:315

6. Sabbatini N., Guardigli M. and Lehn J-M. Luminescent Lanthanide Complexes as Photochemical Supramolecular Devices. Coord. Chem. Rev. 1993; 123:201

7. Yang Y., Cai Q. And Meng J. The High Luminescence of Tb^{3+} (Gd^{3+}) Salicylic Acid Complex.Chinese J. of Lumin. 1991; 12(2):151

8. Rosencwaig A. and Gersho A. Theory of the Photoacoustic Effect with Solids. J. Appl. Phys.1976; 47:64

9. Sikorska A., Sliwinski A. And Zachara S. Photoacoustic Signal Analysis for the Relaxation Study of Dibenzoilmethane. Spectro. Lett. 1995; 28(4):547

10. Su Q., Mao Q. and Zhao G. Photoacoustic Spectra of Nd $(TFA)_3 \cdot 2H_2O$ and Nd $(HFA)_3 \cdot 2H_2O$. Spectrochim. Acta part A 1995;5

11. Su Q. And Zhao G. Studies on Energy Levels of Rare Earth Elements by Photoacoustic Spectroscopy. J. Rare Earths (special issue) 1991; 1:366

12. Dieke GH and Crosswhite HM. The Spectra of the Doubly and Triply Ionized Rare Earths. Appl. Opt. 1963; 2:675

13. Hu J., Chen G. Studies on Luminescent Mechanism and Fluorescent Properties of Rare Earth Complexes(I). Chemical J. of Chinese Universities 1990; 8:817

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