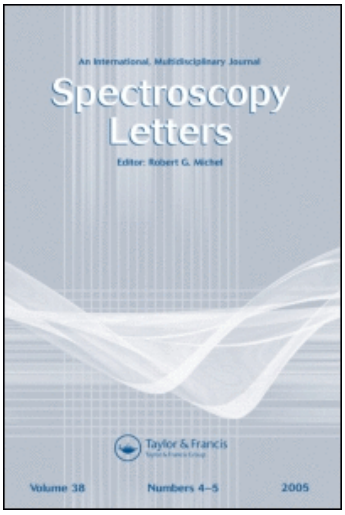

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Photoacoustic Spectra of Sm^3, Eu^3, Dy^3 Complexes

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PHOTOACOUSTIC SPECTRA OF Sm^{3+}, Eu^{3+}, Dy^{3+} COMPLEXES

Key Words: PA spectrum, rare earth, complex, relaxation

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ABSTRACT

The complexes crystals of $Sm(Ac)_3 \cdot 4H_2O$, $Eu(Ac)_3 \cdot 4H_2O$ and a new complex $Dy_2(Ac)(NO_3)_4 \cdot 12H_2O$ were synthesized and their PA spectra were determined firstly. All their PA spectra absorptions are interpreted. The fluorescence properties of Sm^{3+}, Eu^{3+}, Dy^{3+} and the relaxation process models were studied by their PA spectra.

INTRODUCTION

Recently, the photoacoustic measurement have been widely used to investigate the chemical and physical properties of almost all kinds of samples[1,2]. It is because that the PA spectroscopy enables to obtain spectra on any type of solid, whether it be crystalline, powder or gel, and it be a direct monitor of energy gap and the nonradiative relaxation channel, the complement of absorption and photoluminscence spectroscopic technique[3]. However, the PA technique has not be widely used in transition metal complexes system[4,5]. In this work, we used the PA spectroscopy as a direct monitor to study energy gap and relaxation process of complexes.

The so-call "sol-gel" process offers new approaches to the synthesis of inorganic materials[6]. Especially, this process has been used in the synthesis of superconductors, the copper and rare earth complexes, as molecular precursors, have been widely studied[7,8]. Molecular precursors lead to the formation of a solid net work through hydrolysis and polycondensation reactions. Temperature required for material processing can be notably lowered[9]. The molecular precursors are usually inorganic salts or metal alkoxides. They can be chemically modified by chelating ligands such as organic acids or β-diketones and this giving rise to a better control of the process. The so-obtained gels are usually amorphous and therefore characterization of their local structure is generally very delicate. Crystalline compounds are very good models to correlate spectroscopic data with structural information. In this work, we synthesized Sm, Eu acetate complexes and one new Dy complex. And their PA spectra were determined. The electron energy levels and their spectral properties were studied.

EXPERIMENT

Synthesizes

The $Sm(Ac)_3 \cdot 4H_2O$ and $Eu(Ac)_3 \cdot 4H_2O$ complexes crystal were prepared in glacial acetic acid solution. As the Sm_2O_3 and Eu_2O_3 were dissolved in glacial acetic acid system respectively, the PH values were controlled at three. Slowly evaporated at room temperature. After twenty five days, yellow granular crystals of $Sm(Ac)_3 \cdot 4H_2O$ were obtained. Elemental analysis results: Exp. C, 17.10, H, 4.33%; Calc. C,18.00, H, 4.25%. And colorless granular crystal of $Eu(Ac)_3 \cdot 4H_2O$ were grew up in five days from Eu-glacial acetic acid solution. Elemental analysis results: Exp. C,16.60, H, 4.40%; Calc. C, 17.18, H, 4.53%. Their IR and thermal analysis data were correspond to their structural formula.

The $Dy_2(Ac)(NO_3)_4 \cdot 12H_2O$ complex crystal was also prepared from glacial acetic acid solution. The Dy_2O_3 was dissolved in HNO_3 solution and evaporated to dry. Then, this $Dy(NO_3)_3$ was dissolved in glacial acetic acid. After three days, the colorless granular crystals of $Dy_2(Ac)(NO_3)_4 \cdot 12H_2O$ was grew up. Elemental analysis results: Exp. C, 2.62, H, 3.11, N, 6.11%; Calc. C, 2.83, H, 3.18, N, 6.60%. It's IR and thermal properties were also correspond to it's structural formula.

TABLE 1.
The PA Spectra And Assignment of Sm^{3+}, Eu^{3+}, Dy^{3+} Complexes.(nm)

Sm		Eu		Dy	
$^6H_{5/2}$ -	357.2	$^7F_0$ -	368.9	$^6H_{15/2}$ -	359.6
	372.2		390.6		371.9
	387.2	$^5L_6$	405.6		396.3
$^6P_{13/2}$	411.0	$^5D_3$	424.0	$^4G_{11/2}$	436.1
$^4G_{9/2}$	423.5	$^6D_2$	476.0	$^4I_{15/2}$	457.5
$^4F_{5/2}$	449.8	$^5D_1$	543.4	$^4F_{9/2}$	483.5
$^4I_{13/2}$	471.9	$^5D_0$	----	$^6F_{1/2}$	706.7
$^4I_{11/2}$	484.1			$^6F_{3/2}$	758.7
$^4I_{9/2}$	492.7			$^6F_{5/2}$	815.
$^4G_{7/2}$	511.0				
$^4F_{3/2}$	529.4				
$^4G_{5/2}$	547.7				

Photoacoustic spectrum

The photoacoustic spectra of the title complexes were detected with the sample placed in an indigenous photoacoustic cell fitted with an ERM 10 electret microphone in the region of 300-800nm. The light source intensity was modulated by a variable speed mechanical chopper at frequency of 12Hz and the output signal was normalized for the change of lamp intensity by a reference of carbon-black.

RESULTS AND DISCUSSIONS

Usually, for the special electronic structure of Ln^{3+} ions, the shield effect of the $5S^2$, $5P^6$ electrons, the interactions between the f-f transitions and the ligand field were very weak. So, the PA spectra of different ligand rare earth complexes will be a limited technique. But, the transition absorptions of different J energy levels were clearly shown in their PA spectra, see Table 1. And all the PA spectra absorptions were assignment in Table 1.

We know that compound in excited state will be relaxed by two process of radiative and nonradiative. And PA spectrum is a

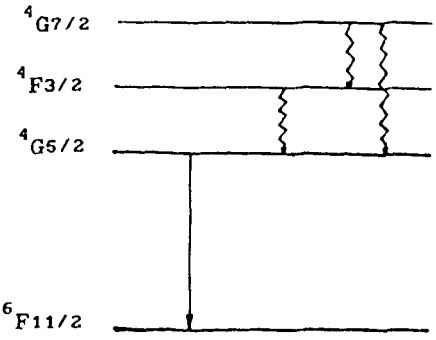

FIG. 1. The relaxation process of Sm^{3+} ion.
~~~~~ nonradiative; ——→ radiative.

technique which is only response to the nonradiative relaxation process. So, the PA signal of fluorescence energy levels which relaxed by radiation process will be very weak or vanished[10]. Among the energy levels of Sm^{3+} ion, the longest life time of excited state is $^4G_{5/2}$ (about 6.26 ms) and it is also a strong fluorescence state. The electron of excited state $^4G_{5/2}$ has a dominant possibility to take nonradiative relaxation process. As see in Fig. 1, when the electron was excited to $^4G_{7/2}$, $^4F_{3/2}$ state, usually their will be relaxed to $^4G_{5/2}$ by nonradiative transition, and then relaxed by radiation process (fluorescence). It is seen that the relaxation process of energy levels $^4G_{7/2}$, $^4F_{3/2}$, $^4G_{5/2}$ are mostly through the radiation process. In PA spectrum, it is seen that their intensity is very very weak. As seen in Fig. 2, the PA signal of $^4G_{7/2}$, $^4F_{3/2}$, $^4G_{5/2}$ are so weak that we could just distinguished. And it is said that these energy levels are strong fluorescence energy levels.

However, the Eu^{3+}, Dy^{3+} ions also have the strong fluorescence properties. In the energy levels of Eu^{3+} ion, the longest life time of excited state is $^5D_0$ (about 9.67ms). According to the PA spectrum, as shown in Fig. 3, the relaxation transitions of $^5D_0$ state can not be monitored by PA technique. And the PA signal of $^5D_1$, $^5D_2$, $^5D_3$ are also quite weak. It can be interpreted that the excited state $^5D_0$ is a very strong fluorescence energy levels and its relaxation process is almost all radiation process. And the electron in excited state $^5D_1$, $^5D_2$, $^5D_3$ may be relaxed to $^5D_0$ by
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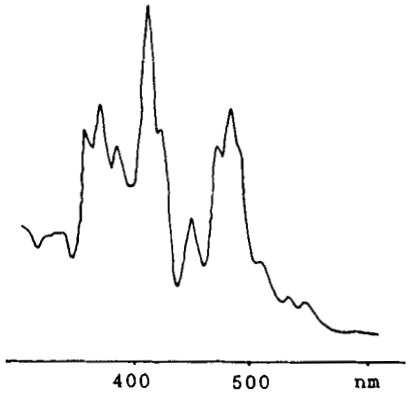

FIG. 2. The PA spectrum of $Sm(Ac)_3 \cdot 4H_2O$ complex.

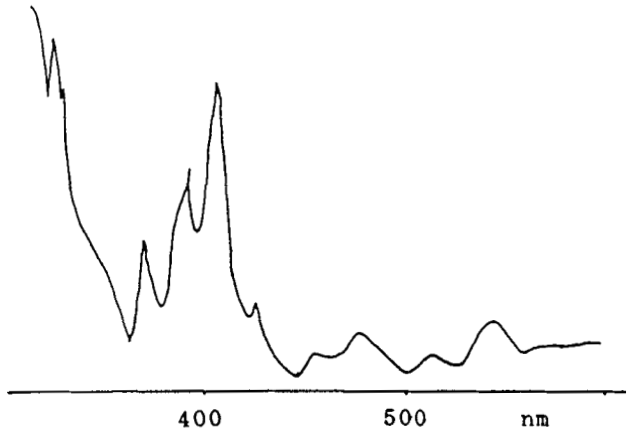

FIG. 3. The PA spectrum of $Eu(Ac)_3 \cdot 4H_2O$ complex.

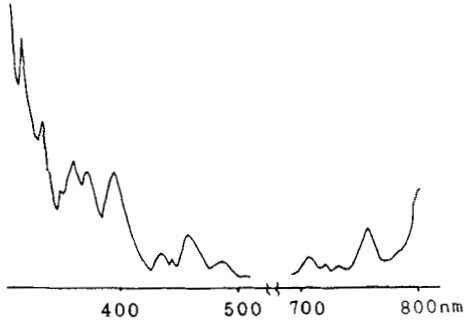

FIG. 4. The PA spectrum of $Dy_2(Ac)(NO_3)_4 \cdot 12H_2O$ complex.

non-radiation model dominantly, then relaxed by radiation process. So, only a weak signal can be monitored in their PA spectra.

The PA spectrum of $Dy_2(Ac)(NO_3)_4 \cdot 12H_2O$ complex was shown in Fig. 4. The PA signal of fluorescence energy levels $^4F_{9/2}$ (life time 9.02ms) was very weak. And the PA signal of neighbor energy levels $^4I_{15/2}$, $^4G_{11/2}$ were also quite weak. It can also be interpreted by a similar relaxation model in Fig. 1.

In conclusion, we could say that the PA spectrum give a clear relaxation process model of strong fluorescence energy level and it's neighbor energy levels of rare earth ions. So, the photoacoustic technique is a very useful method to study the spectral properties of rare earth complexes.

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