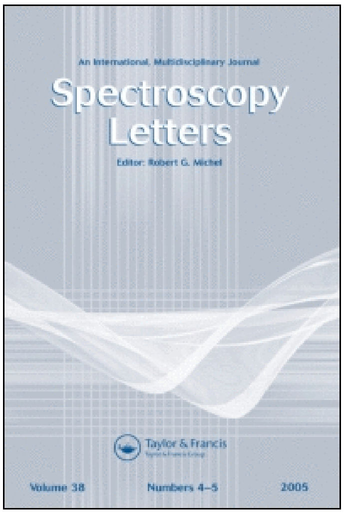

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Photoacoustic Spectra Studies on Neodymium Complexes

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PHOTOACOUSTIC SPECTRA STUDIES ON NEODYMIUM COMPLEXES

Key words: Photoacoustic spectrometer, neodymium complexes,
relaxation processes.

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ABSTRACT

A series of neodymium complexes crystals were synthesized and their photoacoustic spectra were determined. The excited state energy levels of Nd(III) in different complexes were discussed and their relaxation processes were studied. The different coordination environments were shown by comparing the band due to Nd(III) $^4I_{9/2}$ — $^4G_{5/2}, ^2G_{7/2}$ transitions in different complexes. The fine structure of this absorption shows that the Nd-O bond forms a stronger coordinated bond than that of Nd-N system.

INTRODUCTION

The so-call "sol-gel" process offers new approaches to the synthesis of inorganic materials[1,2]. Especially, this process has been used in the synthesis of superconductors, the copper and rare earth complexes, as molecular precursors, and has in general, been widely studied[3,4]. Molecular precursors lead to the formation of a solid network through hydrolysis and polycondensation reactions. The temperature required for material processing can be notably lowered[5]. 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[6], this giving rise to a better control of the process. The gels so-obtained 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.

Recently, photoacoustic (PA) measurements have been widely used to investigate the chemical and physical properties of many kinds of samples[7]. PA spectroscopy enables us to obtain spectra on any type of solid, whether it is crystalline, powder or gel, and it is a method that can monitor of energy gaps and nonradiative relaxation channels directly, the complement of absorption and photoluminescence spectroscopic techniques[8]. However, the PA technique has not been widely used in transition metal complex systems[9,10]. In general, the PA technique shows many advantages when it is used in complex systems. Neodymium complexes have been widely studied in structure, spectral, thermal and some other properties. But, the PA spectra of rare earth metal complexes have been studied in very few cases[11,12]. In this work, the PA spectra of neodymium complexes are determined and the coordination properties of complexes are discussed in terms of their PA spectra.

EXPERIMENT

(1)Synthesis:

Nd(o-phen)$_2$(NO$_3$)$_4$•3H$_2$O (I):

This complex single crystals were prepared by dissolving Nd$_2$O$_3$ in HNO$_3$ solution and then evaporating it. Then acetone was used as a new solvent. Quantitative *o*-phenanthroline was dissolved in this solution, evaporated at room temperature and red granular single crystals grew up from the solution in several days. The crystals were then removed and quickly washed with distilled water. Elemental analysis of the crystalline compound was carried out. Found: C, 35.82; H, 2.91; N, 14.45%; Calc. for $Nd(o\text{-phen})_2(NO_3)_4\cdot 3H_2O$: C, 35.73; H, 2.73; N, 13.90%.

$Nd(2,2'\text{-bipy})_2(NO_3)_3(C_3H_6O)$ (II):

This complex crystals were prepared by the same way as compound (I), but the ligand of *o*-phenanthroline was replaced by the 2,2'-bipydine and pink granular crystals grew up from this solution system. Elemental analysis of this crystalline compound was carried out. Found: C, 37.75; H, 2.94; N, 14.17%; Calc. for $Nd(bpy)_2(NO_3)_3(C_3H_6O)$: C, 39.45; H, 3.14; N, 14.00%.

$Nd(Ac)_3\cdot 3/2H_2O$ (III), $Nd(Ac)_3\cdot H_2O$ (IV), $Nd(Ac)_3\cdot 3H_2O$ (V):

Neodymium triacetate hydrate $Nd(Ac)_3\cdot x\ H_2O$ (x = 1.0, 1.5, 3.0) single crystals were prepared from the Nd oxide (Nd_2O_3)-glacial acetate acid solution system. As the pH value was controlled by aqueous ammonia at 4 and evaporated slowly at room temperature, single, red plate crystals grew from this solution in about ten days. These crystals were then removed and quickly washed with distilled water and acetone. Elemental analysis of the crystalline compound was carried out. Found: C, 20.61; H, 3.47; calc. for $Nd(Ac)_3\cdot 1.5\ H_2O$ (III): C, 20.68; H, 3.45%. However, as the pH value of the neodymium oxide-glacial acetic acid solution was controlled at 1, two kinds of fibrous and cuboid (7 x 2 x 1.5 mm) single crystals with the same color simultaneously grew from the solution in about 3 days at room temperature. These crystals were also isolated and washed, and the results of elemental analysis show that crystal (IV) is $Nd(Ac)_3\cdot H_2O$, found: C, 20.77; H, 3.28; calc., C, 21.23; H, 3.24%; and crystal (V) is $Nd(Ac)_3\cdot 3\ H_2O$, found: C, 19.11; H, 4.19; calc., C, 19.19; H, 4.00%.

(2) CHARACTERIZATION

IR spectra were recorded on a Sakara-440 spectrometer in a frequency range 4000-400 cm^{-1}. The samples were studied as powder dispersals in KBr pellets. The IR spectra of all these neodymium complexes were in agreement with their formula.

In the PA spectra experiment, the excitation source was a 500 W xenon lamp and the optical system was a CT-30F monochromator. The light source was modulated by a variable speed mechanical chopper at a frequency of 12 Hz. The acoustic signal was detected with the sample placed in a locally built photoacoustic cell fitted with an EMR 10 electret microphone. After the preamplification, output of the microphone was fed to a lock-in-amplifier to which a reference signal was input from the chopper. The output signal was normalized for changes in lamp intensity using carbon-black[10].

RESULTS AND DISCUSSION

The PA spectra of $Nd(phen)_2(NO_3)_4 \cdot 3H_2O$ (I), $Nd(bpy)_2(NO_3)_3(C_3H_6O)$ (II) and $Nd(Ac)_3 \cdot 3/2H_2O$ (III) complexes crystals are presented in Figure 1. In Fig. 1, the transition absorptions of different J energy levels are clearly shown in the PA spectra and the properties of different ligand fields are also reflected. As shown in figure 1, a strong absorption at 400 nm in the PA spectra of complexes (I) and (II) is apparently observed, and corresponds to a charge transfer absorption. It means that a charge transfer $L \longrightarrow f$ between with large π conjugation system and the rare earth occurs at a low frequency. This strong charge transfer absorption does not occur in other neodymium complexes, such as Ac^-, sac^- ligands. It shows the specific characteristics of large π conjugation system in the rare earth complexes.

The PA absorptions of $Nd(phen)_2(NO_3)_4 \cdot 3H_2O$ (I), $Nd(bpy)_2(NO_3)_3 \cdot (C_3H_6O)$ (II), $Nd(Ac)_3 \cdot 3/2H_2O$ (III), $Nd(Ac)_3 \cdot H_2O$ (IV), $Nd(Ac)_3 \cdot 3H_2O$ (V), Nd_2O_3 (VI) and the electronic absorptions of

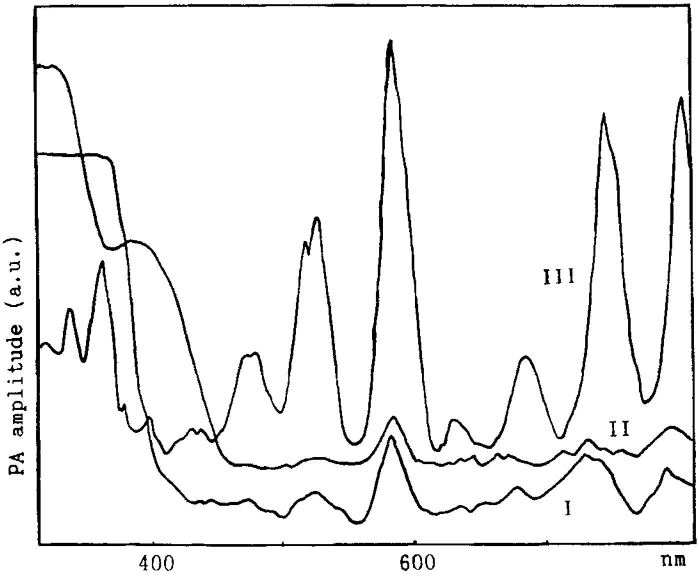

FIG. 1. The PA spectra of Nd(III) complexes.
I: $Nd(phen)_2(NO_3)_4\cdot 3H_2O$; II: $Nd(bpy)_2(NO_3)_3(C_3H_6O)$;
III: $Nd(Ac)_3\cdot 3/2H_2O$.

hydrated Nd(III) ion (VII) in the range of 300-800 nm are presented in Table 1. As seen in Table 1, the changes of f-f transition absorption positions of complexes with different ligand are very small, in general, about 10 nm, and these relative intensities are also basically invariant. This is very different from the behaviour of d-d transitions in d electron metal complexes. Compared with the electronic absorption of hydrated Nd(III) ion, red shifts occur in absorptions of all complexes crystals, $\delta\nu$ is in the range of 0-20 nm. It is due to the interactions between ligand and inner layer f electrons.

We know that electrons in excited states usually relaxed by two processes: a radiative and non-radiative one. PA spectroscopy is a technique in which only the energies of non-radiative process were determined. But all the energies of two relaxation processes

TABLE 1

PA spectra and assignment of different Nd(III) Complexes (nm)*

E.L.	I	II	III	IV	V	VI	VII(ES)
L-L*	<350/400	<340/600					
L-f	365.7(sh)	395/350					
${}^4D_{7/2}$			341.3/27		339.9/38	339.8/20	328/10
${}^4D_{5/2}$			359(sh)	359.6/39	359.8/53	360(sh)	350/34
${}^4D_{3/2}$			362(sh)	362.7/33	364.4/54	364.2/70	353/74
${}^2P_{1/2}$	442.3/18		437.6/13	443.7/13	434.9/16	437.6/15	428/16
${}^4G_{11/2}$	470.5/24		469.7/23	468.2/22	471.7/32	474.3/35	469/11
${}^4G_{9/2}$	512.5/30	511.4/25	517.1/45	517.1/38	519.8/58	517.1/60	512/24
${}^4G_{7/2}$	527.5/37	530.3/32	529.4/56	529.4/52	531.5/63	529.4/70	521/24
${}^4G_{5/2}$	584.4/100	584.8/100	585.0/100	586.5/100	583.6/100	582.9/100	576/100
${}^2H_{11/2}$	632.8/22	633.7/30	628.7/12	631.8/11	629.6/18	633.3/10	
${}^4F_{9/2}$	678.0/50	677.2/30	680.7/12	682.3/22	683.2/32	683.8/20	679/80
${}^4S_{3/2}$	734.9/83	726.1/68	740.4/79	741.9/71	744.5/85		732/82
${}^4F_{7/2}$	745.8/61	745.0/30	746.5/79	744.5/68	749.1/84	754.1/85	740/101
${}^4F_{5/2}$	793.2/68	795.4/86	798.5/80	798.5/75	799.7/87	797.6/80	794/174

* A/B = nm / relative intensity

I: $Nd(phen)_2(NO_3)_4 \cdot 3H_2O$; II: $Nd(bpy)_2(NO_3)_3(C_3H_6O)$; III: $Nd(Ac)_3 \cdot 3/2H_2O$
IV: $Nd(Ac)_3 \cdot H_2O$; V: $Nd(Ac)_3 \cdot 3H_2O$; VI: Nd_2O_3; VII: hydrated Nd(III) ion.

(radiative and non-radiative) are reflected in electronic absorption spectrum. So, the difference of intensities between PA spectrum and electronic absorption spectrum indicates the fluorescence properties of their energy levels. It is demonstrated as the radiative relaxation process which can be reflected only by electronic absorption spectrum, not the PA technique[8,11,12].

Among the energy levels of the Nd(III) ion, the longest life time excited state is ${}^4F_{3/2}$ (about 4×10^{-4} s). As a weak fluorescence system, the excited state ${}^4F_{3/2}$ of Nd(III) has a

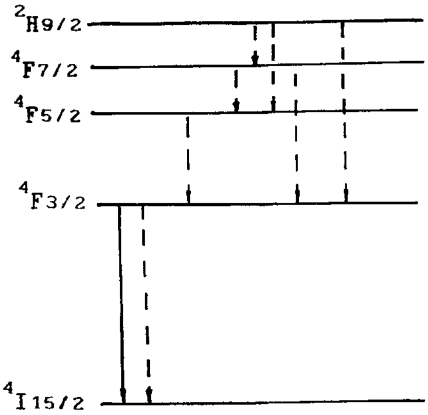

FIG. 2. The relaxation process of the excited state in Nd^{3+} ion.
- - → radiation process; ——→ nonradiation process.

large possibility to undergo non-radiative relaxation to the small energy interval between $^4F_{3/2}$ and the next lower energy level $^4I_{15/2}$.(See Fig. 2). As the electrons are excited to $^4F_{5/2}$, $^4F_{7/2}$ state, usually, they relax to $^4F_{3/2}$ by non-radiative process, and then relax by both non-radiative and radiative process (fluorescence). It is to be seen that both the radiative and non-radiative process all exist in relaxation processes of the excited states of $^4F_{5/2}$, $^4F_{7/2}$. In the PA spectra, it is shown that the intensity is weaker than that of the absorption spectra. From the data of Table 1, we can see the PA relative intensities of $^4F_{5/2}$, $^4F_{7/2}$ are obviously weaker than the absorption intensity of hydrated Nd(III) ion, and these intensity variations are not notable in the higher energy levels.

In Nd(III) complexes, the different coordination environments are shown by comparing the band due to the $^4I_{9/2} \rightarrow {}^4G_{5/2}$ transitions. The absorption of J energy levels are split into fine structure for the effect of the ligand. As the PA spectra are recorded on powder complex sample, this fine structure can not be observed because the PA signal is saturated. Figure 3 shows the

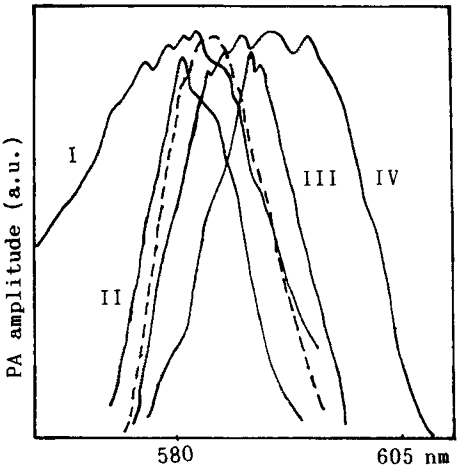

FIG. 3. PA absorptions of Nd^{3+} $^4I_{9/2}$ —$^4G_{5/2}$ transitions.
I: $Nd(phen)_2(NO_3)_4{\cdot}3H_2O$; II: $Nd(Sac)_3{\cdot}4H_2O$;
III: $Nd(Ac)_3{\cdot}3/2H_2O$; VI: $Pr(Nd)(Ac)_3{\cdot}H_2O$;
Dash curve is Nd_2O_3.

absorptions due to the Nd(III) $^4I_{9/2} \rightarrow {}^4G_{5/2}$ transitions in $Nd(phen)_2(NO_3)_4{\cdot}3H_2O$ (I), $Nd(Sac)_3{\cdot}4H_2O$[11](II), $Nd(Ac)_3{\cdot}3/2H_2O$ (III), $Pr(Nd)(Ac)_3{\cdot}H_2O$[11](IV) and for comparison, the Nd_2O_3. In Nd(III) doped $Pr(Ac)_3{\cdot}H_2O$ complex, absorptions due to the Nd(III) are observed at 598.6 and 583.7 nm, and the absorptions due to Pr(III) $^3H_4$—$^3D_2$ are observed at 591 and 596.6 nm. As seen in figure 3, compared to the absorptions of Nd_2O_3, the violet shift is observed in complexes (I) and (II) in which the Nd(III) ion is coordinated by oxygen and nitrogen atoms, but a red shift is observed in complexes (III) and (IV) where the Nd(III) ion is only coordinated by oxygen atoms. That the difference of coordination natures between Nd-O and Nd-N is demonstrated. The coordinated bond and ligand field are stronger in the Nd-O bond, and in general, f-f transitions of Nd(III) ion show large red shift. These characteristics are also verified by the results of XPS and some other technique[11].

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