

Optical properties of a binuclear neodymium complex in phosphorus oxychloride for liquid laser



Guofang Zhang^a, Jiangbo She^{b,*}, Kai Han^a, Rongzhi Nie^b, Dongdong Li^c, Bo Peng^{b,*}

^a Key Laboratory of Applied Surface and Colloid Chemistry, MOE, School of Chemistry and Chemical Engineering, Shaanxi Normal University, Xi'an 710062, PR China

^b State Key Laboratory of Transient Optics and Photonics, Xi'an Institute of Optics and Precision Mechanics, Chinese Academy of Science (CAS), Xi'an, Shaanxi 710119, PR China

^c School of Electronic Engineering, Xi'an University of Post and Telecommunications, Xi'an, Shaanxi 710121, PR China

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ABSTRACT

A novel binuclear neodymium complex $\text{Nd}(\text{CF}_3\text{COO})_3 \cdot (\text{Ph}_3\text{PO})_2$ (Ph_3PO : triphenylphosphine oxide) with high stimulated emission cross-section was presented. The molecular structure of the complex was characterized by single-crystal X-ray diffraction. The optical properties of the complex in liquid medium were studied. From the absorption and luminescence spectra, the Judd–Ofelt parameters of Nd ($\text{CF}_3\text{COO})_3 \cdot (\text{Ph}_3\text{PO})_2$ in phosphorus oxychloride were obtained. Based on the crystal structure, the effects of crystal field and bonding valence properties on three intensity parameters Ω_t ($t = 2, 4, 6$) and emission cross-section were analyzed in detail. The emission cross-section of ${}^4\text{F}_{3/2} \rightarrow {}^4\text{I}_{11/2}$ fluorescence transition ($2.78 \times 10^{-20} \text{ cm}^2$) of the new neodymium compound was higher than those of other Nd(III) complexes and even comparable with some laser glasses.

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1. Introduction

The design and synthesis of complexes with luminescent property have attracted considerable attention due to their photoluminescence, electroluminescence and magnetic properties. The fluorescent properties of lanthanide coordination compounds with organic ligands have great potential applications in chemo- and bio-sensors [1–3], liquid laser medium [4,5], optical fiber lasers and amplifiers [6].

Rare earth containing laser materials have been well studied and applied extensively during the past several decades. Solid state lasers containing Nd(III) have been largely investigated due to its important near infrared luminescence around 1060 nm, which can be used in high-power and high average-power outputs laser systems [7]. However, such lasing materials as crystals and glasses still have quite a few disadvantages that restrict their further applications. For example, (1) it is very costly and difficult to manufacture them in big size homogeneously; (2) the inevitable heat accumulation problems of solid laser, such as thermal lens, thermal birefringence, and thermal stress, which limit the output power and beam quality of solid laser [8].

The rare-earth complex liquid laser material, its luminescent centers are still rare-earth ions, the flowing carrier is the solvent which has no absorption with pumped and output laser. It can avoid the heat accumulation by cycle flowing. At the same time, the complexes can be easily synthesized and dissolved in solvent homogeneously. The size and shape of laser materials are determined by the liquid container, no longer defined by the technology of synthesis and optical process. Accordingly, it combines the excellent optical properties of rare-earth ions and good heat management of liquid, provides a new method for solving the heat management bottleneck of high energy solid laser materials [9].

It is well known that the emission cross-section, one of the most important parameters for laser design, is the key factor of tuning emission properties of trivalent rare-earth ions in the host matrixes. It depends considerably on the surrounding host matrix and ligands. Except some inorganic crystal laser materials, most of laser materials obtain the emission cross-section parameters by calculation of Judd–Ofelt theory [10,11], without the coordinated structure of luminescent centers. In this letter, a novel binuclear neodymium complex $\text{Nd}(\text{CF}_3\text{COO})_3 \cdot (\text{Ph}_3\text{PO})_2$ (Ph_3PO : triphenylphosphine oxide) dissolved in phosphorus oxychloride was reported. The molecular structure of the complex was characterized by single-crystal X-ray diffraction. Based on crystal structure, the effects of crystal field and bond valance properties on three intensity parameters Ω_t ($t = 2, 4, 6$) and emission cross-section were analyzed in detail. The emission cross-section of ${}^4\text{F}_{3/2} \rightarrow {}^4\text{I}_{11/2}$

* Corresponding authors.

E-mail addresses: shejb@opt.ac.cn (J. She), bpeng@opt.ac.cn (B. Peng).

fluorescence transition of this complex was higher than those Nd(III) complexes and even comparable with some laser glasses. It shows a potential application in the field of neodymium liquid lasers in the future.

2. Experimental

2.1. Materials and measurement

All analytical reagents were obtained from commercial sources and used directly without further purification. The infrared spectra were recorded as KBr pellet on a Nicolet 170SX FT-IR spectrometer. Elemental analysis (C, H, O) was determined with a German Vario EL III instrument. The crystal structure was determined with a Bruker Smart-1000 CCD diffractometer. Absorption spectra were measured with Jasco V-570 UV–Vis–NIR scanning spectrophotometer. Photoluminescence (PL) emission spectra were performed using a nanosecond laser (Luce 532, Newopto Corporation) operating, a Zolix Omini- λ 300 fluorescence spectrophotometer and DIn-GaAs1700 detector. The TG–DTG measurements were done with a Thermoanalyzer Systems Q1000DSC+LNCS+FACS Q600SDT of TA company.

2.2. Preparation of $\text{Nd}(\text{CF}_3\text{COO})_3 \cdot (\text{Ph}_3\text{PO})_2$ complex

$\text{Nd}(\text{CF}_3\text{COO})_3 \cdot 2\text{H}_2\text{O}$ was obtained by dissolving Nd_2O_3 in a mixture of trifluoroacetic acid and water and subsequently volatilized the water after refluxing the solution for 4 h. $\text{Nd}(\text{CF}_3\text{COO})_3 \cdot 2\text{H}_2\text{O}$ (2.6 g, 5 mmol) and triphenylphosphine oxide (2.78 g, 10 mmol) were dissolved in 45 ml ethanol and stirred for 2 h under reflux. Then, after removal of solvent under reduced pressure, the pink product, $\text{Nd}(\text{CF}_3\text{COO})_3 \cdot (\text{Ph}_3\text{PO})_2$, was obtained by dried at 120 °C for 10 h under vacuum. The single crystal suitable for X-ray diffraction analysis was obtained from its ethanol solution after one week. Elemental analysis calculated. for $\text{Nd}(\text{CF}_3\text{COO})_3 \cdot (\text{Ph}_3\text{PO})_2$: C 48.51, H 2.91, O 12.31; found: C 48.22, H 2.82, O 12.59%. IR (KBr, cm^{-1}): 3062 ($\nu_{\text{C-H}}$), 1720 ($\nu_{\text{as}(\text{COO})}$), 1438 ($\nu_{\text{s}(\text{COO})}$), 1209 ($\nu_{\text{C-F}}$), 1155 ($\nu_{\text{P=O}}$), 854 ($\nu_{\text{C-H}}$), 725 ($\nu_{\text{C-F}}$), 694 ($\nu_{\text{C-H}}$) (see Scheme 1).

2.3. Single crystal X-ray diffraction analysis

The determination of the unit cell and data collection for $\text{Nd}(\text{CF}_3\text{COO})_3 \cdot (\text{Ph}_3\text{PO})_2$ crystal was performed on a Bruker Smart-1000 CCD diffractometer with graphite monochromated Mo $K\alpha$ radiation ($\lambda = 0.71073 \text{ \AA}$) using $\omega - 2\theta$ scan technique. The structure was solved by direct method using SHELXS-97 [12] and refined against F^2 by full-matrix least-square using SHELXL-97 [12]. All non-hydrogen atoms were refined anisotropic ally. All hydrogen atoms were treated using a riding model. No decomposition was showed in the crystal. A summary of the crystal data, experimental details and refinement results was listed in Table 1.

Table 1

Crystal data and structure refinement of $\text{Nd}(\text{CF}_3\text{COO})_3 \cdot (\text{Ph}_3\text{PO})_2$ crystal.

Empirical formula	$\text{C}_{84}\text{H}_{60}\text{F}_{18}\text{Nd}_2\text{O}_{16}\text{P}_4$
Formula weight	2079.68
Temperature (K)	296(2)
Wavelength (\AA)	0.71073
Crystal system	Monoclinic
Space group	$P2(1)/n$
Unit cell dimensions	$a = 15.2930(4) \text{ \AA}$; $\alpha = 90^\circ$ $b = 18.0766(4) \text{ \AA}$; $\beta = 92.962(2)^\circ$ $c = 15.3723(4) \text{ \AA}$; $\gamma = 90^\circ$
Volume (\AA^3)	4243.92(18)
Z	2
Density (calculated) (mg/m^3)	1.627
$F(000)$	2068
Crystal size	$0.14 \times 0.13 \times 0.10 \text{ mm}$
θ range for data collection	$3.12\text{--}25.99$
Limiting indices	$-18 \leq h \leq 17$, $-22 \leq k \leq 22$, $-18 \leq l \leq 18$
Reflections collected/unique	23170/8092 [$R(\text{int}) = 0.0281$]
Completeness to $\theta = 26.00^\circ$	97.1%
Refinement method	Full-matrix least-squares on F^2
Data/restraints/parameters	8092/21/559
Goodness-of-fit on F^2	1.104
Final R indices [$I > 2\sigma(I)$]	$R_1 = 0.0375$, $\omega R_2 = 0.0904$
R indices (all data)	$R_1 = 0.0515$, $\omega R_2 = 0.1012$
Largest diff. peak and hole (e \AA^{-3})	2.038 and -0.997

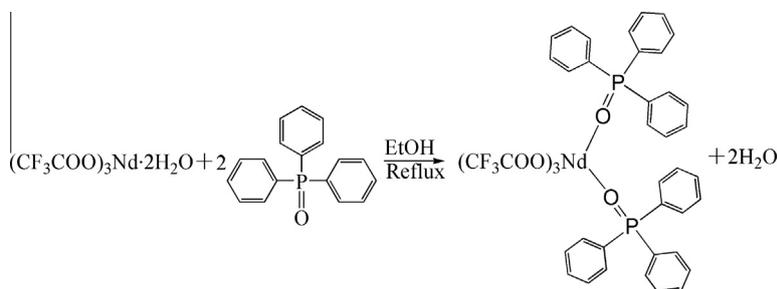
3. Results and discussion

3.1. Crystal structure

The complex $\text{Nd}(\text{CF}_3\text{COO})_3 \cdot (\text{Ph}_3\text{PO})_2$ is crystallized in the monoclinic space group $P2(1)/n$ and consists two Nd(III) ions, six trifluoroacetate anions and four triphenylphosphine oxide ligands in the unit. The selected bond lengths and angles of the complex are listed in Table 2. The molecular structure with the atom-labeling scheme and the detailed coordination sphere around the Nd(III) ion is shown in Fig. 1. It can be seen that the Nd(III) ion is coordinated by eight O atoms, derived from five different trifluoroacetate anions and two triphenylphosphine oxide ligands, which form square anti prism configuration (Fig. 2). The eight oxygen atoms of the four trifluoroacetate anion groups bridge two neodymium atoms together to form a binuclear complex by $\eta^2-\mu^2-k^1\text{O}:k^1\text{O}'$ coordination mode with the distance $4.711(2) \text{ \AA}$ between two Nd(III) ions. The other two trifluoroacetate anions acting as second assistant ligands are bidentate to the Nd(III) ions, and the four triphenylphosphine oxide acting as monodentate ligands to neodymium ions by the oxygen atoms.

3.2. Thermogravimetric analysis

As shown in Fig. 3, the thermogravimetric curve for $\text{Nd}(\text{CF}_3\text{COO})_3 \cdot (\text{Ph}_3\text{PO})_2$ was recorded in N_2 from room temperature



Scheme 1. The synthetic route of $\text{Nd}(\text{CF}_3\text{COO})_3 \cdot (\text{Ph}_3\text{PO})_2$.

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