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钕 4,4′-二甲基-2,2′-联吡啶配合物液体激光介质的合成及其光学特性

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摘 要:合成并用元素分析、红外光谱法表征了一种 4,4′-二甲基-2,2′-联吡啶五氟丙酸钕配合物—$Nd(C_2F_5COO)_3$ · Dmbp (Dmbp: 4,4′-二甲基-2,2′-联吡啶). 将该配合物溶解在 N,N-二甲基甲酰胺中获得了液体介质,依据液体介质的吸收和荧光光谱,通过 Judd-Ofelt 理论计算获得了钕离子的谱线强度参数(Ω_2, Ω_4, Ω_6)和受激发射截面. 计算得到该配合物中钕离子$^4F_{3/2}\rightarrow{}^4I_{11/2}$跃迁的受激发射截面为 5.2×10^{-20} cm^2,表明该钕配合物在液体基质中具有较好的发光特性. 通过荧光发射光谱分析可知,$Nd(C_2F_5COO)_3$ · Dmbp 将是一种有前途的光学增益材料.

关键词:液体激光材料;钕配合物;受激发射截面

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Synthesis and Optical Properties of Neodymium 4,4′-Dimethyl-2,2′-bipyridine complex for Liquid Laser Media

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Abstract: A novel neodymium pentafluoropropionate complex, $Nd(C_2F_5COO)_3$ · Dmbp (Dmbp: 4,4′-dimethyl-2,2′-bipyridine), was synthesized and characterized by elemental analysis, Fourier transform infrared spectra. The optical porperties of the liquid medium which was abtained by dissolving $Nd(C_2F_5COO)_3$ · Dmbp in N, N-dimethylformamide was investigated. Based on absorption and luminescence spectra of $Nd(C_2F_5COO)_3$ · Dmbp in DMF, as well as Judd-Ofelt theory, the three intensity parameters Ω_t(t=2,4,6) and emission cross-section were calculated and analyzed The emission cross-section of $^4F_{3/2}\rightarrow{}^4I_{11/2}$ fluorescence transition of Nd^{3+} ion was 5.2×10^{-20} cm^2, and comparable with some laser glasses, which indicated good radiative properties of this neodymium complex in liquid matrix. According to the photoluminescence spectra, $Nd(C_2F_5COO)_3$ · Dmbp complex will be a promising material for optical gain material in the future.

Key words: Liquid lasers materials; Neodymium complex; Emission cross-section

OCIS Codes: 160.5690; 140.3530; 300.6170

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0 Introduction

Nd(III)-doped inorganic crystals and glasses as high gain medias for lasers have been well studied during the past several decades. However, such lasing materials as crystals and glasses still have few disadvantages that restrict their further application in high energy laser system, such as poor thermal management[1]. Such unsolved stubborn problems have become neck points to the further development of solid state neodymium lasers.

Liquid Nd(III) laser medium is one of the important candidates for a high power and scale tunable laser system, because such liquid laser systems can be acquired easily and cooled by circulation at high power density operation, which may overcome thermal degradation of the component of the system[2].

In this study, a novel neodymium complex $Nd(C_2F_5COO)_3 \cdot Dmbp$ was synthesized and characterized by elemental analysis, Fourier transform infrared spectra (FTIR), ultraviolet visible and near infrared (UV-Vis-NIR) absorption spectra and photoluminescence spectra (PL). The neodymium complex was dissolved in N, N-dimethylformamide to abtain the liquid medium. Based on absorption and luminescence spectra of $Nd(C_2F_5COO)_3 \cdot Dmbp$ in DMF, as well as Judd-Ofelt theory, the three intensity parameters Ω_t ($t=2,4,6$) and emission cross-section were calculated and analyzed in detail.

1 Experimental

1.1 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 Fourier transform infrared spectrometer in a wavenumber range of 4000～400 cm^{-1}. Elemental analyses (C, H, N) were determined with a German Vario EL III instrument. Absorption spectra were measured on JASCO UV-570 ultraviolet visible and near infrared scanning spectrophotometer. Photoluminescence emission spectra were performed using a femtosecond Ti: sapphire laser (UF-T2S) operating, a Zolix Omini-λ 300 fluorescence spectrophotometer and InGaAs1700 detector.

1.2 Preparation of $Nd(C_2F_5COO)_3 \cdot Dmbp$ complex

First, 3.36 g (10 mmol) Nd_2O_3 was dissolved in 10.56g (60 mmol) C_2F_5COOH with 30 ml H_2O. The solution was refluxed for 4 h under stirring. Then, it was concentrated by vacuum rotary evaporation. A pink precipitation, $Nd(C_2F_5COO)_3 \cdot 2H_2O$, was obtained. 4,4′-dimethyl-2,2′-bipyridine 1.47 g (8 m·mol) and $Nd(C_2F_5COO)_3 \cdot 2H_2O$ 5.64 g (8 m·mol) were reacted in 30 ml tetrahydrofuran (THF) and was refluxed with stirring for 2 h. The product, $Nd(C_2F_5COO)_3 \cdot Dmbp$, was achieved after dried in vacuum under 120℃ for 8 h. Elemental analysis calcd. for $Nd(C_2F_5COO)_3 \cdot Dmbp$: C 32.39, H 1.81, N 4.20; found: C 32.35, H 1.77, N 4.26 %. IR (KBr, cm^{-1}): 1731(s, $v_{as(COO)}$), 1662(vs, $v_{as(COO)}$), 1562(m, $v_{(C=N)}$), 1432(s, $v_{s(COO)}$), 1326(m, $v_{s(COO)}$), 1220(vs, $v_{(C\text{-}F)}$), 825(s, $v_{(C\text{-}H)}$), 728(vs, $v_{(C\text{-}F)}$).

2 Results and discussion

2.1 Optical spectroscopy

Fig. 1 shows the Fourier transform infrared (FTIR) spectra of $Nd(C_2F_5COO)_3 \cdot Dmbp$. The free carboxylic acids characteristic absorption bands $v_{as(COO)}$ 1774 cm^{-1}, $v_{s(COO)}$ 1336 cm^{-1} shift to bands of 1662 cm^{-1} and 1326cm^{-1}, which suggest that the oxygen atoms of carbonyl groups are coordinated with neodymium ions. The middle absorption band at 1562 cm^{-1} was attributed to the vibration of C=N[3]. The IR attribution confirmed the compound was the objective product.

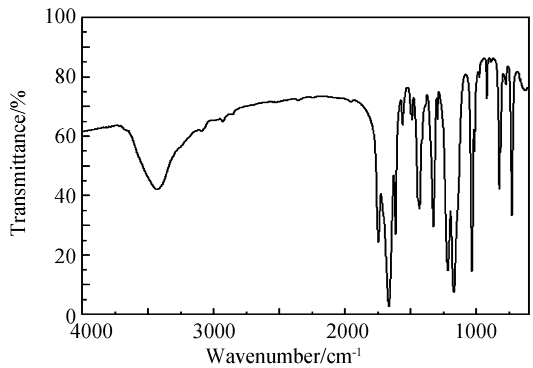

Fig. 1 The Fourier transform infrared spectra of $Nd(C_2F_5COO)_3 \cdot Dmbp$ complex

The UV-Vis-NIR absorption spectra of $Nd(C_2F_5C\text{- -}OO)_3 \cdot Dmbp$ in N, N-dimethylformamide (DMF) solution is shown in Fig. 2. The bands from 450 to 900nm are f-f transitions of the Nd^{3+} ion, corresponding to those from the ground $^4I_{9/2}$ level to the excited levels, respectively[4].

Photoluminescence spectra of $Nd(C_2F_5COO)_3 \cdot$ Dm- -bp in DMF (0.2 mol/L) excited at 801 nm under room temperature is illustrated in Fig. 3. Three characteristic emission bands centered at 877 nm($^4F_{3/2} \rightarrow {}^4I_{9/2}$), 1054 nm ($^4F_{3/2} \rightarrow {}^4I_{11/2}$) and 1329 nm ($^4F_{3/2} \rightarrow {}^4I_{13/2}$) were observed, which indicates that the $Nd(C_2F_5COO)_3 \cdot Dmbp$ complex has good photoluminescence emission.

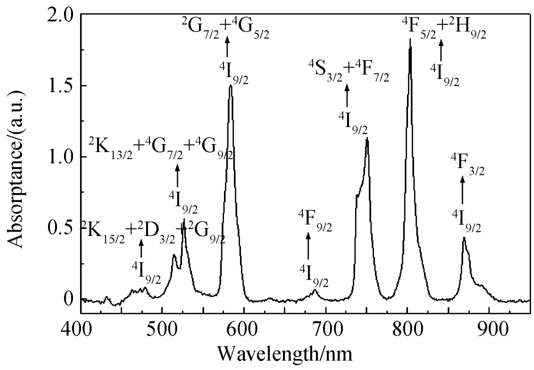

Fig. 2 Absorption spectra of $Nd(C_2F_5COO)_3\cdot$Dmbp in DMF solution

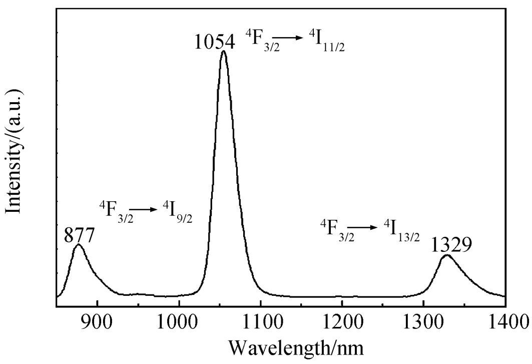

Fig. 3 Photoluminescence emission spectra of Nd $(C_2F_5COO)_3\cdot$Dmbp in DMF solution

2.2 Judd-Ofelt analysis

Judd-Ofelt theory is one of the most successful theories for evaluating the potential radiative properties of rare-earth-doped materials. The Judd-Ofelt analyses of the Nd(III) complex was calculated by use of the absorption bands in the visible range (492～547, 547～610, 714～774, 774～840, and 840～920 nm). The assignment of the bands is given in Fig. 2. The oscillator strength of an absorption band can be determined using the following equation [5]:

$$P_{exp}=\frac{mc^2}{\pi e^2 N\lambda^2}\int\alpha(\lambda)\,d\lambda$$

where m is the mass of the electron, c is the velocity of light, e is the charge of the electron, N is the number density of Nd^{3+} ions, and $\alpha(\lambda)$ is the absorption coefficient at wavelength λ. The refractive index of the solution is 1.431. According to Judd-Ofelt theory, the oscillator strength of an electric-dipole transition between an initial J manifold and $|(S,L)J$ and a terminal J' manifold $|(S',L')J'$ can be determined by[6]:

$$P(aJ;bJ')=\frac{8\pi^2 cm\chi v}{3h(2J+1)}\cdot\sum_{t=2,4,6}\Omega_t\,|\langle 4f^N aJ\,\|\,U^{(t)}\,\|\,4f^N bJ'\rangle|^2$$

where h is the Plank constant and ν is the frequency in inverse centimeter, $\chi=(n^2+2)^2/9n$ is the local field correction factor. J is the total angular momentum quantum number of the initial level (for Nd(III) ion $J=9/2$). $|U(t)|$ are the doubly reduced matrix elements corresponding to the $J\rightarrow J'$ transition. The Judd-Ofelt parameters $\Omega_t(t=2,4,6)$ can be obtained by a least-square method to correlate the oscillator strengths. To estimate the strength of crystal field in the liquid system, we calculated the Judd-Ofelt parameter $\Omega_2=2.1\times10^{-20}\ cm^2$, $\Omega_4=6.2\times10^{-20}\ cm^2$ and $\Omega_6=5.8\times10^{-20}\ cm^2$ of $Nd(C_2F_5COO)_3\cdot$Dmbp. Symmetrical crystal fields of the Nd(III) ions leads to significant decrease in values of the parameter Ω_2 because of domination of magnetic dipole transition along with decrease of electric dipole transition[7]. The Ω_2 of the $Nd(C_2F_5COO)_3\cdot$Dmbp in DMF gives small value, suggesting the symmetrical surrounding environment of Nd(III) ions in this system.

The effective stimulated emission cross-section (σ) is an important parameter for the assessment of a laser material. Knowledge of the σ is essential in evaluating laser system parameters such as maximum gain, saturation power and optimum output mirror reflectivity. The stimulated emission cross-section, σ_{em}, can be evaluated from the emission spectra by:

$$\sigma_{em}=\frac{\lambda^4 A_{ed}(ab)}{8\pi n^2 c\Delta\lambda}$$

where the λ is the peak wavelength of fluorescence as 1057 nm, and $\Delta\lambda$ is the line width of fluorescence peak, determined as the full-width at half-maximum as 29 nm. In case of end-pumped solid-state 4-level laser systems, the threshold pump power is inversely proportional to the effective stimulated emission cross-section of the lasing material. In the design and development of low threshold and high gain laser materials for high power applications, the stimulated emission cross section, σ, of the $^4F_{3/2}\rightarrow{}^4I_{11/2}$ fluorescence transition of the Nd(III) ions is one of the most important parameters and should be as high as possible. In this case, the σ of the $^4F_{3/2}\rightarrow{}^4I_{11/2}$ fluorescence transition of the Nd(III) ions is $5.2\times10^{-20}\ cm^2$, which is higher than some previous works which are listed in Table 1 [8-10]. This complex will be a promising material for liquid laser application.

Table 1 Comparison of the stimulated emission cross-section of $Nd(C_2F_5COO)_3\cdot$Dmbp in DMF with other materials reported

Materials	$\sigma(\times10^{-20}\ cm^2)$	Ref
Nd^{3+} doped silicate glasses	1.5	[8]
Nd(III) doped borate and phosphate glasses	3.2	[9]
$Nd(C_2F_5COO)_3\cdot$ Dipy in DMSO	2.4	[10]
This work	5.2	--

3 Conclusions

In conclusion, a novel neodymium complex Nd $(C_2F_5COO)_3$ · Dmbp was synthesized and dissolved in DMF to abtain the liquid medium. Based on absorption and luminescence spectra of Nd$(C_2F_5COO)_3$ · Dmbp in DMF, as well as Judd-Ofelt theory, the three intensity parameters Ω_t ($t=2,4,6$) and emission cross-section were calculated and analyzed in detail. The emission cross-section of $^4F_{3/2}\rightarrow{}^4I_{11/2}$ fluorescence transition was 5.2×10^{-20} cm^2, and comparable with some laser glasses, which indicated good radiative properties of this neodymium complex in liquid matrix. According to the photoluminescence spectra, Nd $(C_2F_5COO)_3$ · Dmbp complex will be a promising material for laser active medium in the future.

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