Investigation of neodymium doped organic liquid media for laser application

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Luminescence of Nd^{3+} is observed in a new undeuterated organic liquid medium. The measured lifetime τ of 1060-nm emission is 460 μs and the emission cross section is 2.54×10^{-20} cm^2. According to the spectral research results, two pumping schemes are designed and the threshold energies for outputting laser are roughly calculated. Taking 808 nm as pumping wavelength and using single-pulse-mode pumping, the threshold pumping energy of single pulse is evaluated about 250 mJ to ensure the pumped volume enough large and so the peak power of 200-μs pulse is about 1250 W, which is easily obtained today. The rough estimated results prove that this organic solution is a successfully potential laser media.

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Nd^{3+}-doped solid-state laser materials, such as silicates, phosphates, and crystals, have been investigated thoroughly and employed extensively. However, solid-state laser materials have intrinsic problems of heat accumulation, especially on the occasions of high repetition rate, high average power or high energy. Contrast to solid-state materials, liquid can not only eliminate heat by recirculating, but also avoid the permanent damage of laser media. The research on Nd^{3+}-doped liquid laser materials had begun when laser was just invented. However the extraordinary low quantum yield of Nd^{3+} caused by serious radiationless transition in common hydrogen contained liquid made Nd^{3+}-doped liquid laser advance hardly[1]. Many methods[2−8] had been employed to control radiationless transition and enhance quantum efficiency. Until now several Nd^{3+}-doped inorganic liquid solutions had output laser emissions and some properties of them even were better than those of Nd^{3+}-doped glasses or crystals[2−4]. While for Nd^{3+}-doped organic liquid laser materials, there are nearly no organic solutions reported to lasing except in Ref. [5]. In fact, without deuterium or designing coordinating environments, common Nd^{3+}-doped organic liquid solutions are thought nearly impossible to fluorescence, not to mention lasing[6,7].

In this article, an undeuterated Nd^{3+}-doped organic solution is prepared and the solution fluorescence is observed successfully. The performance tests show that the fluorescence lifetime and the quantum efficiency of Nd^{3+} in this solution is unexpectedly high. The preliminary theoretical analysis of laser threshold shows that this undeuterated organic liquid solution is a powerfully potential liquid laser material.

Neodymium (III) tris (thenoyltrifluoroacetonate) ($Nd(TTA)_3$) is synthesized and provided by Fudan University. Then $Nd(TTA)_3$ is dissolved in N,N-dimethylformamide (DMF) and the concentration of Nd^{3+} is about 0.4-mol/L. The refractive index of DMF is about 1.43. The solution is put in a quartz cell with side lengths of 1 cm. Measurement of transmittance spectrum is performed using ultraviolet (UV)-3150 spectrometer at room temperature (see Fig. 1). Fluorescence spectrum is obtained by USB2000 Miniature Fiber Optic Spectrometer, with a tunable Ti:sapphire laser exciting at 800 nm with repetition rate of 1 kHz and the pulse width of about 100 fs. Two obvious fluorescence peaks are observed as shown in Fig. 2. Fluorescence lifetimes are obtained using Thorlabs' DET210 detector and Tektronix TDS380P oscilloscope and the exciting source is the same as that in measured fluorescence spectrum. A 1060-nm total reflecting mirror is used to separate 898- and 1060-nm fluorescences, as shown in Fig. 3, and the lifetimes are respectively 505 and 460 μs. The emission decay curve of 1060 nm is shown in Fig. 4. Because the lifetime of fluorescence is unexpectedly high, for ensuring the reliability, we repeat the experiments and ascertain the above-mentioned results.

From the above results, we can find that the fluorescence lifetime of Nd^{3+} in this organic solution is extraordinarily high. So we will analyze the properties of it from

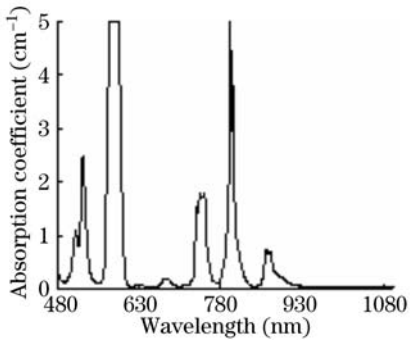

Fig. 1. Absorption spectrum of $Nd(TTA)_3$ in DMF.

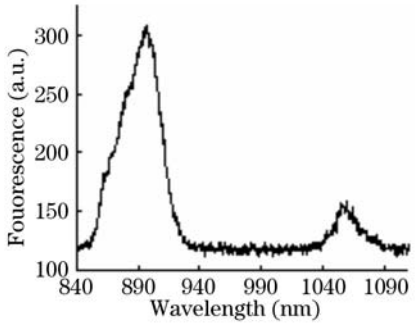

Fig. 2. Fluorescence spectrum of $Nd(TTA)_3$ in DMF.

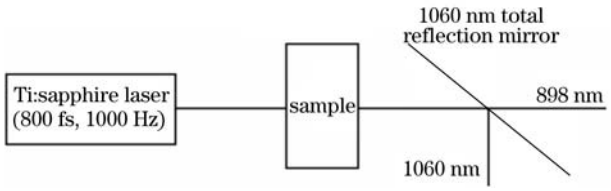

Fig. 3. Setup sketch for measuring fluorescence lifetimes.

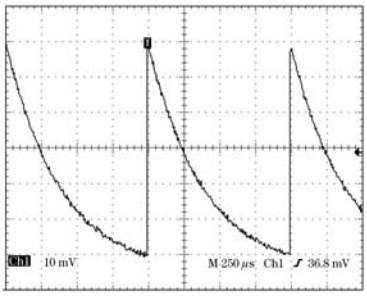

Fig. 4. Emission decay curve of $Nd(TTA)_3$ in DMF at 1060 nm.

the point view of outputting laser. It is well known that emission cross section $\sigma_{\rm em}$ of active ions is one of the most important parameters for laser application. According to Judd-Ofelt theory, the emission cross section $\sigma_{\rm em}$ between two states can be calculated as

$$\sigma_{\rm em} = \frac{\lambda_{\rm p}^4 A_{\rm ed}}{8\pi n^2 c \Delta\lambda_{\rm eff}}, \tag{1}$$

where $A_{\rm ed}$, $\lambda_{\rm p}$, n, $\Delta\lambda_{\rm eff}$, and c are respectively the radiative transition probabilities between two states, the peak wavelength, the refractive index of matrix, the effective fluorescence width, and the light speed in vacuum. $A_{\rm ed}$ and $\Delta\lambda_{\rm eff}$ can be calculated according to

$$A_{\rm ed}(ab) = \frac{64\pi^4 e^2}{3h} \cdot \frac{(n^2+2)^2 \cdot n}{9} \cdot \frac{1}{\lambda_{\rm p}^3} \cdot \frac{1}{2J+1} S_{\rm ed}(a,b), \tag{2}$$

$$\Delta\lambda_{\rm eff} = \frac{\int I(\lambda)\,{\rm d}\lambda}{I_{\max}}, \tag{3}$$

where $I_{\max}$ is the peak intensity of fluorescence peak, $S_{\rm ed}$ is the electric dipole line strength between two intermediate coupling states. So the emission cross section is

$$\sigma_{\rm em} = \frac{8\pi^3 e^2}{3hc(2J+1)} \frac{(n^2+2)^2}{n} \frac{\lambda_{\rm p}}{\Delta\lambda_{\rm eff}} S_{\rm ed}(a,b). \tag{4}$$

According to Judd-Ofelt theory, $S_{\rm ed}$ is

$$S_{\rm ed}(ab) = \frac{1}{e^2} \sum_{a,b} \left| \langle a | \vec{D} | b \rangle \right|^2 = \sum_{t=2,4,6} \Omega_t \left| \langle \alpha [SL] J | U^t | \alpha' [S'L'] J' \rangle \right|^2, \tag{5}$$

where Ω_t is the Judd-Ofelt intensity parameter. The reduced matrix elements of Nd^{3+} can be found in Refs. [9, 10]. From experimental point of view, the absorption line strength between two electric states has another relationship with measured absorption coefficients as

$$\int k(\lambda){\rm d}\lambda = \frac{8N\pi^3 e^2 \lambda_{\rm p}}{3hc(2J+1)} \cdot \frac{(n^2+2)^2}{9n} \cdot S_{\rm ed}, \tag{6}$$

where h, e, N, $k(\lambda)$ and J are respectively Planck's constant, elementary charge, concentration of rare earth ions, absorption coefficient, and angular momentum of beginning electric state. With the measured spectra and Eqs. (5) and (6), three intensity parameters has been calculated using least-square procedure: $\Omega_2 = 4.9 \times 10^{-20}$ cm^2, $\Omega_4 = 5.1 \times 10^{-20}$ cm^2, and $\Omega_6 = 2.5 \times 10^{-20}$ cm^2. And then using the calculated intensity parameters, $S_{\rm ed}$ and $A_{\rm ed}$ between arbitrary two electric states can be obtained according to Eqs. (5) and (2). Then the total radiative probabilities and theoretical radiative lifetime $\tau_{\rm r}$ of certain state can be obtained according to

$$\tau_{\rm r}(a) = \frac{1}{A_{\rm ed}(a)} = \frac{1}{\sum\limits_b A_{\rm ed}(ab)}. \tag{7}$$

All calculated results are shown in Table 1. The results show that not only the organic solution fluoresces successfully, but also the emission cross section at 1060 nm can compare with some Nd^{3+}-doped silicates, and the fluorescence efficiency is about 460/682=0.67 which is very high for Nd^{3+} in solutions. So the solution is a potential laser material. For evaluating the realizability of outputting laser, we should estimate the laser threshold.

Laser diodes are planned to be used as pulsed exciting source and the exciting wavelength is around 808 nm. The length l of active media along laser oscillating direction is designed to be 1 cm. The reflectances of cavity mirrors are respectively R_1=1 and R_2=0.9. Theoretical analysis in the following text is based on this pumping scheme.

Because the absorption cross section of Nd^{3+} at 808 nm in this solution is high ($\sigma_{\rm abs808} \approx 1.29 \times 10^{-20}$ cm^2), so when the concentration of Nd^{3+} is relatively high, side pumping must be chosen to ensure designed volume enough to be pumped, as shown in Fig. 5. The absorption loss at 1060 nm is $\alpha_{1060} \approx 0.27$ cm^{-1}. The pumping area is about 1×0.2 (cm), and the designed enough pumped depth is 0.2 cm. To ensure this depth enough pumped, the concentration of Nd^{3+} has an upper-limit value although the solubility tests indicate that the Nd^{3+} doping concentration can reach above 0.8 mol/L. According to Eq. (8), the upper-limit value is around 0.65 mol/L,

$$\frac{I}{I_0} = e^{-\sigma_{\rm abs808} N l} \geq \frac{1}{e}. \tag{8}$$

The threshold inverted population density $\Delta N_{\rm t}$ is about 0.2 mol/L,

$$\Delta N_{\rm t} = \left[\alpha_{1060} - \frac{\ln(R_1 R_2)}{2l} \right] / \sigma_{\rm em}. \tag{9}$$

The threshold pumping energy $E_{\rm t}$ is

$$E_{\rm t} = \frac{\Delta N_{\rm t} h \nu_{\rm p} V}{\eta}, \tag{10}$$

Table 1. Spontaneous Emission Coefficient A_{ed}, Emission Cross Sections σ_{em}, Branch Ratios β and Radiative Lifetime τ_r

Fluorescence Wavelength (nm)	Transition Energy Levels	A_{ed} (s^{-1})	β	σ_{em} ($\times 10^{-20}$ cm^2)	τ_r (μs)
898	$^4F_{3/2} - ^4I_{9/2}$	842	0.57	0.96	682
1060	$^4F_{3/2} - ^4I_{11/2}$	624	0.43	2.54	682

where c/ν_p is the pumping wavelength. V is the pumping volume and $V = 1 \times 0.2 \times 0.2$ (cm)=0.04 cm^3. Take the total pumping efficiency at 808 nm $\eta = 0.5$, then the threshold pumping energy is E_t=250 mJ. If the pulse width τ is 200 μs, then the pumping peak power P_t is E_t/τ=1250 W. If the duty ratio is 2%, the average power is 25 W .

If end pumping scheme is chosen as shown in Fig. 6, the concentration of Nd^{3+} must be decreased. According to Eq. (8), the upper-limit concentration of Nd^{3+} is estimated to be about 0.13 mol/L. If the enough pumping volume is also designed to be about 0.04 cm^3 and other parameters are the same as those used in side pumping scheme, the threshold energy is still about 250 mJ/pulse.

From the above results, we can find that the quantum efficiency of this organic solution is unexpectedly high. We make preliminary analysis as follows. 1) TTA coordinating ligand has a very low vibrational energy and strong coordination ability simultaneously, and forms close coordination spheres shielding the Nd^{3+} from surroundings, which control the non-radiative transitions. 2) Although there exists C–H bonds and probable O–H bonds in solution, they only exist in outer coordination spheres. So high-energy vibrational bonds contribute little to the radiationless transitions of rare earth ions.

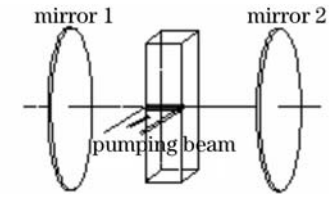

Fig. 5. Sketch of side pumping.

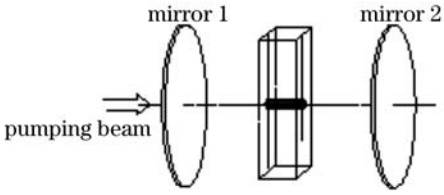

Fig. 6. Sketch of end pumping.

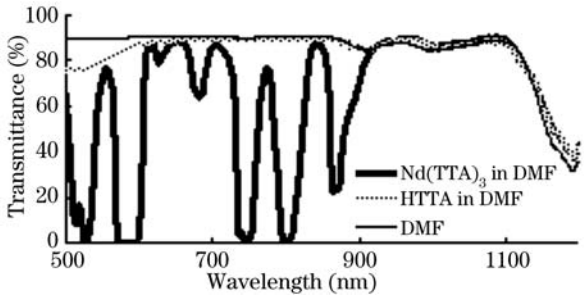

Fig. 7. Transmission spectra of solutions and pure solvent.

In addition, the absorption spectra show that there exists an absorption peak at around 1060 nm which seriously enhances the laser threshold. To analyze the absorption loss around 1060 nm, we prepare the solution of HTTA in DMF and the concentration of TTA is the same as that of $Nd(TTA)_3$ in DMF. The transmission spectra of DMF, HTTA in DMF and $Nd(TTA)_3$ in DMF have been measured as shown in Fig. 7. We can find that the loss at 1060 nm is mainly from solvent. So further experiments must be done to make clear whether the loss at 1060 nm is inherent loss of DMF or the impurities in DMF. If it is caused by impurities in DMF, the threshold may be decreased further by purifying the solvent.

Contrast to inorganic solutions, the organic solution is easily obtained and has low toxicity. However, the troublesome problem of radiationless transition makes them fluorescence unsuccessfully. In this article, the solution of $Nd(TTA)_3$ in DMF is prepared and H is not replaced by D, the solution fluoresces successfully, and the lifetime of fluorescence is very high. The estimated threshold energy is not too high and can be realized in common laboratory. So this organic solution is a potential organic liquid laser material. Furthermore, from the absorption spectrum, we can find that the absorption loss at 1060 nm is mainly caused by solvent, so if the solvent can be purified further, the threshold has the probability to be decreased further. Further work will be done, including analyzing the material to make clear the reason for extraordinary long lifetime and doing experiment of outputting laser.

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