Fluorescence Properties of $Nd:CeF_3$ Crystals

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Fluorescence Properties of Nd : CeF_3 Crystals*

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Four Nd : CeF_3 crystals doped with 0.1, 0.5, 1.0 and 2.0 wt.% Nd^{3+} are grown, their absorption and fluorescence spectra are measured. The absorption bands of Nd : CeF_3 are much wider than that of Nd : YAG. The absorption peak at 353 nm does not depend on Nd^{3+} concentration linearly and there exists no concentration quenching effect while Nd^{3+} concentration is less than 2.0 wt.%. The fluorescence lifetime and the effective stimulated cross section are measured, respectively, as $\tau_r = 300\,\mu s$ and $\sigma_e = 2.4 \times 10^{-20}\ cm^2$.

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In the past decade, the technology of diode lasers has been greatly developed. It also stimulates people to seek new solid laser materials, among which fluoride crystals, such as $YLiF_4$ (Refs. 1 and 2), $LiCaAlF_6$, $LiSrAlF_6$ (Ref. 3), LaF_3 and so on become research emphases. Fan *et al.*[4] made an end-pumped Nd : LaF_3 laser, and thought that long upper energy lifetime and wide absorption band would make Nd : LaF_3 a promising laser material.

We have been undertaking the growth of CeF_3 and have already obtained large high-quality crystals. Based on the growth techniques of CeF_3 crystals, we grew four CeF_3 crystals doped with Nd^{3+} of different concentrations. The purities of CeF_3 and NdF_3 powders are 99.9% and 99.99% respectively. The crystals are grown by Bridgman method in a high vacuum furnace, and the descending rate is 2 mm/h. The concentrations of Nd^{3+} in CeF_3 crystals are 0.1, 0.5, 1.0 and 2.0 wt.% respectively. The crystal size is $\Phi 20 \times 50$ mm. Nd^{3+} ions distribute in the crystals evenly. The crystal is violet, and the color deepens with the increase of Nd^{3+} concentration.

The absorption spectra of Nd : CeF_3 crystals are measured by a Shimadzu UV-265 spectrophotometer. Figure 1 illustrates the comparison of four absorption spectra. The absorption intensity becomes strong with the increase of Nd^{3+} concentration. Generally speaking, the absorption intensity depends on the dopant concentration linearly. Like the absorption peak at 578 nm shown in Fig. 2, other absorption peaks located at 788, 737, 863 and 520 nm surely correspond with the rule. However, the absorption peak at 353 nm is extraordinary. As Nd^{3+} concentration increases to 2.0 wt.%, the peak height increases more quickly and deviates greatly from a line (see Fig. 2). The reason which causes the phenomenon awaits further researches.

The absorption band around 800 nm interests us most for it is commonly used as the pump wavelength in diode semiconductor lasers. Compared with Nd : YAG, the absorption peak of Nd : CeF_3 around 800 nm shifts about 20 nm toward shorter wavelength, and becomes much wider. This characteristic is desirable for the application of lasers, because the wide absorption band does not require so strict a pump wavelength and Nd : CeF_3 crystals can absorb pump light more effectively than Nd : YAG crystals have done.

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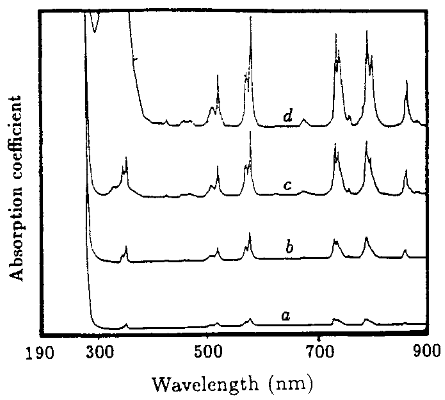

Fig. 1. Absorption spectra of four Nd:CeF$_3$ crystals. *a*—0.1 wt.%, *b*—0.5 wt.%, *c*—1.0 wt.% and *d*—2.0 wt.% Nd^{3+}.

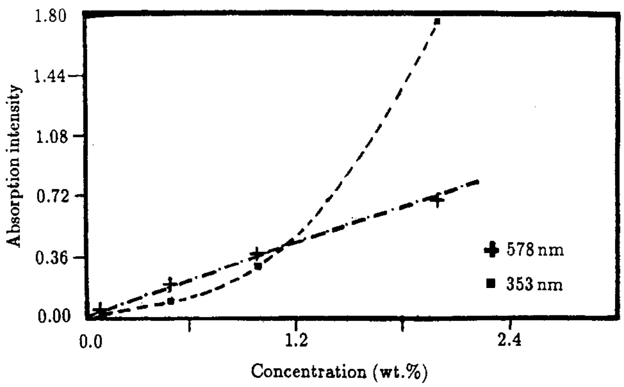

Fig. 2. Absorption intensity vs Nd^{3+} concentration.

The measurement of fluorescence spectra of Nd:CeF$_3$ is accomplished with a fluorescence spectrometer in Shanghai Institute of Optics and Fine Mechanics. Figure 3 gives the result. Between 1.0 and 1.4 μm, there are two fluorescence peaks: one at 1.064 μm, which is stronger and indicates the transition from $^4F_{3/2}$ to $^4I_{11/2}$, the other at 1.328 μm, which is weaker and indicates the transition $^4F_{3/2} \rightarrow {}^4I_{13/2}$.

As for the emitting peak at 1.064 μm, we measured its fluorescence lifetime $\tau_r = 300\,\mu s$ (for 1.0 wt.% Nd^{3+}). It is longer than that of Nd:YAG (200 μs for 1.0 wt.% Nd^{3+}).

Reference 5 gives the relation to calculate the effective stimulated emission cross section σ_e:

$$\sigma_e = \frac{\lambda_g^2 \beta}{8\pi n^2 c \delta v_1 \tau_r},$$

here, λ_g is the wavelength, β is the branching ratio for the transition $^4F_{3/2} \rightarrow {}^4I_{11/2}$, n is the index of refraction, δv_1 is the luminescence effective line width, c is the speed of light and τ_r is the radiative lifetime of the upper energy level $^4F_{3/2}$.

For the transition $^4F_{3/2} \rightarrow {}^4I_{11/2}$, $\lambda_g = 1.064\,\mu m$, $\beta = 0.411$,[6] $n = 1.680$,[7] $\tau_r = 300\,\mu s$, $\delta v_1 = 340\,cm^{-1}$, so the effective stimulated emission cross section is obtained: $\sigma_e = 2.4 \times 10^{-20}\,cm^2$. Comparatively, the σ_e of Nd:LaF$_3$ is $2.2\times10^{-20}\,cm^2$.[4]

The relationship between fluorescence intensity and Nd^{3+} concentration is also argued. As illustrated in Fig. 4, while Nd^{3+} concentration is less than 2.0 wt.%, there exists no concentration quenching effect. It means that higher concentration Nd^{3+} can easily be doped in CeF$_3$ crystals and does not have bad effect on the fluorescence property of Nd:CeF$_3$ crystals. This is another desirable property of Nd:CeF$_3$ crystals. Nevertheless, it has been pointed out that the lifetime of $^4F_{3/2}$ will decrease as Nd^{3+} concentration increases.[4,5] The defects in CeF$_3$ crystals are also observed to increase with the increase of Nd^{3+} concentration, particularly, layer-structure defects occur in the CeF$_3$ crystal doped with 2.0 wt.% Nd^{3+}. How to choose a suitable Nd^{3+} concentration in CeF$_3$ crystals and improve the crystal quality while growing crystals are imminent problems before us in the near future. Our colleagues at the University of Southampton and the University of Sussex in the United Kindom have made an original laser using a Nd:CeF$_3$ crystal we grew, which is pumped by a rhodamine 6G dye laser.[8] The pumping wave is 590 nm, and the threshold value is about 40 mW. The crystal is doped with 1.0 wt.% Nd^{3+} and the size is 5 × 5 × 5 mm.

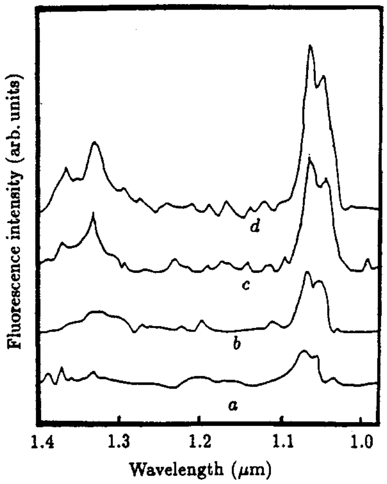

Fig. 3. Fluorescence spectra of four Nd : CeF_3 crystals. *a*—0.1 wt.%, *b*—0.5 wt.%, *c*—1.0 wt.% and *d*—2.0 wt.% Nd^{3+}.

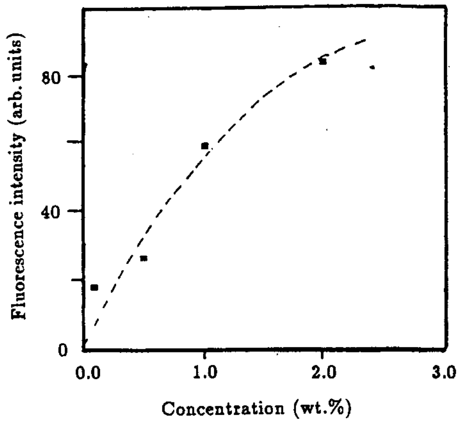

Fig. 4. Fluorescence intensity vs Nd^{3+} concentration (for 1.064 μm peak).

Finally, the following conclusions are obtained: (1) Nd^{3+} can easily enter CeF_3 crystals and distributes evenly. (2) The absorption band of Nd : CeF_3 is broader than that of Nd : YAG and the absorption peaks move about 20 nm toward shorter wavelengths. The height of the absorption peak at 353 nm does not depend on the Nd^{3+} concentration linearly. (3) At the range from 1.0 to 1.4 μm, the fluorescence spectrum of Nd : CeF_3 has two emitting peaks: one at 1.064 μm and the other at 1.328 μm. As for the transition ${}^4F_{3/2} \rightarrow {}^4I_{11/2}$, $\tau_r = 300\,\mu s$, $\sigma_e = 2.4 \times 10^{-20}\,cm^2$ (for 1.0 wt.% Nd^{3+}). While the Nd^{3+} concentration is less than 2.0 wt.%, there is no concentration quenching effect and high concentration Nd^{3+} can be doped in CeF_3 crystals. Because of the characteristics mentioned above, we believe that Nd : CeF_3 is a very promising laser crystal.

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