Optical properties of Dy:YCa\textsubscript{4}O(BO\textsubscript{3})\textsubscript{3} crystal grown by the Czochralski technique

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Abstract

Dy\textsuperscript{3+}-doped YCa\textsubscript{4}O(BO\textsubscript{3})\textsubscript{3} (Dy:YCOB) crystal was successfully grown by the Czochralski technique. The absorption cross section at 453 nm was 0.28 × 10\textsuperscript{−21} cm\textsuperscript{2}, that is related to the \( ^6\text{H}_{15/2} \rightarrow ^4\text{I}_{15/2} \) transition. The Judd-Ofelt parameters \( \Omega_t (t = 2, 4, 6) \) were 1.62 × 10\textsuperscript{−20}, 0.10 × 10\textsuperscript{−20}, 0.41 × 10\textsuperscript{−20} cm\textsuperscript{2}, respectively. The emission cross section assigned to the transition \( ^4\text{F}_{9/2} \rightarrow ^4\text{H}_{13/2} \) was 1.02 × 10\textsuperscript{−21} cm\textsuperscript{2}. The \( ^4\text{F}_{9/2} \) energy level’s fluorescence lifetime was 900 µs.

1. Introduction

The trivalent rare earth (RE) ion Dy\textsuperscript{3+} doped solid material has attracted great attention on account of considerable yellow emission in correspondence with the transition \( ^4\text{F}_{9/2} \rightarrow ^6\text{H}_{13/2} \) located around 580 nm, which has been widely utilized in many fields, for instance, telecommunication, information storage as well as medical treatment [1]. Besides, the absorption transition \( ^6\text{H}_{15/2} \rightarrow ^4\text{I}_{15/2} \) of Dy\textsuperscript{3+} ions is in agreement with InGaN semiconductor’s emission band, extremely advantageous to laser operation. Recent research has concentrated on Dy\textsuperscript{3+} doped different solid materials, including YAG [2], YAP [3], LuLiF\textsubscript{4} [4], LaF\textsubscript{3} [5], ZnWO\textsubscript{4} [6], GdVO\textsubscript{4} [7], KGd(WO\textsubscript{4})\textsubscript{2} [8], YAl\textsubscript{2}(BO\textsubscript{3})\textsubscript{3} [9], etc. So far, visible laser performances have been accomplished in few Dy\textsuperscript{3+} doped laser materials, including Dy:YAG [10], Dy:ZnWO\textsubscript{4} [11], Dy:LLF [12] and Dy:ZBLAN [13].

YCa\textsubscript{4}O(BO\textsubscript{3})\textsubscript{3} (YCOB) crystal has good physical and chemical properties. It is classified into the monoclinic crystal with the Cm space group. The lattice parameters are \( a = 8.046 \) Å, \( b = 15.959 \) Å, \( c = 3.517 \) Å and \( \beta = 101.19^\circ \) with the density of 3.252 g cm\textsuperscript{−3} [14]. To date, there are some analyses on YCOB crystals doped with Tm\textsuperscript{3+} [15], Yb\textsuperscript{3+} [16] and Nd\textsuperscript{3+} [17, 18]. As far as we know, Dy:YCOB’s spectral performance has never been reported.

In this work, we succeeded in synthesizing Dy:YCOB crystal via Czochralski technique. To discuss the spectral properties, the absorbance spectrum, emission spectrum and fluorescence decay curve were detected.

2. Experiments

2.1. Crystal synthesis

We synthesized Dy:YCOB crystal via Czochralski technique. The starting materials were composed of Dy\textsubscript{2}O\textsubscript{3} (99.999%), CaCO\textsubscript{3} (99.999%), Y\textsubscript{2}O\textsubscript{3} (99.999%) and H\textsubscript{3}BO\textsubscript{3} (99.999%) powders. The weighing process was based on stoichiometric ratio and to compensate the loss during the synthesis process, we added 1 wt% additional H\textsubscript{3}BO\textsubscript{3}. The powders were first mixed (3 h) and sintered (900 °C, 7 h, air). Then they were sufficiently ground, mixed, compressed into pellets and sintered (1100 °C, 10 h, air). The weighing and sintering processes followed the chemical equation: \( x\text{Dy}_{2}O_{3} + (1-x)\text{Y}_{2}O_{3} + 8\text{CaCO}_{3} + 6\text{H}_{3}BO_{3} \rightarrow 2\text{Dy}_{x}\text{Y}_{1-x}\text{Ca}_{4}\text{O}(\text{BO}_{3})_{3} + 8\text{CO}_{2} ↑ + 9\text{H}_{2}O \) (\( x = 0.02 \)). The synthesis parameters were shown as follows: growth direction, growth atmosphere, pulling speed, rotation rate, cooling rate, the grown crystal length and diameter. The related parameter values are
crystalline b-axis, nitrogen, 0.5 ~ 1 mm h⁻¹, 10 ~ 20 rpm, 10 ~ 30 °C h⁻¹, 50 mm and 15 mm. Figure 1 demonstrates the polished Dy:YCOB sample. The crystal was cut along the plane (−2 0 1) with the size of 10 mm × 5 mm × 2 mm.

2.2. Structure and spectral examinations
We utilized the x-ray powder diffractometer to obtain the phase calibration of Dy:YCOB crystal. The element content of Dy³⁺ ions was detected by ICP-AES. The absorbance spectra were obtained by a Spectrophotometer (Lambda 900, Perkin-Elmer UV–vis-NIR). The fluorescence spectrum and fluorescence decay curve were measured with a Fluorescence Spectrometer (FLS-980).

Figure 2 demonstrates the XRD pattern of Dy:YCOB powders and pure YCOB. The diffraction peaks coincide with the JCPDS card #50-0403 with no additional ones. The cell parameters of Dy:YCOB were \( a = 8.078 \text{ Å}, b = 16.022 \text{ Å}, c = 3.534 \text{ Å}, \beta = 101.19° \), that are a bit larger than undoped YCOB [14] crystal. The element content and segregation coefficient of Dy³⁺ ions were 1.74 at% and 1.71, respectively.
3. Results and discussion

3.1. Absorbance spectra

Figure 3 presents the absorbance spectra of Dy:YCOB. Within the scope of 200–2000 nm, there are 9 absorption bands centered at 386, 425, 450, 472, 789, 886, 1064, 1254 and 1641 nm. The corresponding transitions were labeled in figure 3. We mainly concentrate on the transition $^6\text{H}_{15/2} \rightarrow ^4\text{I}_{15/2}$ around 450 nm, that is appropriate to be pumped by blue-emitting LDs. At 453 nm, the absorption cross section $\sigma_{abs}$ was $0.28 \times 10^{-21}$ cm$^2$. What’s more, the full width at half maximum (FWHM) was 2.4 nm.

3.2. J–O theory calculations

The Judd-Ofelt theory is generally utilized for analyzing the spectral performance in RE ions doped crystals as well as glasses [19–21].

The experimental line strength $S_{\text{exp}}(J, J')$, calculated line strength $S_{\text{cal}}(J, J')$ as well as the mean wavelength $\bar{\lambda}$ were gathered in table 1, that were calculated from the absorbance spectra. The Root-Mean-Square (RMS) deviation in $S_{\text{exp}}(J, J')$ and $S_{\text{cal}}(J, J')$ is $0.050 \times 10^{-20}$ cm$^2$, manifesting a good consistence between them.

The J–O intensity parameters $\Omega_t$ ($t = 2, 4, 6$) can reflect information about structure and coordination symmetry. The parameter $\Omega_2$ is applied for estimating the covalency and symmetry of crystal field near Dy$^{3+}$ ions [22]. In Dy:YCOB, the value of $\Omega_2$ ($t = 2, 4, 6$) were $1.62 \times 10^{-20}$, $0.10 \times 10^{-20}$, $0.41 \times 10^{-20}$ cm$^2$, respectively and are listed in table 2. In contrast to Dy doped CaGdAlO$_4$ [23], GdScO$_3$ [24], the value of $\Omega_2$ in Dy:YCOB is smaller but larger than that of the relatively symmetrical Dy doped YAG ceramic [25], YSGG [26], CeF$_3$ [27], which implies that the covalency in Dy:YCOB is smaller than CaGdAlO$_4$, GdScO$_3$, but larger than YAG ceramic, YSGG, CeF$_3$.
tunable laser generation. The corresponding to the yellow emission and the FWHM was 15.14 nm, that is benefit of energy storage capacity. The transition $4\text{F}_{9/2} \rightarrow 6\text{H}_{13/2}$ around 581 nm owns the largest $A(J, J')$ and $\beta$, indicating Dy:YCOB has the higher possibility to realize yellow laser operation.

### 3.3. Fluorescence spectrum

Under 450 nm excitation, the fluorescence spectrum of Dy:YCOB ranging from 400 to 800 nm is shown in figure 4. Four emission bands initiate from $4\text{F}_{9/2}$ level to $4\text{H}_{15/2}$, $4\text{H}_{15/2}$, $4\text{H}_{11/2}$, $4\text{H}_{9/2}$ and $4\text{F}_{11/2}$, whose center wavelengths are 485, 581, 671 and 761 nm, respectively. Notably, the yellow emission $4\text{F}_{9/2} \rightarrow 6\text{H}_{13/2}$ is the most intensive, supporting the results described in table 3.

The emission cross section $\sigma_{em}$ is worked out by:

$$\sigma_{em}(\lambda) = \frac{\lambda A(J, J') I(\lambda)}{8\pi c n^2 \int_{\lambda_{band}} I(\lambda) d\lambda}$$  \hspace{1cm} (1)$$

where $I(\lambda)$ is the measured fluorescence intensity. In Dy:YCOB, $\sigma_{em}$ at around 585 nm was $1.02 \times 10^{-21}$ cm$^2$ corresponding to the yellow emission and the FWHM was 15.14 nm, that is beneficial to mode-locked and tunable laser generation.

Figure 5 presents $4\text{F}_{9/2}$ level’s fluorescence lifetime curve. Using the single exponential fitting, the fluorescent lifetime $\tau$ was 900 $\mu$s. The lifetime is higher than most of the oxide host materials, for example, Dy:YAG (400 $\mu$s) [2], Dy:NaGd(WO$_4$)$_2$ (177 $\mu$s) [31], Dy:YAP (185 $\mu$s) [3], suggesting a higher probability of energy storage

### Table 1. The experimental and calculated line strengths of Dy:YCOB.

| Transitions (from $4\text{H}_{13/2}$) | $\lambda$(nm) | $S_{em}(10^{-20}$ cm$^2$) | $S_{rad}(10^{-20}$ cm$^2$) |
|---------------------------------------|---------------|---------------------------|---------------------------|
| $4\text{F}_{7/2} + 4\text{I}_{13/2} + 4\text{M}_{21/2} + 6\text{K}_{27/2}$ | 386           | 0.156                     | 0.127                     |
| $4\text{G}_{11/2}$                    | 425           | 0.026                     | 0.009                     |
| $4\text{I}_{15/2}$                    | 450           | 0.064                     | 0.039                     |
| $4\text{F}_{9/2}$                     | 472           | 0.010                     | 0.013                     |
| $4\text{F}_{7/2} + 4\text{G}_{3/2}$   | 789           | 0.150                     | 0.166                     |
| $4\text{H}_{5/2} + 4\text{F}_{7/2}$   | 886           | 0.408                     | 0.307                     |
| $4\text{H}_{9/2} + 4\text{F}_{9/2}$   | 1064          | 0.354                     | 0.370                     |
| $4\text{H}_{9/2} + 4\text{F}_{11/2}$  | 1234          | 1.792                     | 1.775                     |
| $6\text{H}_{13/2}$                    | 1641          | 0.369                     | 0.415                     |

### Table 2. The J-O intensity parameters $\Omega_i (i = 2, 4, 6)$ ($\times 10^{-20}$ cm$^2$) of dysprosium ions in different materials.

| Materials          | $\Omega_2$ | $\Omega_4$ | $\Omega_6$ | References   |
|--------------------|------------|------------|------------|--------------|
| YCOB               | 1.62       | 0.10       | 0.41       | This work    |
| YSGG               | 0.13       | 0.73       | 1.06       | [26]         |
| YAG ceramic        | 0.20       | 1.11       | 1.46       | [25]         |
| CeF$_3$            | 1.01       | 0.69       | 0.91       | [27]         |
| CaGdAlO$_4$        | 1.80       | 1.00       | 0.50       | [23]         |
| GdScO$_3$          | 2.74       | 2.52       | 0.94       | [24]         |
| PbWO$_4$           | 7.32       | 1.10       | 1.14       | [28]         |

### Table 3. The spontaneous emission possibility $A(J, J')$, fluorescence branching ratio $\beta$ in Dy:YCOB.

| Transitions (from $4\text{F}_{9/2}$) | $\lambda$(nm) | $A$(s$^{-1}$) | $\beta$(%) |
|---------------------------------------|---------------|--------------|------------|
| $4\text{H}_{15/2}$                    | 485           | 51.9         | 11.68      |
| $4\text{H}_{13/2}$                    | 581           | 250.9        | 56.40      |
| $6\text{H}_{11/2}$                    | 671           | 43.0         | 9.66       |
| $6\text{H}_{9/2} + 4\text{F}_{11/2}$  | 761           | 99.0         | 22.26      |
| Radiative lifetime $\tau_{rad}$(ms)   |               |              | 2.2        |
capability. The fluorescence quantum efficiency \( \eta (\eta = \tau_f/\tau_{rad}) \) was 40.0%, which attributes to the cross relaxation caused by high doping concentration. The above-mentioned data denotes that Dy:YCOB is encouraging for realizing yellow laser performance.

### 4. Conclusion

In this article, we succeeded in synthesizing Dy:YCOB by Czochralski technique. At 453 nm the absorption cross section was \( 0.28 \times 10^{-21} \text{ cm}^2 \), corresponding to \( ^{4}\text{H}_{15/2} \rightarrow ^{4}\text{I}_{15/2} \), implying the suitability of pumping by InGaN LDs. The J–O parameters value \( \Omega_i (i = 2, 4, 6) \) were \( 1.62 \times 10^{-20}, 0.10 \times 10^{-20}, 0.41 \times 10^{-20} \text{ cm}^2 \), respectively. The fluorescence spectrum is dominated by the 581 nm yellow emission and the fluorescence branching ratio \( \beta \) was 56.40%. The corresponding emission cross section \( \sigma_{em} \) was \( 1.02 \times 10^{-21} \text{ cm}^2 \) and the FWHM was 15.14 nm. The \( ^{4}\text{F}_{9/2} \) level’s fluorescence lifetime \( \tau_f \) was 900 \( \mu \text{s} \). To sum up, these findings indicate that Dy:YCOB may be applied to succeed in achieving yellow laser oscillation.

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Data availability statement

All data that support the findings of this study are included within the article (and any supplementary files).

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