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The Recent Development of Rare Earth-Doped Borate Laser Crystals

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1. Introduction

As a laser host, borates possess favourable chemical and physical characteristic and higher damnification threshold. Ln$_2$Ca$_3$B$_4$O$_{12}$ (Ln = La, Gd, or Y) double borate family crystals, Ca$_3$(BO$_3$)$_2$ (CBO) and LaB$_3$O$_6$ crystals are the potential laser host materials. They have the suitable hardness and good chemical stability and are moisture free. Furthermore, they melt congruently and can be grown by Czochralski method [1-5], so the high optical quality crystal with large dimension can be easily grown.

The Ln$_2$Ca$_3$B$_4$O$_{12}$ (Ln = La, Gd, or Y) double borate family was first grown by the Czochralsky method with the Nd$^{3+}$ doping [3,5]. The orthorhombic crystallographic structure of Yb$^{3+}$-doped Y$_2$Ca$_3$B$_4$O$_{12}$ (CYB) was determined in Ref. [6], it is made of three sets of M-oxygen distorted polyhedrons and three sets of BO$_3$ planar triangles. The Yb$^{3+}$, Y$^{3+}$ and Ca$^{2+}$ cations occupy statistically the three M sets. This structure disorder contributes to the line broadening of spectra of rare earth doping ions, such as Yb$^{3+}$, Nd$^{3+}$, and can lead to a tunable laser.

In the rare earth-doped CBO crystal, the rare earth ions substitute for the divalent cation (Ca$^{2+}$) and charge compensation is required. Because of the charge compensation effects, the rare earth-doped CBO crystals show partly distorted structure, and the inhomogeneous broadening of the emission similar to amorphous materials can be also expected.[7]

Furthermore, rare earth-doped LaB$_3$O$_6$ crystal can serve as a microchip laser crystal without any processing because of the cleavage of LaB$_3$O$_6$ crystal [8-10].

The study on the rare earth-doped Ca$_3$(BO$_3$)$_2$, LaB$_3$O$_6$ and Ca$_3$Re$_2$(BO$_3$)$_4$ laser crystals will be covered in this chapter. The growth, thermal, optical and spectrum characteristics of these crystals are presented. Their laser characteristics are also covered.

2. Rare earth-doped Ca$_3$(BO$_3$)$_2$ crystals

Ca$_3$(BO$_3$)$_2$ (CBO), which belongs to the trigonal system with the space group R-3C, and the cell parameters are as follows: $a=b=8.6377(8)$ Å, $c=11.849(2)$ Å, $v=765.61$ Å$^3$, $z=6$, and $D_c=3.096$ g/cm$^3$ is a good laser host material. It has the suitable hardness and good chemical
stability and is moisture free. The Ca\(^{2+}\) ion in CBO is surrounded by eight nearest oxygen to form a distorted polyhedron, in which the only symmetry is a two-fold axis passing through the Ca ion. Thereby the calcium ions belong to the C\(_2\) point symmetry. As in this borate the trivalent rare earth ion is introduced on the divalent cation site, a mechanism for charge compensation should be considered.

### 2.1 The crystal growth

Pure, Er\(^{3+}\), Dy\(^{3+}\), and Nd\(^{3+}\)-doped CBO crystals were grown by the Czochralski method along the [0 1 0] orientation (by using the b-axis seeds). The raw materials were analytical grade, CaCO\(_3\), H\(_3\)BO\(_3\), Na\(_2\)CO\(_3\), and some spectral grade, Dy\(_2\)O\(_3\) and Nd\(_2\)O\(_3\). In fact, in the case of rare earth-doped CBO crystal, the co-doping Na\(_2\)CO\(_3\) as charge compensator was introduced to obtain crystal with a large concentration of the rare earth ions. The melt composition ratio of CaCO\(_3\) and H\(_3\)BO\(_3\) is 3:2 for the pure CBO and rare earth (RE)-doped CBO crystals according to the following reactions:

\[
(3-6x)\text{CaCO}_3 + 2\text{H}_3\text{BO}_3 + 3x/2\text{Na}_2\text{CO}_3 + 3x/2\text{Ln}_2\text{O}_3 = (\text{Ca}_{1-2x}\text{Na}_x\text{Ln}_x)_3(\text{BO}_3)_2
\]

\[+ 3\text{H}_2\text{O}↑+ (3-9x/2)\text{CO}_2↑\]

The polished sample of the pure CBO crystal is shown in Fig.2.1. Its optical homogeneity was determined using Zygo optical interferometer (shown in Fig.2.2). Its homogeneity is 2.57x10^{-5}, and its thickness is 5.00 mm.

### 2.2 The thermal characteristic

Measurements of thermal expansion have greatly increased our knowledge of material properties such as lattice dynamics, electronic and magnetic interactions, thermal defects, and phase transitions \[12\]. As a significant part of the power pump is converted into heat inside the material during laser operation, it is important to know its linear thermal expansion coefficients to predict how the material behaves when the temperature increases \[13\]. The figure of linear expansions versus temperature was shown in Fig.2.3. The linear thermal expansion coefficient is defined as:

![Fig. 2.1. The polished sample of the pure CBO crystal](www.intechopen.com)
Fig. 2.2. Interference fringe of CBO crystal.

Fig. 2.3. Thermal expansion of the CBO crystal

\[
\alpha = \frac{1}{T} \frac{\Delta L}{\Delta T} \tag{2.1}
\]

Where \( L \) is the initial length of the sample at room temperature and \( \Delta L \) is the change in length when the temperature changes \( \Delta T \). We can calculate the thermal expansion coefficient from the slope of the linear fitting of the linear relationship between \( \Delta T/T \) and the temperature. In this case, the linear thermal expansion coefficients for different crystallographic directions c-, and b-axes are \( 4.69 \times 10^{-5} \) K\(^{-1} \), \( 1.37 \times 10^{-5} \) K\(^{-1} \), respectively\[^{[14]}\]. The thermal expansion coefficients of the a and b axes are comparable. Thermal expansion
Coefficient along the $c$-axis is about two times larger than those of $b$ and $a$ axes. Although the thermal expansion property of YVO$_4$ crystal has little different from that of CBO crystal, the CBO crystal has no cleavage plane.

\[
\alpha_{ij\text{(CBO)}} = \begin{bmatrix} 1.37 & 0 & 0 \\ 0 & 1.37 & 0 \\ 0 & 0 & 4.69 \end{bmatrix} \times 10^{-5} \degree \text{C} 
\]  

(2.2)

It is well known that the higher the consistency of atom in the crystal structure, the larger the heat expansion coefficient, and vice versa. Obviously, it was demonstrated from the Fig.2.4 that the consistency of atom along $c$ axis is higher than that along $b$ axis, which is comparable to $a$ axis. Therefore, the heat expansion coefficient along $c$ axis is much larger than those along $b$ axis and $a$ axis.

Fig. 2.4. (a) The structure of CBO crystal; (b) The cb section of the structure of CBO crystal

**2.3 The spectrum characteristics**

**2.3.1 The spectrum characteristics of Nd$^{3+}$:Ca$_3$(BO$_3$)$_2$ crystal**

Fig.2.5 shows the transmission spectrum of CBO crystal. It has high transmittance in the 190–3300 nm optical ranges.$^{[14]}$

Fig.2.6 shows the absorption spectrum measured at room temperature in the 300–950 nm ranges.$^{[15]}$. There are three main strong absorption peaks in the spectrum centered at 588, 751 and 808 nm, respectively, corresponding to the transitions from the $4I_{9/2}$ ground state. The
introduction of Na\(^+\) as charge compensator results in the disorder in the local crystal fields acting on the optically active ions.\(^{16}\) Therefore, the absorption and emission peaks can become broadening.\(^{17}\) The full width at half maximum (FWHM) of the absorption peak at 808 nm is about 19 nm, which is larger than that of Nd\(^{3+}\):GdVO\(_4\) (FWHM is 4 nm)\(^{18}\). The absorption coefficient and absorption cross section of Nd\(^{3+}\):CBO crystal at 808 nm are 0.93 cm\(^{-1}\) and 2.12\(\times\)10\(^{-20}\) cm\(^2\), respectively, which are compared with those of Nd\(^{3+}\):GdVO\(_4\) (2.0\(\times\)10\(^{-20}\) cm\(^2\) for \(\pi\) spectrum)\(^{20}\) and Nd\(^{3+}\):YVO\(_4\) (2.0\(\times\)10\(^{-20}\) cm\(^2\) for \(\pi\) spectrum)\(^{19}\). Therefore, Nd\(^{3+}\):CBO crystal is suitable for GaAlAs laser diode pumping.

Fig. 2.7 presents the emission spectrum of Nd\(^{3+}\):CBO crystal, in which there are three main emission peaks in the spectrum centered at 1346, 1060 and 883 nm, respectively, corresponding to the transitions of \(4F_{3/2} \rightarrow I_{J}\) (\(J=13/2, 11/2, 9/2\)). Table 2-1 lists the line strengths and optical parameters of Nd\(^{3+}\) in CBO crystal. Table 2-2 lists the values of intensity parameters of Nd\(^{3+}\) in CBO crystal and those of some other well-known Nd-doped laser crystals. Table 2-3 presents the luminescence parameters of Nd\(^{3+}\) in CBO crystal for the transitions \(4F_{3/2} \rightarrow I_{J}\). The stimulated emission cross-section at 1060 nm is about 8.04\(\times\)10\(^{-20}\) cm\(^2\), which is smaller than those of NdAl\(_3\)(BO\(_3\))\(_4\) (1.43\(\times\)10\(^{-19}\) cm\(^2\))\(^{26}\) and Nd\(^{3+}\):La\(_2\)(WO\(_4\))\(_3\) (11.2\(\times\)10\(^{-20}\) cm\(^2\)) crystals\(^{27}\), but larger than that of Nd\(^{3+}\):LaB\(_3\)O\(_6\) (3.46\(\times\)10\(^{-20}\) cm\(^2\)) crystal\(^{21}\). Fig.2.8 presents the luminescence decay curve excited at 808 nm at room temperature corresponding to the emission line \(4F_{3/2} \rightarrow I_{11/2}\) at 1060 nm. The fluorescence lifetime of \(4F_{3/2}\) is 43.8\(\mu\)s, and the radiative lifetime is 135.03\(\mu\)s. So the luminescent quantum efficiency of the \(4F_{3/2}\) level is about 32.4\%.
Fig. 2.6. The absorption spectrum of Nd$^{3+}$:CBO crystal measured at room temperature.

Fig. 2.7. The emission spectrum of Nd$^{3+}$:CBO crystal.
### Table 2.1. Line strengths and optical parameters of Nd$^{3+}$ in CBO crystal

| Transition final state | Central wavelength $\bar{\lambda}$ (nm) | $S_{\text{nda}} (I \rightarrow J')$ (10$^{-20}$ cm$^2$) | $S_{\text{cal}} (I \rightarrow J')$ (10$^{-20}$ cm$^2$) | $\sigma_{\text{abs}} (\bar{\lambda})$ (10$^{-20}$ cm$^2$) |
|------------------------|--------------------------------------|---------------------------------|---------------------------------|-------------------|
| $4I_{9/2} \rightarrow 4D_{5/2}$ | 359 | 0.837 | 0.772 | 5.342 |
| $4G_{9/2}$ | 528 | 0.920 | 0.949 | 2.020 |
| $4G_{5/2}$ | 588 | 5.529 | 5.529 | 4.419 |
| $4S_{3/2}$ | 751 | 4.564 | 4.620 | 1.373 |
| $3H_{9/2}$ | 808 | 2.475 | 2.377 | 2.303 |

### Table 2.2. The intensity parameters of Nd$^{3+}$ in CBO crystal and those of some other well-known Nd-doped laser crystals

| Crystal | $\Omega_2$ (10$^{-20}$ cm$^2$) | $\Omega_4$ (10$^{-20}$ cm$^2$) | $\Omega_6$ (10$^{-20}$ cm$^2$) | $4F_{5/2} \rightarrow 4I_{11/2}$ | Ref. |
|---------|-------------------------------|-------------------------------|-------------------------------|-------------------------------|------|
| CBO | 4.63 | 2.40 | 10.4 | 0.476 | 15 |
| NAB | 6.07 | 9.14 | 14.58 | 0.518 | 21 |
| LaSc$_3$(BO$_3$)$_4$ | 5.349 | 4.124 | 3.852 | 0.470 | 22 |
| LaB$_2$O$_6$ | 0.54 | 2.31 | 4.51 | 0.538 | 23 |
| YVO$_4$ | 4.667 | 2.641 | 4.047 | 0.509 | 24 |
| GdVO$_4$ | 12.629 | 4.828 | 8.425 | 0.519 | 25 |
| Ca$_2$Sc$_2$Ge$_3$O$_{12}$ | 0.99 | 4.24 | 7.14 | 0.524 | 26 |

### Table 2.3. The luminescence parameters of Nd$^{3+}$ in CBO crystal for the transitions $4F_{3/2} \rightarrow 4I_{J}$.

| Radiation transition | Radiation wavelength (nm) | $\Lambda (I \rightarrow J')$ (s$^{-1}$) | $\beta_{IJ}$ |
|----------------------|---------------------------|---------------------------------|--------------|
| $4F_{3/2} \rightarrow 4I_{9/2}$ | 883 | 3157 | 0.426 |
| $4I_{11/2}$ | 1060 | 3529 | 0.476 |
| $4I_{13/2}$ | 1346 | 720 | 0.097 |
| $4I_{15/2}$ | 1852 | 37.8 | 0.001 |

### 2.3.2 The spectrum characteristics of Er$^{3+}$:Ca$_3$(BO$_3$)$_2$ crystal

Figure 2.9 shows the room temperature (RT) polarized absorption spectra in the 200–1600 nm spectra region of Er$^{3+}$ in the CBO crystal[28]. It consists of a number of groups of lines corresponding to transitions between the ground state $4I_{15/2}$ and higher energy states inside the $4f^{11}$ electronic configuration of the Er$^{3+}$ ion. Due to the high Er$^{3+}$ concentration of the CBO sample, the spectra are well defined. In this sample, eleven absorption bands clearly are located at 1517, 978, 793, 652, 523, 486, 450, 403, 380, 365, and 257 nm, which correspond to the transitions from $4I_{15/2}$ to $4I_{13/2}$, $4I_{11/2}$, $4I_9/2$, $4F_{9/2}$, $2H_{11/2}$, $4F_{7/2}$, $4F_{5/2}$, $2H_{9/2}$, $4G_{11/2}$, $4G_{9/2}$ and $4D_{5/2}$, respectively.
Fig. 2.8. The luminescence decay curve excited at 808 nm at room temperature corresponding to the emission line $^{4}I_{3/2} \rightarrow ^{4}I_{11/2}$ at 1060 nm.

Fig. 2.10 displays the RT polarized emission spectra (in the 1400-1700 nm spectral range). The emission spectra obtained under $^{4}I_{13/2}$ multiplet excitation at 980 nm. And the fluorescence decay curve of the $^{4}I_{13/2} \rightarrow ^{4}I_{15/2}$ transition is also shown in Fig. 2.11. From the curve, the fluorescence lifetime was 2.54 ms.

Fig. 2.12 shows the cross sections of the Er$^{3+}$ ions in the CBO crystal. (a) The absorption cross-section, (b) the emission cross-section derived by the reciprocity method (RM), (c) the emission cross-section derived by the Füchtbauer-Ladenburg (FL) formula, and (d) the emission cross-section derived by the modified method. The maximum values of the emission cross section centered at about 1530 nm are $9.67 \times 10^{-21}$ cm$^2$ for the $\pi$ spectrum and $7.43 \times 10^{-21}$ cm$^2$ for the $\sigma$ spectrum, which can be compared with those reported for other Er$^{3+}$ doped laser crystals [9.3$\times 10^{-21}$ cm$^2$ for Er$^{3+}$:LaGaO$_3$,$^{29}$ 4.5$\times 10^{-21}$ cm$^2$ for Er$^{3+}$:YAG (yttrium aluminum garnet),$^{30}$ and 3.1$\times 10^{-21}$ cm$^2$ for Er$^{3+}$:YAlO$_3$]$^{30}$. The wavelength dependence of the gain cross-section for several values of population inversion $P$ ($P = 0, 0.1, 0.2, \ldots, 1$) is shown in Fig. 2.13. A wide tunable wavelength range from 1530 to 1650 nm is expected when the population inversion $P$ is larger than 0.5, which is encountered in a free-running laser operation. Table 2-4 displays the experimental, theoretical oscillator strengths for Er$^{3+}$ ions in CBO crystal. Table 2-5 presents the comparison of the Judd-Ofelt parameters of Er$^{3+}$:CBO and other Er$^{3+}$ doped crystals. Generally, the $\Omega_2$ parameter is sensitive to the symmetry of the rare earth site and is strongly affected by covalency between rare earth ions.
Fig. 2.9. Room temperature (RT) polarized absorption spectra of Er$^{3+}$ in the CBO crystal.

Fig. 2.10. Room temperature polarized emission spectra of the Er$^{3+}$:CBO single crystal.
and ligand anions. In the present work, the parameter $\Omega_2$ is high, but it is lower than those for YVO$_4$ and NaBi(WO$_4$)$_2$. This possibly indicated that the Er$^{3+}$ doped CBO crystals are more covalent in character. Table 2-6 displays the radiative transition probabilities $A_{J\prime J}$, fluorescence branching ratios $\beta_{J\prime J}$, and radiative decay time $\tau$, for Er$^{3+}$ ions in CBO crystal. From the measured and calculated radiative lifetimes, the luminescent quantum efficiency $\eta=\tau_f/\tau$, for the $^4_{13/2} \rightarrow ^4_{15/2}$ transition of the Er$^{3+}$ :CBO crystal is found to be approximately 84.4%.

Fig. 2.11. Fluorescence decay curve of the $^4_{13/2} \rightarrow ^4_{15/2}$ transition

Fig. 2.12. The cross sections of the Er$^{3+}$ ions in the CBO crystal. (a) The absorption cross-section, (b) the emission cross-section derived by the RM, (c) the emission cross-section derived by the FL, and (d) the emission cross-section derived by the modified method.
Fig. 2.13. The wavelength dependence of the gain cross-section for several values of population inversion $P (P = 0, 0.1, 0.2, \ldots, 1)$ (a) for $\pi$ spectrum (b) for $\sigma$ spectrum,
Table 2.4. Experimental, theoretical oscillator strengths for Er$^{3+}$ ions in CBO Crystal

| Transition (from $^4I_{15/2}$) | $\lambda$(nm) | $f_{\pi}$ $\times 10^6$ | $f_{\sigma}$ $\times 10^6$ |
|--------------------------------|--|---|---|
| $^4I_{13/2}$ | 1517 | 2.73 | 2.46 |
| $^4I_{11/2}$ | 978 | 0.72 | 0.97 |
| $^4I_{9/2}$ | 793 | 0.56 | 0.70 |
| $^4F_{9/2}$ | 652 | 3.82 | 4.32 |
| $^2H_{11/2}$ | 523 | 8.73 | 8.95 |
| $^4F_{7/2}$ | 486 | 4.17 | 4.38 |
| $^4F_{5/2}$ | 450 | 0.91 | 1.09 |
| $^2H_{9/2}$ | 403 | 1.48 | 1.49 |
| $^4G_{11/2}$ | 380 | 16.36 | 16.12 |
| $^4G_{9/2}$ | 365 | 3.85 | 4.11 |
| $^4D_{5/2}$ | 257 | 20.37 | 19.93 |

Table 2.5. Comparison of Judd-Ofelt parameter $\Omega_2$ of Er$^{3+}$: CBO and other Er$^{3+}$ doped crystals

| Transition | $\Omega_2$ ($10^{-20}$ cm$^2$) | $\Omega_2$ ($10^{-20}$ cm$^2$) | $\Omega_2$ ($10^{-20}$ cm$^2$) | Ref. |
|------------|--------------------------------|--------------------------------|--------------------------------|------|
| Ca$_3$(BO$_3$)$_2$ $\Omega_{\text{eff}}^2$ | 5.35 | 4.95 | 2.29 | 28 |
| YAG | 0.66 | 0.81 | 0.71 | 31 |
| YVO$_4$ | 13.45 | 2.23 | 1.67 | 32 |
| LiYF$_4$ | 1.92 | 0.26 | 1.96 | 33 |
| NaBi(WO$_4$)$_2$ | 5.50 | 1.00 | 0.71 | 34 |
| Y$_2$O$_3$ | 4.59 | 1.21 | 0.48 | 35 |

Table 2.6. Radiative transition probabilities $A_{\text{md}}$, fluorescence branching ratios $\beta_{\text{md}}$, and radiative decay time $\tau_r$ for Er$^{3+}$ ions in CBO crystal.
2.3.3 The spectrum characteristics of Dy\(^{3+}:\text{Ca}_3(\text{BO}_3)_2\) crystal

Fig. 2.14 shows the room temperature absorption spectrum of Dy\(^{3+}:\text{Ca}_3(\text{BO}_3)_2\) crystal, which consists of nine groups of bands.\(^{[36]}\) They are associated with the observed transitions from the \(6\text{H}_{15/2}\) ground state. The wavelengths corresponding to the transitions are listed in Table 2-7, which also displays the integrated absorbance, the measured and calculated line strengths of Dy\(^{3+}\): CBO crystal. The room temperature emission spectrum is presented in Fig.2.15, in which there are several bands centered at 479, 575, 663, and 750 nm corresponding to \(4\text{F}_{9/2} \rightarrow 6\text{H}_{15/2}, 6\text{H}_{13/2}, 6\text{H}_{11/2}, \) and \(6\text{H}_{9/2} + 6\text{F}_{11/2}\) transitions, respectively. Fig.2.16 displays the fluorescence decay curves of \(4\text{F}_{9/2} \rightarrow 6\text{H}_{13/2}\) and \(4\text{F}_{9/2} \rightarrow 6\text{H}_{15/2}\) transitions of Dy\(^{3+}\): CBO crystal excited at 397 nm, from which the fluorescence lifetime of the \(4\text{F}_{9/2}\) of Dy\(^{3+}\) in CBO is calculated to be about 1.275 ms. Table 2-8 presents the intensity parameters of Dy\(^{3+}\): CBO crystal and the comparison between the intensity parameters of Dy\(^{3+}\) doped in some other laser crystals and in CBO. The spectroscopic quality factor \(X = \frac{\Omega_4}{\Omega_6}\) for the Dy\(^{3+}\) in CBO is determined to be 2.982. This value for \(X\) suggests that Dy\(^{3+}\): CBO is a promising material for efficient laser action when compared with Dy\(^{3+}\): YVO\(_4\) for which \(X = 2.132\). Table2-9 displays the experimental and calculated oscillator strengths for absorption \(6\text{H}_{15/2}\) ground state of Dy\(^{3+}\) ion in CBO crystal. Table 2-10 demonstrates the calculated radiative transition rate, the branching ratios, and the radiative lifetime for the emission from the \(4\text{F}_{9/2}\) level of Dy\(^{3+}\): CBO. The fluorescence branching ratio is a critical laser parameter because it also characterizes the possibility of attaining stimulated emission from a specific transition. The \(4\text{F}_{9/2} \rightarrow 6\text{H}_{13/2}\) transition has large value of the branching ratios, thereby suggesting that this transition may result in the strongest laser action. This work gives a consistent optical characterization of Dy\(^{3+}\): CBO crystal, which may realize a yellow solid state laser device.

![Absorption spectrum of CBO: Dy\(^{3+}\) crystal](https://www.intechopen.com)
Fig. 2.15. The room temperature emission spectrum of Dy$^{3+}$: CBO (excited by 397 nm).

| Excited state | Wavelength (nm) | Γ (nm/cm) | $S_{\text{mea}}$ (10$^{-20}$cm$^2$) | $S_{\text{cal}}$ (10$^{-20}$cm$^2$) |
|---------------|-----------------|----------|-----------------|-----------------|
| $^6\text{H}_{11/2}$ | 1692 | 2.755 | 0.384 | 0.949 |
| $^6\text{F}_{11/2},^4\text{H}_{9/2}$ | 1262 | 35.411 | 6.619 | 6.564 |
| $^6\text{H}_{7/2},^6\text{F}_{9/2}$ | 1076 | 1.823 | 0.399 | 0.026 |
| $^6\text{F}_{7/2}$ | 901 | 3.841 | 1.001 | 0.698 |
| $^6\text{F}_{5/2}$ | 800 | 1.244 | 0.364 | 0.218 |
| $^4\text{G}_{11/2}$ | 449 | 0.327 | 0.167 | 0.029 |
| $^4\text{M}_{21/2},^4\text{K}_{17/2}$ | 386 | 1.511 | 0.891 | 0.070 |
| $^4\text{H}_{11/2}$ | 366 | 0.440 | 0.272 | 0.512 |
| $^6\text{F}_{7/2}$ | 351 | 1.291 | 0.830 | 0.978 |

Table 2.7. The integrated absorbance, the measured and calculated line strengths of Dy$^{3+}$: CBO crystal

| Crystals | $\Omega_2$ | $\Omega_4$ | $\Omega_6$ | Reference |
|----------|------------|------------|------------|-----------|
| CBO      | 5.216      | 1.858      | 0.623      | This work |
| Y$_3$Sc$_2$Ga$_3$O$_{12}$ | 0.134 | 0.7261 | 0.61 | 36 |
| LiYF$_4$ | 2.01       | 1.34       | 2.39       | 11        |
| YVO$_4$  | 6.59       | 3.71       | 1.74       | 37        |
| YAl$_5$(BO$_3$)$_4$ | 10.04 | 2.04 | 2.31 | 38 |
| KY(WO$_4$)$_2$ | 23.24 | 3.329 | 2.359 | 1 |

Table 2.8. Comparison between the intensity parameters of Dy$^{3+}$ doped in some laser crystals and in CBO ($\Omega_i$ are in units of 10$^{-20}$ cm$^2$)
Fig. 2.16. The fluorescence decay curves of $^4F_{9/2} \rightarrow ^6H_{13/2}$ and $^4F_{0/2} \rightarrow ^6H_{15/2}$ transitions of Dy$^{3+}$: CBO crystal (by 397 nm excited)

Table 2.9. The experimental and calculated oscillator strength $f \times 10^6$ for absorption $^6H_{15/2}$ ground state of Dy$^{3+}$ ion in CBO crystal. Also the $\Delta f \times 10^6$ between the calculated and experimental oscillator (note: rms $f=0.883 \times 10^{-6}$)
Table 2.10. The calculated radiative transition rate, the branching ratios, and the radiative lifetime for the emission from the $^{4}F_{9/2}$ level of Dy$^{3+}$: CBO

| Start levels   | Wavelength (nm) | $A$ (s$^{-1}$) | $\beta$ (A) | $\tau$ (µs) |
|----------------|-----------------|---------------|-------------|-------------|
| $^{6}H_{15/2}$ | 479             | 90.209        | 0.115       | 1275        |
| $^{6}H_{13/2}$ | 575             | 612.77        | 0.781       |             |
| $^{6}H_{11/2}$ | 663             | 66.561        | 0.085       |             |
| $^{6}H_{15/2}+^{6}F_{11/2}$ | 750 | 15.066        | 0.019       |             |

3. Rare earth-doped Ca$_3$Re$_2$(BO$_3$)$_4$ [Re=Y,Gd] crystals

3.1 The crystal structure

An ORTEP drawing of the structure fragment of crystal Yb:Ca$_3$Y$_2$(BO$_3$)$_4$ is shown in Fig. 3.1a. Fig. 3.1b shows the packing diagram of cell units of Yb:Ca$_3$Y$_2$(BO$_3$)$_4$ crystal.[8] In Yb$^{3+}$:Ca$_3$Y$_2$(BO$_3$)$_4$ crystal structure, cations occupy three independent sites statistically, which is similar to Ca$_3$La$_2$(BO$_3$)$_4$[39] and Ba$_3$La$_2$(BO$_3$)$_4$[40]. The basic structure of Yb:Ca$_3$Y$_2$(BO$_3$)$_4$ is composed of three sets of M-oxygen distorted polyhedrons, and three sets of BO$_3$ planar triangles. Ca$^{2+}$ and Y$^{3+}$ ions occupy three independent sites statistically. M1, M2 and M3 were suggested to stand for these three independent sites respectively. They are coordinated by eight oxygen ions to form the distorted polyhedron. From the value of the electronic density of each independent site, and the ion charges of Ca$^{2+}$ and Y$^{3+}$ ions as well as the ratio of their atomic number in the formula, we can calculate their ratio in each site. Concretely, the method for calculating the ratio of Yb/Ca is as follows: we suggest the average atomic number of M$_n$ atom:

$$\bar{Z}_n = Z_Y X_n + Z_{Ca} Y_n$$  \hspace{1cm} (3.1)

Here the atomic number of Y and Ca are: $Z_Y = 39, Z_{Ca} = 20$, and $X_n$ is the occupancies of Y$^{3+}$ ion in M$_n$, $Y_n$ is the occupancies of Ca$^{2+}$ ion M$_n$,

$$X_n + Y_n = 1$$  \hspace{1cm} (3.2)

As we know:

$$\frac{\bar{Z}_n}{Z_{n+1}} = \frac{\rho_n}{\rho_{n+1}}$$  \hspace{1cm} (3.3)

in which $\rho$ is the electronic density of M$_n$. According the formula Ca$_3$Y$_2$(BO$_3$)$_4$, we can get:

$$X_1 + X_2 + X_3 = 2$$  \hspace{1cm} (3.4)

$$Y_1 + Y_2 + Y_3 = 3$$  \hspace{1cm} (3.5)

Combing all the above equations, we can calculate the ratio of Y/Ca in the three sites M1, M2 and M3, the results are as follows: M1=0.61Y+0.39Ca, M2=0.445Y+0.555Ca and M3=0.25Y+0.75Ca. Yb$^{3+}$ ions substitute Y$^{3+}$ ions entering these three lattices. The fact that the
statistical distribution of Ca$^{2+}$, Y$^{3+}$ and Yb$^{3+}$ ions might lead to the increase of width of spectra of this crystal. As a matter of fact, this was confirmed by the next part of this report. Table 3-1 presents the atomic coordinates and thermal parameters.

|     | x     | y     | z     | Wyckoff | U(eq) |
|-----|-------|-------|-------|---------|-------|
| M(1)| 1750  | 2500  | 9687  | 4c      | 20(1) |
| M(2)| -193  | 4164  | 6788  | 8d      | 30(1) |
| M(3)| -1999 | 3738  | 11589 | 8d      | 32(1) |
| O(1)| 4458  | 3275  | 10709 | 8d      | 40(20)|
| O(2)| 1200  | 2500  | 12380 | 4c      | 40(30)|
| O(3)| -1536 | 2500  | 9990  | 4c      | 40(30)|
| O(4)| 1971  | 4849  | 5098  | 8d      | 40(40)|
| O(5)| -970  | 5456  | 8143  | 8d      | 40(50)|
| O(6)| -2537 | 3256  | 7768  | 8d      | 40(30)|
| O(7)| 1120  | 3993  | 9410  | 8d      | 40(80)|
| B(1)| 5110  | 2500  | 11350 | 4c      | 18(4)|
| B(2)| 2790  | 2500  | 6470  | 4c      | 13(3)|
| B(3)| 3267  | 5404  | 5432  | 8d      | 21(3)|

$U_{eq}$ is defined as one third of the trace of the orthogonalized Uij tensor. The Ca$^{2+}$ and Y$^{3+}$ ions coexist in M1, M2 and M3 positions statistically.

Table 3.1. Atomic coordinates ($\times 10^4$) and thermal parameters ($\text{Å}^2 \times 10^3$)

Fig. 3.1a. A structure fragment of crystal Yb:Ca$_3$Y$_2$(BO$_3$)$_4$
3.2 The crystal growth

The crystal was grown by Czochralski method. The crystal growth was carried out in a DGL-400 furnace with KGPF25-0.3-2.5 power supply of intermediate frequency. An Ir-crucible of 60mm diameter by 35 mm high was used.

The initial compounds for the synthesis were AR grade CaCO$_3$, H$_3$BO$_3$ and 4N Y$_2$O$_3$,Yb$_2$O$_3$. A Ca$_3$Y$_2$(BO$_3$)$_4$ compound with 5mol%Yb$_2$O$_3$-doped was synthesized according to the following reactions:

$$6\text{CaCO}_3+0.05\text{Yb}_2\text{O}_3+1.95\text{Y}_2\text{O}_3+8\text{H}_3\text{BO}_3 \rightarrow 2\text{Ca}_3\text{Yb}_{0.05}\text{Y}_{1.95}(\text{BO}_3)_4+6\text{CO}_2+12\text{H}_2\text{O}$$

Thoroughly mixed and pressed mixtures of the stoichiometric composition were slowly heated to 500°C at a rate of 50°C/h and further to the synthesis temperature at the rate of 150°C/h in a Pt-crucible. Then the sintered compound was melt in the Ir-crucible under N$_2$ atmosphere, at a temperature which was 50°C higher than the crystallization temperature, and was kept at this temperature for one hour. Seeding was performed on the Ir-wire. The nitrogen gas pressure is 0.04MPa. Pulling rate and the rotation rate was 1.3~1.5mm/h and 12-20 r.p.m, respectively. When the growth process was ended, the crystal was drawn out of the melt surface and cooled down to room temperature at a rate of 10~30°C/h. The transparent single crystals with a size up to φ20 mm×55 mm was obtained (as shown in Fig.3.2). Fig.3.3 shows the interference fringe of the grown Yb$^{3+}$:Ca$_3$Y$_2$(BO$_3$)$_4$ crystal, the optical homogeneity is $4\times10^{-5}$, it means the crystal has excellent quality. Table 3-2 presents the parameters of crystal growth. In order to estimate the solubility of the doping ion in the
crystal, it is customary to use an “effective segregation coefficient” defined as \[ k_e = \frac{C_s}{C_l} \]

where \( C_s \) is the doped-ion concentration in the crystal and \( C_l \) is the doped-ion concentration in the melt, since the concentration of Yb\(^{3+}\) ion in Yb\(^{3+}\):CYB was measured to be 1.56 wt% by electron probe microanalysis method, the effective segregation coefficient of Yb\(^{3+}\) ion in CYB crystal was calculated to be 0.97.

Fig. 3.2. The grown Yb\(^{3+}\):Ca\(_3\)Y\(_2\)(BO\(_3\))\(_4\) crystal
Fig. 3.3. Interference fringe of Yb\textsuperscript{3+}:Ca\textsubscript{3}Y\textsubscript{2}(BO\textsubscript{3})\textsubscript{4} crystal.

| Nitrogen gas (MPa) | 0.04 | Rotate rate (rpm) | 12-20 |
|--------------------|------|-------------------|-------|
| Soaping temp. (°C) | 1460 | Decreasing rate of temp. (°C/day) | 2~10 |
| Soaping time (h)  | 0.5  | Pulling rate (mm/h) | 1.3~1.5 |
| Crucible size (mm) | φ60mm×35mm | Annealing rate (°C/h) | 10~50 |
| Seeding temp. (°C) | 1410 | Crystal size (mm) | φ20 mm×55 mm |

Table 3.2. The parameters of crystal growth.

### 3.3 The spectrum characteristics

#### 3.3.1 The spectrum characteristics of Tm\textsuperscript{3+}:Ca\textsubscript{3}Y\textsubscript{2}(BO\textsubscript{3})\textsubscript{4} crystal

Fig.3.4 presents the absorption spectrum of Ca\textsubscript{3}Y\textsubscript{2}(BO\textsubscript{3})\textsubscript{4}:Tm\textsuperscript{3+} crystal, in which there are seven peaks centered at 1684 nm, 1215 nm, 792.4 nm, 687.9 nm, 475.6 nm, 359.9 nm, and 262.9 nm, corresponding to the transitions from \textsuperscript{3}H\textsubscript{6} to \textsuperscript{3}F\textsubscript{4}, \textsuperscript{3}H\textsubscript{5}, \textsuperscript{3}H\textsubscript{4}, \textsuperscript{3}F\textsubscript{3}, \textsuperscript{1}G\textsubscript{4}, \textsuperscript{1}D\textsubscript{2}, and \textsuperscript{1}I\textsubscript{6} respectively\textsuperscript{[42]}. The FWHM at 792.4 nm is about 33.9 nm and the cross-section is about 1.5×10\textsuperscript{-21} cm\textsuperscript{2}, which is benefit to the pumping of commercial laser diode. The room temperature emission spectrum of Ca\textsubscript{3}Y\textsubscript{2}(BO\textsubscript{3})\textsubscript{4}:Tm\textsuperscript{3+} crystal excited at 792.4 nm is presented in Fig.3.5, in which there is a broad emission band ranged from 1332.6 nm to 1429.1 nm. The FWHM of this emission band is 63.6 nm, which is resulted from the statistical distribution of Ca\textsuperscript{2+}, Y\textsuperscript{3+} and Tm\textsuperscript{3+} ions.
Fig. 3.4. The absorption spectrum of Ca$_3$Y$_2$(BO$_3$)$_4$:Tm$^{3+}$ crystal

Fig. 3.5. The room temperature emission spectrum of Ca$_3$Y$_2$(BO$_3$)$_4$:Tm$^{3+}$ crystal excited at 792 nm
3.3.2 The spectrum characteristic of Er$^{3+}$:Ca$_3$Y$_2$(BO$_3$)$_4$ crystal

Fig. 3.6 presents the absorption spectrum of Ca$_3$Y$_2$(BO$_3$)$_4$:Er$^{3+}$ crystal, in which there are twelve peaks centered at 244.6 nm, 257.3 nm, 366.4 nm, 379.9 nm, 408.1 nm, 452 nm, 522.7 nm, 544.2 nm, 654.3 nm, 799.3 nm, 976.6 nm, 1518.4 nm, correspond to the transitions from $^4I_{15/2}$ to $^2I_{11/2}$, $^4D_{5/2}$+$^4D_{7/2}$, $^4G_{9/2}$, $^2G_{9/2}$+$^4F_{9/2}$+$^2H_{9/2}$, $^4F_{5/2}$, $^2H_{11/2}$, $^4S_{3/2}$, $^4F_{9/2}$, $^4I_{9/2}$, $^4I_{13/2}$, respectively$^{[43]}$. The room temperature emission spectrum of Ca$_3$Y$_2$(BO$_3$)$_4$:Er$^{3+}$ crystal excited at 530 nm is presented in Fig. 3.7, in which there is a broad emission band ranged from 1429.4 nm to 1662.8 nm. The FWHM of this emission band is 126 nm. The factor contributing to this broad emission is the disordered structure of the crystal, namely, Ca$^{2+}$ and Y$^{3+}$ ions are statistically situated in three different lattices in the crystal structure determined by us. This broad emission will benefit the energy storage. Therefore, this crystal should be useful as a tunable infrared (in the eye-safe region at 1.54 $\mu$m) laser crystal.

Based on the measured absorption spectra of three commutative perpendicularity directions and J-O theory, the J-O parameters are calculated to be $\Omega_2$=1.214×10$^{-20}$ cm$^2$, $\Omega_4$=1.585×10$^{-20}$ cm$^2$, $\Omega_6$=1.837×10$^{-20}$ cm$^2$. The oscillator strength, radiative transition probability $A$, radiative lifetime $\tau_{rad}$ and the fluorescent branching ratio $\beta$ are also calculated, which are shown in Table 3-3~4. The stimulated emission cross-section at 1535nm is 6.4×10$^{-21}$ cm$^2$ and the integral cross-section at 1535 nm is 2.7×10$^{-18}$ cm$^2$. The lifetime measured is about 792 $\mu$s with the luminescent quantum efficiency of 20.8%.

Fig. 3.6. The absorption spectrum of Ca$_3$Y$_2$(BO$_3$)$_4$:Er$^{3+}$ crystal

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Fig. 3.7. The room temperature emission spectrum of $\text{Ca}_3\text{Y}_2(\text{BO}_3)_4$ crystal excited at 530 nm

| Wavelength $\lambda$(nm) | $f_{\text{exp}}\times10^6$ | $f_{\text{cal}}\times10^6$ |
|--------------------------|---------------------------|-------------------------|
| 258                      | 14.380                    | 0.213                   |
| 368                      | 3.276                     | 6.595                   |
| 381                      | 11.034                    | 0.018                   |
| 453                      | 1.261                     | 1.015                   |
| 491                      | 1.895                     | 3.161                   |
| 524                      | 6.618                     | 3.614                   |
| 654                      | 2.926                     | 2.910                   |
| 800                      | 0.681                     | 0.411                   |
| 974                      | 0.728                     | 0.876                   |
| 1534                     | 2.219                     | 2.076                   |

$rms\Delta f=5.864\times10^{-6}$

Table 3.3. Oscillator strengths of 7 at% $\text{Er}^{3+}$ in $\text{Ca}_3\text{Y}_2(\text{BO}_3)_4$ crystal
Table 3.4. Radiative transition probability $A$, radiative lifetime $\tau_{\text{rad}}$ and fluorescent branching ratio $\beta$ of Er$^{3+}$ in 7 at%Er$^{3+}$:Ca$_3$Y$_2$(BO$_3$)$_4$ crystal at room temperature.

### 3.3.3 The spectrum characteristic of Yb$^{3+}$:Ca$_3$Y$_2$(BO$_3$)$_4$ crystal

Fig. 3.8 presents the absorption spectrum of Ca$_3$Y$_2$(BO$_3$)$_4$:Yb$^{3+}$ crystal, in which there is a broad absorption band ranged from 850 nm to 1000 nm, corresponding to the transition from $^2F_{7/2} \rightarrow ^2F_{5/2}$. The FWHM at 977 nm is about 12 nm and the cross-section is about $1.9 \times 10^{-20}$ cm$^2$, which is benefit to the pumping of commercial laser diode. Table 3.5 shows the absorption properties of some ytterbium-doped compounds. The room temperature emission spectrum of Ca$_3$Y$_2$(BO$_3$)$_4$:Yb$^{3+}$ crystal excited at 977 nm is presented in Fig. 3.9, in which there is a broad emission band ranged from 927.95 nm to 1102.7 nm. The FWHM of this emission band is 98 nm and its peak value is located at 1025 nm, which is resulted from the statistical distribution of Ca$^{2+}$, Y$^{3+}$ and Yb$^{3+}$ ions.
Fig. 3.8. The Absorption spectrum of Yb$^{3+}$:Ca$_3$Y$_2$(BO$_3$)$_4$ crystal at room temperature

Fig. 3.9. The room temperature emission spectrum of Ca$_3$Y$_2$(BO$_3$)$_4$:Yb$^{3+}$ crystal excited at 977 nm
| Compound         | n (nm) | p (nm) | \( \lambda_p \) (nm) | \( \sigma_a \times 10^{-20} \text{ cm}^2 \) | FWHM (nm) | References |
|------------------|--------|--------|------------------------|---------------------------------------------|-----------|------------|
| 5at% Yb:CYB      |        |        | 977                    | 1.9                                         | 12        | [6]        |
| 2at% Yb:YCOB     |        |        | 976.1                  | 0.94                                        | 3         | [44]       |
| 1at% Yb:Y2SiO5   |        |        | 977.4                  | 2.1                                         | 7         | [45]       |
| 1at% Yb:Sc2SiO5  |        |        | 979.5                  | 1.9                                         | 4         | [45]       |
| Yb:GdCOB         |        |        | 976                    | 0.87                                        | 2.6       | [46]       |
| 15% Yb:YAG       |        |        | 968                    | 0.94                                        | 2.6       | [47]       |
| 15% Yb:BLuB      |        |        | 966                    | 0.29                                        | 6.4       | [47]       |
| Yb:YAB           |        |        | 975                    | 3.4                                         | 3         | [48]       |

Table 3.5. Absorption properties of the ytterbium-doped compounds

3.3.4 The spectrum characteristic of \( \text{Nd}^{3+}:\text{Ca}_3\text{Gd}_2(\text{BO}_3)_4 \) crystal

Based on the absorption spectra of \( \text{Nd}^{3+}:\text{Ca}_3\text{Gd}_2(\text{BO}_3)_4 \) crystal and the measured absorption spectra in three commutative perpendicularity directions and J-O theory, the J-O parameters are calculated to be \( \Omega_2 = 2.076 \times 10^{-20} \text{ cm}^2 \), \( \Omega_4 = 4.252 \times 10^{-20} \text{ cm}^2 \), \( \Omega_6 = 5.342 \times 10^{-20} \text{ cm}^2 \) [55]. The emission spectra of \( \text{Nd}^{3+}:\text{Ca}_3\text{Gd}_2(\text{BO}_3)_4 \) crystal demonstrates that there are three main emission peaks under excited of 808nm, centered at 912nm, 1064nm and 1337nm, respectively. The stimulated emission cross-section at 1064 nm corresponding to \( ^4I_{15/2} \rightarrow ^4I_{11/2} \) transition is \( 2.28 \times 10^{-20} \text{ cm}^2 \). The fluorescence decay curve displays that the measured lifetime of \( ^4I_{15/2} \) level is 175 ms, and the quantum efficiency is estimated to be 72%.

3.3.5 The spectrum characteristic of \( \text{Er}^{3+}:\text{Ca}_3\text{Gd}_2(\text{BO}_3)_4 \) crystal

Fig.3.10 presents the absorption spectrum of \( \text{Ca}_3\text{Gd}_2(\text{BO}_3)_4:\text{Er}^{3+} \) crystal, in which there are twelve peaks centered at 244.6nm, 257.3 nm, 366.4 nm, 379.9nm, 408.1 nm, 452 nm, 522.7nm, 544.2 nm, 654.3 nm, 799.3 nm, 976.6 nm, 1518.4nm, corresponding to the transitions from \( ^4I_{15/2} \) to \( ^2I_{11/2} \), \( ^4D_{5/2} ^4D_{7/2} \), \( ^4G_{9/2} \), \( ^2G_{9/2} ^4F_{9/2} ^4H_{9/2} \), \( ^4F_{5/2} \), \( ^2H_{11/2} \), \( ^4S_{3/2} \), \( ^4F_{9/2} \), \( ^4I_{13/2} \), \( ^4I_{11/2} \), respectively [56]. The room temperature emission spectrum of \( \text{Ca}_3\text{Gd}_2(\text{BO}_3)_4:\text{Er}^{3+} \) crystal excited at 530nm is presented in Fig.3.11, in which there is a broad emission band ranged from 1460 nm to 1600 nm. The FWHM of this emission band is 126 nm, which is resulted from the statistical distribution of \( \text{Ca}^{2+} \), \( \text{Gd}^{3+} \) and \( \text{Er}^{3+} \) ions. Based on the measured absorption spectra of three commutative perpendicularity directions and J-O theory, the J-O parameters are calculated to be \( \Omega_2 = 4.01 \times 10^{-20} \text{ cm}^2 \), \( \Omega_4 = 0.98 \times 10^{-20} \text{ cm}^2 \), \( \Omega_6 = 1.72 \times 10^{-19} \text{ cm}^2 \). Comparing the parameters with those of the other \( \text{Er}^{3+} \) doped crystal, we found that the parameters are larger. The oscillator strength, radiative transition probability \( A \), radiative lifetime \( \tau_{\text{rad}} \) and the fluorescent branching ratio \( \beta \) are also calculated, which are shown in Tables 3-6~3-8.

The stimulated emission cross-section at 1535nm is calculated to be \( 6.0 \times 10^{-21} \text{ cm}^2 \). Fig.3.12 shows the fluorescence lifetime of Er:CGB crystal under the excitation of 530 nm. The lifetime measured is about 792 ms, so the luminescent quantum efficiency of the \( ^4I_{13/2} \) manifold is estimated to be 20%.
Fig. 3.10. Absorption spectrum of Er:CGB crystal in random direction at RT

Fig. 3.11. The fluorescence spectrum of Er\textsuperscript{3+}:CGB under the excitation of 530nm
Fig. 3.12. The fluorescence lifetime of Er:CGB crystal under the excitation of 530nm

| Wavelength (nm) | $f_{exp} \times 10^6$ | $f_{cal} \times 10^6$ |
|----------------|----------------------|----------------------|
| 380            | 13.969               | 12.976               |
| 489            | 2.343                | 2.797                |
| 523            | 6.415                | 7.33                 |
| 653            | 2.3                  | 2.261                |
| 800            | 0.241                | 0.261                |
| 976            | 0.587                | 0.91                 |
| 1534           | 2.053                | 1.938 ed(a)          |

$rms \Delta f = 5.54 \times 10^{-7}$

(a): ed and md denote electric-dipole and magnetic-dipole transitions respectively.

Table 3.6. Oscillator strengths of Er$^{3+}$ in Ca$_3$Gd$_2$(BO$_3$)$_4$ crystal

| Crystals         | $\Omega_2 \times 10^{20}$ cm$^2$ | $\Omega_4 \times 10^{20}$ cm$^2$ | $\Omega_6 \times 10^{20}$ cm$^2$ | References |
|------------------|----------------------------------|----------------------------------|----------------------------------|------------|
| Er$^{3+}$:Ca$_3$Gd$_2$(BO$_3$)$_4$ | 4.01                             | 0.98                             | 1.72                             | [55]       |
| Er$^{3+}$:YAG    | 0.19                             | 1.68                             | 0.62                             | [57]       |
| Er$^{3+}$:YAlO$_3$ | 1.06                             | 2.63                             | 0.78                             | [58]       |
| Er$^{3+}$:YVO$_4$ | 1.25                             | 1.69                             | 0.61                             | [59]       |
| Er$^{3+}$:YLiF$_4$ | 0.97                             | 1.21                             | 1.37                             | [60]       |

Table 3.7. The Judd-Ofelt parameters for Ca$_3$Gd$_2$(BO$_3$)$_4$: Er$^{3+}$ compared with other Er-doped crystals
Table 3.8. Radiative transition probability $A$, radiative lifetime $\tau_{rad}$ and fluorescent branching ratio $\beta$ of Er$^{3+}$ in Ca$_3$Gd$_2$(BO$_3$)$_4$ crystal at room temperature.

3.3.6 The spectrum characteristic of Yb$^{3+}$:Ca$_3$Gd$_2$(BO$_3$)$_4$ crystal

Fig.3.13 presents the absorption spectrum of Ca$_3$Gd$_2$(BO$_3$)$_4$:Yb$^{3+}$ crystal, in which there is a broad absorption band ranged from 850 to 1000 nm, corresponding to the transition from $^2F_{7/2}$ to $^2F_{5/2}$. The FWHM at 980 nm is about 12 nm and the cross-section is about $5.9 \times 10^{-20}$ cm$^2$, which is benefit to the pumping of commercial laser diode. Table 3-9 shows the absorption properties of some ytterbium-doped compounds. The room temperature emission spectrum of Ca$_3$Gd$_2$(BO$_3$)$_4$:Yb$^{3+}$ crystal excited at 895 nm is presented in Fig.3.14, in which there is a broad emission band ranged from 930 nm to 1100.7 nm. The FWHM of this emission band is 72.6 nm and its peak is located at 1020 nm, which is resulted from the statistical distribution of Ca$^{2+}$, Gd$^{3+}$ and Yb$^{3+}$ ions.
Fig. 3.13. The absorption spectrum of $\text{Ca}_3\text{Gd}_2(\text{BO}_3)_4:\text{Yb}^{3+}$ crystal

Fig. 3.14. Room temperature emission spectra of $\text{Ca}_3\text{Gd}_2(\text{BO}_3)_4:\text{Yb}^{3+}$ crystal excited at 895 nm
| Compound          | $\lambda_p$(nm) | $\sigma_\Delta$ ($\times10^{-20}$ cm$^2$) | FWHM(nm) | References |
|-------------------|-----------------|----------------------------------------|---------|------------|
| 5at%Yb:CGB        | 980             | 5.95                                   | 12      | [5]        |
| 2at%Yb:YCOB       | 976.1           | 0.94                                   | 3       | [61]       |
| 1at%Yb:Y$_2$SiO$_5$ | 977.4           | 2.1                                    | 7       | [62]       |
| 1at%Yb:Sc$_2$SiO$_5$ | 979.5           | 1.9                                    | 4       | [62]       |
| Yb:GdCOB          | 976             | 0.87                                   | 2.6     | [63]       |
| 15%Yb:YAG         | 968             | 0.94                                   | 2.6     | [64]       |
| 15%Yb:BLuB        | 966             | 0.29                                   | 6.4     | [64]       |
| Yb:YAB            | 975             | 3.4                                    | 3       | [65]       |

Table 3.9. Absorption properties of the ytterbium-doped compounds

3.4 The Laser characteristics of Yb$^{3+}$:Ca$_3$Re$_2$(BO$_3$)$_4$[Re=Y,Gd] crystals

3.4.1 The Laser characteristics of Yb$^{3+}$:Ca$_3$Y$_2$(BO$_3$)$_4$ crystal[66-69]

An passively mode-locked Yb:Y$_2$Ca$_3$(BO$_3$)$_4$ (Yb:CYB) laser with a partially reflective semiconductor saturable-absorber mirror was achieved. The 244 fs pulses with a repetition rate of ~55 MHz were obtained at the central wavelength of 1044.7 nm. The measured average output power amounted to 261 mW. This was the first demonstration of femtosecond laser in Yb:CYB crystal. Fig.3.15 shows the experimental setup of the laser oscillator. The input mirror M1 was a flat mirror coated with high reflection (HR) in a broad band from 1010 to 1060 nm and high transmission (HT) at 976 nm. The two folding mirrors, M2 and M3, were concave and had the radii of curvature of 1000 and 500 mm, respectively. Both of which were HR-coated placed near normal incidence (~3º). A SESAM with a reflection of 96% at 1040 nm was employed, which had a modulation depth of 1.6% and saturation fluence of 70 µJ/cm$^2$. Fig.3.16 presents the continuous wave and mode locking average output power versus the absorbed pump power. We can see that the threshold absorbed pump power was 1.9 W and a maximum output power of 783 mW was obtained under the absorbed pump power of 7.0W. The laser oscillation was achieved with the threshold absorbed pump power of 2.8 W when the output coupler was replaced by the SESAM. Within the range of absorbed pump power from threshold to 4.6W, a metastable regime rapidly alter-nating between Q-switched mode locking and continuous wave (CW) mode locking was observed.

Fig.3.17 presents the central wavelength and FWHM of the emission spectrum for mode locking operation. The spectrum was red-shifted obviously at a range from 1041.5 to 1044.7 nm with the absorbed pump power increased from threshold to 7.0 W, which was possibly attributed to the reabsorption effect for quasi-three-level as the short wavelength part of the absorption spectrum overlaps the emission spectrum. Fig.3.18 shows the pulse train of the cw mode-locked laser with the repetition rate of ~55MHz. Fig.3.19 presents the autocorrelation trace of the 244 fs pulse with the average output power of 261 mW at the central wavelength of 1044.7 nm. The corresponding spectrum had a FWHM of 8.1 nm centered at 1044.7 nm, with a time bandwidth product of 0.54. In this job, a partially reflective SESAM was used as the output coupler that would lower the positive dispersion. When the absorbed pump power was fixed at 7.0 W, the adjustment of the Yb:CYB crystal and SESAM in such a resonator (by either moving or rotating that could vary the amount of...
material that the light went through) is critical for the stability of mode-locking operation and pulse duration: an average output power of 375 mW could be obtained but the mode locking was unstable; the duration also fluctuated in a wide range from ~1000 to 244 fs.

Fig. 3.15. Experimental setup of the laser oscillator. The shaded part in the position of the gain medium refers to the change in shape resulting from the thermal expansion

Fig. 3.16. The continuous wave and mode locking average output power versus the absorbed pump power
Fig. 3.17. The central wavelength and FWHM of the emission spectrum for mode locking operation.

Fig. 3.18. The pulse train of the cw mode-locked laser with the repetition rate of ~55MHz.
Q-switching and Q-switched mode-locked Yb:Y_{2}Ca_{3}B_{4}O_{12} lasers with an acousto-optic switch are demonstrated. In the Q-switching case, an average output power of 530 mW is obtained at the pulse repetition rate of 10.0 kHz under the absorbed pump power of 6.1 W. The minimum pulse width is 79 ns at the repetition rate of 1.7 kHz. The pulse energy and peak energy are calculated to be 231 μJ and 2.03 kW, respectively. In Q-switched mode-locking case, the average output power of 64 mW with a mode-locked pulse repetition rate of 118 MHz and Q-switched pulse energy of 48 μJ is generated under the absorbed pump power of 6.1 W. Fig. 3.20 presents the CW and Q-switched average output power versus absorbed pump power. The CW lasers were operated with the absorbed pump power of up to 0.8 W and 1.3 W, respectively, for T = 1% and T = 5% output coupler. When the absorbed pump power reaches 6.1 W, the T = 5% output coupler provides the best performance with an output power of 992 mW, which is much higher than 760 mW by using T = 1% output coupler. Fig.3.21 gives the emission spectra of the Yb:CYB laser with plano-concave cavity configuration. (a) is in the CW situation with T = 5% output coupler. (b)–(d) are in the Q-switching situation with T = 5% output coupler, (e) is in the Q-switching situation with T = 1% output coupler the emission spectra of the Yb:CYB laser. Fig.3.22 shows the pulse width versus absorbed pump power. At the pulse repetition rate of 1.7 kHz and the absorbed pump power 6.1 W, the pulse widths of 79 ns and 114 ns are detected by used of T = 1% and 5% coupler, respectively. Fig.3.23 presents the pulse energy and pulse peak power versus the absorbed pump power at the pulse repetition rate of 1.7 kHz. The pulse energy of 231 μJ and peak energy of 2.03 kW can be obtained with the T = 5% output coupler. Fig.3.24 gives the single pulse profile of the A-O Q-switched Yb:CYB lasers with the pulse width of 76 ns at the absorbed pump power of 6.1 W, and the inset corresponding to the temporal pulse trains with the repetition rate of 1.7 kHz. The beam quality M2 is measured to be about 1.4 by using the knife-edge scanning method.
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Fig. 3.20. The CW and Q-switched average output power versus absorbed pump power for $T = 1\%$ and $5\%$

Fig. 3.21. Emission spectra of the Yb:CYB laser. (a) is in CW situation with $T = 5\%$. (b)-(d) are in Q-switching situation with $T = 5\%$, showing the absorbed pump power dependence. (e) is in Q-switching situation with $T = 1\%$. 

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Fig. 3.22. Pulse width versus absorbed pump power

Fig. 3.23. Pulse energy and pulse peak power versus the absorbed pump power at the pulse repetition rate of 1.7kHz
Fig. 3.24. The single pulse profile of the A-O Q-switched Yb:CYB lasers with the pulse width of 76 ns at the absorbed pump power of 6.1 W

Fig.3.25 depicts the schematic arrangement of the four-mirror resonate cavity for Q-switched mode-locking operation. M1 is the same plane mirror as that in Q-switching case described above. M2 and M3 are two spherical concave mirrors with curvature of 500 mm and 100 mm, respectively, and HR coated from 1010 nm to 1060 nm. The two different concave couplers (r = 75 mm) with transmissions of 1% and 5% are also used as the output coupler M4. The distances L1 from M1 to M2, L2 from M2 to M3, L3 from M3 to M4 are set as 440 mm, 770 mm and 60 mm, respectively. Fig.3.26 shows the emission spectra of the Yb:CYB laser. (a)-(c) is in CW situation with $T = 5\%$ showing the absorbed pump power dependence. (d) is in Q-switched mode-locking situation with $T = 5\%$, (e) is in Q-switched mode-locking situation with $T = 1\%$. Compared with the spectra of the above plano-concave resonator, there are only three or four emission branches in Figs. 3.26 a–c, since the combined etalon effects of the resonant cavity and uncoated Yb:CYB are different between the two-mirror and four-mirror cavity. Under the absorbed pump power of 3.0 W, there are three nonoverlapping emission branches located at 1042 nm, 1047 nm and 1051 nm. Similar to that in the Q-switched mode, the spectrum shifts to the long side with the increase of the absorbed pump power owing to the reabsorption effect. When the absorbed pump power reaches 6.1 W, a new branch in the short side (1040 nm) appears. The CW and Q-switched average output power versus absorbed pump power for $T = 1\%$ and $5\%$ are plotted in Fig.3.27, (a) is $T = 1\%$ and (b) is $T = 5\%$. The average output powers of 64 mW and 87 mW are obtained for $T = 1\%$ and $T = 5\%$ output coupler, respectively. Fig.3.28 shows the pulse energy of the Q-switched envelope versus the absorbed pump power at repetition rate of 1.7 kHz. In Fig.3.29, (a) is the oscilloscope traces of Q-switched pulse train with the $T = 5\%$ output coupler and the repetition rate of 1.7 kHz under the absorbed pump power of 6.1 W in the same situation. (b) is the typical QML pulse envelope of $T = 5\%$ in the same situation. (c) is the expanded traces of mode-locked train. The repetition rate of the periodic mode-locked pulses is about 118 MHz, which matches exactly with the axial mode interval. The output beam density distribution is close to the fundamental transverse mode (TEM00) and the quality parameter M2 factor is about 1.6.
Fig. 3.25. The schematic arrangement of the four-mirror resonate cavity for Q-switched mode-locking operation.

Fig. 3.26. Emission spectra of the Yb:CYB laser. (a)-(c) is in CW situation with $T = 5\%$ showing the absorbed pump power dependence.
Fig. 3.27. The CW and Q-switched average output power versus absorbed pump power for $T = 1\%$ and $5\%$. (a) is $T = 1\%$ and (b) is $T = 5\%$. 
Fig. 3.28. Pulse energy of the Q-switched envelope versus the absorbed pump power at repetition rate of 1.7 kHz.

Fig. 3.29. (a) is the oscilloscope traces of Q-switched pulse train with the $T = 5\%$ output coupler and the repetition rate of 1.7 kHz under the absorbed pump power of 6.1 W in the same situation. (b) is the typical QML pulse envelope of $T = 5\%$ in the same situation. (c) is the expanded traces of mode-locked pulses.

The Yb$^{3+}$-doped $Y_2Ca_3B_4O_{12}$ diode-pumped laser operation in both continuous-wave (CW) and passively Q-switched modes was reached. The differential slopes of the CW output power are in the 22-40 % range under different experimental conditions. Continuous tuning
of the laser wavelength is obtained in the 1020-1057 nm range, in agreement with the broad emission spectra. In pulsed regime the repetition rate occurs up to 1.6 kHz and pulse energies of 30-75 µJ with about 40 ns duration are obtained. Fig.3.30 demonstrates the polarized emission spectra of the CYB:Yb³⁺ crystal used for laser experiments. The two orthogonal polarizations of the eigenstates are labeled as H and V. The main peak at 976.3 nm has 6 nm full width at half maximum (FWHM) and is suitable for diode pumping. Fig.3.31 displays the spectral distribution of the laser emission in CW and passive Q-switch modes. We can see that the more intense one corresponds to the H polarization with a broadband peaking near 1040 nm. The time evolution of the fluorescence was displayed with a 9410 Lecroy oscilloscope. The decay time was found to be 1 ms. Fig.3.32 presents repetition rates and pulse energies obtained in passive Q-switching the Ca₃Y₂(BO₃)₄:Yb³⁺ laser. Lasing was obtained in H polarization in agreement with the polarized emission spectra, near 1045 nm (with the 97.5% transmission coupler) and up to 1 W power. Fig.3.33 shows the tunability of the laser emission obtained from rotation of a birefringent filter. Fig.3.34 presents the laser output power versus pump power obtained under different experimental conditions. The obtained slope efficiencies were in the 29%-40% range with the 5 cm radius curvature output coupler and 22% with the 7.5 cm coupler. Table 3-10 shows the pulse energy obtained in passive Q-switching different Yb³⁺-doped hosts. In particular, we can see that the performances for Yb³⁺ doped GGG and GAB crystals obtained with similar experimental conditions were better than for Yb³⁺:CYB, with no instability of the pulsed regime and less thermal problems. A plausible explanation is the lower laser emission cross section in Yb³⁺:CYB and a too low absorbed pump power (61% absorption) of our sample.

Fig. 3.30. Polarized emission spectra of the CYB:Yb³⁺ crystal used for laser experiments

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Fig. 3.31. Spectral distribution of the laser emission in cw and passive Q-switch modes.

Fig. 3.32. Repetition rates and pulse energies obtained in passive Q-switching the Ca$_3$Y$_2$(BO$_3$)$_4$:Yb$^{3+}$ laser. The inset represents a typical time evolution of the laser pulse.
Fig. 3.33. Tunability of the laser emission obtained from rotation of a birefringent filter

Fig. 3.34. Laser output power versus pump power obtained under different experimental conditions.
Table 3.10. Pulse energy obtained in passive Q-switching different Yb\textsuperscript{3+}-doped hosts

| Crystal         | cw emission wavelength (nm) | Lifetime $\tau$ (µs) | Emission cross section (10^{-20}cm\textsuperscript{2}) at cw lasing wavelength | Pulse energy (µJ) |
|-----------------|----------------------------|----------------------|--------------------------------------------------------------------------------|-------------------|
| Yb\textsuperscript{3+}:KGdW | 1029                       | 951                  | 2.7                                                                              | 3.4\textsuperscript{[70]} |
| Yb\textsuperscript{3+}:KLuW   | 1031.7                     | ...                  | ...                                                                              | 32.4\textsuperscript{[71]} |
| Yb\textsuperscript{3+}:YAG    | 1023                       | 600                  | 2.03                                                                             | 54,100,179,500\textsuperscript{[72]} |
| Yb\textsuperscript{3+}:GGG    | 1025                       | 800                  | 2.0                                                                              | 40,48,87,96\textsuperscript{[73]} |
| Yb\textsuperscript{3+}:GAB    | 1045                       | 800                  | 0.83                                                                             | 125,165\textsuperscript{[74]} |
| Yb\textsuperscript{3+}:CYB    | 1044                       | 1000                 | 0.60                                                                             | 30-70\textsuperscript{[69]} |

3.4.2 The laser characteristics of Yb\textsuperscript{3+}:Ca\textsubscript{3}Gd\textsubscript{2}(BO\textsubscript{3})\textsubscript{4} crystal\textsuperscript{[75]}

The diode-pumped multi-wavelength continuous-wave laser operation of the disordered Yb:Ca\textsubscript{3}Gd\textsubscript{2}(BO\textsubscript{3})\textsubscript{4} (Yb:CGB) crystal was investigated. The number of the oscillating wavelengths varied from two to five in the range from 1045.4 to 1063.6 nm with the absorbed pump power and Yb:CGB crystal length. An output power of 1.4 W was obtained when quadruple wavelengths were emitted simultaneously, corresponding to a slope efficiency of 23.7%. The quintuple-wavelength oscillation at 1049.4, 1051.3, 1053.4, 1055.6 and 1057.4 nm was realized with an output power of 1.0 W. The experiment results exhibited the further possible application of Yb:CGB crystal in terahertz-wave generation. Fig.3.35 represents the experimental setup of the CW Yb:CGB laser oscillator. M1 was a plane mirror with antireflection coating at the pump wavelength and high-reflection coating at a broad band from 1040 to 1070 nm. A concave mirror with 75-mm curvature radius and ~99% reflectance from 1040 to 1070 nm was used as the output coupler M2. Fig.3.36 shows the absorbed pump power and absorption efficiency versus incident pump power for the two Yb:CGB samples, with the same cross section of 3×3 mm\textsuperscript{2} but different lengths of 2 and 5 mm (described as sample 1 and 2, respectively). It can be seen that the absorption efficiency of sample 1 was around 40% if the incident pump power was below 4.0 W. But the efficiency decreased dramatically from 40% to 30% when the incident pump power was increased from 4.0 to 8.0 W. Then the efficiency was stable again, varying within a narrow range of 30% ~ 32%. That was possibly attributed to the saturation of pump absorption to some extent, resulting from the depletion of the population in ground state. The similar phenomenon was observed when sample 2 was tested. Fig.3.37 depicts the relationship between the output power ($P_{\text{out}}$) and absorbed pump power for the two samples. The laser operation was realized with threshold absorbed pump powers of 0.4 and 0.9 W for sample 1 and 2, respectively. The maximum output power was 1.4 W by using sample 2 under the absorbed pump power of 6.8 W, with a slope efficiency of 23.7% and an optical conversion efficiency of 20.6%. The sample 1 exhibited higher slope efficiency of 30.3% and optical conversion efficiency of 27.0% with the output power of 1.0 W under the absorbed pump power of 3.7 W. Fig.3.38 gives the emission wavelengths versus absorbed pump power for the two Yb:CGB samples. Fig.3.39 and Fig.3.40 shows the emission spectra of the simultaneous multi-wavelength Yb:CGB laser with sample 1 and sample 2, respectively. It can be seen that the emission wavelengths at each stage were almost same in intensity. That is
advantageous to the practice terahertz-wave generation. If the quintuple-wavelength simultaneous emission is employed, multiple terahertz waves can be generated theoretically through difference frequency nonlinear interaction. Furthermore, it is interesting to note the separation of emission peaks varied from 1.0 to 2.0 nm with the absorbed pump power and Yb:CGB crystals, which means the multi-wavelength CW Yb:CGB laser could support the tunable terahertz-wave generation from 0.27 to 2.16 THz as calculated from Fig. 3.38. Our experiment also showed that the reabsorption effect in quasi-three-level laser systems depended on the length of laser medium and the level of pump intensity. In addition, this effect had a great influence on the laser characteristics such as output power, optical efficiency and emission wavelength.

Fig. 3.35. Experimental setup of the CW Yb:CGB laser oscillator

Fig. 3.36. Absorbed pump power and absorption efficiency versus incident pump power for the two Yb:CGB samples
Fig. 3.37. Continuous-wave output power versus absorbed pump power of the Yb:CGB laser.

Fig. 3.38. Emission wavelengths versus absorbed pump power for the two Yb:CGB samples. The rapid redshift ranges are marked by squared pattern. The oscillating wavelengths varied in the region from 1045.4 to 1063.6 nm with the absorbed pump power and Yb:CGB sample length.
Fig. 3.39. Emission spectra of the simultaneous multi-wavelength Yb:CGB laser with sample 1. (a) triple-wavelength oscillation with \( P_{\text{out}} = 0.4 \) W and \( P_{\text{abs}} = 2.0 \) W; (b) quadruple-wavelength oscillation with \( P_{\text{out}} = 0.9 \) W and \( P_{\text{abs}} = 3.0 \) W; (c) quintuple-wavelength oscillation with \( P_{\text{out}} = 1.0 \) W and \( P_{\text{abs}} = 3.7 \) W.
Fig. 3.40. Emission spectra of the simultaneous multi-wavelength Yb:CGB laser with sample 2. (a) is dual-wavelength oscillation with $P_{\text{out}} = 0.9$ W and $P_{\text{abs}} = 5.0$ W; (b) is triple-wavelength oscillation with $P_{\text{out}} = 1.2$ W and $P_{\text{abs}} = 6.0$ W; (c) is quadruple-wavelength oscillation with $P_{\text{out}} = 1.4$ W and $P_{\text{abs}} = 6.8$ W.
4. Nd$^{3+}$-doped LaB$_3$O$_6$ crystals

The LaB$_3$O$_6$ [LaBO] single crystal belongs to monoclinic system with the space group of I2/c \cite{76,77}. The cell parameters are as follows\cite{77}: $a=9.946(1)$ Å, $b=8.164(1)$ Å, $c=6.4965(5)$ Å, $\beta=127.06(1)^{\circ}$, \cite{78}. $V=420.9$ Å$^3$, $D_c=4.219$ g/cm$^3$. It melts congruently at 1145°C \cite{76}. Therefore, this crystal can be obtained with large size by the Czochralski technique. Since the ionic radius of La$^{3+}$ in LaB$_3$O$_6$ single crystal is about 1.04 Å \cite{78}, it can be substituted by laser exciting ions of lanthanide such as Nd$^{3+}$, Yb$^{3+}$ ions. Therefore LaB$_3$O$_6$ crystal may be a new potential host for laser crystal. Furthermore, rare earth-doped LaB$_3$O$_6$ crystal can serve as a microchip laser crystal without any processing because of the cleavage of LaB$_3$O$_6$ crystal.

4.1 The crystal growth

Nd$^{3+}$-doped LaBO crystal with size up to φ20 mm×35 mm was grown using the Czochralski technique by Dr.Guohua Jia\cite{4}. When the crystal was cut into laser bulk, it split into the cleavage crystal with the size of 2.5 mm×9 mm×35 mm as shown in Fig.4.1.

![Fig. 4.1. Image of the unprocessed cleavage microchip along the (101) planes directly obtained from the as-grown crystal](image)

4.2 The spectrum characteristics of Nd$^{3+}$-doped LaB$_3$O$_6$ crystal\cite{80}

The room temperature absorption spectrum (Fig.4.2) consists of 10 groups of bands, which are associated with the observed transitions from the $^{4}I_{9/2}$ ground state. The absorption spectrum of the LaB$_3$O$_6$:Nd$^{3+}$ crystal reaches its maximal value at about 800 nm and its FWHM is about 16 nm. The absorption cross-section was measured to be $\sigma_{abs} = 3.37 \times 10^{-20}$ cm$^2$. \cite{7} This stronger absorption band corresponding to the transition $^{4}I_{9/2} \rightarrow ^{2}H_{9/2}$ is very favorable for commercial GaAlAs diode pumping\cite{4}. The room temperature emission spectrum with the light perpendicular to <1 1 1> planes is presented in Fig.4.3. The $^{4}F_{3/2} \rightarrow ^{4}I_{J}$ ($J = 9/2, 11/2, 13/2$) transitions corresponding to the bands centered at 890.7, 1062 and 1329 nm, respectively, are the most important for laser applications. The value of
the emission cross-section at 1062 nm of $\text{LaB}_3\text{O}_6:\text{Nd}^{3+}$ is $3.46 \times 10^{-20}$ cm$^2$, which is a little smaller than that of other Nd$^{3+}$ doped crystals. The emission cross-section and branching ratio ($\beta$) of the $\text{4F}_{3/2} \rightarrow \text{4I}_{9/2}$ transition are centered at 891 nm. The values of the emission cross-section at 891 nm and the branching ratio of this transition are $4.07 \times 10^{-21}$ cm$^2$ and 0.336, respectively. Fig. 4.4 shows the room temperature fluorescence decay curve of $\text{LaB}_3\text{O}_6:\text{Nd}^{3+}$ crystal from which the fitting result of single exponential decay is 44.465 ns.

Table 4-1 shows the integrated absorbance, the experimental and calculated line and oscillator strengths of Nd$^{3+}$:$\text{LaB}_3\text{O}_6$ crystal (note: rms $f = 0.744 \times 10^{-6}$), and Table 4-2 presents the intensity parameters of Nd$^{3+}$:$\text{LaB}_3\text{O}_6$ crystal and the comparison of the intensity parameters of other Nd$^{3+}$ doped crystals. Table 4-3 presents the calculated radiative probabilities, radiative branching ratios and radiative time for the emissions from the $\text{4F}_{3/2}$ level of $\text{LaB}_3\text{O}_6:\text{Nd}^{3+}$. Table 4-4 shows the comparison of the $\text{4F}_{3/2} \rightarrow \text{4I}_{11/2}$ emission cross-section and radiative branching ratios of Nd$^{3+}$ doped crystals.

Fig. 4.2. The room temperature absorption spectrum

![Absorption Spectrum](image)

Fig. 4.3. Room temperature emission spectrum with the light perpendicular to <1 1 1> plane

![Emission Spectrum](image)
Fig. 4.4. Room temperature fluorescence decay curve of LaB$_3$O$_6$:Nd$^{3+}$ crystal

| Excited state | Wavelength (nm) | $I$ (nm/cm) | $S_{\text{mea}}$ $(10^{-20} \text{ cm}^2)$ | $S_{\text{cal}}$ $(10^{-20} \text{ cm}^2)$ | $f_{\text{exp}}$ $(10^{-6})$ | $f_{\text{cal}}$ $(10^{-6})$ |
|---------------|----------------|-------------|---------------------------------|---------------------------------|----------------|----------------|
| $^4F_{3/2}$   | 860            | 35.86       | 0.411                           | 0.778                           | 1.656          | 0.329          |
| $^4F_{5/2},^2H_{9/2}$ | 799           | 240.81      | 2.969                           | 2.885                           | 6.810          | 6.891          |
| $^4F_{7/2},^4S_{3/2}$ | 744           | 221.79      | 2.937                           | 3.081                           | 0.163          | 0.379          |
| $^4F_{9/2}$   | 674            | 41.89       | 0.612                           | 0.210                           | 1.595          | 0.970          |
| $^4G_{5/2},^2G_{7/2}$ | 579           | 127.94      | 2.177                           | 2.204                           | 4.900          | 3.633          |
| $^2K_{13/2},^4G_{7/2},^4G_{9/2}$ | 524           | 79.91       | 1.502                           | 1.114                           | 6.426          | 6.507          |
| $^2K_{13/2},^2G_{9/2},^2P_{3/2},^4G_{11/2}$ | 470           | 20.92       | 0.483                           | 0.267                           | 1.533          | 0.532          |
| $^2P_{1/2},^2D_{3/2}$ | 428           | 1.77        | 0.041                           | 0.095                           | 6.746          | 7.708          |
| $^4D_{3/2},^2D_{3/2},^2I_{1/2},^4D_{1/2}$ | 356           | 51.26       | 1.418                           | 1.435                           | 6.351          | 6.171          |
| $^4D_{3/2},^2D_{3/2},^2L_{17/2}$ | 328           | 10.58       | 0.318                           | 0.063                           | 0.816          | 1.547          |

Table 4.1. The integrated absorbance, the experimental and calculated line and oscillator strengths of Nd$^{3+}$:LaB$_3$O$_6$ crystal (note: rms $f = 0.744 \times 10^{-6}$)

| Crystals         | $\Omega_2$ $(10^{-20} \text{ cm}^2)$ | $\Omega_4$ $(10^{-20} \text{ cm}^2)$ | $\Omega_6$ $(10^{-20} \text{ cm}^2)$ | References |
|------------------|-------------------------------------|-------------------------------------|-------------------------------------|-------------|
| LaB$_3$O$_6$     | 0.54                                | 2.31                                | 4.51                                | [80]        |
| YVO$_4$          | 5.88                                | 4.08                                | 5.11                                | [81]        |
| CaZn$_2$Y$_2$Ge$_3$O$_{12}$ | 0.94                                | 3.25                                | 3.68                                | [82]        |
| Sr$_4$GdGa$_3$O$_7$ | 2.94                                | 6.93                                | 6.96                                | [83]        |
| Gd$_3$Ga$_5$O$_{12}$ | 0.05                                | 2.9                                 | 9.3                                 | [81]        |
| YAG              | 1.0                                 | 2.9                                 | 9.3                                 | [81]        |
| Ca$_2$Sc$_2$Ge$_3$O$_{12}$ | 0.99                                | 4.24                                | 7.14                                | [90]        |
| Lu$_2$ScGa$_3$O$_{12}$ | 0.082                               | 2.844                               | 3.137                               | [84]        |

Table 4.2. The intensity parameters of Nd$^{3+}$:LaB$_3$O$_6$ crystal and the comparison of the intensity parameters of other Nd$^{3+}$ doped crystals
| Start levels | Wavelength (nm) | $\Lambda$ | $\beta$ (s$^{-1}$) | $\tau$ (µs) |
|--------------|-----------------|------------|-------------------|-------------|
| $^4I_{9/2}$  | 891             | 917.29     | 0.336             | 366.03      |
| $^4I_{11/2}$ | 1062            | 1.47 × 10$^3$ | 0.538             |             |
| $^4I_{13/2}$ | 1329            | 326.55     | 0.12              |             |
| $^4I_{15/2}$ | 1852            | 17.05      | 6.24 × 10$^{-3}$  |             |

Table 4.3. The calculated radiative probabilities, radiative branching ratios and radiative time for the emissions from the $^4F_{3/2}$ level of LaB$_3$O$_6$:Nd$^{3+}$

| Crystals                  | Wavelength (nm) | $\sigma_p$ (10$^{-20}$ cm$^2$) | $\beta$ | References |
|---------------------------|-----------------|---------------------------------|---------|------------|
| NdAl$_3$ (BO$_3$)$_4$     | 1060            | 28.4                            | 0.518   | [85]       |
| CaSc$_2$Ge$_3$O$_{12}$:Nd$^{3+}$ | 1060        | 2.6                             | 0.37    | [24]       |
| NdSc$_2$ (BO$_3$)$_4$:Nd$^{3+}$ | 1061         | 2.0 × 10$^2$                    | 0.38    | [86]       |
| La$_2$ (WO$_4$)$_3$:Nd$^{3+}$ | 1058          | 11.2                            | 0.5098  | [87]       |
| NdAl$_3$ (BO$_3$)$_4$     | 1063 ($\sigma$ polarized) | 16.0                       | 0.52    | [88]       |
|                           | 1063.5 ($\pi$ polarized) | 14.3                       | 0.52    | [88]       |
| Gd$_{0.8}$La$_{0.2}$VO$_4$:Nd$^{3+}$ | 1063      | 33.2                            | 0.498   | [89]       |
| LaB$_3$O$_6$:Nd$^{3+}$    | 1062            | 3.46                            | 0.538   | [80]       |

Table 4.4. The comparison of the $^4F_{3/2} \rightarrow ^4I_{11/2}$ emission cross-section and radiative branching ratios of Nd$^{3+}$ doped crystals.

4.3 The laser characteristics of Nd$^{3+}$-doped LaB$_3$O$_6$ crystal

A method utilizing an unprocessed Nd$^{3+}$-doped LaB$_3$O$_6$ crystal cleavage microchip as the solid-state laser gain medium was proposed by Prof. Huang[10]. Pumped by a Ti:sapphire laser at 871 nm, 1060 nm continuous-wave laser emission with slope efficiency of 23% has been achieved in an unprocessed microchip directly obtained from a cleavage Nd$^{3+}$:LaB$_3$O$_6$ crystal. Fig.4.5 shows the infrared laser output power at 1060 nm as a function of absorbed pump power at 871 nm. A maximum output power of 112 mW was obtained when the absorbed pump power was 580 mW. The laser performance of the unprocessed cleavage Nd$^{3+}$:LaBO microchip cannot compare with those of other microchip lasers yet, such as widely investigated Nd$^{3+}$:YAG and Nd$^{3+}$:YVO$_4$.[91~94]

5. Summary

The growth, thermal, optical and spectrum characteristics and laser characteristics of rare earth-doped Ln$_2$Ca$_3$B$_2$O$_{12}$ (Ln = La, Gd, or Y) double borate family laser crystals, Ca$_3$(BO$_3$)$_2$ and LaB$_3$O$_6$ laser crystals were reviewed.

From a passively mode-locked Yb:Y$_2$Ca$_3$(BO$_3$)$_4$ (Yb:CYB) laser, the 244 fs pulses with a repetition rate of ~55 MHz were obtained at the central wavelength of 1044.7 nm. The measured average output power amounted to 261 mW. Q-switching and Q-switched mode-locked Yb:Y$_2$Ca$_3$B$_4$O$_{12}$ lasers with an acousto-optic switch were also demonstrated. In the Q-switching case, an average output power of 530 mW was obtained at the pulse repetition rate of 10.0 kHz under the absorbed pump power of 6.1 W. The minimum pulse width is 79 ns at the repetition rate of 1.7 kHz. The pulse energy and peak energy are calculated to be 231 µJ and 2.03 kW, respectively. In Q-switched mode-locking case, the average output...
power of 64 mW with a mode-locked pulse repetition rate of 118 MHz and Q-switched pulse energy of 48 µJ was generated under the absorbed pump power of 6.1W. Meanwhile, Yb\(^{3+}\)-doped \(Y_2Ca_3B_4O_{12}\) diode-pumped laser operation in continuous-wave (CW) was reached. The differential slopes of the CW output power are in the 22-40% range under different experimental conditions. Continuous tuning of the laser wavelength is obtained in the 1020-1057 nm range, in agreement with the broad emission spectra. Also, the diode-pumped multi-wavelength continuous-wave laser operation of the disordered Yb:Ca\(_3\)Gd\(_2\)(BO\(_3\))\(_4\) (Yb:CGB) crystal was reached. An output power of 1.4 W was obtained when quadruple wavelengths were emitted simultaneously, corresponding to a slope efficiency of 23.7%.

Finally, the laser property of microchip \(Nd^{3+}:LaB_3O_6\) crystal are reviewed. Pumped by a Ti:sapphire laser at 871 nm, 1060 nm continuous-wave laser emission with slope efficiency of 23% has been achieved in an unprocessed microchip directly obtained from a cleavage \(Nd^{3+}:LaB_3O_6\) crystal. A maximum output power of 112 mW was obtained when the absorbed pump power was 580 mW.

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