



# Polarized spectroscopy and diode-pumped laser operation of disordered $\text{Yb}:\text{Ca}_3\text{Gd}_2(\text{BO}_3)_4$ crystal

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**Abstract:** We report on the growth, structure, polarized spectroscopy and efficient continuous-wave laser operation of an  $\text{Yb}^{3+}$ -doped disordered calcium gadolinium borate crystal,  $\text{Yb}^{3+}:\text{Ca}_3\text{Gd}_2(\text{BO}_3)_4$  (Yb:GdCB). Yb:GdCB belongs to the orthorhombic class [sp. gr. *Pnma*, lattice parameters  $a = 7.1937(0)$  Å,  $b = 15.5311(3)$  Å,  $c = 8.6140(7)$  Å]. The structure disorder of this material originates from a random distribution of  $\text{Ca}^{2+}$  and  $\text{Gd}^{3+}|\text{Yb}^{3+}$  cations over three non-equivalent lattice sites. This leads to broad and smooth (“glassy-like”) absorption and emission spectra at room and low temperatures. The stimulated-emission cross-section of  $\text{Yb}^{3+}$ ,  $\sigma_{\text{SE}}$  is  $0.42 \times 10^{-20}$  cm<sup>2</sup> at 1025.1 nm for light polarization  $E \parallel c$  and the luminescence lifetime of the  $^2\text{F}_{5/2}$  state is 644 μs. Continuous-wave laser performance of the Yb:GdCB crystal was evaluated under high-power diode-pumping at 976 nm for three crystal orientations along the crystallographic axes. For an *a*-cut crystal, a maximum output power of 5.58 W was achieved at ~1057 nm with a slope efficiency of 51.7% and a linear laser polarization ( $E \parallel c$ ). The demonstrated power scaling capabilities and broadband emission properties of Yb:GdCB indicate that it is promising for generation of sub-50 fs pulses from passively mode-locked lasers at ~1 μm.

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## 1. Introduction

Borates represent an important class of host crystals very suitable for doping with ytterbium ( $\text{Yb}^{3+}$ ) ions for highly efficient laser operation at ~1 μm. The monoclinic (sp. gr. *Cm*) calcium rare-earth oxoborates,  $\text{Ca}_4\text{REO}(\text{BO}_3)_3$ , where RE = Y and Gd (abbreviated YCOB and GdCOB, respectively) [1,2] represent just one such example. They feature good thermal and thermo-optical properties [3–5], high doping levels (tens of at.%) and attractive spectroscopic properties for  $\text{Yb}^{3+}$  doping [6], such as large ground-state splitting ( $^2\text{F}_{7/2}$ ,  $> 1000$  cm<sup>-1</sup>) leading to broad wavelength

tuning and low lasing threshold, strongly polarized and broad emission spectra, a relatively long fluorescence lifetime ( ${}^2F_{5/2}$ ,  $>2.6$  ms), and high absorption cross-sections at zero-phonon line (ZPL) suitable for in-band pumping by commercial high power InGaAs diode lasers at  $\sim 980$  nm. Efficient and high-power continuous-wave (CW) [4,7] diode-pumped lasers (including thin-disk one [8]) based on such crystals were demonstrated. Due to their disordered structure,  $\text{Yb}^{3+}$ -doped YCOB and GdCOB crystals exhibit relatively broad and flat gain profiles supporting sub-100 fs pulse generation from mode-locked (ML) lasers [9,10].

There exists another type of  $\text{Yb}^{3+}$ -doped disordered borate crystals, i.e.,  $\text{Yb}^{3+}$ -doped calcium borate crystal, i.e.,  $\text{Yb}:\text{Ca}_3\text{RE}_2(\text{BO}_3)_4$ , where RE stands for Y, Gd or La. They are orthorhombic (sp. gr. *Pnma*). In the host crystals, the cations (M:  $\text{Ca}^{2+}$  and  $\text{RE}^{3+}$ ) statistically occupy three non-equivalent crystallographic sites (M1, M2 and M3). The crystal structure is composed of three sets of M-oxygen distorted polyhedrons ( $\text{MO}_n$ ) and three sets of isolated  $\text{BO}_3$  planar triangles [11,12]. The dopant ions ( $\text{Yb}^{3+}$ ) replace for the  $\text{RE}^{3+}$  cations in all three M1 – M3 sites. This leads to a variety of multi-ligands around the active ions and a pronounced inhomogeneous spectral line broadening. Thus, the absorption and luminescence spectra of  $\text{Yb}^{3+}$  ions in  $\text{Ca}_3\text{RE}_2(\text{BO}_3)_4$  crystals resemble those in borate glasses (a “glassy-like” spectroscopic behavior). This makes  $\text{Yb}:\text{Ca}_3\text{RE}_2(\text{BO}_3)_4$  crystals attractive for ML lasers.

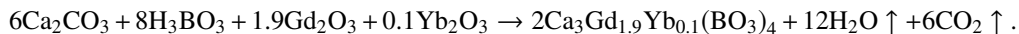
Calcium gadolinium borate,  $\text{Ca}_3\text{Gd}_2(\text{BO}_3)_4$  (abbreviated: GdCB), represents one of these disordered materials displaying extraordinary spectroscopic features when doped with  $\text{Yb}^{3+}$  ions. By virtue of the  $\text{Ca}^{2+}$  and  $\text{Gd}^{3+}|\text{Yb}^{3+}$  cations statistically occupying the M1 – M3 lattice sites [13],  $\text{Yb}:\text{GdCB}$  manifests a “glassy-like” spectroscopic behavior at the cost of a relatively low thermal conductivity of 0.92 W/mK at room temperature [14]. It melts congruently at a relatively low temperature of 1400°C and it can be easily grown by the conventional Czochralski (Cz) method [15]. So far, only unpolarized spectroscopic properties of the  $\text{Yb}:\text{GdCB}$  crystal were investigated at room temperature (RT) [13]. Xu *et al.* reported on a CW  $\text{Yb}:\text{GdCB}$  laser pumped by a multi-transverse mode fiber-coupled InGaAs diode laser at 976 nm yielding an output power of 1.4 W at  $\sim 1060$  nm with a relatively low slope efficiency of 23.7% [16]. Zeng *et al.* demonstrated a diode-pumped  $\text{Yb}:\text{GdCB}$  laser ML by a semiconductor saturable absorber mirror delivering pulses as short as 96 fs at 1045 nm with an average output power of 205 mW at a pulse repetition rate of 67.3 MHz [17].

In the present work, we report on the crystal growth, structure refinement, polarized RT, as well as low temperature (LT, 10 K) spectroscopy, and efficient and power-scalable CW laser operation of the  $\text{Yb}:\text{GdCB}$  crystal at  $\sim 1$   $\mu\text{m}$ . Our results indicate the prospects of the  $\text{Yb}:\text{GdCB}$  crystal for ultrashort pulse generation, as well as for power scalable operation.

## 2. Crystal growth and structure

### 2.1. Crystal growth

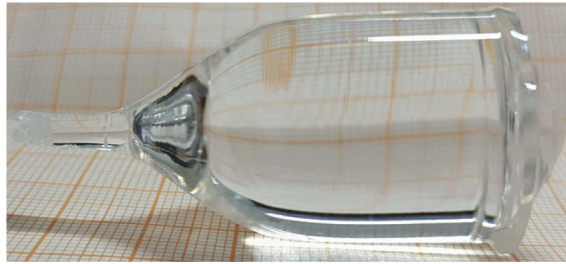
A 5 at.%  $\text{Yb}^{3+}$  (in the melt) doped GdCB crystal was grown by the Cz method under an argon (Ar) atmosphere in an iridium crucible. The starting materials were  $\text{CaCO}_3$  (4N),  $\text{Gd}_2\text{O}_3$  (5N),  $\text{H}_3\text{BO}_3$  (5N) and  $\text{Yb}_2\text{O}_3$  (5N). They were weighed according to the stoichiometric composition with 5 at.%  $\text{Yb}^{3+}$  (with respect to  $\text{Gd}^{3+}$ ),  $\text{Ca}_3\text{Gd}_{1.9}\text{Yb}_{0.1}(\text{BO}_3)_4$ , and an excess of 3 wt%  $\text{H}_3\text{BO}_3$  was added to compensate the evaporation of  $\text{B}_2\text{O}_3$  during the crystal growth. The compound was synthesized via the following solid-state reaction:



For that, the starting materials were mixed, ground and heated at 1173 K for 10 hours (h) in a platinum crucible. Once the crucible cooled down to RT, the mixture was pressed into pellets and reheated at 1373 K for 10 h. The synthesized polycrystalline material was placed in an iridium crucible and melted by an intermediate-frequency heater. To release the bubbles in the melt and

to avoid the formation of polycrystals during the crystal growth process, a temperature of 30 - 50 K higher than the melting point is required. The melt was held at this temperature for about 2 - 3 h before starting the growth. An [010] oriented seed from undoped GdCB was used. After dipping the seed into the melt and adjusting the heating power of the furnace, the crystal growth was performed with a pulling rate of 0.5 - 2.0 mm/h and a rotation speed of 10 - 15 revolutions per minute. After growth was completed, the crystal was slowly removed from the melt and cooled down to RT at a stepped rate of 15 to 25 K/h.

Figure 1 shows a photograph of an as-grown Yb:GdCB crystal boule. It had a cylindrical shape with dimensions of  $\Phi 20 \times 25 \text{ mm}^2$ . The crystal did not display any cracks, inclusions and scattering centers under illumination by a He-Ne laser, indicating an excellent optical quality. It was colorless and transparent.



**Fig. 1.** Photograph of an as-grown 5 at.% Yb:GdCB crystal.

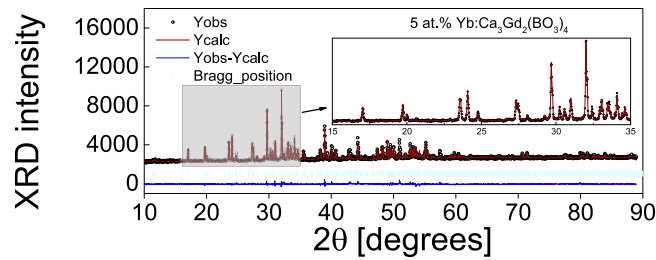
The actual doping level was determined by Inductively Coupled Plasma Mass Spectrometry (ICP-MS) to be  $N_{\text{Yb}} = 4.15 \times 10^{20} / \text{cm}^3$  (5.0 at.%). The segregation coefficient for  $\text{Yb}^{3+}$  ions,  $K_{\text{Yb}} = C_{\text{crystal}} / C_{\text{melt}}$ , was close to unity.

## 2.2. Structure refinement

The crystal structure and the phase purity were confirmed by X-ray powder diffraction (XRD). The XRD pattern was measured using a Bruker D2 Phaser diffractometer with  $\text{CuK}\alpha$  radiation ( $1.5418 \text{ \AA}$ ) in the range of diffraction angles  $2\theta = 10\text{--}88^\circ$  with a step size of  $0.02^\circ$  and a step time of 2 s. All the reflections in the XRD pattern were assigned to a single crystalline phase isostructural to undoped GdCB.

The crystal structure of 5 at.% Yb:GdCB was refined by the Rietveld method using the Match3 software. The structural data for  $\text{Ca}_3\text{Y}_2(\text{BO}_3)_4$  [12] were taken as a starting model. The observed, calculated and residual XRD patterns are shown in Fig. 2. Yb:GdCB belongs to the orthorhombic class (sp. gr.  $Pnma - D_{2h}^{16}$ , No. 62) with lattice constants  $a = 7.1937(0) \text{ \AA}$ ,  $b = 15.5311(3) \text{ \AA}$ ,  $c = 8.6140(7) \text{ \AA}$  (number of formula units per unit-cell:  $Z = 4$ ). The unit-cell volume is  $V = 962.419 \text{ \AA}^3$  and the calculated crystal density  $\rho_{\text{calc}} = 4.790 \text{ g/cm}^3$ . The refinement  $R$ -factors are  $R_{\text{wp}} = 2.97\%$ ,  $R_{\text{exp}} = 1.67\%$  and  $\chi^2 = (R_{\text{wp}}/R_{\text{exp}})^2 = 3.16$  indicating good convergence of the fit. More details about the Rietveld refinement can be found in Table 1. The refined lattice parameters of Yb:GdCB are slightly smaller compared to undoped GdCB [ $a = 7.1953(3) \text{ \AA}$ ,  $b = 15.5348(7) \text{ \AA}$  and  $c = 8.6197(4) \text{ \AA}$ ] [14], due to the difference in ionic radii of  $\text{Yb}^{3+}$  ( $0.985 \text{ \AA}$ ) and  $\text{Gd}^{3+}$  ( $1.053 \text{ \AA}$ ) for VIII-fold oxygen coordination.

Table 2 shows the fractional atomic coordinates ( $x, y, z$ ), the site occupancy factors (O.F.) and the isotropic displacement parameters  $B_{\text{iso}}$  obtained via the Rietveld refinement. There exist three non-equivalent cationic sites: M1 -  $4c$ , M2 -  $8d$  and M3 -  $8d$  (designation - Wyckoff symbol). They are statistically occupied by  $\text{Ca}^{2+}$ ,  $\text{Gd}^{3+}$  and  $\text{Yb}^{3+}$ . The corresponding O.F. are: 0.390 - 0.575 - 0.035 (M1), 0.555 - 0.425 - 0.020 (M2) and 0.750 - 0.235 - 0.015 (M3).



**Fig. 2.** Rietveld refinement plots for the 5 at.% Yb:GdCB crystal: the experimental ( $Y_{obs}$ ), the calculated ( $Y_{calc}$ ) and the difference ( $Y_{obs} - Y_{calc}$ ) patterns, vertical dashes - the Bragg positions; *Inset*: zoomed view on the  $2\theta$  range of 15 - 35°.

**Table 1. Rietveld Refinement Data for the 5 at.% Yb:GdCB**

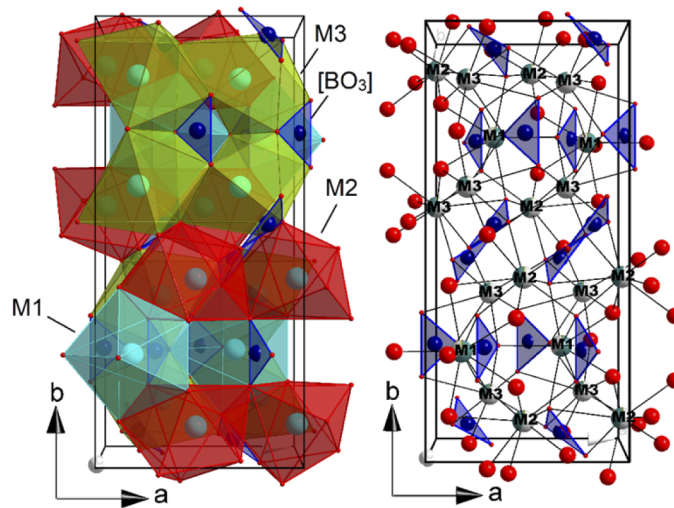
Parameter	Value
Crystal system	Orthorhombic
Space group (IT number)	$Pnma - D_{2h}^{16}$ (No. 62)
Number of formula units	$Z = 4$
Reduced number of S.O.	4
General multiplicity	8
Calculated density ( $\text{g}/\text{cm}^3$ )	4.790
Lattice constant $a, b, c$ ( $\text{Å}$ )	7.1937(0), 15.5311(3), 8.6140(7)
Unit-cell volume $V$ ( $\text{Å}^3$ )	962.419
$2\theta$ range (deg)	10–88
$2\theta$ step (deg)	0.02
Radiation	Cu-K $\alpha$ 1 ( $\lambda = 1.5418 \text{ Å}$ )
No. of reflections	862
Refinement software	Match3 (crystal impact) software
Reliability factors	$R_p = 2.09\%$ , $R_{wp} = 2.97\%$ , $R_{exp} = 1.67\%$ and $\chi^2 = 3.16$

**Table 2. Fractional Atomic Coordinates (x, y, z), Sites, Occupancy Factors (O.F.) and Isotropic Displacement Parameters  $B_{iso}$  for 5 at.% Yb:GdCB**

Atom	Wyckoff	x	y	z	O.F.	$B_{iso}, \text{Å}^2$
M1 <sup>a</sup> s	4c	0.1740(0)	1/4	0.9651(0)	0.390 - 0.575 - 0.035	1.959(0)
M2	8d	-0.0199(1)	0.4164(1)	0.6759(6)	0.555 - 0.425 - 0.020	1.269(0)
M3	8d	-0.1969(5)	0.3729(5)	1.1566(0)	0.750 - 0.235 - 0.015	0.552(0)
B1	4c	0.4925(7)	1/4	1.1030(0)	1	1.421(0)
B2	4c	0.3031(0)	1/4	0.6293(6)	1	1.026(0)
B3	8d	0.2988(9)	0.5357(9)	0.5058(3)	1	1.658(0)
O1	8d	0.4641(0)	0.33068	1.0708(0)	1	3.158(0)
O2	4c	0.1502(5)	1/4	1.2367(0)	1	3.158(0)
O3	4c	-0.1867(4)	1/4	1.0079(0)	1	3.158(0)
O4	8d	0.2037(5)	0.4910(0)	0.4884(1)	1	3.158(0)
O5	8d	-0.1103(0)	0.5336(4)	0.8169(5)	1	3.158(0)
O6	8d	-0.2430(2)	0.3147(7)	0.7670(2)	1	3.158(0)
O7	8d	0.1095(4)	0.3878(5)	0.9494(5)	1	3.158(0)

<sup>a</sup>M = Ca, Gd and Yb.

A fragment of the crystal structure is shown in Fig. 3(a), drawn according to the refined structural data using the Diamond4 program. The structure of Yb:GdCB is determined by facet- and edge-sharing M-oxygen ( $\text{MO}_n$ ) polyhedra of an irregular shape separated by isolated  $\text{BO}_3$  triangles. The species in M1 sites are surrounded by eight oxygen atoms with bond distances ranging from 2.1947(6) to 2.6211(1) Å, while the species in M2 and M3 sites are coordinated by seven oxygen atoms with bond distances ranging from 2.2839(9) Å to 2.5884(8) Å and from 2.3005 (5) to 2.6994 (9) Å, respectively. Each M3-based polyhedron is surrounded by four M1- and four M2-based polyhedra, Fig. 3, creating a disordered pseudo-cube with the M3 polyhedron inside and the M1- or M2-based polyhedra at the corners. The M1- and M2-based polyhedra from two neighboring pseudo-cubes are lying approximately within the same  $a$ - $b$  plane. The full set of interatomic distances for M-oxygen polyhedra is given in Table 3.



**Fig. 3.** A fragment of the crystal structure of 5 at.% Yb:GdCB: (a) a projection onto the  $a$ - $b$  plane showing the different M-oxygen polyhedra; (b) local environment around the cationic sites M1, M2 and M3.

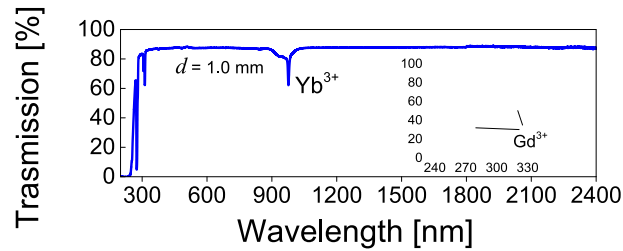
**Table 3. Selected Interatomic Distances for 5 at.% Yb:GdCB**

M1 - O, Å	M2 - O, Å	M3 - O, Å
M1-O3 = 2.6211(1) 1	M2-O1 = 2.5107(5) 1	M3-O5 = 2.6532(2) 1
M1-O7 = 2.1947(6) 2	M2-O6 = 2.3838(4) 1	M3-O1 = 2.6994(9) 1
M1-O2 = 2.3458(1) 1	M2-O4 = 2.4129(5) 1	M3-O3 = 2.3005(5) 1
M1-O6 = 2.3165(2) 1	M2-O5 = 2.2839(9) 1	M3-O2 = 2.3873(4) 1
M1-O1 = 2.5989(0) 2	M2-O4 = 2.5575(2) 1	M3-O5 = 2.4358(7) 1
M1-O6 = 2.3165(2) 1	M2-O7 = 2.5715(9) 1	M3-O4 = 2.3307(4) 1
	M2-O6 = 2.5884(8) 1	M3-O1 = 2.6310(8) 1

### 3. Optical spectroscopy

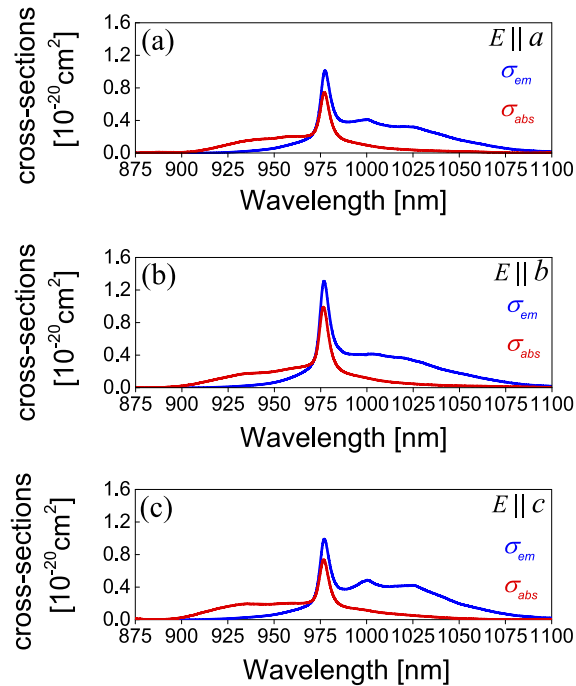
The RT transmission spectrum of a 1 mm-thick 5 at.% Yb:GdCB crystal is shown in Fig. 4. In the visible, no signs of absorption due to color centers and  $\text{Yb}^{2+}$  ions are observed. The absorption at  $\sim 1 \mu\text{m}$  is due to the  ${}^2\text{F}_{7/2} \rightarrow {}^2\text{F}_{5/2}$  transition of the  $\text{Yb}^{3+}$  ion. In the UV, the sharp bands at

274 - 280 nm and 301–312 nm are due to the host-forming  $\text{Gd}^{3+}$  ion. The UV absorption edge of the host matrix is observed at  $\sim 255$  nm.



**Fig. 4.** RT unpolarized transmission spectrum of a 1 mm-thick 5 at.% Yb:GdCB crystal plate, *inset* – a close look at the UV spectral range.

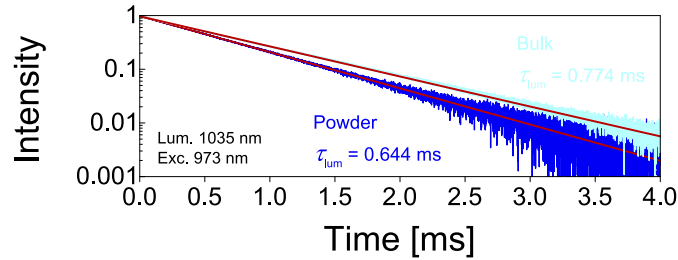
Orthorhombic Yb:GdCB is an optically biaxial crystal. Thus, its spectral properties were characterized for three principal light polarizations,  $E \parallel a$ ,  $b$  and  $c$ . The polarized RT absorption ( $\sigma_{\text{abs}}$ ) cross-section spectra of Yb:GdCB are shown in Fig. 5. The maximum  $\sigma_{\text{abs}}$  reaches  $0.99 \times 10^{-20} \text{ cm}^2$  at 976.5 nm (ZPL) and the corresponding absorption bandwidth (determined at full width at half maximum, FWHM) is 7.3 nm for light polarization  $E \parallel b$ . Such a broad bandwidth releases the limitations for pumping the Yb:GdCB crystals with high-power InGaAs laser diodes related to the possible temperature drift of the diode wavelength. For other polarizations, the peak  $\sigma_{\text{abs}}$  is lower,  $0.74 \times 10^{-20} \text{ cm}^2$  at 977.1 nm ( $E \parallel a$ ) and  $0.73 \times 10^{-20} \text{ cm}^2$  at 976.8 nm ( $E \parallel c$ ), while the absorption bandwidth is similar (7.5 nm).



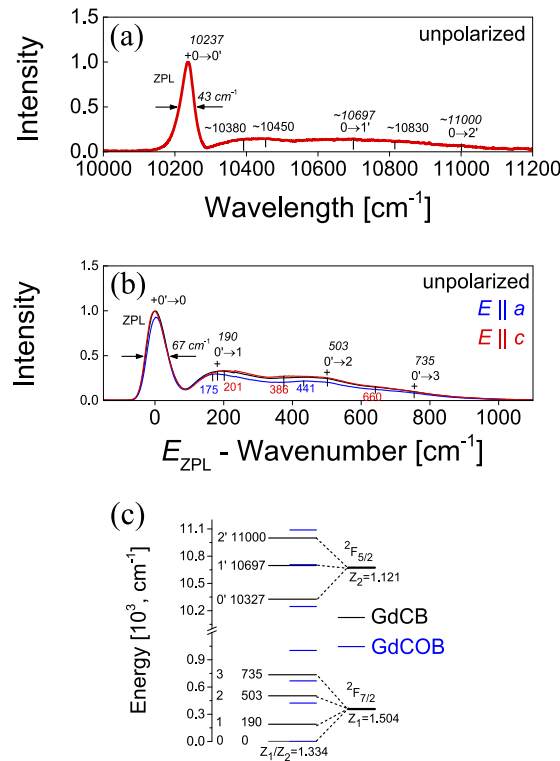
**Fig. 5.** Polarized RT absorption ( $\sigma_{\text{abs}}$ ) and stimulated-emission (SE,  $\sigma_{\text{SE}}$ ) cross-sections of  $\text{Yb}^{3+}$  in the Yb:GdCB crystal. The light polarization is: (a)  $E \parallel a$ ; (b)  $E \parallel b$  and (c)  $E \parallel c$ .

The stimulated-emission (SE,  $\sigma_{\text{SE}}$ ) cross-sections were calculated based on a combination of the Füchtbauer–Ladenburg equation and the reciprocity method (RM). A good agreement

between the two methods (considering the effect of reabsorption on the measured luminescence spectra) was observed for a radiative lifetime of the  ${}^2F_{5/2}$   $\text{Yb}^{3+}$  multiplet  $\tau_{\text{rad}} = 0.65 \pm 0.05$  ms. A mean refractive index  $\langle n \rangle = 1.70$  was used for calculations. The combined  $\sigma_{\text{SE}}$  spectra are shown in Fig. 5. The maximum  $\sigma_{\text{SE}}$  is  $1.31 \times 10^{-20}$   $\text{cm}^2$  at 976.8 nm (ZPL) for light polarization  $E \parallel b$ . In the spectral range where laser operation is expected (at wavelengths well above the ZPL,  $> 1 \mu\text{m}$ ),  $\sigma_{\text{SE}}$  reaches  $0.42 \times 10^{-20}$   $\text{cm}^2$  at 1025.1 nm for  $E \parallel c$ . For other two polarizations in this spectral range, the peak  $\sigma_{\text{SE}}$  is lower, namely  $0.36 \times 10^{-20}$   $\text{cm}^2$  at 1019.9 nm ( $E \parallel b$ ) and  $0.32 \times 10^{-20}$   $\text{cm}^2$  at 1025.0 nm ( $E \parallel a$ ). The intrinsic anisotropy of the SE cross-sections



**Fig. 6.** RT luminescence decay curve for  $\text{Yb}^{3+}$  ions in the 5 at.% Yb:GdCB crystal (bulk and powdered samples), red lines – single-exponential fits,  $\lambda_{\text{exc}} = 973$  nm,  $\lambda_{\text{lum}} = 1035$  nm.



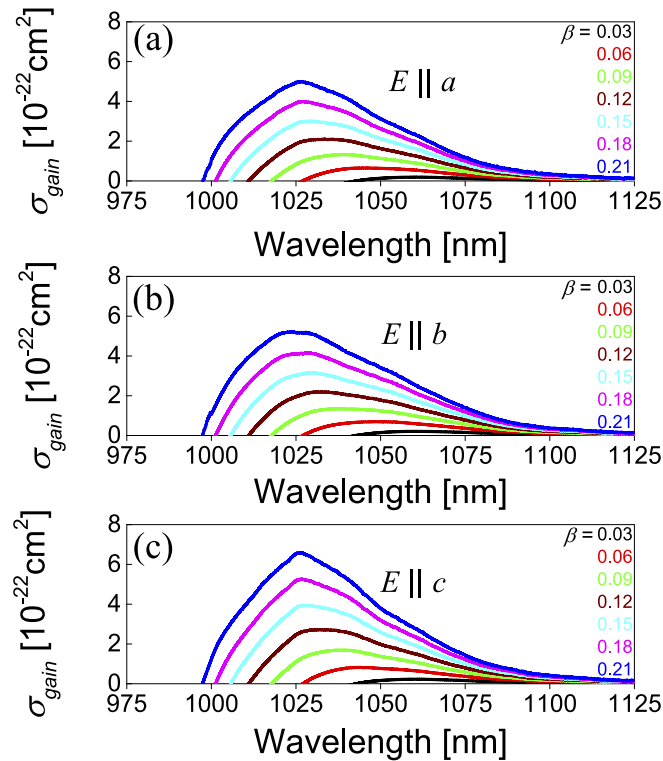
**Fig. 7.** LT (10 K) spectroscopy of the 5 at.% Yb:GdCB crystal: (a) absorption spectrum and (b) luminescence spectra,  $\lambda_{\text{exc}} = 973$  nm; (c) suggested energy-level scheme of  $\text{Yb}^{3+}$  in one of the sites in the GdCB crystal, the data for GdCOB [2] are shown for comparison.  $Z_{1(2)}$  are the partition functions.

indicates that a linearly polarized radiation is expected to be generated from Yb:GdCB lasers without polarization-selective elements ( $E \parallel c$  or  $E \parallel b$ , depending on the crystal cut).

The luminescence decay curve was measured using a finely powdered crystalline sample to avoid the effect of radiation trapping (reabsorption). The  $\text{Yb}^{3+}$  ion luminescence in GdCB exhibits a single-exponential decay corresponding to a luminescence lifetime of  $\tau_{\text{lum}} = 644 \mu\text{s}$ , Fig. 6.

It indicates that the transition intensities of  $\text{Yb}^{3+}$  ions residing in M1 – M3 sites are relatively close. The determined  $\tau_{\text{lum}}$  value agrees well with the estimated radiative lifetime. To further reveal the inhomogeneous spectral broadening for  $\text{Yb}^{3+}$  ions in GdCB, the LT absorption and luminescence spectra were measured, Fig. 7(a,b). The luminescence was studied under non-selective excitation.

The broadband spectral properties of Yb:GdCB were preserved even at 10 K. The ZPL in absorption centered at  $10237 \text{ cm}^{-1}$  (976.8 nm) had a bandwidth (FWHM) of  $43 \text{ cm}^{-1}$  which is at least one order of magnitude broader than that for ordered crystals. An attempt to assign the electronic transitions for one of the  $\text{Yb}^{3+}$  species in GdCB (the dominant one) was made following the previously reported crystal-field splitting for Yb:GdCOB (site I, Gd) [2]. The energy levels of the ground-state ( $^2F_{7/2}$ ) were numbered as 0–3 and those of the excited-state ( $^2F_{5/2}$ ) – as 0' – 2'. This resulted in the following crystal-field splitting:  $^2F_{7/2} = (0, 190, 503, 735) \text{ cm}^{-1}$  and  $^2F_{5/2} = (10327, 10697, 11000) \text{ cm}^{-1}$ , cf. Figure 7(c). The partition functions for the lower and upper  $\text{Yb}^{3+}$  manifolds were then calculated to be  $Z_1 = 1.504$  and  $Z_2 = 1.121$ , respectively, yielding a ratio  $Z_1/Z_2 = 1.334$  used for the calculations of the SE cross-sections by the reciprocity method.

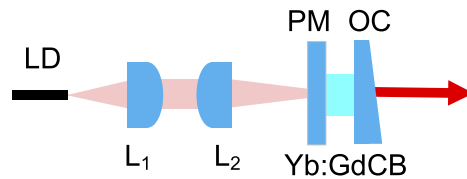


**Fig. 8.** RT polarized gain cross-section ( $\sigma_{\text{gain}}$ ) spectra for Yb:GdCB crystal,  $\beta$  is the inversion ratio. The light polarization is: (a)  $E \parallel a$ ; (b)  $E \parallel b$  and (c)  $E \parallel c$ .

According to the quasi-three-level nature of the Yb laser, the gain cross-sections,  $\sigma_{\text{gain}} = \beta\sigma_{\text{SE}} - (1 - \beta)\sigma_{\text{abs}}$ , were calculated, where  $\beta = N_2/N_{\text{Yb}}$  is the inversion ratio and  $N_2$  is the population of the upper laser level ( ${}^2F_{5/2}$ ). The polarized gain profiles are shown in Fig. 8. With increasing the inversion ratio, the spectral maximum shifts to shorter wavelengths, e.g., from 1060 nm for small  $\beta = 0.03$  to 1027 nm for high  $\beta > 0.15$  (for  $E \parallel c$ ). The gain bandwidths for an intermediate  $\beta = 0.12$  are 48 nm ( $E \parallel a$ ), 51 nm ( $E \parallel b$ ) and 46 nm ( $E \parallel c$ ). These values, as well as the extremely broad and smooth gain spectra indicate the high potential of the Yb:GdCB crystal for broadly tunable operation and sub-50 fs pulse generation from ML lasers.

#### 4. Diode-pumped laser operation

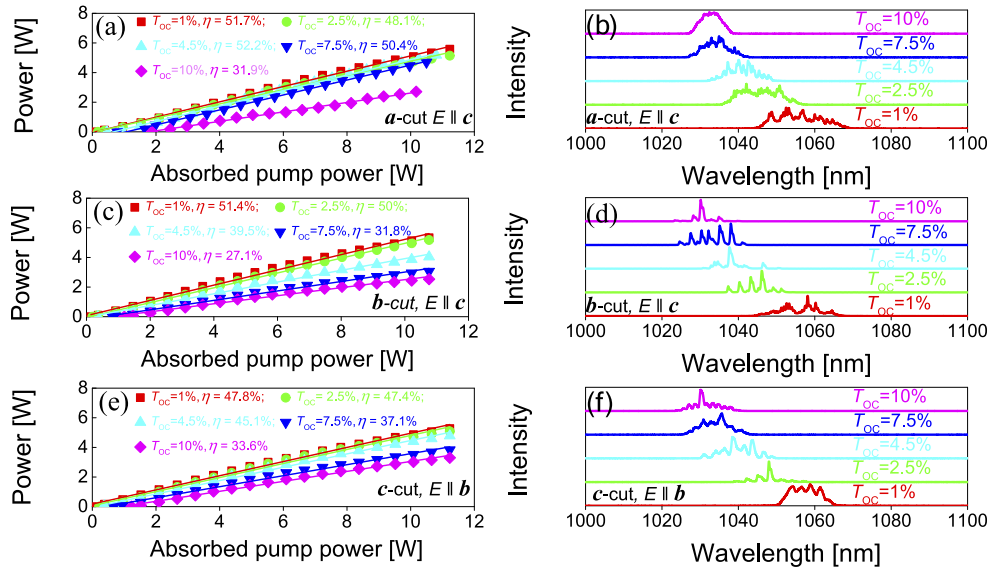
The schematic of the diode-pumped compact Yb:GdCB laser is shown in Fig. 9. Three rectangular samples with 5 at.% Yb<sup>3+</sup> doping were oriented for light propagation along the three crystallographic axes (denoted as *a*-cut, *b*-cut and *c*-cut) having identical dimensions (aperture: 4 mm × 4 mm, thickness: 3 mm). Their input and output faces were polished to laser quality and left uncoated. The crystals were wrapped in Indium foil and repetitively mounted into the same copper holder cooled by circulating water (coolant temperature: 15°C). The pump source was a multi-transverse mode, fiber-coupled InGaAs diode laser emitting up to 50 W of unpolarized radiation at 976 nm. The fiber had a core diameter of 105 μm and a numerical aperture (N.A.) of 0.15. The emission wavelength of the diode laser was locked by a fiber Bragg grating (FBG) over the entire operation range with a linewidth of ~0.7 nm. The pump beam was reimaged into the laser crystal by a pair of antireflection-coated doublet lenses with identical focal lengths ( $f = 50$  mm) yielding a beam waist of ~63 μm (radius).



**Fig. 9.** Schematic of the diode-pumped Yb:GdCB laser. LD: fiber-coupled laser diode;  $L_1$  and  $L_2$ : lenses; PM: pump mirror; OC: output coupler.

The laser cavity consisted of a flat pump mirror (PM) coated for high transmission at 0.9-1.01 μm and high reflection at 1.02-1.2 μm, and a plane-wedged output coupler (OC) with a set of transmissions at the laser wavelength ( $T_{\text{OC}} = 1\% - 10\%$ ). Both cavity mirrors were placed as close as possible to the laser crystal oriented for normal incidence resulting in a microchip-type design. The geometrical cavity length of such a micro-laser was ~3 mm. The obtained laser operation in a plano-plano cavity with all the studied crystal cuts indicated a positive (focusing) thermal lens in Yb:GdCB for laser polarizations  $E \parallel b$  and  $E \parallel c$ . The maximum incident pump power was limited to 18.7 W to avoid the risk of thermal fracture of the crystal. The single-pass pump absorption efficiency was measured under lasing condition yielding values between 54.4% and 60.1% depending on the crystal orientation and the transmission of the OC.

The CW laser performance for different OCs with the three Yb:GdCB samples of different cuts is shown in Fig. 10. The best performance was observed for the *a*-cut crystal: the laser generated a maximum output power of 5.58 W at 1045 - 1067 nm (a broad spectrum) with a slope efficiency  $\eta$  of 51.7% (vs. the absorbed pump power) and an optical-to-optical efficiency of 49.7%, Fig. 10(a) (for  $T_{\text{OC}} = 1\%$ ). With increasing the output-coupling, the laser threshold gradually increased from 0.137 W ( $T_{\text{OC}} = 1\%$ ) to 1.188 W ( $T_{\text{OC}} = 10\%$ ). A comparison of these results with those obtained for *b*-cut and *c*-cut crystals can be found in Table 4.



**Fig. 10.** CW diode-pumped Yb:GdCB lasers: (a), (c) and (e) input – output dependences,  $\eta$  – slope efficiency; (b), (d) and (f) typical spectra of laser emission. Crystal orientation and laser polarization: (a) and (b) *a*-cut,  $E \parallel c$ ; (c) and (d) *b*-cut,  $E \parallel c$ ; (e) and (f) *c*-cut,  $E \parallel b$ .

**Table 4. Continuous-Wave Diode-Pumped Laser Performance<sup>a</sup> of 5 at.% Yb:GdCB Crystals with Different Orientations**

Cut	Polarization	$P_{\text{out}}$ , W	$\lambda_L$ , nm	$\eta$ , %	$P_{\text{th}}$ , W	$\eta_{\text{opt}}$ , %
<i>a</i> -cut	$E \parallel c$	5.58	1045–1057	51.7	0.137	49.7
<i>b</i> -cut	$E \parallel c$	5.33	1030–1058	51.4	0.137	49.8
<i>c</i> -cut	$E \parallel b$	5.27	1030–1057	47.8	0.069	46.9

<sup>a</sup> $P_{\text{out}}$  – output power,  $\lambda_L$  – laser wavelength,  $\eta$  – slope efficiency,  $P_{\text{th}}$  – laser threshold,  $\eta_{\text{opt}}$  – optical efficiency.  $T_{\text{OC}} = 1\%$ .

For all three crystal cuts, the laser emission was linearly polarized, and the polarization state was naturally selected by the anisotropy of the gain. The laser polarization was  $E \parallel c$  (*a*-cut and *b*-cut crystals) and  $E \parallel b$  (*c*-cut crystal). This agrees well with the anisotropy of the SE cross-sections for the  $\text{Yb}^{3+}$  ions in the GdCB crystal, cf. Figure 5. The same polarization state was preserved over the entire studied range of pump powers. Typical laser emission spectra of the three samples are shown in Fig. 10(b), (d) and (f). They exhibited a similar dependence on the OC transmission, e.g., varying from 1045–1067 nm ( $T_{\text{OC}} = 1\%$ ) to 1028–1038 nm ( $T_{\text{OC}} = 10\%$ ) for the *a*-cut crystal. The observation of a red-shift of the laser wavelength with the reduction of the OC transmission is typical for quasi-three-level Yb lasers with intrinsic reabsorption at the laser wavelength and it is in line with the calculated polarized gain cross-section spectra of the Yb:GdCB crystal, cf. Figure 8. The broad free-running spectra are due to the very flat  $\text{Yb}^{3+}$  gain profiles, and their multi-peak structure is attributed to etalon (Fabry-Perot) effects between the mirror / crystal interfaces.

## 5. Conclusion

To conclude,  $\text{Yb}^{3+}:\text{Ca}_3\text{Gd}_2(\text{BO}_3)_4$  (Yb:GdCB), is a promising laser material with broadband emission properties at  $\sim 1 \mu\text{m}$ . It features a variety of cationic sites (M1 – M3) with a distorted VIII-fold (M1) and VII-fold (M2, M3) coordination randomly populated by the  $\text{Ca}^{2+}$  and

$\text{Gd}^{3+}|\text{Yb}^{3+}$  cations leading to an extremely strong inhomogeneous broadening of absorption and emission bands of  $\text{Yb}^{3+}$  ions (a “glassy-like” spectroscopic behavior). Moreover, it offers a notable polarization-anisotropy of stimulated-emission cross-section spectra which determines a linear polarization in Yb:GdCB lasers ( $\mathbf{E} \parallel \mathbf{b}$  or  $\mathbf{E} \parallel \mathbf{c}$ , depending on the crystal orientation). Yb:GdCB is characterized by a large total Stark splitting of the ground-state ( ${}^2\text{F}_{7/2}$ ,  $735 \text{ cm}^{-1}$ ), as well as long fluorescence lifetime ( $644 \mu\text{s}$ ), which are favorable for low-threshold laser operation. The broad absorption linewidth ( $\sim 7.3\text{--}7.5 \text{ nm}$  at  $976 \text{ nm}$  corresponding to the  $\text{Yb}^{3+}$  zero-phonon-line (ZPL) releases the constraints on the bandwidth and temperature drift of the emission wavelength for commercially available InGaAs diode lasers. Finally, the extremely broad, flat and smooth gain profiles of the  $\text{Yb}^{3+}$  ion in GdCB being superior in this regard to those for well-known  $\text{Yb}^{3+}$ -doped monoclinic calcium oxoborate crystals (e.g., Yb:YCOB and Yb:GdCOB), indicate the high potential of the former crystal for applications in sub-50 fs pulse generation from ML lasers, particularly in terms of shortening the pulse duration of low-to-moderate power seeding lasers for ultrafast amplifiers.

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**Data availability.** Data underlying the results presented in this paper are not publicly available at this time but may be obtained from the authors upon reasonable request.

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