Growth, thermal properties and laser operation of Nd:Ca₃La₂(BO₃)₄: A new disordered laser crystal

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Abstract: A novel disordered laser crystal Nd:Ca₃La₂(BO₃)₄ is characterized including its crystal growth, structure, thermal properties, inhomogeneously broadened spectra, and laser performance, which result that this crystal should be a promising gain material for the high-power ultrashort pulsed neodymium laser. The complete set of anisotropic thermal properties were systematically studied for the first time. It has been found that thermal contraction happens in the c direction and all the thermal conductivities increase with temperature, indicating a glass-like behavior. Polarized absorption and fluorescence spectra of Nd:Ca₃La₂(BO₃)₄ crystal were measured at 298.15 K and 77.3 K, respectively. The results show that both the absorption and the emission spectra of Nd³⁺ have been inhomogeneously broadened, and thus it is very promising to be used in laser systems to produce femtosecond pulses. CW laser operations at 1.06 µm along the three crystallographic directions has been demonstrated for the first time. A maximum power of 1.08 W with an optical conversion efficiency of 10.6% and slope efficiency of 12.4% was achieved in the acut sample.

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OCIS codes: (140.3530) Lasers, neodymium; (160.3380) Laser materials.

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1. Introduction

Recently, the rapid development of ultrashort laser pulse technology has triggered great progress on the frontier of many fundamental sciences. It has now been found that ultrashort laser pulses have got wide applications in telemetry, microcosmic exploration, hightemperature plasma generation, etc [1-3]. Based on the uncertainty principle, the width of pulses is determined by the mode-locked frequency, which indicates that the gain materials should have broad emission spectra. Neodymium doped glass is one of the most commercial femtosecond laser gains due to its inhomogenously broadened fluorescence spectra. However, its totally disordered structure generates the unpolarized emission and relative poor thermal properties. In crystals, there is a kind of host materials named as disordered crystals. In their structures, there is partly replacement of the ions in the lattices which induces broad inhomogenously broadened spectra like glass and their crystal merits induce the better thermal properties and polarized emission. Therefore, the disordered crystal was considered to be promising candidate for the generation of femtosecond pulses and a substitute for Nd glass. For the instance of Nd:CNGG crystal, its absorption bandwidth (FWHM) near 807 nm is 7 nm, almost 5 times larger than that of Nd:YAG crystal; its emission bandwidth (FWHM) near 1067 nm is 17 nm, 30 times larger than that of Nd:YAG [4], and the mode-locked pulse is about 660 fs [5]. With a simple hybrid of Nd:CNGG and CLNGG disordered crystals, the pulse of 534 fs was achieved and should be an inspiring result in the disordered crystal lasers [6].

Among the disordered crystal group, a new borate family $Ca_3RE_2(BO_3)_4$ (RE = Y, La, Gd) draws people's attention, and Nd: $Ca_3La_2(BO_3)_4$ is one of current interest [7]. In the lattice, the Re and Ca ions randomly replace each other generating their disordered structure. In the last few years, a lot of research work has been focused on the Yb³⁺-doped Ca₃RE₂(BO₃)₄ crystals and recently, a minimum pulse duration of 244-fs with a repetition rate of 55 MHz was obtained in the Yb: $Ca_3Y_2(BO_3)_4$ crystal [8, 9]. However, Nd³⁺-doped crystals of this family have not been systematically studied but are important for the possible generation of femtosecond Nd lasers. For Nd: $Ca_3La_2(BO_3)_4$, although it has been known for many years, the important thermal properties and laser performance have not demonstrated up to now. We believe that this lack is due to the difficulty in obtaining suitable sized Nd: $Ca_3La_2(BO_3)_4$ crystals with good optical quality. Besides, the polarized spectroscopic properties were also needed to gain a better understanding of the lasing mechanism in Nd: $Ca_3La_2(BO_3)_4$ [7]. In this

paper we report the Czochralski growth of large sized $Nd:Ca_3La_2(BO_3)_4$ crystal. The phase purity, lattice constants and effective segregation coefficient of Nd^{3+} in the as-grown crystal were measured. Furthermore, its complete set of anisotropic thermal properties and polarized spectroscopic properties were well characterized. The laser operation of $Nd:Ca_3La_2(BO_3)_4$ was carried out along three different crystallographic directions and its laser performance was evaluated for future applications.

2. Experiment details

A Nd:Ca₃La₂(BO₃)₄ single crystal was grown by the Czochralski method under a nitrogen atmosphere containing 2% oxygen (v/v) in an iridium crucible. The as-grown Nd:Ca₃La₂(BO₃)₄ crystal has an excellent quality (no scatter pellets can be observed under 5 mW He-Ne laser). Figure 1(a) is the photograph of the as-grown Nd:Ca₃La₂(BO₃)₄ crystal boule grown along the *b* direction. Its dimensions are about Φ 25 × 32mm². The Nd concentrations in Nd:Ca₃La₂(BO₃)₄ crystal was measured to be 0.495 at.% by the X-ray fluorescence method.



Fig. 1. (a) The as-grown Nd:Ca₃La₂(BO₃)₄ crystal boule; (b) X-ray powder diffraction pattern of Nd:Ca₃La₂(BO₃)₄ crystal; (c) X-ray rocking curve of the as-grown Nd:Ca₃La₂(BO₃)₄ single crystal.

Several samples with different sizes were prepared from this crystal boule for the experiments. The phase purity of the as-grown crystal was first checked by X-ray powder diffraction (XRPD). As shown in Fig. 1(c), accurate unit cell parameters were further calculated by using the Pawley fitting of the whole powder pattern decomposition (WPPD) procedure in the TOPAS v.3 software. The background was fitted using a Chebyshev Polynomial of 8th order and the peak shape was assumed to be a modified Thompson-Cox-Hasting pseudo-Voigt (TCHZ_PV) function. The results show that the unit cell parameters are a = 7.2657 (1), b = 16.0444 (3), c = 8.6802 (1) Å, and V = 1011.88 (8) Å³ with an orthorhombic space group *P*nma, Rwp = 10.141%.

The rocking curves were measured by using the high resolution X-ray diffraction method to test the lattice integrity of the as-grown crystals. The result is shown in Fig. 1(b), the full

width at half-maximum (FWHM) values is only 29.34". The diffraction peaks show good symmetry without any splitting, which indicates that the $Nd:Ca_3La_2(BO_3)_4$ single crystal has highly excellent quality and is suitable for laser applications.

A thermal mechanical analyzer (Perkin Elmer model: Diamond TMA) was used to measure the average linear thermal expansion tensor components of Nd: $Ca_3La_2(BO_3)_4$. The sample used for the thermal expansion measurement was processed into a rectangular piece of dimensions 6.14 \times 7.00 \times 7.94 mm³ ($a \times b \times c$). The specific heat was measured by the differential scanning calorimetry method using a simultaneous thermal analyzer (Perkin Elmer Diamond: DSC). The thermal diffusivity coefficient was measured by the laser flash method using a laser flash apparatus (NETZSCH LFA457), from which the thermal conductivity can be calculated. Three square wafers used for the measurements with dimensions of $[4.02 \times 4.01 \times 1.00 \text{ mm}^3 (a \times b \times c), 4.01 \times 4.00 \times 1.00 \text{ mm}^3 (a \times c \times b)$ and $4.00 \times 4.00 \times 1.01 \text{ mm}^3$ ($b \times c \times a$)] were coated with graphite on opposite sides.

A cuboid with dimensions of $5.0 \times 5.7 \times 6.7 \text{ mm}^3$ ($a \times b \times c$) was cut from the grown crystal. All the surfaces of the sample were polished for spectral experiments. The polarized absorption spectra were measured at room temperature by a V-570 JASCO ultraviolet/visible/near infrared (UV/Vis/NIR) spectrophotometer. Scan speed was 60 nm / min and sampling interval was 0.5 nm.

With the same sample that mentioned above, the fluorescence spectra from 850 to 1500 nm at room temperature and 77.3 K were recorded by a spectrofluorimeter (Edinburgh Instrument FLS920). The exciting source is a 450 W stable xenon lamp with the wavelength of 355 nm light. The fluorescence decay curve at 1064 nm was measured with the same spectrofluorimeter which was pumped by a 10 ns pulsed OPO laser (Opolette 355 II) with the wavelength of 355 nm.

With the laser samples cut along a, b and c directions, CW laser operations were demonstrated by using a plano-concave resonator. The laser experimental setup is shown schematically in Fig. 2. The pumping source was a fiber-coupled LD with the emission wavelength centered at 806 nm. The output beam of the LD was focused onto the Nd:Ca₃La₂(BO₃)₄ crystal sample with a spot radius of about 0.2 mm and a numerical aperture of 0.22 achieved by using a focusing lens. The length between M1 and M2 was about 17 mm. M1 was a plano mirror, antireflection (AR) coated at 806nm on the pump face, high reflectance (HR) coated at the range of 1020 to 1200 nm, and high-transmittance (HT) coated at 806 nm on the other face. The output coupler M2 was a concave mirror with a radius of curvature of 80 mm, and the output transmission is 2.0% at 1.06μ m. The samples were cut to the dimensions $3 \times 3 \times 6 \text{ mm}^3$ and the $3 \times 3 \text{ mm}^2$ faces perpendicular to the *a*, *b* and *c* directions were polished. During the experiments, the crystal were wrapped with indium foil and mounted on a copper block cooled by water. The cooling water was maintained at a temperature of 10 °C.



Fig. 2. Schematic diagram of the experimental laser setup.

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3. Results and discussions

3.1 Linear thermal expansion

Figure 3(a) shows the thermal expansion curves of Nd:Ca₃La₂(BO₃)₄ versus temperature. From the curves, it can be seen that the thermal expansion curves along the *a*- and *b*-axis are almost linear over the entire temperature range from 303.15 to 770.15K. It shows only thermal expansion, no thermal contraction occurs when the crystal is heated along the the *a*- and *b*-axis. However, the thermal expansion along the *c*-axis shows anomaly that there is not only thermal expansion but also thermal contraction within the measuring temperature range.

According to the measured thermal expansion curves, the mean values of the average linear thermal expansion coefficients along the *a* and *b*-axis were calculated to be $a_a = 2.27 \times$ 10^{-5} /K, $a_{\rm b} = 7.49 \times 10^{-6}$ /K over the temperature range of 293.15-757.15 K, which shows large positive thermal expansion. Since the thermal expansion along the *c*-axis shows not only thermal expansion but also thermal contraction, the curve of *c*-axis was cut into two parts. The average linear thermal expansion coefficient of c-axis in the range of 293.15 K to 500.15 K shows a negative value of -4.36×10^{-6} /K, while in the range of 500.15 K to 757.15 K the average linear expansion coefficient was turned to be positive as 8.97×10^{-6} /K. The interesting negative thermal expansion makes the crystal suitable for many technological applications. The primary one is to be used as components of composites to adjust the overall thermal expansion of composites to some particular value [10, 11]. Additionally, it can be found that the linear thermal expansion coefficient value along the *a*-axis is 5 times larger than that along *c*-axis. Thus, there is a large anisotropy in the thermal expansion of Nd:Ca₃La₂(BO₃)₄. Therefore, to protect Nd:Ca₃La₂(BO₃)₄ from cracking caused by thermal expansion, a smaller cooling rate should be used during crystal growth, especially when the temperature dropped below the 500.15 K, the cooling rate should be slower because of the negative thermal expansion.

Additionally, a large temperature gradient should be avoided during processing and application. In this crystal-growing process, the cooling rate was chosen to be 30-40 °C/h at the beginning and a cooling rate of 15-20 °C/h when the temperature dropped to 500.15 K.



Fig. 3. (a) Thermal expansion versus temperature; (b) Specific heat versus temperature; (c) Thermal diffusivity versus temperature; (d) Thermal conductivity versus temperature.

#182818 - \$15.00 USD (C) 2013 OSA Received 7 Jan 2013; revised 16 Feb 2013; accepted 16 Feb 2013; published 4 Mar 2013 11 March 2013 / Vol. 21, No. 5 / OPTICS EXPRESS 6095

3.2 Specific heat

The dependence of the specific heat (C_p) of Nd:Ca₃La₂(BO₃)₄ on temperature is shown in Fig. 3(b). It can be seen that the specific heat varies approximately linearly with temperature, increasing smoothly from 0.616 to 0.863 J g⁻¹ K⁻¹, when the temperature is increased from 298.15 K to 568.15 K. The specific heat of the crystal is 0.651 J g⁻¹ K⁻¹ (98.60 cal mol⁻¹ k⁻¹) at 330 K. In comparison with Nd:YCOB (82.4 cal mol⁻¹ k⁻¹) and Nd:YVO₄ (24.6 cal mol⁻¹ k⁻¹) [12], Nd:Ca₃La₂(BO₃)₄ has a relatively large specific heat. Since Nd:YCOB and Nd:YVO₄ both have a high optical damage threshold [13], it follows that Nd:Ca₃La₂(BO₃)₄ should also have a high damage threshold.

3.3 Thermal diffusion coefficient

The thermal diffusion coefficient a_{ij} of the crystal is also a symmetric second-rank tensor, analogous to the thermal expansion coefficient. Figure 3(c) shows the thermal diffusion coefficients of the Nd:Ca₃La₂(BO₃)₄ crystal. It can be seen that the thermal diffusivities along the *a*, *b* and *c*-axis decreases slowly with increasing temperature. At 295.35 K, the thermal diffusivity along the *a*-axis is 0.42 mm²/s, and along the *b*- and *c*-axis 0.44 mm²/s and 0.40 mm²/s, respectively.

3.4 Thermal conductivity

Figure 3(d) shows the temperature dependence on the thermal conductivities of Nd:Ca₃La₂(BO₃)₄ along the *a*-, *b*- and *c*-axis, determined by using the formula $k = \lambda \times \rho \times C_p$

here λ is the thermal diffusivity coefficient, $\rho = 4.187 \text{ g/cm}^3$ is the measured density, and C_p is the specific heat. It can be seen that the thermal conductivity of Nd:Ca₃La₂(BO₃)₄ increases with increasing temperature, a behavior that is not typical of most crystals. When the temperature increases from 295.35 to 572.55 K, the thermal conductivity along the *a*-, *b*- and *c*-axis increases from 1.08 to 1.30 W/m-K, 1.12 to 1.45 W/m-K, and 1.03 to 1.35 W/m-K, respectively. Though the thermal conductivity of Nd:Ca₃La₂(BO₃)₄ is relatively low, it is still larger than the Nd:glass.

The thermal conductivity of $Nd:Ca_3La_2(BO_3)_4$ is similar to that of $Nd^{3+}:SrGdGa_3O_7$ because both have an approximately linear temperature dependence [1], which indicates glasslike behavior. This behavior of $Nd:Ca_3La_2(BO_3)_4$ is possibly related to the disordered structure of the crystal.



Fig. 4. (a) Polarized absorption spectrum of Nd:Ca₃La₂(BO₃)₄; (b) Polarized absorption crosssection of Nd:Ca₃La₂(BO₃)₄ over the range of 720-910 nm; (c) Fluorescence decay curve of Nd:Ca₃La₂(BO₃)₄.

The polarized absorption spectra of the 0.495 at. % Nd³⁺-doped Ca₃La₂(BO₃)₄ crystal over the range of 330-1000 nm is shown in Fig. 4(a). E represents the electric field of the incident light. Figure 4(b) shows an enlargement of the 720-910 nm region for clarity. Obviously, the polarization spectrum helps to gain a better understanding of the optical properties of Nd: $Ca_3La_2(BO_3)_4$ in contrast with the previously measured unpolarized spectrum [5]. It can be seen from the two figures that the absorption spectrum shows a relatively strong directional dependence on the polarization due to the effect of anisotropy. From Fig. 4(b), it can be seen that the absorption for E//b is the strongest one among the three directions, and the peak absorption cross-section at 806 nm is about 2.96×10^{-20} cm² with a broad bandwidth (FWHM) of about 15 nm. Therefore, the E//b polarized direction can be treated as the most effective pump direction, more efficient 1.06um laser output may be realized in a *a*- or *c*-cut Nd: $Ca_3La_2(BO_3)_4$ crystal. For the E//a and E//c polarizations, the maximum absorption crosssections near 806 nm are $2.68 \times 10^{-20} \text{cm}^2$ and $2.55 \times 10^{-20} \text{cm}^2$, respectively, and the bandwidths (FWHM) are both of 17 nm. In comparison with the Nd:KY(WO₄)₂, Nd:YAG and Nd:YVO4 crystals with ordered structures (see Table 1) [14–17], the Nd³⁺-doped Ca₃La₂(BO₃)₄ crystal has a large FWHM at 806 nm, which is about 24 times larger than that of the Nd:YAG crystal, and is 8.5 times larger than that of the Nd:YVO₄ crystal. The wide bandwidth signifies that Nd:Ca₃La₂(BO₃)₄ is quite suitable for diode pumping and indicates inhomogeneous broadening behavior [18], which is probably due to the structural disorder of the crystal [5]. The fluorescence decay curve of Nd: $Ca_3La_2(BO_3)_4$ is shown in Fig. 4(c). By linear fitting, the fluorescence lifetime is found to be 76 μ s, which is very similar to that of the Nd: $Sr_3Y_2(BO_3)_4$ crystal which was reported in our previous work.



Fig. 5. Fluorescence spectra of Nd:Ca₃La₂(BO₃)₄: (a) room temperature polarized emission spectra; (b) 77.3 K polarized spectra emission spectrum.

The room temperature and low temperature (77.3 K) fluorescence spectra are shown in Fig. 5. The peak wavelength in the room temperature fluorescence spectrum for E//a is located at 1064 nm with a broad bandwidth (FWHM) of about 27 nm, while for E//b and E//c polarizations, the peak wavelengths are located at 1061 nm and 1062 nm, and the broad bandwidths (FWHM) are 27 nm and 30 nm, respectively. Additionally, compared with the room temperature fluorescence spectra, the values of FWHM in the 77.3 K for E//a and E//bpolarizations are both 25 nm, while for E//c the value of FWHM is 26 nm, all of which show a very small change. The broad bandwidth is similar to Nd:glass (20-30nm), which can support pulses of less than 100fs [19, 20]. Thus, such a large bandwidth shows that Nd: $Ca_3La_2(BO_3)_4$ may also possibly be used in laser systems to produce femtosecond pulses. Additionally, because of the relatively high thermal conductivity, the crystal can be even used in the high-power system [21]. It can be concluded that the broad room temperature absorption and emission bands together with the 77.3 K fluorescence spectrum show an inhomogeneous broadening behavior of the Nd: $Ca_3La_2(BO_3)_4$ crystal. Generally, the major broadening mechanism at room temperature is homogeneous broadening from the thermal vibration of lattice and inhomogeneous broadening from disordered crystal lattice. While in the low temperature, the inhomogeneous broadening dominates due to the weakening of lattice vibration. Here we can find that the inhomogeneous broadening behavior plays a decisive role, not only in the room temperature, but also in the low temperature. We know that Nd:Ca₃La₂(BO₃)₄ crystal is a homology of Nd:Ca₃Gd₂(BO₃)₄, and the inhomogeneous broadening behavior in the Nd: $Ca_3Gd_2(BO_3)_4$ crystal has been discussed in our paper before [6]. Thus, we believed that the inhomogeneous broadening of the Nd^{3+} lines is also attributed to the variation of the local crystal field surrounding the Nd^{3+} ions resulting from the high degree of structural disorder in that Nd³⁺, Ca²⁺ and La³⁺ ions are randomly situated at three different symmetry sites in the Nd:Ca₃La₂(BO₃)₄ structure [5].

Crystals	Nd:Ca ₃ La ₂ (BO ₃) ₄	Nd:KY(WO ₄) ₂	Nd:YAG	Nd:YVO ₄
Crystal system	Orthorhombic	Monoclinic	Cubic	Tetragonal
Growth method	CZ	TSSG	CZ	CZ
Peak absorption	806 (E//a)	812	808	808.7
wavelength λ_a (nm)				
FWHM at λ _a (nm)	17	4	0.7	2
Peak emission	1064 (E//a)	1058	1064	1064
wavelength λ_e (nm)				
FWHM at λ _e (nm)	27	/	0.8	1.1
Fluorescence lifetime	76	154	248	84
(µs)				
Reference	This work	14	15	16, 17

Table 1. Comparison of Spectroscopic Properties of Nd³⁺-doped Ca₃La₂(BO₃)₄ Crystal with Other Well-known Crystals

3.6 Laser performance



Fig. 6. Average output power versus incident pump power along the *a*-, *b*- and *c*-cut.

Continuous-wave (CW) laser performances at 1.06 mm in three directions were demonstrated for the first time. The output power under various incident pump power values was measured using a power meter, and the results are shown in Fig. 6. In can be seen that the *a*-cut sample shows the best laser performance among the three directions. For *a*-cut sample, the pump threshold is 1.5 W, and a maximum output power of 1.08 W at 1.06 μ m was achieved at a pump power of 10.24 W. The optical-to-optical conversion efficiency can be calculated to be 10.6%, and a slope efficiency of 12.4% was derived from the linear part of the curve. We can also found in Fig. 6 that the output power in the three directions were not saturated, but because of the thermal effect, when the pumping power increased the values that larger than 10.24 W, 8.3 W and 8.9 W for the three directions, the samples used in the experiment were broken. Thus, if we try to reduce the thermal effect, we believe that larger pumping power can be used, so higher output power may be achieved. Additionally, the samples used in the laser experiment were not coated, and only one output coupling with 2.0% transmission was used in the experiment. Therefore, more efficient laser output can be realized if the samples and the transmission output coupling are optimized.

4. Conclusion

A large sized and high quality Nd: $Ca_3La_2(BO_3)_4$ laser crystal has been successfully grown by the Czochralski method. The unit cell parameters are calculated by Pawley fitting of the whole powder pattern decomposition (WPPD) procedure to be a = 7.2657 (1), b = 16.0444 (3), c = 8.6802 (1) Å, and V = 1011.88 (8) Å³ with orthorhombic space group Pnma. Furthermore, its complete thermal, spectroscopic and laser performance were reported. The average linear thermal expansion coefficients along the a- and b-axis were measured to be a_a $= 2.27 \times 10^{-5}$ /K, $a_b = 7.49 \times 10^{-6}$ /K over the whole temperature range of 293.15-757.15K. However, along the *c*-axis, it first shows a thermal contraction of -4.36×10^{-6} /K till 500.15 K, then turns to a positive thermal expansion of 8.97×10^{-6} /K up to 757.15 K. The specific heat was measured to be 0.616 to 0.863 J g^{-1} K⁻¹ over the temperature range of 298.15-568.15 K. The thermal conductivity of Nd:Ca₃La₂(BO₃)₄ increases with the rising of temperature, indicating a glass-like behavior. Polarized absorption spectra and fluorescence spectra of $Nd:Ca_3La_2(BO_3)_4$ crystal were measured at room temperature and 77.3 K, respectively. The results show that the absorption and emission spectra of Nd^{3+} are inhomogeneously broadened, which is attributed to the disordered structure of the host lattice. Such broad emission spectra suggest that $Nd:Ca_3La_2(BO_3)_4$ is very potential to be utilized in laser systems to produce femtosecond pulses. Due to the relatively large thermal conductivity, Nd: $Ca_3La_2(BO_3)_4$ crystal can be even used in the high-power systems. Finally, CW laser operations at 1.06 µm were demonstrated along the three crystallographic directions for the first time. A maximum power of 1.08 W was obtained with an optical conversion efficiency of 10.6% and slope efficiency of 12.4% in *a*-cut sample. All these results indicate that the Nd:Ca₃La₂(BO₃)₄ is a very promising optical material featuring future laser applications.

Acknowledgment

This work was supported by the National Natural Science Foundation of China (Grant Nos. 51025210, and 51021062), the National Basic Research Program of China (Grant No. 2010CB630702), and the Program of Introducing Talents of Discipline to Universities in China (111 program).