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Growth, structural, spectral and high-power continuous-wave laser operation of $Yb_{0.11}Gd_{0.89}COB$ crystal

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Abstract: A $Yb_{0.11}Gd_{0.89}Ca_4O(BO_3)_3$ crystal with new composition was grown by the Czochralski method. The crystal structure was measured and analyzed. The unit-cell parameters of the $Yb_{0.11}Gd_{0.89}COB$ were calculated to be a=0.8089(7) nm, b=1.5987(6) nm, c=0.3545(8) nm, β=101.22°. The absorption and fluorescence spectra were measured. The maximum absorption cross-section of $Yb_{0.11}Gd_{0.89}COB$ crystal was 0.79×10^{-20} cm^2, which occurred at 976 nm with Y polarization. The emission cross-section at 1027 nm was calculated to be 0.33×10^{-20} cm^2. The radiative lifetime τ_{rad} was calculated to be 2.74 ms. The Stark energy-level diagram of Yb^{3+} in the $Yb_{0.11}Gd_{0.89}COB$ crystal field at room temperature was determined. The ground-state energy level $^2F_{7/2}$ splitting was calculated to be as large as 1004 cm^{-1} and the zero-line energy was 10246 cm^{-1}. A maximum output power of 9.35 W was achieved in continuous-wave (CW) mode, with the slope efficiency being 42.1%. Chemical etching experiment revealed that the dominating imperfections in the studied $Yb_{0.11}Gd_{0.89}COB$ crystal were dislocations and sub-grain boundaries. The existence of crystal defects could cause light scattering, and degrade laser output efficiency. The influence of crystal defects on laser properties was discussed.

Keywords: optical materials; rare earths; optical properties; crystal structure; defects

$RECa_4O(BO_3)_3$ (RECOB, RE=La, Nd, Sm, Gd, Er and Y) were firstly synthesized by Norrestam et al., and structural investigations demonstrated that the compounds of RCOB had possible applications as host medium for minilaser materials[1]. Shortly after that, the calcium gadolinium oxoborate [$GdCa_4O(BO_3)_3$, GdCOB] bulk crystal was grown by the Czochralski method, and structural investigations demonstrated that it belongs to the monoclinic space group *Cm* (point group m)[2]. Very soon after GdCOB was grown, it was found to be not only an efficient nonlinear optical crystal, but also an ideal candidate as laser host medium for Yb^{3+} [3–6]. Yb:GdCOB combines a relatively small emission cross section and a broad fluorescence spectrum. In addition, it has long radiative lifetime, which provides good energy storage properties. Furthermore, a large splitting of $^2F_{7/2}$ Stark levels of Yb^{3+} in Yb:GdCOB, makes the population of the transition lower level much less sensitive to temperature[7]. Finally, Yb:GdCOB permits a high doping rate of Yb^{3+} without concentration quenching. Based on these advantages, a lot of work has been conducted on Yb-doped GdCOB crystal for its spectroscopy[8], tunability[9,10], mode-locking[11], CW[12] and passively Q-switched laser operations[13,14]. Although laser outputs were realized in different modes, the laser performance seemed still less impressive, especially, the CW output power was limited to only 5–7 W level[12,13]. Until 2016, Chen et al. demonstrated efficient high-power CW operation of Yb:GdCOB laser. An output power as much as 18.2 W was generated at 1031.5 nm in CW mode, with slope efficiency up to 70%[15]. The impressive output power and energy conversion efficiency achieved very recently indicated that there were still rooms for improvement in laser performance of Yb:GdCOB crystal.

It is well-known that one of the crucial factors governing the laser performances is the optical homogeneity of laser crystals. However, the existence of various defects can limit the improvement of the optical homogeneity as well as laser performances. Actually, crystal defects, such as straight and curved dislocations, growth strains, inclusions, have been revealed from GdCOB

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crystals many times[16–19]. And furthermore, the measured inhomogeneity distribution of Ca^{2+} and Gd^{3+} cations in GdCOB crystal was reflected in changes of the crystal lattice parameters. As for Yb-doped GdCOB laser crystals, the disordered distribution of Yb^{3+}, Gd^{3+} and Ca^{2+} may further distort the crystal structure and induce crystal defects. Unfortunately, up to now, only few papers devote to investigate crystal lattice defects of Yb-doped GdCOB crystal, and much work needs to be done to understand the relationship between crystal quality and the Yb doping level. In this paper, $Yb_{0.11}Gd_{0.89}COB$ crystal was grown by Czochralski method. The spectral and CW laser properties were studied in detail. The homogeneity of $Yb_{0.11}Gd_{0.89}COB$ crystal was analyzed. The crystal defects were revealed by chemical etching method. The relationship between the crystal quality and optical properties was discussed.

1 Experimental

1.1 Crystal growth

The compounds of $Yb_{0.1}Gd_{0.9}Ca_4O(BO_3)_3$ were prepared by a conventional solid-state reaction method. The starting materials of Gd_2O_3, Yb_2O_3, $CaCO_3$ and B_2O_3 with 99.99% purity were weighed and mixed according to the compositions of $Yb_{0.1}Gd_{0.9}Ca_4O(BO_3)_3$. In a first step, the compounds were ground and thoroughly mixed. The mixture was then pressed into pellets and put into a platinum (Pt) crucible. These pellets were sintered in air at 900 ºC for 9 h. In a second step, the pellets were heated at 1100 ºC for 12 h to prepare polycrystalline material and subsequently used for single-crystal growth.

Czochralski method was used to grow Yb:GdCOB crystals[20,21]. The polycrystalline compounds prepared by solid-state reaction method were then put into an iridium (Ir) crucible. And the Ir crucible with the size of 55 mm in diameter and 40 mm in height was heated by a 2.5 kHz radio medium-frequency generator. Single crystalline bars of 3 mm×3 mm×30 mm of pure GdCOB (*b* axis along the long axis) were used as seeds. The rotation was started at 10–15 r/min, and the pulling rate was 0.5–1 mm/h after the size of the new crystal had reached 20 mm in diameter. After the growing process ended, the crystal was lifted out of the melt, and annealed for 24 h at 1100 ºC to release thermal stress. Fig. 1 shows the as-grown Yb:GdCOB crystal.

1.2 Compositions and structural characterization

An X-ray fluorescent analysis was performed to determine the proportions of Yb and Gd in grown crystal. Samples for analysis were cut off from the top part of the crystal and ground into fine powder. X-ray powder diffraction (XRPD) was used to determine the crystal structure, using nickel-filtered Cu Kα radiation. XRPD was measured on a Bruker D8 ADVANCE diffractometer equipped with a graphite monochromator, employing an exposure time of 1.2 s for each step of 0.01945º wide for a 2θ range of 10.0º–70.0º. X-ray diffraction patterns of the as grown crystal were recorded. The lattice parameters were calculated and refined by using the MDI Jade 5 program.

1.3 Absorption and photoluminescence spectra measurements

The crystal samples used for spectra measurement were cut along its principal optical axes (*X*, *Y*, *Z*), with an aperture of 3 mm×3 mm and a thickness of 4 mm. And the principal optical axes of Yb:GdCOB crystals biaxial crystal were determined in a similar way to Ref. [22]. The polarized absorption spectra were measured by a Cary-500 UV-VIS-NIR spectrophotometer (Varian Corp. America) at room temperature. The room-temperature fluorescence spectra at infrared range of 970–1125 nm were recorded using an Edinburgh Instruments FLSP 920 spectrophotometer when the crystal samples were pumped by a 964 nm laser diode.

1.4 CW laser performance measurement

The crystal samples of Yb:GdCOB cut along the principal optical axes of *X*, *Y*, and *Z*, with an aperture of 3 mm×3 mm and a thickness of 5 mm, were polished to serve for laser performance measurement. A simple plano-concave resonator was employed to study the CW laser performance[15]. The plane mirror was coated for high reflectance (>99.9%) at 1020–1200 nm and high transmittance (>98%) at 820–990 nm. As output coupler, a concave mirror of 25 mm radius-of-curvature was utilized, and the transmittance could be chosen in a wide range from T=0.5% to T=60% (at 1030 nm). An uncoated Yb:GdCOB crystal with the size of 3 mm×3 mm×5 mm was fixed in a water-cooled copper holder and placed close to the plane mirror inside the cavity. The cavity length was about 25 mm. The physical cavity length was 23 mm. A 50 W high-brightness fiber-coupled diode laser emitting at 976 nm (band width of less than 0.5 nm), with fiber core diameter of 100 μm and numerical aperture (NA) of 0.22, was used as the pump source.

1.5 Optical homogeneity measurement and chemical etching experiments

(010) Slices (Fig. 1) with a thickness of about 2 mm were cut from a Yb:GdCOB crystal and polished to serve as samples for optical homogeneity measurement and chemical etching experiments. A Mark II Zygo interferometer was used to quantitatively determine the optical homogeneity of the crystal samples. A water solution of 4%HCl was selected as etchant for the (010) slices. The etching process was performed at room temperature dur-