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Growth of $GdVO_4$ composite single-crystal rods by the double-die edge-defined film-fed growth technique

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Abstract The growth of composite-structured Nd : $GdVO_4$ single crystal rods by the double die EFG method is reported. Two crucibles are combined with an outer and inner die for ascending of different melt. The composite-structured Nd : $GdVO_4$ single crystal rods with a length of 50 mm and an outer diameter of 5 mm including of inner Nd-doped core region with diameter 3 mm were grown successfully. Nd distribution in the radial direction has graded profile from result of EPMA. Absorption coefficient in the core region at 808 nm was 42 cm^{-1}. Finally, we demonstrated the laser oscillation using our composite crystal and 2-W output was obtained.

Key words A2. Edge defined film fed growth, B1. Oxides, B1. Rare earth compounds

1. Introduction

There has been interest in microchip lasers because of their various advantages for optical applications [1-3]. In order to attain high power and efficient laser operation of microchip lasers, an edge-pumping scheme with composite-type laser materials was investigated [4, 5]. These composite materials consist of inner cylindrical material with dopant ions and surrounding transparent material. These were fabricated by bonding processes as diffusion bonding of single crystals, and by sintering process in transparent ceramics. From the viewpoint of the suppression of an excessive heat generation, high-powered microchip lasers require high-energy conversion efficiency from incident power to output. Although Nd : $GdVO_4$ are very useful for highly efficient microchip lasers [6], no polycrystalline ceramic composite of Nd : $GdVO_4$ for laser media has been realized because of the uni-axial crystal structure of Nd : $GdVO_4$. Therefore it has been considered that only diffusion bonding can provide composite-type Nd : $GdVO_4$, while it requires high fabrication levels of cutting, polishing and annealing.

Authors paid attention to the edge-defined film-fed growth (EFG) method to solve the difficulty of synthesizing composite-type Nd : $GdVO_4$ crystal rods. This method has been usually applied to grow sapphire crystals, TiO_2 crystals, and other crystals with fiber-shape. Recently, rod-type composite single crystals of Nd, Cr:$LiNbO_3$ have been grown successfully by using the improved EFG method, so-called the double-die EFG (DD-EFG) method [7].

In this work, authors adopted a DD-EFG method for growing composite-type Nd : $GdVO_4$ single crystal rods. We experimentally proved the possibility of optical devices fabricated from grown composite rods. The spectroscopic properties of these devices were also examined.

2. Experimental Procedure

For growth of the composite-type Nd : $GdVO_4$ single crystal rods, Nd : $GdVO_4$ as an inner core material and undoped $GdVO_4$ as an outer clad one were prepared. Chemical compounds Gd_2O_3 (Nippon Yttrium Co., Ltd.: 4 N), V_2O_5 (Kojundo Kagaku Lab.: 3 N) and Nd_2O_3 (Nippon Yttrium Co., Ltd.: 4 N) were used to synthesize $GdVO_4$ and Nd : $GdVO_4$ polycystalline materials. The stoichiometric composition was used as each initial charge. Doping concentration of Nd was 1.0 at% to Gd. Each mixed powder was calcined at 600°C for 10 hr in air to prevent evaporation of V_2O_5 and then sintered at 1350°C for 12 hr in air to prepare each polycrystalline material through solid reaction. X-Ray powder diffraction was used to make sure each synthesized material was consistent with the JCPDS data of $GdVO_4$.

For our DD-EFG, a conventional Czochralski furnace with a 30 kW RF generator was used as the heat source. Figure 1 shows a setup of a DD-EFG die and crucibles for growing composite-type $GdVO_4$ crystal rods, where two crucibles were used as the double crucible method

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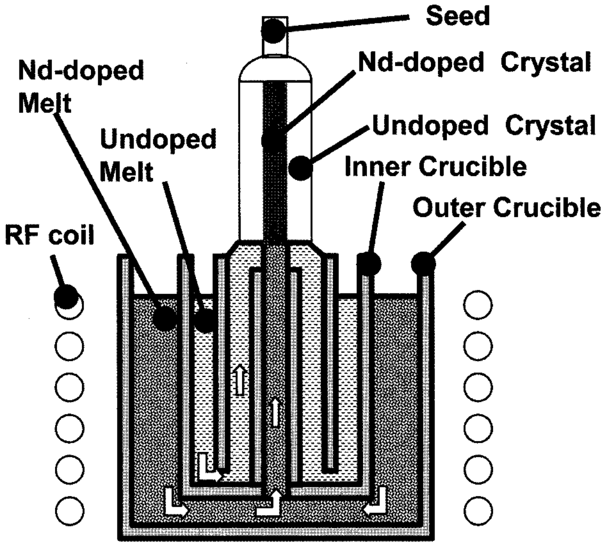

Fig. 1. Schematic cross-section of experimental set-up for DD-EFG. The arrows in crucibles show the directions of the melt flow.

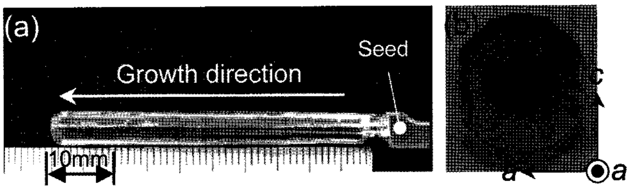

Fig. 2. Photographs of crystal grown by the DD-EFG method. (a) Side view. (b) Cross-section.

[8]. In this work we use the die and the crucibles made of iridium and N_2 gas atmosphere contained 0.5--1% O_2. The inner crucible (35-mm diameter, and 43-mm height) was centered on the outer crucible (50-mm diameter, and 50-mm height) and contained the melt of undoped $GdVO_4$, while the outer crucible was filled with the melt of 1-at% Nd-doped $GdVO_4$. The die with a diameter of 5 mm and a height of 41 mm was fixed at the bottom of inner crucible. The diameter of central bore in the die that was connected to the outer crucible was 1.0 mm. The melt in the inner crucible was drawn through an outer path of width of 0.5 mm. The composite-type Nd : $GdVO_4$ single crystal rod was grown using a seed with <100> orientation at a pulling rate of 0.5~20 mm/h and no rotation. The melting temperature of these melt is 1800°C. In order to grow the crystal rods, the growing temperature at these dies is a little bit higher than the melting temperature.

3. Results and Discussion

3.1. Crystal growth

A composite-type Nd : $GdVO_4$ single crystal rod grown by the DD-EFG method is shown in Fig. 2(a), and it had a length of 50 mm with an outer diameter of 5 mm. The pulling rate of this crystal was 3 mm/h under the temperature gradient of 150°C/cm. As can be seen from the figure, visible cracks were not generated. Growing a good quality of composite-type rods, the die height which relate to temperature gradient, the shape of the die top and the pulling rate were considered. Cracks in crystal rods were occurred at the pulling rate more than 7 mm/h. Composite structure could not be made when temperature gradient was less than 120°C/cm.

In order to make sure a composite structure, wafers were cut perpendicular to the growth axis for measurement of the Nd distribution in the radial direction by electron probe microanalysis (EPMA). The cross-section of the grown composite rod was also shown in Fig. 2(b), where core and clad regions can be visibly distinguished. Ir particle could not be seen by microscope and was not detected from the result of glow discharge mass spectroscopy (GDMS). Figure 3 shows the radial distribution of Nd measured by EPMA along center line of wafers taken from the sections parted 0.5 mm, 5 mm and 15 mm from the seed. These results show that composite-type crystal rods with graded Nd distribution can be grown by this method as shown in Fig. 3(b) and Fig. 3(c), on contrary no core region can be seen at the initial part of the composite rod as shown in Fig. 3(a). Nd distribution like Fig. 3(a) occurred at initial growth because melts (Nd-doped and undoped ones) were mixed before seed touch. And then the core region was fabricated gradually along the growth. It should be noted that the core region became wider along the growth and there is still some Nd content about 0.5 at% at the edge from Fig. 3(b) and Fig. 3(c). And Nd content in core region is 0.7 at% which is not equal to unity. It is considerable that outer (Nd-doped) and inner (nondoped) melts mixed each other under the growth and amount of nondoped melt arising from ring shape slit is smaller than that of Nd-doped melt arising from 1.0 mm hole. Moreover, the diameter of core region was found to be about 3 mm which is larger than the inner die diameter of 2.5 mm, obviously due to the spreading effect reported at ref. 7. To suppress expanding the core region, lower meniscus height and higher pulling rate are needed. However this expanding could not be suppressed when we tried to grow the crystal whose growth rate was 20 mm/h and meniscus height was almost 0 mm judged

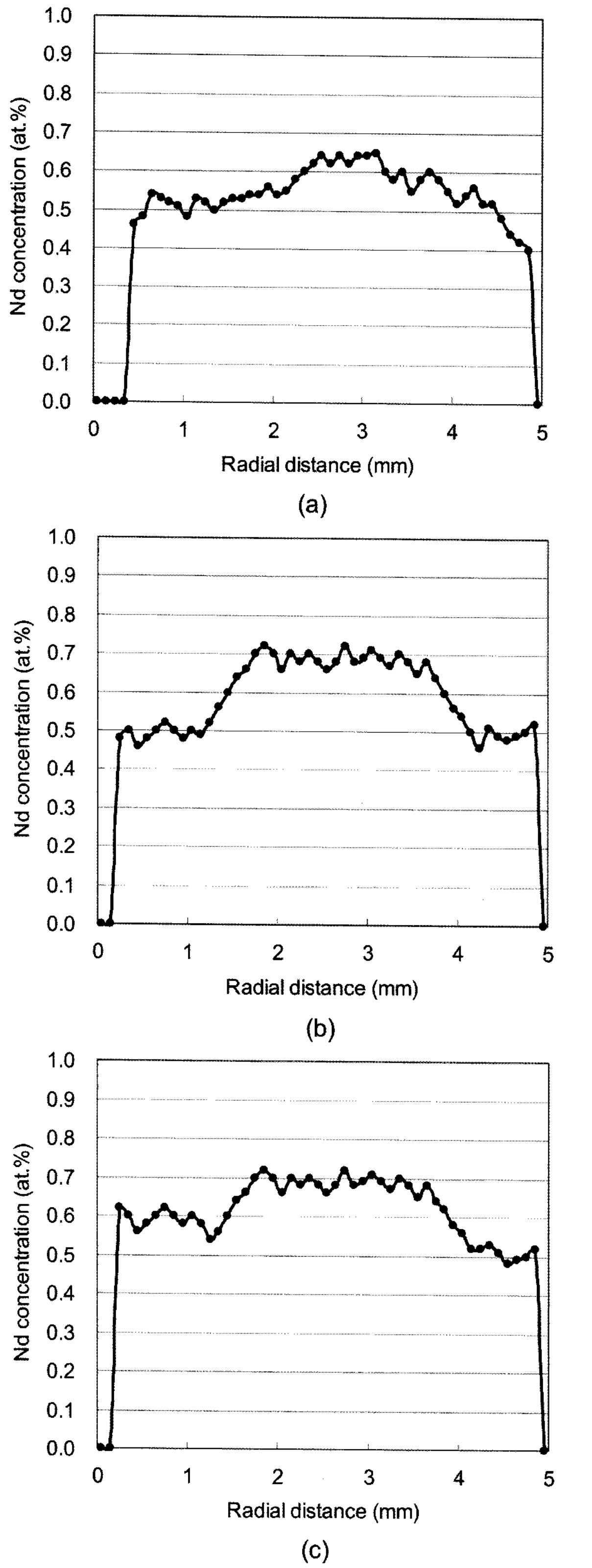

Fig. 3. The radial Nd^{3+} distribution of Nd : $GdVO_4$ crystal using EPMA. (a) 0.5 mm, (b) 5 mm, (c) 15 mm apart from the seed.

from the noise of load cell signal. From this result, spreading effect only can't explain this expanding phenomenon and we are looking for other factors.

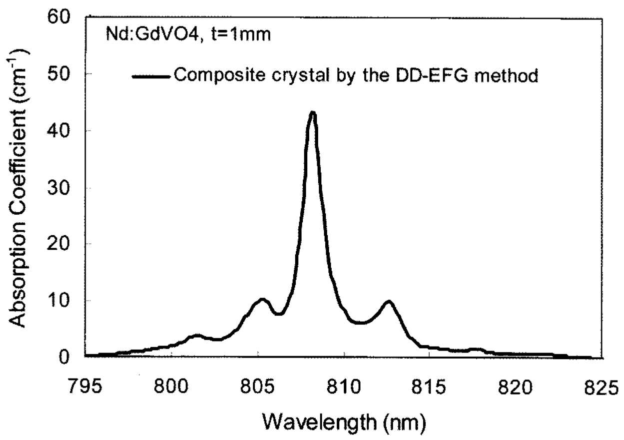

Fig. 4. Absorption coefficients around 808 nm of the core region in Nd : $GdVO_4$ grown by the DD-EFG method. Sample thickness is 1 mm.

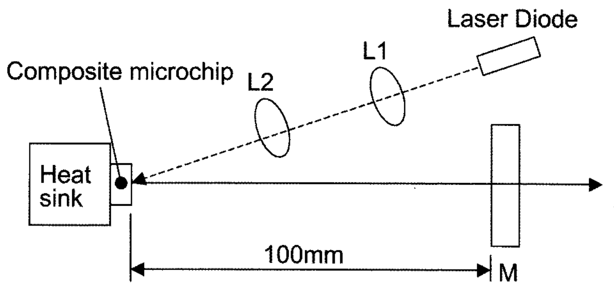

Fig. 5. Experimental setup for laser oscillation of composite-type Nd : $GdVO_4$ wafer grown by the DD-EFG method. L1 is the collimation lens, L2 is the focusing lens, M is the output flat mirror T = 3 %@1063 nm.

3.2. Laser experiment

Before laser experiment, the absorption measurement of wafer cut from grown composite rod was carried out. The absorption coefficient of the core region at 808 nm using 1-mm thickness sample in wavelength was 42 cm^{-1}, as shown in Fig. 4. This absorption coefficient was lower than that of 1-at% Nd : $GdVO_4$ bulk crystals which is 63 cm^{-1}. The result of the EPMA was that the Nd concentration was measured uniformly 0.7 at% in core region, which coincided the absorption coefficient of 42 cm^{-1}.

In order to demonstrate laser oscillation of grown composite-type crystal rods, wafers were cut perpendicular to the growing axis and formed to microchip shape that were polished on both cutting surfaces with optical coatings. We used thinner thickness 0.25-mm sample for this demonstration, because the thickness of 1-mm is too thick to demonstrate the laser oscillation from the result of the absorption coefficient 42 cm^{-1}. The laser

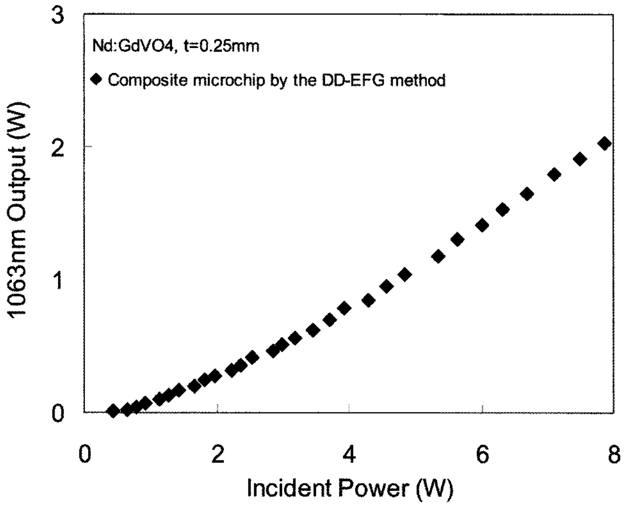

Fig. 6. Laser characteristics of composite-type Nd : $GdVO_4$ microchip grown by the DD-EFG method under 808 nm laser diode. Sample thickness is 0.25 mm.

experiment of microchip-shaped grown composite rod was carried with fundamental set up, as shown in Fig. 5. The pumping beam from 808-nm laser diode beam was focused to 27-μm radius spot on the surface of microchip-shaped grown composite rod. Figure 6 shows 2-W output was obtained from microchip-shaped grown composite rod with coating. It is found that our sample has a potential of high power laser materials from this result.

4. Conclusions

We successfully grew the composite-type Nd : $GdVO_4$ rods using DD-EFG method. We evaluated their radial Nd distribution and absorption in core region. From EPMA result, we obtained graded Nd profile in the radial direction of grown composite sample. We expect that this profile is more effective for high power laser microchip than the step profile which is fabricated from the diffusion bonding or the ceramic procedure, because no optical loss occur at the boundary between core and clad in graded profile. We also successfully demonstrated the laser oscillation of microchip-shaped grown composite rod with coated surfaces and obtained 2-W output.

In this work it was found that composite-type laser active media of single crystal rods can be directly grown by the DD-EFG method. We consider that this technology is very promising for developing the future design of solid-state lasers.

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References

[1] Y. Asakawa, R. Kawai, K. Ohki and K. Otsuka, "Laser-diode-pumped microchip $LiNdP_4O_{12}$ lasers under different pump-beam focusing condition", Jpn. J. Appl. Phys. 38 (1999) 515.

[2] T.Y. Fan, "Optimizing the efficiency and stored energy in quasi-three level lasers", IEEE J. Quantum Electron. 28 (1992) 2692.

[3] C. Stewen, K. Contag, M. Larionov, A. Giesen and H. Hugel, "A 1-kW CW thin disc laser", IEEE J. Sel. Top. Quantum Electron. 6 (2000) 650.

[4] M. Tsunekane and T. Taira, "High-power operation of diode edge-pumped, glue-bonded, composite Yb : $Y_2Al_5O_{12}$ microchip laser with ceramic undoped YAG pump lightguide", Jpn. J. Appl. Phys. 44 (2005) 1164.

[5] T. Dascalu, N. Pavel and T. Taira, "90 W continuous-wave diode edge-pumped microchip composite Yb : YAG laser", Appl. Phys. Lett. 83 (2003) 4086.

[6] V. Lupei, N. Pave, Y. Sato and T. Taira, "Highly efficient 1063-nm continuous-wave laser emission in Nd : $GdVO_4$", Opt. Lett. 28(23) (2003) 2366.

[7] K. Shimamura, N. Kodama and T. Fukuda, "A new crystal growth method for in situ core doping", J. Cryst. Growth 142 (1994) 400.

[8] K. Kitamura, Y. Furukawa, S. Takekawa and S. Kimura, "Single crystal of lithium niobate or tantalate and its optical element, and process and apparatus for producing an oxide single crystal", U. S. Patent No. 6,464,777 B2.