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G. B. Loutts

C. Bonner

C. Meegoda

H. Ries

M. A. Noginov

See next page for additional authors

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Authors

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Crystal growth, spectroscopic characterization, and laser performance of a new efficient laser material Nd:Ba₅(PO₄)₃F

G. B. Loutts^{a)} C. Bonner, C. Meegoda, and H. Ries

Center for Materials Research, Norfolk State University, Norfolk, Virginia 23504

M. A. Noginov, N. Noginova, M. Curley, and P. Venkateswarlu

Department of Physics, Center for Nonlinear Optics and Materials, Alabama A&M University, Normal, Alabama 35672

A. Rapaport and M. Bass

Center for Research and Education in Optics and Lasers, University of Central Florida, Orlando, Florida 32816-2700

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High quality single crystals of neodymium doped barium fluorapatite have been grown by the Czochralski technique and evaluated as an optical gain medium. A product of the emission cross section and lifetime of Nd³⁺ luminescence of more than 1.8×10^{-22} cm² s at 1055 nm, and laser performance with slope efficiency up to 65% have been obtained. © 1997 American Institute of Physics. [S0003-6951(97)01929-3]

Neodymium doped crystals of fluorapatites, Ca₅(PO₄)₃F (FAP) and Sr₅(PO₄)₃F (SFAP), have been demonstrated as low threshold, high efficiency laser media.¹⁻³ Laser operation at 0.94, 1.06, and 1.3 μm has been obtained with both flashlamp and diode pumping.²⁻⁵ In this letter, we report the synthesis, spectroscopic characterization, and laser performance of their analog, Nd³⁺ doped barium fluorapatite, Ba₅(PO₄)₃F or BFAP. Previous attempts to synthesize BFAP were mentioned in Refs. 1 and 6, however they resulted in poor quality, polycrystalline samples, so that no characterization was reported.

All the three fluorapatites crystallize in the hexagonal system, space group P6₃/m, with Nd ions substituting Ca²⁺, Sr²⁺, or Ba²⁺ ions in the sevenfold coordinated cationic site II.^{1,4} Since Ba²⁺ ion is larger than both Sr²⁺ and Ca²⁺ ions, the average distance between the Nd³⁺ ions in BFAP is expected to be the longest. This condition may reduce the energy exchange between Nd³⁺ ions in the host and consequently weaken the self-quenching of Nd³⁺ luminescence.

Single crystals of undoped and neodymium-doped BFAP, 30 mm in diameter and 120 mm long, were grown at Norfolk State University by the Czochralski technique.⁷ The charge was synthesized from barium carbonate, phosphorous pentoxide, and barium fluoride of 99.99% purity. A mixture of the first two components was sintered at 950 °C for several hours, grinded in a mortar, mixed with barium fluoride, and hot loaded into a 3 in. iridium crucible. Neodymium was introduced in the melt as neodymium oxide in concentrations of 0.4, 2.0, and 4.0 at. % (in respect to Ba). The crystals were pulled at 1.5 mm/h under nitrogen ambient atmosphere in the direction perpendicular to the “c” axis of the hexagonal unit cell.

An undoped BFAP crystal had the density of 4.75 (1) g/cm³ and the apatite crystal structure with lattice parameters of $a = 10.174(2)$ Å and $c = 7.724(1)$ Å. In Nd doped BFAP crystals, both lattice parameters were reduced by 0.005–0.02

Å. The Nd concentration, determined in the bottom and top parts of the crystals by the electron microprobe analysis, was 4 to 5 times lower than that in the melt. The effective neodymium distribution coefficient in BFAP is about 0.2. (In what follows, the Nd concentration referred to is the actual concentration in samples, given in atomic percent.) In spite of the overall good optical quality, we found several types of defects in the BFAP crystals including fine smoke, linear inclusions oriented along the *c* direction, and cracks. All these imperfections have been reported in other fluorapatites as well, however the cleavage along the *c* plane is more pronounced in BFAP than in FAP and SFAP.

The absorption spectrum of a BFAP sample, containing 0.8% Nd or 1.2×10^{20} Nd³⁺ ions/cm³, is shown in Fig. 1. The main absorption line in the 800 nm region is centered at 802.8 nm with full-width at half-maximum (FWHM) of about 1.6 nm and peak absorption cross section of 1.6×10^{-19} cm² in π polarization (**E**||**c**).

The luminescence spectrum of Nd:BFAP in the 1.0–1.4 μm region, shown in Fig. 2, is characteristic of all Nd doped fluorapatites.^{2,3} It features intense, narrow lines at 1055.5 and 1321 nm which are much stronger in π polarization than in σ polarization. Based on the emission spectrum, we have par-

FIG. 1. Room temperature polarized absorption of 0.8% Nd:BFAP. Thin line corresponds to **E**||**c**, bold line **E**⊥**c**.

^{a)}Electronic mail: g_loutts@vger.nsu.edu

FIG. 2. Room temperature Nd^{3+} luminescence in BFAP.

tially reconstructed the Stark energy diagram of Nd:BFAP, shown in Fig. 3. Characteristic of all fluorapatite crystals, the Stark splitting of the $^4\text{F}_{3/2}$ level is very large, 373 cm^{-1} . This implies that at room temperature, about 86% of the net $^4\text{F}_{3/2}$ population is accommodated in the lower Stark component. The transitions originating from the upper and lower components are represented in the emission spectrum as two virtually separate and identically spaced sets of lines shifted by 373 cm^{-1} . The spectrum also features short-wavelength weak satellite lines accompanying sharp emission peaks at 1055.5 and 1321 nm with the frequency shifts of 25 and 38 cm^{-1} , respectively. Relative intensities of the satellite lines were found to vary at different excitation wavelengths used. For example, the intensity of a 1052 nm satellite line normalized to that of the 1055.5 nm line is stronger at a 488 nm excitation than at 514.5 nm excitation. Such a behavior implies a multisite occupancy of Nd^{3+} ions in BFAP. Most likely, they substitute in both Ba_I and Ba_II sites in the apatite

FIG. 3. Room temperature diagram of Stark energy levels in Nd:BFAP. Position of the levels were determined with an accuracy of better than 5 cm^{-1} . Energy level marked with (*) was defined with greater uncertainty than the others. Arrows indicate most intense emission lines.

crystal lattice.⁴ Based on the relative intensities of the main and the satellite lines, we estimate that more than 87% of Nd^{3+} ions occupy the Ba_II site. In the $^4\text{I}_{13/2}$ manifold, we defined accurately only the state corresponding to the strongest emission line. Other Stark levels are grouped within a cluster shown schematically in Fig. 3 as a shaded box. At each of the transitions, $^4\text{F}_{3/2} \Rightarrow ^4\text{I}_{9/2}$, $^4\text{F}_{3/2} \Rightarrow ^4\text{I}_{11/2}$, and $^4\text{F}_{3/2} \Rightarrow ^4\text{I}_{13/2}$, the line terminating at a lowest component of the manifold is more intense and sharper than the others.

The room temperature decay of $^4\text{F}_{3/2}$ luminescence in 0.08% Nd:BFAP, excited with 100 ns pulses of light at 803 nm, was found to be a single exponential, with the decay time (τ) of 0.37 ms. At higher Nd concentrations, the effective $^4\text{F}_{3/2}$ decay time decreased most likely due to self-quenching. However, even in a 0.8% Nd doped sample, the effective luminescence decay time was as high as 0.30 ms. The fact that no deviation from the exponential function or variation in decay time was detected within the experimental accuracy of $\pm 5\%$, when the samples was excited at different wavelengths in the 802–805 nm range, implies that the decay times of Nd^{3+} ions in different sites are about the same.

The laser experiments were conducted with both pulsed and cw laser pumping. The cavity was formed by a 5-cm-high-reflective (HR) mirror and a flat output mirror. The distance between the mirrors in different experiments was varied from 4.0 to 4.8 cm. The BFAP crystal was placed in the cavity closer to the output mirror. It was longitudinally pumped from the end of the back mirror. A 3.75-mm-thick 0.4% Nd doped BFAP sample and a 0.95-mm-thick 0.8% Nd doped BFAP sample were used in the laser experiments. Both samples were cut along the plane containing the c axis and did not have any optical coating.

In the pulsed laser experiment, the 0.4% doped sample was excited at $\text{E} \parallel c$ with 805 nm radiation of a tunable flashlamp pumped Cr:LiSAF laser operating in free running regime. Lasing at 1055.5 nm was very stable, virtually insensitive to small misalignments in the setup. The input/output curve of the pulsed Nd:BFAP laser, obtained with a 10% output coupler, is shown in Fig. 4(a). The slope efficiency was equal to 55%, and the threshold absorbed pumping energy was less than 1 mJ.

In the cw laser experiment, the BFAP crystal was excited at $\text{E} \parallel c$ with a Ti:sapphire laser tuned to 803 nm. The laser operation at 1055.5 nm was obtained in the cavity using one of the following output couplers: an HR dielectric mirror, dielectric mirrors with transmission of $T=1\%$, $T=5\%$, and $T=10\%$, and an aluminum-coated neutral density filter of variable density (a wheel). The input/output curve obtained with the 0.8% Nd:BFAP sample and a $T=10\%$ output coupler is shown in Fig. 4(b).

Using slope efficiencies, determined in cw experiments with different output couplers, we estimated the optical losses to be less than 0.7% and the intrinsic slope efficiency around 70%. Apparently, the slope efficiency observed in the pulsed experiment was lower than that in the cw regime due to the different optical qualities of the laser samples as well as the quality and focusing conditions of the pumping beam.

From the laser experiments, following the approach suggested in Refs. 3 and 8 we determined that the emission cross section (σ) in Nd:BFAP at 1055.5 nm was more than

(a)

(b)

FIG. 4. Input/output curves of Cr:LiSAF pumped pulsed 0.4% Nd:BFAP laser (a) and Ti sapphire pumped cw 0.8% Nd:BFAP laser (b) operating at 1055 nm.

$6 \times 10^{-19} \text{ cm}^2$. The estimated value of σ , obtained from the emission spectra measurements, is $4 \times 10^{-19} \text{ cm}^2$. Assuming that the emission cross section in Nd:BFAP is greater than $5 \times 10^{-19} \text{ cm}^2$, one can show that the product $\sigma\tau$ (an important parameter in characterizing the laser efficiency) in Nd:BFAP is one of the largest among the several advanced neodymium laser materials, listed in Table I.

The cw laser operation was also obtained at the $^4F_{3/2} \Rightarrow ^4I_{11/2}$ transition (1320.9 nm) with a 25% slope efficiency and a $L=1.2\%$ loss in a cavity with a 5% output coupling. Apparently, the performance was limited by thermal effects. Since BFAP has a higher molecular weight than SFAP, we expect its heat conductivity to be lower than the value of 2 W/mK for SFAP.³

In conclusion, we have grown high optical quality Nd:BFAP single crystals and determined their major struc-

TABLE I. Effective emission cross sections at the $^4F_{3/2} \Rightarrow ^4I_{11/2}$ transition, σ , lifetimes, τ , and products $\sigma\tau$ in Nd:BFAP and some of the advanced laser materials.

Material	σ , cm^2	τ , s	$\sigma\tau$, cm^2/s
Nd:BFAP	$> 5 \times 10^{-19}$	3.7×10^{-4}	$> 1.85 \times 10^{-22}$
Nd:SFAP	5.4×10^{-19} a	2.98×10^{-4} a	1.61×10^{-22}
Nd:YVO ₄	10.5×10^{-19} b	9.8×10^{-5} b	1.03×10^{-22}
Nd:YAG	3.04×10^{-19} b	2.7×10^{-4} b	8.3×10^{-23}
Nd:YAB	10×10^{-19} c	2.0×10^{-5} c	2×10^{-23}

^aRef. 3.

^bRef. 10.

^cRef. 11.

tural and spectroscopic parameters. The product of Nd^{3+} emission cross section at 1055.5 nm ($> 5 \times 10^{-19} \text{ cm}^2$) and radiative lifetime (0.37 ms) was found to be one of the highest among Nd doped laser materials. Low threshold, high efficiency lasing was demonstrated in both pulsed and cw operation at 1055.5 nm.

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¹K. B. Steinbrugge, T. Heningsen, R. H. Hopkins, R. Mazelsky, N. T. Melamed, E. P. Riedel, and G. W. Roland, *Appl. Opt.* **11**, 999 (1972).

²X. X. Zhang, G. B. Loutts, M. Bass, and B. H. T. Chai, *Appl. Phys. Lett.* **64**, 10 (1994).

³X. X. Zhang, P. Hong, G. B. Loutts, J. Lefaucheur, M. Bass, and B. H. T. Chai, *Appl. Phys. Lett.* **64**, 3205 (1994).

⁴X. X. Zhang, M. Bass, B. H. T. Chai, P. J. Johnson, and J. C. Oles, *J. Appl. Phys.* **80**, 1280 (1996).

⁵X. X. Zhang, P. Hong, and B. H. T. Chai, in *OSA Trends in Optics and Photonics* (OSA, Washington, DC, 1996), Vol. 1, p. 428.

⁶L. D. DeLoach, S. A. Payne, B. H. T. Chai, and G. Loutts, *Appl. Phys. Lett.* **65**, 1208 (1994).

⁷G. B. Loutts and B. H. T. Chai, *Proc. SPIE* **1963**, 31 (1993).

⁸T. Y. Fan and R. L. Byer, *IEEE J. Quantum Electron.* **24**, 895 (1988).

⁹A. J. Alfrey, *IEEE J. Quantum Electron.* **25**, 760 (1989).

¹⁰R. A. Fields, M. Birnbaum, and C. L. Fincher, *Appl. Phys. Lett.* **51**, 1885 (1987).

¹¹G. Huber, in *Current Topics in Materials Science* (North-Holland, Amsterdam, 1980), Vol. 4, p. 1.