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Growth of laser-quality single crystals of Nd³⁺-doped calcium fluorapatite and their efficient lasing performance

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The Czochralski growth of laser-quality Nd³⁺-doped calcium fluorapatite single crystals and their lasing characterization are reported. Low threshold and high efficiency lasing performances were achieved in both continuous-wave and long pulse laser-pump-laser operation. The effect of concentration quenching on laser performance is discussed.

Low threshold, high efficiency lasing is demonstrated for calcium fluorapatite crystals, Ca₅(PO₄)₃F or FAP, doped with Nd³⁺. As demonstrated by their excellent lasing properties these crystals have excellent optical properties. Crystal growth techniques resulting in these crystals are also described. FAP crystals were successfully grown and demonstrated as a promising laser host in the 60's.^{1,2} However, due to its poor thermomechanical properties³ and inadequate crystal quality, the application of FAP as a laser host was neglected for many years. The use of diode lasers as pump sources greatly reduces the size of the laser crystal required and the thermal load it must bear. As a result the material strength requirements are appreciably relaxed. On the other hand, to achieve low threshold, efficient diode pumped lasing it is desirable to select materials which have a large product of stimulated emission cross section and radiative decay time as well as strong, broad absorption in the emitting region of the pump diode lasers. Nd³⁺-doped FAP has an estimated emission cross section of $5 \times 10^{-19} \text{ cm}^2$ and a radiative fluorescent decay time about 250 μs .² It is therefore expected to be a useful host for diode pumping provided the crystal quality is adequate.

Our laser-quality FAP crystals were grown by the Czochralski method using a 3-in.-diam iridium crucible. A neutral ambient atmosphere was provided by continuous nitrogen flow through the furnace. The growth process was under automatic control. A dual, closed loop control system was utilized to maintain a desirable crystal diameter. It consisted of a mass loop with a crystal weighing feedback, a power loop with a power feedback, and independent proportional integral differential controllers for each loop. Because of the complicated chemical nature of calcium fluorapatite,¹ special attention was paid to the charge preparation. The compound was synthesized from calcium hydrogen phosphate, calcium carbonate, calcium fluoride, and neodymium oxide according to the following reaction:

A mixture of the first three components was sintered in a

platinum crucible at 1000 °C for several hours then pounded in a mortar, mixed with calcium fluoride and hot loaded into the iridium crucible.

During a FAP growth run fluoride is lost continuously through evaporation. To compensate this loss and to diminish gas bubble trapping, 2 mol % excess calcium fluoride was usually added in the melt. A cracking problem, which is often faced when growing FAP crystals and is attributed to the relatively low thermal conductivity of FAP, was solved with the use of a low thermal gradient ($<100 \text{ }^\circ\text{C}/\text{cm}$ above the melt) furnace and slow cooling of as-grown crystals ($>24 \text{ h}$). Gas bubble trapping is a common imperfection in apatite crystals. These bubbles are not spherical. They look like bent channels or tubes oriented along the *c* axis and are concentrated in the core region of the crystal. To minimize this region a low rotation rate (not higher than 20 rpm) was used. The bubbles can be totally eliminated by adding 5 mol % excessive fluoride, which, however, leads to the formation of fine scattering centers, probably due to the ex-solution of calcium fluoride.

Optimal growth conditions were found to be as follows: pull rate 1 mm/hr, rotation rate 10–20 rpm, and amount of the melt crystallized not more than 25%. Initial spontaneous nucleation was started on an iridium wire, and the crystal quickly became single grain after about 1 cm of growth. Subsequent crystals were pulled along the $[10\bar{1}0]$ axis. Typical FAP boules weighed 200–300 g and were approximately 25–30 mm in diameter and 110 mm in length.

Room-temperature absorption of Nd:FAP in the 800 nm region is partially polarized with π polarization stronger than σ . The main absorption peak is centered at $\approx 807 \text{ nm}$ with full width at half-maximum about $\approx 2 \text{ nm}$ and peak absorption coefficient of 16 cm^{-1} . The absorption was measured with an FAP sample doped with a nominal Nd³⁺ concentration of 1 at. % in the melt. Since the distribution coefficient of Nd³⁺ ions in FAP is about 0.52,⁴ the actual Nd³⁺ concentration in the sample is estimated to be 0.52 at. % (in what follows Nd³⁺ concentration refers to the estimated actual concentration unless otherwise specified), or $9.9 \times 10^{19} \text{ Nd}^{3+} \text{ ions/cm}^3$. As a result, the peak absorption cross section is about $1.62 \times 10^{-19} \text{ cm}^2$, which is slightly higher than that of Nd:YAG. Room-temperature emission in the 1 μm region consists mainly of an intense, narrow line at 1.063 μm and is almost three times as strong in π polarization as in σ . The unique emission properties result from the large crystal split-

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ting of the $^4F_{3/2}$ manifold of Nd^{3+} ions in FAP. The splitting in FAP is about 360 cm^{-1} (Ref. 2) substantially larger than that in YAG [88 cm^{-1} (Ref. 5)] and most other hosts. The strongest line at $1.063\text{ }\mu\text{m}$ originates from the lower sublevel of the $^4F_{3/2}$ manifold which accommodates about 82% of the total population of the manifold at room temperature.

The room-temperature decay of the $1\text{-}\mu\text{m}$ emission of 0.52 at. % Nd^{3+} :FAP is nonexponential. The decay time, obtained by normalizing the fluorescence intensity at $t=0$ to one and then integrating the entire decay curve over time, was found to be $197\text{ }\mu\text{s}$ at room temperature. The room-temperature decay of 0.052 at. % Nd^{3+} :FAP is exponential with a decay time of $256\text{ }\mu\text{s}$. The nonexponential decay and the shorter decay time for 0.52% Nd^{3+} :FAP result from concentration quenching.⁶

A 6-mm-long (with a diameter of $\approx 15\text{ mm}$) sample with a nominal Nd^{3+} concentration of 0.52 at. % was cut with flat and parallel faces containing the c axis for laser experiments. These faces were antireflection (AR) coated at $1.06\text{ }\mu\text{m}$. The laser test employed a concave (radius= 5 cm) reflector [high reflectivity (HR) at $1.0\text{--}1.1\text{ }\mu\text{m}$ and high transmission at $790\text{--}810\text{ nm}$] and a flat partial reflector (partial reflectivity at $1.0\text{--}1.1\text{ }\mu\text{m}$ and high transmission at $790\text{--}810\text{ nm}$) to form a 4.5-cm-long laser cavity. Different partial reflectors with reflectivities of 98.8%, 97.0%, and 95.0% were used to test the laser performance. Both pulsed and continuous-wave (cw) laser pumped operation were studied. Pulsed excitation was achieved with a long pulse Cr:LiSAF laser (pulse width $\approx 100\text{ }\mu\text{s}$) and cw pumping with a Ti:sapphire laser. Both lasers were tuned to $\approx 807\text{ nm}$ to match the absorption peak of the Nd^{3+} ions in FAP. The spectral band width was about 1 nm for Cr:LiSAF laser and less than 0.2 nm for the Ti:sapphire laser. More than 95% of the pump power was absorbed in both pump schemes. The pump light was focused through the HR mirror into the laser crystal about 4 mm in front of the flat mirror (output coupler) with a 10 cm focal length lens.

Lasing from Nd^{3+} :FAP is linearly polarized along the c axis (π polarization) and occurs at $1.063\text{ }\mu\text{m}$. The cw laser output as a function of absorbed power is plotted in Fig. 1(a) for different output couplers. The laser output energy in long-pulse operation as a function of absorbed energy is given in Fig. 1(b). The thresholds and slope efficiencies for both operations are summarized in Table I. It is seen from Fig. 1(b) that the output vs input characteristics in pulsed operation is pump-energy dependent (i.e., the laser has higher slope efficiency for higher pump energy). The slope efficiencies listed in Table I for pulsed operation were measured from the straight portions of the curves in Fig. 1(b) at higher absorbed energy ($>4\text{ mJ}$). It can be seen from Table I that the thresholds are very low for both modes of operation. The pulsed slope efficiencies are high and in all cases higher than observed in cw operation.

Information on the intrinsic slope efficiency and passive loss in the crystal can be derived from the variation of measured slope efficiency with the output coupler transmission through the following simple relation:⁷

$$\eta = \eta_0 T / (T + L), \quad (2)$$

FIG. 1. Laser output as a function of pump input for different output couplers: (a) cw operation and (b) long-pulse operation.

where η is the measured slope efficiency, η_0 the intrinsic slope efficiency, T the transmission of the output coupler, and L the double-pass passive loss. A plot of $1/\eta$ vs $1/T$ will give a straight line with a slope of L/η_0 and an intercept of $1/\eta_0$. Data given in Table I are plotted in Fig. 2, curve a for pulsed and curve b for cw operation. The solid lines are the calculated results based on Eq. (2) using parameters $\eta_0 = 76\%$ and $L = 0.85\%$ for pulsed operation, and $\eta_0 = 59\%$ and $L = 1.29\%$ for cw operation, respectively.

The intrinsic slope efficiency η_0 in cw operation can be written as

$$\eta_0 = \eta_q \lambda_p / \lambda_1, \quad (3)$$

TABLE I. Summary of laser performance.

$T(\%)$	Threshold		Slope efficiency (%)	
	pulsed(μJ)	cw(mW)	pulsed	cw
1.2	18	7.4	44	29
3	23	10	61	41
5	31	13	67	48

FIG. 2. Slope efficiency as a function of output coupler transmission for both cw and long-pulse operation.

where η_q , λ_p , and λ_l are the quantum efficiency, the pump, and lasing wavelengths, respectively. Since the pump and lasing wavelengths are 807 and 1063 nm, respectively, the maximum intrinsic slope efficiency would be 76% assuming unit quantum efficiency. In the presence of concentration quenching the quantum efficiency is equal to the ratio of the effective decay time to the radiative decay time, which is 77% ($=197 \mu\text{s}/256 \mu\text{s}$) for 0.52% Nd³⁺:FAP. One therefore expects an intrinsic slope efficiency of 59% which is consistent with the experimental data shown in Fig. 2.

As mentioned above, pulsed slope efficiencies are higher than the observed cw counterparts in all cases and they project a quantum-defect-limited intrinsic slope efficiency, 76%. That is, in pulsed lasing, as used in this work, concentration quenching does not seem to affect the laser performance. This is understandable if one examines the fluorescence and lasing dynamics. As mentioned earlier, the effect of concentration quenching is the introduction of an additional nonradiative decay resulting in a more rapid decay of the fluorescence. The effective nonradiative decay time can be estimated from the observed fluorescence decay time in the presence of concentration quenching and the radiative decay time and is about 855 μs for 0.52% Nd³⁺:FAP. The lasing dynamics can be seen from Fig. 3 which gives the pump and lasing waveforms for low and high pump energies, respectively. Figure 3(a) shows the typical results observed for the total absorbed energy less than 3 mJ. Similar results as shown in Fig. 3(b) were observed for the total absorbed energy above 4 mJ, above which the output vs input curve becomes straight with a higher slope as seen in Fig. 1(b). It can be seen from Fig. 3(b) that no measurable delay between the pump and lasing is observed and that almost every spike in the pump waveform has a corresponding one in the lasing wave form (i.e., every spike of the pump light was enough to cause lasing with hardly any time delay). That is, the nonradiative process, concentration quenching, does not have

FIG. 3. Pump and lasing waveforms in pulsed operation for different absorbed energies: (a) 0.5 mJ and (b) 4 mJ. The vertical axes are energies in arbitrary units for both figures.

enough time to affect the population and all the population contributes to lasing. In these circumstances a quantum-defect-limited slope efficiency is to be expected. For lower pump levels, however, there is a delay between the first spikes of the lasing and pump waveforms and every spike in the pump waveform does not have its corresponding spike in the lasing wave form, as clearly shown in Fig. 3(a). The delay can be as long as 100 μs just above threshold though it decreases with increasing pump level. The concentration quenching at low pump levels has time to affect the population and lower laser efficiency is expected and seen in Fig. 1(b).

In summary, we have successfully grown high optical quality FAP single crystals and demonstrated their low threshold, high efficiency lasing for both pulsed and cw operation. A quantum defect limited intrinsic slope efficiency has been projected from the pulsed lasing performance and an efficiency of 67% has been observed using a 5% output coupler. The lower slope efficiency observed in cw operation was attributed to the effect of concentration quenching. Therefore, higher slope efficiency is expected for laser crystals with optimized Nd³⁺ concentration. The double-pass passive loss derived from the lasing data is $\approx 1\%$ for a 6-mm-long crystal, which indicates that the crystal quality is much better than previously obtained. Having a very high absorption for diode pumping and high emission cross section makes Nd:FAP attractive for applications in low to medium power, miniature diode-pumped lasers.

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¹ R. Mazelsky, R. H. Hopkins, and W. E. Kramer, *J. Cryst. Growth* **3/4**, 260 (1968).

² R. C. Ohlman, K. B. Steinbruegge, and R. Mazelsky, *Appl. Opt.* **7**, 905 (1968).

³ R. H. Hopkins, D. H. Damon, P. Piotrowski, M. S. Walker, and J. H. Uphoff, *J. Appl. Phys.* **42**, 272 (1971).

⁴ K. B. Steinbruegge, T. Henningsen, R. H. Hopkins, R. Mazelsky, N. T. Melamed, E. P. Riedel, and G. W. Roland, *Appl. Opt.* **11**, 999 (1972).

⁵ J. A. Koningstein and J. E. Geusic, *Phys. Rev.* **136**, 711 (1964).

⁶ X. X. Zhang, A. B. Villaverde, M. Bass, G. Loutts, and B. H. T. Chai, *SPIE Proc.* **1863**, 35 (1993).

⁷ J. A. Caird, S. A. Payne, P. R. Staver, A. J. Ramponi, L. L. Chase, and W. F. Krupke, *IEEE J. Quantum Electron.* **QE-24**, 1077 (1988).