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Intracavity frequency doubling of a Nd:YAG laser with an organic nonlinear optical crystal

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We have demonstrated intracavity second-harmonic generation of green 532 nm light in a quasi-cw 1064 nm Nd:YAG laser using organic nonlinear optical crystals of 4-(N,N-dimethylamino)-3-acetamidonitrobenzene (DAN) immersed in index matching fluid contained in an antireflection-coated cuvette. This technique permits crystals to be used directly from solution growth without polishing or antireflection coating them. Up to 0.56 mW peak power of 532 nm light was generated from 2.3 W of intracavity 1064 nm peak power in 100 μs pulses. We also report preliminary results on true cw intracavity harmonic generation with antireflection-coated DAN crystals.

Intracavity second-harmonic generation (SHG) and frequency mixing using inorganic nonlinear optical (NLO) crystals such as KTP and $KNbO_3$ have recently been demonstrated[1] to be a practical means of obtaining milliwatts of cw blue or green laser light from infrared diode lasers and other sources. A further enhancement in the achievable conversion efficiency could in principle be obtained using organic nonlinear crystals such as 4-(N,N-dimethylamino)-3-acetamidonitrobenzene (DAN),[2-5] and more recently, 3-methyl-4-methoxy-4′-nitrostilbene (MMONS)[6] which have higher phase-matched SHG figures of merit (d^2/n^3) than the inorganic NLO crystals. While intracavity SHG requires very low insertion loss, placing stringent limits on crystal optical quality as well as on absorption, there has been significant recent progress in growing high optical quality crystals such as DAN,[7] 2-N-(α-methylbenzylamino)-5-nitropyridine (MBA-NP),[7] 2-methyl-4-nitroaniline (MNA),[8] urea,[9] and N-(4-nitrophenyl)-L-prolinol (l) (NPP).[10] This work reports the first successful cw intracavity SHG using an organic NLO crystal thus demonstrating that laser grade optical quality can be achieved in highly nonlinear organic crystals.

In the present work, DAN crystals with large-area (001) faces and high internal optical quality have been grown and used to generate green 532 nm light using phase-matched SHG when placed in the cavity of a 1064 nm Nd:YAG laser (to take advantage of the high intracavity power). Surface reflection, distortion, and scattering loss have been significantly reduced by immersing the crystals in index matching fluid contained in an antireflection-coated spectroscopic cuvette. This technique permits insertion of nonlinear optical crystals as grown, without polishing or antireflection coating, directly into the cavity of a cw laser and is therefore an efficient means of screening many crystals.

DAN was prepared by a two step synthesis. First, 3-amino-4-fluoronitrobenzene was acetylated in chloroform with acetic anhydride. Then, the resulting acetamide was reacted with dimethylamine in dimethylsulfoxide (DMSO). The yellow DAN powder was then purified by repeated recrystallization from solution in a mixture of ethanol and water. Additional purification was performed by column chromatography on silica gel with a mixture of ethyl acetate and hexane followed by further recrystallizations from a mixture of methylene chloride and hexane. The purity of the DAN was confirmed by high-pressure liquid chromatography.

Single crystals of DAN were grown from DMSO solution in a tube with excess feed material at the bottom.[11] Thermal convection within the tube was created by maintaining the temperature at the bottom of the tube at 29 °C while the upper portion of the tube was held at 27 °C. High quality crystals of up to $10\times7\times2$ mm^3 were obtained in three to four weeks. DAN belongs to the monoclinic space group $P2_1$ (point group 2)[12] and the crystals grown in solution have large (001) facets and are generally trapezoidal in shape with smaller $(0\bar{1}0)$ (011), $(0\bar{1}1)$ and (112) facets.

Loss due to the crystal surface reflections and roughness was reduced by immersing the as-grown crystals in index matching fluid. The Cargille Series A Refractive Index Fluids (a mixture of hydrogenated terphenyl and 1-bromonapthalene) were contained in a BK7 glass spectroscopic cuvette which was antireflection coated for 1064 nm on the outer faces [Fig. 1(a)]. Total reflection loss from the two cuvette-fluid and two fluid-crystal interfaces was calculated to be 0.4% for an optimum fluid index of $n = 1.615$ and less than 1.0% for $1.5 < n < 1.7$ at 1064 nm. However, the refractive index fluid absorbed enough of the laser power to cause thermal blooming and convection and slowly dissolved the crystal as well. These effects worsened with higher index fluids, presumably due to the increasing concentration of the 1-bromonapthalene component. The convection was effectively eliminated by placing a shutter in the cavity, as described below. Lower absorption and solvation might be obtained with another choice of index matching fluid.

Intracavity second-harmonic generation (SHG) of the 1064 nm line of Nd:YAG was achieved by type I phase matching in DAN for a p-polarized fundamental beam traveling at approximately 22° from the normal to the (001) facet in a plane tilted by 2° from the $(0\bar{1}0)$ plane. The effective SHG coefficient d is 27 ± 3 pm/V and the output at 532 nm is polarized along the crystalline (010) axis.[3] The phase-matched index of refraction[5] is 1.732 ± 0.005.

The end-pumped concentric Nd:YAG laser is depicted schematically in Fig. 1(b). The TEM_{00} output of a Ti:sapphire laser pumped by a cw argon laser was focused by a 60

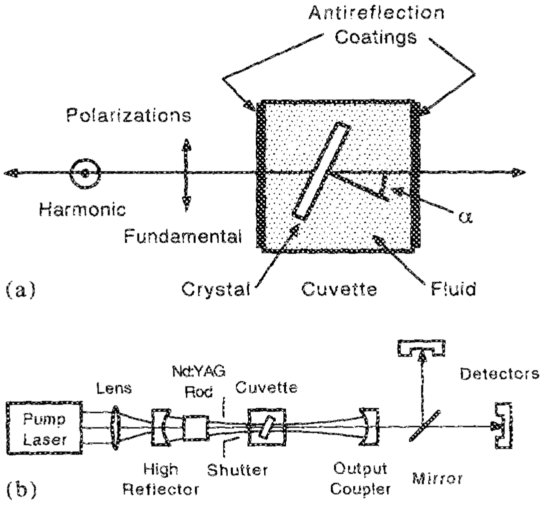

FIG. 1. (a) Diagram of the spectroscopic cuvette containing refractive index fluid and the crystal oriented at the phase-matching angle α. Both the entrance and exit faces of the cuvette are antireflection coated for 100% transmission at 1064 nm. (b) Diagram of the end-pumped Nd:YAG laser showing the locations of the high reflector, output coupler, pump focusing lens, and the cuvette containing the DAN crystal. The dichroic mirror reflected the 1064 nm laser output into one detector and transmitted the 532 nm harmonic to the other detector. (Both detectors were preceded by an appropriate interference filter, not shown, to block unwanted light.)

mm focal length lens into the 6 mm Nd:YAG rod located near one end of the cavity. The output coupler and high reflector were coated for 99.9 and 100.0% reflection, respectively, and the YAG laser rod was antireflection coated for 1064 nm. The high reflector was coated for maximum transmission at the pump wavelength of 810 nm. Both the high reflector and the output coupler had radii of curvature of 75 mm and were separated by approximately 150 mm, resulting in a near-concentric resonator configuration. The output coupler transmitted 0.1% of the incident 1064 nm laser power and 88.4% of the incident 532 nm harmonic. The fundamental and harmonic outputs of the laser were separated by a dichroic mirror and directed onto silicon photodiode detectors.

First the laser was aligned for maximum TEM_{00} mode output to yield approximately 2–5 W of cw intracavity power at 0.5 W of pump power, without the cuvette or crystal. Then the 1 cm path length cuvette [see Fig. 1(a)] containing the index matching fluid (but not the crystal) was inserted into the cavity with the antireflection-coated entrance and exit faces perpendicular to the cavity axis. The laser was realigned and, when operated cw, exhibited strong power fluctuations and poor transverse mode quality. The fluctuations were due primarily to convection in the refractive index fluid which in turn was caused by heating of the fluid by residual absorption (less that 1%) of the laser and pump light. To reduce fluctuations caused by heating, a shutter was inserted between the laser rod and the cuvette [see Fig. 1(b)] and opened for 10 ms at a repetition rate of 1 to 5 Hz. The low average power eliminated the convection, but the laser output was essentially quenched after about 100 μs by thermal blooming. Because of this, multiple pulses would often arise within the 10 ms shutter window and the laser could also be adjusted to yield gain-switched spikes of duration less than the 20 μs rise time of the detector. The most stable output was obtained with a single 100 μs wide pulse and a near-TEM_{00} spatial mode, with a peak height fluctuating between 60–80% of the empty cavity cw power, indicating that the cuvette and fluid introduced moderate linear loss.

The DAN crystal was mounted on a six-axis stage (three translation and three rotation axes) and the crystal suspended in the fluid filled cuvette located in the cavity of the Nd:YAG laser. The laser cavity was realigned while the crystal orientation and position were adjusted to maximize both the fundamental laser output and the harmonic output. The crystal introduced a small amount of astigmatism and distortion into the resonator, which was clearly apparent in the shape of the output beam, as well as additional linear loss, but did not noticeably increase the thermal blooming. The peak laser output fluctuated between 15 and 60% of the empty cavity cw power. Figure 2 shows the time dependence of the fundamental (lower curve) and harmonic (upper curve) outputs from the laser. Note that the second peak in the SHG output is much smaller than the second peak in the fundamental because of the quadratic dependence of the SHG on the fundamental power.

The highest SHG output was obtained with a 0.77-mm-thick crystal immersed in $n = 1.624$ index fluid. With a peak intracavity Nd:YAG power (in short spikes of duration less than 10 μs) of 2.3 W, the peak SHG power exiting one crystal face was 0.28 mW, or 0.012% power conversion efficiency. (The crystal emits the same power from the other crystal face, but this light was not collected.) The expected SHG output power from Boyd and Kleinman[13] (in SI units) is $P_{2\omega} = (2\pi n L h/\lambda)(8\pi^2 d^2/\epsilon_0 c \lambda^2 n^3)\exp(-\alpha' L)(P_\omega)^2$. Here, P_ω is the fundamental power, $\lambda = 1064$ nm, $n = 1.732$ is the crystal index of refraction, L is the distance traversed by the beams in the crystal, ϵ_0 is the permittivity of free space, c is the speed of light, $\alpha' \approx (1/2)\alpha_{2\omega} \approx 2.5\ \text{cm}^{-1}$, and

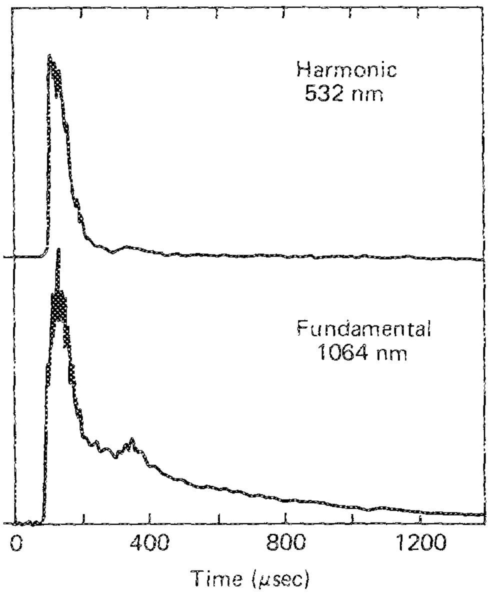

FIG. 2. Fundamental (lower curve) and second-harmonic (upper curve) outputs from the laser. The amplitude of the initial peak of each trace was used to determine the SHG efficiency. The second smaller peak was not always present.

w_0 is the Gaussian beam waist radius. In the limit of weak focusing ($L \ll 2\pi n w_0^2/\lambda$), but significant beam walk-off ($\rho L/w_0 \gg 1$), $2\pi n L h/\lambda \approx L^2 A(L)/\pi w_0^2$ where ρ is the beam walk-off angle due to double refraction (for DAN, the walk-off angle is 10.8°).[5] The value of $A(L)$ is a slowly decreasing function of $\rho L/w_0$ and is equal to one in the absence of beam walk off. Therefore, $P_{2\omega} = S(P_\omega)^2$ where[13]

$$S = (8\pi^2 d^2/\epsilon_0 c\lambda^2 n^3)[L^2 A(L)/\pi w_0^2]\exp(-\alpha' L)$$
$$= 3.7\times10^{-6}\ \mathrm{W/W^2}\times[L^2 A(L)/\pi w_0^2]\exp(-\alpha' L). \tag{1}$$

The Gaussian beam waist in the crystal $w_0 = 70\ \mu\mathrm{m}$ was determined by Gaussian mode resonator calculations (including the effect of the YAG rod) and direct measurement of the YAG output spot radius. For a 0.77-mm-thick crystal at the phase-matching angle, $A(L) = 0.59$, and the calculated SHG power is 0.43 mW which is in good agreement with the observed value (0.28 mW).

Figure 3 shows the SHG power exiting the crystal versus the intracavity fundamental power for a 1.3-mm-thick crystal in $n = 1.589$ index fluid. The pump power was constant at 0.5 W but the laser output fluctuated from pulse to pulse and each point represents the peak SHG and intracavity powers from a single pulse. The laser output was a slightly distorted and astigmatic Gaussian TEM_{00} mode which also fluctuated from shot to shot. We attribute the majority of the scatter in Fig. 3 to the mode quality fluctuation which results in a fluctuation of the peak intensity of the fundamental wave at the crystal. The solid line is a least-squares fit to $P_{2\omega} = S(P_\omega)^2$ with $S = 8\times10^{-5}\ \mathrm{W/W^2}$. The calculated value of S using Eq. (1) [here $A(L) = 0.43$] is $S = 14\times10^{-5}\ \mathrm{W/W^2}$ which is in excellent agreement with the measured value.

This is the first report, to our knowledge, of intracavity harmonic generation by an organic nonlinear optical crystal. A novel technique of immersing the crystal in index matching fluid has been used which is a useful way to evaluate a new material or to aid in optimization of the growth technique. Crystals with only fair surface quality, that is with nonplanar and moderately rough surfaces, can be inserted in the cavity without polishing or antireflection coating. We have shown that the refractive index of the fluid is not overly constrained ($1.50 < n < 1.70$ at 1064 nm should be suitable for DAN) but reduced absorption at the fundamental wavelength and chemical compatibility with the crystal are very important. It is likely that, with proper choice of fluid and cuvette size, stable cw intracavity SHG is possible. Harmonic conversion efficiencies up to 0.012% of the quasi-cw intracavity power has been achieved using this technique.

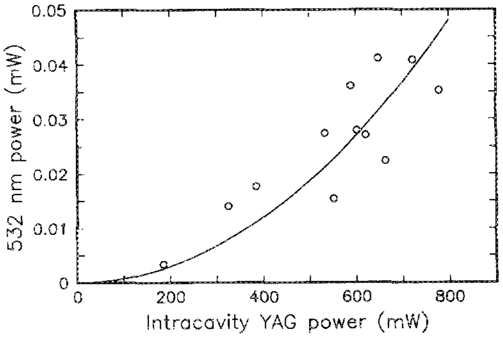

FIG. 3. The peak SHG power vs the peak fundamental intracavity power in a 1.3-mm-thick crystal. The line is a least-squares fit to the relationship $P_{2\omega} = S(P_\omega)^2$ with $S = 8\times10^{-5}\ \mathrm{W/W^2}$.

We have also recently demonstrated true cw intracavity harmonic generation using a crystal which has been polished on the (001) faces and subsequently coated for low reflection loss (0.5% per face) in air (without the cuvette and index matching fluid). 4 μW cw power (from each crystal face) of 532 nm light was generated from 137 mW of intracavity power in a 0.6-mm-thick crystal in the Nd:YAG laser described above. The output power calculated using Eq. (1) is 1.3 μW assuming a beam waist radius $w_0 = 70\ \mu\mathrm{m}$.

Successful laser operation and harmonic generation with an organic NLO crystal in the laser cavity is an important and crucial step in the quest for efficient generation of short wavelength laser light with compact laser diode sources. With its large phase-matched figure of merit and the internal quality attained thus far, DAN is beginning to fulfill some of the early predictions of its suitability for this purpose. Although the absorption edge of DAN is at approximately 500 nm, resonance enhancement partially compensates for absorption, producing efficient SHG for pump wavelengths as short as 970 nm.[14]

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