Efficient optical parametric generation in an organomineral crystal

I. D. W. Samuel, B. Villacampa, D. Josse, S. Khodja,
and J. Zyss
*France Telecom, CNET, Centre Paris B, Laboratoire de Bagneux, 196 Avenue Henri Ravera,
BP107, 92225 Bagneux Cedex, France*

(Received 3 August 1994; accepted for publication 6 February 1995)

Organomineral crystals are engineered to combine the favorable properties of organic and inorganic materials. High gain parametric emission and amplification at telecommunications wavelengths are demonstrated in an organomineral crystal, 2-amino-5-nitropyridinium-dihydrogen phosphate. A novel angle-noncritical type-II phase-matching configuration is observed in parametric emission, and parametric amplification is demonstrated at 1.5 μm. © *1995 American Institute of Physics.*

The continuing development of photonics has created the demand for ever-improving optically nonlinear materials. There are many applications of materials with large second-order susceptibility $\chi^{(2)}$ such as second harmonic mixing, sum-frequency generation, optical parametric generation, and electro-optic modulation. The existing materials can be classified as either organic or inorganic. Organic materials for $\chi^{(2)}$ generally consist of donor-acceptor nonlinear molecules following the paranitroaniline blueprint. They can have very large nonlinearities, but there are often problems of crystal growth associated with the dipolar character of such molecules.[1] Dipolar interactions tend to favor an energy-minimizing antiparallel packing of molecular dipoles, leading to an undesirable centrosymmetric crystal structure. Furthermore, in some cases intermolecular bonding is weak, limiting mechanical robustness. In many inorganic materials the growth techniques have now been mastered, and mechanical properties are usually favorable. However, the nonlinearities available are limited.

A new approach is provided by so-called "organomineral" materials that contain both organic and inorganic components.[2–4] The aim of this approach is to combine the favorable properties of both classes of material; to benefit from the enhanced nonlinearities of organic molecules, and also from the structural cohesion and facility of growth of some inorganic materials. Strong ionic and hydrogen bonding interactions between organic cations and mineral anions overcome the usual drawbacks of more traditional van der Waals structures. A successful example of this approach is 2-amino-5-nitropyridinium-dihydrogen phosphate (2A5NPDP).[2,3] This material has been precisely tailored towards near-infrared applications, whereas other work has been directed towards the blue/near-ultraviolet region of the spectrum.[4]

In this letter we report studies of optical parametric emission and amplification in 2A5NPDP. We observe a novel angularly noncritical phase-matching configuration, and demonstrate parametric amplification at 1.5 μm, a wavelength of strategic importance for telecommunications. The crystal of 2-amino-5-nitropyridine (2A5NP) is typical of many dipolar nonlinear materials; its constituent molecules consist of an aromatic part linking a donor to an acceptor end group [see Fig. 1(a)]. In the 2A5NPDP crystal, the 2A5NP is present as the cation, $2A5NP^+$, between sheets of a polymeric anionic matrix of phosphate ions. These phosphate sheets provide shielding that permits a herring-bone type polar packing of the nonlinear $2A5NP^+$ groups. Each $2A5NP^+$ ion is bonded to a phosphate group by an ionic bond and two hydrogen bonds. The strong bonding in 2A5NPDP, in contrast to much weaker van der Waals interactions in some molecular solids, leads to good mechanical properties. The crystal structure is orthorhombic, space group $Pna2_1$, point group *mm*2. The *XYZ* dielectric axes coincide with the *abc* crystal directions. The crystal used in this study was grown in solution by Crismatec S. A.[5] It was cut and polished perpendicular to the *Y* axis, and was 4 mm thick.

Excitation at 612 nm was provided by an amplified dye laser system based on a design by Meyer *et al.*,[6] giving light

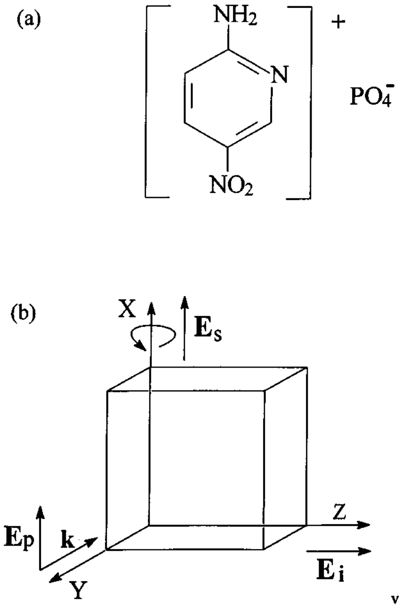

FIG. 1. (a) The 2-amino-5-nitropyridinium-dihydrogen phosphate molecule. (b) Configuration of the experiment, showing the crystal orientation, and the pump (E_p), signal (E_s), and idler (E_i) polarizations. The crystal was rotated about its X axis.

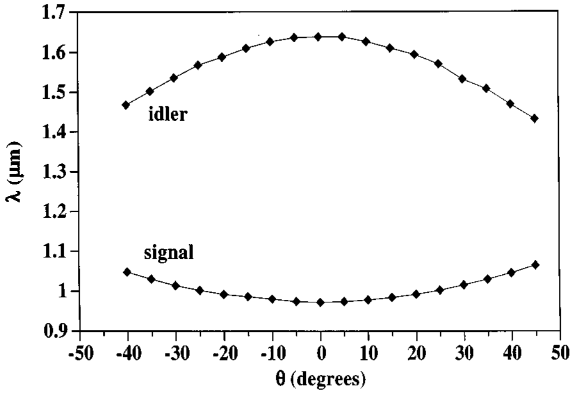

FIG. 2. Signal and idler wavelengths as a function of crystal angle for parametric emission in 2A5NPDP. θ is the external angle.

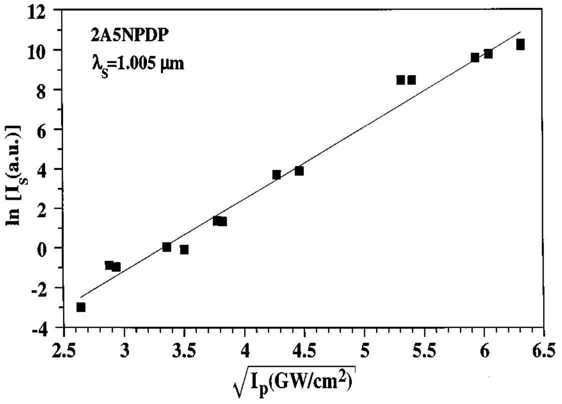

FIG. 3. Dependence of the intensity of parametric emission in 2A5NPDP at 1005 nm (I_s) as a function of the pump intensity (I_p).

pulses of energy 200 μJ and duration 2 ps, at a repetition rate of 10 Hz. The beam was focused onto the crystal by a lens of 0.5 m focal length, and the size of the beam (FWHM) at the crystal position was measured to be 425 μm×425 μm by an optical multichannel analyzer. Excitation was polarized parallel to the X axis, and the crystal could be rotated about this axis [see Fig. 1(b)]. The emission was separated from the excitation beam by bandpass filters and then passed through a 0.25 m monochromator to the detector, which was either a germanium photodiode or an infrared-enhanced photomultiplier tube (for the shorter wavelengths).

The first series of experiments involved studying the emission. With the crystal at normal incidence, the signal wavelength was 974±2 nm and the idler wavelength 1642±4 nm. The signal and idler were polarized parallel to the X and Z axes, respectively, indicating a type-II phase match [see Fig. 1(b)]. The crystal was rotated about the X axis, and the signal and idler wavelengths measured. The resulting experimental phase-matching curve is shown in Fig. 2. The most striking feature is the angle noncritical phase matching around 0°. This behavior arises because the phase-matching curve crosses the Y dielectric axis.

The parametric gain was estimated by measuring the intensity of the parametric emission as a function of the pump intensity, which was varied using neutral density filters. For large gain, the gain G is given by

$$(\tfrac{1}{4})\exp(2\Gamma l_{\mathrm{eff}}), \tag{1}$$

where

$$\Gamma^2=(8\pi^2 d_{\mathrm{eff}}^2 I_p)/(\varepsilon_0\lambda_i\lambda_s n_i n_s n_p c), \tag{2}$$

and l_{eff} is the effective length of the crystal, I_p the pump intensity ranging from 5 to 30 GW/cm^2, and d_{eff} is the nonlinear coefficient at phase match. λ_i and λ_s are the signal and idler wavelengths, while n_i, n_s, and n_p are the refractive indices at the signal, idler, and pump wavelengths.

Figure 3 shows the intensity of the emission at 1005 nm versus the square root of the pump intensity in a semilogarithmic plot, measured with the crystal at an angle of 24° to normal incidence. The graph is a straight line, as expected and from its slope we deduce $\Gamma=29\pm3\ \mathrm{cm}^{-1}$ for $I_p=30$ GW/cm^2. From this and Eq. (2), we deduce $d_{\mathrm{eff}}=2.6\pm0.5$ pm/V, assuming that the effective length of the crystal is equal to the physical length of the crystal. We note that this is a factor of 2 smaller than the previously reported value of 6±1 pm/V for second harmonic generation at 1.34 μm.[3] There are several factors that may contribute to the difference including gain saturation effects, beam walkoff, imperfections in the crystal, and the fact that the effective length of the crystal may have been overestimated. There are also many sources of error, such as estimating the intensity of the pump beam, and assuming a "tophat" beam profile. Moreover, gain saturation and pump depletion effects [which are not accounted for in Eqs. (1) and (2)] may be important as the gain G corresponding to our value of Γ is $>10^9$. We note that in previous measurements of parametric emission in other organic crystals,[7,8] the values of d_{eff} were also smaller than in corresponding second harmonic generation measurements.

We have also demonstrated parametric amplification at 1.5 μm in 2A5NPDP. In these experiments, light from a continuous-wave 1.5 μm diode laser was combined collinearly with the picosecond pump beam by a dichroic mirror. The angle of the crystal (26°) was optimized to maximize the amplification at this wavelength, and ac coupling to a boxcar integrator was used to eliminate the continuous component. The emission was compared with and without injection by the diode laser. Without injection, emission was observed at 1.5 μm and its complement at 1.0 μm. When the laser was injected, much stronger emission was observed at both these wavelengths. The gain was measured as before by measuring the intensity of the amplified signal as a function of the pump intensity, and Γ was deduced to be $19\pm3\ \mathrm{cm}^{-1}$ at both 1.5 and 1.0 μm. This corresponds to a gain G of the order of 10^6. We have calculated from the Sellmeier coefficients[3] that noncritical phase matching for parametric amplification at 1.55 μm would be achieved for a pump wavelength of 606 nm.

In conclusion, we have demonstrated parametric emission and amplification at telecommunications wavelengths in the organomineral crystal 2A5NPDP. We have observed a novel noncritical phase-matching configuration in parametric emission, and demonstrated parametric amplification at 1.5 μm close to this configuration. We believe that this material is promising for optical parametric oscillation in the near infrared, building on our earlier work on optical parametric oscillators with organic crystals.[9] Organomineral crystals are a recent idea, and we believe that there is considerable scope for optimization of their nonlinearity.

We are very grateful to Dr. S. Gauvin for the construction of the autocorrelator used to measure the pulse duration in this work. We also gratefully acknowledge the Crismatec company, and in particular Dr. Guerder, Dr. Derrouineaux, Dr. Iltis, and D. Bigot for expert growth, cutting, and polishing of 2A5NPDP samples. This work was partially supported by a US Navy grant for ''Highly efficient optically nonlinear organic materials and by a DRET Contract No. NR93366.''

[1] J. Zyss, I. Ledoux, and J. F. Nicoud, in *Molecular Nonlinear Optics: Materials, Physics and Devices*, edited by J. Zyss (Academic, Boston, 1993).

[2] R. Masse and J. Zyss, Mol. Eng. **1**, 141 (1991); R. Masse, M. Bagieu-Beucher, J. Pecaut, J.-P. Levy, and J. Zyss, Nonlin. Opt. **5**, 413 (1993).

[3] Z. Kotler, R. Hierle, D. Josse, J. Zyss, and R. Masse, J. Opt. Soc. Am. B **9**, 534 (1992).

[4] D. Eimerl, S. Velsko, L. Davis, F. Wang, G. Loiacono, and G. Kennedy, IEEE J. Quantum. Electron **QE-25**, 179 (1989); C. B. Aakeroy, P. B. Hitchcock, B. D. Moyle, and K. R. Seddon, J. Chem. Soc. Chem. Commun. **23**, 1856 (1989); H. O. Marcy, L. F. Warren, M. J. Rosker, P. Cunningham, C. A. Ebbers, L. E. Davis, and S. P. Velsko, Technical Digest of Conference on Lasers and Electro-Optics, Paper CFF6, Anaheim, CA, May 8–13, 1994.

[5] French patent 9014743 (held by R. Masse and J. Zyss, CNET) extended to major industrial countries (1990).

[6] Y. H. Meyer, M. M. Martin, F. Nesa, and E. Breheret, J. Phys. (Paris) Colloq. **48**, C7-397 (1987).

[7] J. Zyss, I. Ledoux, R. Hierle, R. K. Raj, and J.-L. Oudar, IEEE J. Quantum Electron. **QE-21**, 1286 (1985).

[8] I. Ledoux, J. Badan, J. Zyss, A. Migus, D. Hulin, J. Etchepare, G. Grillon, and A. Antonetti, J. Opt. Soc. Am. B **4**, 987 (1987).

[9] D. Jose, S. X. Dou, J. Zyss, P. Andreazza, and A. Périgaud, Appl. Phys. Lett. **61**, 121 (1992); D. Josse, S. Khodja, J. Badan, I. D. W. Samuel, and J. Zyss, Appl. Phys. Lett. **64**, 3655 (1994).