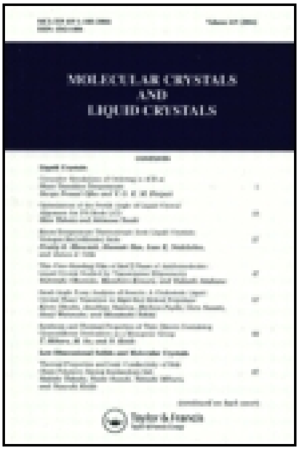

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Linear and Nonlinear Optical Properties of New Organic Materials

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Linear and Nonlinear Optical Properties of New Organic Materials

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Single crystals of new organic nonlinear optical materials, *N*-(2,4-dinitrophenyl)-1-chloro-3-phenyl-2-propanamine(DNCPA) and *N*-(5-nitro-2-pyridyl)leucinol(NPLO) have been grown by a seeded solution growth technique. Linear and nonlinear optical properties of these materials have been investigated. Angle-tuned type I and type II phase matching for frequency doubling of 1064 nm radiation at room temperature were achieved for DNCPA and NPLO crystals. The effective nonlinear coefficients were d_{eff} = 0.13 pm/V (type I), d_{eff} = 1.1 pm/V (type II) for DNCPA and d_{eff} = 40 pm/V (type I), d_{eff} = 3.0 pm/V (type II) for NPLO, respectively.

Keywords: dinitrophenyl-chlorophenyl-propanamine(DNCPA), nitropyridyl-leucinol(NPLO), organic crystal, phase-matched SHG

1. INTRODUCTION

Organic materials are considerably attractive as an extremely useful material for a number of applications of nonlinear optics, such as second-harmonic generation, frequency-mixing, electro-optic modulation, optical parametric oscillation. Some organic nonlinear optical materials exhibit eminently large optical nonlinearity compared with most inorganic nonlinear optical materials. A systematic approach with both organic and inorganic structure was facilitated at the end of the 1960s by using a method for testing of second-harmonic generation efficiency of powder samples.[1,2] After that many organic materials have been found with superior second-harmonic efficiency than the inorganic materials.[3–5] The largest second order molecular hyperpolarizabilities are found in molecules possessing both electron donor and acceptor at opposite ends of the π conjugated system. It is well known that the *p*-nitroaniline and 2,4-dinitroaniline molecules have large nonlinearities, however, they never show the efficiency for second-harmonic generation in each crystal. This fact means that optically nonlinear active molecule does not guarantee

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that it will be a useful material for second-harmonic generation with the noncentrosymmetric crystal structure. The concept of molecular engineering was introduced to optimize both molecular and crystal nonlinear properties. The introduction of molecular chirality for nonlinear optical organic material have been proposed, because the molecular chirality guarantees the noncentrosymmetric crystal structure. A chiral auxiliary has been utilized to optically nonlinear active molecules like 2,4-dinitroaniline derivatives. Ouder *et al.*[6] reported that methyl-(2,4-dinitrophenyl)amino-2-propanoate(MAP), which has the optically active amino acid as a substituent, exhibits very attractive properties for nonlinear optics.

On the other hand, there is a trade-off between molecular hyperpolarizability and optical transparency of its molecule. It is well known that the absorption maximum wavelength (λ max) is related to the energy gap between the ground state and the excited charge transfer state. The effect on the energy gap and the hyperpolarizability due to the introduction of substituents and heteroatoms to a conjugated molecule can be predicted by using a molecular orbital calculation. The molecular orbital calculation demonstrate that the replacement of carbon at the *ortho* or *para* position to an electron donor in the conjugated molecular ring by an electron negative atom produces a large hypsochromic shift. The pyridine analog molecules produce hypsochromic shift compared with benzene analog molecules. Twieg *et al.*[7] pointed out that the donor-acceptor substituted pyridine derivative with chiral auxiliary, 2-(α-methylbenzylamino)-5-nitropyridine(MBANP), has large optical second-harmonic efficiency in powder form and its absorption cut-off wavelength measured in an ethanol solution exists in a relatively short wavelength region. The MBANP crystal has short absorption cut-off wavelength of 430 nm and noncentrosymmetric crystal structure with large nonlinear coefficients.[8,9]

We report here on the linear and nonlinear optical properties of new organic nonlinear materials, *N*-(2,4-dinitrophenyl)-1-chloro-3-phenyl-2-propanamine(DNCPA), and *N*-(5-nitro-2-pyridyl)leucinol(NPLO), which are developed and grown to the single crystal in our laboratory. DNCPA has relatively longer-cut-off wavelength than NPLO. Both crystals are shown to be highly birefringent, to be phase-matchable for YAG wavelength with large nonlinear coefficients.

2. CRYSTAL PROPERTIES

2.1. DNCPA

Single crystal has been grown by using a seeded and slow solvent evaporation technique from toluene solution. Seed crystals were obtained by the spontaneous nucleation from toluene solution. The optical quality of seed crystal was examined with a polarized microscope. The seed was fixed by fusion at the end of a platinum wire. The apparatus was a closed double-jacket glass vessel whose temperature was stabilized within 0.1°C by circulating thermostatic water. The highly optical-quality DNCPA crystal with dimensions of up to 19 × 16 × 5 mm^3 was grown for 30 days. The mechanical Vickers hardness of DNCPA crystal was found to be 25, thus DNCPA crystal has better mechanical hardness among some optical nonlinear organic crystals.[10]

The structure of the crystal was determined with single crystal X-ray diffractometer. The DNCPA crystal system was found to be orthorhombic with space group $P2_12_12_1$. The lattice parameters are a = 14.09 Å, b = 15.61 Å, c = 7.15 Å and the other parameters are listed in Table I.

2.2. NPLO

Single crystal was grown by the seeded slow cooling method from ethanol/toluene mixed solution. Seeds were also obtained by the slow cooling of ethanol/toluene mixed solution. The typical cooling rate was −0.1°C in 20 hours. A crystal with dimensions of up to $22.4 \times 12.3 \times 6.3$ mm^3 was grown for two months. The mechanical Vickers hardness of NPLO crystal was found to be 18.

The NPLO crystal system was found to be monoclinic with space group $P2_1$. The lattice parameters are a = 10.04 Å, b = 5.883 Å, c = 11.60 Å and the other parameters are also listed in Table I.

3. OPTICAL PROPERTIES

3.1. Optical Properties of Molecules and Crystals

The molecular absorption spectra of DNCPA and NPLO were measured in dichloromethane solution. As shown in Figure 1, intense charge transfer absorption bands for both molecules were observed in the near ultraviolet wavelength region.

TABLE I

Crystal properties of DNCPA and NPLO

		DNCPA	NPLO
Crystal system		Orthorhombic	Monoclinic
Space group		$P2_12_12_1$	$P2_1$
Lattice parameter	a(Å)	14.09	10.04
	b(Å)	15.61	5.88
	c(Å)	7.15	11.60
	V(Å^3)	1573	641.6
	ß(deg.)	90	110.43
Z Value		4	2
Density	(g/cm^3)	1.418	1.240

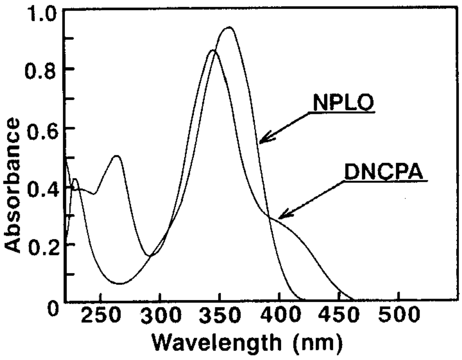

FIGURE 1 Molecular absorption spectra of DNCPA and NPLO in dichloromethane.

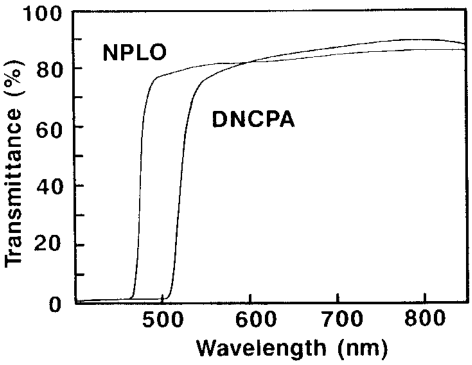

FIGURE 2 Transmission spectra of DNCPA crystal along [101] crystal axis and NPLO crystal along [101] crystal axis.

The DNCPA has shorter absorption maximum wavelength than the NPLO, but it has a shoulder around 420 nm. Thus NPLO has more blue shifted cut-off wavelength than DNCPA. The origin of the shoulder was analyzed by the molecular orbital calculation, which made clear that the shoulder was caused by the nitro substituent at ortho position to the amino substituent.[11]

Figure 2 shows the transmission spectra along [101] crystal axis of DNCPA and [100] crystal axis of NPLO. The crystals were cut with a diamond wire-saw and polished with alumina-water suspension. The cut-off wavelengths are less than 530 nm for the DNCPA crystal and 460 nm for the NPLO crystal.

3.2. Refractive Index

The principal dielectric axes were determined by observing conoscopic figure at the wavelength of He-Ne laser. As DNCPA crystal belongs to the primitive lattice system with point group 222, the principal dielectric axes of the crystal coincide with the crystallographic axes. On the other hand, as NPLO crystal belongs to the primitive lattice system with space group 2, the only one principal dielectric axis (Y-axis) of the crystal is parallel to the crystallographic axis (b-axis) and the other axes are in the crystallographic a–c plane. The direction of X and Z axes most likely have the wavelength dependence, however, we have neglected this dependence because of its complicated nature. The refractive indices of both crystals were measured by the minimum deviation method at the wavelength of 488 nm, 514 nm, 532 nm, 633 nm and 1064 nm.

The three prisms of DNCPA crystal were made for the measurements of refractive indices. The two crossed surfaces were polished. The ridgeline made by the two surfaces was parallel to the principal dielectric axes of crystal. The polarized beam which was parallel to the dielectric axis was used for the measurements.

The two prisms of NPLO crystal were cut and polished. The ridgeline of each prism was parallel to the Y or Z principal dielectric axis. These prisms allow the direct measurements of the refractive indices of n_y and n_z. The refractive index of n_x was obtained by solving the equation of index ellipsoid.

The wavelength dependence of refractive indices have been fitted with the Sellmeier's equation

$$n^2 = \mathrm{A} + [\mathrm{B}/(\lambda^2 + \mathrm{C})] - \mathrm{D}\lambda^2,$$

where λ is wavelength and A, B, C and D are the constants. The results of the measurements and the constants are shown in Table II.

Both crystals have found to be highly birefringent, which can be explained with the molecular orientation in a crystal unit.

4. NONLINEAR OPTICAL PROPERTIES

4.1. DNCPA

Phase-matched second-harmonic generation from DNCPA crystal was studied for type I and type II at the Nd:YAG wavelength 1064 nm. The light source was injection seeded Q-switched Nd:YAG laser operating at 10 Hz with the typical pulse width of 8 nsec. The crystal samples were mounted on a goniometric stage, and irradiated with linearly polarized laser light of 2 mm diameter. The polarization state of second-harmonic wavelength 532 nm were analyzed. The intensity of the second-harmonic generation were measured as the sample rotating around Z-axis.

As DNCPA crystal belongs to point group 222, the effective nonlinear coefficients (d_{eff}) are given by; $d_{\mathrm{eff}} = -d_{36} \sin\theta \sin 2\phi$ for type I and $d_{\mathrm{eff}} = -0.5\ (d_{14} + d_{25}) \sin\theta \sin 2\phi$ for type II, where d_{ij} are elements of coefficients for X, Y and Z axes. θ and ϕ indicate the angles of rotation around the Z and X axes, respectively. The phase matching angles were calculated from the dispersion of refractive indices. Since the largest values for these effective nonlinear coefficients are obtained at $\theta = 90°$, we have calculated the phase matching angles which were $\phi_{\mathrm{PM}} = 28°$ for type I and $\phi_{\mathrm{PM}} = 39°$ for type II in X–Y plane. Type I and type II phase matching were experimentally studied using the cut and polished crystal plates of which surfaces were perpendicular to each phase matching direction at $\theta = 90°$.

Optimum second-harmonic generations of DNCPA crystal were observed at $\phi_{\mathrm{PM}} = 27.8°$ for type I and $\phi_{\mathrm{PM}} = 38.3°$ for type II. The angle tuned phase-matched second-harmonic intensity for type I is shown in Figure 3. The angular bandwidth

TABLE II

Measured refractive indices and coefficients of the Sellmeier's equations for DNCPA and NPLO crystals

	DNCPA			NPLO		
Wavelength(nm)	nx	ny	nz	nx	ny	nz
488	—	—	—	1.470	1.712	2.218
514	1.523	1.909	1.990	1.463	1.681	2.116
532	1.517	1.887	1.945	—	—	—
633	1.511	1.825	1.853	1.457	1.631	1.933
1064	1.499	1.764	1.786	1.451	1.598	1.812
COEFFICIENT						
A	3.1204	3.2368	2.2970	2.124	2.5607	3.2123
B	0.0563	0.0456	0.0006	0.0011	0.0257	0.1302
C	-0.1598	-0.2030	-0.2458	-0.2108	-0.1700	-0.1625
D	0.2588	0.0849	0.0448	0.0174	0.0299	0.0559

for both phase matching were obtained to be about 0.13 mrad-cm. The effective nonlinear coefficients of DNCPA crystal for type I and type II are determined by comparing with the phase-matched second-harmonic intensity from KDP crystal (d_{36} = 0.63 pm/V).[12] They were 0.13 pm/V for type I and 1.1 pm/V for type II.

The walk-off angles were calculated by the refractive indices with following equation

$$\tan^2\rho = 1/[n_x^4 \cos^2\phi/(n_x^2 - n^2) + n_y^4 \sin^2\phi/(n_y^2 - n^2)].$$

The results were 0.20 rad for type I and 0.22 rad for type II. These values are one order magnitude larger than those of the inorganic crystals.

4.2. NPLO

Phase-matched second-harmonic generation for type I and type II were also studied with NPLO crystal. As NPLO crystal belongs to point group 2, the effective nonlinear coefficients on X–Z plane are given by: $d_{\text{eff}} = -d_{21}\cos^2\theta - d_{23}\sin^2\theta +$

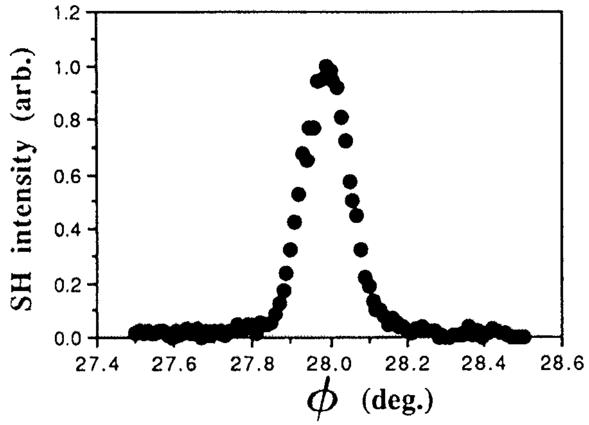

FIGURE 3 Angle-tuned type I phase-matched second-harmonic generation of DNCPA crystal at 1064 nm.

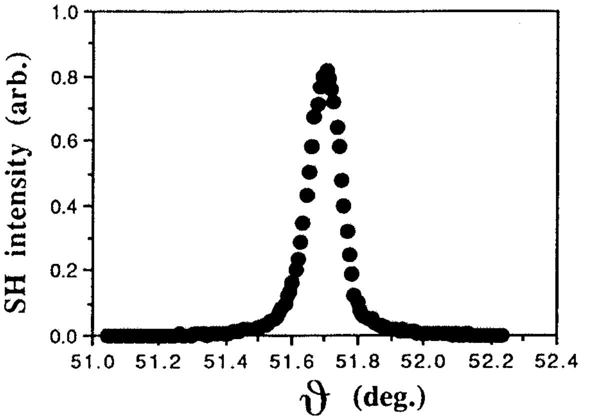

FIGURE 4 Angle-tuned type I phase-matched second-harmonic generation of NPLO crystal at 1064 nm.

d_{25} sin 2θ for type I, $d_{\mathrm{eff}} = d_{14} \sin\theta \cos\theta - d_{16} \cos^2\theta - d_{34} \sin^2\theta + d_{36} \sin\theta \cos\theta$ for type II, where the notation of coefficients are the same as the formulation for DNCPA.

We also have calculated the phase matching angles in X–Z plane. They were $\theta_{PM} = 55.4°$ for type I and $\theta_{PM} = 29.2°$ for type II. The type I and type II phase matching were also studied with the cut and polished crystal plates which were perpendicular to the phase matching direction in the X–Z plane. The experimental apparatus used were the same as that for DNCPA crystal, but the sample rotation was around Y-axis.

Optimum second-harmonic generation of NPLO crystal were observed at $\theta_{PM} = 52°$ for type I and $\theta_{PM} = 33°$ for type II. The angle–tuned phase matching second-harmonic intensity for type I is shown in Figure 4. The angular bandwidth for both phase matching were obtained to be about 0.30 mrad-cm. The effective nonlinear coefficients of NPLO crystal for type I and type II were determined by comparing with the type II phase-matched second-harmonic intensity for KTP crystal ($d_{\mathrm{eff}} = 5.2$ pm/V), of which the effective nonlinear coefficient for type II was also measured by comparing with the phase-matched second-harmonic intensity from KDP crystal. They were 40 pm/V for type I and 3.0 pm/V for type II.

The walk-off angles were also calculated by the following equation

$$\tan^2\rho = 1/[n_x^2 \sin^2\theta/(n_x^2 - n^2) + n_z^4 \cos^2\theta/(n_z^2 - n^2)].$$

The results were 0.22 rad for type I and 0.24 rad for type II.

5. CONCLUSIONS

We have demonstrated that DNCPA and NPLO are useful nonlinear optical materials for phase-matched frequency doubling at YAG laser wavelength. In addition, both materials possess crystal growth properties to a suitable size for the applications. These crystals have good transmittance for the visible wavelength and good processability due to their hardness.

The effective nonlinearity of DNCPA is comparable to the inorganic nonlinear optical materials and NPLO is superior to some of organic nonlinear optical materials having similar linear optical properties.

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