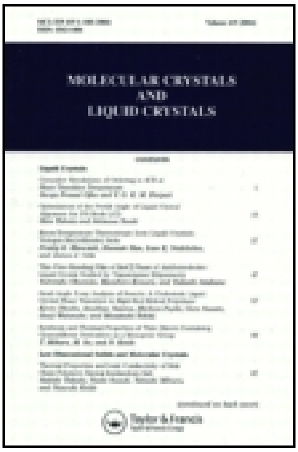

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Phase-Matching Properties of a PI Symmetry Crystal, (-)-1-(4-Dimethylaminophenyl)-2-(2-Hydropropylamino)Cyclobutene-3, 4-Dione

Takao Tomono [a], Shinsuke Umegaki [b], Tomonori Usagawa [b], Lyong Sun Pu [a] & Keisuke Sasaki [b]

[a] Foundation Research Laboratory, Fuji Xerox Co., Ltd., 2274, Hongo, Ebina, Kanagawa, 243-04, Japan

[b] Department of Electrical Engineering, Faculty of Science and Technology, Keio University, 3-14-1, Hiyoshi, Kouhoku, Yokohama, Kanagawa, 223, Japan

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PHASE-MATCHING PROPERTIES OF A P1 SYMMETRY CRYSTAL, (–)-1-(4-DIMETHYLAMINOPHENYL)-2-(2-HYDROPROPYLAMINO) CYCLOBUTENE-3,4-DIONE

TAKAO TOMONO[1], SHINSUKE UMEGAKI[2], TOMONORI USAGAWA[2], LYONG SUN PU[1] AND KEISUKE SASAKI[2]
[1]Foundation Research Laboratory, Fuji Xerox Co., Ltd., 2274, Hongo, Ebina, Kanagawa 243-04, Japan. [2]Department of Electrical Engineering, Faculty of Science and Technology, Keio University, 3-14-1, Hiyoshi, Kouhoku, Yokohama, Kanagawa 223, Japan.

ABSTRACT Phase-matching properties of a P1 symmetry crystal, (-)-1-(4-dimethylaminophenyl)-2-(2-hydropropylamino) cyclobutene-3,4-dione, are theoretically and experimentally investigated. The nonlinear-optical coefficients d_{ij} are calculated by the oriented-gas model and the effective coefficients are estimated to be 243 pm/V and 23 pm/V at a fundamental wavelength of 1064 nm for the type I and the type II phase-matching of the second-harmonic generation, respectively. The experimental results of the type II second-harmonic generation using the largest plane of the as-grown crystal are given.

INTRODUCTION

A large number of organic molecules based on non-localized π-conjugated systems have been proposed for nonlinear-optical applications such as frequency-doubling and electro-optic modulation of light. The molecules with the appropriate donor-acceptor pair exhibit the large second-order optical nonlinearities.[1-2] In general, however, these molecules tend to form centrosymmetrical structures in crystallization because of their dipole-dipole interaction. Chirality, hydrogen bonds, bulky substituents and so on have been introduced for the non-centrosymmetrical structure.

We already showed that the cyclobutenedione derivatives have the first hyperpolarizabilities several times larger than their nitro-substituted counterparts[3-5] and in addition, that the crystal of (-)-1-(4-dimethylamino-phenyl)-2-(2-hydroxypropylamino)cyclobutene-3,4-dione (DAD) belongs to the non-centrosymmetrical space group P1 of the triclinic crystal system. Its nonlinear optical coefficient d_{11} for the second-harmonic generation (SHG) was estimated to be 200±40 pm/V experimentally by the Maker-fringe method and to be 400 pm/V theoretically by the oriented-gas model.[6]

According to the relation between the microscopic and the macroscopic nonlinearity analyzed by J.Zyss et. al.,[7] in the P1 crystal, the dielectric x-axis coincides with the intramolecular charge-transfer (CT) axis and the largest nonlinear-optical coefficient is d_{11}. It is concluded in this case that the effective coefficient d_{eff} reduces to $(2/3\sqrt{3})d_{11}$ at its maximum. There, however, exist the cases[6,8] that any one of the dielectric axes does not coincide with the CT axis.

In this paper, we will show that the DAD crystal, whose dielectric axes do not coincide with the CT axis, can possess the larger effective coefficients. We will give the experimental results, which confirms the theoretical values of the effective coefficients for the type Ⅱ SHG using an as-grown crystal.

CALCULATION OF NONLINEAR-OPTICAL COEFFICIENTS

Nonlinear-optical coefficients d_{IJK} can be calculated by the oriented-gas model. There, the relation between the intramolecular CT axis and the dielectric axes, the principal refractive indices and the first hyperpolarizabilities are required.

The molecular structure of DAD is shown in Fig.1.[3] The DAD crystal belongs to the triclinic system. Therefore, its crystallographic a-, b- and c-axes do not correspond to the dielectric x-, y- and z-axes and the crystal is optically biaxial. Using as-grown crystals, the crystallographic axes were assigned from x-ray analysis and the dielectric axes were determined from microscope observation of the conoscopic image.[5] The largest plane of the crystal shown in Fig.2 was a crystallographic a-c and dielectric x-z plane. The dielectric x and z axes could be assigned from the dichroism.

In Fig.2, a projection of DAD molecules onto the plane is also shown.

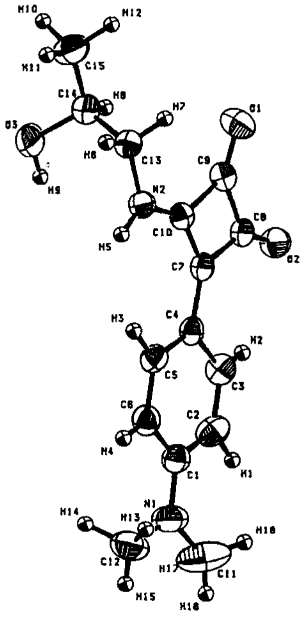

FIGURE 1 Molecular structure of DAD.

The molecules are aligned parallel to each other, reflecting the P1 symmetry. It should be noted that the orientation of molecules differs from the direction of alignment. This results in that any one of the dielectric axes does not coincide with the orientation of molecules or the CT axis. One of the dielectric axes might lie between the two directions of orientation and alignment, although the three-dimensional packing of molecules also affects configuration of the axes. In the case of DAD, the dielectric x-axis lies between the c-axis and the projection of the CT axis onto the a-c plane and makes an angle of 15.2° against the c-axis and 10.0° against the projection of the CT axis. Here, the direction from N1 of a dimethylamino substituent to O1 of a cyclobutenedione ring can be regarded as the CT axis.

Figure 3 represents the relation between the CT axis and the dielectric and crystallographic axes. From this, the directional cosines of the CT axis required for calculation by the oriented-gas model were determined to be (0.665, -0.737, -0.117) for the dielectric x-, y-, and z-axes.

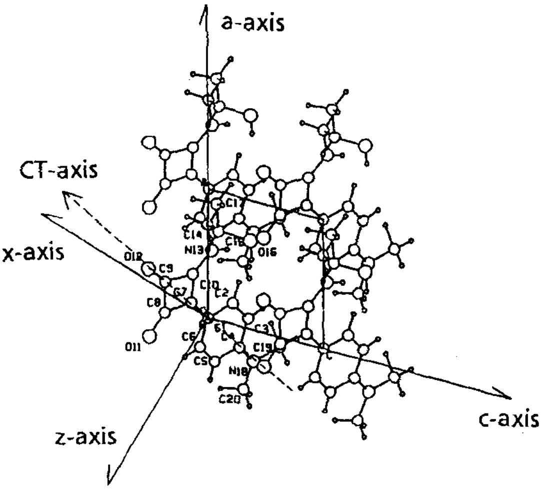

FIGURE 2 Projection of DAD molecules onto a crystallographic a-c plane. The largest plane of the as-grown crystal is a crystallographic a-c and dielectric x-z plane.

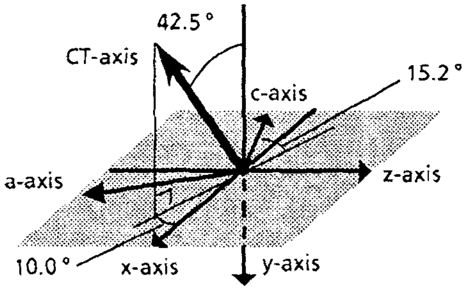

FIGURE 3 Intramolecular CT axis, dielectric x-, y- and z-axes and crystallographic a- and c-axes. The hatched area indicates the largest plane of the as-grown crystal.

TABLE 1 Parameters used for calculation in the oriented-gas model.

Crystallographic data	Z value	1
	Density (g/cm^3)	1.275
	Directional cosines	(0.6653, -0.7373, -0.1173)
Optical data	β_{CT} (esu)	140 x 10^{-30}
	n_x^{ω}, n_y^{ω}, n_z^{ω}	1.760, 1.595, 1.557
	$n_x^{2\omega}$, $n_y^{2\omega}$, $n_z^{2\omega}$	2.21, 1.81, 1.63

Refractive indices already determined [6] at a wavelength of 1064 nm (ω) and of 532 nm (2ω) are (n_x^{ω}, n_y^{ω}, n_z^{ω})=(1.760, 1.595, 1.557) and ($n_x^{2\omega}$, $n_y^{2\omega}$, $n_z^{2\omega}$)=(2.21, 1.80, 1.63). These refractive indices reflect the above directional cosines. The linear polarizabilities of molecules contribute themselves more to the x- or y-polarizability than to the z-polarizability, that is, more to n_x or n_y than to n_z. Moreover, n_x is larger than n_y, since the packing density of molecules in the x-direction is greater than that in the y-direction.

The nonlinear-optical coefficient d_{IJK} can be expressed as

$$d_{IJK} = N f_I^{2\omega} f_J^{\omega} f_K^{\omega}\ b_{IJK} \tag{1}$$

where

$$b_{IJK} = \frac{1}{Z} \sum_{s=1}^{z} \sum_{i,j,k=1}^{3} \cos(I, i(s)) \cos(J, j(s)) \cos(K, k(s)) \beta_{ijk}(s) . \tag{2}$$

In Eqs.(1) and (2), N and Z denote the number of molecules in a unit volume and in a unit cell, respectively, and (i(s), j(s), k(s)) and $\beta_{ijk}(s)$, the Cartesian coordinates and the hyperpolarizability of the s-th molecules in a unit cell, respectively. The local-field-correction factor f_I^m ($m=\omega$ or 2ω) is calculated by

$$f_I^m = \frac{(n_I^m)^2 + 2}{3} \tag{3}$$

Since the DAD crystal consists of a single molecule and the molecules are aligned parallel, $(1/Z)\Sigma_s^z$ in Eq.(2) can be set equal to unity. In addition, only the hyperpolarizability β_{CT} in the direction of the CT axis can be used , while the other components β_{ijk} are neglected. Parameters used in the calculation are listed in Table 1.

The calculated nonlinear-optical coefficients in pm/V are as follows.

$$\left|\begin{array}{cccccc} d_{11} & d_{12} & d_{13} & d_{14} & d_{15} & d_{16} \\ d_{21} & d_{22} & d_{23} & d_{24} & d_{25} & d_{26} \\ d_{31} & d_{32} & d_{33} & d_{34} & d_{35} & d_{36} \end{array}\right| = \left|\begin{array}{cccccc} 319.5 & 311.7 & 7.5 & 48.3 & -48.9 & -315.6 \\ -269.5 & -262.9 & -6.3 & -40.7 & 41.2 & 266.2 \\ -38.1 & -37.2 & -0.9 & -5.8 & 5.8 & 37.6 \end{array}\right| \tag{4}$$

It is seen in Eq.(4) that contributions of the directional cosines of the CT axis to the nonlinear polarizabilities are similar to those to the linear polarizabilities or the refractive indices. The coefficients are classified by their magnitudes into four groups; (a) d_{33}, which does not include either x or y component of the directional cosines, (b) d_{13}, d_{23}, d_{34} and d_{35}, which include only one x or y component, (c) d_{14}, d_{15}, d_{24}, d_{25}, d_{31}, d_{32} and d_{36}, which include two x or y components, and (d) d_{11}, d_{12}, d_{16}, d_{21}, d_{22} and d_{26}, which do not include the z component. Here, it should be noted that the off-diagonal d_{12}, d_{21}, d_{16} and d_{26} of the last group are extremely large, which is different from the conclusion for the P1 symmetry crystals by J. Zyss.[7] We can expect excessively large effective nonlinear-optical coefficients for the phase-matched SHG.

EFFECTIVE NONLINEAR-OPTICAL COEFFICIENTS FOR PHASE-MATCHED SHG

In the DAD crystal, type I and type II phase-matching are possible for SHG of the fundamental wavelength of 1064 nm.

For a unit vector $s^m = (s_x^m, s_y^m, s_z^m)$ of the wave-normal in the biaxial crystal, two refractive indices corresponding to the longest (-) and shortest (+) axes of the index ellipse are written as

$$n_\pm^m = \frac{\sqrt{2}}{\sqrt{(A^m \pm \sqrt{((A^m)^2 - 4B^m))}}}, \tag{5}$$

where

$$A^m = (s_x^m)^2\left(\frac{1}{(n_y^m)^2} + \frac{1}{(n_z^m)^2}\right) + (s_y^m)^2\left(\frac{1}{(n_z^m)^2} + \frac{1}{(n_x^m)^2}\right) + (s_z^m)^2\left(\frac{1}{(n_x^m)^2} + \frac{1}{(n_y^m)^2}\right)$$

and

$$B^m = (s_x^m)^2 \frac{1}{(n_y^m n_z^m)^2} + (s_y^m)^2 \frac{1}{(n_z^m n_x^m)^2} + (s_z^m)^2 \frac{1}{(n_x^m n_y^m)^2}. \tag{6}$$

In Eqs.(5) and (6), the superscript m denotes ω or 2ω.

The phase-matching conditions for the type I and the type II SHG are given by

$$n_-^\omega = n_+^{2\omega} \tag{7a}$$

and

$$\frac{1}{2}(n_+^\omega + n_-^\omega) = n_+^{2\omega}, \tag{7b}$$

respectively.

For unit vectors $e_\pm^m$ of the electric fileds corresponding to $n_\pm^m$, the effective nonlinear coefficients for the type I and type II SHG are calculated by[9]

$$d_{eff}(\mathrm{I}) = \begin{vmatrix} (e_+^{2\omega})_x & (e_+^{2\omega})_y & (e_+^{2\omega})_z \end{vmatrix} \begin{vmatrix} d_{11} & d_{12} & d_{13} & d_{14} & d_{15} & d_{16} \\ d_{21} & d_{22} & d_{23} & d_{24} & d_{25} & d_{26} \\ d_{31} & d_{32} & d_{33} & d_{34} & d_{35} & d_{36} \end{vmatrix} \begin{vmatrix} (e_-^\omega)_x (e_-^\omega)_x \\ (e_-^\omega)_y (e_-^\omega)_y \\ (e_-^\omega)_z (e_-^\omega)_z \\ 2(e_-^\omega)_y (e_-^\omega)_z \\ 2(e_-^\omega)_z (e_-^\omega)_x \\ 2(e_-^\omega)_x (e_-^\omega)_y \end{vmatrix} \tag{8a}$$

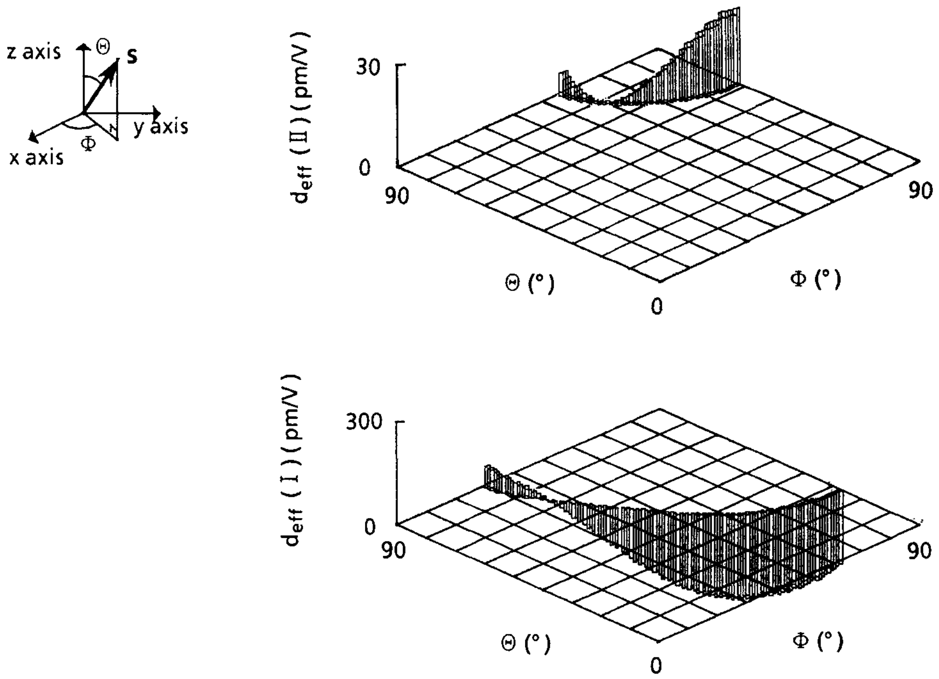

FIGURE 4 Effective nonlinear-optical coefficients d_{eff} (I) and d_{eff} (II) for type I and II SHG as a function of phase-matching direction (Θ, Φ).

and

$$d_{eff}\,(\mathrm{II}) = \left| (e_+^{2\omega})_x \;\; (e_+^{2\omega})_y \;\; (e_+^{2\omega})_z \right| \left| \begin{matrix} d_{11} & d_{12} & d_{13} & d_{14} & d_{15} & d_{16} \\ d_{21} & d_{22} & d_{23} & d_{24} & d_{25} & d_{26} \\ d_{31} & d_{32} & d_{33} & d_{34} & d_{35} & d_{36} \end{matrix} \right| \left| \begin{matrix} (e_+^{\omega})_x (e_-^{\omega})_x \\ (e_+^{\omega})_y (e_-^{\omega})_y \\ (e_+^{\omega})_z (e_-^{\omega})_z \\ (e_+^{\omega})_y (e_-^{\omega})_z + (e_-^{\omega})_y (e_+^{\omega})_z \\ (e_+^{\omega})_z (e_-^{\omega})_x + (e_-^{\omega})_z (e_+^{\omega})_x \\ (e_+^{\omega})_x (e_-^{\omega})_y + (e_-^{\omega})_x (e_+^{\omega})_y \end{matrix} \right| . \qquad (8b)$$

Under the condition that $s^{\omega} = s^{2\omega} = s$, where s can be represented as $s = (\sin\Theta\cos\Phi, \sin\Theta\sin\Phi, \cos\Theta)$ by the angles Θ and Φ of the polar coordinates, the combination of phase-matching angles Θ and Φ or the phase-matching direction (Θ, Φ) is calculated by Eqs.(7a) and (7b) with Eqs.(5) and (6).

Using the directions $e_+^{2\omega}$ and $e_\pm^{\omega}$ corresponding to this phase-matching direction, the effective nonlinear coefficients for the DAD crystal were calculated by Eqs.(8a) and (8b). The results are shown in Fig.4, which illustrates the effective coefficients d_{eff} (I) and d_{eff} (II) for the phase-matching directions (Θ, Φ).

Generally speaking, the effective coefficients increase, when Θ decreases and Φ increases. The maximum value of d_{eff} (I) is 243 pm/V for

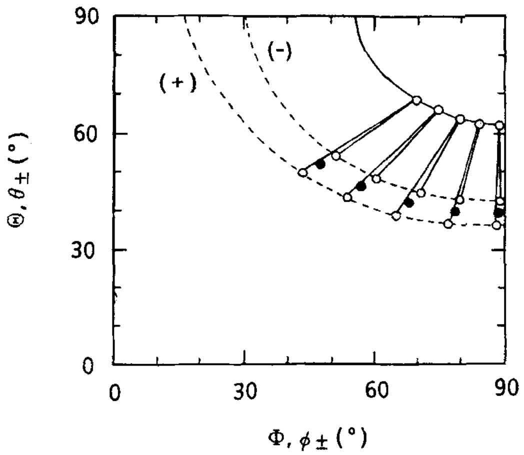

FIGURE 5 Phase-matching directions ($\theta\pm$, $\phi\pm$) of two orthogonally polarized fundamental waves external to the crystal for internal phase-matching directions (Θ, Φ). The external and the internal directions are represented by the broken lines and the solid line, respectively. Several internal phase-matching directions and the corresponding external ones denoted by the open circles are connected by straight lines. The closed circles represent the experimental points.

the phase-matching direction (32°, 68°). The coefficients d_{16} (=-316 pm/V) mainly contributes itself to this value. On the other hand, the maximum value of d_{eff} (II) is 23 pm/V for the phase-matching direction (62°, 89°). This value is not so large in spite of the main contribution of the coefficient d_{26} (=266 pm/V), since other coefficients are concerned and the angle Θ is large.

It is noted that quite a large effective coefficient can be obtained from the DAD crystal in the case of type I SHG. To our knowledge, this is the largest phase-matchable coefficient that has ever been reported on organic nonlinear-optical crystals.

EXPERIMENTAL RESULTS OF TYPE II SHG

In the experiment of SHG, we could use only the as-grown crystal, whose typical size was $3\times0.5\times2$ mm^3. The plane usable for incidence of the fundamental wave was only the x-z plane. In this case, the fundamental wave cannot be made incident for the type I phase-matching. The external angles corresponding to the type I phase-matching as given in Fig.4, which represents the angles internal to the crystal, does not exist.

The type II SHG requires two orthogonally polarized fundamental waves, e_+^{ω} and e_-^{ω}, whose incidence angles are different from each other because of the different refractive indices n_+^{ω} and n_-^{ω}. For each combination of the internal angles Θ and Φ, the incidence angles characterized by $\theta\pm$ and $\phi\pm$ can be calculated according to Snell's law. The results are shown in Fig.5, where a solid line and two broken lines denote the

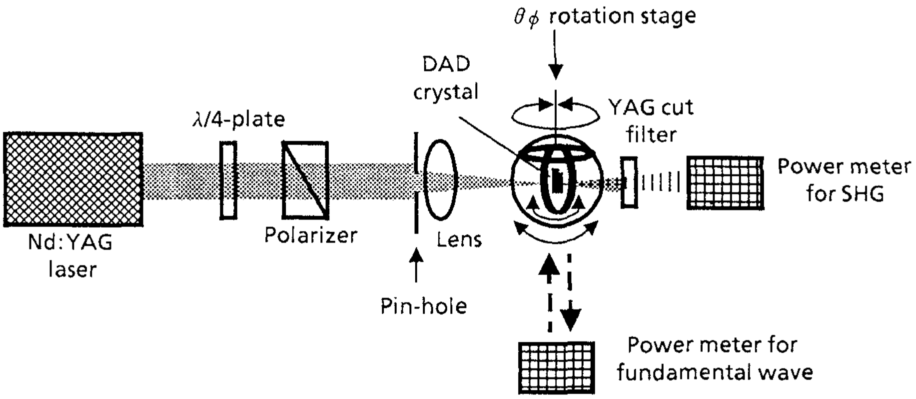

FIGURE 6 Experimental setup for type II SHG.

internal (Θ, Φ) and the external ($\theta\pm$, $\phi\pm$), respectively. The difference of the incidence angles decreases with an increase of $\phi\pm$ and a decrease of $\theta\pm$. In the range of ϕ over 50 degrees, it is around 4 degrees.

The experimental setup is shown in Fig.6. The two differently directed fundamental beams were made by using an appropriate lens for a fundamental laser beam. Since the experiment was made in the above range of $\phi\pm$, the focal length of the lens was selected to be 20 mm for a fundamental beam diameter of 1 mm, which yielded the angular aperture of 3.8 degrees. A quarter-wave plate and a polarizer for a linearly polarized laser was used to adjust the polarization or divide the polarization equally into $\mathbf{e}_\pm{}^\omega$ for the maximum second-harmonic (SH) power. This means that $\mathbf{e}_\pm{}^\omega$ in Eq.(8b) should be multiplied approximately by $1/\sqrt{2}$, although the directions of the fundamental electric fields, $\mathbf{e}_+{}^\omega$ and $\mathbf{e}_-{}^\omega$, are not perpendicular to each other in the crystal.

The effective coefficient $d_{eff}(\mathrm{II})$ was calculated from the measured fundamental power P_ω and the measured maximum SH power $(P_{2\omega})_{max}$ by

$$(P_{2\omega})_{max} = \frac{\omega^2}{2\,\varepsilon_0 c^3} \frac{d_{eff}(\mathrm{II})^2}{n_+^{2\omega}\, n_+^{\omega}\, n_-^{\omega}} \frac{P_\omega{}^2}{\pi\, W_0{}^2} L^2\, t_\omega{}^4\, T_{2\omega}\ , \qquad (9)$$

where ε_0 and c are the dielectric constant of vacuum and the velocity of light in vacuum, respectively, L is the effective thickness of the crystal, and t_ω and $T_{2\omega}$ denote the amplitude transmission factor of the fundamental wave and the energy transmission factor of the SH wave, respectively. The diameter $2W_0$ of the fundamental Gaussian beam waist at the focal point was estimated to be 24μm.

Table 2 lists the experimental values $d_{eff}{}^{exp.}$ and the theoretical values $d_{eff}{}^{theo.}$ at several phase-matching directions together with the measured fundamental and the SH power. The observed phase-matching directions (θ, ϕ), which are represented by the closed circles in Fig.5, were between (θ_+, ϕ_+) and (θ_-, ϕ_-).

TABLE 2 Measured and theoretical values $d_{eff}^{exp.}$ and $d_{eff}^{theo.}$ of type II effective nonlinear-optical coefficients for phase-matching directions (Θ, Φ).

(Θ,Φ) (°,°)	(θ_+, ϕ_+) (θ_-, ϕ_-) (°,°)	(θ, φ) (°,°)	P_ω (W)	$(P_{2\omega})_{max}$ (mW)	$d_{eff}^{exp.}$ (pm/V)	$d_{eff}^{theo.}$ (pm/V)
(62,89)	(36,87) (44,88)	(39, 88)	6.5	2.25	21.1	22.9
(63,85)	(37,77) (45,80)	(41, 79)	6.6	1.67	18.9	20.9
(64,80)	(40,65) (47,70)	(43, 68)	6.7	1.25	17.6	19.0
(66,75)	(45,54) (51,61)	(48, 58)	6.7	0.46	10.6	14.8
(69,70)	(50,44) (55,53)	(54, 49)	6.7	0.23	6.7	9.1

External phase-matching directions ($\theta_\pm$, $\phi_\pm$) and (θ, φ) are explained in the text.

As seen from Table 2, the experimental results are in good coincidence with the theoretical ones, although the two independent fundamental beams with orthogonal polarizations were not used. The somewhat smaller experimental values are attributed to the use of the lens, which cannot provide the completely phase-matchable fundamental beams.

CONCLUSION

We have theoretically demonstrated that the DAD crystal of space group P1 possesses the large effective nonlinear-optical coefficients and have confirmed it by the experiment of the type II SHG using the as-grown crystal. If we succeeded in growing the crystal in the direction of the dielectric y-axis, we could use the x-y or y-z plane and could confirm the extremely large value 243 pm/V of d_{eff} (I), which can generate the SH power of 0.4 mW for L = 10 mm and $W_0 = 50$ μm from the fundamental power of only 10 mW. There, waveguides and cavities to enhance the fundamental intensity are not necessary for practical uses.

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