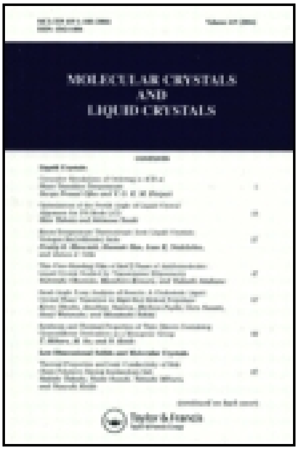

Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals

Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl19

Organic Crystals for Nonlinear Optics and Devices

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To cite this article: A. Yokoo, T. Kaino & I. Yokohama (1998): Organic Crystals for Nonlinear Optics and Devices, Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals, 316:1, 7-14

To link to this article: http://dx.doi.org/10.1080/10587259808044448

Mol. Cryst. Liq. Cryst., 1998, Vol. 316, pp. 7–14
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Organic Crystals for Nonlinear Optics and Devices

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Abstract: We have devised an indirect laser-heated pedestal growth method to obtain organic nonlinear optical (NLO) devices with high wavelength conversion efficiency through the second-order NLO effect of materials. Using the method, the growth direction of organic NLO crystal can be controlled and a long interaction length in the phase-matched direction is attained. As an organic NLO crystal, 2-adamanthylamino-5-nitropyridine (AANP) has been grown and its optical properties are characterized. The results show that Type II angle-tuned phase-matched wavelength conversion is possible in the wavelength region from 1.2 to 1.7 μm. To reduce the absorption of the AANP crystal in the 1.55 μm wavelength region, we have fabricated deuterated derivartives of AANP and succeeded in increasing the wavelength conversion efficiency.

Keywords: nonlinear optics, wavelength conversion, organic crystal, crystal growth, deuterated derivartive

INTRODUCTION

Large-capacity optical communications systems based on time division multiplexing or wavelength division multiplexing require wavelength-conversion devices to evaluate ultra-short pulses and to obtain wavelength tunable coherent light sources. Semiconductor devices, such as a wavelength-conversion laser diodes, have a relatively slow response and a low repetition rate because their effect depends on the excitation of carriers. On the other hand, devices which use nonresonant nonlinear optical (NLO) effects have a fast response and large repetition rate because they don't need carrier excitation. In particular, the second-order NLO effect is thought to result in larger efficiency and devices using this effect are expected to be applied in the wavelength region of their systems.

A high wavelength-conversion efficiency can only be obtained if the materials have a large effective d-coefficient, phase-matching ability and sufficient interaction length in the phase-matched direction. Various inorganic NLO crystals, such as $LiNbO_3$ (LN) [1], $KTiOPO_4$ (KTP) [2] and β-BaB_2O_4 (BBO) [3], have been used in actual optical systems, but all of these crystals have relatively small effective d-coefficients of less than 20 pm/V.

Organic NLO crystals with π-electron conjugation, on the otherr hand, have the potential for large d-coefficients. Several such crystals, i.e., 2-(N,N-dimethylamino)-5-nitroacetanilide (DAN) [4], 3,5-dimethyl-1-(4-nitrophenyl) pyrazole (DMNP) [5], N-(4-nitrophenyl)-L-prolinol (NPP) [6], and 2-adamantylamino-5-nitropyridine (AANP) [7] have been reported. However, few satisfy the necessary requirements for practical use.

To develop NLO devices for optical communications systems, we chose AANP, which has a d-coefficient of 80 pm/V and provide second harmonic generation (SHG) in the wavelength region of optical communications systems. AANP crystal for SHG at a wavelength of 1.32 μm obtained by the Bridgman-Stockbarger method has a length of 2.2 mm at most in the phase-matched direction because it is easily cleaved. This is a little bit short for actual applications. In addition, its optical properties, such as its absorption spectrum and phase-matching direction, have not been sufficiently evaluated.

In this paper, we describe the linear and nonlinear optical properties of AANP crystal and show that its wavelength conversion efficiency can be improved by using a deuterated derivartive of AANP.

CRYSTAL GROWTH METHOD

To grow organic crystals with a controlled crystal growth direction, i.e., the phase-matched direction, we have devised an indirect laser-heated pedestal growth (ILHPG) method [8]. Fig. 1 shows the ILHPG method. A source rod and a seed crystal are inserted into a glass tube from opposite sides of the tube. In this crucible-less approach, a CO_2 laser beam is focused on the glass tube circularly with 360° axially symmetric irradiance. Heat is emitted from the surface of the glass tube and the tip of the rod is melted by it. An oriented seed crystal is dipped into the molten zone, and then the crystal with the same orientation with that of seed crystal is grown by pulling the seed crystal away from the molten zone while simultaneously feeding the source rod into it. We used this method to grow AANP single crystal that is long enough in the phase-matched direction. The chemical structure of AANP is shown in Fig. 2 along with that of a partially deuterated one, which is discussed later. AANP crystals belong to the orthorhombic system with space group $Pna2_1$ and point group mm2. The cleaved planes was found to be (010) plane, i.e., an ac plane. The melting point of AANP is 167 °C. Rod-like single crystals can be obtained in any orientation with this method. The ILHPG method was also used to grow the deuterated derivative of AANP.

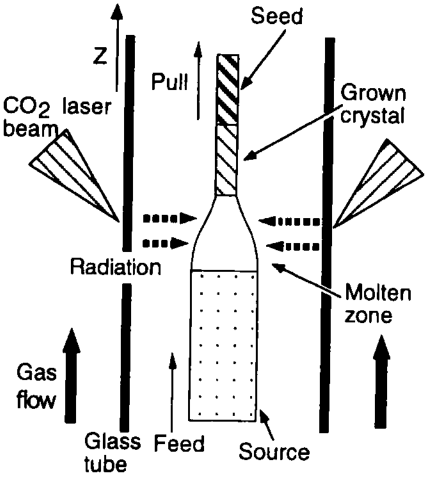

FIGURE 1 ILHPG method

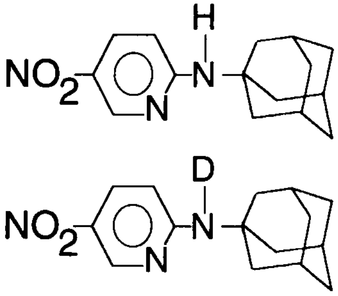

FIGURE 2 Chemical structure of AANP (top) and AANP-amnD (bottom)

OPTICAL PROPERTIES AND APPLICATION OF AANP CRYSTAL

To apply a NLO crystal in actual devices, it is important to clarify the crystal's optical properties, such as its absorption spectrum and phase-matching orientation. The optical absorption spectrum of AANP crystal was measured

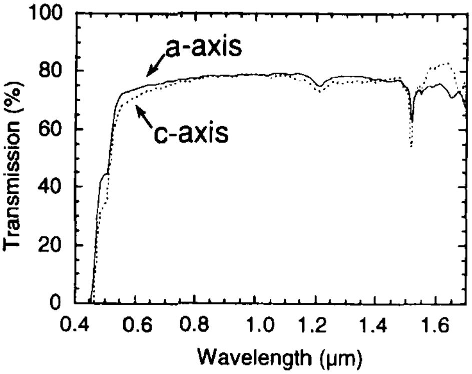

FIGURE 3 Transmission spectrum of AANP

using a 0.4-mm-thick cleaved plate of AANP along the ac plane [9]. Fig. 3 shows the transmission spectra with light polarizations parallel to the a-axis and c-axis. The upper limit of the transmission was below 80 % because of Fresnel reflection and scattering loss in the crystal. The large absorption in the wavelength region below 0.55 μm is due to the π-π* transition. There are small absorption peaks at 1.21 and 1.52 μm. They are thought to arise from the overtone and combination absorption of IR stretching vibrations in the molecule. Dichroism between the absorption along the c-axis and a-axis was observed. These differences reflect the anisotropy of the arrangement of molecules in the crystal. Near-IR absorption with a peak at 1.52 μm may influence the wavelength conversion in the wavelength region around 1.55 μm. However, the crystal is transparent in the wavelength region around 1.32 μm and from 0.6 to 1.1 μm. These regions include the wavelengths for optical communications systems and the wavelengths of second-harmonic and sum-frequency light generated from light in the optical communications wavelength region. We will discuss how to reduce the near-IR absorption later.

The possibility of Type II phase-matched SHG with a large effective d-coefficient in the fundamental wavelength region from 1.2 to 1.7 μm was revealed by numerical analysis using Sellmeier equation. Type II phase-matching was experimentally confirmed and the result is in good agreement with theoretical data [9]. SHG output intensities from AANP were compared with the conventional inorganic crystal BBO at the fundamental wavelengths of 1.32 and 1.55 μm [10]. The BBO crystal was 5-mm long and was oriented along the Type I phase-matching direction for both fundamental wavelengths. Nearly conforcal focuses were achieved. Table 1 summarizes the results of the comparison. For both fundamental wavelengths, AANP has much higher conversion efficiencies than BBO. However, the efficiency ratio at 1.55 μm is lower than that at 1.32 μm. This is because the fundamental light is attenuated in the crystal because of absorption around 1.55 μm. In spite of this disadvantage, AANP shows higher SHG efficiency than BBO. These results mean that AANP is more suitable than conventional inorganic crystals for SHG or sum-frequency generation (SFG) in the wavelength region from 1.3 to 1.6 μm.

TABLE 1 SHG efficiency of AANP

Fundamental wavelength	crystal direction		crystal length (mm)	Normarized SHG efficiency (/W)	η_{AANP}/η_{BBO}
	θ (°)	ϕ (°)			
1.32 μm	90	60	4.5	2.1×10^{-3}	72
1.55 μm	60	90	1.8	0.27×10^{-3}	6.7

TABLE 2 Crystal characteristics of AANP-amnD and AANP

	AANP-amnD	AANP
Point group	mm2	mm2
Space group	$Pna2_1$	$Pna2_1$
a	7.989	7.990
b	26.372	26.316
c	6.588	6.594
α	90	90
β	90	90
γ	90	90

As an actual devise application of AANP crystal, it was used in an optical sampling measurement system. Optical sampling measurement systems require Type II phase-matched SFG crystal for the evaluation of sub-picosecond optical pulses with wavelengths in the region of optical communications systems. Optical sampling measurements of 100Gbit/s optical signal using the AANP crystal and conventional KTP crystal revealed that the signal to noise ratio of the measured waveform is improved by the AANP crystal [11]. As far as we know, this is first example of the actual application of organic nonlinear optical crystal.

IMPROVEMENT OF WAVELENGTH CONVERSION EFFICIENCY USING A DEUTERATED DERIVARTIVE OF AANP

The SHG efficiency of the AANP crystal at 1.55 μm is lower than expected, as mentioned above. We think that absorption in the fundamental wavelength region of AANP influences the SHG efficiency. As shown in Fig. 3, there is absorption in the wavelength region from 1.47 to 1.59 μm with the peak at 1.52

μm. This absorption limits the effective interaction length to below 2 mm for SHG at 1.55 μm. To increase the SHG efficiency at 1.55 μm, the absorption in the wavelength region should be decreased. The absorption is thought to arise from the overtone and combination absorption of stretching vibrations in the molecule. The deuteration of AANP may cause a shift in the absorption wavelength. We found that deuteration of the amino part of AANP reduces the absorption[12]. The chemical structure of the amino-deuterated AANP (AANP-amnD) is shown in Fig. 2. Table 2 compares the crystal characteristics of the two types. The transmission spectrum of AANP-amnD crystal is compared with that of AANP crystal in Fig. 4, where the scattering loss in the crystals is omitted to clarify the effect of deuteration. Absorption loss caused by intra-molecular stretching vibrations at 1.55 μm is 0.1 dB/mm for the AANP-amnD, whereas it is 1.0 dB/mm for the AANP. The small absorption peak at 1.52 μm means that AANP still remains in the AANP-amnD used here. Angle-tuned phase-matching SHG measurements show that the phase matching conditions of AANP-amnD are almost the same as those of AANP. Using the ILHPG method, the rod-like AANP-amnD crystal shown in Fig. 5 was grown in the phase-matching direction for SHG at 1.55 μm.

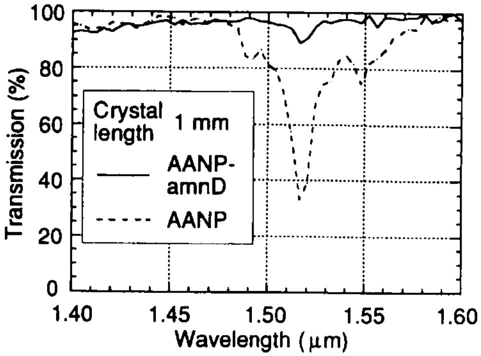

FIGURE 4 Transmission spectrum of AANP-amnD and AANP

To evaluate the performance of the AANP-amnD crystal, SHG efficiency of 3.5-mm-long AANP-amnD was compared with that of 1.8-mm-long AANP. The SHG efficiencies of

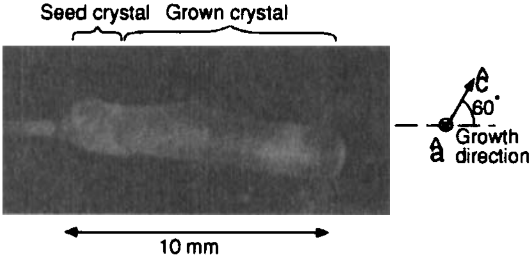

FIGURE 5 ILHPG-grown AANP-amnD crystal

TABLE 3 SHG efficiency of AANP-amnD and AANP

	Absorption loss (dB/mm)	Crystal length (mm)	Normarized SHG efficiency (/W)
AANP-amnD	0.1	3.5	0.45×10^{-3}
AANP	1.0	1.8	0.27×10^{-3}
		4.2	0.18×10^{-3}

the crystals are shown in Table 3. We found that the efficiency of AANP crystal is almost the same for lengths of 4.2 and 1.8 mm. That means that the effective interaction length is limited to about 2 mm at a fundamental wavelength of 1.55 μm. On the other hand, the AANP-amnD crystal shows 1.7 times higher SHG efficiency than the AANP crystal at 1.55 μm. Fig. 6 shows the dependence of the relative conversion efficiency on fundamental wavelength. AANP shows a strong dependence, and the efficiency is at its lowest point at 1.52 μm. This data is in good agreement with the absorption at wavelengths between 1.51 and 1.56 μm, which shows a peak at 1.52 μm. On the other hand, it's very clear that the conversion efficiency is better and the dependence on the fundamental wavelength is weaker for AANP-amnD.

We have confirmed that deuteration does not influence the $\chi^{(2)}$ of the material and that the reduction of absorption is effective in improving SHG efficiency and uniformity of SHG efficiency. These results demonstrate that AANP-amnD is a promising material for Type II angle-tuned phase-matched wavelength conversion with high efficiency in the optical communications wavelength region.

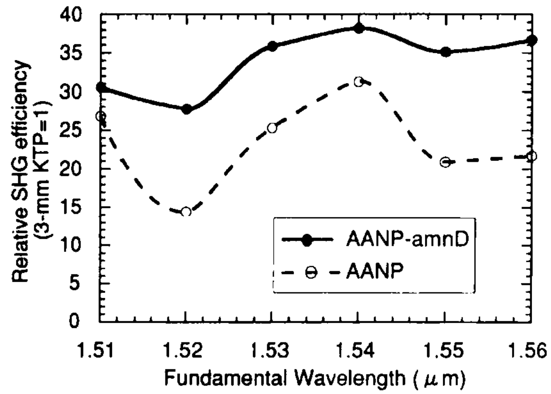

FIGURE 6 Fundamental wavelength dependency of SHG efficiency

CONCLUSIONS

The indirect laser-heated pedestal growth (ILHPG) method is an effective growth technique by which the growth direction of organic crystal can be controlled. We have successfully applied it to grow AANP crystal. The optical properties of AANP show that the Type II angle-tuned phase-matched wavelength conversion is possible in the wavelength region from 1.2 to 1.7 μm. In addition, reduction of absorption in the AANP crystal by using a deuterated derivartive of AANP increases the SHG efficiency at 1.55 μm.

Acknowledgements

The authors thank Drs. S. Tomaru, H. Takara, H. Itoh, Y. Matsuoka, and H. Iwamura for discussions and encouragement.

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