Organic nonlinear optical devices

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Indirect laser-heated pedestal growth (ILHPG) is used to produce a single crystal of organic nonlinear optical material that is long enough in the phase-matched direction for application to nonlinear optical devices. Single crystals of 2-adamanthylamino-5-nitropyridine (AANP) with length of more than 20 mm and diameters ranging from 300 μm to 2 mm have been grown. The efficiencies of second harmonic and optical parametric generation are compared with those of inorganic crystals. The results show that organic crystals can be used for a practical wavelength converter.

1. INTRODUCTION

In making second-order nonlinear optical devices that exhibit second-harmonic and optical parametric effects, it is better to use organic nonlinear optical materials with a π-electron conjugation than inorganic materials such as $LiNbO_3$. This is because organic materials have a higher nonlinear susceptibility ($\chi^{(2)}$) and a higher laser damage threshold than inorganic materials. However, only a few of the organic materials have been crystallized in reasonable crystal size suitable for possible applications to wavelength conversion devices, though a long interaction length in the phase-matched direction is required to obtain high wavelength conversion efficiency.

Three growth methods for organic crystals, that is, the solution method, the Bridgman-Stockbarger method and the capillary method, have mainly been researched. The solution growth method is used for materials like N-(4-nitrophenyl)-(L)-prolinol (NPP) and 3-methyl-4-nitro-pyridine-1-oxide (POM) [1,2]. It is usually the basic method to be tried because it is very simple and there are no problems with thermal decomposition. The relatively low growth rate of the method makes it difficult to grow large crystals, and the formation of solvent inclusions can degrade the optical quality. The Bridgman-Stockbarger method is a familiar bulk-crystal-growth method. AANP and 4-nitro-4'-methyl-benzilidene aniline (NMBA) have been crystallized by this method [3,4]. However, a disadvantage is that the contact with the growth container induce mechanical stress in the crystal. Capillary growth is used for 2-acetamido-4-nitro-N:N-dimetyl aniline (DAN) and 3,5-dimetyl-1-(4-nitrophenyl) pyrazole (DMNP), which are employed in Cherenkov-type phase-matched second harmonic generation (SHG) devices [5,6]. The advantage of this method is that small core size is achievable, and hence high power density can be obtained for device application. Unfortunately, it is applicable to very few kinds of material.

The biggest problem common to all the above methods is that there is no way to control the crystal growth direction. To attain high efficiency of wavelength conversion, nonlinear optical crystals have to be long enough in the phase-matched direction. Therefore, a growth method for organic nonlinear optical crystals with a long size in a phase-matched direction has been strongly required.

This paper reports a crystal growth technique that produces a phase-matched organic crystal with highly efficient optical nonlinearity and describes the features of wavelength converters formed from the grown crystal.

2. FABRICATION METHOD

Fig. 1 shows a schematic of the ILHPG method and a side view photograph of the molten zone of the crystal growth in progress [7]. Extra features of the ILHPG method are a glass tube and the use of gas flow. The source rod and seed crystal are inserted into the glass tube from opposite sides of the tube. CO_2 laser beam is focused on the glass tube circularly in an axially symmetric irradiance. The laser beam is absorbed by

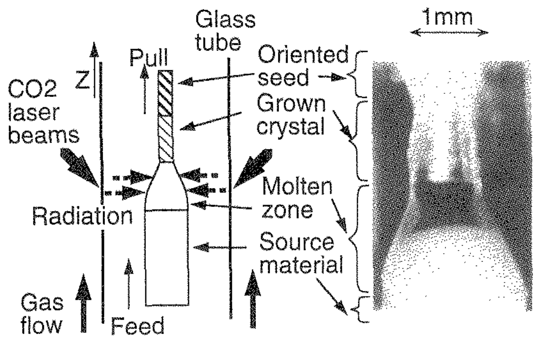


Fig. 1 Schematic of the ILHPG method (left) and side view of the molten zone (right)

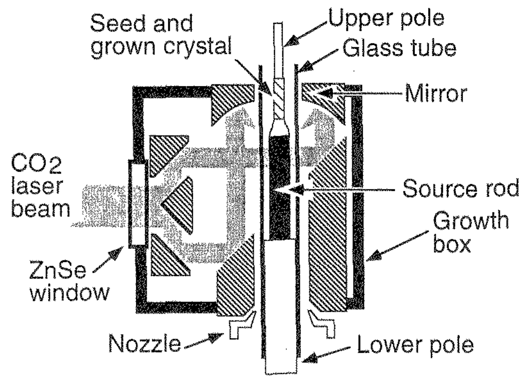


Fig. 2 ILHPG growth apparatus

the glass tube for a time and heat radiation is emitted from the surface of the glass tube. As a result, direct and localized heating of the source rod is avoided. The tip of the rod is melted by the radiation from the glass tube, and then, a molten zone is formed by dipping the oriented seed crystal. Then the crystal is grown by pulling it out of the melt while simultaneously feeding the source rod into the molten zone.

The shape of molten zone is maintained by a balance between the effects of gravity and the surface tension which depends on the viscosity of the melt. It is important to keep the molten zone at an optimum size to stabilize crystal growth. Otherwise, the balance between gravity and surface tension is destroyed by excessive broadening of the molten zone, and the zone is broken down. So, not only the temperature, but also the size of the molten zone should be controlled. It is difficult to maintain the molten zone only by adjusting the laser power, because rising the laser power broaden the heated part of the glass tube due to thermal conductivity. Thus we added a gas flow around the tube to suppress the excessive broadening of heated zone. Then broadening of the molten zone is prevented.

The growth apparatus is shown in Fig. 2. The focusing optics are in the growth box with holes at the top and bottom. The seed crystal and the source rod are attached to the tips of the poles. Their position can be adjusted, and they can also be moved up or down. The 3 mm-diameter glass tube is attached to the lower pole. The laser beam is passed through a ZnSe window and focused on the glass tube by the optics. Fluctuation of the laser beam power is less than 2 %. Helium gas is introduced into the growth box from the lower hole using nozzles and ejected from upper hole to make the gas flow around the glass tube. An example of the temperature gradient is shown in Fig. 3. The main effect of the gas flow is to narrow the heated zone. Therefore, the temperature gradient and maximum temperature in the tube are optimized by controlling the power of the laser beam and gas flow so as to maintain the molten zone at an optimum size.

The advantages of the ILHPG method for organic crystal are as follows: (1) Large growth rate: Growth rates as high as 5 mm/hr are attainable. (2) No stress from the growth container. (3) No solvent inclusions. (4) Precise temperature and temperature gradient control over wide range. (5) Short period in molten form: The temperature of the compound is above the melting point for only about 10 minutes. (6) Any crystal growth direction.

Therefore, crystals can be easily grown long enough in the phase-matched direction, which is the biggest advantage of the ILHPG method.

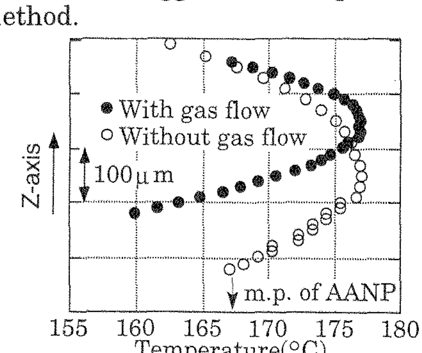
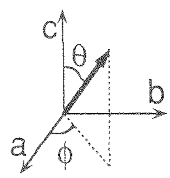


Fig. 3 Temperature gradient in the glass tube. Z-axis is shown in Fig. 1

Table 1 Correspondence between crystal growth direction and crystallographic axes

Crystal No.	θ (°)	φ (°)	
1	90	0	Cut from Bridgman bulk
2	90	20	
3	90	40	
4	90	60	SHG at 1.32 μm
5	0	90	Cut from Bridgman bulk
6	20	90	
7	40	90	
8	60	90	SHG at 1.55 μm



3. CRYSTAL GROWTH OF AANP

We chose 2-adamantylamino-5-nitropyridine (AANP) for this study. Optical properties of AANP crystal were determined using a single crystal obtained by the Bridgman-Stockbarger method. It has been reported to have a large second-order optical nonlinearity of d_{31}=80 pm/V and the possibility of angle-tuned phase-matched SHG in the wavelength region between 1.06 and 1.55 μm [3]. The melting point of AANP is 167 °C. AANP crystals belong to the orthorhombic system with space group $Pna2_1$ and point group mm2. The cleaved plane was found to be a (010) plane, that is, an ac plane.

These crystals are easily cleaved and have to be polished to obtain the correct orientation, so the final length in the phase-matched direction is too small for nonlinear optical devices. For example, the AANP crystal for SHG at a wavelength of 1.32 μm we obtained by the Bridgman-Stockbarger method has orientation of 60° from the ac plane and length of 2.2 mm at the most in the phase-matched direction. The length is a little bit short for actual applications.

To fabricate an AANP single crystal long enough in a phase-matched direction, we have applied the ILHPG method. Table 1 shows the crystal growth direction of crystals we grew. No. 4 (θ=90°, φ=60°) corresponds to the crystal direction of the phase-matched angle for SHG from 1.32 μm. As mentioned above, a Bridgman bulk crystal easily grows along the c-axis (θ=0°). The crystal cleaves naturally along the a-c plane, so the length in the b direction is very small. That is, it is almost impossible to get a seed crystal with sufficient length in the phase-matched direction. So to obtain crystal No. 4, we had to grow a series of crystals starting from No. 1, then No.2 and No.3 each with a different direction, until we obtain the crystal No. 4. We grew the series of crystals from No. 5 to No. 8 in the same way. Rod-like single crystals were obtained in any orientations. Fig. 4 shows a photograph of a grown crystal. The dimensions depend on the diameter and length of the source rod and the reduction ratio. The diameter typically ranges from 300 μm to 2 mm, and the length can be over 20 mm. In a stable grown region, fluctuation of the diameter is within 5 %. The side view and cross section of the crystal is observed with crossed polarizing microscope. The stable grown crystal shows uniform extinction in the side view and cross section throughout its length. The orientation and characteristics of the crystal are identified with a Buerger-precession camera. It was confirmed that the orientation of the seed crystal and that of the grown crystal are the same throughout its length. These results mean that crystal grown by the ILHPG method keeps the orientation of the seed crystal and it is a single crystal.

4. NONLINEAR OPTICAL CHARACTERISTICS OF THE GROWN CRYSTALS

The performance of the grown crystals was evaluated in terms of SHG efficiency at fundamental wavelengths of 1.55 and 1.32 μm. AANP crystal shows type II phase-matched SHG with the fundamental wavelengths. SH intensity was compared

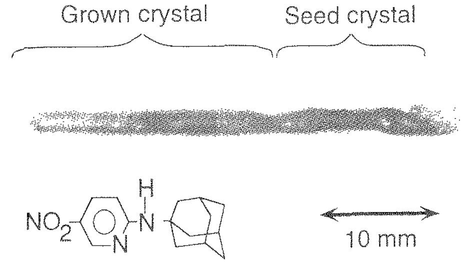


Fig. 4 ILHPG grown AANP crystal

Table 2 SH intensity ratio for AANP vs. BBO

Fundamental wavelength	crystal direction		crystal length (mm)	SH (AANP) / SH (BBO*)
	θ(°)	φ(°)		
1.32 μm	90	60	4.5	72
1.55 μm	60	90	1.8	6.7

* Length of the BBO crystal is 5 mm

with 5-mm-long beta-barium borate (BBO) crystal oriented along the type I phase-matched direction for each fundamental wavelengths. The ratios of the SH intensity of the AANP crystals to that of the BBO crystal are shown in Table 2. In both cases, AANP crystals show higher conversion efficiencies. However, SH intensity at 1.55 mm is much lower than expected. We think that absorption in the fundamental wavelength region of AANP influences the SHG efficiency.

We observed optical parametric generation (OPG) using a 2.5-mm-long AANP crystal oriented at θ=90° and φ=62°. The crystal was rotated around the c-axis to change the wavelength of the signal and idler beam. Pump-beam wavelength was 0.61 μm, peak power was 5 MW, duration was 0.2 ps and polarized perpendicular to the c-axis. The crystal configuration and the output wavelength dependence on crystal rotation are shown in Fig. 5. A signal beam from 1.63 to 1.42 μm and an idler beam from 0.98 to 1.06 μm were obtained. The polarization of signal and idler beam was perpendicular and parallel to the c-axis respectively, which indicates the type II phase-matching.

Output intensity of the AANP crystal is compared with a potassium titanyl phosphate (KTP) crystal in Fig. 6. The output intensity of the 2.5-mm-long AANP crystal is 10 times higher than that of a 5-mm-long KTP crystal pumped at 0.61 μm.

5. CONCLUSIONS

Using the ILHPG method, long rod-like single crystals of organic material in any orientation have been successfully fabricated.

ILHPG makes it possible to grow long rod-like AANP crystals with phase-matched direction and higher wavelength conversion efficiency is expected. We confirmed second harmonic and optical parametric generation using ILHPG-grown AANP crystals. AANP crystals show higher efficiency than conventional inorganic ones. These results show that the practical application of organic AANP crystals is possible.

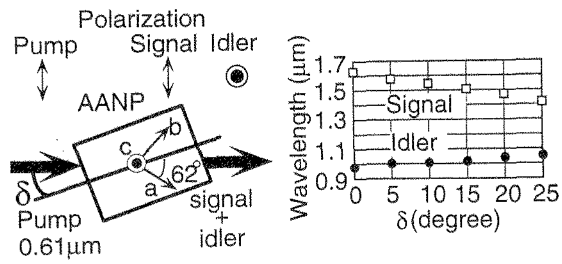


Fig. 5 OPG crystal configuration (left) and wavelength dependence on crystal rotation (right)

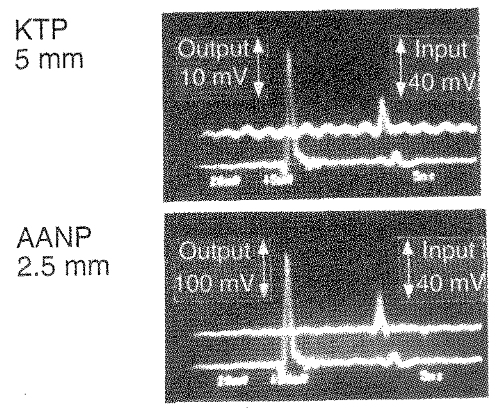


Fig. 6 OPG intensity of AANP and KTP

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