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GROWTH OF ORGANIC CRYSTAL THIN FILM BY A NEW METHOD—RECTANGULAR HEATER HEATED PEDESTAL GROWTH METHOD

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In the present investigation, to make a phase matched crystal for any wavelength, we report the growth of thin film of 2-adamantylamino-5-nitropyridine (AANP) from molten state by a new and simple technique namely rectangular heater heated pedestal growth method. Using this method crystal thin film has been grown along a, b, c-directions and along the phase matching direction at 1.55 μm *wavelength (60° from c-axis towards b-axis). Temperature profile of the growth cell has been studied to confirm its stability. X-ray diffraction studies confirmed the direction in which the film has been grown. Second harmonic light from 1.55* μm *laser was clearly detected just in plane of the crystal grown towards the phase matched angle of the wavelength.*

Keywords: phase matched crystal; rectangular heater heated pedestal growth; temperature profile; x-ray diffraction

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INTRODUCTION

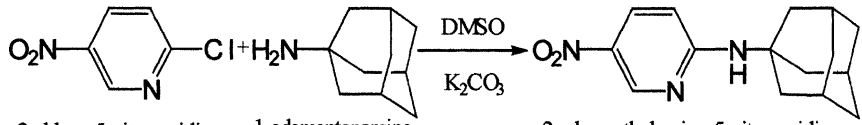
Organic nonlinear optical (NLO) materials have been the subject of very intensive studies in the recent days because of their high potential applicability owing to their large nonlinearity. Among the recently discovered organic NLO materials 2-admantylamino-5-nitlopyridine (AANP) is reported to have good NLO properties [1–6]. AANP has emerged as an attractive organic NLO crystal since it has a higher wavelength conversion efficiency than the conventional inorganic NLO crystals. It belongs to orthorhombic system with space group $Pna2_1$ and point group mm2 [1]. Melting point of AANP is about 167°C. The transparency range extends from 500 to 1600 nm and it has an absorption coefficient of 8%/mm at 1.55 μm [2]. It has a large second-order optical nonlinearity of $d_{31} = 80$pm/V and a large second harmonic efficiency, 30 times than that of potassium titanyl phosphate (KTP) at 1.55 μm wavelength [3]. Angle-tuned phase matched second harmonic generation (SHG) in the wavelength region between 1.06 and 1.55 μm is possible with AANP. It is suitable for optical sampling as a sum frequency generation (SFG) crystal because the signal-to-noise ratio is very low because of small influence by SHG [4]. The cleavage plane is the (010) plane [3].

There are many reports on the growth of AANP single crystal from molten state [1–6]. However, there are no reports on the growth of thin film crystal of AANP along the phase matching direction. In the present investigation, we report the growth of thin film crystal of AANP from molten state by a novel technique namely rectangular heater heated pedestal growth (RHHPG) method. The main advantage of this method is that the thin film crystal can be grown along any desired direction. Using this method, for the first time thin film crystal of AANP has been grown along the three crystallographic directions, a, b, c directions and along the phase matching direction at 1.55 μm wavelength.

EXPERIMENT

Synthesis

AANP has been synthesised using 2-chloro-5-nitropyridine and 1-adamantanamine with potassium dicarbonate dissolved in dimethylsulphooxide according to the following chemical reaction:



2-chloro-5-nitropyridine 1-adamantanamine 2-adamanthylamino-5-nitropyridine

$+KCl + CO_2 + H_2O$

The synthesised salt is recrystallised twice by dissolving it in methanol followed by filtration under dry vacuum. Further purification is carried out by sublimation.

Crystal Growth

An attempt has been made to grow AANP thin film using the RHHPG method. The experimental set up is shown in Figure 1. In this method a rectangular heater was used to create a molten state. A nichrome wire of thickness, 0.15 mm was wound around a rectangular glass tube of dimension $6 \times 4 \times 12\,\text{mm}^3$ to fabricate a rectangular heater. The rectangular heater was inserted into a glass tube of 1 cm diameter. The length of the glass tube was such that the film passed through a gradient of temperature and did not directly come in contact with room temperature. AANP crystal powder, sandwiched between two thin glass plates formed the source. The source and the seed crystal were inserted into the rectangular heater from opposite sides of the tube. The tip of the glass plate was melted by the radiation from the rectangular heater and then a molten zone was formed by bringing the seed crystal in contact with the tip of the glass plate. Then

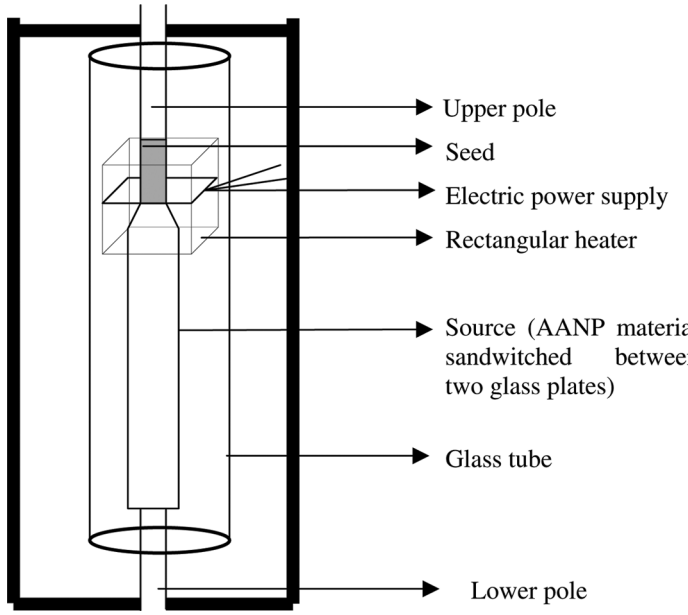


FIGURE 1 Experimental set up for RRHHPG method.

the thin film crystal was grown by pulling it at a rate of 2.3 mm/hr out of the melt while simultaneously feeding the source into the molten zone.

Advantages of using this method are that large growth rate can be attained. Crystal grown is free of stress from the growth container and solvent inclusions. Precise temperature control over a wide range can be obtained using this method. Moreover, the crystals can be grown in the desired direction.

Preparation of the Glass Plate and Surface Treatment

The glass plates for the source were prepared according to the steps shown in Figure 2. The surface of the glass plates played an important role in determining the quality of the thin film. To increase the quality of the

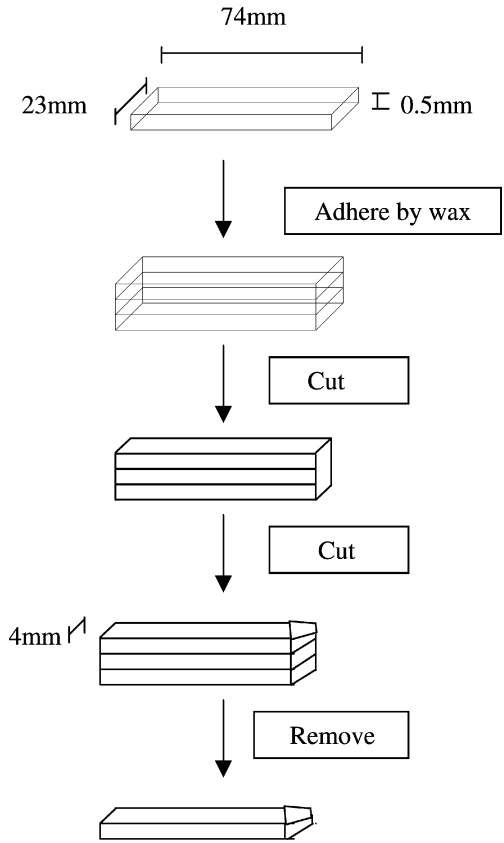


FIGURE 2 Preparation of glass plates.

surface of the glass plate, the glass plates were treated with 5 w% sodium hydroxide solution in an ultrasonic cleaner for 1 hour and then treated with 5 w% nitric acid solution in an ultrasonic cleaner for 1 hour and then washed in water. The glass plates were then treated with 3 w% timethylchlorosilane in chloroform at 80°C for about 2 hours to make them hydrophobic. This treatment improved the quality of the thin film grown.

X-Ray Diffraction Studies and Thickness Measurement

X-ray diffraction pattern have been recorded for the grown thin films of AANP using Mac Science, M18XHF22-SRA with CuKα ($\lambda = 1.54056$ Å) radiation. The sample was scanned over the range 5–35 degree at a rate of 5 degree/min. The thickness of the thin films have been measured using surface measuring method-DEKTAK^3 ULVAC model.

RESULTS AND DISCUSSION

The temperature stability of the rectangular heater with respect to time has been studied to be highly stable. Figure 3 shows the temperature profile of the sample inside the glass tube, pulled at the rate of 2.3 mm/hr. AANP thin film has been grown along a, b and c-directions, respectively. The grown

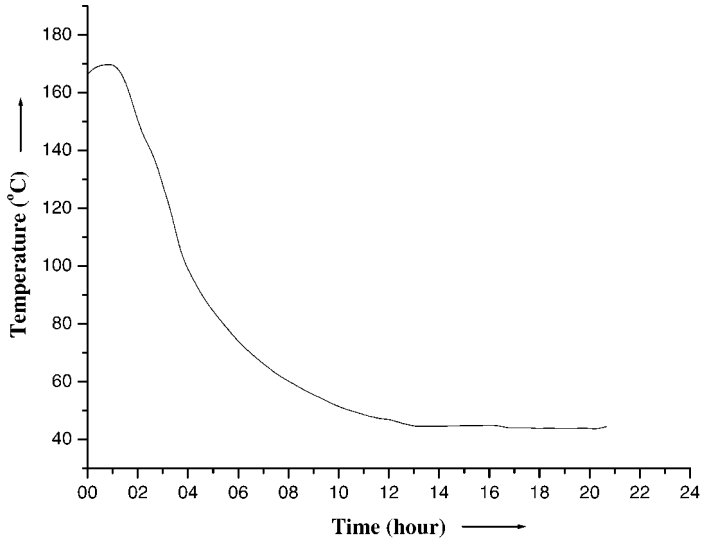


FIGURE 3 Temperature profile of the sample inside the glass tube, pulled at the rate of 2.3 mm/hr.

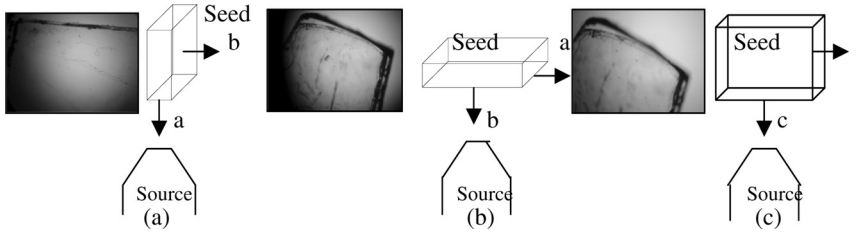


FIGURE 4 AANP thin film grown along (a) a, (b) b and (c) c-directions. Magnification 4X.

thin film along a, b and c-directions along with the schematic diagram of the growth of the AANP thin film along a, b and c-directions are shown in Figure 4 a, b and c respectively. Thin film grown along the phase matching direction at 1.55 μm wavelength is shown in Figure 5. To grow the crystal along the phase matching direction, the seed was mounted such that it made an angle of 60° from c-axis towards b-axis. The x-ray diffraction patterns of the thin film grown along a, b and c-directions are shown in Figure 6 a, b and c respectively. The tables inscribed in the Figure 6 a, b and c show the calculated and experimental d-spacing and their respective indices for the AANP thin films grown along a, b and c-directions, respectively. The experimental values were found to correspond well with the calculated d values. Table 1 shows the thickness of the AANP film grown along a, b, c directions and along the phase matching direction at 1.55 μm, respectively. All the thin film crystals had the thickness less than 14 μm. The SHG intensity as a function of the incident angle for the thin film grown along the phase matching direction has been measured at 1.55 μm wavelength as shown in Figure 7. The figure shows that the SHG intensity peak was observed very near to 0 degree. This depicts that the grown crystal was phase matchable at 1.55 μm wavelength.

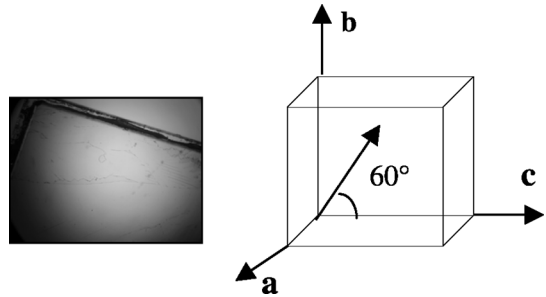


FIGURE 5 AANP thin film grown along the phase direction. Magnification 4X.

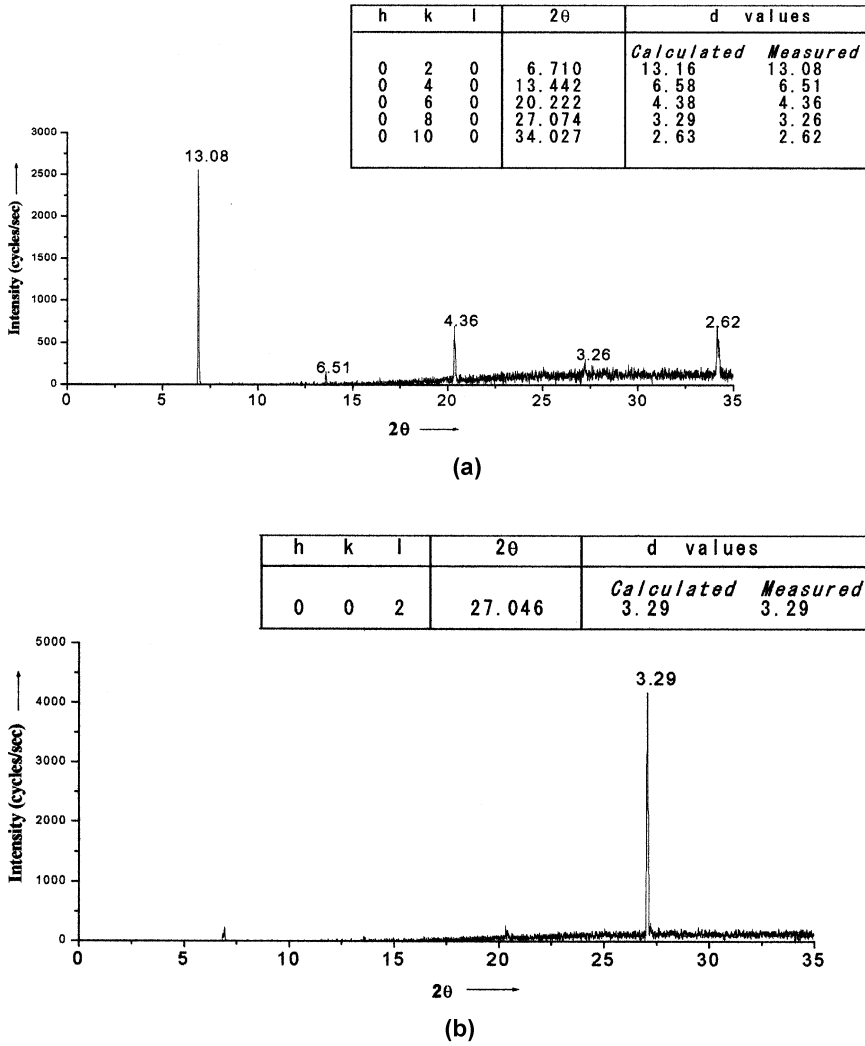


FIGURE 6 (a) X-ray diffraction pattern of AANP thin film grown along a-direction (b) X-ray diffraction pattern of AANP thin film grown along b-direction (c) X-ray diffraction pattern of AANP thin film grown along c-direction.

CONCLUSION

The RHHPG method we proposed is a good method for the growth of organic thin film crystals in a desired orientation. AANP material has been synthesized and a pulling rate of 2.3 mm/hr was employed for the growth of

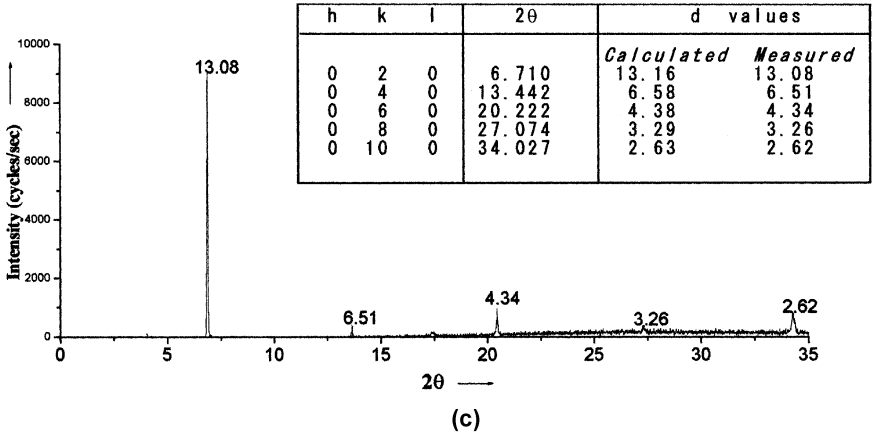


FIGURE 6 (Continued)

TABLE 1 Thickness of the Thin Films grown along a, b, c and Phase Matching Directions

Growth direction	a	b	c	Phase matching direction
Thickness (μm)	6.8	13.2	10.2	12.4

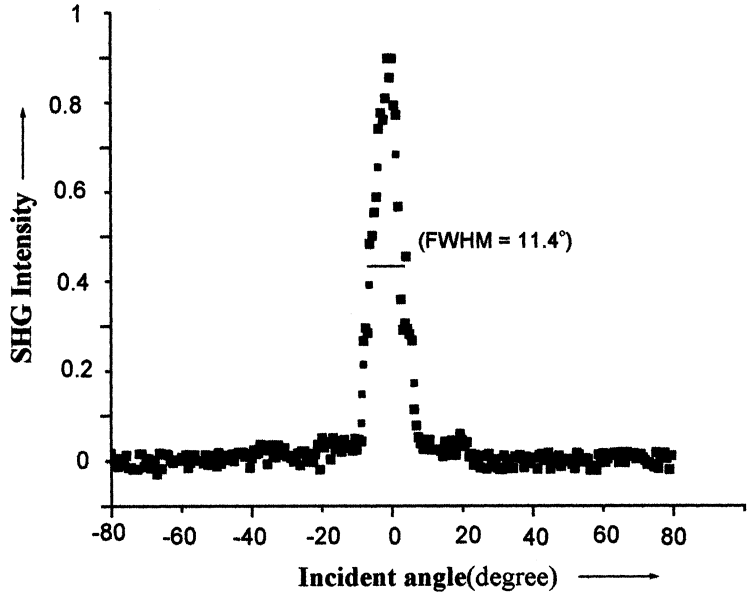


FIGURE 7 SHG intensity measured as a function of incident angle for the phase matched thin film crystal of AANP at 1.55 μm.

AANP thin film using RHHPG method. Thin film of AANP has been grown successfully along the a, b, c directions and phase matching direction at 1.55 μm wavelength using this method. The temperature stability inside the rectangular heater and the temperature profile of the sample inside the glass tube during the growth have been examined. The grown thin films have been characterized using X-ray diffraction studies to confirm the orientation of the grown crystal. The thickness of the grown thin films have been determined to be around $6 \sim 14$ μm. SHG intensity as a function of the incident angle has been measured for the phase matched crystal at 1.55 μm wavelength. Second harmonic light from 1.55 μm laser was clearly detected just in plane of the crystal grown towards the phase matched angle of the wavelength.

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