JOURNAL OF MATERIALS SCIENCE 27 (1992) 3200–3202

Crystal growth of bulk and cored fibre of 4-(*N,N*-dimethylamino)-3-acetamidonitrobenzene (DAN)

GONG-FAN HUANG*, MING-YI HWANG, J. T. LIN
Center for Research in Electro-Optics and Lasers (CREOL), University of Central Florida, 12424 Research Parkway, Orlando, FL 32826, USA

Large crystals of 4-(*N,N*-dimethylamino)-3-acetamidonitrobenzene (DAN) were grown from solutions by lowering the temperature; and bulk and cored fibre DAN crystals were grown by the Bridgman–Stockbarger (BS) method. The growth conditions and factors which affect the crystal quality were investigated.

1. Introduction

The crystals of 4-(*N,N*-dimethylamino)-3-acetamidonitrobenzene (DAN) exhibit a high nonlinear optical coefficient of $d_{23} = 50\ \mathrm{Pm\,V^{-1}}$ [1] with $d_{\mathrm{eff}} = 27\ \mathrm{Pm\,V^{-1}}$ [2]. The largest size previously reported of bulk DAN crystal was $15 \times 7 \times 2\ \mathrm{mm^3}$ (grown from solutions) [1] and the longest recorded cored fibre of DAN crystal was 20–30 mm [3]. We have grown single crystals of DAN from solutions with sizes of 26, 12 and 8 mm along the a, b and c axes, respectively (as shown in Fig. 1) and the crystalline portion of cored fibre was longer than 30 mm. Bulk and fibre crystals both exhibit good optical quality.

The chemical formula of DAN is $C_{10}H_{13}N_3O_3$. DAN crystals belong to the monoclinic system with space group $P2_1$ and unit-cell parameters of $a = 0.4785$ nm, $b = 1.3050$ nm, $c = 0.8733$ nm, $Z = 2$ and $\beta = 94.36°$ [4]. The melting point of the raw materials of DAN synthesized in this work was 166.4°C. The powder second harmonic generation (SHG) intensity was measured to be 500 times that of potassium dihydrogen phosphate (KDP). We also show the transmission of DAN in Fig. 2.

2. Experimental procedure and results

2.1. Growth from solutions

Solution growth by lowering temperature involves simple equipment and a temperature controller. However, finding suitable solvents is difficult. Through crystalline experiments, anhydrous acetic acid, butyl acetate and ethyl acetate were selected as solvents for crystal growth. The seeds were obtained by evaporating a saturated solution of anhydrous acetic acid. A small seed is a long five-sided column with the main axis along the *a* axis and with an inclined plane on the end. A seed used for crystal growth should have a small volume of about $3 \times 1.5 \times 1.0\ \mathrm{mm^3}$ with good macroperfection.

The solubility of DAN in anhydrous acetic acid was determined with a curve as shown in Fig. 3.

$$W = 0.34\ T - 6.05$$

where T (°C) is the temperature of the saturation point and W (g) is the weight of solute dissolved in a 100 g solvent. The oversaturation (or stable region) of this curve is about 2.2 °C. A seed of $4 \times 1.5 \times 1.5\ \mathrm{mm^3}$ was mounted in a glass stand and put into a 90-ml saturated solution of anhydrous acetic acid. The rotation of the crystal stand is reversible with a speed of 3 rotations $\mathrm{min^{-1}}$. The temperature of the growth solution was reduced from 38 to 25 °C in 3 months. The average rate of temperature reduction was 0.1 °C per day for the first 2 months and 0.2 °C per day in the last month. The as-grown crystal is shown in Fig. 2 with size of $26 \times 12 \times 8\ \mathrm{mm^3}$. The rate of growth in the directions of *a*, *b* and *c* axes are 0.30, 0.13 and 0.09 mm $\mathrm{day^{-1}}$, respectively. The DAN crystal was taken out directly from the solution without an annealling procedure. No cleaved phenomena occurred.

2.2. Growth by the Bridgman method

The growth rate of single-crystal DAN is enormously increased by the Bridgman–Stodebarger (BS) technique [5] which is particularly suitable for organic materials that have no decomposition reaction near the melting point. In our laboratory, we have succeeded in growing DAN single crystals of bulk (Fig. 4) and cored (Fig. 5) fibre. The rate of growth is 100 times greater than that in solutions.

The furnace consisted of three glass tubes. The high and low sections were separated by an insulator (2.5-cm thick) of aluminium oxide in order to obtain a sufficiently sharp axial temperature gradient of about 70 °C between the high and low surfaces of an insulator. The chamber of the furnace was the interior tube that was wound by resistance wire. The middle and external tubes were the thermal insulating layers. The

* *Present address*: *KAIFA Technology Inc., Santa Clara, CA* 95054, *USA*.

0022–2461

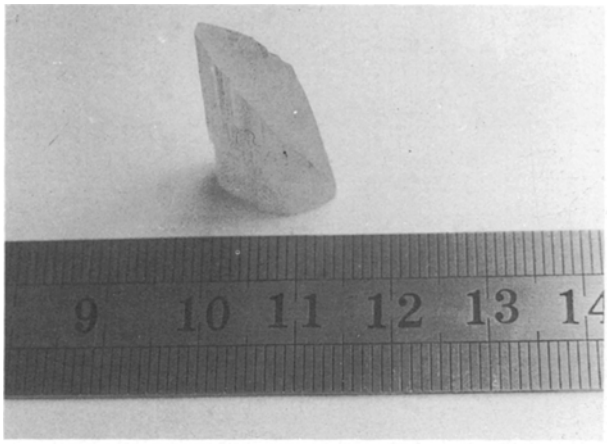

Figure 1 Bulk crystal of DAN grown from solution.

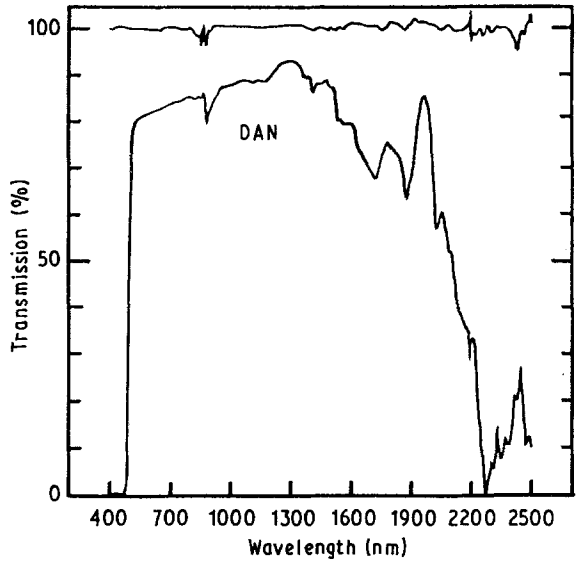

Figure 2 Transmission curve of DAN crystal.

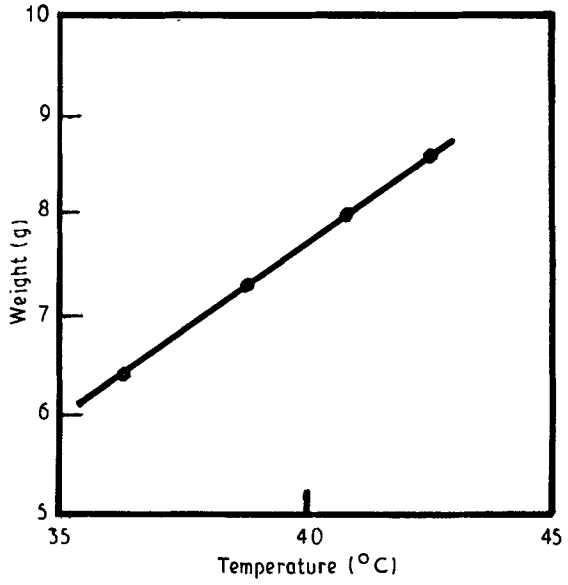

Figure 3 Solubility curve of DAN in anhydrous acetic acid.

diameters of the three tubes are 1.8, 3.0 and 9.5 cm, respectively. The furnace height was 60 cm. The power of the furnace for high and low sections was 60 W for use by both the BS and inverted Bridgman (IBS)

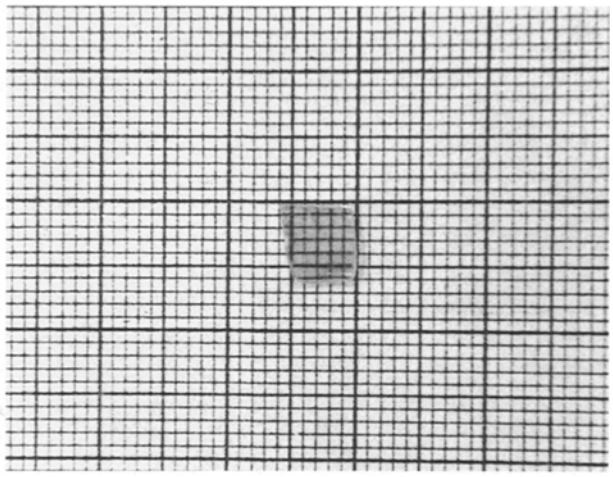

Figure 4 Bulk crystal of DAN grown by Bridgman method.

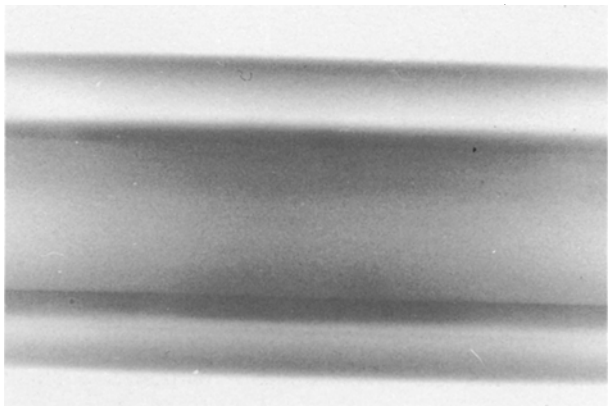

Figure 5 Amplified photo of the cored fibres of DAN crystal (magn × 170).

methods. The furnace was basically a sealed system to prevent thermal convection. Both high- and low-section temperatures were independently controlled to better than 0.1 °C. An ampoule was moved along the vertical direction by a minute motor with a yarn connector.

The crystal growth of DAN cored fibre was carried out by the IBS method. The quartz capillary cladding had an inner diameter of 150–200 μm. DAN filled the capillaries by means of capillary action. This procedure was performed in air where the DAN powder was put in a long, thin ampoule immersed in a bath of silicon oil. Before melting the DAN powder, the capillaries were suspended in the ampoule in order to preheat the capillaries and make it easier to fill. When the powder was completely melted the capillaries were inserted into the melt and the fill was finished in several seconds. The lengths of the filling substance were about 7–10 cm. In order to eliminate effects by radial temperature gradients, few or single cored fibres were mounted in an ampoule enclosed in the growth process. The vertical temperature gradient of the furnace was measured with no load. This can be used as a reference, although conditions are different when there is a load. The temperature gradient, from the position of the solid–liquid boundary to 1 cm away, was

32.6 °C, and the average gradient was 19.1 °C cm^{-1} within 3 cm from the boundary in the direction of growth. The height of the melt was controlled to be about 12 mm. Using a pull rate of 2–4 mm h^{-1}, we have successfully grown cored fibre of 30 mm length with good quality.

The bulk crystal of DAN was also grown by the BS method. DAN powder was filled in an ampoule and melted in an oil bath. As soon as the DAN solids were completely melted, the mouth of the ampoule was enclosed in order to reduce the air density and retain the chemical stability of DAN in the growth process. The temperature gradient (no load), from the solid–liquid boundary to 1 cm away, was 10.3 °C, and the average gradient was 23.3 °C cm^{-1} within 3 cm from the boundary along the growth direction. The height of the melt was controlled about 9 mm. The ampoule was lowered at a rate of 0.5–1 mm h^{-1}. Single crystals of DAN were grown with dimensions of 8 mm in diameter and 20 mm in length.

3. Discussion

We have observed that a gaseous bubble will cause a fault in cored fibres (Fig. 6). Zone melting by the BS procedure was found to be effective for removing bubbles and in this process a faster lowering rate was adopted. General spontaneous nucleation in the fibre was about 25 mm, which is the transition from polycrystal to monocrystalline. Since we adopt an effective step, only the 2–5 mm transition occurred. For the bulk crystal grown by the BS method, the small amount of decomposed substance, which is darker than single crystal of DAN, was removed to the upper monocrystalline and cleavages occurred in some of the bulk. The measure indicated that this cleavage plane is (0 0 1) face and the angle is 38° between the *b* axis and the axis of the ampoule (even if in the vertical direction). As to growth by solution, different solvents give crystals of different size and appearance. The largest crystal was grown in anhydrous acetic acid (see Fig. 2) while in ethyl acetate only a thin piece was grown (see Fig. 7). The butyl acetate also exhibits good crystallinity for DAN.

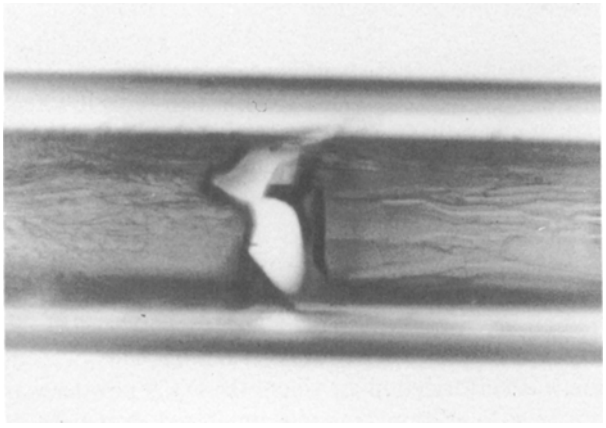

Figure 6 Fault photo of DAN cored fibre (magn × 150).

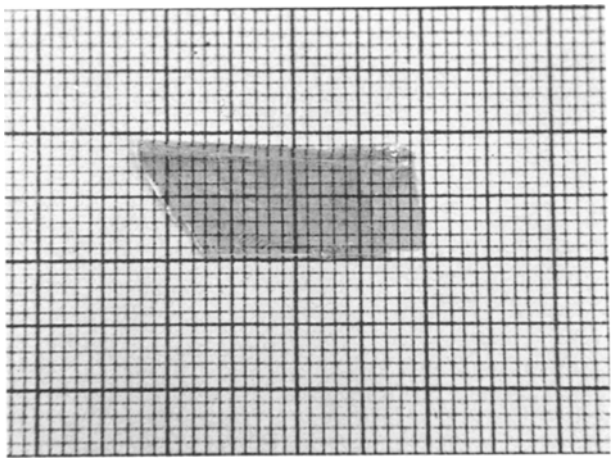

Figure 7 A thin piece of DAN crystal.

Acknowledgements

This study was supported by the Florida High Tech Council and the Chinese 863 project. The authors would like to acknowledge Yong-Lin Huang for his assistance in the growth furnace.

References

1. P. KERKOC and J. HULLIGER, *ICCG-9 Abs.* **251** (1989).
2. J. C. BAUMERT, R. J. TWIEG, G. C. BJORKLUND, J. A. LOGAN and C. W. DIRK, *Appl. Phys. Lett.* **51** (1987) 1484.
3. P. KERKOC, CH. BÖSSHARD, H. AREND and P. GÜNTER, *ibid.* (1989) 487.
4. P. A. NORMAN, D. BLOOR, J. S. OBHI, S. A. KARAULOV, M. B. HURSTHOUSE, P. V. KALINSKY, R. J. JONES and S. R. HALL, *J. Opt. Soc. Amer. B* **4** (1987) 1013.
5. A. CARENCO, J. JERPHAGNON and A. PERIGAUD, *J. Chem. Phys.* **66** (1977) 3806.

Received 14 November 1990
and accepted 10 April 1991