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Investigation on the growth and characterization of 4-aminobenzophenone single crystal by the vertical dynamic gradient freeze technique

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ABSTRACT

Growth of bulk single crystal of 4-Aminobenzophenone (4-ABP) from the vertical dynamic gradient freeze (VDGF) setup designed with eight zone furnace was investigated. The experimental parameters for the growth of 4-ABP single crystal with respect to the design of VDGF setup are discussed. The eight zones were used to generate multiple temperature gradients over the furnace, and video imaging system helped to capture the real time growth and solid–liquid interface. 4-ABP single crystal with the size of 18 mm diameter and 40 mm length was grown from this investigation. Structural and optical quality of grown crystal was examined by high resolution X-ray diffraction and UV–visible spectral analysis, respectively and the blue emission was also confirmed from the photoluminescence spectrum. Microhardness number of the crystal was estimated at different loads using Vicker's microhardness tester. The size and quality of single crystal grown from the present investigation are compared with the vertical Bridgman grown 4-ABP.

1. Introduction

For the past few years, great efforts have been made on the design and development of novel nonlinear optical materials because of their impending applications [1,2]. Especially, special attention has been paid to the growth of organic single crystals as they are promising candidates for nonlinear optical (NLO) applications due to their high nonlinearity, flexibility in terms of molecular structure and high optical damage threshold [3,4]. 4-Aminobenzophenone (4-ABP) is one among them was first reported by Frazier et al. in 1987 [5]. It crystallizes in monoclinic system with space group $P2_1$ [6]. The optical transmission range of 4-ABP extends from 420 to 1400 nm and its powder second harmonic generation (SHG) efficiency is ~360 times that of ADP [7]. But, the real barrier to exploit the potential applications of 4-ABP is the unavailability of crystals with bulk size and minimum defects. However, various attempts were made on the growth of bulk 4-ABP single crystals from the solution and melt growth techniques [8–11]. In general, melt growth techniques are preferable than solution growth because, its rate of growth is high and the crystals are free from solvent inclusion. But, the reports [8,11] concluded that the 4-ABP single crystals grown from the vertical Bridgman technique were small in size and less in quality. It is well known that for the growth of organic materials, temperature control is particularly more important because, they are very sensitive to overheating due to the thermal and chemical instability. Also, in directional solidification process like the conventional Bridgman technique, the crucible containing melt is moved from higher temperature to lower temperature region. This kind of motion is accompanied with vibrations of crucible which disturb growth. Thus, the unavoidable thermal fluctuations and mechanical vibrations occurred during growth are the major problems of the conventional Bridgman method. Therefore, in order to overcome these, a modified melt technique with precise control of temperature and vibrationless growth system is required. The vertical dynamic gradient freeze (VDGF) technique has advantages in which the temperature control is more effective (due to multizone) and crucible containing melt is cooled from one end to another end without any mechanical translation. The VDGF method was reported as one of the versatile methods for growing high-quality semiconductor single crystals such as GaAs, InP, etc., [12,13] especially with controlled thermal and vibration free growth environment. Hence, in the present study we have proposed an indigenously designed modified eight zone vertical dynamic gradient freeze technique and

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investigated the various growth parameters for the growth of organic NLO single crystals of 4-ABP.

2. Experimental details

2.1. Furnace and growth setup design

The vertical dynamic gradient freeze system used in the present investigation consists of four major parts; furnace, programmable logical controller (PLC) based control system, translation assembly and image capturing device. The furnace was made up of quartz glass tube with 2 mm in wall thickness, 50 mm in diameter and 500 mm in length. Eight individual C-type (C-shaped) heaters having nichrome wire of 0.8 mm thick were used as heating element. This heating arrangement provided an operating temperature range from 50 to 500 °C. Zone temperatures were controlled using thyristor based SPC1-35 power controller and measured by K-type thermocouples. To monitor and capture the growth related features through the charge coupled device (CCD) based video camera, a window of 24 × 3 cm^2 was made at the outer cover of furnace. A metal rod used to hold the growth ampoule was fitted with the translation assembly driven by a CSK series high-torque 2-phase stepping motor having open chassis type driver and photo coupler I/O specification. Even though, in the VDGF technique growth is achieved by changing the temperature gradient electronically without any mechanical translation, the translation setup included in the present design was used to position the ampoule at particular zone. The entire function of the VDGF system was monitored, controlled and recorded through a computer interfaced PLC using lab view software package. The photograph of VDGF system used for the growth of 4-ABP single crystal is shown in Fig. 1 and the detailed explanations on design, principle and function of all the components embedded in the VDGF setup are reported in our earlier communication [14].

3. Crystal growth

3.1. Thermal profile study of eight zone furnace for 4-ABP growth

In order to know the temperature distribution and magnitude of temperature gradient along the axis (center) of the eight zone furnace, axial temperature profile characteristics of furnace for the set temperatures of zones (Z_1–Z_8) were studied. Zone temperatures were set at the outer wall of the inner tube using K type thermocouples fixed at the center of the each zone. The temperature profile of the furnace was measured per cm from top to the bottom through the axis of furnace. These profiles were recorded corresponding to each zone which was in 'ON' condition while all other zones were in 'OFF' condition. The thermal profiles measured along the axis of the furnace for the set temperature of 200 °C applied at each zone individually are shown in Fig. 2. From the figure, it is observed that the temperature inside the furnace for the same set temperature of different zones varies and it decreases from zone 1 (Z_1) to zone 8 (Z_8). This is because, the heat loss is minimum at the top of the furnace and increases towards the bottom of the furnace. Variation in heat loss occurs due to the difference in air density inside the furnace and the insulation made on the top of the furnace. Also, it is clear from Fig. 2 when the set temperatures of all the zones are same simultaneously, the temperature is maximum at the top of the furnace and decreases exponentially towards the bottom of the furnace. Therefore, instead of setting same set temperature for all zones, different set temperatures were provided to achieve the isothermal profile at the growth region. After several profile measurements with different set temperatures, the initial set temperature values of zones for the growth of 4-ABP single crystal were optimized and are given in Table 1. The thermal profile of eight zone furnace along its axis for the optimized initial set temperatures is shown in Fig. 3. The dotted lines in Fig. 2 and Fig. 3 indicate the starting point of the corresponding zones.

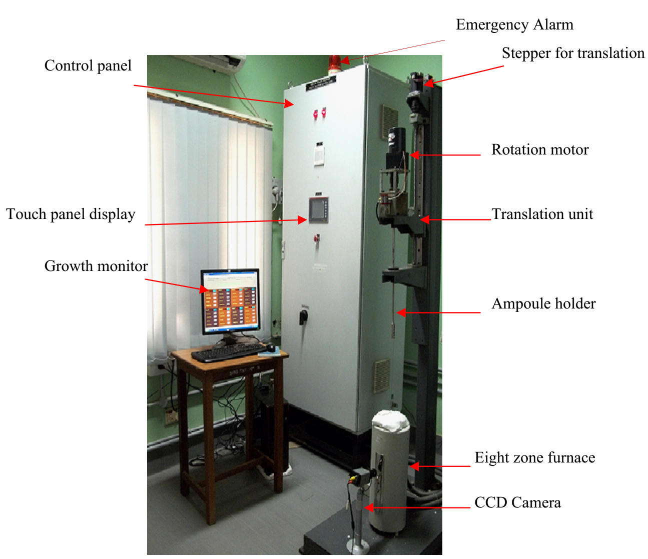

Fig. 1. VDGF system used for the growth of 4-ABP single crystal.

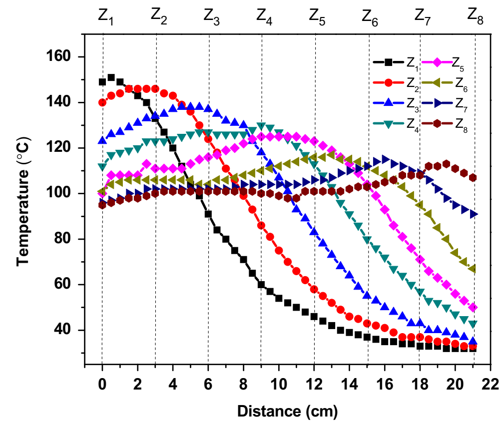

Fig. 2. Temperature profile of the eight zone furnace for the set temperature 200 °C applied at each zone individually.

Table 1
Optimized initial set temperatures for 4-ABP single crystal growth from the VDGF technique

Zone	Temperature (°C)
1	118
2	118
3	121
4	121
5	125
6	125
7	130
8	130

3.2. Growth of 4-ABP single crystal

4-Aminobenzophenone was purchased from Sigma Aldrich with the purity of about 99%. Glass ampoule having wall thickness of