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A Simple Inexpensive Bridgman-Stockbarger Crystal Growth System for Organic Materials

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Direct observation of solid-liquid interface is important for the directional solidification to determine the desired interface shape by controlling the growth parameters. To grow good quality single crystals of novel organic nonlinear optical materials, a simple inexpensive Bridgman-Stockbarger (BS) crystal growth system has been designed and fabricated. Two immiscible liquids have been utilized to create two zones for this crystal growth system. Bulk single crystals of benzil derivative and n-salicylidene-aniline have been successfully grown in this system. The optimum lowering rate has been found to be 0.1 mm/h for the flat interface. Results on the crystal growth and other parameters of the grown crystals are presented.

Significant efforts have been made in the field of organic nonlinear optical materials because of their potential applications such as second-harmonic generation(SHG), frequency mixing and electro-optic modulation. Organic molecules have been reported to have larger nonlinear optical susceptibilities in many cases than those of most inorganic materials within the 0.5-2.0 micron transparency domain (Sutter, 1988). Laser damage thresholds of some organic single crystals are much higher than conventional inorganic single crystals (Nitti, 1993). Most of the organic single crystals are more difficult to grow than inorganic crystals due to their low thermal conductivity, their large supercooling tendencies and thermal instability. Organic single crystals have been grown from the solution (Kotler, 1992), vapor and melt growth (Aggarwal, 1992). Melt growth is superior to solution growth in that the crystal can be grown faster and the grown crystal is free from the solvent inclusions. Materials that have lower thermal conductivity take more time to solidify from the melt. For this reason, organic crystals are grown at a slower rate. A Bridgman-Stockbarger method(Aggarwal, 1993) has been used to grow single crystal of organic materials because of relatively simple geometry of system and ease of controlling growth parameters during the growth processing. The solid-liquid interface shape and location are the important factors in Bridgman-Stockbarger growth system. The interface shapes strongly influence the dislocation, grain size, and dopant concentration during directional solidification (Corriel, 1979; Favier, 1977). Interface shape and position can be controlled by material properties and furnace control such as temperature gradient and lowering rate. Therefore understanding of growth parameters is important for the Bridgman-Stockbarger system to determine the desired interface shape during the process.

Post-processing techniques have been used to determine interface shape and location for the opaque system (Feigelson, 1980; Capper, 1983). They were able to change the interface shape by changing the growth parameters. However, these techniques do not allow the real-time observation and controlling interface shape and location during crystal growth. The x-ray radiographic techniques have also been developed to enable the direct visualization for opaque system (Barber,1986,1995).

To grow novel organic materials, the control of the growth parameters is more advantageous using real time observation. Therefore a transparent furnace and observing system is required for real-time measurement. A simple, inexpensive transparent BS system is designed and fabricated in our laboratory that is described in the next section. The interface shape, location and growth rate are determined as a function of lowering rate to understand influence on growth factors.

II. Experimental set-up

The Bridgman-Stockbarger melt growth system is shown in Fig.1. It consists of a growth chamber, crystal lowering mechanism and temperature control system. A Glass beaker is used as growth chamber that contains two immiscible liquids. Deionized water is used for lower temperature zone as heat transfer medium and silicon oil is used for higher temperature

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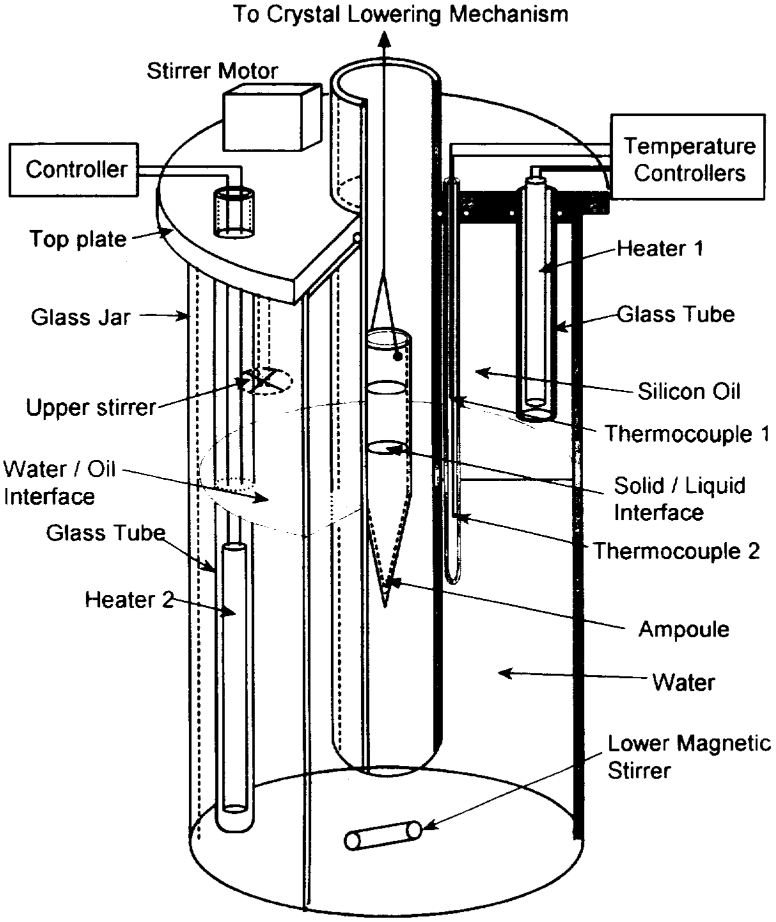

Fig. 1 Schematic diagram of the crystal growth chamber

zone. Two tubular shaped heaters that are sealed in glass tubes, fabricated in our laboratory are used for the hot(temperature above the melting point) and cold(temperature below the melting point) zones. Two separate proportional temperature controllers YSI 72 and Eurotherm 818 are used for controlling the temperature of the two zones. The control thermocouples in the two zones are located near the growth ampoule. Both zones are stirred to keep the temperature uniform in the individual zones. A hot plate with stirring function is used as lower zone stirrer and a DC motor is attached at the top of the growth chamber for hot zone stirring. The lowering arrangement is designed and fabricated using Velmex slide that is operated using Hurst stepping motors and gear reducer. Each zone can be set at any desired temperature and the temperature is controlled to within ±0.1°C. For benzil-aniline (melting point 95°C) crystal growth, temperatures of 97.5°C and 82.5°C are set up for hot and cold zones, respectively. The vertical temperature gradient can be obtained up to 25°C to prevent supercooling during growth. Once the seed is formed at the tip of the ampoule then the growth process can be observed through the growth chamber. The lowering rate was controlled by observing interface shape until we could get flat interface. After successful growth of the crystal, the ampoule is slowly cooled at a rate of few degrees per hour. No wetting and cracks induced from difference of thermal expansion between grown single crystal and quartz ampoule were found.

III. RESULTS AND DISCUSSION

Single crystals of benzil, benzil aniline and salicylidene-aniline have been successfully grown in this system. Fig. 2 shows a typical ampoule containing the grown crystal. A typical crystal growth run consists in filling the conical

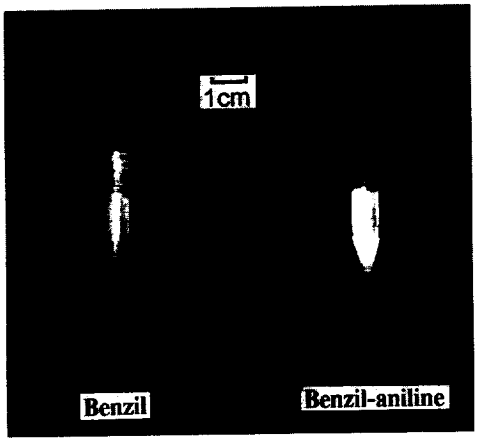

Fig.2 Photograph of benzil and benzil-aniline crystals

ampoule with the organic material, melting it in the hot zone and slowly transporting it to the cold zone thereby crystallizing a small layer of material at a time. Because of the transparency of the system, the temperature of the hot and cold zones are adjusted such that the solid-liquid interface is clearly visible in one of the zones (Fig. 3). The temperature gradient is adjusted to 10 -15°C to initiate the nucleation at the tip of the conical ampoule for benzil and benzil-aniline. However cold zone has to be cooled below the room temperature (~15°C) for nucleation of salicylidene-aniline(melting point 55°C) that has larger supercooling tendency(> 25°C). Then the cold zone temperature is slowly increased until the flat solid-liquid interface is achieved.

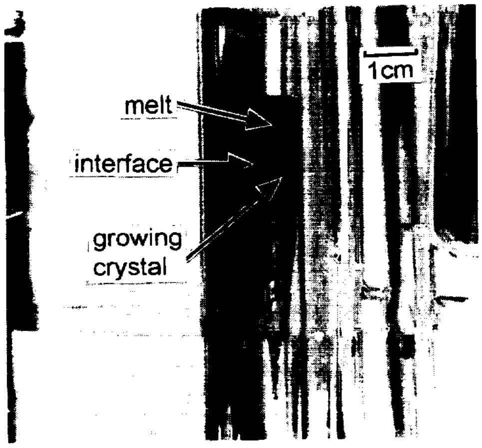

Fig.3 Photograph of a cross-section of the growth chamber showing solid -liquid interface

Various lowering rates are used during the crystal growth experiments and the shape of the interface was recorded after viewing through the telemicroscope which is mounted on a x-z translator. Normally the interface is divided in 10 points and the motion of each is monitored as the crystal growth proceeds. It has been found that the faster lowering rate increases the concavity of the solid liquid interface towards the growing crystal. From these experiments the optimum lowering rate has been found to be 0.1 mm/h for the flat interface.

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