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Growth and characterization of organic single crystal benzyl carbamate

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ABSTRACT

Benzyl carbamate single crystal is grown by a solution and vertical Bridgman technique for the first time. The cell parameters and morphologies are assessed from single crystal X-ray diffraction analysis. High resolution X-ray diffraction analysis indicates the crystalline perfection of the grown benzyl carbamate crystal. Fourier Transforms Infrared spectroscopy study has been applied to arrive at the different functional groups. Thermo gravimetric analysis and differential scanning calorimetry are used to study its thermal behavior. The microhardness test is carried out and the load dependent hardness is measured.

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1. Introduction

The benzyl group plays a central role in many protecting groups of alcohols, carboxylic acids, and amines, among other functional groups. The benzyl carbamate group in particular is one of the most widely used protecting groups for amines [1] to the extent of serving as anticancer drugs. The parent benzyl carbamate is a compound of benzyl and carbamate having low melting point lower than the room temperature, as is the general tendency of the benzyl family (namely, benzyl acetate, benzyl alcohol, benzyl salicylate, benzyl methacrylate, benzyl benzoate and benzyl butyl phthalate [2]). The compound has a melting point of 93 °C. it is a single crystal of non-hygroscopic, noncentrosymmetry crystalline organic compound of the space group $Pca2_1$ having molecular formula $C_8H_9NO_2$ [3], which finds a key application in second- and third-order non-linear optics that include harmonic generation, optical switches, photonic devices, electro-optical modulators, memory, and other interconnects [4,5]. Crystal growers have been adopting various crystal growth methods to grow bulk single crystals of the two prevalent methods i.e. the solution growth method and melt growth method [6]. The experimenters prefer the latter due to its minimum solvent inclusion problems and rapid growth. The priority for the vertical Bridgman method over the Czochralski method is because of its feasibility to grow large size single organic crystals, cracking and solid–liquid interface can be easily avoided [7].

The organic solvent acetone, ethanol and methanol are used to grow benzyl carbamate crystals, but of smaller size as well as molecules being scattered around the inner wall of the beaker. Hence the endeavor is to grow bulk size (length 8.8 cm) single crystals by the vertical Bridgman technique. The study assesses the growth and various analyses such as single-crystal X-ray diffraction (XRD), high resolution X-ray diffraction (HRXRD). Fourier transform infrared transmission (FTIR) spectrum, thermo gravimetric (TG) and differential scanning calorimetry (DSC) and Vicker's microhardness outcomes.

2. Crystal growth

2.1. Solution growth

Initial attempt has been made with a solution growth method. Most organic compounds do not dissolve in water. Hence organic solvents like methanol, ethanol and acetone are used to dissolve the sample compound. The material is dissolved in methanol and stirred for 8 h using magnetic stirrer to ensure complete dissolution. The grown crystal is found to be of size $2.2 \times 0.3 \times 0.3$ cm^3 and treated with ethanol ($1.7 \times 0.3 \times 0.25$ cm^3) and acetone (irregular shape), though the procedure is repeated the resultant outcome is the same as before. Hence, the venture is shifted to melt growth (Fig. 1(a)).

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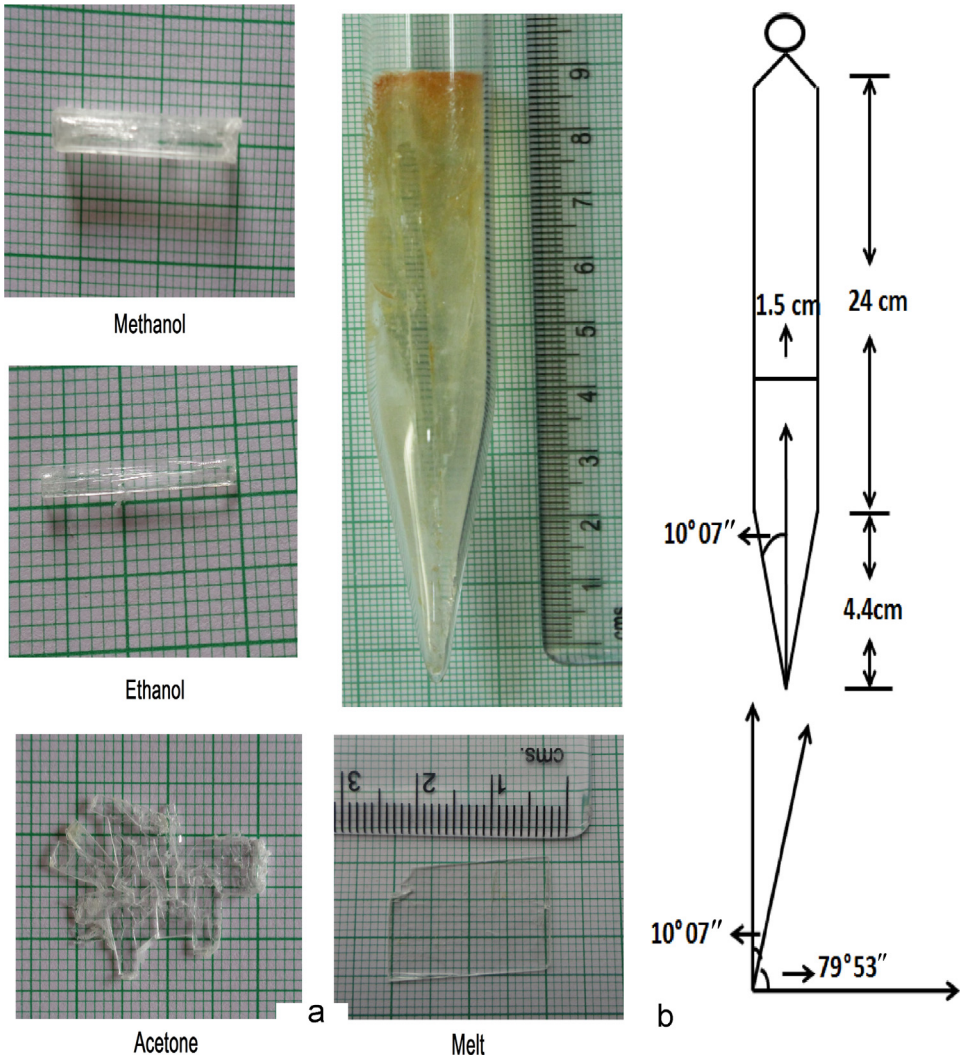

Fig. 1. Photographs of the (a) methanol, ethanol and acetone solvent used grown crystals with cut and polished portion of the vertical Bridgman technique grown crystal and (b) schematic diagram of single wall ampoule with cone angle.

2.2. Melt growth

In the vertical Bridgman technique for growing organic single crystals the ampoule design is the determining factor [8]. The experiment for study uses borosil glass to construct single walled ampoule. The total ampoule length is 28.4 cm, with a cone length of 4.4 cm, its diameter being 1.5 cm and 24 cm height above the cone angle. The cone angle of ampoule is 10 ° 07 ''. The diagram of optimized single wall ampoule with cone angle is shown in Fig. 1 (b). Deionised water and acetone are used to clean the ampoule and finally annealed at 200 °C for 12 h.

The benzyl carbamate material is loaded into the ampoule. The ampoule is evacuated at room temperature (33 °C) to 10^{-4} Torr using a vacuum pump; this vacuum level is maintained for 1 h, after the ampoule is sealed. The sealed ampoule is placed inside the furnace at above melting point region and is allowed to remain at the elevated temperature for 48 h to attain homogeneity [9]. The sealed ampoule starts its downward translation after half a day. The translation rate of the ampoule is 0.2 mm/h. Once the material reaches the freezing point, it starts to solidify suddenly. The grown crystal in the ampoule is not good so the strategy is repeated but small single crystal of (3 mm) size settles at the bottom of the ampoule. The crystal grows sequence seed on the small single crystal. After the growth is complete; the cooling rate is lowered slowly to the room temperature [10]. In order to avoid cracks due to their difference in the thermal expansion coefficient between the glass and the crystal. The range of cooling rate is 1 °C/h, 2 °C/h and 3 °C/h for 93 °C to 83 °C, 83 °C to 65 °C and 65 °C to room temperature respectively. The formed crystal is colorless and it grown in (010) plane. The crystal is removed carefully from the growth ampoule using a standard diamond wheel cutter to avoid cut and crack on the grown crystal. The cut and polished cross-section of benzyl carbamate single crystal with solution growth crystals is shown in Fig. 1(a).

The identification of the morphology and crystallographic direction of the grown crystal gives the complete structure of the material. The analysis of the grown crystals indicates that the growth direction is independent for all directions in solution grown crystals and controlled manner for melt grown crystal. The morphologies of the benzyl carbamate crystals grown by methanol and ethanol are comparable and identical with the reported values [3], it indicates the growth in (010) plane is prominent for the material. In melt growth, the crystal grows in the (010) plane. Crystal is grown in acetone show irregular formation.

2.3. Characterization

Single crystal XRD analysis is used with an Enraf-Nonius CAD4 diffractometer using Mo Kα rays to identify the lattice parameters. FTIR spectral parameters are determined by a Perkin-Elmer

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