



In-situ observation of faceted growth of benzophenone single crystals



V. Natarajan^a, M. Arivanandhan^{b,*}, P. Anandan^b, K. Sankaranarayanan^c, G. Ravi^c,
Y. Inatomi^d, Y. Hayakawa^b

^a Department of Physics, Dr. Sivanthi Aditanar College of Engineering, Tiruchendur, India

^b Research Institute of Electronics, Shizuoka University, Johoku 3-5-1, Naka-ku, Japan

^c Department of Physics, Alagappa University, Karaikudi, India

^d Institute of Space and Astronautical Science, Japan Aerospace Exploration Agency, 3-1-1 Yoshinodai, Sagami-hara, Kanagawa 229-8510, Japan

HIGHLIGHTS

- Faceted growth of benzophenone was in-situ observed.
- Growth rate of various faces were obtained from $t-x$ plot.
- The results were explained based on attachment energy model.

ARTICLE INFO

Article history:

Received 24 June 2013

Received in revised form

12 December 2013

Accepted 4 January 2014

Keywords:

Interfaces

Optical materials

Crystal growth

Crystallography

ABSTRACT

Melt growth of benzophenone was in-situ observed under various cooling rate and temperature gradient. The melt growth experiments were performed for various cooling rate of melt and various temperature gradients. The movement of growth interface with time was measured for various growth faces such as (001), (101) and (011) and the growth rates of the respective faces were calculated. It was found that the growth rate of all the faces increased with cooling rate of the melt. Steady state growth was observed in the experiments with low temperature gradient while, the steep gradient leads to unstable growth of crystal. The observed growth rate variation was explained using the attachment energy model.

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1. Introduction

Understanding of crystal growth process is quite important not only for the fundamental science but also for the industrial crystallization. Many factors associated with structure of a crystal such as morphological stability and shape of growth units influence in controlling the growth process [1]. Therefore, it is indispensable to understand the primary growth process taking place during crystallization from solution and/or melt. The growth process at an initial stage of growth can be understood by in-situ observing the growing crystal and the solid–liquid interfaces.

At the nucleation stage supersaturation provides the driving force for the formation and agglomeration of solute or growth units in solution/melt. The theory provided by Burton, Cabrera and Frant (BCF) in 1951 laid the foundation for understanding the structure of

the crystal growth interface and growth mechanism with respect to the supersaturation of solution [2]. Due to the different arrangement of atoms or molecules of the various crystal faces, each crystallographically unique face may grow by different interface kinetic process. The variation of surface binding energy with crystal orientation brings about anisotropic growth which results in various morphologies from prismatic to tabular, needle like etc.

Benzophenone is a promising organic NLO material with good optical properties, and non hygroscopic nature and thereby proposed as a best alternate material for urea [3–5]. The benzophenone crystals were grown by various methods and studied its structural and optical properties by many researchers [5–7]. Moreover, the growth anisotropy was observed in the unidirectional growth of benzophenone from solution and discussed in relation to the interface kinetics [8]. However, there is no detailed report about the growth mechanism of benzophenone single crystal.

Many microscopic methods have been employed for observing the growth process of various materials [9–11]. Among the reported methods, atomic force microscopy (AFM) [9], laser

* Corresponding author. Tel./fax: +81 53 478 1338.

E-mail addresses: marivu@ipc.shizuoka.ac.jp, arivucz@gmail.com (M. Arivanandhan).

interferometer technique [10] and optical microscopy [11] are the more reliable techniques to in-situ observe the growing crystal and its surrounding solution and/or melt. In the present work, to understand the growth process of benzophenone, melt growth of benzophenone from undercooled melt was in-situ observed by Mach–Zehnder interferometer.

2. In-situ observation experiment

Fig. 1 shows the schematic diagram of the optical system which was used for the in-situ observation experiment. A laser diode (LD) with 780 nm wavelength was used as the light source. The sample cell was set perpendicular to the optical axis in the interference loop of a Mach–Zehnder type interferometer. The evolution of the interface morphology was observed by bright field images obtained in the same optical path.

Fine powders of high purity benzophenone were filled in the quartz glass cell as shown in Fig. 2. The dimension of the sample cell is $50 \times 30 \times 1 \text{ mm}^3$ with 1 mm thickness. A thicker cell would provide a larger displacement of fringes but in the same time the thicker cell may allow for unwanted convection in the melt and leads to polycrystallization during the growth process. Two K-type thermocouples of 100 μm thickness were placed at both end of the cell to measure the temperature gradient of the melt. Both end of the cell had two Peltier heating and cooling units which were controlled by two K-type thermocouples attached on the respective Peltier units. The Peltier heaters were used to heat the material up to its melting point. Once the material gets melted completely, the temperature at one end is decreased slowly to establish a temperature gradient between hot and cold end of the cell. The temperature gradient was varied by varying the cold end temperature. Once the desired temperature gradient was established, the temperature of both end were cooled slowly at a particular cooling rate to observe the growth process. Thus the directional growth experiments could be controlled by the temperature gradient and the cooling rate. The growth direction was from cold end to the hot end. The experiment was conducted for three different temperature gradients such as 0.4, 0.6 and $0.8 \text{ }^\circ\text{C mm}^{-1}$. At each gradient, the melt was undercooled at three different cooling rates such as 1, 1.5, and $2 \text{ }^\circ\text{C min}^{-1}$ to observe the growth rate variation of different growth faces of benzophenone. The growth was initiated at the cold end of the cell when the cold end temperature reaches around $43 \text{ }^\circ\text{C}$. The growth temperature was varied with cooling rate of the experiments. The growth was observed at $43 \text{ }^\circ\text{C}$ when the cell

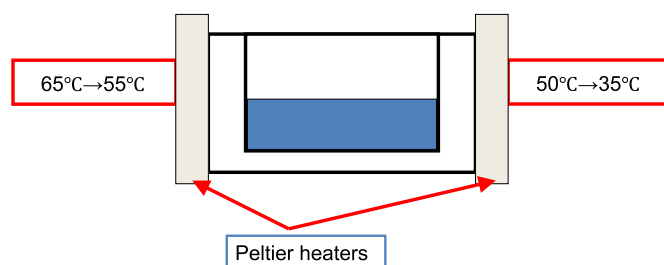


Fig. 2. Schematic diagram of the sample cell.

cooled at the rate of $2 \text{ }^\circ\text{C min}^{-1}$ whereas growth was started at $45 \text{ }^\circ\text{C}$ when the cell cooled at the rate of $1 \text{ }^\circ\text{C min}^{-1}$. It is noteworthy to mention that the temperature is measured at the outside of the cold end of sample cell and thus the temperature at the melt must be relatively differs from the measured temperature. The benzophenone growth process was recorded using a Sony video recorder. After the experiments, the video was carefully analysed to measure the growth rates.

3. Result and discussion

Temperature and concentration gradients in the vicinity of solid–liquid interface are known as the important factors to control the morphological instability of the interface. Released latent heat accompanied with solidification is removed quickly through the grown crystal and thus the temperature gradient in liquid is the same even near the solid–liquid interface. However, the latent heat for faceting material is in general large enough to influence the temperature gradient in the melt. Therefore the temperature profile in the melt is necessary to estimate more precisely during crystal growth.

According to Jackson's [12] theoretical calculations about the structure of solid–liquid interface, the factor known as Jackson's α factor is defined as follows;

$$\alpha = (L_o/kT_e)(\eta/z) \quad (1)$$

where L_o is the enthalpy of fusion, k is Boltzmann's constant, T_e is the equilibrium growth temperature, η and z are the number of atoms within the plane and the bulk crystal, respectively. Here the enthalpy of fusion is also known as latent heat of the material which is defined as the energy needed to change the state of a material from solid to liquid and vice-versa. Moreover, the η/z value depends on the crystal structure of a material.

In general, the liquid has a higher internal energy than the solid phase and thus the energy must be released when it crystallizes. The theoretical analysis showed that materials for which $\alpha > 2$ are generally faceted on one or more planes. Since, benzophenone has high α factor ($\alpha = 6.3$), faceted growth is to be expected [13]. Fig. 3a and b shows the examples of bright field image and interference image of faceted growth of benzophenone crystal.

Fig. 4a–d shows the snapshots of the faceted growth of benzophenone under the temperature gradient of $0.4 \text{ }^\circ\text{C mm}^{-1}$ between hot and cold end of sample cell and the growth was observed at the cooling rate of $1 \text{ }^\circ\text{C min}^{-1}$. The equilibrium morphology of benzophenone crystal was shown in Fig. 5. From the figures, it is obvious that the benzophenone grown from the melt was clearly faceted and three of the growth facets such as (001), (101) and (011) were identified based on morphology (Fig. 5) and carefully in-situ observed during the growth. The growth rates of each facet were measured as a function of time by monitoring the

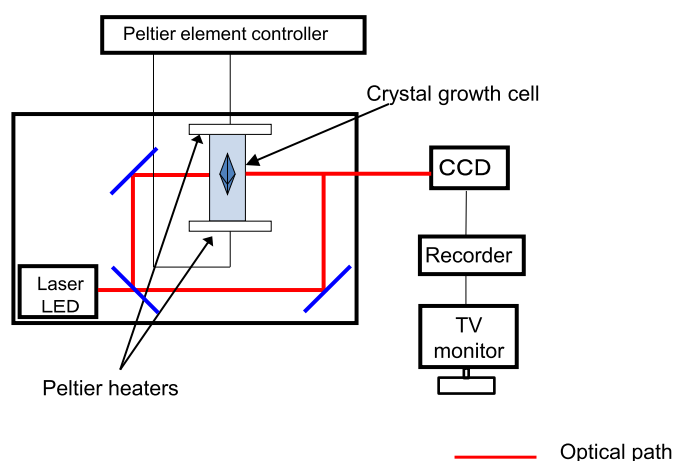


Fig. 1. Schematic view of in-situ observation system based on Mach–Zehnder interferometer.

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