

Research Letter

Unsteady Growth of BaB₂O₄ Single Crystal from High-Temperature Solution

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Two-dimensional growth of BaB₂O₄ single crystal from high-temperature solution was performed, and the motion of solid-liquid interface was observed in real time by differential interference microscopy. Results show that the solid-liquid interface exhibits the morphology of a vicinal face where steps with height of several microns are observed. The measurements of growth rate V and step propagating velocity v show that both V and v fluctuate by up to 40~50% of their average values, respectively, under constant external conditions. Such intrinsic fluctuations with time interval of the order of one second is mainly the result of step bunching, which has been confirmed by the gradual decrease of step spacing when approaching the edge of the growing interface. Besides above fluctuations, a longer-period oscillation of V (period interval of 4~5 seconds) is obtained for relatively rapid growth, which is triggered by the periodical alteration of step propagating directions.

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1. INTRODUCTION

Fluctuations of growth rate with time typically result in compositional and structural variations in crystals which inevitably deteriorate the crystal qualities. In general, the growth fluctuation is possibly correlated with the externally imposed modulations of crystal-growth conditions. Nevertheless, some recent researches have proved that the fluctuation of growth rate occurs even with constant conditions, which may be an intrinsic characteristic of crystal growth [1–4].

Up to now, however, almost all the investigations about the intrinsic fluctuation of crystal growth rate were performed under low-temperature conditions. There are few attempts on the unsteady growth of single crystal for high-temperature case, mainly due to the difficulty in observation. Moreover, the majority of previous studies dealt with the fluctuations of growth rates in the time scale of minutes or hours. Meanwhile, Onuma et al. [5] had confirmed that even in the time scale of seconds, unsteady growth still occurs. In our previous work [6, 7], the in situ observation of barium metaborate (BaB₂O₄, BBO) crystal growth under high-temperature conditions has been realized experimentally by an optical method. The aim of this paper is to visual-

ize the profile of the solid-liquid interface during BBO crystal growth in real time focusing on the problem of growth rate fluctuation in the time scale of seconds, as well as the instability of interfacial morphology.

2. EXPERIMENTAL PROCEDURE

The crystal growth was performed in a high-temperature in situ observation system developed previously [8]. The main part of crystal growth is a loop-shaped Pt wire heater. As shown in Figure 1, the Pt wire (ϕ 0.2 mm) is employed to heat and suspend the melt/solution during the in situ observation experiment. A Pt-10Rh thermocouple (ϕ 0.08 mm) with the resolution of ± 1 K is used to measure the temperature of the loop. The inner diameter of the loop is about 1.6 mm. A V-shaped electrode is used to prevent the deformation of the loop-shaped heater at high temperature.

Differential interference microscope (DIM) coupled with Schlieren technique was applied to visualize the whole growth process. During the experiments, the object lens of the microscope was vertical to the horizontal heater so that the motion of the solid-liquid interface could be observed

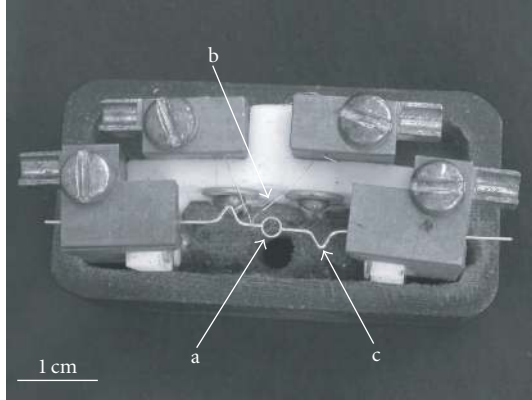


FIGURE 1: The photo of crystal-growth system: (a) loop-shaped Pt wire heater; (b) Pt-Rh thermocouple; (c) V-typed electrode.

directly. The video from the microscope (through CCD) was recorded digitally into a computer for further analysis.

The crystal growth was performed in the following manner. Firstly, the mixture of $\text{Li}_2\text{B}_4\text{O}_7$ - BaB_2O_4 (65 wt %) was melted and suspended on the loop-shaped heater. To improve the image, the melt/solution was adjusted to be optically transparent under the microscope by precisely adjusting its amount. Secondly, a tiny BBO crystal seed formed in the center of the solution. Then a temperature drop was given and the crystal was allowed to grow in two dimensions with a polyhedral shape. The morphology of the growing solid-liquid interface (S-L interface) was observed in real time by the DIM. By measuring the front displacement of the growing interface between the subsequent growth stages with time, the growth rate was calculated.

3. RESULTS AND DISCUSSION

3.1. Morphology of BBO solid-liquid interface

The crystal growth was performed in two dimensions, and the movements of $\{10\bar{1}0\}$ and $\{\bar{1}010\}$ interfaces were visualized by optical method. Owing to the addition of $\text{Li}_2\text{B}_4\text{O}_7$ flux, the BBO crystal grows at about 1093 K, which is much lower than the melting point of pure BBO ($T_m = 1368 \pm 5$ K). In such cases, growth usually occurs in layer-by-layer style as a result of the existence of step-free energy [9, 10]. Figure 2 shows the optically observed typical morphology of the growing $\{\bar{1}010\}$ interface during the growth of BBO single crystals, where the growth layers (crystal steps) are obvious.

Since the thickness of one layer (i.e., the height of step) in Figure 2 is up to several microns, they are macrosteps, which are formed by a series of elementary steps. Although the growing interface seems flat as a whole, the macrosteps do not propagate in the direction parallel to the solid-liquid interface. This indicates that the interface is a vicinal face, which can be explicitly sketched by the inset photo in Figure 2. In present observation, the velocity of vicinal face V , that of local singular face R , and the step velocity v can be

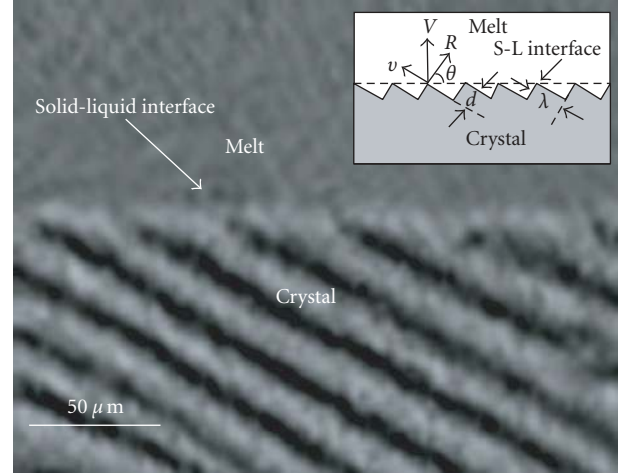


FIGURE 2: Typical profile of stepped morphology of $\{\bar{1}010\}$ interface visualized by the optical method; the inset is the schematic figure of the interfacial morphology.

quantitatively measured. The values of step height d and step spacing λ can also be obtained.

3.2. Fluctuations in growth rate and observation of step bunching

In our observation system, growth rate V was measured at the center of the solid-liquid interface, and local velocity R was measured at a fixed position situated about $20 \mu\text{m}$ away from the interface center where the established “step group” is visible. Here, a “step group” consists of a series of adjacent steps that have nearly the same orientation. The velocities were calculated for every 0.2 second by a video analysis software. Due to the facility limitation, the maximum measurable time for V and R was about 15 seconds and that for v was even less. The variations of velocities with time for the growing $\{\bar{1}010\}$ interface were shown in Figure 3. From the figures, one can see that V and v are not steady and fluctuate in an irregular way. The fluctuation amplitude is about 40~50% of their average values, and the average periodicity is one second or so. From the obtained frequency values, it is clear that this periodical pattern is not related to the observational frequency. The temperature was monitored and the record did not follow any oscillatory rhythm. Then one can conclude that the periodical behavior is not the result of growth condition fluctuations.

Generally, the oscillation of growth rates can appear from both extrinsic and intrinsic reasons. Fluctuation of a concentration field by melt convection is the most representative extrinsic effect. This is, however, a fluctuation of the order of minutes or hours in case of buoyancy convection [11], which cannot be adopted in the present case. Furthermore, the value of dimensionless Marangoni number $\text{Ma} = \sigma_T \Delta T d / \eta \kappa$ characterizing the strength of thermocapillary convection was also calculated for investigating the effect of Marangoni flow. Here $\sigma_T = d\sigma/dT$ is the temperature coefficient of surface tension σ , ΔT is the horizontal temperature difference

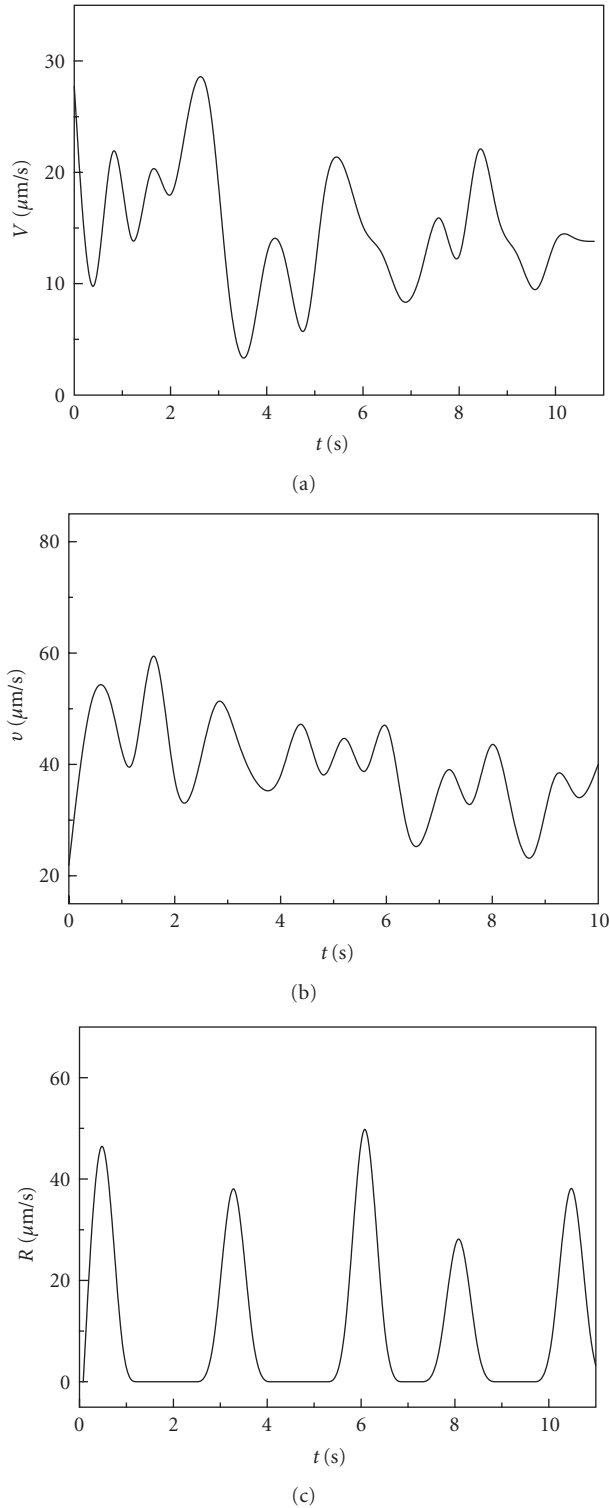


FIGURE 3: Time traces of normal growth rate V , step velocity v , and local growth rate R for the $\{1010\}$ interface.

along the heater, d is the characteristic length of the liquid, η is the dynamic viscosity, and κ is the thermal diffusivity. For a coarse estimate [12], the value of Ma is about 20 in present solution system, which cannot trigger oscillatory Marangoni

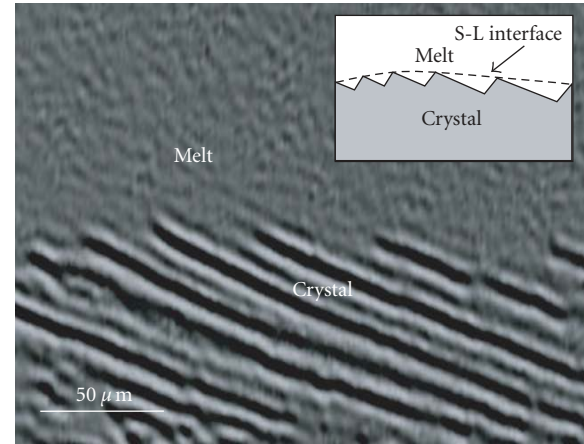


FIGURE 4: Step bunching showing the interfacial instability of a vicinal face.

flows for BBO solution according to the discussions in our previous work [12, 13].

One most possible intrinsic reason is bunching of the steps, which has been identified in some cases of crystal growth from aqueous solutions [14, 15]. For bunching investigation, an effective method is used to trace the variation of step height and spacing with time, which can be suggested by the variation of R with time t . If the step heights and spacing are completely constant, one should expect that some fixed values of growth rates and several points of zero appear repeatedly in the R - t curve. The value of zero in the R profile means that the step does not move to the next pixel within the measurement duration. However, in Figure 3(c), the apex values of R vary with time, and the intervals between two adjacent apexes also change during the growth. This hints that both the height and the spacing of steps vary with time; namely, bunching of elementary steps occurs.

Although the bunching of elementary steps is difficult to be detected directly in our present observation system, the bunching of macrosteps can be easily visualized. In general, crystal steps are generated firstly at the edges of the growing face due to the higher concentration of solute [16]. For BBO crystal growth, such phenomenon has also been detected in previous paper [7]. In present experiments, however, the majority of the macrosteps were found to propagate easily from the face center to the face edges. This may be correlated with the effect of impurities on the binary phase solution. Figure 4 shows the morphology of solid-liquid interface near the face edges. It can be seen that the spacing of the macrostep decreases when approaching the edge, which leads to the local deformation of the interfacial shape as depicted by the sketched map inlet.

The step spacing depending on the position of the surface is controlled by two factors. One is the nonuniformity of surface supersaturation, and the other is bunching of step due to impurity. As discussed by Kuroda et al. [17], the step spacing is adjusted to compensate for the distribution of concentration on the following surface so as to keep the

macroscopic growth rate constant. So a step advances faster near the edge of a crystal, and the step spacing becomes wider than the central region of a face. However, in our observation, the opposite result was obtained. The step spacing became narrower near the edge. According to the discussion, if the impurities are the only cause to affect the step spacing, the height of each step should increase with the distance from the step source. This is just the fact in present observation. Then it can be concluded that the step bunching, which is responsible for the fluctuation of growth rate and step velocity, is mainly induced by the impurities in the solution.

3.3. Long period of growth rate oscillation

Figure 5 shows the growth rate of $\{10\bar{1}0\}$ interface versus time t . For this interface, two styles of rate oscillations were found. The basic oscillation of rate V (the solid line) is very familiar with that of $\{\bar{1}010\}$ interface, with oscillation period of about one second. Nevertheless, upon the basic oscillation, a longer period of growth rate oscillation was obtained for the motion of $\{10\bar{1}0\}$ interface, as shown by the dashed line in Figure 5. The interval of the long-period fluctuation is 4 seconds or so. Very instructively, accompanying the long growth rate oscillation is the oscillation of step direction, which can be clearly seen from the microstructure of the as-grown crystal surface, as shown in Figure 6. In situ observation shows that at one moment the step group arising from the face central region runs to the right edge of the growing interface; however, the step group formed in the next interval runs to the left edge of the growing interface. This proceeds periodically and the period is just about 4~5 seconds. It is the periodical changes of the step propagating direction that give rise to the long period of growth rate oscillations. In effect, the oscillation of step direction occurs for the motion of $\{\bar{1}010\}$ interface too. Meanwhile, in that case the long-period oscillation is impossibly detectable due to the comparatively larger face area and the consequently longer periodicity of directional alterations. The possible reason responsible for the oscillation of step propagating directions may be the structural variation of step sources, which has been considered as another important mechanism that induces the intrinsic oscillation of growth rates [18].

It is interesting to notice that this type of long-period oscillation was observed only with comparatively rapid growth (namely, large supercooling). If the average growth rate is extremely slow, no intersectional step groups are observed in the as-grown crystal, and the long period of oscillation will disappear. However, the short-period oscillation exists in any case. This will be helpful especially to the improvement of rapid growth technique, which has been given much attraction in recent years [19, 20].

4. CONCLUSIONS

The existence of growth rate V and step propagating velocity v fluctuations during BBO single crystal growth has been confirmed. In the second scale, V and v both vary with time

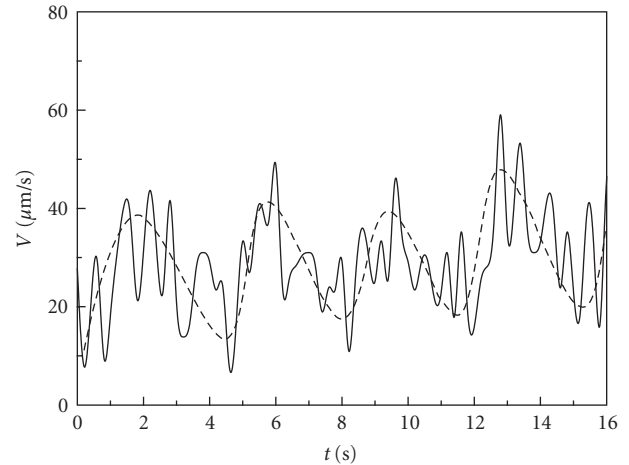


FIGURE 5: Time traces of normal growth rate V for the $\{10\bar{1}0\}$ interface.

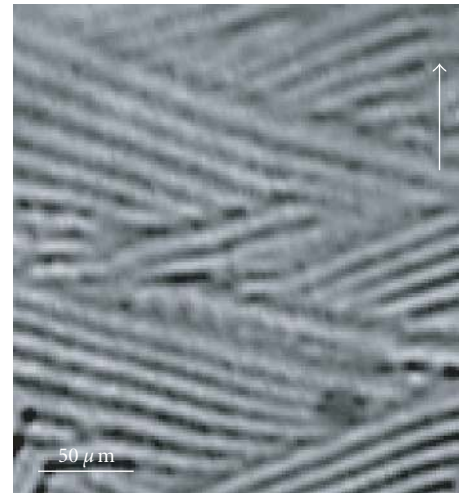


FIGURE 6: Microstructure of intersectional step groups in the as-grown crystal; the arrow indicates the growing direction of the $\{10\bar{1}0\}$ interface.

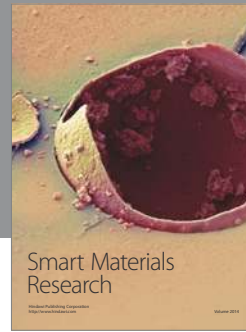
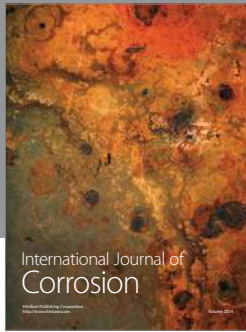
in a very irregular way, which is proved to be an intrinsic oscillation related to the step bunching. By a differential interference microscope, the bunching of macrosteps was visualized and observed experimentally. Additionally, for the case of rapid growth, a long period of oscillation of V was found with the periodicity of 4~5 seconds. It is the periodical alternation of growth source orientation that is responsible for this long-period oscillation.

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