Optical and atomic force microscopic study on step bunching in BaB_2O_4 crystal growth*

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The formation of macrostep during high-temperature phase of barium meta-borate (α-BaB_2O_4) single crystal growth has been investigated by both optical *in-situ* observation system and atomic force microscopy (AFM). The *in-situ* observation results demonstrate that the critical linear size of growing facet exceeding the size that the macrostep generates is significantly anisotropic. The critical linear sizes are around 280 μm and 620 μm for $\{10\bar{1}0\}$ and $\{\bar{1}010\}$ planes, respectively. AFM study illustrates that macrostep train with a height of 150 nm∼200 nm is one typical morphological feature of the as-grown crystal surface. The riser of each macrostep consists of several straight and parallel sub-steps, indicating the occurrence of step bunching. Additionally, triangular sub-steps with heights of several nanometers on the treads of the macrosteps are found to be another typical feature of surface morphology, which implies a microscopically competitive bunching of sub-steps between various crystallographic orientations.

Keywords: step bunching, optical *in situ* observation, atomic force microscopy, BaB_2O_4 crystal

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1. Introduction

Step bunching (namely formation of macrostep) is one of the characteristic morphological features of single crystal, which can result in striations within the grown crystals.[1] Unlike striations induced by variations of external temperature or compositions, the bunch-induced striations are intrinsic phenomenon and cannot be eliminated by stabilizing external conditions.[2] Therefore, it is important to understand how and when step bunching occurs. Moreover, the investigation of step bunching will help to optimize the technology of the crystal growth.

Although some investigations have experimentally shown the evolution of step bunching during crystal growth in a low temperature solution,[3−5] little effort has been made to investigate step bunching phenomenon under the condition of high temperature. This paper introduces an optical *in-situ* observation system as well as an atomic force microscopic *ex-situ* investigation technique and its application in crystal growth mechanism study, especially in the formation process of macrosteps. The coupling of these two techniques experimentally provides a chance to discover the mechanism of step bunching in crystal growth under high temperature conditions.

2. Experimental procedure

The crystal growth was performed in a high-temperature *in-situ* observation system developed in our previous work.[6,7] The growth device was a loop-shaped heater with a diameter of 1.6 mm, which was made of Pt wire (ϕ0.2 mm) as shown in Fig. 1.

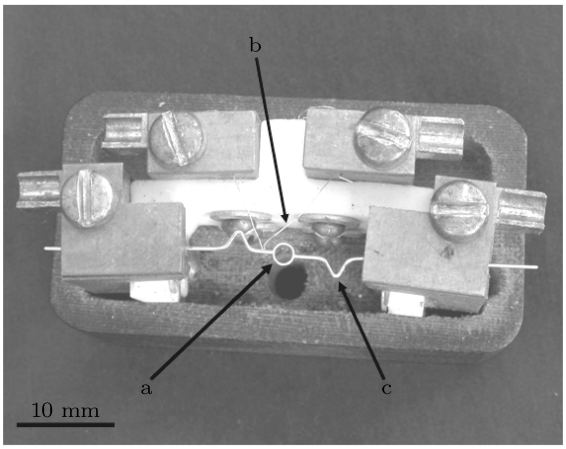


Fig. 1. Photo of crystal growth device, composed of a-loop-shaped Pt wire heater, b-Pt-Rh thermocouple, and c-V-typed electrode.

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The heater was placed horizontally. Its temperature was controlled by a stabilized DC power supply. A Pt-10%Rh thermocouple (ϕ0.08 mm) was applied to measure the temperature and two V-typed electrodes were used to prevent the loop from deforming at high temperature.

The single crystal was grown from BaB_2O_4–$Li_2B_4O_7$ fluxed melt. The starting material used was a mixture of 75 wt% BaB_2O_4 and 25% $Li_2B_4O_7$. Firstly, the mixture was melted and suspended on the Pt loop with a temperature of 930 °C. A tinny BaB_2O_4 crystal seed was formed in the melt centre by adjusting the temperature. Then the temperature was reduced to 880 °C so as to allow the crystal to grow in two dimensions. The phase of the grown crystal is the high-temperature phase of barium meta-borate (α-BaB_2O_4) which has been identified by x-ray diffraction (XRD) analysis in our previous paper.[8] The interfacial morphology and the crystal shape were observed in real time during the growth by differential interference microscopy. The video from the microscope (through CCD) was recorded digitally into a computer for further analysis. After growth, the sample was withdraw from the loop-shaped heater and slowly cooled down to room temperature. Finally, the surface morphology of the as-grown crystal was observed by an atomic force microscope (AFM) system without any chemical or mechanical treatment.

3. Results and discussion

3.1. Formation of macrostep observed by optical *in-situ* observation method

Figure 2 shows the two-dimensional growth of one BaB_2O_4 single crystal visualized by the differential interference microscopy. The initial shape of the crystal seed is triangular as shown in Fig. 2(a). However, its shape becomes hexagonal within a very short time with the exterior interfaces being $\{\bar{1}010\}$ and $\{10\bar{1}0\}$ facets respectively (Fig. 2(b)). When the linear size of the hexagon-shaped crystal is small, the growing interfaces are all smooth and flat and the as-grown part of the crystal is transparent under optical microscopy. Nevertheless, when the size of the horizontal facet exceeds one critical value L_c, macrostep appears along the moving interface as indicated by the arrow in Fig. 2(c). After that, crystal growth proceeds significantly in layer-by-layer style and a terraced morphology is obtained.

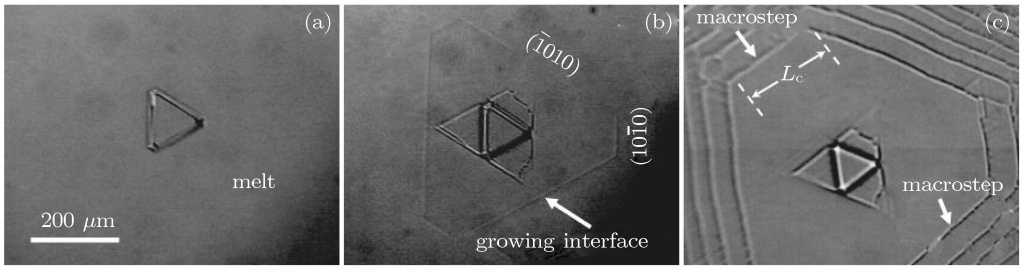


Fig. 2. Consecutive stages of BaB_2O_4 single crystal growth observed by differential interference microscope, showing how macrosteps form at different times: (a) time $t = 0$ (initial), (b) $t = 5.0$ s, and (c) $t = 10.0$ s.

Generation of macrostep in crystal growth is primarily due to the morphological instability of growing interface. In general, interfacial instability is correlated with the inhomogeneous solute distribution along the interface, which has been verified in oxide crystal growth by electron-microprobe analyses in our previous study.[9] On the other hand, the shape stabilizing factor is related to the anisotropy in the surface growth kinetics. If the anisotropy of kinetic coefficient is not sufficient to compensate for the inhomogeneity in the concentration distribution over the growing interface, morphological instability in the crystal facets takes place.

One important parameter characterizing the occurrence of interfacial instability is the critical size L_c, above which the shape preserving-growth is impossible. The value of L_c has been measured in the present experiment, which is found significantly to be anisotropic: around 280 μm for $\{10\bar{1}0\}$ facets while 620 μm for $\{\bar{1}010\}$ facets. The regime of crystal growth is usually governed by coupled interfacial kinetics and interfacial mass transport. For one specific

growth system the mass transfer keeps almost steady under constant external conditions. In the present experiment, therefore, the discrepancy of critical facet size between different crystallographic orientations is primarily due to the high anisotropy of interfacial kinetic coefficients.

For the faceted nature of BaB_2O_4 crystal growth, the critical size L_c is usually proportional to the kinetic coefficient β as $L_c \sim \beta^{-1/2}$, where β is the interfacial kinetic coefficient which is closely correlated with the incorporating rate of growth unit into the growing interface. α-BaB_2O_4 crystal belongs to trigonal system with space group $R\bar{3}C$, and the basic growth unit in its melt is anionic coordination growth unit $[B_3–O_6]^{3-}$. Since the incorporation rate of $[B_3–O_6]^{3-}$ into $\{\bar{1}010\}$ facet is usually slower than that into $\{10\bar{1}0\}$ facet,[10] it is reasonable that the former facet has larger critical size than the latter one. It should be noted that this finding is greatly helpful not only for understanding the crystal growth mechanism, but also for technically optimizing the large crystal growth. It is obvious that when the growing direction is selected to be perpendicular to the facet with a lower interfacial kinetic coefficient, a larger crystal without defect may be obtained.

Furthermore, our *in-situ* observation result shows that L_c value depends strongly on growth temperature which determines the moving velocity of the growing interface. This can be interpreted when transport phenomenon is taken into account. A larger growth rate generally leads to the enhancement of diffusion as well as the reduction of convection in melt.[11] As a result, the non-uniformity of the concentration distribution is promoted and the value of critical facet size is inevitably changed.

3.2. Step bunching revealed by AFM

Optical *in-situ* observation system can visualize only the surface morphology on the micron scale and the detail information about surface height in scale of nanometer is impossible to achieve. Nevertheless, this can be realized by AFM.[12] In this part, AFM is used to *ex-situ* investigate the surface morphology of as-grown crystal when it is cooled down to room temperature so as to deeply understand the growth mechanism of BaB_2O_4 crystal. The investigated area is focused on the region where significant macrosteps are observed under optical microscope.

AFM observation demonstrates some significant giant macrosteps on the crystal surface, whose height ranges from 150 nm to 200 nm or so. Figure 3(a) shows a typical AFM image of the giant macrostep with a scan area of 40×40 μm^2. Figure 3(b) displays the cross-sectional profiles of the surface heights along the line AB in Fig. 3(a). The height of the macrostep as illustrated by the thick arrow in Fig. 3(a) can be determined from corresponding section analysis shown in Fig. 3(b), which is about 180 nm.

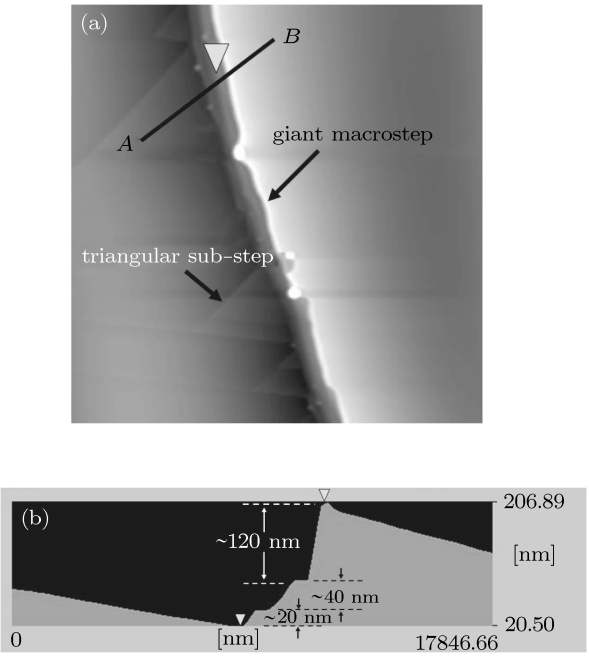


Fig. 3. (a) AFM image of the as-grown BaB_2O_4 crystal surface with a scan area of 40×40 μm^2, and (b) cross-sectional profiles of the surface heights along the line AB in Fig. 3(a).

A more interesting phenomenon from the height profile analysis is that several heights of sub-step are clearly obtained in the riser region of the macrostep. This hints that the giant macrostep observed under differential interference microscopy is the result of bunches of several sub-steps. Such a giant macrostep is the so-called "real macrostep" as described by Chernov.[13] A "real macrostep" is composed of a shape-preserving step riser, which is surrounded by two flat treads whose linear sizes are both large as compared with that of the riser. The riser of the "real macrostep" is not flat but is composed of curved surfaces, which can be simply sketched in Fig. 4. AFM results show that in the present experiment the linear size of the riser L_R is only ~1 μm–3 μm, while that of the flat tread L_T is up to ~60 μm.

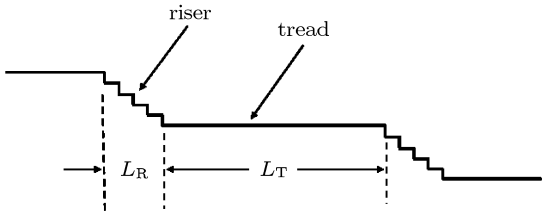


Fig. 4. Schematic form of real macrostep.

In Fig. 3(b) there are a total of three heights of sub-step which are around 20 nm, 40 nm and 120 nm respectively. This means that the density of sub-steps involved in one specific curved riser varies with position. The height of the upper sub-step is usually greater than that of the lower one, just hinting a tendency of bunching. Furthermore, the morphologies of such sub-steps can be visualized by a magnified AFM image as shown in Fig. 5 where the scanned area is 2×2 μm^2. Clearly, the sub-steps are usually straight and parallel.

The other striking feature of surface morphology is that some triangular sub-steps are clearly seen on the tread of the macrostep as typically indicated in Fig. 3(a). Section analysis shows that the heights of these triangular sub-steps are around several nanometers. Triangular shape is in some sense due to the growth anisotropy of the single crystal.[14] It can be considered as a result of joining of couples of steps which are in different directions. The formation of triangular shape here implies a microscopically competitive bunching of steps between various crystallographic orientations.

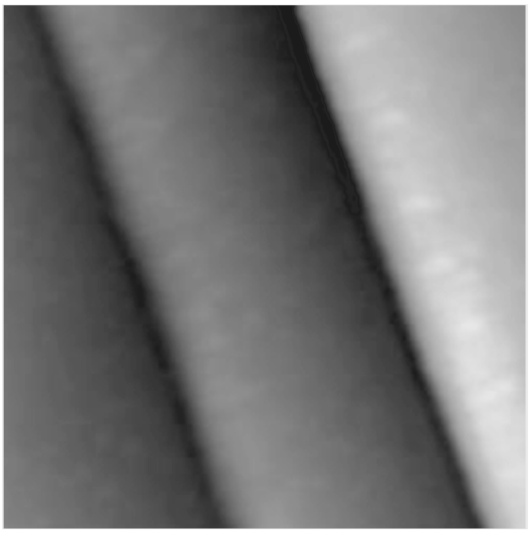


Fig. 5. Magnified AFM image of one macrostep riser with a scan area of 2×2 μm^2, showing straight and parallel sub-steps.

4. Conclusions

Two-dimensional growth process of α-BaB_2O_4 single crystal was observed in real time by optical microscopy, and the critical facet size exceeding the size that the macrostep forms is found to be significantly anisotropic. Additionally, the surface morphology of the as-grown crystal is systemically revealed by AFM. The AFM study illustrates some "real macrosteps" on the surface with heights up to around 200 nm, and each macrostep riser is composed of several sub-steps. Nevertheless, on the flat treads of the "real macrosteps", triangular sub-steps with heights of several nanometers or so are typically found.

References

[1] Chernov A A 2004 *J. Cryst. Growth* **264** 199

[2] Vekilov P G, Rosenberger F, Lin H and Thomas B R 1999 *J. Cryst. Growth* **196** 261

[3] Ristic R I, Shkunov B and Shewood N 1996 *J. Cryst. Growth* **160** 330

[4] Li C R and Tsukamoto K 2001 *J. Cryst. Growth* **233** 336

[5] Onuma K, Kameyama T and Tsukamoto K 1994 *J. Cryst. Growth* **137** 610

[6] Jin W Q, Chen J Y, Li W S and Yan H P 1993 *Ferroelectrics* **142** 13

[7] Pan X H, Jin W Q, Liu Y and Ai F 2008 *Cryst. Res. Technol.* **43** 152

[8] Cai L X, Jin W Q, Pan Z L, Liang X A and Liu Z H 2001 *J. Synthetic Crystals* **30** 280 (in Chinese)

[9] Pan X H, Jin W Q, Liu Y, Ai F and Jin F 2009 *Chin. Phys.* B **18** 699

[10] Zhong W Z, Hong H C, Lu Z P, Zhao T D, Hua S K, Tang D Y and Zhao Q L 1994 *Sci. Chin.* Ser. B **4** 798 (in Chinese)

[11] Pan X H, Ai F, Jin W Q, Liu Y and Zhang Y 2007 *Sci. Chin.* Ser. G **50** 539

[12] Ohira S, Arai N, Oshina T and Fujita S 2008 *Appl. Surf. Sci.* **254** 7838

[13] Chernov A A and Nishinaga T 1987 in *Morphology of Crystals* ed. Sunagawa I (Tokyo: Terra Scientific Publishing Company) p. 254

[14] Yin L W, Li M S, Xu B, Song Y J and Hao Z Y 2002 *Chin. Phys. Lett.* **19** 1707