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A Study on Stratification of Concentration in Crystal Growth of α-LiIO$_3$ by Holographic Interferometry

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Abstract A new thermoplastic-photoconductor laser holographic recording system has been used for real-time and *in situ* observation of α-LiIO$_3$ crystal growth. The influence of crystallization-driven convection on the concentration stratification in solution has been studied under gravity field. It is found that the stratification is closely related to the seed orientation of α-LiIO$_3$ crystal. When the optical axis of crystal seed $\boldsymbol{C}$ is parallel to the gravity vector $\boldsymbol{g}$, the velocity of the concentration stratification is two times larger than that in the case of $\boldsymbol{C} \perp \boldsymbol{g}$.

It needs 40 h for the crystalline system of α-LiIO$_3$ to reach stable concentration distribution (expressed as τ) at 47.6℃. The time τ is not sensitive to the seed orientation. Our results provide valuable data for designing the crystal growth experiments in space.

Keywords: α-LiIO$_3$ crystal, laser holographic interferometry, thermoplastic photoconductor, crystal growth in microgravity, crystallization-driven convection, stratification.

1 Introduction

Microgravity resource will be one of the main space resources under the near-earth space to be exploited in the coming 21st century.

The principal physical phenomena under the microgravity environment may be summed up as follows: the buoyancy-driven convection decreases by six orders of magnitude; the deposition and segregation almost disappear; the gradient of static pressure in fluid tends towards zero[1,2]. Since the first space experiment on the crystal growth at the beginning of 1970s by US skylab, the experimental simulation under the microgravity on the earth and crystal growth in space about the effect of gravity on crystal growth have been widely carried out[3-6]. Experimental results indicate that the industrialization and commercialization of the space crystal growth have optimistic prospect. For these purposes, it is very important to make a deep-going investigation of the fundamental problems of the crystal growth in microgravity conditions.

Crystal growth is both a process of solid/liquid interfacial reaction and thermodynamical phase transition. Since fluid phase is the mother phase for crystal growth from solution, both growing rate and crystal quality depend on the interfacial kinetics and the transference of mass and heat in fluid phase. Thus, the distribution and stratification of solution concentration in the surrounding fluid phase is one of the most important fundamental topics in crystal growth. On the earth, there exist natural convection, Stokes convection and crystallization-driven flow in fluid system. Under microgravity conditions, although the natural convection is greatly weakened, the crystallization-driven convection still exists. Therefore, how to diagnose the crystallization-driven convection and study its behavior is of vital importance to understanding the rules of crystal growth.

Scholars engaged in the field of microgravity sciences and its application at the National Aeronautics and Space Administration (NASA) and the European Space Agency (ESA) believe that if the laser holographic interferometry is used for the real time and *in situ* observation on the crystal growth, our knowledge on the fluid effect of crystal growth will move forward with giant strides, and that the study on space crystal growth will enter a new stage, that is to say we will be able to study the kinetic process of crystal growth[7-8].

This paper will report our experimental results on the process of α-LiIO$_3$ crystal growth by laser holographic interferometry.

2 Choice of the Crystallization System

α-LiIO$_3$ crystal is an electric-polarization, nonlinear optial crystal with space group of C_6^6. This crystal was found to have the second harmonic generation effect in 1968. Since then, a large high-quality α-LiIO$_3$ single crystal has been grown from solution by a constant temperature evaporation method[9]. Since 1970s, α-LiIO$_3$ has been extensively used to the manufacture of the second harmonic generation (SHG) laser and ultrasonic transducer[10]. The mechanism of crystal growth in the gravitational field on the earth has been already studied systematically[11,12].

α-LiIO$_3$ crystals were grown in a Chinese recovery satellite recently[13]. By comparing the characteristics of space-grown and earth-grown crystals, it is found that the α-LiIO$_3$ crystals grown in space is the same as that grown on the ground-hexagonal double pyramid. In other words, the crystal is a polyhedron formed by the hexagonal double pyramidal faces $\{10\bar{1}1\}$ and hexagonal prismatic faces $\{10\bar{1}0\}$. However, there are obvious difference in the growth rate. Let R be the ratio between the growth rates in the positive and negative optical axes. i.e. $R = V_{[0001]}/V_{[000\bar{1}]}$. It is found that for α-LiIO$_3$ crystal growth in low pH value solution, the value of R under ordinary gravity conditions is much higher than that under microgravity conditions.

Why does the value of R decrease under microgravity conditions? The physical mechanism is not clear yet. In the study of the fluid flow effect of crystal growth, it is necessary to perform a real time and *in situ* observation on the process of crystal growth.

3 Experimental Technique

The experimental apparatus consists of two parts: an optical system of laser holographic interferometry and a system of thermostatical crystallization (see Fig. 1).

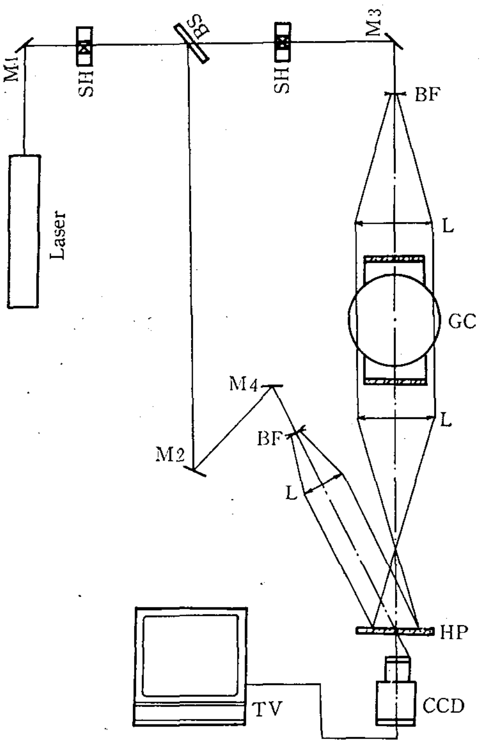

Fig. 1. Scheme of the holographic set-up for the real time and *in situ* observation of α-LiIO$_3$ crystal growth. laser, He-Ne laser; M, mirror; SH, shutter; TV, TV set. BS, beam splitter; BF, beam spreader; L, lens; GC, growth cell; HP, holographic plate.

3.1 *Laser Holographic System*

The He-Ne laser was used as light source with 10 mW output power. The transverse model TME$_0$ was adopted. The laser light was split into an object beam and a reference beam by a beam splitter (BS). The power ratio of the object beam to the reference beam is 1/5. The object beam was expanded and collimated to be a light beam 150 mm in diameter and then injected onto the input plane of a thermostatical crystallizer (GC). After passing through GC, the output beam was focused and injected onto a holographic plate (HP). The reference beam was expanded by a spreader and collimated by a collimator and then injected onto the holographic plate (PH) too. The object beam and the reference beam was overlapped at HP. The angle between the object and reference beam was about 25°. A new type thermoplastic photoconductor was adopted as a holographic record plate, which was made of materials without silver. The system has the following advantages:the period to take a hologram is shorter than the traditional method; the *in situ* recording, developing and reconstructing of the interferogram can be realized; furthermore, the hologram can be conserved for a long time.

3.2 *Thermostatical Crystallization System*

The thermostatical crystallization system consisted of two concentric cylinders with optical window. The wall of the tubular cylinder was processed by a special stainless steel as required by the holographic experiment. A double-wall container was made up of two concentric cylinders. The outer container was filled up with water, and the inner one with the mother solution for crystal growth. In order to maintain a constant temperature during the growing process, two sets of microresistance wire were used as the heater, which was controlled by an electric controller. No stirring unit was set in the thermostat in the crystal cell. The temperature fluctuations in the crystal cell was less than 0.1℃.

3.3 *Hologram Formation and Its Photography.*

α-LiIO$_3$ crystal was grown by slow solution evaporation method at 47.6℃. The synthesis and purification of the α-LiIO$_3$ powder materials as well as the preparation of supersaturated solution are the same as those reported in Ref. [11]. The seed plate was cut from an α-LiIO$_3$ crystal grown on the earth and possessed left-handed optical activity. The seed was 25 mm in diameter and 1.5mm in thickness. The normal direction of the end faces was parallel to the optical axis and the crystalline orientation was in [0001] direction. For the determination of the seed orientation, please refer to Ref. [12]. At the beginning of the experiment, the seed was put in a supersaturated solution of α-LiIO$_3$, then the solution was slowly heated at a rate of 2.5℃/h. After the solution reached equilibrium, a reference hologram was taken. In the process of the crystal growth, the initial object beam reconstructed from the reference hologram and the real object beam were overlapped and formed the interferogram pattern. The pattern could be photographed by a camera and recorded by a CCD. The process of crystal growth was observed by the real time and *in situ* procedure. This experiment had been running for 10 days. 140 interferograms were photographed. The system was stable and the pattern was clear during the experiment.

4 Experimental Results

The anisotropy of the crystal growth rate is one of the obvious characteristics in the α-LiIO$_3$ crystal growth. The growth rate in [0001] direction is much faster than the one in [10$\bar{1}$0] direction in growing process from neutral mother solution. In order to investigate the influence of the crystallization-driven convection on the growth rate, two sets of experiments were designed, one with the optical axis of the seed, $\boldsymbol{C}$, parallel to the gravity direction $\boldsymbol{g}$, and the other with $\boldsymbol{C}$ perpendicular to $\boldsymbol{g}$. The experimental results are described as follows:

4.1 *The Process of Crystal Growth in $\boldsymbol{C} \| \boldsymbol{g}$ arrangement*

Fig. 2 shows the real time holographic interferograms when growing a crystal

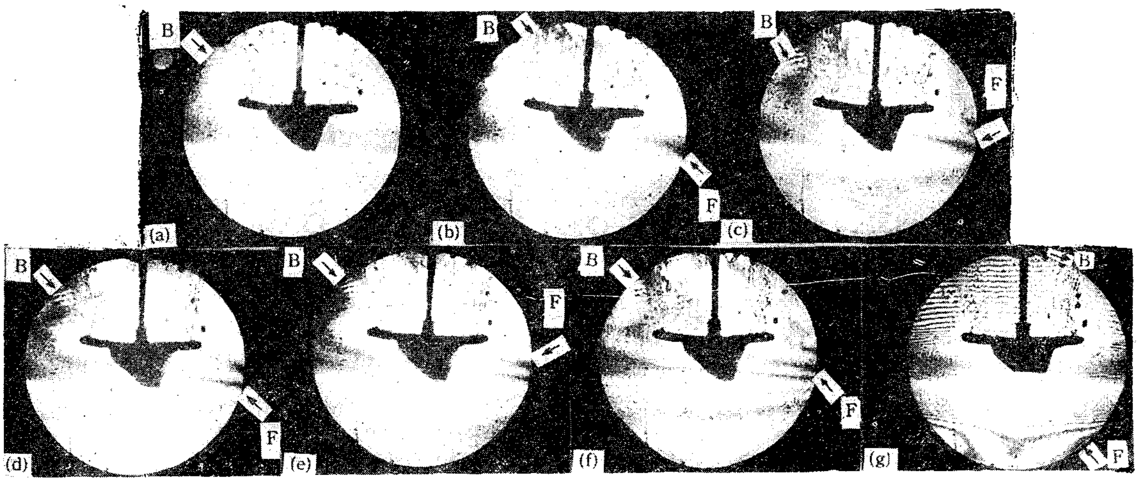

Fig. 2. Real holographic interferograms of α-LiIO$_3$ crystal growth in the case of $\boldsymbol{C} \| \boldsymbol{g}$. B, background fringes; F, interferograms.

of α-LiIO$_3$ with $\boldsymbol{C}\|\boldsymbol{g}$. The black stick, which is perpendicular to the plane in the figure is a seed stick. The circular plate, which is perpendicular to the stick (since the injected beam is parallel to the plate, it is shown as a black line that is also perpendicular to the stick), is the seed fitting plate. The seed in [0001] direction was fitted on the plate below it. An extension of the seed is the growing crystal of α-LiIO$_3$.

Fig. 2(a) is an initial reference hologram showing the growing process at $t = 0$ without any fringe below the seed plate. But there are some fringes and spots above the seed plate implying a buoyant plume rising from the solution. The origin of the plume is related to solution evaporation and vapour freezing on the crystal cell.

Fig. 2(b)—(f) show the holograms taken at = 11,21,31,41 and 49 min, respectively. In Fig. 2(b), there is only one fringe showing the occurrence of the concentration stratification after 11 min in growing process. Ten minutes later, the second fringe appeared, another 10 min, the third······. In the crystal-growing process, the density of the fringes increases consecutively and the gap between neighboring fringes decreases continuously. 40.16 h after the beginning of the growing process, the fringes started to degenerate near the crystal/solution interface. At a distance from the interface, there were a few stable fringes with larger curvature indicating that the system of supersaturated solution reached the steady concentration distribution, and the interference pattern no longer changed with the time.

4.2 *The Process of Crystal Growth in $C\perp g$ Arrangement*

Fig.3 shows the real time and *in situ* laser holograms of concentration distribution in the growing solution of α-LiIO$_3$ crystal when $\boldsymbol{C}\perp\boldsymbol{g}$. Compared with the $\boldsymbol{C}\|\boldsymbol{g}$ case, the seed plate was rotated by 90°, so the plate is parallel to the seed stick.

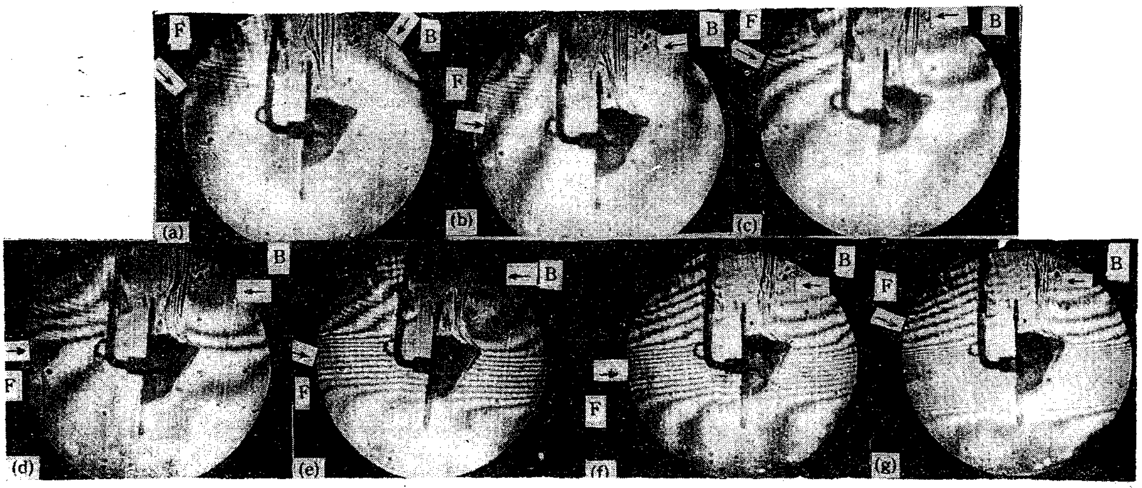

Fig. 3. Real holographic interferograms of α-LiIO$_3$ crystal growth in the case of $\boldsymbol{C}\perp\boldsymbol{g}$. B, background fringes; F, interferograms.

Fig. 3(a) is an initial reference interferogram. The shadow part at the upper left (marketed by B) is the background spots and plume pattern, which was not erased in the thermoplastic photoconductor. A black fringe in F region of the figures indicates that a gradient of the concentration in this region has been constructed. The gradient orientation is parallel to the $\{10\bar{1}1\}$ face. In the case of $\boldsymbol{C}\|\boldsymbol{g}$, the initial interferograms are also parallel to $\{10\bar{1}1\}$ face. It means that the crystallization-driven convection plays an important role in the formation of stratification at the initial growing process. Fig. 3 (b)—3(e) illustrates the evolution of the concentration distribution. Fig. 3(b) is a hologram taken at $t=100$ min. Three fringes were shown in the figure. The fringes are still parallel to $\{10\bar{1}1\}$ face. Fig. 3(c) and 3(d) were taken at 165 th and 230 th min, with 5 and 7 fringes in them, respectively. In this state, a new fringe was formed every 33 min. It was worthy to note that the direction of the interferograms deviated gradually from the original direction to the direction of the gravity $\boldsymbol{g}$. Fig. 3(e) and 3(f) give the concentration distribution corresponding to the growing process at $t=15.75$ and 17.75 h, respectively. At that moment, more than 10 parallel straight fringes were formed near the crystal/solution interface region, with their direction perpendicular to $\boldsymbol{g}$. But the orientation of fringes localized above the seed and at a distance from the interface was not perpendicular to $\boldsymbol{g}$. When distribution reached equilibrium, almost all the fringes in the solution above the seed became perpendicular to $\boldsymbol{g}$. The gap between the fringes decreased with time and tended towards degeneration, as shown in Fig. 3(g). The time τ, from initial state to the stable distribution, is equal to 39.96 h.

5 Conclusion

The following conclusions could be drawn.

1. The newly developed thermoplastic-photoconductor laser holographic record system could be adopted to study the process of crystal growth by real time observation in a transparent solution system. The period to make a hologram is shorter than any traditional methods, and the *in situ* operation process for recording, developing and reconstructing the holograms could be realized.

2. There is a steady concentration distribution field in an aqueous solution of α-LiIO$_3$ crystal grown by using the constant temperature evaporation method. In both $\boldsymbol{C}\|\boldsymbol{g}$ and $\boldsymbol{C}\perp\boldsymbol{g}$ experimental arrangements, the steady distribution periods τ are the same. When the temperature in the solution was maintained at 47.6℃, $\tau=40$ h.

3. The seed orientation of α-LiIO$_3$ influences the stratifying velocity of solution concentration dramatically. The stratifying velocity under the $\boldsymbol{C}\|\boldsymbol{g}$ condition is 2 times larger than that in the $\boldsymbol{C}\perp\boldsymbol{g}$ case.

4. It is possible to study the effect of the secondary force through the "rotary effect of interferogram" on the earth, which was caused by crystallization-driven convection at the initial stage of crystal growth. So far, people always think that the gravity is a first-class force for driving the fluid effect of the crystal growth

on the earth, other forces are all secondary ones that can only be investigated under microgravity conditions.

The experiments in space show that the crystal site may be drifted and the crystal orientation may be rotated in the process of crystal growth. This phenomenon brings trouble to theoretical workers because any site drift and the orientation change will certainly destroy the concentration distribution field, making the solution of the diffusive differential equation meaningless. We have found that in the system of α-LiIO$_3$ crystal growth, the steady distribution periods and the stable interference patterns are the same for both cases of $\boldsymbol{C} \perp \boldsymbol{g}$ and $\boldsymbol{C} \| \boldsymbol{g}$, implying that if only the process of crystal growth is kept stable, the solution of the convective-diffusion differential equation still possesses some conservatism, even though the crystal site is drifted and the crystal direction rotated.

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