Barium Nitrate Single Crystals Growth by Aqueous Solution Method

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Abstract The growing conditions of barium nitrate Ba(NO$_3$)$_2$ single crystals using the aqueous solution method have been studied. Supersaturation can be calculated by measuring the temperature of the solution and its equilibrium temperature. Supersaturation of Ba(NO$_3$)$_2$ was 0.7% at 32.0 °C and about 3% at 34.0 °C. The obtained single crystals have three kind of morphology: tetrahedral, cubic, and, rarely, dodecahedral. The normal growth rate is proportional to the supersaturation; it is necessary to make the solution below 5% supersaturation in order to obtain transparent Ba(NO$_3$)$_2$ single crystals. The normal growth rate for {111} faces was 2.51 × 10$^{-6}$ mm/s for the 0.7% supersaturation condition (32.0 °C), 6.43 × 10$^{-6}$ mm/s for the 3.0% supersaturation, and 7.01 × 10$^{-6}$ mm/s for the condition of 5.0% supersaturation. The quality of the grown crystals depends on the nature of the seed, the cooling rate employed, and the agitation of the solution. The faces of the obtained crystals have been identified using an X-ray diffractometer. The surface diffusion is responsible for the low growth rates of the {111} faces.

Key words Barium nitrate Ba(NO$_3$)$_2$, supersaturastion, aqueous solution method, growth rate.

1. Introduction

Barium nitrate Ba(NO$_3$)$_2$ is a new material for stimulated Raman scattering (SRS) converters that provides non-linear conversion of frequency radiation in lasers due to stimulated Raman scattering effect.\cite{1-3} Ba(NO$_3$)$_2$ single crystal is remarkable for optical applications. For example, as frequency converter in tunable lasers for expansion tuning range, for production of additional emission band combined with elements of doubling and summation of frequency, as optical filter for wave band 1.8-2.4 µm and so on.\cite{4,5}

Optical uniformity of barium nitrate single crystals is comparable with the quality of barium- and calcium-fluoride optical crystals. Anomalous birefrigence in some areas does not exceed 5 nm/cm. Barium nitrate crystals ensure the radiation wavelength for 40-50% conversion (@ 580 nm) of second-harmonic generation (SHG)-conversion for Nd-laser(0.53 µm). Achieved radiation conversion efficiencies into first and second Stock's are 60% and 19%, respectively.\cite{6}

The growth mechanisms of crystals from aqueous solution have been investigated either by interpreting surface topographies\cite{7,8} or by analyzing the normal growth rate of a crystal versus supersaturation.\cite{9,10} In those studies, dislocations of various types and stacking faults are observed.\cite{11,12} However morphological instability has been studied experimentally in the growth from dilute Ba(NO$_3$)$_2$ aqueous solution of crystal films with free surfaces.\cite{13} It has been also increasingly realized that kinetic parameters should be measured in situ on individual growth hillocks or growth layers instead of a face or a crystal as a whole, so as to obtain better understanding of the growth mechanism of crystal. The growth hillocks whose dislocations are identified on growing particular faces of Ba(NO$_3$)$_2$ crystals grow under well-controlled conditions.\cite{14} Recently, a new technique of real-time phase-shift interferometry was developed for precise in situ observation and measurement of crystal growth.\cite{15,16} However, an evaporation method was used to generate enough supersaturation for crystal growth and to compensate for the decrease of solute concentration during the growth.

In this study, we chose barium nitrate crystals, which grow in the aqueous solution under well-controlled con-
2. Experimental Procedure

The apparatus to grow crystals is illustrated in Fig. 1(a). To maintain the particular temperature, we used a water bath and a heater. The temperature stability was measured both by a Pt-100 resistance thermometer and by an auto-temperature controlling system. The 1 l Pyrex beaker was kept in the 25 l water bath with a temperature stability of ±0.1 °C. The vertical enamel-coated wire of 1 mm diameter with seed holder was rotated in the beaker by a speed-controllable motor.

The chemical purity of the Ba(NO$_3$)$_2$ reagent powder (Aldrich co.) was 99.99%. To obtain the seed crystals, Ba(NO$_3$)$_2$ solution was made by adding 45 g Ba(NO$_3$)$_2$ powder to 500 ml distilled water in a beaker of about 80 °C, and that aqueous solution without any Ba(NO$_3$)$_2$ solids was cooled in 3 days to room temperature, at which several small Ba(NO$_3$)$_2$ crystals appeared in the solution bottom, with decrease of solution level by evaporation. The small crystals have three kinds of morphology(Fig. 1(b)), which would be used as seed. The solubility of Ba(NO$_3$)$_2$ in water at several temperature was measured, and supersaturation was calculated by following expression.\(^\text{(1)}\)

\[
\sigma = \frac{c - c^*}{c^*} = S - 1
\]

where \(\sigma\) is the relative supersaturation, \(c\) is the concentration of the solution, \(c^*\) is the equilibrium saturation concentration and \(S\) is the degree of supersaturation.

A seed crystal, 3–5 mm long, was put in the seed holder with a \{111\} face perpendicular to the direction of rotation at a distance of 4 cm from the center. The solution in the Pyrex beaker was not running due to the rotation of the crystal. The growth duration was typically three days and the solution was slowly cooled with rate of about 0.7 °C/day.

The growth rate was measured by dividing crystal size increase by a given time, which was typically from two hours to three days. And we checked the relation between the growth rate and the rotation speed for 20 rpm and 40 rpm, respectively.

RINT2000 wide angle goniometer at 30 kV/mA using standard sample holder was used for the morphology of as-grown crystals and several faces of crystals was identified.

3. Results and Discussion

The data of solubilities Ba(NO$_3$)$_2$ in water was in Fig. 2. The solubility curves give mass soluble in a given volume of solvent, or saturation is often expressed by weight percent of solute in the saturated solution. Temperature and concentration, at which spontaneous crystallization occurs, are represented by the upper broken curve, generally referred as the super-solubility curve. Supersaturation
ration can be calculated by measuring the temperature of the solution and its equilibrium temperature. Supersaturation of Ba(NO$_3$)$_2$ was 0.7% at 32.0°C and 3% at 34.0°C. Provided that the solution is dilute, a plot of the logarithm of the solubility is a linear function of the reciprocal temperature. This plot gives solubilities proportional to 1/T. Through the calculation and simulation, Bennema obtained the linear law.

In order to make supersaturation of Ba(NO$_3$)$_2$ aqueous solution, there are two methods; evaporation of water and cooling of the solution. Sometimes two methods are used together. The Ba(NO$_3$)$_2$ crystals in Fig. 1(b) were grown by evaporation. When the evaporation process at constant temperature with above 5% supersaturation was continued to get larger crystals, the grown crystals were not transparent and became to be polycrystalline. But the Ba(NO$_3$)$_2$ crystal growth with 3% saturation make transparent single crystals (Fig. 3) both by evaporation method or by temperature decrease from 51.0°C to 34.0°C.

The growth rates of as-grown Ba(NO$_3$)$_2$ crystals with a {1̅1} face perpendicular to the direction of rotation (20 rpm) are as follows; the normal growth rate for {1̅1} faces was $2.51 \times 10^{-6}$ mm/s for the 0.7% supersaturation condition (32.0°C), and $6.43 \times 10^{-6}$ mm/s for the 3.0% supersaturation, and $7.01 \times 10^{-6}$ mm/s for the 5.0% supersaturation. So we conclude that the normal growth rate is proportional to the supersaturation. Besides temperature control, the uniform rotation of seeds is required so that stagnant regions or re-circulating flows are not produced, otherwise inclusions in the crystals will be formed. To study and achieve uniform and optimum transport of solute to the growing crystals, various seed rotation mechanisms have been used. When the rotation speed increased twice from 20 rpm to 40 rpm, the size of Ba(NO$_3$)$_2$ crystal grown at 40 rpm was almost same to that at 20 rpm. So rotation speed difference of 20 rpm is thought not to affect largely to growth rate. Growth rates for various growing conditions were summarized in Table 1.

All unwanted nuclei and the surface damage on the seed are removed by dissolving at a temperature above the saturation point. Growth is initiated after lowering the temperature to the equilibrium saturation. The quality of the grown crystal depends on the nature of the seed, cooling rate employed and agitation of the solution. Fig. 4 shows the morphology for one of as-grown Ba(NO$_3$)$_2$ single crystals (supersaturation of 3.0% at 34.0°C). We de-

![Fig. 3. Ba(NO$_3$)$_2$ crystals grown in 3% supersaturation; (a) Ba(NO$_3$)$_2$ crystals in 3% supersaturation by evaporation and (b) Ba(NO$_3$)$_2$ crystals in 3% supersaturation by lowering temp(51.0°C → 34.0°C).](image)

| Table 1. Growth rates of barium nitrate single crystals for various growing conditions. |
|------------------|------------------|----------|-------------------|
| temperature      | supersaturation  | rpm      | growth rate (mm/s) |
| 32.0°C           | 0.7%             | 20       | $2.51 \times 10^{-6}$ |
| 34.0°C           | 3.0%             | 20       | $6.43 \times 10^{-6}$ |
| 51.0°C           | 5.0%             | 20       | $7.01 \times 10^{-6}$ |
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Fig. 4. Morphology of barium nitrate single crystals (Supersaturation of Ba(NO$_3$)$_2$ was 3.0% at 34.0 °C).

terminated 1, 2 (the opposite side of 1), 3 and 4 faces by X-ray diffraction. 1, 2 and 3 revealed {111} faces and 4 revealed {100} face. By the crystallographic consideration, we could determine the other faces, like Fig. 4.

Ba(NO$_3$)$_2$ crystals take the habit with well-developed {111}, medium-{001} faces, occasionally smaller {210} faces. In other words, the following participate in the faceting: the {111} and {111} tetrahedron faces, the {100} cube face and rarely the {120} dodecahedron face. The present studies showed that the optimum growth rate of the crystal in the [100] direction, with the direction perpendicular to the direction of rotation, is $2.5 \times 10^{-6} - 6.4 \times 10^{-6}$ mm/s in the temperature interval 32-34 °C. Tendency of the growth rates for crystal faces as a function of supersaturation of the solution was also analyzed on the basis of the surface-diffusion model of Burton, Cabrera, and Frank (BCF).19 It was shown that surface diffusion is responsible for the low growth rates of {111} faces; in the case of {001} face, the mechanism is less important at higher values of supersaturation than volume diffusion. The growth rate of a face, i.e. advancement of its surface in the normal direction per unit time, depends upon many factors. Internal factors are the surface structure of faces, which in turn are related to the bulk crystal structure, and their degree of perfection. External factors are supersaturation, solute concentration which is related to solubility, temperature of the solution, solution composition, or stirred solution, presence of impurities. The dependency of crystal morphology and quality on growth temperature using seed obtained from the growth solution and at the crystal growth temperature is being studied.

4. Conclusion

We have grown transparent Ba(NO$_3$)$_2$ single crystals by aqueous solution method. The normal growth rate is proportional to the supersaturation, and it is necessary to make the solution in below 5% supersaturation to get transparent Ba(NO$_3$)$_2$ single crystals.

Supersaturation of Ba(NO$_3$)$_2$ was 0.7% at 32.0 °C and 3% at 34.0 °C. The rotation speed was not relative to the normal growth rate of Ba(NO$_3$)$_2$ crystals in solution. The quality of the grown crystal depends on the nature of the seed, cooling rate employed and agitation of the solution. As-grown Ba(NO$_3$)$_2$ crystals take the habit with well-developed {111} face, at which [111] direction is perpendicular to the rotation direction. Tendency of the growth rates for crystal faces as a function of supersaturation of the solution was also analyzed on the basis of the surface-diffusion model. The surface diffusion is responsible for the low growth rates of {111} faces. Rotation speed difference of 20 rpm is thought not to affect largely to growth rate.

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