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 by aqueous solution method have been studied. Supersaturation of $Ba(NO_3)_2$ was 0.7% at 32.0 ℃ and about 3% at 34.0 ℃. The obtained single crystals have three kind of morphology; the tetrahedron, the cube and rarely dodecahedron face. The faces of obtained crystals have been identified by X-ray diffractometer.

1. Introduction

The growth mechanisms of crystals from aqueous solution have been investigated either by interpreting surface topographies[1, 2] or by analyzing the normal growth rate of a crystal versus supersaturation.[3, 4] In these studies, dislocations of various types and stacking faults are observed.[5, 6] However morphological instability has been studied experimentally in the growth from dilute $Ba(NO_3)_2$ aqueous solution of crystal films with free surfaces.[7] 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.[8] Recently, a new technique of real-time phase-shift interferometry was developed for precise in situ observation and measurement of crystal growth.[9, 10] 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 conditions, in order to investigate how the growth of crystals is influenced by the growing conditions.

2. Experimental

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 a auto-temperature controlling system. The 1 ℓ Pyrex beaker was kept in the 25 ℓ water bath with a temperature stability of ± 0.1 ℃. The enamel coated wire of 1 mm diameter was rotated in the beaker by a rapid controlled motor.

The chemical purity of the $Ba(NO_3)_2$ reagent powder 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 of about 80 ℃, and that aqueous solution was cooled in 3 days to room temperature, at which several small $Ba(NO_3)_2$ crystals appeared in the solution bottom. 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.[11]

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

where σ 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 hanged to wire with a $\{1\bar{1}1\}$ 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 ℃/day.

The growth rate was measured by dividing crystal size increasement 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.

Figure 1(a), (b)

3. Results and Discussions

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. Supersaturation of $Ba(NO_3)_2$ was 0.7 % at 32.0 ℃ and 3 % at 34.0 ℃. 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.

Figure 2.

Through the calculation and simulation, Bennema obtained the linear law.[12] The growth rates of as-grown $Ba(NO_3)_2$ crystals with a $\{1\bar{1}1\}$ face perpendicular to the direction of rotation are summarized as follows; the normal growth rate for $\{1\bar{1}1\}$ faces for the one of supersaturation condition(0.7 %) was 2.51×10^{-6} mm/s and the other(3 %) was 6.43×10^{-6} mm/s. So we conclude that the normal growth rate is proportional to the supersaturation.[12]

The size of $Ba(NO_3)_2$ crystal grown at 40 rpm is almost same to that at 20 rpm. So rotation speed difference of 20 rpm is thought no to effect largely to growth rate.

Figure 3 shows the morphology for one of as-grown $Ba(NO_3)_2$ single crystals. We determined 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 crystallographical consideration, we could determine the other faces, like Fig. 3.

Figure 3

$Ba(NO_3)_2$ 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 $\{1\bar{1}1\}$ 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 $[1\bar{1}1]$ direction, with the direction perpendicular to the direction of rotation, is $2.5\times10^{-6}\sim6.4\times10^{-6}$ mm/s in the temperature interval 34~30 ℃.

4. Conclusions

We have grown $Ba(NO_3)_2$ single crystals by aqueous solution method.

Supersaturation of $Ba(NO_3)_2$ was 0.7 % at 32.0 ℃ and 3 % at 34.0 ℃. The rotation speed was not relative to the normal growth rate of $Ba(NO_3)_2$ crystals in solution. As-grown $Ba(NO_3)_2$ take the habit with well-developed $\{1\bar{1}1\}$ face, at which $[1\bar{1}1]$ direction is perpendicular to the rotation direction.

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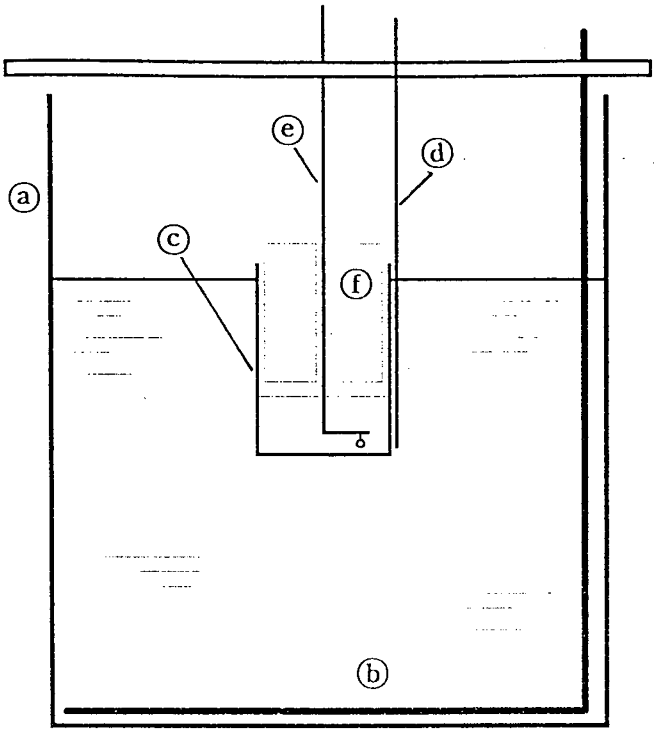
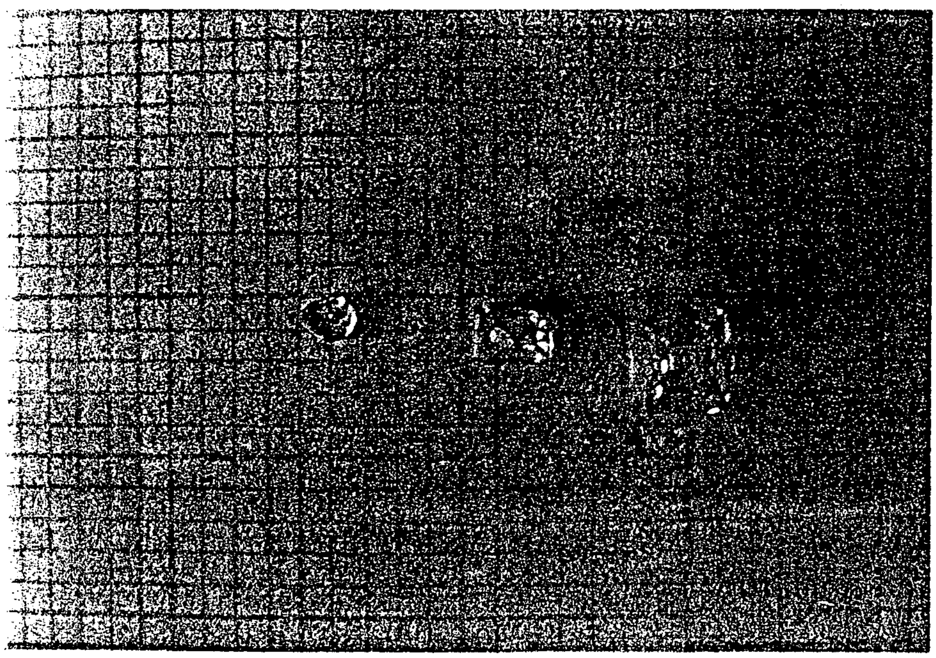


Fig. 1(a). A schematic drawing of the apparatus to grow $Ba(NO_3)_2$ crystals
ⓐ water bath ⓑ heater ⓒ Pyrex beaker ⓓ thermometer
ⓔ sample holder ⓕ insulator cover



1(b). Obtained three kinds of seed

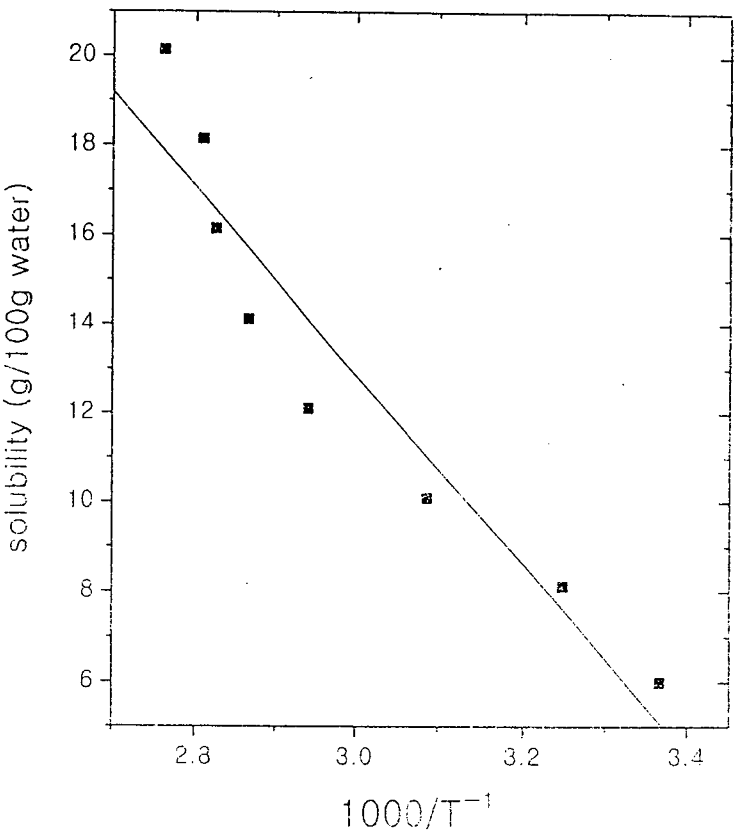


Fig. 2. Solubilities as a function of temperature

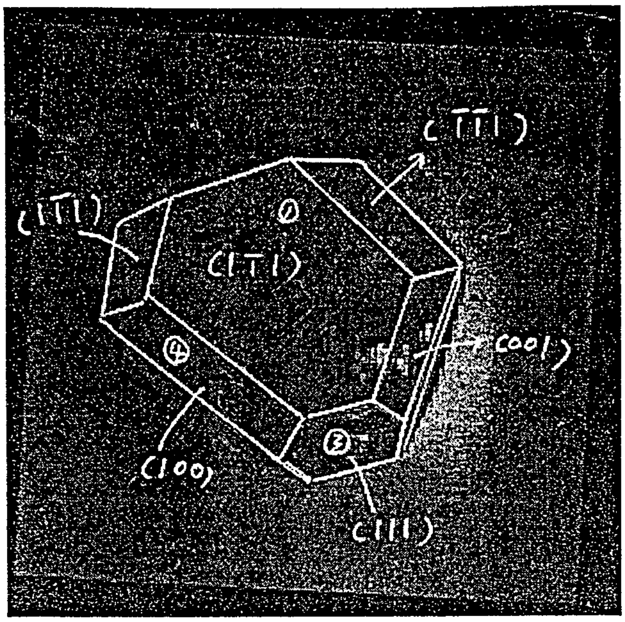


Fig. 3. Morphology of barium nitrate single crystals