Growth mechanism of NaBrO_3 crystals from aqueous solutions

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Abstract. To study the growth mechanism of $\{111\}$ faces of NaBrO_3 , crystals were grown at different supersaturations ranging from 2% to 8%. The growth mechanisms were investigated based on the growth rate versus supersaturation relation and from the surface features observed on $\{111\}$ faces. The growth mechanism of these crystals appear to be due to 2D nucleation. The growth rate curve has been further investigated using Ohara and Reid equations. Polynucleation model in two-dimensional nucleation growth theory is suggested as the most possible growth mechanism for these crystals in the present supersaturation range.

Keywords. NaBrO_3 ; supersaturation; growth rate.

1. Introduction

To understand the mechanism of growth of crystals from solution, several investigators have focused attention on growth kinetics. Among the crystals grown from solution, extensive studies have been made on K-alum (Bennema 1965), KCl (Klein-Haneveld 1971), ADP (Mullin and Gaska 1969), and KDP (Mullin and Amatavivadhana 1967). Kitamura *et al* (1982) carried out simultaneous growth and dissolution studies on NaClO_3 crystals.

Sodium bromate (NaBrO_3) belongs to the cubic tetrahedral class with point group 23. NaBrO_3 is isomorphous with NaClO_3 and exhibits properties like optical activity (Chandrasekharan and Madhava 1967) and piezoelectricity (Mason 1946). Although considerable information is available on the growth of NaClO_3 , there is no report on the growth of NaBrO_3 . Hence we planned to study the growth of NaBrO_3 crystals systematically. Preliminary results of these studies are reported in this paper.

2. Experimental

2.1 Solubility and supersaturation of sodium bromate

Solubility data on sodium bromate at various temperatures are not available. Hence solubility measurements were made at temperatures ranging between 25°C and 60°C. For this purpose approximate saturated solutions were prepared at the required temperatures by adding a known amount of solute to 100 ml of double distilled water. Sufficient care was taken to see that the solution was always slightly undersaturated. Then a crystal of known size and mass was introduced into the solution and held in the middle of the solution with the help of a holder. In most of the experiments, initially the crystal dissolved slightly and then it stabilized with the solution. The

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crystal was allowed to remain in this condition for about 6–8 h. When the crystal appeared to start growing, it was removed from the solution and its size and mass were again measured. During the whole process the solution in the jar was stirred and the process observed using a cathetometer. All these experiments were conducted in a constant temperature bath. The mass of the solute plus the loss of mass of crystal gives the solubility at that temperature. For each temperature, the solubility measurements were made at least 4 to 5 times and the average value taken as the solubility at that temperature. The variation of solubility with temperature is shown in figure 1.

Supersaturation of the solution is expressed as

$$S = \frac{C}{C_s} - 1, \quad (1)$$

where C is the concentration of the dissolved substance at a given moment, C_s the saturation concentration, and S the supersaturation.

2.2 Crystallization

All the crystals were grown from aqueous solutions at a constant temperature of 30°C at different supersaturations between 2% and 8%. A water circulation thermostat obtained from INSREF was employed which provides $\pm 0.05^\circ\text{C}$ constancy of temperature. The thermostat was initially adjusted to a temperature of 30°C.

Figure 1. Solubility data of sodium bromate.

Supersaturated solutions were prepared at temperature 2–3°C above 30°C and transferred into the crystallization jar (250 ml) until two thirds of it was filled with the solution. The jar was then closed with a rubber cork fitted with a thermometer. When the temperature reached 30°C, a seed crystal was introduced into the supersaturated solution. Seed crystals were grown in another beaker at 30°C by slow evaporation. The seed crystals were mounted on a plastic platform with the help of an adhesive. For growth rate measurements, initial and final dimensions of the crystal were measured using a travelling microscope. From these values and time of growth, the growth rates were estimated. The time of crystallization was not constant for all the crystals but varied from 10 to 36 h depending upon the supersaturation of the solution. In the present work all the crystals were allowed to grow in a static system.

3. Results and discussion

3.1 Growth rate versus supersaturation

Sodium bromate crystals grow in tetrahedral form bounded by two sets of $\{111\}$ faces as shown in figure 2a. Figure 2b shows the line diagram of the crystal faces. One set of $\{111\}$ faces grows to a larger size than the other. The larger faces are called major (111) faces and the other faces minor (111) faces. The present studies are confined to the major (111) faces which are more stable.

As the crystals are bounded by triangular $\{111\}$ faces, the edges of each face are along $\langle 110 \rangle$ direction. Hence, for the rate-of-growth experiments the initial and final dimensions of the crystals before and after the growth were measured along the three

Figure 2a.

Figure 2. a. Sodium bromate crystals grown at different supersaturations ($\times 3$) and b. line diagram of sodium bromate crystal faces.

$\langle 110 \rangle$ directions. The average of these was taken as the size of the crystal. Figure 2a shows some of the crystals grown at various supersaturations. It can be seen from the photograph that all the crystals grown under these supersaturations are bounded by two sets of $\{111\}$ faces as mentioned above with no change in morphology.

Growth rates of (111) faces of sodium bromate crystals were measured in about 50 different runs in a relative supersaturation range 2% to 8%. The measured growth rates were in the range 8×10^{-6} to 40×10^{-6} cm/sec. The rate of-growth data for different supersaturations is given in tables 1 and 2.

Figure 3a shows the plot of rate of growth versus supersaturation. Each point is the average of at least six measurements. Figure 3b shows the same plot with all the data points. It is clearly seen that the rate of growth increases parabolically with supersaturation with some scattering of data points at higher supersaturations. A similar observation was made in growth rate studies on sodium chlorate (Hosoya and Kitamura 1978) and barium nitrate crystals (Tsukamoto *et al* 1983). Tsukamoto *et al* (1983) attributed the scattering of data points at higher supersaturation in barium nitrate crystals to rapid nucleation of material on the walls of the vessel. In the present study no such nucleation was observed. But small tiny crystals were found on the base of the jar at higher supersaturation. This could be the reason for the scattering of data points at higher supersaturations. The variation of growth rate at the same supersaturation (figure 3b) could be due to differences in external and internal conditions in each growth experiment, such as turbulence, mass transfer caused by convection, temperature distribution in the crystallization chamber, or defect densities already present in the seed crystal. Growth rates at supersaturation lower than 2% were not measured due to the limitations in the present experimental conditions.

Table 1. Summary of the experimental data.

S (%)	$R(10^{-6})$ (cm/sec)
2.0	6.10
2.0	6.81
2.2	8.30
2.3	11.40
2.4	9.75
2.4	9.75
2.4	11.30
2.4	14.20
2.4	10.60
2.8	14.00
2.8	13.70
2.8	16.60
2.8	17.00
2.8	10.00
2.8	13.00
2.8	18.00
4.0	18.60
4.1	24.40
4.2	24.40
4.2	18.60
4.3	19.40
4.3	21.00
5.0	29.40
5.0	30.00
5.3	27.00
5.6	22.00
6.0	28.40
6.8	24.00
6.8	40.00
6.8	40.30
7.0	51.00
7.8	45.00
8.2	40.00

Table 2. Values (with standard errors) of slope and intercept in equations for 2D growth mechanism, which are calculated from curve fitting.

Parameter	Growth models		
	Mononuclear	Polynuclear	Birth and spread
Intercept	- 8.49 (± 0.18)	- 1.56 (± 0.22)	- 7.77 (± 0.18)
Slope	- 0.0078 (± 0.0025)	- 0.029 (± 0.003)	- 0.012 (± 0.002)
Regression coefficient	0.73	0.96	0.42

Figure 3. a. Plot of growth rate (R) versus supersaturation (S) for sodium bromate crystals and b. shows all the data points.

In growth rate studies on NaClO_3 crystals Hosoya *et al* (1978) obtained a parabolic curve at higher supersaturation, but the data of Bennema (1965) gave a linear growth rate plot at lower supersaturation. They concluded that the linear plot indicates growth due to screw dislocation mechanism and the parabolic curve points to growth due to two-dimensional mechanism. In the present work, the supersaturation range is higher than 2%. Hence it appears that the parabolic plot obtained in sodium bromate could be due to two-dimensional growth mechanism.

In two-dimensional nucleation growth theory three models have been put forward by Ohara and Reid (1973). The normal growth rates are expressed by the following equations:

(i) Mononuclear (mono-) model,

$$R = A_{\text{mono}} [\ln(1 + S_B)]^{1/2} \exp[-3B/T_g^2 \ln(1 + S_B)]; \quad (2)$$

(ii) Polynuclear (poly-) model,

$$R = [A_{\text{poly}}/T_g^2 (\ln(1 + S_B))^{3/2}] \exp[-3B/T_g^2 \ln(1 + S_B)]; \quad (3)$$

(iii) Birth and spread (B and S) model,

$$R = [A_{\text{B\&S}} S_B^{2/3} / \ln(1 + S_B)]^{1/6} \exp[-B/T_g^2 \ln(1 + S_B)]; \quad (4)$$

where the constants are given as

$$A_{\text{mono}} = \left(\frac{2}{\pi}\right) n_1^2 \bar{V} \left(\frac{V_m}{h}\right)^{1/2} S, \quad (5)$$

$$A_{\text{poly}} = 2\bar{V} \left(\frac{\sigma n_1}{k}\right)^2 h^{1/2} V_m^{5/2}, \quad (6)$$

$$A_{\text{B\&S}} = 2h^{1/6} V_m^{5/6} \left(\frac{\bar{V}}{\pi}\right)^{1/3} \left(\frac{n_1 D_s C_{\text{SE}}}{X_s}\right)^{2/3}, \quad (7)$$

where n_1 is the equilibrium number of mono-molecules on the surface, $\bar{V}$ the average speed of surface adsorbed molecule, V_m the volume of a molecule, h the step height as lattice constant, D_s the solution diffusion coefficient on the surface, C_{se} the equilibrium surface concentration, X_s the mean diffusion distance in mean lifetime of adsorbed molecule on the surface, S_B the solution supersaturation, T_g the growth temperature and σ the interfacial free energy.

$$B = \frac{\pi h \sigma^2 V_m}{3 K^2}. \quad (8)$$

The three equations can be rewritten as follows:

$$\ln \left[\frac{R}{[\ln(1 + S_B)]^{1/2}} \right] = - \frac{3B}{T_g^2 \ln(1 + S_B)} + \ln A_{\text{mono}}, \quad (9)$$

$$\ln [R \cdot T_g^2 (\ln(1 + S_B))^{3/2}] = - \frac{3B}{T_g^2 \ln(1 + S_B)} + \ln A_{\text{poly}}, \quad (10)$$

$$\ln \left[\frac{R}{S_B^{2/3} [\ln(1 + S_B)]^{1/6}} \right] = - \frac{B}{T_g^2 \ln(1 + S_B)} + \ln A_{B \& S}. \quad (11)$$

In the present work, an attempt has been made to assess the applicability of (9), (10) and (11). It can be seen from these equations that a linear plot should be obtained by plotting left hand side versus $1/[\ln(1 + S_B)]$ for all the three equations. The three-plots are shown in figures 4a, 4b and 4c. The solid lines are obtained by least-squares fit. All the three plots are roughly linear with some scattering of data points. It can be seen from these plots that the data points fit best with (10) (figure 4b); next comes (9); the fit with (11) is clearly the poorest. The values of slopes, intercepts and regression coefficients were obtained by computation and are given in table 2 along with their standard errors. From an observation of the values of regression coefficient in the three models, relation (10) for the poly-model fits best with the present experimental data.

However, it is not possible to draw conclusions about the relative merits of the three equations very forcefully because of the limitations in the experimental facilities. Under the present conditions it appears reasonable to attribute the growth mechanism of sodium bromate to polynuclear model in two-dimensional nucleation theories.

3.2 Surface studies

It is known that when well-developed crystal faces are observed under the microscope, they sometimes reveal typical growth features, from which the growth mechanism can be understood. To probe the growth mechanism of NaBrO_3 crystal further, surface studies were carried out on these crystals. The crystals grown were gently dried with tissue paper and immediately transferred to a Meopta reflection microscope to study the surface. Figure 5a shows a photomicrograph of typical growth steps observed on (111) faces of NaBrO_3 . These steps are triangular with curved edges, the edges are parallel to $\langle 110 \rangle$ direction, and the steps are distributed randomly on the surface. The shape of the spiral steps or hillocks is controlled by the roughness of the steps. If

Figure 4. Plots of the data for examination of **a.** mononuclear model, **b.** polynuclear model and **c.** birth and spread model for sodium bromate crystals.

the step is rough, i.e. kink density is high, the step can advance independently of crystallographic direction, which leads to a circular step. If the step is smooth it becomes more polygonalized. Perhaps higher kink density is responsible for the formation of the present steps.

Figure 5. a - b.

Figure 5. a. Independent macroconcentric steps on (111) faces of sodium bromate crystals ($\times 120$); b. and c. interlaced pattern on (111) faces of sodium bromate crystals ($\times 300$).

Figures 5b and 5c show an interlacing pattern of the steps of neighbouring sources. Different types of cooperation or interaction among the steps may take place depending on the mutual separation, step height, etc. Figure 5b shows smooth interlacing of the steps of two neighbouring sources, whereas a line is observed along the boundary at the intersection of the steps from the two neighbouring sources shown in figure 5c. This could be due to the interaction of steps of different heights which appear similar to a fault line. In the present study no growth spirals were recorded on these crystals.

These surface features together with the growth rate studies show that the growth mechanism of NaBrO_3 crystal in the present supersaturation range could not be due to screw dislocation mechanism but appears to be due to two-dimensional growth mechanism.

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References

- Bennema P 1965 *The rate of growth of crystals from slightly supersaturated solutions*, PhD Thesis, Technical University of Delft, Delft
- Chandrasekharan S and Madhava M S 1967 *Acta Crystallogr.* **23** 911
- Hosoya S and Kitamura M 1978 *Miner. J.* **9** 73

- Hosoya S, Kitamura M and Miyata T 1978 *Miner. J.* **9** 147
Kitamura M, Kouchi A, Hosoya S and Sunagawa T 1982 *Miner. J.* **11** 119
Klein-Haneveld H B 1971 *J. Crystal Growth* **10** 111
Mason W P 1946 *Phys. Rev.* **70** 529
Mullin J W and Gaska G 1969 *Canadian J. Chem. Eng.* **47** 483
Mullin J W and Amatavivadhana A 1967 *J. Appl. Chem.* **20** 153
Ohara M and Reid R C 1973 in *Modelling crystal growth rates from solutions* (New Jersey: Prentice-Hall, Inc.)
Tsukamoto K, Ohba H and Sunagawa T 1983 *J. Crystal Growth* **63** 18