Growth mechanism of NaClO$_3$ and NaBrO$_3$ crystals from aqueous solutions

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Abstract. A study of growth rates of NaClO$_3$ and NaBrO$_3$ has been carried out using a small growth cell by *in situ* observation. Normal growth rates of {100} faces of NaClO$_3$ and {111} faces of NaBrO$_3$ along $\langle 110 \rangle$ direction are measured under relatively high supersaturation ranging from 3–8%. In the initial stages of growth, {100}, {110} and {111} faces develop in NaClO$_3$ and gradually all the faces are replaced by the {100} faces only. In the case of NaBrO$_3$, mostly {111} faces develop with occasional occurrence of small {100} faces at the intersection of {111} faces. The growth mechanisms are investigated from growth rate vs supersaturation plots and from the observations of surface features. In the present supersaturation range, the growth mechanism appears to be due to two-dimensional growth mechanism.

Keywords. NaClO$_3$; NaBrO$_3$; supersaturation; growth mechanism.

1. Introduction

The mechanism of crystal growth from aqueous solutions has been extensively studied both theoretically and experimentally. Growth rate measurements under well controlled growth parameters such as temperature, supersaturation and impurities are of great importance in such studies.

Considerable amount of work has been reported on the growth rate measurements from solutions using different growth apparatus. Botsaris *et al* (1966) studied rate of growth of KCl crystal from the change in weight after the experiment. Bennema (1965) and Schuz (1968) studied the growth rates of K-alum, KCl etc using sensitive weighing methods at different supersaturations and proposed possible growth mechanisms.

By the above methods, though growth mechanisms can be understood, no information on actual growth process can be obtained. Hence, several research workers (Kozlovskii 1958; Albon and Dunning 1959; Lemmlein *et al* 1960) have focused their attention on *in situ* observation of growth of single crystals. Davey and Mullin (1974) investigated the movement of growth layers on {100} faces of ADP crystals using a small growth cell. Hosoya and Kitamura (1978) developed a sophisticated apparatus for *in situ* observation and studied the growth of NaClO$_3$ crystals. Tsukamoto and Sunagawa (1990) made a systematic study of the growth of KCl in the presence of Pb ions.

Though we have reported studies on growth of NaClO$_3$ and NaBrO$_3$ crystals, they were largely confined to bulk

growth, etching and physical properties (Kishan Rao and Sirdeshmukh 1978, 1983; Kishan Rao and Surender 2001; Kishan Rao *et al* 2002). A systematic study on the growth of NaBrO$_3$ crystals at various supersaturations was undertaken and the possible growth mechanism was explained (Surender and Kishan Rao 1995). To understand the actual growth process of NaBrO$_3$ crystals a study by *in situ* observation of the growth of these crystals is undertaken. In order to standardize the apparatus used, we have also undertaken the study of growth of NaClO$_3$ crystals, though there is considerable amount of work on these crystals.

Although NaClO$_3$ and NaBrO$_3$ are isomorphous, practically no work is reported on the growth of NaBrO$_3$ by this method. This may be because of its inconvenient pyramidal growth habit. By further studies it may be possible to find ways for modifying the habit of these crystals to suit practical applications.

2. Experimental

All the crystal growth experiments were carried out using a small constant temperature bath made up of perspex with dimensions $l = 20$ cm, $b = 14$ cm, $h = 12$ cm, procured from INSREF which provides a temperature constancy of $\pm 0.05°C$. The lid of the temperature bath was slightly modified as in figure 1 so that the growth cell can be fixed properly. In the present work, the growth cell used was made up of glass with dimensions $l = 4$ cm, $b = 4$ cm, $h = 3.5$ cm. It was completely closed with a glass window having a small hole for inserting a thermocouple. The

thermocouple was connected to a digital temperature indicator for recording the actual growth temperature of the solution. The complete set up was kept under a Meopta transmission microscope without touching it. All the growth experiments were observed under a low power magnification of 4×6. The line diagram of the experimental set up is shown in figure 1.

In the present work, all the crystal growth experiments were carried out at a constant temperature of 30°C and at different supersaturations ranging from 3–8%. The supersaturated solution (already prepared in another bath) was transferred into the growth cell after the temperature of the bath reached 30°C. It was allowed to stabilize for about 10–15 min to attain constancy in temperature (30°C) of the solution. A good quality seed crystal was introduced into the solution and kept at the bottom of the growth cell (seed crystals were already prepared in another beaker by slow evaporation). Then the temperature of the solution was slowly raised by 1 or 2°C above the growth temperature in order to dissolve any microparticles present in the solution. Then the temperature of the solution was brought back to 30°C. When the temperature of the solution was raised, the seed crystal started dissolving initially due to the instantaneous slight undersaturation of the solution. It recovered to its initial size after the temperature reached 30°C. When the stability was established,

the growth rate measurements were initiated with the help of graticule attached to the eye-piece and photographs were taken at fixed intervals.

3. Results and discussion

3.1 *Growth of sodium chlorate and sodium bromate crystals*

Figure 2 shows photographs of the complete recovery process of a seed crystal of $NaClO_3$ of size 1·5 mm in length and 1 mm in breadth. As discussed in the earlier section, the seed crystal gets dissolved as the temperature is raised above saturation temperature giving rise to rounded edges. As the temperature is brought back to 30°C, the seed continues to have rounded edges at 0 min as shown in figure 2a. During the recovery process, small {110} and {111} faces appear in addition to predominant {100} faces during the first 4 min as shown in figures 2c and d. As growth proceeds further, {110} and {111} faces gradually diminish while {100} faces develop and eventually the crystal is bounded by {100} faces only. These results are similar to those observed by Hosoya and Kitamura (1978) on $NaClO_3$ crystals.

It is interesting to note that the time of complete recovery depends upon the size of the seed crystal employed. It has been observed that for smaller seeds of length 1·5 mm and breadth 1 mm, it takes about 8 min to recover completely, while for still larger seeds, the time of complete recovery increases. It is observed in the growth experiments that some thick growth layers are formed as shown in figure 2e. It appears that the growth layers originate from the edges and spread towards the centre of the crystal faces. These growth layers are called as kinematic waves (Kitamura *et al* 1982).

It is well known that $NaBrO_3$ crystals grow in pyramidal form bounded by two sets of {111} faces. Hence, in the present growth experiments small pyramidal seed crystals of $NaBrO_3$ about 1·0 mm along ⟨110⟩ direction are used for growth experiments (seed crystals were already grown by slow evaporation). The same growth procedure as that of $NaClO_3$ has been adopted for the growth of these crystals also. The growth process is completely recorded with the help of photographs. Figure 3 shows complete recovery of $NaBrO_3$ seed crystal with time for a supersaturation of 3%. It can be observed from these photographs that in the initial stages of growth {100} faces also appear to grow apart from {111} faces. However, {111} faces grow at a faster rate than {100} faces and eventually the crystals are by and large bounded by usual {111} faces and some {100} faces at the intersection of {111} faces. Further, it may also be observed from these photographs that some small tiny crystals appear at the base of the jar apart from the crystal under observation. This may be due to small fluctuations in the supersaturation during the growth process.
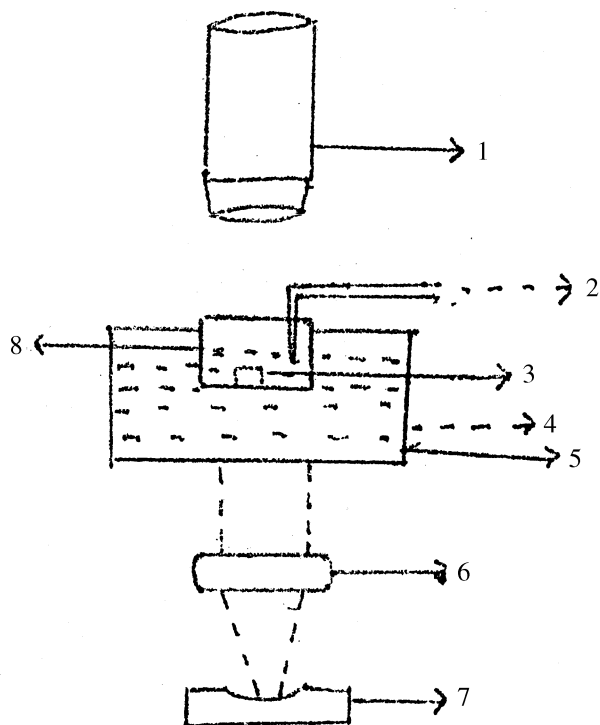

Figure 1. Line diagram of *in situ* growth set up (1. Microscope (eye-piece), 2. thermocouple, 3. seed crystal, 4. water, 5. temperature bath, 6. light condensing system, 7. light source and 8. growth cell).
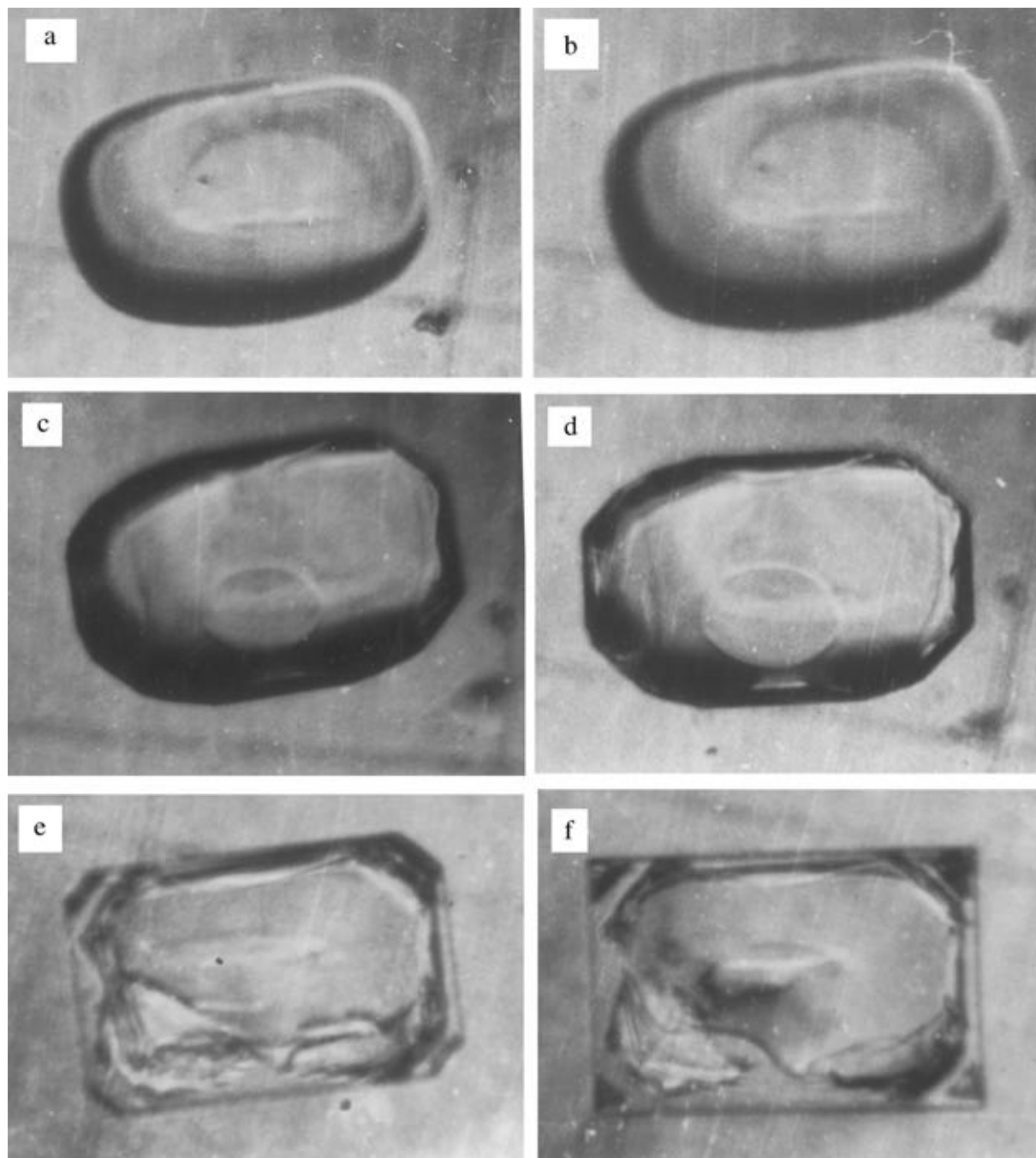
Figure 2. Series of photographs showing the growth process of $NaClO_3$ seed crystal with time in min ($M \times 25$): **a**. 0 min, **b**. 2 min, **c**. 4 min, **d**. 6 min, **e**. 10 min and **f**. 12 min.

3.2 *Growth rate vs supersaturation of sodium chlorate and sodium bromate crystals*

For $NaClO_3$ crystals, the change in size (shift) along $\langle 100 \rangle$ direction is taken for growth rate measurements whereas shift along $\langle 110 \rangle$ direction is taken for sodium bromate crystals. From the linear plots of length vs time obtained for $NaClO_3$, the growth rates at different supersaturations are estimated from their slopes. In case of $NaBrO_3$, as these plots are not linear, total increase in the size of the crystal per unit time is taken as the growth rate parameter.

Figures 4a and b show the plots of growth rate vs supersaturation for $NaClO_3$ and $NaBrO_3$ crystals, respectively. Each data point in both the plots is an average of atleast six measurements. It is clearly seen that the growth rate increases parabolically with supersaturation in both the crystals with some scattering of data points at higher supersaturations. Similar parabolic trend was observed in sodium
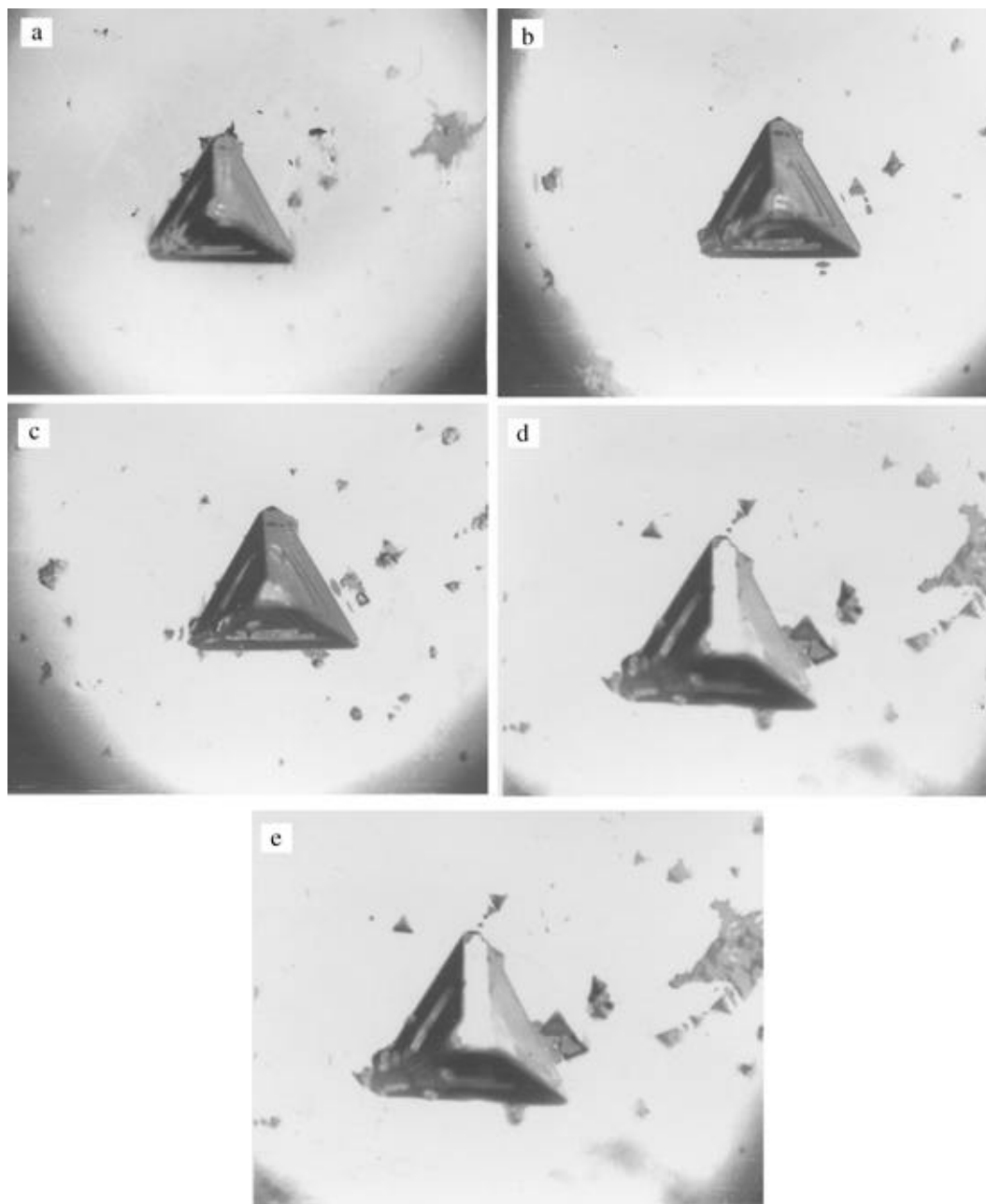
Figure 3. Series of photographs showing the growth process of $NaBrO_3$ seed crystal ($M \times 25$): **a**. 0 min, **b**. 2 min, **c**. 5 min, **d**. 10 min and **e**. 30 min.

chlorate (Hosoya *et al* 1978) at relatively higher super-saturations above 2% whereas a linear trend was observed by Bennema (1965) at lower supersaturations. They concluded that the linear plot indicates growth due to screw dislocation mechanism and the parabolic curve indicates the growth due to two-dimensional mechanism.

In the present work the supersaturation starts from 3%. Hence, it appears that the parabolic trend observed in both the crystals suggests that the growth of these crystals could be due to two-dimensional growth mechanism. Similar observation was made (Surender and Kishan Rao

1995) in the case of bulk growth of $NaBrO_3$ crystals. To understand the growth mechanism further, surface studies also have been carried out on these crystals.

3.3 *Surface studies*

It is well known that when freshly grown crystal faces are observed under a reflection microscope, sometimes they reveal typical growth features from which the growth mechanism can be understood. Hence, to probe further
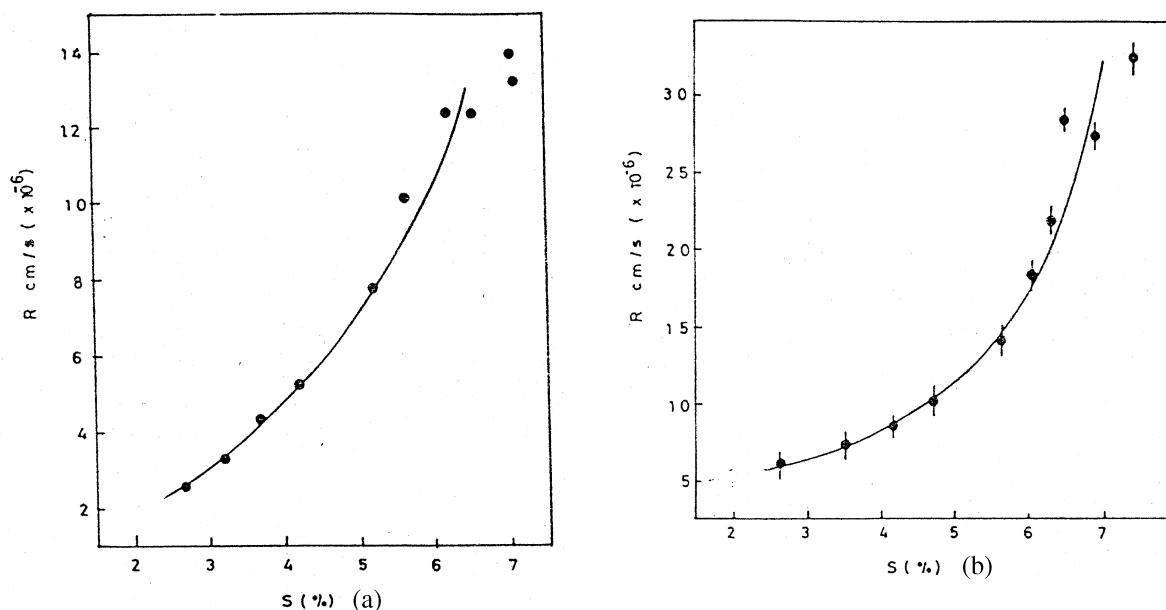
Figure 4. Plot of growth rate versus supersaturation for **a**. $NaClO_3$ and **b**. $NaBrO_3$.
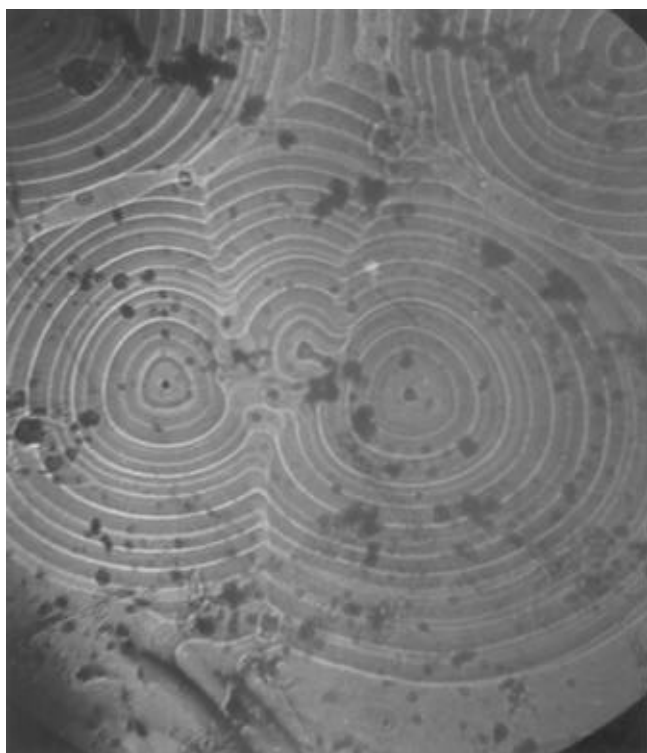

Figure 5. Typical surface features observed on (111) faces of $NaBrO_3$ ($M \times 150$).

the growth mechanism of these crystals, surface studies have been carried out on as-grown faces of these crystals. The crystals grown are gently dried with a tissue paper and are immediately transferred to the Meopta reflection

microscope. It is interesting to note that none of the as-grown {100} faces of $NaClO_3$ revealed any growth features whereas as-grown {111} faces of $NaBrO_3$ revealed typical triangular concentric pattern of hillocks. Similar observations were reported on {111} faces of $NaBrO_3$ crystals (Kishan Rao and Surender 2001) during bulk growth rate studies of these crystals and on $Pb(NO_3)_2$ (Solc and Sohnel 1973). Figure 5 shows a typical interlacing growth hillocks pattern. These hillocks are triangular in shape with their edges slightly curved and oriented parallel to the edges of the crystal faces i.e. along ⟨110⟩ direction, reflecting the three-fold rotational symmetry of the faces. No satisfactory interpretation of these hillocks has been given in the literature. However, Sangwal (1989) points out that they are produced when the supersaturation at some points on the growing surface of a crystal is higher than at other parts of it. Thus these points act as centres of repeated two-dimensional nucleation for growth fronts, which spread and pile up on the growing surfaces. Further, he pointed out that the number and location of the growth centres probably depends on temperature, supersaturation, crystal face etc. Depending upon these factors, sometimes, independent growth hillocks and interlacing growth patterns are observed. It is important to mention that no spirals were observed on these crystal faces.

The surface features together with the parabolic trend of the growth rate studies suggest that the growth mechanism of $NaBrO_3$ crystals appear to be due to two-dimensional growth mechanism. Though no surface features are observed on {100} faces of $NaClO_3$ crystals, the parabolic trend of growth rate studies suggests that the growth of $NaClO_3$ crystals also takes place via a two-dimensional growth mechanism.

However, it is not possible to draw conclusions very forcibly because of the limitations in the experimental facilities. Finally, we conclude that under present conditions it appears reasonable to attribute the growth mechanism of these crystals in the present supersaturation range to two-dimensional growth mechanism. However, further studies are needed to understand about the absence of growth features in $NaClO_3$ crystals.

References

Albon N and Dunning W J 1959 *Acta Crystallogr.* **12** 219

Bennema P 1965 *The rate of growth of crystals from slightly supersaturated solutions*, Ph.D. Thesis, Technical University of Delft, Delft
Botsaris D G, Mason E A and Reid R C 1996 *J. Chem. Phys.* **45** 1893
Davey R J and Mullin J W 1974 *J. Cryst. Growth* **26** 45
Hosoya S and Kitamura M 1978 *Miner. J.* **9** 73
Hosoya S, Kitamura M and Miyata T 1978 *Miner. J.* **9** 147
Kishan Rao K and Sirdeshmukh D B 1978 *J. Cryst. Growth* **44** 533
Kishan Rao K and Sirdeshmukh D B 1983 *Cryst. Res. Technol.* **9** 1125
Kishan Rao K and Surender V 2001 *Bull. Mater. Sci.* **24** 665
Kishan Rao K, Surender V and Saritha Rani B 2002 *Bull. Mater. Sci.* **7** 641
Kitamura M, Kouchi A, Hosoya S and Sunagawa I 1982 *Miner. J.* **11** 119
Kozlovskii M I 1958 *Sov. Phys. Cryst.* **3** 206
Lemmlein G G, Dukova E D and Chernov A A 1960 *Sov. Phys. Cryst.* **5** 634
Sangwal K 1989 *Prog. Crystal Growth & Charact.* **19** 216
Schuz W 1968 *Z. Kristallogr.* **128** 36
Solc Z and Sohnel O 1973 *Krist. Technol.* **8** 811
Surender V and Kishan Rao K 1995 *Bull. Mater. Sci.* **18** 289
Tsukamoto K and Sunagawa I 1990 *J. Cryst. Growth* **99** 150