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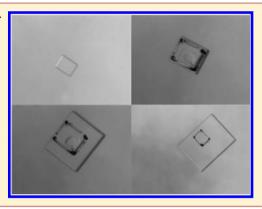
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Nongrowing Faces of Sodium Chlorate Crystals in Supersaturated Solution

Branislava M. Misailović, Dragana A. Malivuk, Andrijana A. Žekić, and Mićo M. Mitrović*,

ABSTRACT: The results of investigations of {100}, the nongrowing faces of sodium chlorate crystals in supersaturated solutions, are presented. It occurred that some of the faces did not grow, whereas the neighbor faces of the same crystals grew. The dissolution and refaceting of the crystals did not affect the probability of the nongrowing face appearance and the reduction of the range of face growth rates. Nongrowing faces are very stable; they start to grow at a relatively high supersaturation, face by face or several faces simultaneously. The order of the start of the growth is random, subsequently grown neighbor or opposite faces. Possible reasons for coexistence of growing and nongrowing faces, Ostwald ripening, microscopic conditions in the crystallization cell, microstructure of crystal face, and the impurity effects are discussed.



■ INTRODUCTION

Under the same external conditions, different crystals of the same material grow at different rates. 1-3 This phenomenon, termed as growth rate dispersion, is still not understood well. The dispersion of growth rates can be described by the finite mixture of normal distributions. Distribution maxima probably correspond to different activities of dominant dislocation groups, while the maxima width correspond to the dislocation perimeter.⁴ The maxima shift during the growth is probably a consequence inherent to crystal growth rate changes.^{5,6}

It is shown that in the supersaturated solution, there exist among the growing crystals those that did not grow in particular directions: sodium chlorate in (100), 7,8 KDP in [001],^{6,7,9} Rochelle salt in [001],⁷ calcium sulfate in [001],¹⁰ and sodium perborate crystals.¹¹ Many of these crystals stopped their growth after significant dissolution and refaceting. Otherwise, a small amount of dissolution and refaceting does not affect growth rate significantly.5

The existence of the "dead zone" for crystal growth, which was confirmed for many substances, is usually explained by the presence of impurities. 12 Immobile impurities adsorbed on the crystal face may completely block step propagation. 13,14 Dithionate impurity gradually decreased the step velocity of the {111} faces of sodium chlorate crystals. 15 It has been shown recently 16 that at a low supersaturations coexistence of growing, nongrowing, and dissolving sodium chlorate crystals exist.

In this paper, the results of investigations of {100} nongrowing faces of sodium chlorate crystals in supersaturated solutions will be presented. The stability of these faces and influence of dissolution and refaceting on their appearance was investigated.

EXPERIMENTAL SECTION

The aim of our experiments was to investigate the growth of small sodium chlorate crystals with nongrowing faces in aqueous solution. The analar grade of this system (99% purity) was used. The relative solution supersaturation $\sigma = (C - C_0)/C_0$ (C and C_0 are the actual and saturated solution concentrations) was changed during the experiment by varying the solution temperature T. The concentration C was calculated on the basis of the empirical formula $C = 0.226T(^{\circ}C) +$ 44.38 (g of NaClO₃/100 g of solution).¹⁵ The solution was prepared by equilibrating an excess of crystals with deionized water for 3 days at a saturation temperature of $T_s = (31.0 \pm 0.1)$ °C. Corresponding concentration, C = 51.386 g of NaClO₃/100 g of solution, was kept constant the during growth runs in all experiments. Saturated solute concentrations C_0 at growth temperatures T are calculated using the previous formula.

The crystal growth carried out in a crystallization cell, described previously. 17 The cylindrical crystallization chamber had the solution capacity of about 15 mL. The velocity of the solution at the bottom (around the crystals) and at the top of the chamber was about 0.05 and 0.5 mm/s, respectively. Crystals were nucleated in the cell by introducing air bubbles through a needle into the cell. The nucleation of the crystals was performed at $T_p = (28.0 \pm 0.1)$ °C.

Between 10 and 20 of the crystal nuclei, sufficiently distant from their closest neighbors as to avoid intergrowth during the growth, were selected for detailed growth observation during one growth run. Initial crystal sizes were 0.024-0.313 mm.

Our attention was occupied by the crystals with nongrowing faces. Growth in (100) direction of sodium chlorate evolves through growth of two {100} faces at opposite sides of the crystal. Growth rate in the $\langle 100 \rangle$ direction is the sum of growth rates of $\{100\}$ and $\{\overline{1}00\}$ faces, that is, $R_{\langle 100 \rangle} = R_{\{100\}} + R_{\{\overline{1}00\}}$. The distinction between the growth rates of opposite faces was difficult. The calculation of $R_{(100)}$ from the

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crystal length—time dependence is simple. For determination of the {100} face displacement, a reference point is necessary.

An optical microscope Nikon SMZ800 supplied by camera Luminera, Infinity 1, is used for analysis of the pictures of the crystals. We measured the crystal length changes in $\langle 100 \rangle$ directions and displacement of $\{100\}$ faces with an accuracy of about $\pm 2~\mu m$.

Without a reference point, it is impossible to conclude whether one of the opposite faces are nongrowing. The reference point (object) can be inside the crystals (visible defects) or near the crystal in the cell (marker on the bottom of the cell). Because of that, we performed two types of experiments.

Type 1: Experiments with dissolution and refaceting. Most of the observed crystals had no visible defects. If defects are present in the crystals, they changes during growth, so they cannot be a reference points. The reliable reference points were obtained by partial dissolution followed by the refaceting of crystals. Defects formed on the border between seed and the newly grown portion had no further changes; they were good reference points for face displacement measurement.

Type 2: Experiments with external markers. The bottom of the cell was randomly scratched. These scratches were reference objects for the crystal length measurements. The problem in this type of the experiments was that the crystal movements were due to the solution flow. Only motionless crystals could have scratches as reference objects. Approximately during the first hour of growth, most of the crystals moved on the bottom of the cell. Approximately 1–3 of the 10–20 observed crystals, after that period, became motionless in different moments. They stayed at the same positions for 1–2 h.

As we will show later on, the dissolution and refaceting did not affect the probability of appearance of nongrowing faces, and crystals continued their growth at rates practically independent of the conditions of nucleation, which are difficult to control. Besides that, the reference points were easier to obtain in type 1 experiments, and the motionless period in the type 2 experiments was relatively short. Because of that, we performed many more type 1 experiments in which the light movement of the crystals had no influence on measurement errors; therefore it was possible due to a longer observation (markers moving with crystals). Experiments of type 2 were performed only in order to test the influence of dissolution and refaceting on the existence of nongrowing faces.

The type 1 experiments consisted of three parts. In the first part, the crystals were nucleated and grown for about 3 h at a $T = (28.0 \pm 0.1)$ °C. The dissolution and refaceting of crystals were performed during the second part of the experiments. The temperature of the solution was increased to the dissolution temperature $T_{\rm d}$ = (34.0 \pm 0.1) °C with heating rate of about 0.5 °C/min. The solution was kept at this temperature for about 25 min. In that period, the dissolution and rounding of the observed crystals occurred. At the end of dissolution, crystal size in (001) direction was decreased for a minimum of 20%. Some crystals completely dissolved, the others were used as seeds for further growth performed in the third part of the experiments. After the dissolution, the temperature of the solution was rapidly decreased to a growth temperature of $T = (28.0 \pm 0.1)$ °C, the same as in the first part of the experiments. Meanwhile, the refaceting of the crystals was completed. This procedure provided instantaneous refaceting of the crystals, which had clear borders between the dissolved and newly growing portion.

In order to test stability of nongrowing faces, the third part of experiments was performed in two ways: (a) the growth temperature was kept for about 3 h at 28.0 °C in five experiments; (b)the growth temperature was decreased below 28.0 °C. During these parts of the experiments, we observed the behavior of the crystals that had only and at least one nongrowing face. After the growth at T = 28.0 °C, the solution temperature gradually decreased in steps of 1.0 °C until 18.0 °C. At each growth temperature, the solution was kept for about 30 min.

Decreasing the temperature during the third part of the experiments caused a significant increase in the crystal growth rate. Because of that they started intergrowing with their neighbors. Experiments were ended when the last crystal with a nongrowing face intergrew with its

neighbors. Only two experiments were prolonged to a temperature of 18.0 $^{\circ}\mathrm{C}.$

The $R_{\langle 100\rangle}$ was determined from crystal length versus time dependence, whereas $R_{[100]}$ and $R_{[\overline{100}]}$ were determined from corresponding face displacement versus time dependence. The initial crystal growth rates were calculated using the first two experimental data points, pertaining to the first 20–30 min of growth. The stabilized growth rates were calculated using two experimental data points measured after 3 h of growth. Average growth rates of motionless (at least 1.5 h) crystals, in type 2 experiments, as well as the average growth rates after the dissolution and refaceting in experiments type 1, were determined by the least-squares method.

RESULTS

Significant growth rate dispersion of sodium chlorate crystals in $\langle 100 \rangle$ direction was occurred during the first 3 h of growth in experiments of type 1 (before the dissolution), as is shown previously.^{4,17–21}

It was also confirmed that growth rates in the $\langle 100 \rangle$ direction of most of the crystals change during this period, as was shown recently. The majority of the measured growth rates (80–90%) significantly decreased in the initial growth period. Less than 10% of the growth rates increased predominantly in the first stage of the growth run or did not change significantly at all. About 4% of all growth rates were zero all the time or decreased to zero, even though the solution was supersaturated and the other neighboring crystals grew. In Figure 1, the time evolution of the growth rates in one typical growth run is presented.

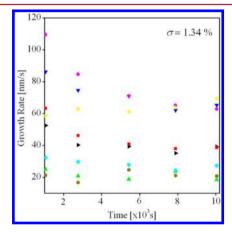


Figure 1. Time evolution of the growth rates in one typical growth run prior to dissolution.

During the dissolution, many of the small crystals totaly dissolved. The scatter diagram, which represents the correlation between the growth rate after rafaceting and the growth rate of the same crystals before dissolution (stabilized growth rates) is shown in Figure 2.

Figure 3a–d shows histograms that represent (a) the dispersion of the initial growth rates (during the first 20–30 min), rates in (100) direction in experiments of type 1, (b) the growth rate dispersion of stabilized growth rates in (100) direction, about 3 h of growth, for both types of experiments, (c) the dispersion of average growth rates of {100} faces after refaceting in experiments of type 1, and (d) the dispersion of average growth rates of {100} faces of motionless crystals in experiments of type 2. To describe the growth rate distributions, the fitting of finite mixture normal distributions to the frequency distributions was performed. Details of the

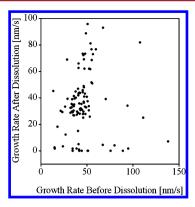


Figure 2. Scatter diagram representing the correlation between the growth rate after rafaceting and the growth rate of the same crystals before dissolution.

fitting procedure were described previously. ^{7,18,22} According to the histograms, some of the growth rates at the beginning and the end of the distributions did not pertain to any of the maxima. These growth rates were eliminated from the fitting procedure. The distributions obtained are also included in Figure 3. The growth rate dispersion in Figure 3d did not fit because growth rates were not measured at the same time from the beginning of the growth runs (crystals became motionless at different moments).

Parameters describing the growth rate dispersions, namely, N, the number of growth rates; \overline{R} , the arithmetic mean of

growth rates; and R_1 , R_2 , and R_3 , the growth rates that correspond to the first, second, and third distribution maxima, are shown in Table 1. It can be seen from Figure 3a—c and Table 1 that the growth rate distributions have one to three well-defined maxima.

Table 1. Parameters That Describe Growth Rate Distributions of Small Sodium Chlorate Crystals

	N	\overline{R} [nm/s]	$R_1 [nm/s]$	R_2 [nm/s]	R_3 [nm/s]
Figure 3a	528	56 ± 1	27 ± 1	53 ± 1	74 ± 1
Figure 3b	536	47 ± 1	24 ± 2	43 ± 1	68 ± 3
Figure 3c	286	18.5 ± 0.4	21 ± 2		
Figure 3d	296	23 ± 2			

The nongrowing faces either existed when crystal observation began or were the result of growth rates decreasing to zero in experiments without dissolution (type 2) or before dissolution (type 1). In experiments of type 1, nongrowing faces exist after the refaceting. There was no occurrence of growth stopping of the faces that grew after refaceting.

Appearance of the crystals with nongrowing faces is independent of the crystal position in the crystallization cell, the crystal orientation with respect to the solution flow direction, the distance between the closest neighbors, and the crystal size.

Several groups of sodium chlorate crystals with nongrowing faces appeared at the beginning (experiments of types 1 and 2)

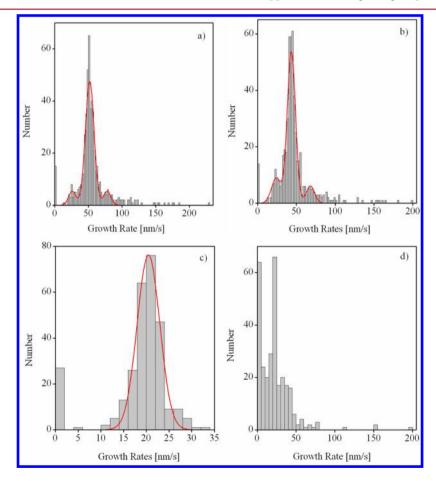


Figure 3. Histograms representing the dispersion of (a) initial growth rates, (b) stabilized growth rates, (c) average growth rates after refaceting, and (d) average growth rates of motionless crystals.

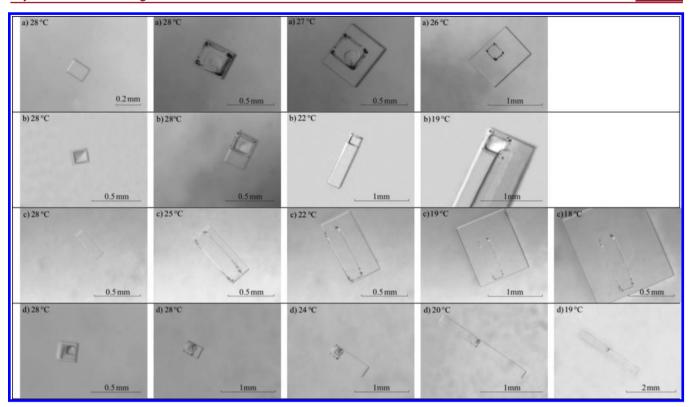


Figure 4. Examples of time evolution of the crystals denoted a, b, c, and d. First image of crystal, 28 °C, before dissolution; second image of crystal, 28 °C, after refaceting; other images, crystals at specific temperatures after refaceting.

Table 2. Time (Supersaturation) Evolution of a Number of Different Groups of Non-Growing Crystals

T (°C)	28	27	26	25	24	23	22	21	20	19	18
σ (%)	1.34	1.79	2.25	2.71	3.19	3.65	4.12	4.60	5.08	5.57	6.06
N_4	31	31	28	28	25	25	20	13	10	0	0
N_3	6	6	7	6	6	4	0	2	4	2	0
N_2	19	19	20	20	19	18	15	10	12	7	5
N_1	18	18	16	15	18	17	6	2	0	4	0
N_0	0	0	3	5	6	10	0	4	2	3	0

or during growth (experiments of type 2). Crystals that are in horizontal plane (1) grew through the growth of three adjacent faces, (2a) grew through the growth of two opposite faces, (2b) grew through the growth of two adjacent faces, (3) grew through the growth of only one {100} face, or (4) did not grow at all.

The examples of time evolution of the crystals after the solution temperature decreased are shown in Figure 4. The crystals pertaining to groups listed above can be recognized in this figure. Similar forms also occurred at the beginning of the growth.

The main results from experiments with temperature decreasing below 28.0 °C are presented in Table 2. During 27 growth runs we observed the behavior of 74 crystals with nongrowing faces. The table presents the time (supersaturation) evolution of a number of different groups of nongrowing crystals. N_4 , N_3 , N_2 , N_1 , and N_0 are the number of crystals with 4, 3, 2, 1, and 0 nongrowing faces, respectively. In the other words, N_4 is the number of crystals that did not grow in all the observed directions, whereas N_0 is the number of crystals growing in all the observed directions, developed from any group of nongrowing crystals. It has been noticed that the evolution from the shape 3 to 2a or 2b has the same probability

(equal probability to start the growth of opposite or adjacent faces).

The temperature decreasing significantly increases crystal growth rates. This results in neighboring crystals intergrowing after the temperature decreases below 23 °C. Intergrown crystals were exluded from further observation. Because of that, the total number of observed crystals at lower temperatures decreases.

Temperature decreasing below 28.0 $^{\circ}$ C stimulates some of the nongrowing faces to grow. We can see in Table 2 that some of the nongrowing faces did not start to grow until after 6 h of temperatures decreasing to 18 $^{\circ}$ C (undercooling 13 $^{\circ}$ C). Less than 20% of the observed crystals with nongrowing faces start to grow in all directions after 3 h of temperature decreasing to 23 $^{\circ}$ C.

The number of crystals with nongrowing faces is higher than number of nongrowing directions, because zero growth in particular direction is the result of zero growth of opposite crystal faces. Because of that, the mentioned 4% nongrowing directions are the consequence of higher percents of nongrowing faces. Using the ratio between numbers of different types of nongrowing crystals (Table 2), we can estimate that at

 $28\ ^{\circ}\text{C}$ (supersaturation 1.34%) about 10% of all crystals had at least one nongrowing face.

Examples of time evolution of these crystals after temperature decreases below 28 °C are shown in Figure 4. The corresponding temperatures are denoted on the pictures. The first and second images of each crystal show crystals at 28 °C before dissolution and after refaceting, respectively. We cannot conclude anything about the order of the start of the nongrowing faces' growth (first neighboring or the opposite). Crystal (a) with all nongrowing faces at 28 °C starts simultaneous growth of three faces at 26 °C with approximately the same rates, while the fourth face starts growth at 23 °C. Different faces of other crystals started the growth at different temperatures. The order of the start of the growth is random, subsequently grown neighboring or opposite faces.

We have recently shown¹⁷ that sodium chlorate crystals can dissolve in low supersaturated solutions but cannot grow in undersaturated ones; all crystals dissolve just above the saturation temperature. In those experiments, we could not observe particularly nongrowing faces (no markers) so that possibly different behavior could occur.

Now, particular attention was paid to the dissolution of crystals with nongrowing faces. We have shown that all nongrowing faces start to dissolve a step above the saturation temperature, while the temperature slowly increases, at (31.02 \pm 0.02) °C. During the temperature decrease, a refaceting of the crystal was noticed at (30.98 \pm 0.02) °C. In other words, dissolution and refaceting of nongrowing and growing faces started at the same temperatures.

Crystals with all nongrowing faces and some crystals with one to three nongrowing faces stay small at $28\,^{\circ}\text{C}$ (the first part of experiment) and completely dissolve at a temperature of 34 $^{\circ}\text{C}$ (the second part of experiment).

DISCUSSION

The main result of our investigation is the coexistence of nongrowing and growing sodium chlorate crystal faces in supersaturated solution. Nongrowing faces are very stable; they exist at very high solution undercooling (supersaturation). In other words, particular crystal faces had a wide "dead zone" for the growth, while the others did not have.

Since many of growing faces stopped growing after refaceting, we expected that dissolution and refaceting increased the probability of the appearance of nongrowing faces. However, as mentioned before, the probability of an appearance of nongrowing faces is similar (approximately the same) for primary nucleated crystals and crystals after refaceting (about 10%). This indicated that dissolution and refaceting have no influence on the appearance of nongrowing faces. As mentioned, many crystals with nongrowing faces dissolved in type 1 experiments, and none of the growing crystals stopped the growth after refaceting. Nongrowing crystals either existed from the beginning of observation, or they were the result of growth rate decreasing to zero in experiments without dissolution (type 2).

As is shown in Figure 2, the dissolution and refaceting essentially changed growth rates of almost all observed crystals. Some crystals growing at high rates before dissolution grew at low rates after dissolution, and vice versa. After the dissolution and refaceting, many of the crystals had nongrowing faces, even some of those that were fast growing crystals before dissolution. A similar result was obtained for growth of KDP and Rochelle salt crystals in [001] direction. This indicates that the

significant dissolution and refaceting practically destroyed the "memory" effect, which probably existed for small dissolution and refaceting.⁵ In other words, after refaceting, crystals continued their growth at rates practically independent of conditions of nucleation, which are difficult to control.

By comparison of the growth rate distributions with initial and stabilized growth rates (Figure 3a,b and Table 1), it can be seen that growth rates corresponding to maxima decrease for the first 3 h of crystal growth. This is probably a consequence inherent to crystal growth rate changes, that is, independent of macroscopic external growth conditions. ^{5,6} For example, in Figure 1, the time evolution of the growth rates in one growth run is presented.

As is proposed in ref 4, the maxima positions correspond to different activities of dominant dislocation groups, while the width of each maximum corresponds to its perimeter. According to Figure 3c,d, after the dissolution and refaceting fast growing faces disappeared. All faces either grow at rates that correspond to one maximum, that is, to one activity of a dominant dislocation group, or they did not grow.

Because the growth in the $\langle 100 \rangle$ direction evolves through growth of two $\{100\}$ faces at opposite sides of the crystal, the first maximum in Figure 3b corresponds to their minimal growth rates. In other words, the growth rate of $\{100\}$ is zero, while the growth rate of the $\{\overline{1}00\}$ face is (24 ± 2) nm/s and corresponds to a minimal activity of a dominant dislocation group. It confirms Figure 3c presenting the distribution of growth rates of $\{100\}$ faces. The first and only maximum corresponds to a minimal activity of the dominant dislocation group. Within the error limits, the position of the maximum is the same, (21 ± 2) nm/s. Similar growth rates of all faces can be noticed by observing the evolution of the crystals (Figure 4). Displacements of all faces are similar during the same time, that is, on the subsequent images.

Summary:

- nongrowing and growing sodium chlorate crystal faces coexisted in supersaturated solution,
- nongrowing faces are very stable,
- dissolution and refaceting did not affect the probability of appearance of nongrowing faces,
- after the dissolution and refaceting, the crystal faces do not grow or grow with similar rates.

It was shown recently¹⁶ that at low supersaturations (below 0.18%) coexistence of growing, nongrowing, and dissolving sodium chlorate crystals exist. As possible reasons for coexistence of growing and dissolving crystals such as the Ostwald ripening, microscopic conditions in the crystallization chamber, microstructure of growing face, overall crystal lattice strain, the Gibbs—Thompson effect, and the presence of impurities are discussed. Some of them can be the reason for existence of nongrowing faces in highly supersaturated solutions and will be discussed in the following paragraphs.

Ostwald Ripening. Ostwald ripening²³ is identified with the growth of large crystals at the expense of smaller ones which dissolve. The dissolution of the smaller crystals (C₃H₇NH₃)₂CuCl₄ near the bigger one was observed earlier in the supersaturated solution.²⁴ Accordingly, it could be expected that there exists a size ratio between closest small and big crystals at which the small crystal does not grow. In our experiments crystals with nongrowing faces appeared independently of distance between the closest neighbors and the crystal size. Consequently, the existence of nongrowing faces

observed in our experiments, cannot be explained by Ostwald ripening.

Microscopic Conditions in the Crystallization Cell. As was noticed, ¹⁶ sodium chlorate crystal growth and dissolution was independent of the crystal position, its orientation in respect to the solution flow, and the distance between the closest neighbors. Consequently, the existence of the nongrowing crystal faces in a supersaturated solution cannot be explained by different microscopic growth conditions around the crystals.

Microstructure of the Crystal Face. Classical BCF dislocation theory of the crystal growth, ^{25,26} predicts that a crystal face with higher activity of the dominant dislocation group emerging at the surface grows at a higher rate. Higher activity of dislocation could be expected for crystals with more structure defects. According to this theory, the dislocation sources free faces as well as those that have sources of opposite sign and cancel one another will not grow at all.

According to the BCF theory the transition of the dominant dislocation source from one face to the neighboring one can be a reason for crystal faces ceasing to grow. Namely, the crystal growth rate can change regardless of the growth conditions, as the result of a transition of the dominant dislocation source from one face to a neighboring one (growth sector changed). 17,27,28 Stopping of the face growth can be the result of leaving of unique dislocation sources to a neighboring face or transition of the dislocation source of opposite sign from neighboring face, which cancel one another. Transition of dislocation sources to neighbor faces can increase their growth rates. Stopping of the growth of any face in our experiments did not cause the increase of the growth rate of neighboring faces. Because of that, transition of the dominant dislocation sources from one face to the neighboring one is probably not the reason for growth stopping of previously grown faces.

The dissolution and refaceting induce additional defects in crystal structures, which probably change the dislocation structure ^{25,26} and the "overall" lattice strain ^{29–31} of the crystals. The dissolution and refaceting have no influence on the appearance of nongrowing faces in the experiments presented. This means that the defects probably do not influence the appearance of nongrowing faces.

Impurity Effects. The presence of small amounts of impurities at the growing face affects the crystal growth. Random perturbations in impurity concentrations near the crystal surface are the usual explanation for growth rate changes. Growth rate dispersion and zero and negative values of the growth rates of calcium sulfate crystals were explained by the effects of impurities. ^{10,32}

The existence of a "dead zone" for crystal growth was confirmed for many substances. ¹² This phenomenon might be explained by the presence of impurities. Immobile impurity particles can adsorb on the surface and completely abrogate step spreading at low supersaturations. They also may block the entrance of growth units to kinks ^{13,14} and progressively decrease the step velocity. ¹⁵

The presence of impurities affects the crystal solubility. Solubility changes lead to surface free energy changes, ^{33,34} which result in crystal growth rate changes. Crystal growth rate increase will happen if an adsorbed impurity has solubility higher than that of a crystallizing substance, and vice versa. ¹²

In experiments described above, the analar grade of sodium chlorate (99% purity) was used. It was proposed recently ¹⁷ that for this system, a possible reason for coexistence of growing,

nongrowing and dissolving crystals (faces) are the absorbed impurities in crystals. If it is true, the impurity at the nongrowing faces had solubility lower than sodium chlorate. Why those impurities incorporate only onto particular crystals or particular faces, when even the external growth conditions were the same is a question that arises. The answer may lie in the differences in the bulk or the surface structure (differences in affinities of the faces on particular impurity) generated during the nucleation or the growth processes.

As is proposed in the literature, 35,36 the "dead zone" was

As is proposed in the literature, 35,36 the "dead zone" was clearly recognized, both for growth and the dissolution of (001) faces of $K_2Cr_2O_7$. Our results show that all nongrowing faces start to dissolve at (31.02 ± 0.02) °C during slow temperature increase. In other words, the "dead zone" exists only for growth of sodium chlorate crystals.

CONCLUSION

We have shown that growing and nongrowing {100} sodium chlorate crystal faces coexist in supersaturated solutions. Dissolution and refaceting have no influence on the probability of appearance of nongrowing faces. These processes significantly reduce the range of face growth rates. All nonzero growth rates pertain to one maximum of the growth rate distribution. It is probably a consequence of the minimal activity of the dominant dislocations groups. Nongrowing faces are very stable; some of them exist at a relatively high undercooling of 13 °C. The crystal faces can start to grow subsequently or simultaneously in random order, subsequently grown neighbor or opposite faces. We have concluded that possible reasons for coexistence of growing and nongrowing faces can be the microstructures of crystal face and the impurity effects.

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Author Contributions

The manuscript was written through contributions of all authors. All authors have given approval to the final version of the manuscript.

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Notes

The authors declare no competing financial interest.

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REFERENCES

- (1) Randolph, A. D.; White, E. T. Chem. Eng. Sci. 1977, 32, 1067.
- (2) Janse, A. H.; de Jong, E. J. In *Industrial Crystallization '78*; de Jong, E. J.; Jančić, S. J., Eds.; North-Holland: Amsterdam, 1979; pp 135–142.
- (3) Virone, C.; ter Horst, J. H.; Kramer, H. J. M.; Jansens, P. J. J. Cryst. Growth 2005, 275, 1397.
- (4) Žekić, A. A.; Mitrović, M. M. J. Cryst. Growth 2003, 258, 204.
- (5) Mitrović, M. M. J. Phys. Chem. 1995, 99, 5438.
- (6) Mitrović, M. M. Chem. Phys. Lett. 1997, 265, 315.
- (7) Mitrović, M. M.; Žekić, A. A.; Ilić, Z. Z. Chem. Phys. Lett. 2002, 361, 312.

- (8) Mitrović, M. M.; Žekić, A. A. J. Cryst. Growth 2005, 275 (1-2), e337.
- (9) Mitrović, M. M.; Žekić, A. A. Cryst. Res. Technol. 2002, 37, 57.
- (10) Linnikov, O. D. Desalination 2000, 128, 47.
- (11) Söhnel, O.; Bravi, M.; Chianese, A.; Mazzarotta, B. J. Cryst. Growth 1996, 160 (3-4), 355.
- (12) Sangwal, K. Prog. Cryst. Growth Charact. 1996, 32, 3.
- (13) Mullin, J. W.; Amatavivadhama, A.; Chakraborty, M. J. Appl. Chem. 1970, 20, 153.
- (14) Mullin, J. W. Crystallisation, 2nd ed.; Butterworths: London, 1972.
- (15) Ristić, R.; Shekunov, C. Yu.; Sherwood, J. N. J. Cryst. Growth 1994, 139, 336.
- (16) Malivuk, D. A.; Žekić, A. A.; Mitrović, M. M.; Misailović, B. M. J. Cryst. Growth 2013, 377, 164
- Cryst. Growth 2013, 377, 164. (17) Mitrović, M. M.; Žekić, A. A.; Elezović-Hadžić, S.; Malivuk, D. A. Ind. Eng. Chem. Res. 2011, 50 (14), 8726.
- (18) Mitrović, M. M.; Žekić, A. A. In Recent Research Developments in Crystal Growth; Pandalai, S. G., Ed.; Transworld Research Network: Kerala, India, 2009; pp 33–60.
- (19) Ristić, R. I.; Sherwood, J. N.; Wojciechowski, K. J. Cryst. Growth 1988, 91, 163.
- (20) Harding, M. M.; Rule, R. J.; Oldman, R. J.; Davey, R. J. J. Cryst. Growth 1992, 123 (3-4), 373.
- (21) Mitrović, M. M.; Žekić, A. A.; Baroš, Z. Z. Chem. Phys. Lett. 2008, 464, 38.
- (22) Mitrović, M. M.; Žekić, A. A.; Petruševski, Lj. S. J. Cryst. Growth 1999, 198/199, 687.
- (23) Ostwald, W. Z. Phys. Chem. 1901, 37, 385.
- (24) Mischgofsky, F. H. J. Cryst. Growth 1983, 65, 500.
- (25) Burton, W. K.; Cabrera, N.; Frank, F. C. Philos. Trans. R. Soc., A 1951, 243, 299.
- (26) Chernov, A. A.; Rashkovich, L. N.; Smolskii, I. L.; Kuznetsov, Yu.G.; Mkrtchan, A. A.; Malkin, A. A. In *Rost Kristallov*; Givargizov, E. I., Ed.; Nauka: Moscow, 1986; Vol. 15.
- (27) Zaitseva, N.; Carman, L.; Smolsky, I. J. Cryst. Growth 2002, 241, 363.
- (28) Klapper, H.; Becker, R. A.; Schmiemann, D.; Faber, A. Cryst. Res. Technol. 2002, 37, 747.
- (29) van der Heijden, A. E. D. M.; van der Eerden, J. P. J. Cryst. Growth 1992, 18, 14.
- (30) Mitrović, M. M.; Ristić, R. I.; Ćirić, I. Appl. Phys. 1990, A51, 374.
- (31) Zacher, U.; Mersmann, A. Cryst. Growth 1995, 147, 172.
- (32) Linnikov, O. D. Desalination 2000, 128, 35.
- (33) Sangwal, K. J. Cryst. Growth 1989, 97, 393.
- (34) Sangwal, K. In *Elementary Crystal Growth*; Sangwal, K., Ed.; Saan: Lublin, Poland, 1994; Chapter 4.
- (35) van Enckevort, W. J. P. J. Cryst. Growth 1996, 166, 156.
- (36) Ceyhan, A. A.; Bulutcu, A. N. J. Cryst. Growth 2011, 327, 110.