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Article

NaClO₃ Crystal Growth and Dissolution by Temperature Cycling in a Sessile Droplet

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Abstract: Sodium chlorate is the most popular compound used to study spontaneous symmetry breaking by means of crystallization. Therefore, it is important to know the behavior of the solid particles. NaClO₃ crystal growth and dissolution are investigated in an aqueous sessile droplet subjected to numerous temperature cycles. On cooling, in addition to the classical formation of repeated elongated fluid inclusions, there is a reproducible appearance of prismatic fluid inclusions (PFIs) at the corners of single crystals. The underlying mechanism involves the complete termination of the (110) face growth and the propagation of the {100} faces, which can close the PFIs. This study reports that on heating, transient donut-like single crystals formed, which could lead to their segmentation, even without stirring the suspension. The systematic addition of other sodium salts with chlorine atoms at different oxidation states did not change these observations.

Keywords: NaClO₃; aqueous solution; crystal growth; dissolution; temperature cycling; fluid inclusions; donut formation



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1. Introduction

Sodium chlorate (NaClO₃) is a material of choice for the study of the emergence of homochirality by stereoselective nucleation [1], deracemization via Viedma ripening [2], and temperature-cycling-induced deracemization (TCID) [3]. Because the solid state shows chirality in the cubic system (SG P2₁3), it is easy to spot the handedness of every single crystal by simply using a polarized optical microscope [4]. Over the last decade, almost all papers have been investigating the global effect of stereospecific nucleation or deracemization by using a flux of energy passing through the suspension; these researchers have studied mechanical energy [5], temperature gradients in space [6], temperature cycling [7,8], ultrasounds [9,10], microwaves [11], types of stirring [12–15], impurities [16], etc. Recently, a study on the scale of a single droplet has revealed the possibility of deracemization with or without chiral flipping by using Viedma ripening or TCID [17]. In the case of temperature cycling under quiescent conditions, repetitive inclusions appear on cooling, but their shapes are unusual when considering the well-accepted Roedder classification [18]. Therefore, it seems necessary to know more about the basics of the growth and dissolution of sodium chlorate crystals when undergoing repeated heating and cooling, such as when applying TCID, but without stirring.

The aim of this paper is to gain insights into the growth and dissolution of sodium chlorate crystals at a small scale under stagnant conditions. This study is performed by using a hot-stage microscope equipped with a camera to ensure continuous monitoring.

2. Materials and Methods

2.1. Products

Sodium chlorate (NaClO_3) (99%+ extra pure) was provided by Acros Organics. It was used without purification or recrystallization in water. Sodium perchlorate (NaClO_4) was prepared from soda (tablets at 97%, provided by Afla Aesar, Karlsruhe, Germany) and perchloric acid (solution at 70% provided by Sigma-Aldrich, Burlington, VT, USA) and then recrystallized in water. Sodium chlorite (NaClO_2) was supplied by Honeywell. It was used after processing it into a slurry in acetone for 3 h. Sodium bromate (NaBrO_3) was provided by Alfa Aesar (99.5% pure) and was used without purification. Sodium dithionate ($\text{Na}_2\text{S}_2\text{O}_6$) was prepared by the same procedure as that described in [19]. Hexadecane (99% pure) was provided by Acros Organics. Distilled water was used for this study.

2.2. Monitoring of the Crystal Growth and Dissolution

Crystals were observed with a Nikon Microscope equipped with a Leica camera: Flexacam C3; software camera Leica Application Suite X (5.0.2.24429). A Linkham THMS 600 programmable hot stage with the software Linksys32 was used to control the sample temperature. The temperature cycles were recorded as follows. At cooling and heating rates of 2 K/min, one photo was recorded per minute. At cooling and heating rates of 5 and 10 K/min, one photo was recorded every 20 s. The images were processed via DaVinci Resolve.

2.3. Experimental Parameters

Temperature cycling was performed between 20 °C and 60 °C. The heating and cooling rates were adjusted from 2 K/min to 10 K/min. Then, ca. 1 μL of saturated solution at 20 °C was deposited as a sessile drop on a silica crucible. Small pieces of sodium chlorate crystals were carefully added. The rest of the small crucible was filled with hexadecane to prevent evaporation of water. A cover slip glass was then adjusted on the edges of the silica crucible.

2.4. Identification of the Crystal Faces

The chosen crystals were attached to glass fiber and mounted on a kappa goniometer Bruker D8-VENTURE diffractometer (Madison, WI, USA) equipped with a PHOTON CAPD detector that had dual microfocus sources ($\text{I}\mu\text{S}$ 3.0 copper and $\text{I}\mu\text{S}$ DIAMOND II molybdenum) Mo radiation was used. A series of 180 frames were recorded by φ scan (1 sec/frame, 0.5°). The unit cell parameters were determined, and face indexation was performed by APEX 4ref software suite (APEX 4, data collection software, V2022.10-1, Bruker AXS Inc., Madison, WI, USA, 2021).

3. Results

3.1. Crystal Growth Induced by Cooling at 10 K/min or 5 K/min

3.1.1. Evidence of Prismatic Fluid Inclusions (PFIs)

On cooling, no primary or secondary nucleation can be observed. Figure 1a–f (extracted from Video S1) show the sequence of events that can be observed, with the cooling profile represented in Figure 1g. Starting from a rounded contour, the particle is rapidly re-faceted (after ca. 2 min; see Figure 1b). The faces with the major morphological indices (MIs) are {100} and {110}. Occasionally, {111} and {120} can also be identified. The (110) face seems to have a fast normal-growth rate, so its morphological index decreases (Figure 1b–d). Nevertheless, at one point, face (110) completely stops its growth (Figure 1e). In the meantime, the {100} faces propagate and close a prismatic fluid inclusion (PFI), as schematized in Figure 2. Figure 3 shows another PFI with a high level of magnification.

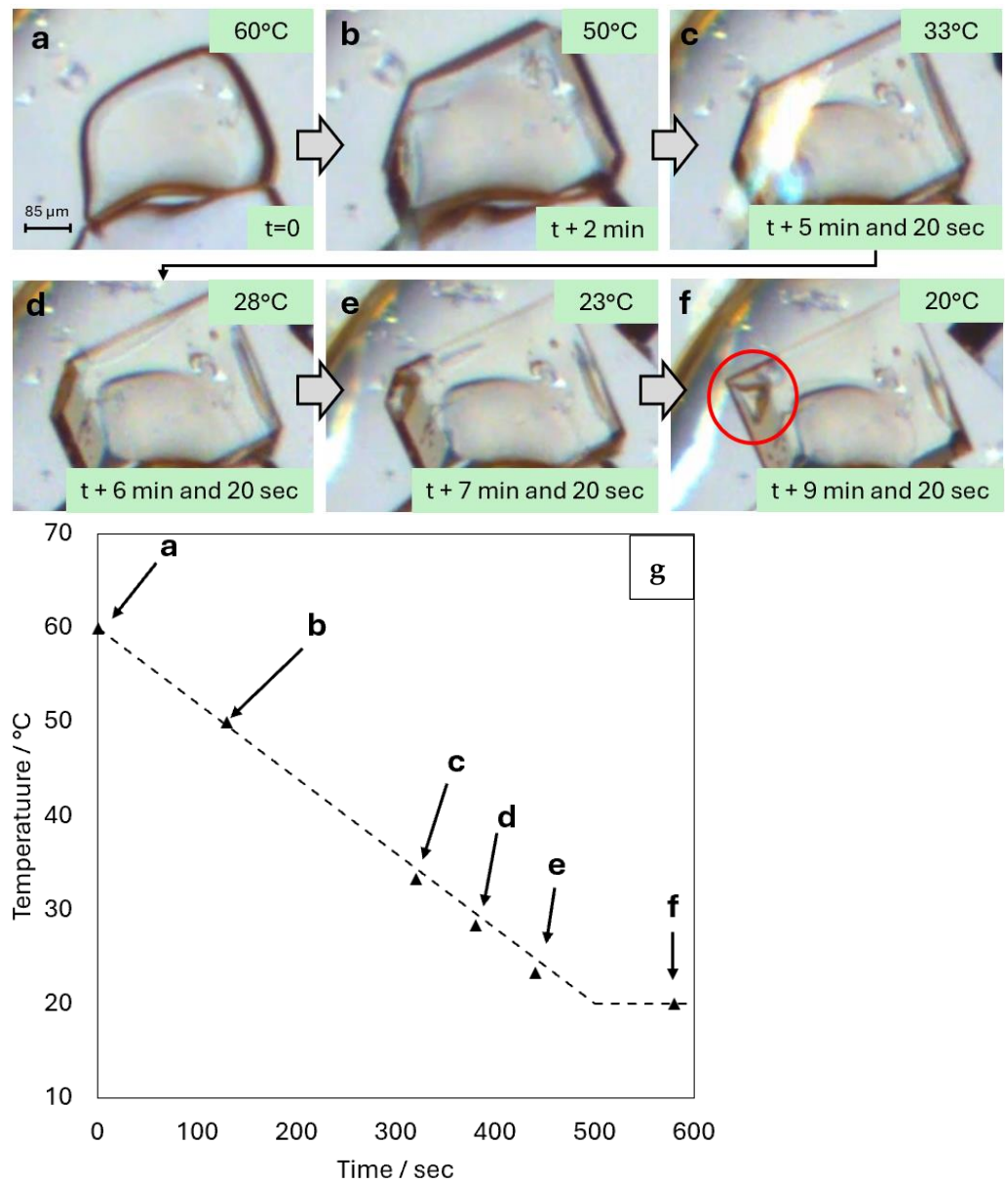


Figure 1. PFI formation at a cooling rate of 5 K/min from 60 °C to 20 °C (a–f). The temperature of each frame is indicated in the top right corner, and the time in the bottom right corner; (g) Specific temperature profile for this inclusion. Black triangles represent the temperature and the time from a to f for each picture.

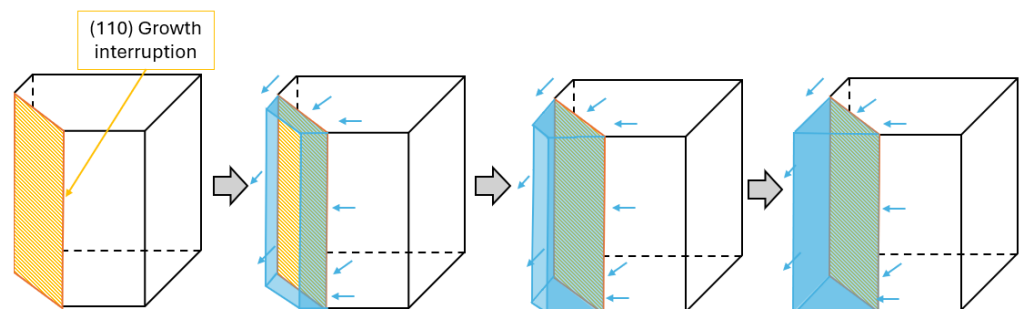


Figure 2. Schematic representation of a prismatic fluid inclusion (PFI) formation. The blue arrows show the propagation of {100} faces, which form the PFI after the complete termination of the growth of the (110) face. As a result, the blue prism contains the mother liquor; cf. Video S1.

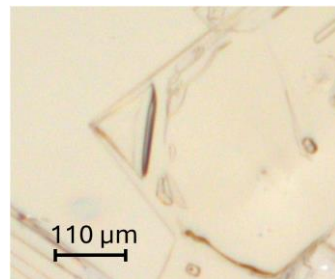


Figure 3. Detailed top view of a prismatic fluid inclusion (PFI).

3.1.2. Reproducibility in the Formation of a PFI

In the SI, the film (Video S2) shows a high degree of reproducibility in the formation of a PFI. No less than twenty-three times, the prismatic fluid inclusions reappear at every cooling (-10 K/min) at approximately the same location, showing an apparent memory effect. However, the highest temperature at which the growth of the $\{110\}$ faces stops oscillates between 50 °C and 40 °C. In Figure 4, the starting temperatures at which the $\{110\}$ faces stop growing are represented by lozenges. The temperatures of the PFI closures are symbolized by triangles. On the same graphic, the surface of the PFI is reported (i.e., the volume, if we assume no variation in the thickness), showing almost no correlation between the temperature at which $GR(110) = 0$ ($GR(hkl)$ stands for growth rate of face (hkl)) and the time elapsed between the termination of the growth of the (110) face and the PFI closure.

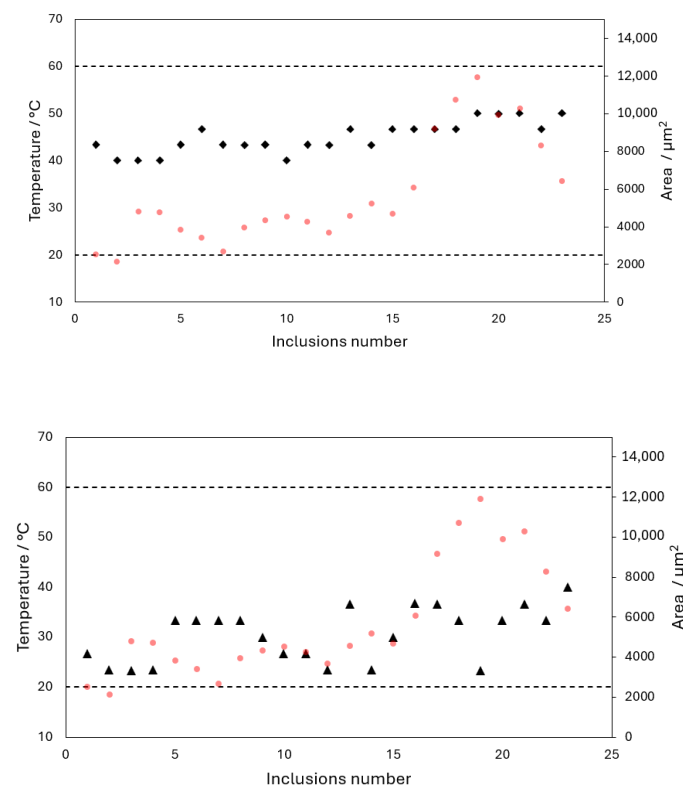


Figure 4. (Top): Starting temperatures (\blacklozenge) at which the successive (110) faces stop growing and thus initiate a PFI. **(Bottom):** Closure temperatures (\blacktriangle) of the PFIs. Heating and cooling performed at $+10$ K/min and -10 K/min, respectively. In the same graphics, the surfaces of the PFIs are reported with red dots (i.e., the volume, if we assume no variation in the thickness), showing almost no correlation between the temperature at which $GR(110) = 0$ and the time elapsed between the termination of the growth of the (110) face and the PFI closure.

3.2. Crystal Growth Induced by Cooling at 2 K/min

When the cooling rate is decreased down to 2 K/min, repetitive elongated inclusions parallel to $\{110\}$ can appear. A similar fact has been described for ammonium perchlorate [20,21]. Indeed, as depicted in Figure 5, an inclusion begins to form at 56 °C because of the interruption of the growth of (110). The low cooling rate gives the opportunity for the crystal to heal by closing the elongated fluid inclusion and to resume the growth of the (110) face at a temperature slightly higher than 54 °C. Later, at 52 °C, the growth of the (110) face stops again without resuming its growth, leading to a PFI.

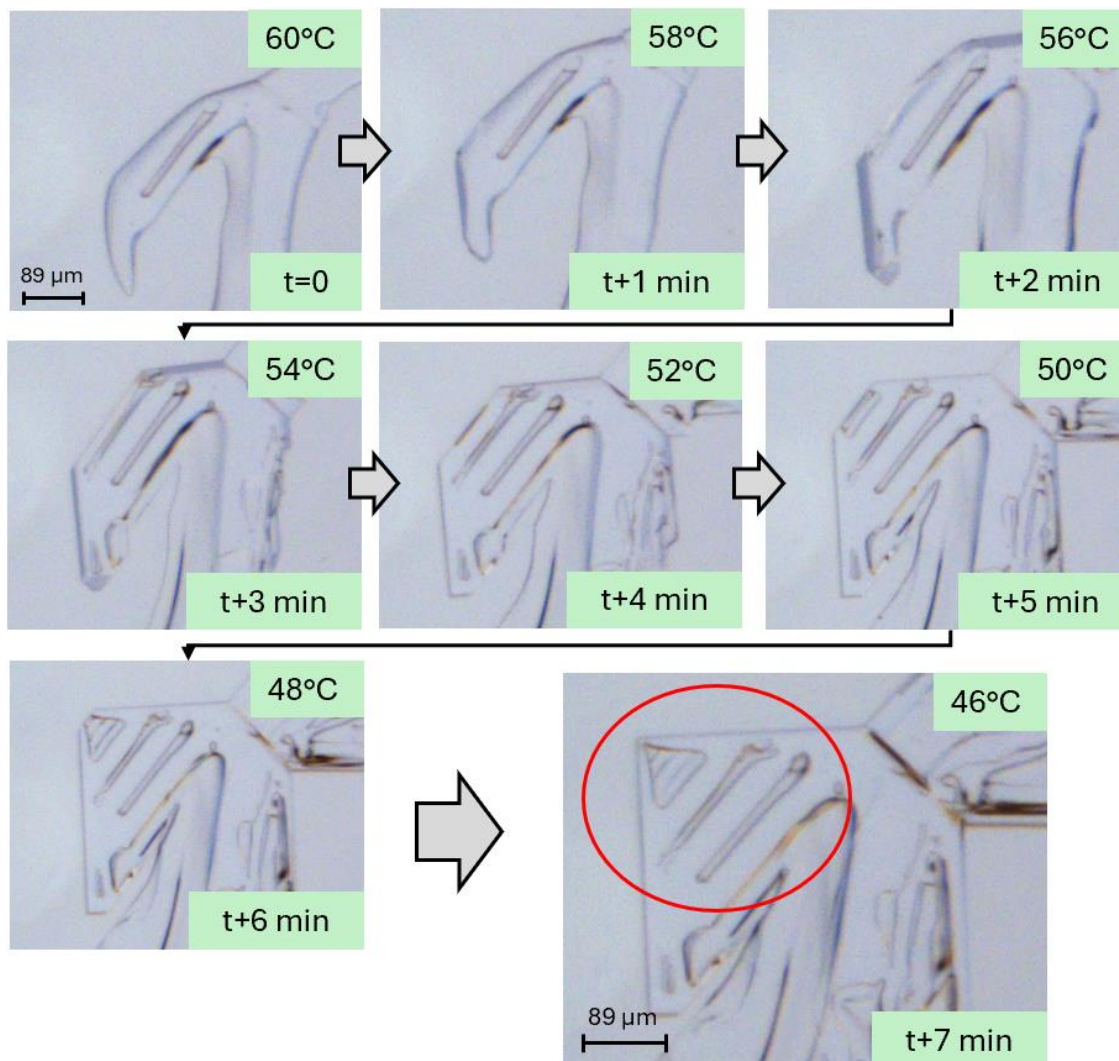


Figure 5. Elongated and prismatic fluid inclusion (PFI) formation during crystallization at 2 K/min between 60 °C and 46 °C. The temperature of each frame is shown in the top right corner, and the time in the bottom right corner. A zoom of these fluid inclusions at 46 °C is encircled in red. Extracted from Video S3.

The growth rates of (110), (100), and (010) can be compared against the time when the crystal closes a PFI (Figure 6). The (110) face growth rate peaks at 14 $\mu\text{m}/\text{min}$. The closure of an elongated FI induces the reappearance of (110). However, while the PFI is forming, $\text{GR}(110) = 0$. $\text{GR}(100)$ is low and relatively constant (the fluctuations are much smaller than for $\text{GR}(110)$), ensuring an isosceles triangle shape for the top view of the PFIs.

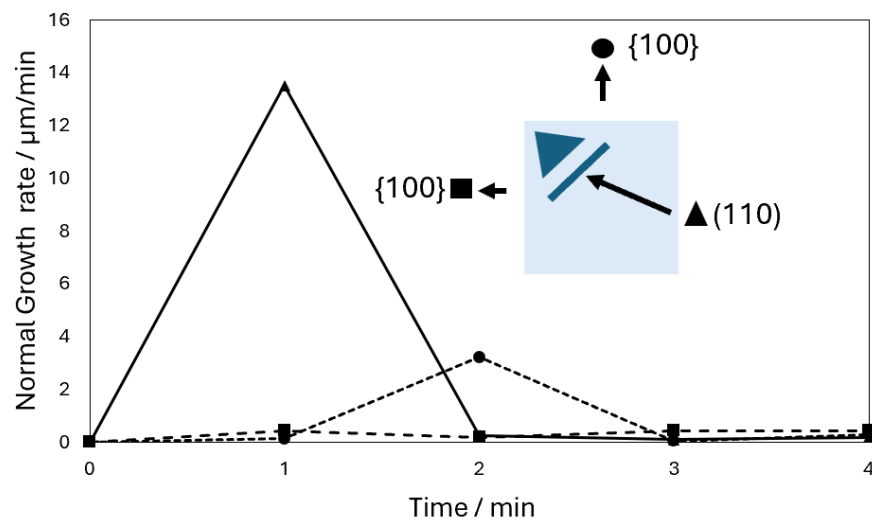


Figure 6. The {100} and (110) growth rates vs. time (GR{100}: ■ and ● and GR(110): ▲). The ▲ face has its growth interrupted once, and then it resumes. However, growth stops again after the formation of an elongated fluid inclusion. The faces ■ and ● have nearly constant and low growth rates. The dashed lines are visual guides. The inset presents the schematic formation of an elongated FI and PFI.

Christmas Tree Shaped Inclusions

At the same cooling rate of -2 K/min (Figure 7), the fluid inclusions can take the shape of a Christmas tree. Different incomplete (110) faces are visible during the crystal growth. These attempts to close a cavity are aborted many times.

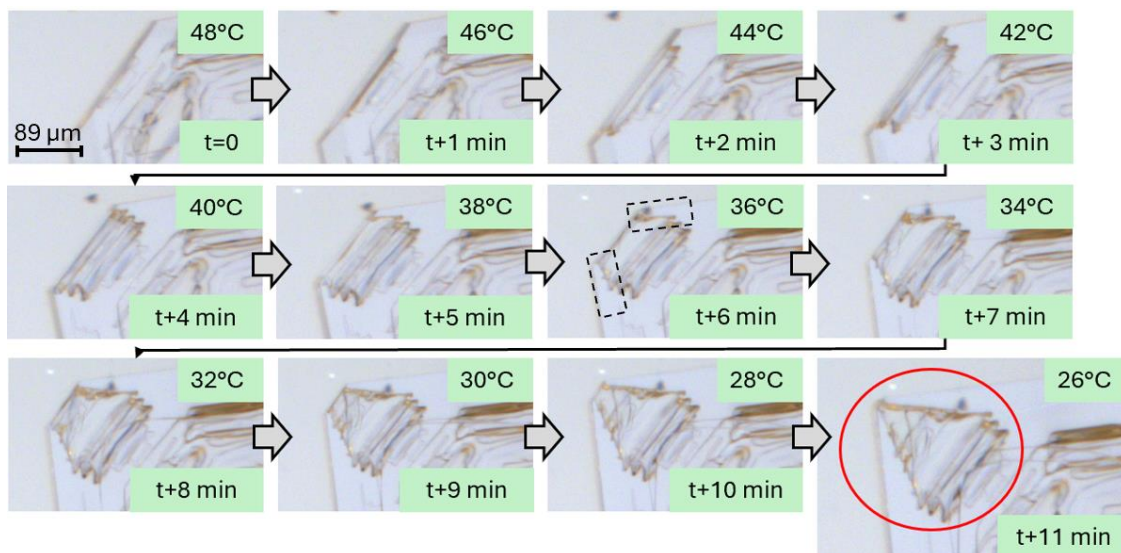


Figure 7. Christmas tree inclusion formation during crystallization at -2 K/min between 48 °C and 26 °C. The zoom at 26 °C highlights the encircled Christmas tree. Extracted from Video S4.

The lateral boundaries of the PFIs exhibit numerous indentations, each of them being an unsuccessful attempt to close an elongated FI. As the formation of the PFI progresses by the propagation of the {100} faces and $GR(110) = 0$, the renewal of the mother liquor inside the open cavity becomes more delayed. The convection movements ensure the growth of the (110) face to a progressively lesser degree. The PFI formation is a somewhat autocatalytic process; as soon it starts, it self-amplifies. Figure 8, schematizes the formation of a Christmas tree inclusion.

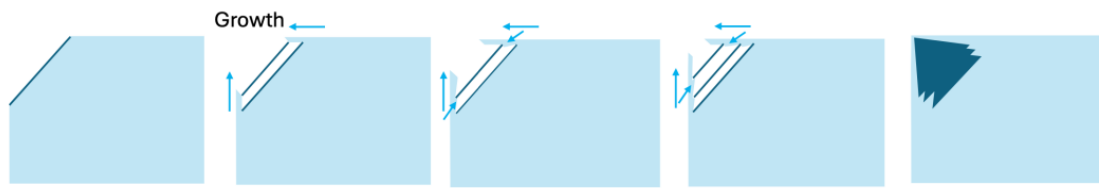


Figure 8. Mechanism of Christmas tree inclusion formation. The (110) face shows a growth interruption (in blue). The blue arrows represent the propagation of the {100} faces, which progressively close the PFIs. The dark blue part represents the projection of the PFIs in the shape of a Christmas tree that is filled by the mother liquor.

The normal growth speeds of the faces emphasize the kinetic regime changes during FI formation (Figure 9). Every time the inclusion is closed, the GR(110) accelerates ($29 \mu\text{m}/\text{min}$ and $37 \mu\text{m}/\text{min}$). At some point, the crystal can no longer close the inclusion, as represented by a zero-velocity growth speed of the center of the (110) face. Moreover, the {100} faces continue their constant normal growth and propagation processes.

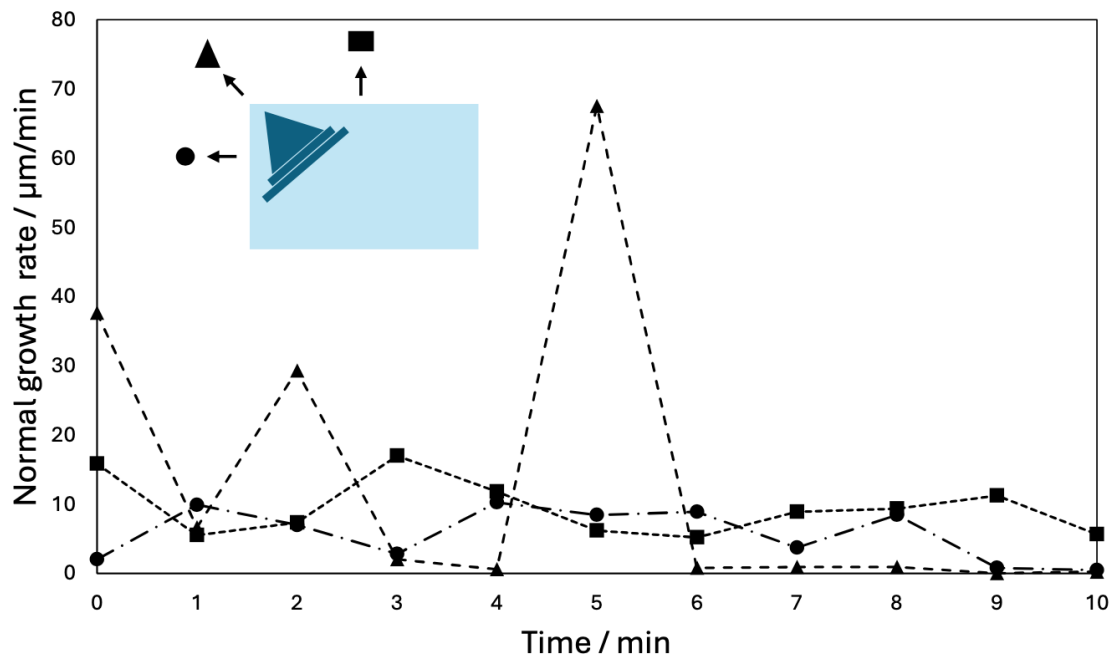


Figure 9. Normal growth rate (GR) of the {100} faces are symbolized as: ■, ● and GR(110) face symbolized as: ▲. The dashed lines are visual guides. The growth interruption of the face (110) is represented by the up-and-down motion of the dashed line. Black arrows represent the faces' GR. The blue triangle represents the mother liquor.

In contrast to GR{110}, which fluctuates greatly, the {100} faces show a nearly constant speed of growth. In that case, the propagation rate of {100} (referred to as PR{100} hereafter) can be measured (Figure 10). As seen below, PR{100} is nearly constant in both cases, meaning that the Christmas tree formation does not affect their propagation rates. As expected, it can be seen that the PR(100) and PR(010) faces are similar, leading to a symmetrical PFI.

Both of the inclusion mechanisms observed at $2 \text{ K}/\text{min}$ could be concomitant. The difference may be attributed to the differing convection movements within the feeding solution. A precise examination of the lateral faces of an FI in the shape of a Christmas tree shows that the indentations are relatively large and closer to the stopped (110) face than to the tip of the PFI. This may result from the renewal capability of the mother liquor being better at the beginning of PFI formation than near the closure of the PFI.

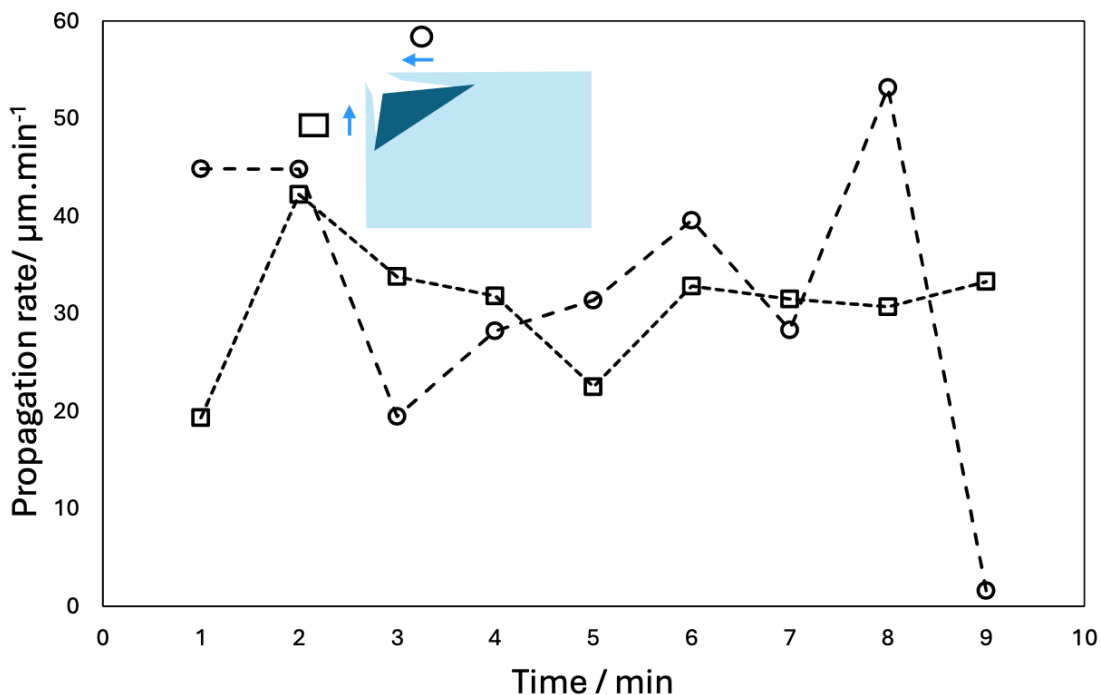


Figure 10. Propagation rate (PR) of equivalent faces (100) (○) and (010) (□) that close the FI in the shape of a Christmas tree; (001) and (00-1) are not visible. The dashed lines are visual guides. Blue arrows represent the PRs of the faces. The blue triangle contains the mother liquor.

3.3. Crystal Dissolution in a Stagnant Suspension Induced by Heating

On heating, the formation of holes inside single crystals can be observed many times. Progressively, as the number of temperature cycles increases, the hole increases in size, forming a donut-like shape. The ultimate evolution corresponds to the fragmentation of a single crystal, even if no stirring is implemented in the suspension. The only existing movements are eddies of the solution associated with convection. Figure 11 below illustrates the evolution during several temperature cycles.

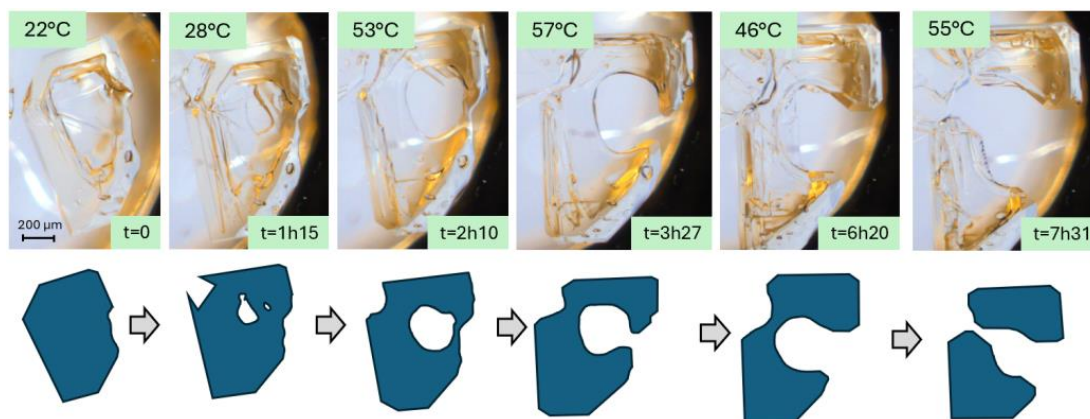


Figure 11. (Top): Formation of a donut and fragmentation of a NaClO₃ single crystal undergoing repetitive 20–60–20 temperature cycles in a sessile droplet. Photos extracted from Video S5, given in the SI. (Bottom): Schematic representation of the segmentation of the single crystal after the formation of a donut. The formation of a PFI helps in the subsequent fragmentation of the single crystal. NB: there is no stirring during these experiments.

3.4. Investigations with Various Impurities: Sodium Chloride, Sodium Hypochlorite, Sodium Chlorite, Sodium Perchlorate, Sodium Bromate, and Sodium Dithionate

Sodium chlorate undergoes spontaneous disproportionation [22]. Several competitive mechanisms exist, which are driven by pH, temperature, and possible irradiation by energetic photons, i.e., photodecomposition. In order to check if one of the possible secondary anions could be the impurity responsible for the formation of PFIs, systematic tests with the addition of chloride Cl^- , hypochlorite ClO^- , chlorite ClO_2^- , and perchlorate ClO_4^- are performed. The addition of small amounts of those sodium salts does not change the two phenomena described in this study, which thus appear to be quite robust. PFIs form upon cooling and donuts form upon heating; these phenomena are also observed with sodium bromate.

Sodium dithionate is a special impurity that is able to bind strongly to the {111} faces [23–26]. Through this binding, this impurity is able to invert the chirality of the crystals on each side of the {111} interfaces and at larger amounts, this impurity can modify the morphology of single crystals. When 0.1% is added to the solution (with reference to the total mass of sodium chlorate) at ± 10 K/min and ± 2 K/min the ‘cubic’ habitus of the crystal is preserved, but the number of PFIs decreases. The interruption of (110) without the propagation of {100} can be observed. The formation of donuts remains globally unchanged (Video S6).

When 0.5% of sodium dithionate is added to the solution, the same protocols of temperature cycling (± 10 and ± 2 K/min) are applied. The cubic morphology is strongly disrupted, a trend toward tetrahedral morphology can be observed, and this change is concomitant to a near absence of PFIs (Video S7). The morphological changes do not prevent the formation of donuts, but these holes scarcely lead to the fragmentation of single crystals. As a result, the effects of sodium dithionate necessarily delay the deracemization via temperature cycling under stagnant conditions.

4. Discussion

In mixing tanks or in Couette–Taylor reactors, the sodium chlorate particles have a rounded shape [3,6–8]. There are no edges nor visible corners due to attrition, shocks, friction, and agglomeration. In our experiments performed without stirring, only natural convection renews the mother liquors on the growing surfaces. Under such conditions at temperatures below ca. 40 °C, single crystals appear faceted with visible edges and corners. Within the -10 K to -2 K/min cooling rate range, repeated elongated FIs together with PFIs can be observed with a high frequency of occurrence. The {110} faces have a dead zone of supersaturation larger than that of the more stable {100} faces. Once the dead zone is passed, it can grow faster than {100}. Nevertheless, when supersaturation is below this threshold, {110} faces completely stop. This is consistent with X-ray topography, which indicates that {110} faces are defective and highly strained [27].

The formation of donuts can be interpreted as follows: when a growing crystal under stagnant conditions reaches a certain size, it is clear to see that the central part of the crystal base in contact with the bottom of the vial is not properly fed. This phenomenon results in a cavity at the lower part of the crystal sitting on the surface of the vial. In contrast, the surrounding edges can grow, forming a kind of ‘hopper’ crystal. On heating, the resulting thin central part of the crystal leads to the formation of a regular hole and then a large hole, i.e., the formation of a donut and, later on, the segmentation of the crystal, as detailed in this study. This segmentation produces very small particles that rapidly dissolve according to the Gibbs–Thompson effect. Thus, even without stirring, the formation of donuts helps the deracemization.

The two phenomena described here do not prevent irreversible evolution towards homochirality [17] but clearly impact the kinetics and mechanisms involved in symmetry breaking. Moreover, the formation of PFIs and donuts is not likely to be related to the presence of the other oxidation states of chlorine atoms, such as chloride, hypochlorite, chlorite, and perchlorate (all tested as sodium salts). Instead, these phenomena are related

to the kinetics and the cubic morphology of the single crystals. In contrast, when adding sodium dithionate (ca. 0.5% *w/w*), the single crystals adopt a tetrahedral morphology, and the phenomena observed on heating and cooling almost vanish.

5. Conclusions

This study on the growth and dissolution of NaClO₃ crystals in an aqueous sessile droplet undergoing temperature cycling between 20 °C and 60 °C leads to the following conclusions:

- (i). On cooling, prismatic fluid inclusions (PFIs) can be observed at the corners of cubic single crystals. This is very reproducible for cooling rates between 2 and 10 K/min. After multiple temperature cycles, a PFI can reappear more than twenty times at nearly the same location. The underlying mechanism involves the complete stopping of the growth of the (110) faces and the propagation of the {100} faces, which close the PFIs.
- (ii). On heating, transient donut-like single crystals form, leading to their segmentation, even without stirring the suspension.

The following impurities, added in the range of 0 to 5%, do not prevent the two phenomena described here: chloride, hypochlorite, chlorite, perchlorate, and bromate (all sodium salts). In contrast, it seems that sodium dithionate, even in small quantities of ca. 0.5%, can mostly suppress the formation of PFIs and donuts by changing the morphology of the crystals and the growth kinetics.

Supplementary Materials: The following supporting information can be downloaded at: <https://www.mdpi.com/article/10.3390/min14090898/s1>, Video S1: Formation of a PFI; Video S2: Feprroducibility of PFI formation; Video S3: Elongated + PFI; Video S4: Christmas tree formation; Video S5: Donut formation; Video S6 and Video S7 respectively visualize the effects of 0.1% and 0.5% of sodium dithionate on dissolution and crystallization by temperature cycling of sodium chlorate.

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Conflicts of Interest: The authors declare no conflicts of interest.

Glossary

TCID	temperature-cycling-induced deracemization
FI	fluid inclusion
PFI	prismatic fluid inclusion
MI	morphological index, i.e., the relative importance of the face (hkl) in the morphology of a single crystal. The smaller the distance from face (hkl) is to a central point of a single crystal, the greater the MI(hkl).
GR{hkl}	normal growth rate of the face {hkl}
PR{hkl}	propagation growth rate of the face {hkl}

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