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Chiral hide-and-seek: Retention of enantiomorphism in laser-induced nucleation of molten sodium chlorate

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We report the observation of non-photochemical laser-induced nucleation (NPLIN) of sodium chlorate from its melt using nanosecond pulses of light at 1064 nm. The fraction of samples that nucleate is shown to depend linearly on the peak power density of the laser pulses. Remarkably, we observe that most samples are nucleated by the laser back into the enantiomorph (dextrorotatory or levorotatory) of the solid prior to melting. We do not observe a significant dependence on polarization of the light, and we put forward symmetry arguments that rule out an optical Kerr effect mechanism. Our observations of retention of chirality can be explained by decomposition of small amounts of the sodium chlorate to form sodium chloride, which provide cavities for retention of clusters of sodium chlorate even 18 °C above the melting point. These clusters remain sub-critical on cooling, but can be activated by NPLIN via an isotropic polarizability mechanism. We have developed a heterogeneous model of NPLIN in cavities, which reproduces the experimental data using simple physical data available for sodium chlorate. © *2011 American Institute of Physics*. [doi:10.1063/1.3637946]

I. INTRODUCTION

Nucleation is a fundamental physical process that occurs in many areas of natural science. Despite its widespread occurrence, our understanding of the mechanisms involved is quite hazy. The pathways that build up to the critical point of nucleation, and the structures and dynamics of the species involved, continue to provoke investigation.[1] A prime example of nucleation in chemistry is in crystallization, i.e., from a solvent or in a liquid-to-solid phase transition.[2]

The use of photochemistry to initiate nucleation has been known for a long time, but more recently, the effect of non-photochemical laser-induced nucleation (NPLIN) was discovered by Garetz, Myerson, and co-workers.[3,4] NPLIN employs short pulses of light that deliver a transient high-strength electric field to the sample, resulting in nucleation. The mechanism for NPLIN is still not completely understood; it is believed that the field acts to stabilize clusters of solute, but this is still a matter for debate.[5–8] The effect can be distinguished from other laser-induced nucleation phenomena that use even more intense pulses to induce photomechanical effects in the solvent;[9,10] these typically employ focussed or femtosecond laser pulses.[11] Crystallization has also been demonstrated at interfaces using focussed continuous-wave laser beams, which are thought to induce trapping and aggregation of solute prior to nucleation.[12] A key advantage of NPLIN over photochemical nucleation is that the integrity of the material is not compromised, although it appears that not all substances exhibit the effect.[13] The effect evidently induces some structural rearrangement, but not as the result of a chemical reaction; in this sense, it more closely resembles assisted homogeneous nucleation of the sample. For this rea-

son, NPLIN offers a powerful tool with which we may initiate nucleation essentially on demand; the random and infrequent nature of homogeneous nucleation is a major impediment to its study in real time by physical techniques.

Studies of NPLIN thus far have been carried out almost exclusively in liquid solution. The role of the solvent in NPLIN is not fully understood, and moreover the solvent would make molecular dynamics computer simulations much more challenging and costly.[14] To the best of our knowledge the only other non-solution phase study of NPLIN has been that carried out by Sun *et al.*, who demonstrated NPLIN of a nematic phase from a pure supercooled liquid crystal.[15] We decided to investigate the scope for NPLIN of solid phases from pure liquid samples. Sodium chlorate was chosen because it is an inorganic salt with a remarkably low melting point (262 °C) which crystallizes in a cubic space group.[16] The salt is unusual in that it exhibits enantiomorphism (chiral packing of the component ions) and the crystals can be separated easily into dextrorotatory (*d*) and levorotatory (*l*) forms by measuring their optical rotation.[17] The retention and transfer of chirality in molecular and supramolecular systems is a hot topic in chemistry,[18] and of particular relevance to understanding biohomochirality.[19]

The main purpose of the present study is to determine if NPLIN can be observed for supercooled molten sodium chlorate (i.e., without solvent), and to explore the laser power regime in which it occurs. We also wish to elucidate features of the NPLIN mechanism, such as whether pre-nucleating clusters are implicated in the process, and to exclude spurious causes for the effect, such as dust or impurities.

II. METHODS

The experimental apparatus is based on our recent study of the spontaneous crystallization of molten sodium

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chlorate.[20] Approximately 2.0 g of sodium chlorate (Sigma–Aldrich, 99+%) was placed in a glass sample tube (diameter 12 mm), to which was added a polytetrafluoroethene (PTFE) stir bar (8 × 2 mm). The form of the solid used was generally coarse grained (as supplied); however, in later experiments, the sodium chlorate was recrystallized from aqueous solution and separated into crystals of pure *l* or pure *d* enantiomorphs. Sample tubes were placed in a brass heating block with two 10 mm window ports to allow complete passage of the laser beam, and another two ports to view the sample. The heating block was placed on a hotplate stirrer with temperature feedback control (Heidolph MR2002). The melting point of the cubic chiral phase (phase I) of $NaClO_3$ has been measured to be 262 °C.[16, 21] This temperature is higher than the widely quoted value of 248 °C,[22] which can be attributed to the existence of other polymorphs with lower melting points. Samples were held at 280 °C for 20 min in order to melt fully, while stirring at 750 rpm (this stirring rate was chosen to ensure rapid but smooth mixing of the melt). The temperature of the sample was then reduced to 265 °C (at ~1 °C per minute), where the experiments on temperature dependence and power dependence were commenced, as detailed in Sec. III. Single pulses (7 ns width) from the fundamental output (1064 nm) of a Nd^{3+}:YAG (yttrium aluminium garnet) laser were used. The peak laser power density was calculated using a ray-tracing method to take into account slight focussing of the beam in the tube.[23] Pulses of 100 mJ pulse^{-1} with a beam diameter of 5.8 mm corresponded to a peak power density of 0.140 GW cm^{-2}.

III. RESULTS

A. General observations

In general, it was found that not all samples could be induced to nucleate using the laser, even at the highest laser powers available (0.350 GW/cm^2); possible causes for this will be discussed below. When NPLIN did occur, a few small particles (<1 mm^3) were observed to form within seconds, and these were rapidly circulated in the remaining melt due

to stirring. Solidification following NPLIN did not take place instantaneously, even when the temperature was as much as 7 °C below 262 °C. Over a period of minutes, a clear glass-like layer of crystalline $NaClO_3$ was formed on the inner surface of the sample tube, which then grew inwards, eventually trapping the stirring bar.

In the majority of cases (~88% of 64 samples), the final product was found to be a pure enantiomorph, either *l* or *d*. The reason for obtaining a pure enantiomorph can be explained by the autocatalytic nature of the crystallization with rapid stirring.[17, 20, 24] An initial nucleus of, say, *l*-$NaClO_3$ is formed, which matures to become a seed. The action of mixing causes this seed to produce more nuclei of the same enantiomorph (secondary nucleation), which in turn grow to produce more seeds, and so on, eventually leading to the entire sample being crystallized as pure *l*-$NaClO_3$.

We found that in most cases it was possible to determine the handedness of the enantiomorph by using optical rotation *in situ* (see Figure 1). The *in situ* determination of chirality was verified by analysis of the cooled solid, which was crushed and used to seed supersaturated (105%) aqueous solutions of sodium chlorate at room temperature.[20] All crystals grown in the resulting solution were found to match the observed *in situ* assignment. In very few cases, we found that it was not possible to determine the chirality *in situ*: these samples were found to form translucent white solids, and were normally formed at temperatures lower than 255 °C. Using the seeding method, such samples were found to be mixtures (*dl*) of the enantiomorphs, as discussed in detail elsewhere.[20]

The ~10% occurrence of mixed *dl* samples resulting from NPLIN is less than that observed due to spontaneous nucleation (~30%).[20] This supports our earlier conclusion that spontaneous nucleation below 255 °C can form one of the achiral polymorphs of $NaClO_3$ (phase II or III), leading to the observation of racemic conglomerate (*dl*) products. In the present work, we find that if NPLIN occurs, it will generally happen at temperatures above 255 °C, where formation of the achiral polymorphs is thermodynamically unfavourable.[16, 20]
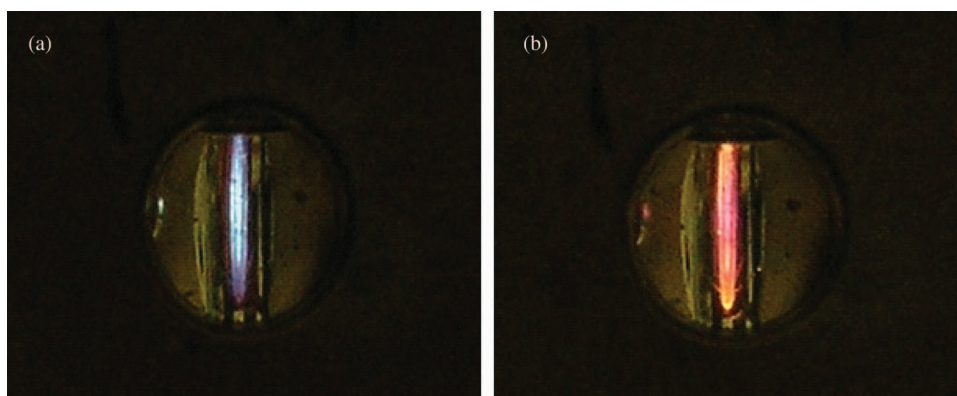
FIG. 1. The crystallized sodium chlorate sample is observed through one of the pairs of ports of the heating block. The sample is viewed here between a pair of crossed polarizers using a white-light torch. Due to optical rotary dispersion, (a) the sample appears blue when the polarizers are crossed, and (b) appears red when the analysing polarizer is turned clockwise (looking into the oncoming beam) for a *d*-$NaClO_3$ sample. An *l*-$NaClO_3$ sample would appear red on turning the analysing polarizer anti-clockwise. No color change is observed when viewing a molten sample. More details on the determination of optical rotation can be found elsewhere (Refs. 20 and 25).

B. Temperature dependence

To study the temperature dependence of NPLIN, the laser power density was fixed at ~0.350 GW cm^{-2}. Once the sample was stabilized at 265 °C, 4 laser pulses were fired into the sample. In the case where no crystallization was observed, the sample was left for 1 min and then shot with another set of 4 pulses, and so on until a total of 20 pulses. The temperature was reduced by 1 °C, the sample was allowed to stabilize for a few minutes, and then another sequence of laser pulses was fired. During this stepwise cooling process, some samples nucleated spontaneously (i.e., not resulting from the laser). If nucleation had not occurred by about 248 °C, either by NPLIN or spontaneously, then the sample would inevitably undergo spontaneous nucleation (not due to the laser pulses). NPLIN occurred in 64 samples out of 79, and the temperature at which each sample nucleated was recorded. The mean temperature for NPLIN was found to be 262 ± 3 °C, close to the nominal melting point of cubic NaClO$_3$ (phase I), suggesting that samples do not need to be highly supercooled for NPLIN to occur. A set of 20 control samples, following the same time frame for cooling but without the use of the laser, gave identical results to our previous observations:[20] most samples nucleated spontaneously near 248 °C to give approximately equal proportions (~1/3 each) of d, l, and dl samples.

C. Laser power dependence

The effect of laser power density was investigated by cooling molten NaClO$_3$ samples to a fixed temperature of 259 °C. Starting at the lower laser power density of 0.140 GW cm^{-2}, the sample was shot with 50 laser pulses. If no crystallization occurred, the power density was increased and the sample shot again with 50 pulses. This procedure was repeated until a maximal power density of 0.350 GW cm^{-2} was reached. A total of 18 samples were tested, of which 9 were shot with linearly polarized light, and 9 were shot with circularly polarized light. No significant dependence on laser polarization was observed in the results. The cumulative fraction of samples to nucleate at a given power density was calculated.[5] It is assumed that samples found to nucleate at a given power density would have nucleated at any higher power density, as has been verified for NPLIN of aqueous KCl.[5,6] As can be seen in Fig. 2, the results show a nearly linear increase in the cumulative fraction of samples nucleated versus laser power density. The solid line in Fig. 2 represents a linear fit to the first 13 data points. The plateau at high power densities suggests that there are some samples resistant to NPLIN, even at high power densities. Also evident is a threshold power density of 0.161 ± 0.013 GW cm^{-2}. A threshold for NPLIN has been seen in several other systems in aqueous solution,[6] although the reasons for it are not yet resolved.[26]

D. Memory of enantiomorphism

With a view to investigating dust or impurities as causes of NPLIN, fresh crystals of sodium chlorate were prepared by recrystallization from aqueous solution. The crystals were
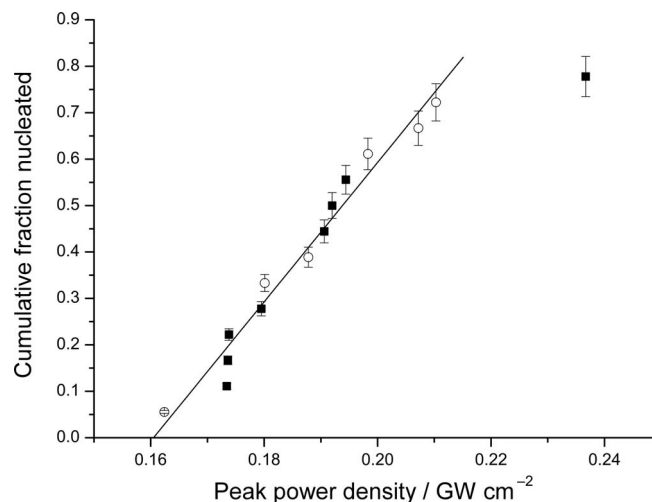

FIG. 2. Cumulative fraction of samples nucleated by NPLIN of molten sodium chlorate. Solid squares and open circles represent samples nucleated with linearly polarized and circularly polarized light, respectively. The solid line represents a fit to the first 13 data points, giving a slope of 15.0 ± 0.8 cm^2 GW^{-1}, with threshold peak laser power density of 0.161 ± 0.013 GW cm^{-2}.

separated into d and l enantiomorphs, briefly rinsed with water, and dried. Samples of pure d- and l-NaClO$_3$ were prepared, and the stirred, molten samples were shot with the laser as described in Sec. III B. The results show a remarkable memory of the chirality, as detailed in Table I. Of the 23 samples tested, 20 crystallized into the enantiomorph of the original sample prior to melting: this is quite surprising, given that the samples were melted and held at 20 °C above the melting temperature for a considerable time (20 min). We note that experiments under similar conditions on stirred, molten NaClO$_3$ without use of the laser (i.e., by spontaneous nucleation), do not exhibit such memory of enantiomorphism.[20]

The most plausible explanation for the memory of enantiomorphism is that some of the original sample survives the melting process. First, we consider the ingress of airborne particles (dust) into the sample; it is possible that some sodium chlorate may resist melting by being trapped inside or in contact with such dust particles.[27] In a preliminary test, a set of 4 samples (2 d and 2 l) were prepared using fresh, solid crystals, taking great care to exclude all external contamination.

TABLE I. NPLIN results of 23 samples of molten NaClO$_3$, where the chirality of the pure enantiomorph was known prior to melting. Samples were melted, cooled, and shot with the laser at a power density of 0.350 GW cm^{-2}, and the chirality of the product was determined (see text for details). The results exhibit a remarkable memory of enantiomorphism, with 20 of 23 samples (87%) showing the same chirality after the melting and NPLIN cycle.

| Enantiomorph		
Before melting	After NPLIN	Number of samples
d	d	9
l	l	11
l	dl	1
d	l	1
d	dl	1

TABLE II. NPLIN of molten $NaClO_3$, where the chirality of the pure enantiomorph was known prior to melting. All samples were crushed and stored for three days. Of the 14 samples in total, 6 samples were exposed to airborne dust over this period, while 8 samples were kept covered prior to testing for NPLIN (see also Table I and text for details). Five out of six samples (83%) exposed to dust, and six out of eight samples (75%) kept covered, showed memory of chirality after melting and NPLIN. The results suggest that crushing rather than exposure to airborne dust can promote NPLIN.

| Sample type | Enantiomorph | | Number of samples |
	Before melting	After NPLIN	
Exposed to dust	d	d	2
	l	l	3
	d	dl	1
Covered	d	d	3
	l	l	3
	d	dl	1
	l	dl	1

It was found that none of the samples exhibited NPLIN: all 4 samples eventually nucleated spontaneously at around 250 °C to form mixed (dl) solids. At face value, this result appears to support the idea that dust is required for NPLIN of molten sodium chlorate.

To verify these results, a larger set of 14 samples (7 d and 7 l) was prepared. The fresh crystals were crushed before placing them into the tubes prior to melting. Eight of the samples were covered while the other six were left exposed for a few days to gather airborne dust. The samples were melted and shot with the laser, according to the procedure detailed in Sec. III B. The results, shown in Table II, again show an extraordinary memory of the chirality of the original solid sample, with 11 of the 14 samples (79%) giving the same enantiomorph after the melting and NPLIN procedure. Taken together, these results suggest that dust is *not* a critical component for NPLIN, but that crushing the crystals promotes NPLIN.

We consider the possible mechanisms by which crushing the $NaClO_3$ could promote NPLIN. On reviewing the timescales for preparation of samples, we noted that ageing (over 24 h) of the sample prior to melting also appears to increase the likelihood of observing NPLIN. Our results suggest that a chemical transformation may be taking place in the $NaClO_3$, which is promoted by crushing and ageing of the sample. Begg *et al.* studied the thermal decomposition of single sodium chlorate crystals, and observed mass losses of 0.1%–1% between 177 and 262 °C.[21] They found evidence to support preferential decomposition due to dislocations emerging at the surface. Crystals doped with impurities were also more prone to decomposition. Although there may be intermediate products formed during decomposition, the mass loss would be consistent with reduction to form oxygen as follows:

$$2NaClO_3(s) \rightarrow 2NaCl(s) + 3O_2(g). \quad (1)$$
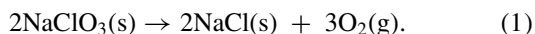
This reaction produces sodium chloride, which has a melting point of 801 °C, substantially higher than that of sodium chlorate. We postulate that during crushing, ageing, and heating of the $NaClO_3$, small particles of NaCl are formed which allow some of the $NaClO_3$ to resist melting, even at

TABLE III. NPLIN of molten $NaClO_3$, for a series of samples prepared with freshly prepared solid crystals and powder in the ratio 1:1 by mass. The enantiomorphs of the solid and powder are given in the first column, e.g., $d–l$ represents a sample containing 1 g of d crystals and 1g of l powder. These were melted and shot with the laser as described in Sec. III B. Of the 12 samples, 10 samples were nucleated by NPLIN to give the same enantiomorph of the original powder, and 1 sample to the enantiomorph of the original solid crystals; 1 sample did not exhibit NPLIN but nucleated spontaneously. In total, 83% of samples were nucleated by NPLIN to give the same enantiomorph as the original powder, supporting a mechanism whereby decomposition allows some of the original sample powder to survive the melting process.

Solid–powder enantiomorph mix before melting	After NPLIN	Number of samples
$d–l$	l	5
$d–l$	Spontaneous	1
$l–d$	d	5
$l–d$	l	1

280 °C. The residual unmelted $NaClO_3$ may be in contact with NaCl particles or protected in pits on the surfaces of NaCl particles.[28] Although it is possible to test for Cl^- by quantitative analysis, we have been unable to verify the formation of particles to support our hypothesis; we expect these particles to be very small (<100 nm).

To further investigate the possibility that decomposition may be responsible for the memory of chirality, another set of 12 samples was prepared. It was noted from the previous trials that samples made up with fresh solid crystals rather than being powdered, appeared more resistant to NPLIN. This would be consistent with the powder having a larger surface area, and being more prone to decomposition. Small d and l crystals (~0.1 cm^3) were grown by recrystallization, and fractions of these were finely powdered separately to produce d and l powders. Sample tubes were made up that contained 50% by weight of small solid crystals of one enantiomer, with the other 50% being powder of the opposite enantiomer, e.g., 50% d crystals, with 50% l powder. After 24 h, each of the samples was melted and shot with the laser in turn, as detailed above (Sec. III B). The results are shown in Table III. As can be seen, there is an overwhelming propensity for samples to nucleate into the enantiomorph of the original powder rather than the solid crystal, further supporting the hypothesis that decomposition allows some of the original sodium chlorate to evade melting.

IV. DISCUSSION

A. Optical Kerr effect model of NPLIN

We have considered possible photomechanical mechanisms that could induce nucleation, e.g., cavitation of bubbles,[9,10] or sound-induced nucleation.[8] Photomechanical effects have been observed at much higher laser power densities obtained by focussing the laser pulses. In the present study, however, we used unfocussed pulses and sodium chlorate does not absorb the 1064 nm light. Garetz *et al.* proposed an optical Kerr-effect mechanism for NPLIN to explain observations of NPLIN for glycine and other small molecules from supersaturated aqueous solutions.[3–5] In this mechanism,

it is energetically favourable for the molecules to align with the most polarizable axis along the direction of the electric field. It should be noted that the frequency of the electric field of near-infrared light is too high to cause orientation of a permanent dipole moment.[3]

In the case of sodium chlorate, the chlorate anion has a trigonal pyramid structure with a disk-like electronic polarizability that can be represented by a prolate ellipsoid. The C_3 axis is the least polarizable ($\alpha_z = 5.172$ Å^3), and the most polarizable axes lie in the plane of the ellipsoid ($\alpha_x = \alpha_y = 6.490$ Å^3), which is the plane of the three oxygen nuclei.[29] At a peak power density of 0.200 GW cm^{-2}, we have an electric field strength $E = 3.883 \times 10^7$ V m^{-1}, giving the interaction energy $H = 4\pi\varepsilon_0(\alpha_z - \alpha_x)\frac{1}{2}E^2 = -1.50 \times 10^{-5} k_B T$ (at 262 °C). This interaction energy is very small compared to the mean thermal energy, and it has been suggested that the combined interaction energy for a cluster of molecules would be sufficient to cause a cluster to become a critical nucleus.[30]

The unit cell for the cubic form of sodium chlorate (chiral space group P2$_1$3) is shown in Fig. 3.[31] The degree of alignment of an ellipsoid along each cell axis can be given by the angle θ between the ellipsoid axis (z) and each cell axis: e.g., for the c axis, the degree of alignment, $K_c = \cos^2\theta_c$ (note that $K_a + K_b + K_c = 1$).[32] If we calculate the average ellipsoid alignment for each axis in the unit cell, we find $\langle\cos^2\theta_a\rangle = \langle\cos^2\theta_b\rangle = \langle\cos^2\theta_c\rangle = \frac{1}{3}$, i.e., the average alignment is spherically symmetric. This result is significant: it means that polarized light cannot be used to promote an alignment of anions in a sodium chlorate cluster that would be commensurate with the crystal structure. Moreover, left- or right-circularly polarized light could not be used to favor nucleation of one enantiomorph over another.[17] In other words, the optical Kerr effect cannot operate in this case; we do not, however, rule out the viability of the Kerr effect mechanism for other systems.

The above symmetry arguments are supported by our experimental results: we see no significant difference between using linearly or circularly polarized light and, moreover, the
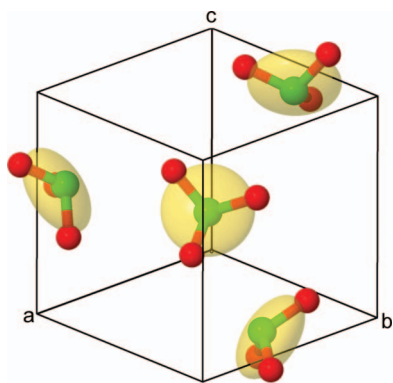
Kerr effect mechanism by itself does not explain the memory of chirality that we observe. We, therefore, look instead at the isotropic polarizability of sodium chlorate clusters.

B. Isotropic polarizability model of NPLIN

A simple isotropic polarizability model based on classical nucleation theory (CNT) has been developed by Alexander and Camp for NPLIN of solids from supersaturated solutions.[6] There are more sophisticated and accurate models of nucleation than CNT;[1] however, while details of the mechanism for NPLIN are still being explored, a simple model is appropriate for providing basic insight into the effect. In the present work, we adapt the CNT model to consider the free energy change for homogeneous (hom = homogeneous) formation of a spherical cluster of radius r from the melt in presence of an electric field,

$$\Delta G_{hom}(r, E) = 4\pi r^2 \gamma - \frac{4}{3}\pi r^3(B\Delta T_- + aE^2). \quad (2)$$

Here, γ is the cluster–melt interfacial tension, $\Delta T_- = T_m - T > 0$ is the degree of supercooling below the melting point T_m, and E is the electric field strength due to the laser light. The parameters a and B depend on simple physical properties of the material; further details of the parameters and the model are given in the Appendix.

To explain the remarkable retention of chirality in the system, we posited that some of the NaClO$_3$ evades melting by being attached to NaCl that is formed by decomposition. In the simplest model of heterogeneous nucleation developed by Volmer, the growth of a hemispherical cluster on the flat surface of a foreign solid substrate was considered.[2,34] The free energy for formation of a cluster (Eq. (2)) is then modified by a factor to give $\Delta G_{het} = f(\theta)\,\Delta G_{hom}$ (het = heterogeneous), where

$$f(\theta) = \frac{1}{4}(2 + \cos\theta)(1 - \cos\theta)^2. \quad (3)$$

The angle θ is the contact angle between the cluster and substrate. At the limit where there is no affinity between cluster and substrate (complete de-wetting), $\theta \to 180°$ and $f(\theta) \to 1$, i.e., homogeneous nucleation applies. In the limit of complete affinity between the nucleus and the foreign substrate, $\theta \to 0°$ and $f(\theta) \to 0$, and the barrier to nucleation vanishes. In the case of NPLIN, we suggest that the presence of the foreign substrate might have two effects:

(a) Even in the absence of the electric field, the barrier to nucleation is lowered relative to that for homogeneous nucleation when $f(\theta) < 1$, i.e., when $\theta < 180°$.

(b) The foreign substrate may contribute an additional energy-lowering polarization term proportional to $-a_{NaCl}V_{NaCl}E^2$ to Eq. (2), where V_{NaCl} is the volume of the foreign body, and a_{NaCl} is the corresponding polarization parameter (Eq. (A2), substituting ε_{NaCl} for ε_s). The dielectric permittivity of NaCl ($\varepsilon_{NaCl} = 2.3204$) is close to the value for solid NaClO$_3$.

FIG. 3. Unit cell structure of cubic NaClO$_3$ (chiral space group P2$_1$3) with unit cell axes labelled a, b, and c (Ref. 31). The structure for the dextrorotatory enantiomorph is shown. The chlorate anions are represented by the balls and sticks, the sodium cations are omitted for clarity. The shape of the polarizability ellipsoid for each anion is superimposed (Ref. 33).

To quantify the heterogeneous nucleation, we include $f(\theta)$ in our model. Using the model outlined in the Appendix (see Eq. (A8)), we find that the number of critical nuclei activated by field of the laser pulse (N_{nuc}) depends linearly on the peak laser power density, which is in turn proportional to square of the peak electric field, E^2. This relationship reproduces the linear dependence of nucleation events versus peak power density as observed in Fig. 1, with the exception that the model predicts a zero threshold power density, different from that observed experimentally (0.161 GW cm^{-2}). The origin of the threshold has not yet been resolved, and experiments are currently underway to explore this region of power in more detail. Even though a transient nucleus may be formed by NPLIN below the threshold, it is possible that the nucleus does not survive for long enough to become sustainable, and therefore, we would observe no subsequent crystallization at that laser power.

The numbers of critical nuclei N_{nuc} at electric fields corresponding to peak laser powers of 0.161 and 0.210 GW cm^{-2} were calculated, and the corresponding linear slope was determined. We found that the experimental slope (15.0 ± 0.8 cm^2 GW^{-1}) was reproduced by a value of the wetting function $f(\theta) = (2.21 \pm 0.01) \times 10^{-5}$, which corresponds to $\theta = (5.98 \pm 0.01)°$. This value suggests a high degree of affinity between the NaClO$_3$ and the NaCl.

An extension of the heterogeneous nucleation theory to incorporate the effects of cavities in foreign substrates was developed by Turnbull.[28] The cavity model is successful in explaining the effect of thermal history of a sample, where it was found that samples exposed to increased temperatures $\Delta T_+ = T - T_m > 0$ above the melting point require increasing degrees of supercooling ΔT_- to bring about nucleation. Turnbull considered the free energy of a cluster of solid retained inside a cylindrical cavity of radius r and height h in a foreign body and found that the cluster can remain stable when $T > T_m$, only if the contact angle $\theta < 90°$.

For the simple geometry of the cylindrical cavity, the following simple relationship is obtained:[40]

$$\frac{\Delta T_-}{\Delta T_+} = \tan\theta. \qquad (4)$$

This equation assumes a single substance as the foreign substrate, and is valid only for relatively small values of ΔT_-, so as to rule out random thermal fluctuations causing nucleation to occur at locations other than at the cavities. In the present work, the sodium chlorate was heated to $\Delta T_+ = 18\,°C$ above the melting point. NPLIN was found to occur close to T_m, so we assume a nominal supercooling of $\Delta T_- = 1\,°C$, which gives $\theta = 3.17°$. Indeed, since θ is small, $\tan\theta \approx \theta$, we can write $\theta \approx 3.17°\,(\Delta T_-/K)$. This value of the contact angle is remarkably close to the value obtained from the fit using our heterogeneous NPLIN model. Although the model of heterogeneous NPLIN that we have developed appears simplistic in its scope, it does remarkably well in reproducing our experimental results. We hope that these results will stimulate more detailed numerical models of heterogeneous nucleation in general, and NPLIN in particular.[35]

V. CONCLUSIONS

In summary, we have demonstrated the effect of non-photochemical laser-induced nucleation in molten sodium chlorate. We found that sodium chlorate can be nucleated into its cubic chiral phase (phase I, $T_m = 262\,°C$) by 7 ns pulses of 1064 nm light. The dependence of the fraction of samples nucleated upon peak laser power density was found to be linear at low power densities, with a threshold of 0.161 GW cm^{-2}, and it was noted that not all samples could be induced to nucleate by the laser. The system was shown to exhibit a remarkable retention of chirality: in total, over 80% of samples tested were nucleated by the laser back into the enantiomorph (dextrorotatory or levorotatory) of the solid prior to melting. Similar experiments on stirred, molten NaClO$_3$ without use of the laser show no such systematic recall of the original enantiomorph.

We did not observe any significant effects of polarization of the light used in NPLIN. We considered an optical Kerr effect mechanism for NPLIN, which operates via the interaction between polarizability anisotropy of ClO$_3^-$ anions and the electric field of the light. However, by consideration of the symmetry of the unit cell of NaClO$_3$, we have shown that this mechanism cannot operate in this case.

In order to explain the observed retention of chirality, we proposed that some of the NaClO$_3$ decomposes to form NaCl, which acts as a solid foreign body to give sites where some of the NaClO$_3$ can resist melting. Upon cooling, these sites can be activated by the laser to induce nucleation of the surviving enantiomorph. A heterogeneous NPLIN model returned a best-fit value of the cluster–substrate contact angle $\theta = (5.98 \pm 0.01)°$. This value was compared to the heterogeneous nucleation model of Turnbull, which considers a distribution of cylindrical cavities as sites for retention of clusters of NaClO$_3$. Using the Turnbull model, we find $\theta \approx 3.17°\,(\Delta T_-/K)$, where $\Delta T_- = T_m - T > 0$ is the degree of supercooling, which is in very close agreement with the experimental results.

APPENDIX: DETAILS OF THE NPLIN MODEL

Equation (2) in Sec. IV B incorporates the well-known electrostatic result that the free energy of a homogeneous dielectric particle is lowered in the presence of an electric field when immersed in a medium of lower permittivity.[36] The classical interfacial tension γ is assumed to be independent of cluster radius. We note that Eq. (2) can be generalized to

consider formation of clusters of any shape; however, we assume spherical clusters to simplify the discussion.

A value of the crystal–melt interfacial tension for sodium chlorate can be estimated using the semi-empirical model of Digilov,[37]

$$\gamma \approx \frac{3}{8} \frac{k_B T_m}{\Omega_{Sm}^{2/3}} \exp\left(\frac{\Delta H_{fus}}{3 N_A k_B T_m}\right),$$ (A1)

where k_B is Boltzmann's constant, N_A is Avogadro's constant, T_m is the melting temperature (535.15 K), ΔH_{fus} is the molar enthalpy of fusion (22.6 kJ mol^{-1}),[22] and Ω_{Sm} is the molecular volume at the melting point, which we calculate from the density of the solid (ρ_S) at the melting point. Using Eq. (A1), we find $\gamma = 85.9$ mJ m^{-2}. The polarization parameter a is given by

$$a = \frac{3\varepsilon_0 \varepsilon_m}{2}\left(\frac{\varepsilon_S - \varepsilon_m}{\varepsilon_S + 2\varepsilon_m}\right),$$ (A2)

where $\varepsilon_S = 2.2210$ and $\varepsilon_m = 2.0976$ are the relative dielectric permittivities of the solid and the melt, respectively, and ε_0 is the vacuum dielectric permittivity. The dielectric permittivities are obtained from the refractive indices (at 1064 nm) of the solid and melt at the melting temperature T_m using the relation $\varepsilon = n^2$.[38] The parameter B is obtained by consideration of the bulk free energy change for the solid–liquid phase transition,

$$B = \frac{\rho_S \Delta H_{fus}}{M T_m},$$ (A3)

where ρ_S is the density of the solid at T_m (2.4056 g cm^{-3}),[39] and M is the molar mass (106.44 g mol^{-1}).

As discussed in detail elsewhere,[6] Eq. (2) predicts a free-energy barrier to nucleation at a critical cluster radius,

$$r_c(E) = \frac{2\gamma}{B\Delta T_- + aE^2}.$$ (A4)

In the absence of the field ($E = 0$), it can be seen that as temperature steadily decreases below T_m, smaller clusters will become critical. When the field is turned on ($E > 0$), a range of clusters with radii, $r_c(E) \leq r \leq r_c(0)$, which are sub-critical in the absence of the field, become critical and may nucleate.[6] The number of NaClO$_3$ molecules, n, in a spherical cluster of radius r may be calculated from the density of the solid phase,

$$n = \frac{4\pi \rho_S N_A}{3M} r^3.$$ (A5)

For the model calculations, we can rewrite Eq. (2) in terms of n,

$$\Delta G_{hom}(n, E) = (36\pi A^2 n^2)^{1/3}\gamma - An(B\Delta T_- + aE^2),$$ (A6)

where $A = M/(\rho_S N_A)$. The distribution of probability of clusters containing n molecules in zero-field is given by the Boltzmann factor, $P(n) \propto \exp[-f(\theta)\Delta G_{hom}(n, 0)/k_B T]$, in the range $1 \leq n \leq n_c(0)$. The heterogeneous nucleation parameter $f(\theta)$ is given by Eq. (3). The number of clusters is

given by

$$N_{clusters} = \frac{N_{molec}}{\langle n \rangle},$$ (A7)

where $\langle n \rangle = \sum_{n=1}^{n_c(0)} n P(n)$ is the mean pre-critical cluster size. From these expressions, we can calculate the number of clusters that become critical due to the presence of the field,

$$N_{nuc} = N_{molec}\left[\sum_{n=n_c(E)}^{n_c(0)} P(n)\right]\left[\sum_{n=1}^{n_c(0)} n P(n)\right]^{-1},$$ (A8)

where $n_c(0)$ and $n_c(E)$ are, respectively, the critical numbers of molecules in a cluster in zero-field and in the presence of the field. The number of molecules of molten NaClO$_3$ in the volume V (0.2033 cm^3) illuminated by the laser pulse can be estimated as

$$N_{molec} = \frac{N_A \rho_m V}{M},$$ (A9)

where ρ_m (2.1022 g cm^{-3}) is the density of the melt at T_m.

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