

5-5-2011

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Recommended Citation

B. C. Knott, J. L. LaRue, A. M. Wodtke, M. F. Doherty, B. Peters, Communication: Bubbles, crystals, and laser-induced nucleation, *J. Chem. Phys.* 2011, 134, 171102, DOI: 10.1063/1.3582897

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Comments

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The following article appeared in

B. C. Knott, J. L. LaRue, A. M. Wodtke, M. F. Doherty, B. Peters, Communication: Bubbles, crystals, and laser-induced nucleation, *J. Chem. Phys.* 2011, 134, 171102, DOI: 10.1063/1.3582897

and may be found at DOI: [10.1063/1.3582897](https://doi.org/10.1063/1.3582897).

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Communication: Bubbles, crystals, and laser-induced nucleation

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(Received 21 February 2011; accepted 6 April 2011; published online 5 May 2011)

Short intense laser pulses of visible and infrared light can dramatically accelerate crystal nucleation from transparent solutions; previous studies invoke mechanisms that are only applicable for nucleation of ordered phases or high dielectric phases. However, we show that similar laser pulses induce CO₂ bubble nucleation in carbonated water. Additionally, in water that is cosupersaturated with argon and glycine, argon bubbles escaping from the water can induce crystal nucleation without a laser. Our findings suggest a possible link between laser-induced nucleation of bubbles and crystals. © 2011 American Institute of Physics. [doi:10.1063/1.3582897]

I. BACKGROUND

Recent experiments in which laser pulses accelerate nucleation of crystals from supersaturated solutions raise fundamental questions concerning the nature of the crystal nucleation process.¹ These experiments show that intense nanosecond laser pulses can reduce the induction time for crystal nucleation in supersaturated solutions from several weeks to seconds or perhaps even to the duration of a nanosecond laser pulse.² The phenomenon, termed nonphotochemical laser-induced nucleation (NPLIN) by the discoverers, has been demonstrated in aqueous solutions of urea,^{3–5} glycine,^{2–4} L-histidine,⁵ potassium chloride,⁶ hen egg lysozyme,⁷ potassium chloride in agarose gel,⁸ and also for a liquid crystal precursor.⁹ The effect was classified “nonphotochemical” because the solutes and solvents have no absorption bands within the range of the applied laser light (wavelengths of 532 and 1064 nm).¹⁰ The hypothesis of a nonphotochemical mechanism was strengthened by a number of observations, including that the effect is intensity dependent but seems to have little wavelength dependence. Additionally, for some systems at certain supersaturations, linearly and circularly polarized laser light induce the nucleation of different polymorphs.^{3–5}

Several mechanisms have been proposed to explain these experimental results. The optical Kerr effect hypothesis proposes that the oscillating electric field of the laser induces a temporary dipole in individual molecules (or clusters of molecules).^{2,10} These induced dipoles are largest when the molecule’s most polarizable axis is aligned with the oscillating field. The laser thus produces a weak torque that aligns all of the molecules with their most polarizable axis parallel to the oscillating field.^{2,10} The optical Kerr hypothesis posits that aligned molecules are more easily arranged into a crystalline lattice. Another hypothesis suggests that the growing

nucleus is stabilized in the presence of the electric field due to a dielectric constant in the nucleus that exceeds that in the surrounding medium.^{6,11}

As previously noted,¹² these mechanisms require the laser-induced nucleation event to occur within the nanosecond laser pulse, thus implying approximately thirteen orders of magnitude reduction in the induction time for nucleation.^{1,4} The remarkable rate enhancements that are observed stand in contrast to theoretical predictions from these two mechanistic hypotheses. Estimates based on the dielectric stabilization model suggest a negligible nucleation rate enhancement at the experimental laser intensities that induce nucleation.⁶ Similarly, the optical Kerr effect has been estimated to give an exceedingly small dipole alignment energy of $10^{-4} k_B T$.² Both effects seem too weak to explain the rate enhancements that have been observed.^{2,6} It has been suggested that these mechanisms may act cooperatively on many molecules in very large nuclei.^{2,3} Recent Monte Carlo simulations using a hybrid Potts lattice gas model of laser-induced nucleation (LIN) suggest that even when cooperative effects are treated for large nuclei in both classical and two-step nucleation pathways, the nucleation rate enhancement from the optical Kerr effect remains negligible at experimental laser intensities.¹³

We report that lasers of similar intensity, wavelength, and pulse duration to those that induce crystal nucleation can also induce bubble nucleation when the aqueous solution is supersaturated with a volatile solute. Laser-induced bubble nucleation is demonstrated for carbonated water. We examine the laser intensity threshold for laser-induced bubble formation as a function of supersaturation. Using an aqueous solution that is cosupersaturated with argon and glycine, we also demonstrate that bubbles can induce crystal nucleation, independent of a laser. Finally, we emphasize that neither of the previously proposed mechanisms could enhance bubble formation. We conclude by discussing some of the possible alternative mechanisms for LIN.

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II. LASER-INDUCED BUBBLE NUCLEATION

Supersaturated aqueous carbon dioxide solutions were prepared in a custom glass vessel with height of 46 cm and diameter of 5 cm (picture available in supporting information¹⁴). The vessel was soaked overnight in an isopropanol/KOH bath to dissolve impurities on the glass surface. The vessel was then rinsed and filled with approximately 600 mL of ultrapure water obtained from a Barnstead Nanopure Infinity water purification system (resistivity > 17.9 M Ω -cm). 99.999% pure CO₂ (Praxair, Inc.) was then flowed through the vapor head space of the vessel to flush out all air. The vessel was then repeatedly pressurized with CO₂ and shaken to accelerate CO₂ uptake. When the gauge pressure was constant over several minutes of shaking, the solution was assumed to be at equilibrium with the pressurized CO₂. The pressures of solutions prepared in this manner remained constant for several days subsequent to shaking.

The vessel was then positioned with the laser beam (diameter of 3 mm) perpendicular to the glass surface. After waiting approximately 20 min after shaking to allow the solution to return to a quiescent state, the top valve was slowly opened to release the pressure while minimizing spontaneous bubble nucleation. After releasing all gauge pressure from the head space, the remaining CO₂ solution was at a supersaturated condition. The supersaturation of the resulting solution is expressed as the ratio c/c_{sat} where c is the solution concentration of CO₂ and c_{sat} is the saturation concentration. These concentrations were computed using Henry's law, which relates the solution phase concentration of a solute to its partial pressure in the gas phase. For CO₂ we use the solubility coefficients tabulated by Weiss.¹⁵ We neglected the high pressure correction which introduces an error of at most 0.3% in our computed supersaturations.

At some supersaturations, a small number of spontaneous bubbles were observed immediately after the valve was opened (generally less than ten), generally ceasing within a few minutes. After this, the time between spontaneous bubble nucleation events was at least 10³ s in the absence of a laser, based on our visual observations.

Keeping the valve open to the atmosphere, the solution was exposed to single 9 ns laser pulses of linearly polarized light generated by a Q-switched Nd:YAG laser (Continuum Powerlite 7010) at wavelengths of 355, 532, or 1064 nm. For pulses of sufficiently high energy, the bubbles nucleated instantaneously, i.e., within one second from the moment of the pulse. Figure 1 shows a photo taken immediately after exposure to a high energy pulse with energy far beyond the threshold. The figure shows that many bubbles have nucleated along the laser beam.

A characteristic feature of previous laser-induced experiments is the existence of a minimum laser intensity (threshold) required to induce nucleation.^{4,6,16} Laser-induced bubble nucleation exhibits a similar threshold. We systematically increased the pulse energy at different CO₂ supersaturations to identify the threshold laser intensity for bubble nucleation as a function of supersaturation. At each laser power, ten single laser pulses are fired into the solution at a rate of about one pulse per second. The threshold pulse energy to induce bub-



FIG. 1. Bubbles form along the laser beam line in response to a single laser pulse. The supersaturation was $c/c_{\text{sat}} = 2.50$. The laser produced 280 mJ/pulse at a wavelength of 532 nm, far above the threshold for laser-induced bubble nucleation.

ble nucleation at a given supersaturation is defined here as the minimum pulse energy that produces at least one bubble from the ten pulses. Figure 2 shows that the threshold pulse energy for laser-induced CO₂ bubble nucleation decreases as the supersaturation (the driving force for nucleation) is increased.

In addition to the ultrapure solutions described above, solutions were also prepared with municipal tap water and 99.5% pure CO₂, labeled “532 nm (tap)” in Fig. 2. These results parallel those with ultrapure reagents, indicating that the threshold is not sensitive to trace impurities. Comparison of the 355, 532, and 1064 nm results indicates that the wavelength of the applied laser light also does not strongly affect the threshold. We also observed laser-induced bubble nucleation in store bought seltzer water. Control experiments were performed with pure water (with no CO₂) and with concentrated carbon dioxide solutions at equilibrium with the gas phase (i.e., with the pressure relief valve not opened to the atmosphere). No visible bubbles were generated in either case even at the maximum power output of the laser (295 mJ/pulse).

III. BUBBLE-INDUCED CRYSTAL NUCLEATION

Bubble-induced crystallization was investigated by cosupersaturating an aqueous solution with both a crystal-forming solute (glycine) and a gaseous solute (argon). No laser was involved in these experiments. Glycine was first dissolved in ultrapure water by heating the solution. Experiments are performed at 22 °C, at which the solubility of glycine is 3.23 mol glycine/L H₂O. We studied solutions with glycine supersaturation $c/c_{\text{sat}} = 1.253$, although this figure may be affected by the presence of the argon gas. After cooling to room

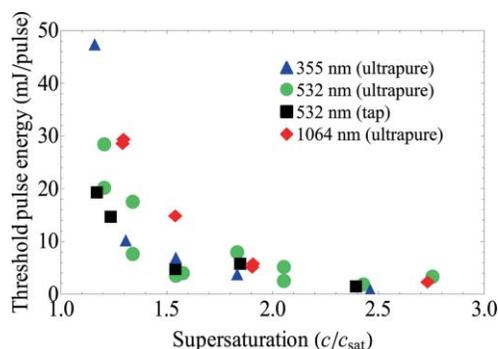


FIG. 2. Supersaturation dependence of the threshold laser pulse energy to induce bubble nucleation in aqueous carbon dioxide solutions at three different laser wavelengths. The “ultrapure” solutions are prepared with 99.999% pure CO₂ and ultrapure H₂O; “tap” solutions are prepared with 99.5% pure CO₂ and municipal tap H₂O.

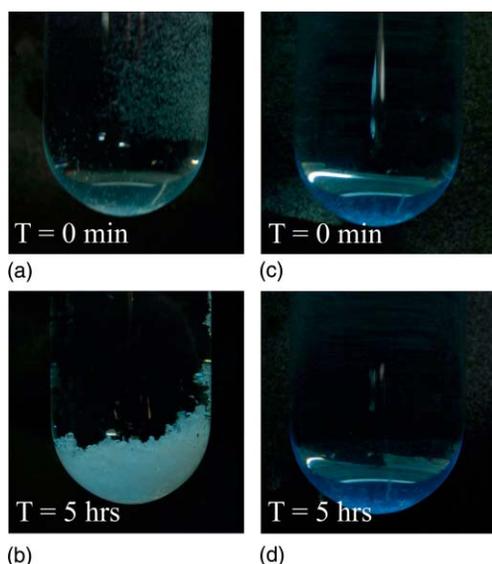


FIG. 3. Bubble-induced crystallization. Panels (a) and (b) show glycine crystal formation from a solution that is supersaturated with both glycine and argon and then shaken, whereas panels (c) and (d) show an absence of crystal formation when argon is absent.

temperature where the glycine is supersaturated, the solution was pressurized under 50 psig of 99.998% pure argon gas and shaken to speed argon uptake in the manner described previously. At this pressure, Henry's law suggests the argon concentration in solution was approximately 6.24×10^{-3} mol Ar/L H_2O . This corresponds to a supersaturation of $c/c_{\text{sat}} = 4.5$; however, the dissolved glycine may alter the argon solubility. After reheating under pressure to dissolve any glycine that may have crystallized during pressurization, the solution was again cooled to room temperature. Next, the pressure valve was opened to the atmosphere. The resulting solution was now supersaturated with respect to argon gas as well as to glycine. The valve was then closed and the vessel was gently shaken by hand to release argon bubbles. Videos of the shaking procedure are available in the supporting information.¹⁴ A myriad of argon bubbles formed throughout the solution volume.

Two control experiments were performed in a similar fashion. In the first, no argon gas was dissolved. In the second, the solution was pressurized with 50 psig of argon gas, as before. However, the pressure release valve was not opened to the atmosphere, thus the solution is only saturated with argon, not supersaturated. In each control experiment, a comparably small number of bubbles were visible after shaking the control solution, but these are due to the entrainment of air.

In the solution that was cosupersaturated with both glycine and argon, the myriad of bubbles was shortly followed by visible glycine crystals falling throughout the solution toward the bottom of the vessel. Nucleation and crystal growth continued for many minutes thereafter. The control experiment in which the pressure relief valve was never opened was performed once, giving no crystals. The control experiment with no argon in solution, was performed twice, with one instance giving no crystals and the other giving only a few. Photographs taken immediately after shaking and five hours after shaking are shown in Fig. 3 both with and without supersaturated argon.

IV. DISCUSSION

The present work constitutes the first example of laser-induced nucleation with a volatile solute, in which the nucleated phase is a vapor. All previous LIN studies focused on nucleating an ordered phase, either a crystal or a liquid crystal.^{2–10,16} Our investigation was motivated by questions about the validity of previously hypothesized mechanisms for LIN. As mentioned in the background, simple estimates as well as Monte Carlo simulations¹³ suggest that previously proposed mechanisms for LIN will have negligible impact on nucleation rates at the laser intensities of LIN experiments.

The nucleation of a gas bubble begins as a fluctuation in the solvent structure¹⁷ and would not be facilitated by enhanced interactions between CO_2 molecules or alignment of CO_2 molecules, thus ruling out an optical Kerr-type alignment mechanism for aqueous carbon dioxide solutions. A CO_2 bubble also has a smaller dielectric constant than the surrounding medium, so the bubble nucleus would not be stabilized according to the model of Isard.^{6,11} Our findings suggest that lasers must induce bubble nucleation by a mechanism that is different from those previously proposed LIN mechanisms.

Earlier work has shown that laser-induced cavitation in pure water,^{18–21} water with polystyrene beads present,²² and water with dye²³ can be achieved by nanosecond or near-nanosecond laser pulses of visible and near infrared light. These cavitation bubbles have maximum radii in the range of $O(10^1)$ – $O(10^3)$ micrometers and microsecond lifetimes,^{18–20,23} and collapse because they are an unstable phase. Similar bubbles are clearly implicated as an intermediate in the femtosecond laser-induced crystal nucleation of protein in agarose gel^{24,25} as well as anthracene in cyclohexane.²⁶

In addition, focused lasers of similar wavelength, pulse length, and pulse energies to those utilized in our experiments have previously been shown to induce solidification of supercooled liquid water, with cavitation bubbles serving as an intermediate in the process.²⁷ The cavitation bubbles are observed to form and collapse within about 100 μs . High speed images reveal that ice nuclei form at the sites where the bubbles have collapsed. Sonication of supersaturated solutions^{28–30} or supercooled water³¹ also induces crystallization (“sonocrystallization”). In sonocrystallization, the crystallization is also mediated by collapse of cavitation bubbles, perhaps due to associated compression in a pressure wave.^{27,31} Similar images and results have been obtained at similar laser parameters in experiments of laser-induced nucleation from solution, although these solutions have added dye.³²

NPLIN studies^{2–10,16} did not report the presence of cavitation bubbles. However, cavitation bubbles in those systems would also be microscopic (or smaller), unstable, and thus invisible to the naked eye. We note that both transient laser-induced cavitation bubbles²¹ and our laser-induced bubble nucleation events become more numerous with increasing laser intensity. We also note that laser-induced crystal nucleation experiments give larger numbers of crystals with increasing laser power.⁶

The current work shows that unfocused laser pulses such as those used in the NPLIN^{2–10,16} experiments can

induce bubble nucleation and additionally that small bubbles can induce crystal nucleation. Previous evidence shows that more focused laser pulses can generate micron-scale cavitation bubbles, which can induce crystal nucleation upon collapse.^{24–27} The combined evidence suggests that extremely small (possibly nanoscale) and transient bubbles may form in NPLIN experiments with unfocused lasers and catalyze crystal nucleation without being observed. A bubble may facilitate crystal nucleation by serving as a heterogeneous nucleation site^{33–35} or by the large pressure gradients created upon bubble collapse.^{36,37}

More work is needed to understand several aspects of the laser-induced nucleation mechanism. Nucleation often involves rare fluctuations in local structure or local composition and these important precursors may not be visible in the absorption spectrum of the bulk solution. We should, therefore, not draw conclusions about photochemical mechanisms from a lack of absorption bands in the bulk solution. Furthermore, our study and also previous studies of LIN only investigated laser-induced nucleation thresholds and probabilities at a few wavelengths. Thus, we should also not exclude or assert photochemistry before more thoroughly measuring laser-induced nucleation probabilities across a full spectrum of wavelengths. Systematic analysis of wavelength dependence of laser-induced nucleation with a continuously tunable light source would therefore be an excellent direction for future work.

V. CONCLUSIONS

Laser-induced nucleation of crystals was previously demonstrated for several molecules, salts, and proteins. Although the mechanism for laser-induced nucleation remains unknown, we have now demonstrated that laser pulses of similar duration, intensity, and wavelengths can also induce the nucleation of CO₂ bubbles in carbonated water. We have also demonstrated that the threshold pulse energy to induce CO₂ bubble nucleation decreases with increasing solution supersaturation and that the threshold is not a strong function of solution purity or laser wavelength. Importantly, alignment of molecules in a bubble is entropically disfavored, and vapor bubbles form because solute–solute and solute–solvent interactions are weak. Thus the previously-proposed optical Kerr mechanism which suggests that lasers align molecules to help them assemble into the crystal structure cannot explain laser-induced CO₂ bubble nucleation. Furthermore, the CO₂ bubble has a lower (not higher) dielectric than water, so the dielectric stabilization hypothesis is also unable to explain laser-induced CO₂ bubble nucleation. Additionally, we have shown in solutions supersaturated with both a crystal-former and a gaseous species that the presence of gas bubbles can induce the nucleation of the crystalline species.

ACKNOWLEDGMENTS

The authors thank Michael J. Gordon, Travis Koh and Isaac Riisness, as well as Gregg T. Beckham, Anamaria Soare, Herman J. M. Kramer, and John Frostad for helpful discussions and suggestions. B.P. was supported by the NSF CAREER Award No. 0955502.

- ¹D. W. Oxtoby, *Nature (London)* **420**, 277 (2002).
- ²J. Zaccaro, J. Matic, A. S. Myerson, and B. A. Garetz, *Cryst. Growth Des.* **1**, 5 (2001).
- ³X. Y. Sun, B. A. Garetz, and A. S. Myerson, *Cryst. Growth Des.* **6**, 684 (2006).
- ⁴B. A. Garetz, J. Matic, and A. S. Myerson, *Phys. Rev. Lett.* **89**, 175501 (2002).
- ⁵X. Y. Sun, B. A. Garetz, and A. S. Myerson, *Cryst. Growth Des.* **8**, 1720 (2008).
- ⁶A. J. Alexander and P. J. Camp, *Cryst. Growth Des.* **9**, 958 (2009).
- ⁷I. S. Lee, J. M. B. Evans, D. Erdemir, A. Y. Lee, B. A. Garetz, and A. S. Myerson, *Cryst. Growth Des.* **8**, 4255 (2008).
- ⁸C. Duffus, P. J. Camp, and A. J. Alexander, *J. Am. Chem. Soc.* **131**, 11676 (2009).
- ⁹X. Y. Sun, B. A. Garetz, M. F. Moreira, and P. Palfy-Muhoray, *Phys. Rev. E* **79**, 021701 (2009).
- ¹⁰B. A. Garetz, J. E. Aber, N. L. Goddard, R. G. Young, and A. S. Myerson, *Phys. Rev. Lett.* **77**, 3475 (1996).
- ¹¹J. O. Isard, *Philos. Mag.* **35**, 817 (1977).
- ¹²B. C. Knott, N. Duff, M. F. Doherty, and B. Peters, *J. Chem. Phys.* **131**, 224112 (2009).
- ¹³B. C. Knott, M. F. Doherty, and B. Peters, *J. Chem. Phys.* **134**, 154501 (2011).
- ¹⁴See supplementary material at <http://dx.doi.org/10.1063/1.3582897> for supplemental figure, video 1, and video 2. Supplemental figure: Custom glass vessel used for all experiments. The vessel height is 46 cm and the diameter is 5 cm. Video 1: Shaking procedure for bubble-induced crystallization experiment. The solution is supersaturated with glycine but the solution contains no argon. This control experiment corresponds to the photographs in Fig. 3, panels (c) and (d). Video 2: Shaking procedure for bubble-induced crystallization experiment. The solution is supersaturated with both glycine and argon. The glycine supersaturation is the same as in video 1. Shaking induces the formation of many argon bubbles. This experiment corresponds to the photographs in Fig. 3, panels (a) and (b).
- ¹⁵R. F. Weiss, *Mar. Chem.* **2**, 203 (1974).
- ¹⁶J. Matic, X. Y. Sun, B. A. Garetz, and A. S. Myerson, *Cryst. Growth Des.* **5**, 1565 (2005).
- ¹⁷Z. J. Wang, C. Valeriani, and D. Frenkel, *J. Phys. Chem. B* **113**, 3776 (2009).
- ¹⁸V. Venugopalan, A. Guerra, K. Nahen, and A. Vogel, *Phys. Rev. Lett.* **88**, 078103 (2002).
- ¹⁹A. Vogel, S. Busch, and U. Parlitz, *J. Acoust. Soc. Am.* **100**, 148 (1996).
- ²⁰P. Giovanneschi and D. Dufresne, *J. Appl. Phys.* **58**, 651 (1985).
- ²¹H. Lubatschowski, G. Maatz, A. Heisterkamp, U. Hetzel, W. Drommer, H. Welling, and W. Ertmer, *Graef's Arch. Clin. Exp. Ophthalmol.* **238**, 33 (2000).
- ²²Y. Q. Jiang, Y. Matsumoto, Y. Hosokawa, H. Masuhara, and I. Oh, *Appl. Phys. Lett.* **90**, 061107 (2007).
- ²³K. Y. Lim, P. A. Quinto-Su, E. Klaseboer, B. C. Khoo, V. Venugopalan, and C. D. Ohl, *Phys. Rev. E* **81**, 016308 (2010).
- ²⁴H. Y. Yoshikawa, R. Murai, S. Sugiyama, G. Sazaki, T. Kitatani, Y. Takahashi, H. Adachi, H. Matsumura, S. Murakami, T. Inoue, K. Takano, and Y. Mori, *J. Cryst. Growth* **311**, 956 (2009).
- ²⁵R. Murai, H. Y. Yoshikawa, Y. Takahashi, M. Maruyama, S. Sugiyama, G. Sazaki, H. Adachi, K. Takano, H. Matsumura, S. Murakami, T. Inoue, and Y. Mori, *Appl. Phys. Lett.* **96**, 043702 (2010).
- ²⁶K. Nakamura, Y. Hosokawa, and H. Masuhara, *Cryst. Growth Des.* **7**, 885 (2007).
- ²⁷B. Lindinger, R. Mettin, R. Chow, and W. Lauterborn, *Phys. Rev. Lett.* **99**, 045701 (2007).
- ²⁸H. Li, J. K. Wang, Y. Bao, Z. C. Guo, and M. Y. Zhang, *J. Cryst. Growth* **247**, 192 (2003).
- ²⁹R. K. Bund and A. B. Pandit, *Chem. Eng. Process.* **46**, 846 (2007).
- ³⁰R. K. Bund and A. B. Pandit, *Ultrason. Sonochem.* **14**, 143 (2007).
- ³¹R. Chow, R. Blindt, R. Chivers, and M. Povey, *Ultrasonics* **43**, 227 (2005).
- ³²A. Soare, R. Dijkink, M. Rodriguez Pascual, C. Sun, P. Cains, D. Lohse, A. Stankiewicz, and H. J. M. Kramer, *Cryst. Growth and Des.* (in press).
- ³³A. F. Heneghan and A. D. J. Haymet, *Chem. Phys. Lett.* **368**, 177 (2003).
- ³⁴D. Kashchiev, *Nucleation: Basic Theory with Applications* (Butterworth-Heinemann, Oxford, 2000).
- ³⁵M. J. Davis and P. D. Ihinger, *Am. Mineral.* **83**, 1008 (1998).
- ³⁶C. Virone, H. J. M. Kramer, G. M. van Rosmalen, A. H. Stoop, and T. W. Bakker, *J. Cryst. Growth* **294**, 9 (2006).
- ³⁷K. Ohsaka and E. H. Trinh, *Appl. Phys. Lett.* **73**, 129 (1998).