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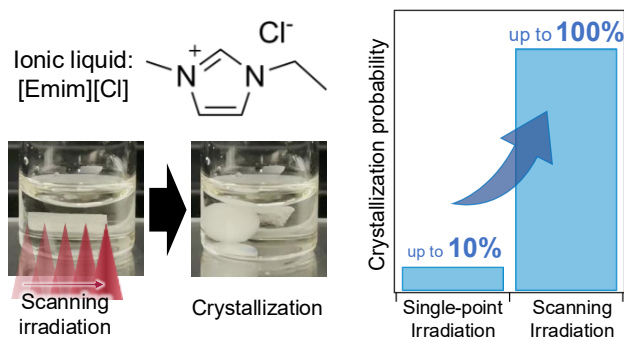
Enhancement of Crystallization of Ionic Liquids by Scanning Irradiation with Focused Ultrashort Laser Pulses

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ABSTRACT

This study investigates the crystallization behavior of the ionic liquid 1-ethyl-3-methylimidazolium chloride ([Emim][Cl]) induced by focused irradiation with ultrashort laser pulses with the pulse duration of 100 fs or 5 ps. The crystallization was significantly enhanced through scanning irradiation compared to single-point irradiation, probably due to an increase in numbers of laser-induced bubbles and less temperature elevation. The scanning irradiation with 5-ps laser pulses resulted in a higher crystallization probability than that with 100-fs laser pulses, which is attributed to the larger bubbles generated by 5-ps pulses (≥ 1 mm) compared to those with 100-fs pulses ($\ll 1$ mm). Our findings that focused scanning irradiation with 5-ps laser pulses can efficiently induce crystal nucleation will offer a guiding principle for the efficient crystal nucleation of various compounds, impacting a broad range of scientific and industrial fields such as crystal engineering and materials science.



TOC Graphic

1. Introduction

Laser ablation, defined by macroscopic morphological changes of materials induced by pulsed laser irradiation above a certain energy threshold, has widely been utilized for fine-tuned material processing in various scientific and industrial fields such as nano/micro-structuring,^{1, 2} nanoparticle fabrication^{3, 4}, chemical analysis^{5, 6}, and so on. Here, one typically uses laser ablation to achieve etching and crushing of solids, namely, as a tool for top-down processing (downsizing of materials). On the other hand, the features of laser ablation have also shown promise for bottom-up fabrication processes such as chemical synthesis of nanomaterials,^{7, 8} thin film formation (pulsed laser deposition),^{9, 10} and promotion of crystal nucleation and growth.¹¹⁻¹⁵ Notably, crystal nucleation induced by laser ablation of supersaturated/supercooled liquids is a unique processing for the fabrication of crystals in liquids.¹¹ This technique was initially demonstrated for protein crystallization¹⁶⁻²³, which is known to be particularly difficult to be achieved due to very weak intermolecular interactions. So far, the laser ablation-based control of crystallization (e.g., crystal size, shape, quality, polymorphs, etc.) has also been reported for various organic²⁴⁻³³/inorganic³⁴⁻³⁹ compounds. More recently, our group demonstrated control of ice crystallization with a spatiotemporal precision of micrometers and microseconds by ultrashort laser ablation of supercooled water, which enabled the monitoring of the early dynamics of ice crystallization with a high-speed framing camera (125,000 fps).³⁸ These results clearly indicate that laser ablation is prominent in the advanced control of crystal nucleation that cannot be achieved by conventional methods alone.

To develop the controllability of crystal nucleation by laser ablation, the dependence of crystal nucleation on various laser parameters has systematically been studied so far. For instance, laser energy is one of the key parameters that can significantly influence the crystal nucleation

probability, as increasing laser energy often promotes crystal nucleation (for urea, anthracene, glycine, sulfathiazole, ice, potassium chloride),^{25-27, 31, 38-40} while some compounds experience suppression above a certain energy (for white hen egg lysozyme, glacial acetic acid, sodium acetate).^{32, 41, 42} The impact of repetition rates was also reported for 4-dimethylamino-*N*-methyl-4-stilbazolium tosylate and urea,^{24, 43} with higher repetition rates (e.g., ≥ 1000 Hz) resulting in lower crystallization probability than that with lower repetition rates (e.g., ≤ 500 Hz). Additionally, laser pulses with the duration of a few picoseconds often provide higher crystallization probability of glacial acetic acid, urea, and ice than those with laser pulses with femtoseconds and few hundred picoseconds.^{32, 38, 40} As for the mechanism of crystal nucleation, recent studies experimentally and theoretically suggested that bubble generation and temperature elevation are profoundly involved in crystal nucleation by laser ablation.^{32, 33, 38-40, 44} Specifically, bubble generation promotes crystal nucleation by increasing local concentration and/or enhancing heterogeneous nucleation, while temperature elevation suppresses it by decreasing supersaturation/supercooling.^{32, 33, 38-40, 44} The above-mentioned past studies indicate that the regulation of bubble generation and temperature elevation may achieve further improvement of crystal nucleation.

In this work, we report the systematic study of laser-induced crystallization of ionic liquids, which are typically defined as salts with a melting point below 100 °C.⁴⁵ Ionic liquids often have significantly lower vapor pressure (e.g., ≤ 1 Pa).⁴⁶⁻⁴⁸ Therefore, laser ablation of ionic liquids should mainly produce gas bubbles produced by photochemical/photothermal reactions (e.g., decomposition) of ionic liquid rather than thermally induced vapor bubbles (cavitation bubbles), which is in contrast to other compounds where both vapor and gas bubbles appear after laser ablation (e.g., water, vapor pressure: 2300 Pa at 20 °C).^{49, 50} Here we used a supercooled melt of 1-ethyl-3-methylimidazolium chloride ([Emim][Cl]) with a melting point of 84 °C,⁵¹ facilitating

the experiments at room temperature. To clarify the impact of the laser irradiation on crystal nucleation of [Emim][Cl], we systematically investigated the crystallization probability under various laser conditions, including laser energy (60 – 180 $\mu\text{J/pulse}$), pulse durations (100 fs or 5 ps), scan speed (0 mm/s: single-point irradiation, 0.16 – 4.0 mm/s: scanning irradiation), and irradiation patterns (one-line or square). To obtain statistically reliable data sets that address the impact of laser irradiation conditions on crystallization behavior, ten samples were tested in each condition. Finally, the crucial parameters that can promote the laser-induced crystal nucleation are discussed.

2. Material and Methods

2.1 Sample preparation

[Emim][Cl] (> 98.0%), purchased from Tokyo Chemical Industry Co., Ltd., was used without further purification. Firstly, crystals of [Emim][Cl] were incubated at 100°C for over 1 h to completely melt. Then, an aliquot of the melt (~ 0.5 mL) was dispensed into a glass vial (S-7, Nichiden-Rika Glass Co., Ltd.) on a heating stage. The melt was then incubated at room temperature (~ 20 °C) for more than 30 min, often remaining in a supercooled state for about another hour. Supercooling, defined as the subtraction of room temperature from melting point, was estimated to be 64 °C. Finally, the glass vial was mounted on the motorized stage of an inverted microscope (IX71, Olympus) for the subsequent laser experiments.

2.2 Optical setup for laser-induced crystallization

The optical setup is shown in Figure S1. Laser pulses from a regenerative amplified Ti:Sapphire laser system (Astrella, Coherent) were introduced to the microscope and focused into the melt of ionic liquid through an objective lens (10×, NA = 0.40, Plan Apo, Olympus). Note that the bottom surface of the glass vial has a converging meniscus lens-like geometry, which may slightly alter the focusing via the objective lens. The central wavelength (λ), pulse durations (Δt), and repetition rate of the laser pulses were 800 nm, 100 fs or 5 ps, and 1 kHz, respectively. The pulse durations were tuned by varying the angle of a grating in the stretcher in the chirped pulse amplification system. The focal radius is estimated to be ~ 1.2 μm according to Rayleigh's criterion ($0.61 \times \lambda/\text{NA}$). The scanning irradiation was performed using a programmable motorized stage (controller: SHOT-702, Sigma, stage: BIOS-Light, Sigma) with scan speeds (V) of 0.16, 0.80, and 4.0 mm/s. Since the repetition rate of laser pulses is 1 kHz, the distances between laser pulses are

0.16, 0.80, and 4.0 μm at $V = 0.16, 0.80,$ and 4.0 mm/s , respectively. Laser energy was adjusted by a combination of a half-wave plate (WPH10M-808, Thorlabs) and a polarizing beam splitter (GL15-B, Thorlabs). The irradiation time was controlled with an electric shutter (controller: SC10, Thorlabs, shutter: SH1/M, Thorlabs). Macroscopic images of crystallization dynamics were captured with a camera (iPhone 12 mini, Apple, 30 fps), while microscopic images through the objective lens were captured with a CMOS camera (WRAYCAM-CIX830, WRAYMER, 30 fps) or a high-speed camera (HPV-2, Shimazu, $\leq 1 \text{ Mfps}$). Image analysis was performed using ImageJ software (NIH).

3. Result and Discussion

3.1. Crystallization behavior of [Emim][Cl] induced by laser ablation

Figure 1a and 1b (Movie S1 and S2) show representative dynamics of [Emim][Cl] crystallization induced by focused irradiation with laser pulses at a single-point (without laser scanning) for 30 s. In the case of 100-fs laser pulses (Figure 1a), fine bubbles (diameter: $\sim 10 \mu\text{m}$) were continuously generated from the laser focus, which is likely attributed to gas bubbles that were produced by photochemical/photothermal effects of [Emim][Cl] (denoted as long-lasting bubbles).⁴⁹ These bubbles slowly moved up at a velocity of $\sim 10 \mu\text{m/s}$ (cf. Figure S2a). Then, crystals of [Emim][Cl] were formed around these bubbles ($t = 60 \text{ s}$, observed as a spherical mass) and gradually grew until the entire melt was filled. On the other hand, the focused irradiation with 5-ps laser pulses (Figure 1b) produced larger bubbles (diameter: $\sim 1 \text{ mm}$) compared with 100-fs laser pulses. In fact, it was reported that the gas yield upon picosecond laser ablation of organic liquids is more than femtosecond laser ablation.⁵² The bubbles generated by 5-ps laser pulse rapidly ascended at a velocity of $> 100 \mu\text{m/s}$ (cf. Figure S2b). Similar to the case with 100-fs laser

pulses (Figure 1a), crystals were formed around these bubbles (see $t = 30$ s in Figure 1b). These results indicate that laser ablation of the ionic liquid can induce its crystal nucleation.

Since the incident laser pulses at a single-point may largely hit bubbles that are produced with preceding laser pulses (cf. Movie S1 and S2), we next investigated crystallization by one-dimensional scanning of laser pulses during irradiation (Figure 1c and 1d, Movie S3 and S4). The motorized stage was reciprocated perpendicularly to the observation direction. The scan length (L) and the scan speed (V) were set to ~ 8 mm and ~ 4.0 mm/s, respectively. In the case of 100-fs laser pulses (Figure 1c), numerous fine bubbles (~ 10 μ m) were formed along the scan line and then became like a veil. On the other hand, the irradiation with 5-ps laser pulses (Figure 1d) initially provided several larger bubbles with a diameter of ~ 1 mm, sometimes coalescing into even larger bubbles during scanning (e.g., > 2 mm in diameter). In both cases, the [Emim][Cl] crystals that were observed as a spherical mass were formed around the bubbles.

It should be noted that crystal nucleation of [Emim][Cl] sometimes took place after cessation of laser irradiation (e.g., Figure 1a). This result implies that laser-induced long-lasting bubbles that remain in the liquid on the scale of minutes play a crucial role in the crystal nucleation, of which detailed mechanism is discussed in the later section (Section 3.3).

3.2. Experimental parameters impacting crystallization probability.

In addition to the difference in the crystallization behaviors between single-point and scanning irradiation (Figure 1), the crystallization probability also significantly varied according to these irradiation manners. Figure 2a and 2b show the crystallization probability for single-point and scanning irradiation, respectively. Crystallization probability is defined as the ratio of the number of nucleated samples to the total number of samples tested. To distinguish the spontaneous

crystal nucleation and laser-induced crystal nucleation, trials where crystals were formed within 180 s after the start of irradiation were counted as successful outcomes (note that laser pulses were shot for 30 s). The single-point irradiation seldom induced crystal nucleation with the probability of 10%, while the scanning irradiation resulted in the crystallization probability of $> 50\%$ under all conditions. Pearson's chi-square test with $P = 5\%$ level confirmed a significant difference in the probabilities between these irradiation manners ($\chi^2(1) > 5.5$, $P < 2.0\%$), indicating that scanning irradiation could enhance the crystal nucleation of [Emim][Cl].

We then investigated the influence of scan speed (V) on the crystallization probability. Figure S3 shows the crystallization behavior at $V = 0.16$ and 0.80 mm/s (see also Figure 1, $V = 0.0$ and 4.0 mm/s). In the case of 100-fs laser pulses (Figure S3a, S3b, 1a, and 1c), the space occupied by the bubbles tended to increase as the scan speed increased from 0 mm/s (single-point) to 0.16 and 0.80 mm/s, while it remained similar between $V = 0.80$ and 4.0 mm/s. Similarly, the irradiation with 5-ps laser pulses (Figure S3c, S3d, 1b, and 1d) provided more bubbles with increasing the scan speed. The average $\pm$ standard deviation numbers of long-lasting bubbles with diameters of ≥ 1 mm (visible to the naked eyes) were 2.4 ± 0.5 at $V = 0$ mm/s, 5.3 ± 0.9 at $V = 0.16$ mm/s, 9.8 ± 1.8 at $V = 0.80$ mm/s, and 16.9 ± 3.4 at $V = 4.0$ mm/s ($n = 10$ per condition). The increment of the numbers of bubbles is probably because the laser pulses could be largely absorbed into the ionic liquid without disturbance from pre-produced bubbles. Figure 3 shows the dependence of crystallization probability on scan speed. At $V = 0.16$ mm/s, the crystal nucleation probability with 100-fs laser pulses was the same as that at single-point irradiation (10%), while that with 5-ps laser pulses was improved (40%). Further increase in scan speed resulted in higher crystallization probabilities: $\geq 50\%$ with 100-fs laser pulses and $\geq 80\%$ with 5-ps laser pulses. This result suggests

that faster scan speeds (e.g., $V = 0.8$ and 4.0 mm/s) tend to provide higher crystallization probabilities than no and slow scanning ($V = 0$ and 0.16 mm/s).

To further investigate the crystallization probability dependence on scanning irradiation, we altered the scanning pattern from the one-line to a square (Figure S4a). Regarding 100-fs laser pulses (Figure S4b and S4c), long-lasting bubbles were formed along the scanning lines of the square, similar to the one-line scanning (Figure 1c, S3a, and S3b). The irradiation with 5-ps laser pulses also provided bubbles along the scanning lines (Figure S4c and S4d), with the number of bubbles increasing with the side length of the square pattern. Figure 4 shows the dependence of crystallization probability on the side length. In the case of 100-fs laser pulses, the nucleation probability increased with increasing the side length. On the other hand, the irradiation with 5-ps laser pulses resulted in a probability of 100% under all conditions. These results indicate that longer scanning lengths with square patterns can improve crystallization probability, which is possibly attributed to the increase in the number of long-lasting bubbles. Notably, the irradiation with 5-ps laser pulses can induce crystallization more efficiently than that with 100-fs laser pulses (Figure 2, 3, and 4).

3.3 Proposed mechanism of enhancement of crystallization probability.

This study revealed that scanning irradiation promotes the crystal nucleation of [Emim][Cl]. Past studies of laser ablation-induced crystallization have reported that laser-induced bubbles (cavitation and long-lasting bubbles) play a pivotal role in crystal nucleation by increasing local concentration, enhancing heterogeneous nucleation, and so on.^{20, 22, 26, 31-34, 38-41, 44, 53} Our typical results (Figure 1, S2, S3, and S4) showed crystal formation around long-lasting bubbles, which may be one of the major triggers for crystal nucleation of [Emim][Cl]. Meanwhile, we also found

that the crystallization sometimes took place from the bottom of glass vials where the laser was not focused (cf. Figure S3a). To clarify the mechanism, we observed the bottom of the glass vials after laser irradiation and then found the formation of a row of fine bubbles (Figure S5). Besides, crystallization was sometimes observed after the cessation of laser irradiation (Figure S6). As a representative example, Figure S7 shows the crystallization behavior from long-lasting bubbles after scanning irradiation ($V = 4.0$ mm/s) with focused 100 fs-laser pulses with $E = 180$ μ J/pulse. The nucleation timing was estimated to be $t > 140$ sec (> 110 sec after cessation), considerably later than the early-stage dynamics of laser ablation-induced phenomena such as shockwave propagation and cavitation bubble generation (typically within ~ 100 μ s after the laser shot).⁵⁰ According to these facts, the enhancement of crystallization probability by scanning irradiation (Figure 2, 3, and 4) was possibly attributed to increase in the numbers of laser-induced bubbles.

In addition to the long-lasting bubble generation, temperature elevation should also be an important factor that influences the crystal nucleation. Several studies suggested that temperature elevation accompanied by laser irradiation suppresses crystal nucleation by decreasing supersaturation and supercooling.^{24, 32, 33, 40} To evaluate the influence of temperature elevation on crystal nucleation of [Emim][Cl], we simply assessed the temperature distribution in the following model. Here we ignore heat diffusion due to liquid flows and also assume that the temperature distribution after a single laser shot is governed by the following diffusion equation.

$$\frac{\partial T}{\partial t} = \alpha \frac{\partial^2 T}{\partial x^2} \quad (1)$$

Here, T and α are temperature and thermal diffusivity of [Emim][Cl], respectively. Assuming that (1) the temperature at $x = \pm\infty$ is constant regardless of time and (2) the irradiation with a single laser pulse raises the temperature at an infinitesimally small spot at $x = 0$ mm by T_0 at $t = 0$ ms, the solution of eq.(1) is as follows at $t > 0$ ms.

$$T(x, t) = \frac{T_0}{\sqrt{4\alpha\pi t}} \exp\left(-\frac{x^2}{4\alpha t}\right) \quad (2)$$

We additionally assume the following situation: (I) laser pulses start to shot from $t = 0$ ms with 1 kHz for 2 s (2,000 pulses, note that the laser irradiation finishes at $t = 1999$ ms), (II) scan speed is $V = 0.0, 0.16, 0.80$ or 4.0 mm/s ($t \geq 0$ s), (III) the laser pulses are absorbed in [Emim][Cl] without disturbance from pre-produced bubbles, and (IV) laser scanning starts from $x = V_{\text{num}}$ mm toward negative x -direction, where V_{num} is the numerical value of V expressed in millimeters. In this condition, the temperature distribution at $t = 2$ s is expressed as sum of the eq.(2) with different time and location, as follows.

$$T(x, V) = T_0 \sum_{t=1}^{2000} \frac{1}{\sqrt{4\alpha\pi t}} \exp\left[-\frac{\{x + V(1 - 10^{-3}t)\}^2}{4\alpha t}\right] \quad (3)$$

Since Zhao et al. reported the thermal diffusivity of $0.11 - 0.12$ mm²/s for ionic liquids with structures similar to [Emim][Cl] (e.g., 1-methyl-3-octylimidazolium chloride, 1-butyl-3-methylimidazolium tetrafluoroborate),⁵⁴ herein α was set to 0.1 mm²/s. Besides, T_0 was normalized so that $T(0 \text{ mm}, 0 \text{ mm/s})$, which gives the maximum value, becomes 1.0. Figure 5 shows temperature distribution at $t = 2$ s. Increment of scan speed decreased the maximum temperature (0.96 at $V = 0.16$ mm/s, 0.50 at $V = 0.80$ mm/s, and 0.10 at $V = 4.0$ mm/s). Since crystal nucleation often take place in the vicinity of laser focus (e.g., $\leq \sim 100$ μm),³⁸ the less temperature elevation at nucleation sites with increasing scan speed should contribute to the improvement in crystallization probability.

Regarding the effect of pulse duration, the irradiation with 5-ps laser pulses provided higher crystallization probability than that with 100-fs laser pulses (Figure 2b, 3, and 4), except for the case of single-point irradiation (Figure 2a). We considered this to be attributable to differences in bubble generation since past studies of laser ablation-induced crystallization have

shown higher crystallization probability at laser condition where larger bubbles (or cavitation bubbles) were produced.^{31, 32, 38, 40} One of the interpretations for this may be enhancement of adsorption and ordering of the molecules (and/or clusters) at the bubble surface, being attributed to the distinct surface tension and/or curvature. In this study, the long-lasting bubbles generated by 5-ps laser pulses (e.g., ~ 1 mm) were considerably larger than those generated by 100-fs laser pulses (e.g., ~ 10 μm), which may contribute to higher crystallization probability. In addition, the long-lasting bubble generated by 100-fs laser pulses remained around the laser focus for a long time (ascending speed: ~ 10 $\mu\text{m/s}$, cf. Figure S2a), while those generated by 5-ps laser pulses quickly floated up (ascending speed: > 100 $\mu\text{m/s}$, cf. Figure S2b), indicating that long-lasting bubbles generated by 5-ps laser pulses can move away from the laser focus, that is, the region of temperature increased. This should also contribute to the enhancement of crystal nucleation with 5-ps laser pulses.

In addition to the final size of the bubbles, we also found that the dynamics of bubble generation was considerably different between 100-fs and 5-ps laser pulses. Figure 6 shows the high-speed images of bubble generation behavior upon a single laser pulse ($E = 180$ $\mu\text{J/pulse}$). In the case of the 100-fs laser pulse, a strong flash, presumably attributed to the generation of plasma and/or supercontinuum light, was observed immediately after laser irradiation ($t \sim 0$ μs). The next frame shows a blurred dark shadow, probably attributed to the assembly of bubbles. They gradually shrank over time (see time-space diagram). A single bubble with diameter of ~ 10 μm finally appeared at the laser focus ($t \sim 1$ s). In contrast, the irradiation with a 5-ps laser pulse provided a clearer bubble without flash. It initially expanded but subsequently maintained almost the same size (~ 130 μm in diameter). Notably, the bubble size at $t = 98$ μs was almost identical with that at $t \sim 1$ s. This result suggests that the favorable sites for nucleation given by laser-

induced bubble lasted significantly longer for the 5-ps laser pulse than for the 100-fs laser pulse, which well explains the higher crystallization probabilities. Overall, this study revealed the optimal laser conditions (focused scanning irradiation with 5-ps laser pulses in a square pattern) that regulate bubble generation and temperature elevation, which can lead to the efficient crystal nucleation of the ionic liquid [Emim][Cl] (up to 100%).

4. Conclusion

This study investigated crystallization of the ionic liquid 1-ethyl-3-methylimidazolium chloride ([Emim][Cl]) by ultrashort laser ablation. Focused laser irradiation into the supercooled state of [Emim][Cl] produced bubbles at the laser focus, serving as crystal nucleation sites of [Emim][Cl]. Notably, scanning irradiation significantly enhanced crystal nucleation compared with single-point irradiation, probably due to the increment of the numbers of laser-induced bubbles and less temperature elevation. In addition, 5-ps laser pulses provided a higher crystallization probability than 100-fs laser pulses, probably because 5-ps laser pulses generated larger laser-induced bubbles, enhancing adsorption and ordering of molecules (and/or clusters) at the bubble surface. We foresee that our findings —focused scanning irradiation with picosecond laser pulses can promote crystal nucleation— will enable the efficient crystal nucleation of various materials. Moreover, ionic liquids are known to exhibit diverse polymorphism attributed to their high conformational flexibility.⁵⁵ We also expect that laser ablation will contribute to the precise control of polymorphism of ionic liquids, impacting various research fields such as materials science.

FIGURES

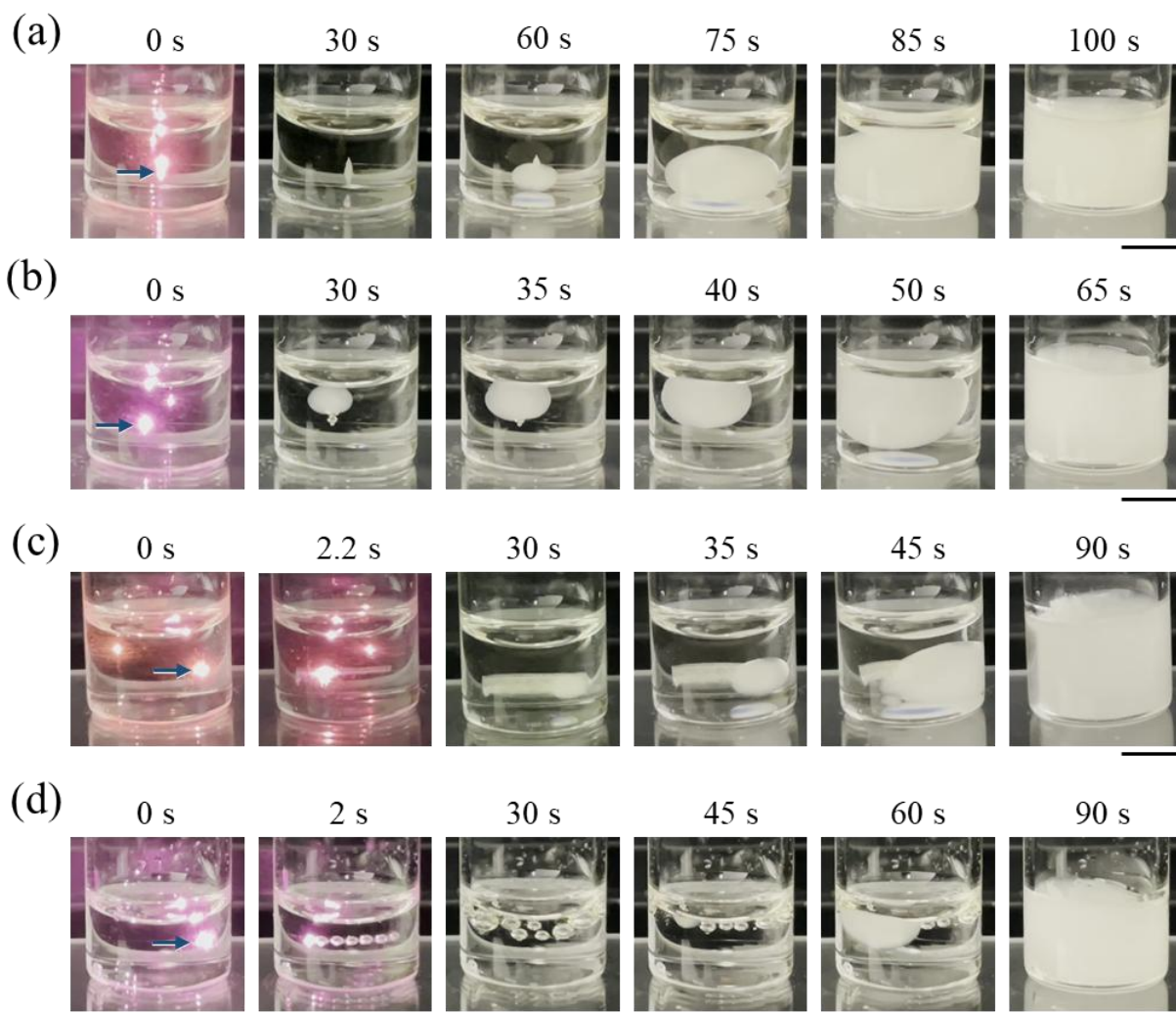


Figure 1. Crystallization behavior of [Emim][Cl] triggered by irradiation with ultrashort laser pulses. (a,b) Single-point irradiation and (c,d) scanning irradiation ($V = 4.0$ mm/s). (a,c) Focused 100-fs laser pulses and (b,d) 5-ps laser pulses with $E = 180$ μ J/pulse were irradiated into the melt for 30 seconds with repetition rate of 1 kHz. Laser pulses were focused ~ 3 mm above the bottom of the glass vial. The blue arrows indicate the focal spots. The timing upon laser irradiation was defined as $t = 0$ s. Scale bars represent 5 mm.

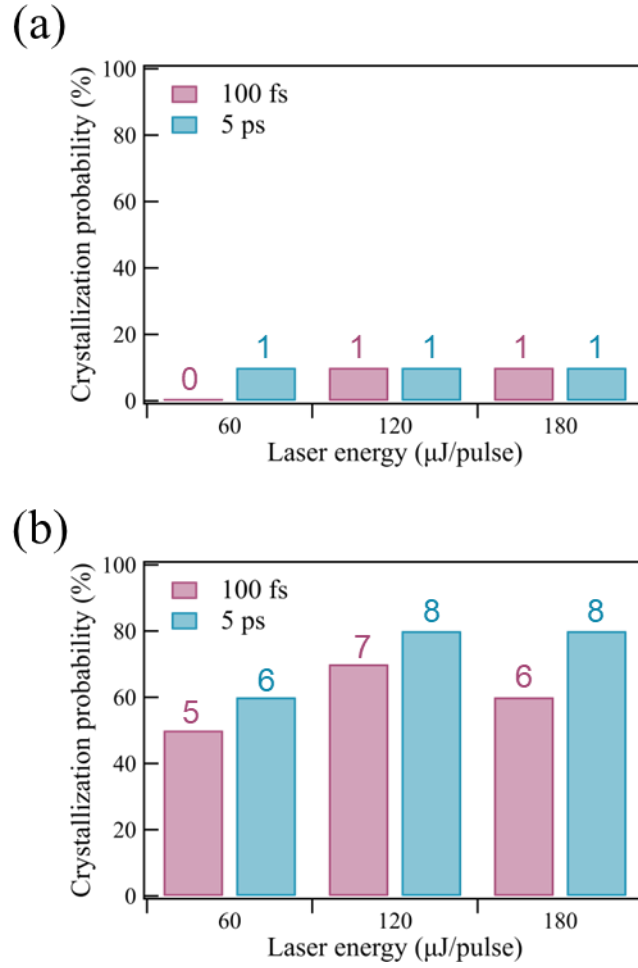


Figure 2. Laser energy dependence of crystallization probability with the scan speed of (a) 0 mm/s (single-point irradiation) and (b) 4.0 mm/s. The laser pulses were shot for 30 s. Ten samples were tested at each condition. The number of nucleated samples is shown for each condition.

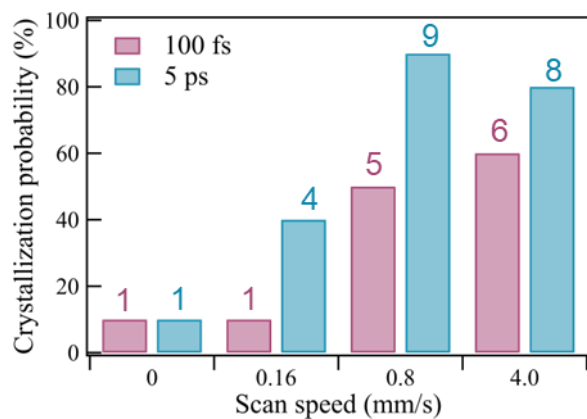


Figure 3. Dependence of crystallization probability on scanning speed. Laser energy was set to $E = 180 \mu\text{J/pulse}$. The laser pulses were shot for 30 s. Ten samples were tested at each condition. The number of nucleated samples is shown for each condition.

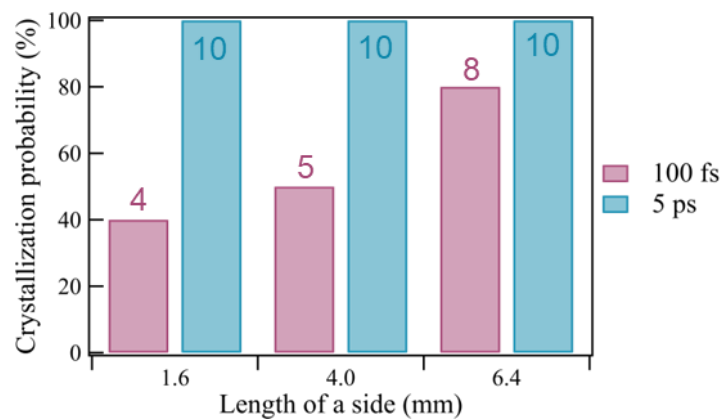


Figure 4. Dependence of crystallization probability on the length of a side. Laser energy and scan speed were set to $E = 180 \mu\text{J/pulse}$ and $V = 4.0 \text{ mm/s}$. The laser pulses were shot for 30 s. Ten samples were tested at each condition. The number of nucleated samples is shown for each condition.

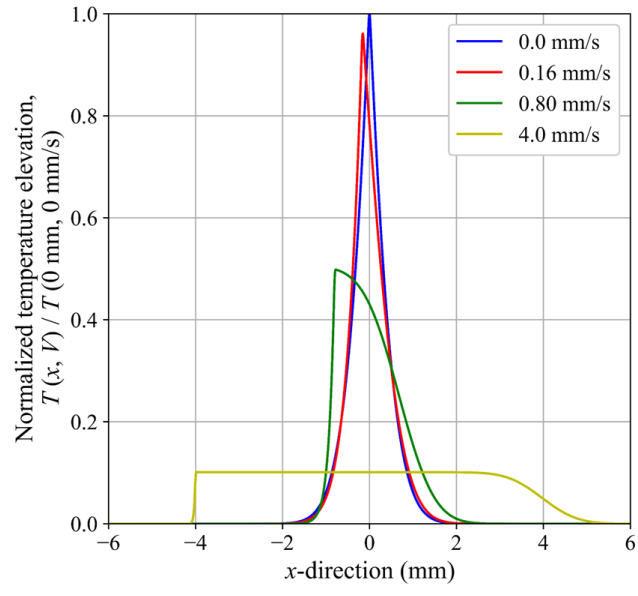


Figure 5. Temperature distribution at $t = 2$ s after the onset of laser irradiation.

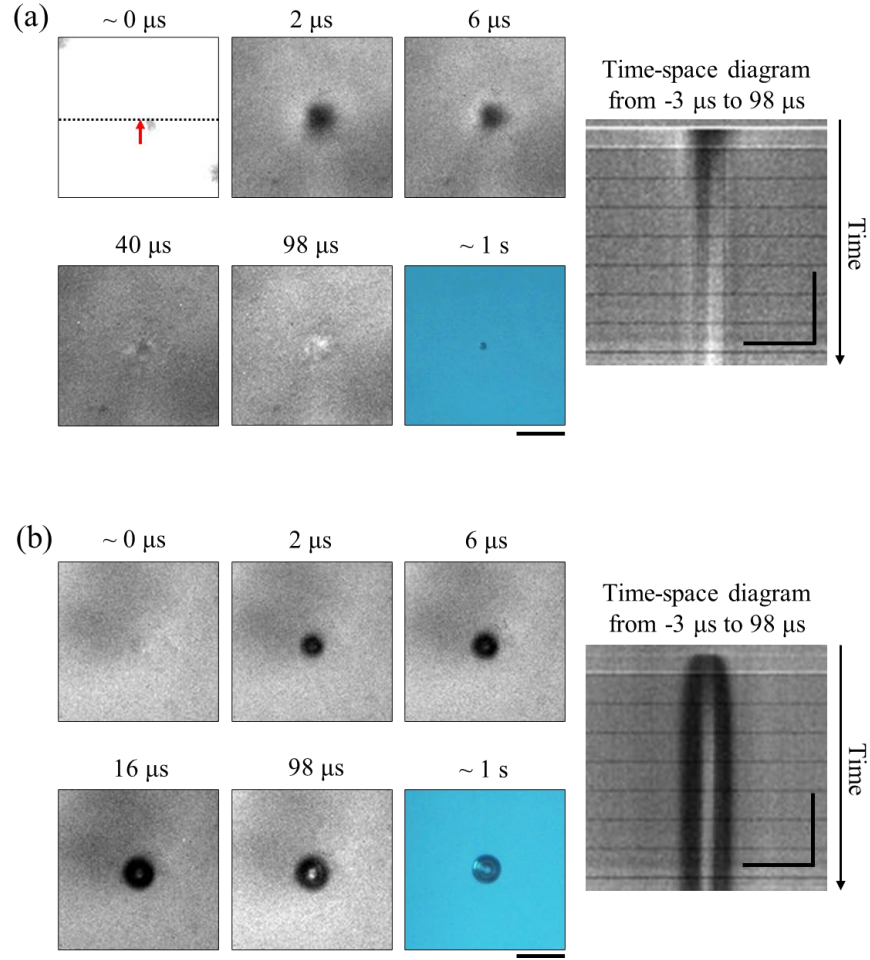


Figure 6. Dynamics of early stage of bubbles generation induced by focused irradiation with (a) 100-fs laser pulse and (b) 5-ps laser pulse with $E = 180 \mu\text{J/pulse}$. The right part shows the space-time diagram of the bubble generation obtained along the dashed line at $\sim 0 \mu\text{s}$. The horizontal and vertical scale bars represent $200 \mu\text{m}$ and $30 \mu\text{s}$, respectively. The images at $0 - 98 \mu\text{s}$ and $\sim 1 \text{ s}$ were separately captured using the distinct cameras that were operated with a frame rate of 1 Mfps and 30 fps, respectively. Red arrows indicate the focal spots.

ASSOCIATED CONTENT

Supporting Information.

The following files are available free of charge.

Illustration of the optical setup, ascending behavior of long-lasting bubbles, crystallization behavior upon scanning irradiation with scan speed of 0.16 and 0.80 mm/s, crystallization behavior upon scanning irradiation with square pattern, crystallization behavior observed after the cessation of laser irradiation, image of the glass bottom after scanning irradiation (PDF)

Movie S1: Crystallization behavior upon single-point irradiation with focused 100-fs laser pulses (corresponding to Figure 1a) (MP4)

Movie S2: Crystallization behavior upon single-point irradiation with focused 5-ps laser pulses (corresponding to Figure 1b) (MP4)

Movie S3: Crystallization behavior upon scanning irradiation with focused 100-fs laser pulses (corresponding to Figure 1c) (MP4)

Movie S4: Crystallization behavior upon scanning irradiation with focused 5-ps laser pulses (corresponding to Figure 1d) (MP4)

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Notes

The authors declare no competing financial interests.

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