#### **Supplementary Information**

# Metastable-Phase Crystallization of Potassium Acetate Triggered by Focused Irradiation with Ultrashort Laser Pulses

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### > <u>Supplementary Figures</u>



**Figure S1.** Temperature of the AcOK solution as a function of incubation time. The dashed line indicates room temperature (22 °C). The error bars represent the standard deviation of 10 measurements.



**Figure S2.** The optical setups for (a) laser-induced crystallization and (b) observation of laser-induced cavitation bubbles.



Figure S3. Absorbance spectra of pure water and the AcOK aqueous solution with m = 32.6 mol/kg. The spectra were measured by a UV-Vis spectrometer (UV-255, Shimadzu).



**Figure S4.** (a) Crystallization behavior in AcOK solution at m = 33.9 mol/kg. The time upon incubation was defined as t = 0 min. (b) Bright-field and crossed polarizing images of plate-like and needle-like crystals. The blue and orange arrows indicate representative needle-like and plate-like crystals, respectively. The scale bar represents 0.5 mm.



**Figure S5.** Raman spectra of needle-like crystals (orange lines) and plate-like crystals (green lines) in AcOK solution. A blue continuous-wave laser with a wavelength of 488 nm (Sapphire 488 LP, Coherent) was utilized as the excitation source. The Raman scattering light was introduced into a spectrometer (ACTON SpectraPro SP-2500, Princeton Instruments) and measured using a cooled CCD camera (DU420A-BEX2-DD-N, Andor). SOLIS software (Andor) was employed for spectral analysis. The Raman spectra were normalized to the peak at ~920 cm<sup>-1</sup>. The resolution of the detector is < 1.6 cm<sup>-1</sup>/pixel.



**Figure S6.** Probability of spontaneous crystallization as a function of incubation time. 30 samples were tested at each incubation time.



**Figure S7.** Crystallization behavior of the metastable form AcOK upon application of (a) mechanical shock and (b) ultrasound. The AcOK solution with m = 32.6 mol/kg was employed. (a) The mechanical shock was applied by manually slamming down the glass vial containing AcOK solution on a desk. (b) Ultrasound was applied for 1 min using an ultrasonic cleaner (ASU-3M, AS ONE) operating at a frequency of 42 kHz. The scale bars represent 5 mm.



**Figure S8.** Dependence of laser energy and pulse duration on the maximum volume of the cavitation bubble. The dashed lines represent fitting curves. Because the maximum volume of the cavitation bubble was approximated by  $4\pi/3 \times (\text{length}/2) \times (\text{width}/2)^2 = \pi/6 \times (\text{length}) \times (\text{width})^2$ , a cubic logarithmic function of  $\pi/6 \times (A \cdot \ln(E) + B) \times (C \cdot \ln(E) + D)^2$  was used for the fitting (*A*, *B*, *C*, and *D* is the fitting coefficients).

## Supplementary Tables

Laser energy	Pulse duration								
(µJ/pulse)	0.1 ps	0.5 ps	1 ps	5 ps	10 ps				
0.10	0% (0/10)	0% (0/10)	0% (0/10)	0% (0/10)	0% (0/10)				
1.0	0% (0/10)								
2.5	0% (0/10)								
5.0	10% (1/10)								
7.5	70% (7/10)	0% (0/10)							
10	100% (10/10)	20% (2/10)		0% (0/10)	0% (0/10)				
15	100% (10/10)	50% (5/10)	0% (0/10)						
22			10% (1/10)						
25				10% (1/10)					
30	100% (10/10)	90% (9/10)	60% (6/10)		0% (0/10)				
40				10% (1/10)					
45		100% (10/10)	100% (10/10)		10% (1/10)				
50				20% (2/10)					
60	100% (10/10)	100% (10/10)	100% (10/10)	10% (1/10)	40% (9/20)				
90				30% (3/10)	30% (3/10)				
120					15% (3/20)				
140				80% (8/10)	60% (6/10)				
165					70% (7/10)				
210				100% (10/10)	70% (7/10)				
255					90% (9/10)				
300					100% (10/10)				

**Table S1.** Raw data of laser-induced crystallization probability. The fractions represent the ratio of crystallized sample numbers to total sample numbers.

		Pulse duration						
		0.1 ps	0.5 ps	1 ps	5 ps	10 ps		
Length	<i>k</i> [µm]	111	111	121	158	176		
	$E_{\rm th}$ [µJ/pulse]	0.57	0.87	1.2	3.1	4.8		
Width	<i>k</i> [µm]	49	81	98	136	150		
	$E_{\rm th}$ [µJ/pulse]	0.80	1.4	1.9	3.3	4.6		

**Table S2.** The raw data of coffecients of the fitting curves  $(k \cdot \ln(E/E_{th}))$  in Figure 5.

## Supplementary Movies

- Movie S1: Crystallization behavior of AcOK in the solution with a molality of 33.9 mol/kg (corresponding to Figure S4a). The time label on the upper left represents mm:ss. (MP4)
- Movie S2: Macroscopic crystallization triggered by laser irradiation (corresponding to Figure 1a). A single laser pulse was shot approximately 1-s after the video began. The movie was played at 8 times faster than real time (MP4)
- Movie S3: Microscopic crystallization triggered by laser irradiation (corresponding to Figure 1b). A single laser pulse was shot approximately 6-s after the movie began. (MP4)
- Movie S4: Crystallization behavior of AcOK upon mechanical shock (corresponding to Figure S7a). (AVI)
- Movie S5: Crystallization behavior of AcOK upon ultrasound application (corresponding to Figure S7b). (AVI)
- Movie S6: Cavitation bubble generation induced by a single laser shot (corresponding to Figure 3 and 4). AcOK aqueous solution with m = 20.9 mol/kg, which is 36% lower than that of the solution used in the laser experiments, was employed. A dummy movie was inserted to show a temporal label in the section of 10 ps laser pulses with  $E = 2 \mu J/pulse$ , where no bubble generation was observed. (MP4)