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4 **Supplementary Materials for**

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6 **First-Order Liquid-Liquid Transition without Density Discontinuity**
7 **in Molten Sodium Acetate Trihydrate and Its Influence on**
8 **Crystallization**
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26 EXPERIMENT DETAILS

27 Materials

28 Sodium acetate trihydrate with a purity of 99.9% is purchased from Aladdin Organics and used as
29 received.

30 In situ NMR

31 The in situ NMR experiments were carried out using a Bruker Avance III 500WB spectrometer
32 with a magnetic field of 11.7 T. The temperature was carefully calibrated over the whole
33 temperature range by ethylene glycol. The accuracy of temperature control is ± 0.2 K. A standard
34 one pulse with 90° pulse width of $3 \mu\text{s}$ was used for the ^{23}Na experiments. The resonance frequency
35 of ^{23}Na ($I=3/2$) is 132.43 MHz. The recycle delay was 50 s, and 4 scans (about 200 s) were
36 accumulated in each measurement. All the ^{23}Na spectra were referenced to 1 mol/L NaCl aqueous
37 solution. A standard one pulse with 90° pulse width of $2.3 \mu\text{s}$ was used in the ^{13}C experiments. The
38 resonance frequency of ^{13}C is 156.43 MHz. 64 scans were accumulated in the measurement with a
39 recycle delay of 50s. Waltz16 decoupling sequence was applied to remove the coupling of ^1H . All
40 ^{13}C spectra were referenced to dilute TMS in CDCl_3 . Spin-lattice relaxation time (T_1) of ^{13}C of
41 carboxyl group were measured using an inversion-recovery pulse sequence of $180_x^\circ - \tau - 90_x^\circ$ with
42 the delay τ varied from 0.1 s to 100 s. T_1 was extracted by fitting the data with exponential
43 decaying according to $M = M_0(1 - 2e^{-\tau/T_1})$, where M is the magnetization that is proportion to
44 integral area of NMR peak, τ is the variable delay time and M_0 indicates the equilibrium
45 magnetization.

46 Density measurement

47 Density was measured by Anton Paar DMA 5000 Density Meter. The accuracy of temperature
48 control is ± 0.01 K. Calibration was performed using air and water. The repeatability accuracy is 10^{-6}
49 g/cm^3 . The sample was firstly held at 365.00 K for 720 min, then cooled down step by step to

50 353.00 K with an interval of 0.02 K. Density was measured isothermally at each step after
51 equilibrating the system for 1.5 min.

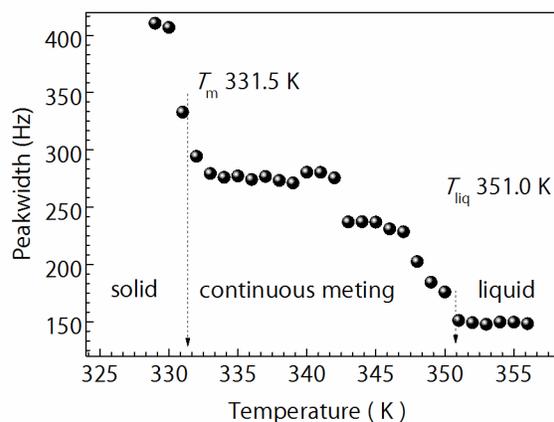
52 **DSC characterization of the crystallization dynamics**

53 DSC experiments were conducted using a DSC Q2000 (TA Instruments, USA) equipped with an
54 RCS90 cooling accessory. The temperature was calibrated by Indium with the purity of 99.99%.
55 Dry N₂ was used as purge gas at a flow rate of 100 cm³/min. Measurements were performed using
56 30 mg sample enclosed in a hermetic aluminum pan. The samples were firstly heated to certain
57 predetermined temperature T_{initial} and held there isothermally for 60 min. Then the samples were
58 cooled down to 273.0 K at a rate of 3.0 K/min. The sodium acetate crystallization temperatures T_{SA}
59 is determined by the onset of the exothermic peak. T_{SA} were systematically measured with T_{initial}
60 ranging from 353.0 K to 365.0 K. The range of T_{SA} is determined by five repeated measurements.

61 **X-ray diffraction characterization of the crystallization product**

62 X-ray powder diffraction (XRD) data of the crystallization products were collected using a Cu K α
63 Source ($\lambda = 1.5418\text{\AA}$) on a PANalytical X'Pert Pro MPD. The powder samples was placed on a
64 zero background holder and smoothed with a glass slide. The data were collected at 2θ ranging
65 from 5 to 50°. The minimum step size of 2θ is 0.016°. The measurements were conducted in
66 'continuous' mode. The acquired data were processed using X'Pert Highscore Plus software. The
67 HTL crystallization products were obtained by cooling the samples from 366.0 K to 233.0 K at a
68 rate of 3 K/min. Similarly, The LTL crystallization products were obtained by cooling the samples
69 from 356.0 K to 233.0 K at a rate of 3.0 K/min. The solid products consisting of SA and SAT were
70 further ground to powder at room temperature for XRD characterization.

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75 **Figure. S1. Determination of the melting temperature T_m and liquidus temperature**76 T_{liq} . The melting process of SAT crystals is characterized by static ^{23}Na NMR. When the

77 sample is in solid state, the quadrupole interactions and the chemical shift anisotropy would

78 significantly increase the linewidth of the ^{23}Na peak. However, when the sample is in liquid79 state and the ^{23}Na atoms are highly mobile, the motional averaging of the local magnetic

80 field would significantly narrow the resonance line, which is known as motional narrowing

81 effect. In addition, when the sample is partially melted, residual solids can lead to

82 inhomogeneity of magnetic field, giving rise to line broadening. Thus, the T_m and T_{liq} can83 be well determined by studying the evolution of peakwidth of ^{23}Na spectra. The sample was

84 heated consecutively from 329.0 K to 356.0 K with a temperature interval of 1.0 K. The

85 ^{23}Na spectrum was taken after the sample was kept isothermally at each temperature for 40

86 minutes. The dramatic narrowing of peak width at 331.5 K suggests the appearance of the

87 liquid, which should be the melting temperature T_m . The peak width gradually decreases

88 from 331.5 K to 351.0 K indicates the decrease of the residual solids. When the temperature

89 is higher than 351.0 K, the peak width cease to change, which suggests that 351.0 K is

90 liquidus temperature T_{liq} .

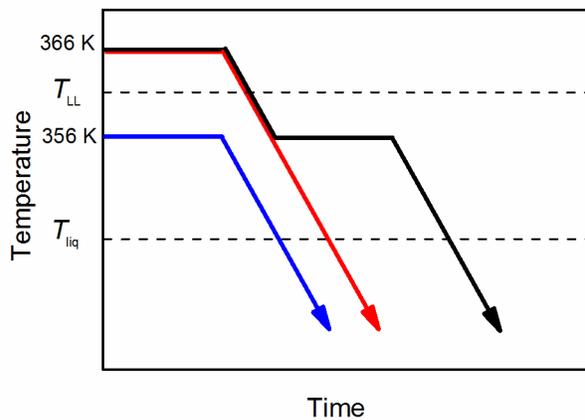
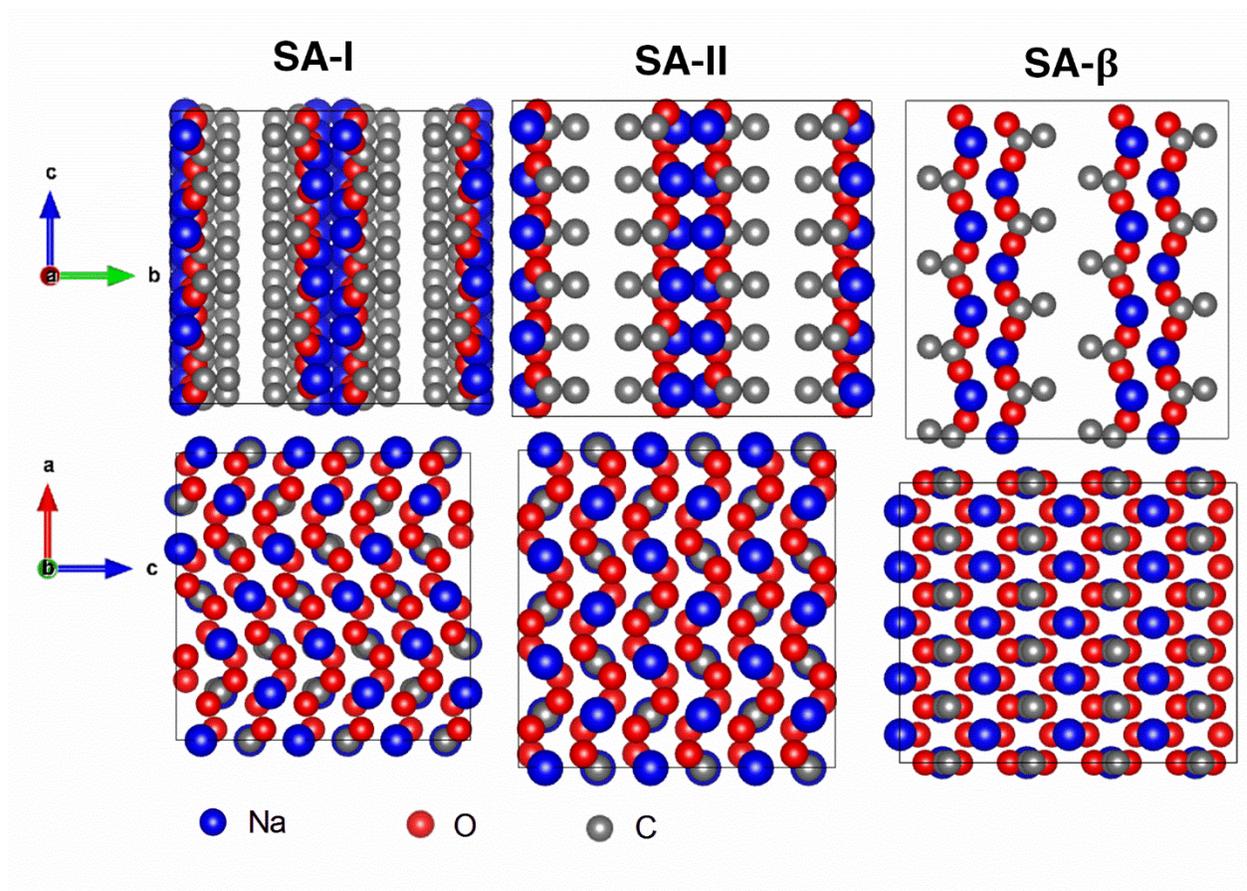


Figure. S2. The temperature protocols in DSC experiments. HTL(red) was held isothermal at 366 K for 60 mins and then cooled down to 233.0 K at a cooling rate of 3K/min. LTL(blue) was held isothermal at 356 K for 60 mins and then cooled down to 233.0 K at a cooling rate of 3K/min. The annealed HTL held isothermal at 356 K for 60 min before further cooling.



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Figure. S3. Crystal structure of SA-I II and β . The Upper panel is the crystal structure viewed from a axis and the lower panel is the crystal structure viewed from b axis.

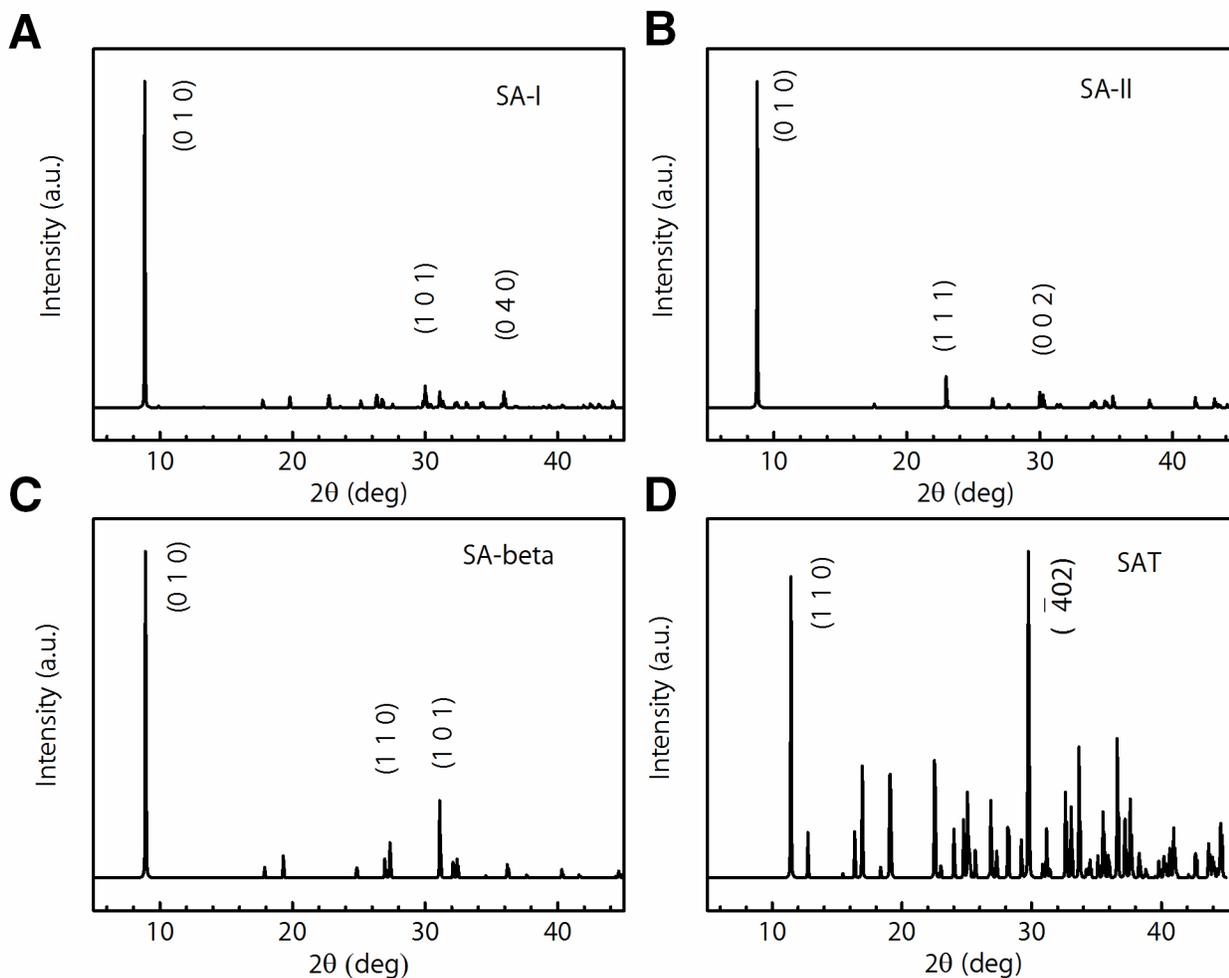
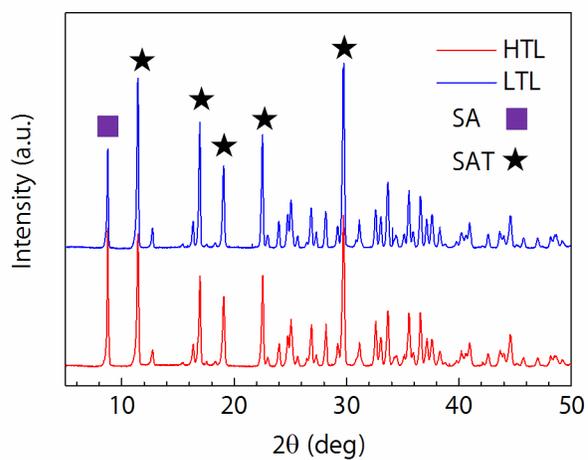


Figure. S4. Calculated XRD patterns. (A) SA-I. (B) SA-II, (C) SA- β and (D) SAT. The characteristic diffraction peaks of (010) plane of SA-I, SA-II and SA- β are located at $2\theta=8.75^\circ$, 8.85° and 8.90° , respectively. The characteristic diffraction peaks of SAT are located at $2\theta=11.45^\circ$ (110) and 29.75° ($\bar{4}02$). There's no diffraction peak below 10° in the XRD pattern of SAT.



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Figure. S5. Powder XRD pattern of crystallization products of HTL and LTL. The square denotes the characteristic peaks of SA, and the star denotes the characteristic peaks of SAT.

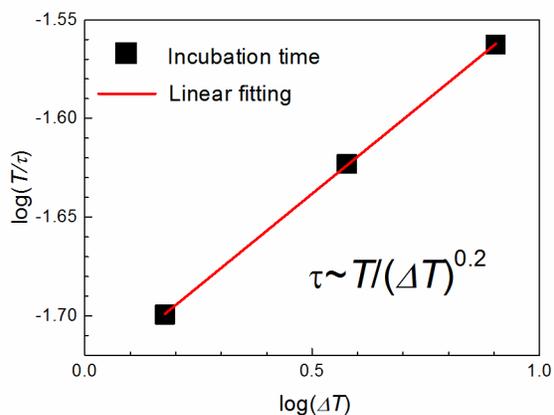


Figure S6. Kinetics of LLT. The incubation time τ versus degree of undercooling $\Delta T = 361.0 \text{ K} - T$. The inset plots $\log(T/\tau)$ versus $\log(\Delta T)$ and the slope of the straight line is 0.2.

The change of incubation time can be described empirically by: $\tau \propto T / (\Delta T)^m$. The linear fitting of $\log(T/\tau)$ versus $\log(\Delta T)$ was performed. The slope of the fitting curve is about 0.2. Thus, the characteristic value of m which describe the kinetics of this phase transition is 0.2.

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Cell parameter								
	Crystal system	Space group	a (Å)	b (Å)	c (Å)	Alpha (°)	Beta(°)	Gamma(°)
SA-I	Orthorhombic	Pmnm	5.2081	9.9481	3.4674	90.00	90.00	90.00
SA-II	Orthorhombic	Pcca	5.956	10.091	5.896	90.00	90.00	90.00
SA-β	Orthorhombic	Pmn2	3.4517	9.9123	5.1864	90.00	90.00	90.00
SAT	Monoclinic	C2/c	12.358	10.45	10.414	90.00	111.75	90.00

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Table 1. The lattice parameters of SA-I, SA II, SA-β and SAT.

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