

# Taming heat with tiny pressure

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Received: August 13, 2023; Accepted: January 7, 2024; Published Online: January 11, 2024; <https://doi.org/10.1016/j.xinn.2024.100577>

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## GRAPHICAL ABSTRACT



## PUBLIC SUMMARY

- Taming heat via external fields other than temperature remains a formidable challenge in the field of thermal engineering.
- A controllable approach for heat is proposed in 2-amino-2-methyl-1,3-propanediol based on its supercooled plastic crystal state with high sensitivity to pressure.
- A proof-of-concept device with an ultrahigh external work-to-heat conversion efficiency of  $\sim 383$  is demonstrated.
- Such delicate and efficient heat tuning may notably facilitate the rational utilization of waste heat.



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Received: August 13, 2023; Accepted: January 7, 2024; Published Online: January 11, 2024; <https://doi.org/10.1016/j.xinn.2024.100577>

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Citation: Zhang K., Zhang Z., Pan H., et al., (2024). Taming heat with tiny pressure. The Innovation 5(2), 100577.

Heat is almost everywhere. Unlike electricity, which can be easily manipulated, the current ability to control heat is still highly limited owing to spontaneous thermal dissipation imposed by the second law of thermodynamics. Optical illumination and pressure have been used to switch endothermic/exothermic responses of materials via phase transitions; however, these strategies are less cost-effective and unscalable. Here, we spectroscopically demonstrate the glassy crystal state of 2-amino-2-methyl-1,3-propanediol (AMP) to realize an affordable, easily manageable approach for thermal energy recycling. The supercooled state of AMP is so sensitive to pressure that even several megapascals can induce crystallization to the ordered crystal, resulting in a substantial temperature increase of 48 K within 20 s. Furthermore, we demonstrate a proof-of-concept device capable of programable heating with an extremely high work-to-heat conversion efficiency of ~383. Such delicate and efficient tuning of heat may remarkably facilitate rational utilization of waste heat.

## INTRODUCTION

Heat is an essential form of energy that originates from atomic and molecular kinetic energies and is crucial in various industrial and civil processes.<sup>1–4</sup> It can be spontaneously transferred from a high-temperature object to a low-temperature one. Currently, ~90% of energy use involves heat generation or manipulation over a wide range of temperatures.<sup>5</sup> Unfortunately, the current ability to control heat is highly limited. Thermal insulation is an effective method of controlling heat,<sup>6</sup> wherein heat can be temporarily confined in a low-temperature environment by using thermally insulating materials such as foams. Recently, optical illumination and pressure have been used to switch endothermic/exothermic responses of materials via phase transitions.<sup>7–9</sup> However, these strategies are either less cost-effective, complicated, or unscalable. Consequently, it is necessary to establish an affordable and easy solution to tame heat.

Crystals and glasses are the most common solid states of matter.<sup>10–12</sup> A crystal has a well-defined atomic structure in which constituent units are arranged in a periodic pattern with certain crystallographic symmetries, whereas glass (more specifically, structural glass) usually lacks a positional and/or an orientational order and forms a relatively disordered state. As a hybrid solid state of matter, a glassy crystal state combines both crystalline and glassy features in a single-phase material. It represents a structure in which the mass centers of molecules develop a high-symmetry lattice with the molecular orientations randomly frozen over the lattice sites, resulting in static orientational disorder.

A crystal is formed when a melt is gradually cooled below its solidification point, whereas a glassy state can be obtained by quenching a melt at a fast rate to achieve supercooling and avoid crystallization. Resembling the well-known volume-versus-temperature curve for a glass-forming liquid,<sup>13</sup> we have schematically plotted the counterpart of the glassy-crystal glassy transition in Figure 1A. Plastic crystals are orientationally disordered molecular crystals in which molecules dynamically reorient over high-symmetry lattices. A glassy crystal state can be obtained by quenching a plastic crystal

at a moderate cooling rate. Between the glassy-crystal glass transition temperature ( $T_g$ ) and plastic-to-ordered crystal transition temperature ( $T_l$ ), the system is in a metastable supercooled plastic crystal state, in which reorientation dynamics are continuously slowed down.<sup>14</sup> The supercooled plastic crystal state and glassy crystal state are essentially the same; only the relaxation times are different.

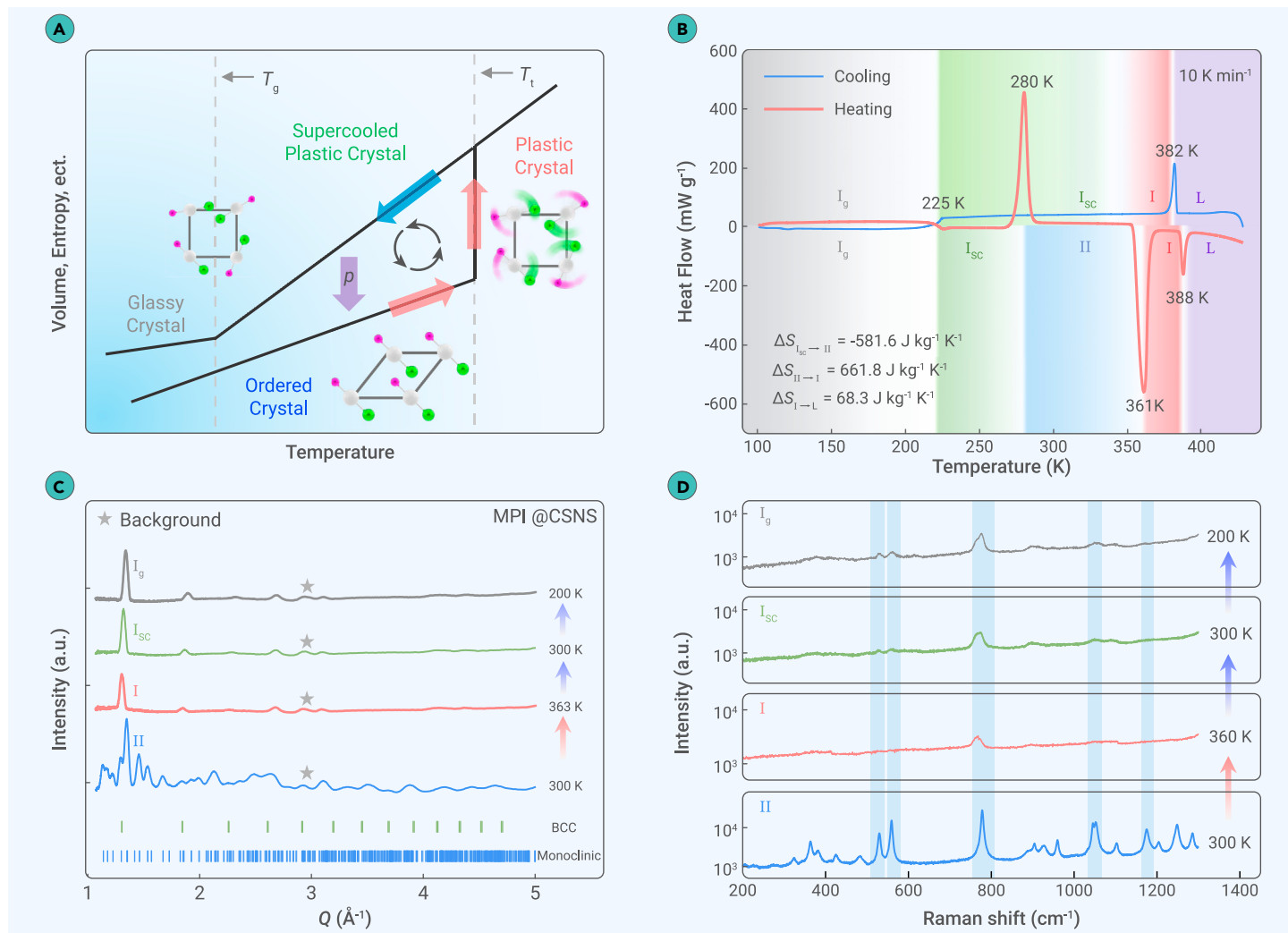
The glassy crystal state was first proposed in cyclohexanol by Adachi et al. ~60 years ago, following which few potential systems have been reported; however, a comprehensive understanding of its response to pressure and manipulation mechanisms remains elusive, as do the possible technological applications owing to its thermal irreversibility.<sup>10–12,15–21</sup> Here, we reveal and confirm the existence of a glassy crystal state in 2-amino-2-methyl-1,3-propanediol (AMP:  $\text{H}_2\text{N}(\text{CH}_3)\text{C}(\text{CH}_2\text{OH})_2$  or  $\text{C}_4\text{H}_{11}\text{NO}_2$ ) via neutron scattering and dielectric spectral measurements. The thermal irreversibility of AMP prevents its barocaloric refrigeration application; however, its ultrasensitive response to pressure at the supercooled state underlies a temperature–pressure cycle in which enormous heat is harvested and can be controlled via the application of a small amount of pressure. In the waste heat spectrum, low-grade waste heat at temperatures less than 373 K accounts for ~63% of the considered waste heat.<sup>22</sup> This could assist in tackling the thermal energy paradox: heat production accounts for >50% of global final energy consumption, whereas the waste heat potential analysis reveals that 72% of primary global energy consumption is lost after conversion mainly in the form of heat.<sup>23</sup>

## RESULTS AND DISCUSSION

### Material and phase transitions

AMP has been widely used as a chemical agent in many industrial processes.<sup>10</sup> At room temperature, it crystallizes into a monoclinic structure in the thermodynamic equilibrium state. At ~353 K, it transforms into a cubic structure,<sup>24,25</sup> which is considered a plastic crystal transition accompanied by enormous latent heat (~244 J g<sup>−1</sup>). Upon cooling back down, either substantial thermal hysteresis or supercooling is observed. Figure 1B presents heat flow data over the temperature region between 100 and 425 K for cooling and heating. Here, we identify four solid states: orientationally disordered plastic crystal (I), ordered crystal (II), supercooled plastic crystal ( $I_{sc}$ ) and glassy crystal ( $I_g$ ) states (labeled in Figure 1B). As the complete name suggests, state  $I_{sc}$  is thermodynamically metastable and able to crystallize if nucleation occurs. After solidification at ~382 K, state I enters the regime of state  $I_{sc}$  and further becomes state  $I_g$  at 225 K. Upon heating, state  $I_g$  transforms into state  $I_{sc}$  at 225 K, followed by crystallization to state II at 280 K with an entropy change of −581.6 J kg<sup>−1</sup> K<sup>−1</sup>. At 361 K, state II undergoes plastic crystal transition to phase I with 661.8 J kg<sup>−1</sup> K<sup>−1</sup> entropy change. The nature of these phases is clarified in detail below.

The evolution of crystal structures of these phases is monitored using temperature-dependent neutron powder diffraction (NPD) and X-ray diffraction (XRD). The NPD pattern of a partially deuterated sample taken at 300 K is identified as that of a monoclinic phase ( $P2_1/n$ ,  $a = 8.6194$  Å,  $b = 11.0419$  Å,  $c = 6.1207$  Å, and  $\beta = 93.6^\circ$ ) (Figure 1C). Only a very few Bragg peaks are observed

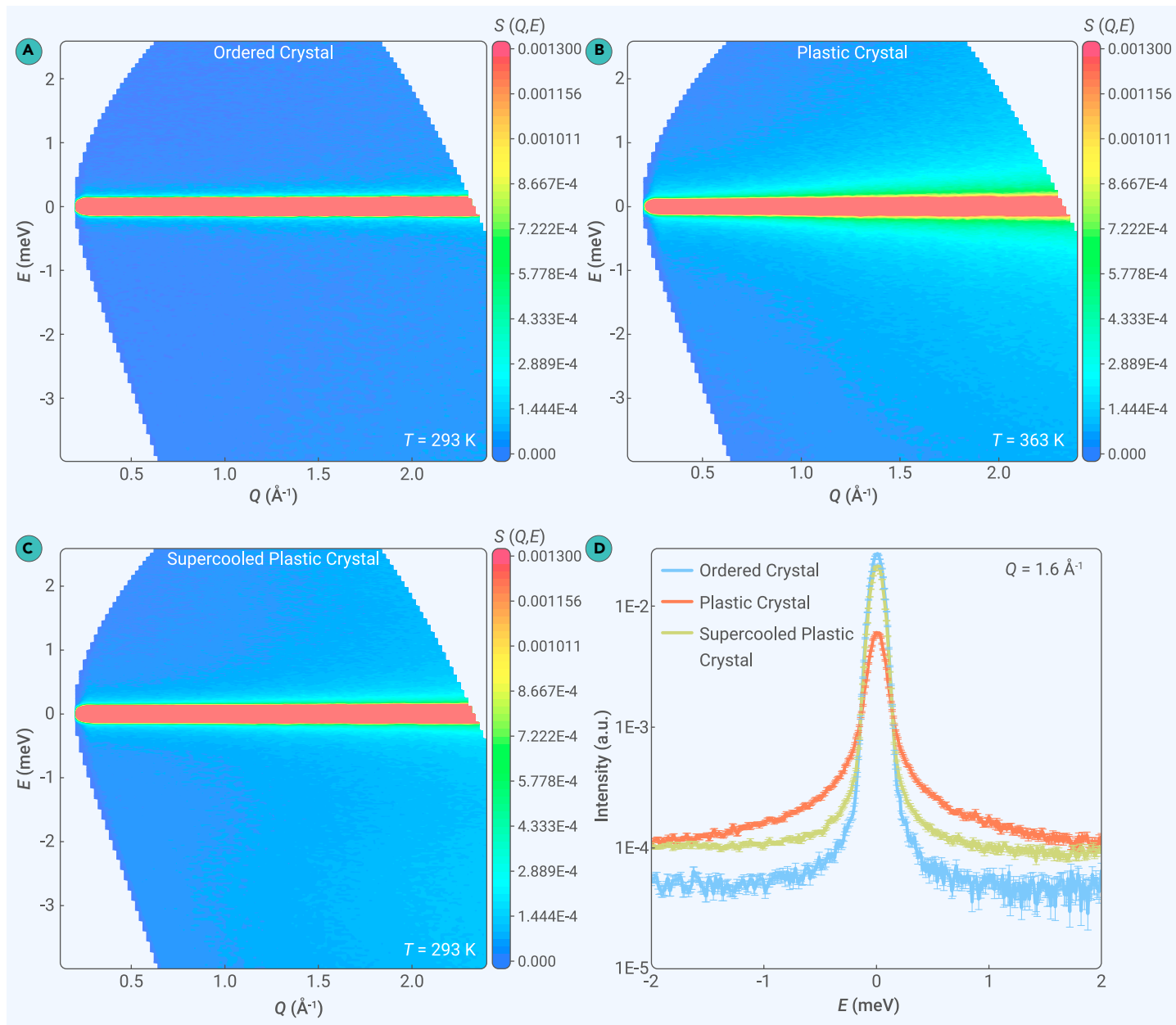


**Figure 1. Phase transitions of AMP at ambient pressure** (A) A glassy-crystal glassy transition. The ordered crystal state is heated to the plastic crystal state at  $T_t$ . Upon cooling, the supercooled plastic crystal state emerges, and finally the glassy crystal state is formed at  $T_g$ . The arrow marked  $P$  means that pressure induces the crystallization of the supercooled plastic crystal. The atomic structures of these states are also illustrated. (B) Heat flow data on cooling and heating of AMP at ambient pressure over the temperature region between 100 and 425 K. Each phase region is marked with a different background color. (C) NPD patterns at different temperatures on a partially deuterated AMP sample obtained at MPI, CSNS. The red (blue) arrows represent the heating (cooling) runs. The positions of Bragg peaks of 2 phases are ticked. (D) Temperature-dependent Raman spectra. The red and blue arrows represent the heating (cooling) runs. In the heating run, five strong peaks (highlighted) are observed at room temperature, whereas at 360 K, most peaks disappear, with only 1 strong peak observed at  $765\text{ cm}^{-1}$ . Thus, a transition from phase II to I is confirmed. The basic profiles of the Raman spectra remain the same upon cooling to 200 K, which shows that the cubic lattice symmetry is retained. Notably, the peak at  $765\text{ cm}^{-1}$  is slightly shifted to higher frequencies. This is a common hardening effect due to suppressed thermal fluctuations. Therefore, some weaker peaks become visible at 200 K, for example, that at  $\sim 562\text{ cm}^{-1}$ .

upon heating to 363 K, indicating a high-symmetry crystal structure indexed by a body-centered cubic (BCC) structure ( $Im3m$ ,  $a = 6.8194\text{ Å}$ ). The BCC phase is maintained with a reduced lattice constant ( $Im3m$ ,  $a = 6.7840\text{ Å}$ ) after cooling back to room temperature. It persists upon further cooling to 200 K. These observations were further confirmed by the temperature-dependent XRD patterns and the diffraction pattern collected using the time-of-flight cold neutron spectrometer Pelican (Figures S1A and S1B). Apparently, the supercooled BCC phase has a  $\sim 9.1\%$  larger unit cell volume than the monoclinic phase (Figures S1C and S1D),<sup>26</sup> which indicates a “free volume” of this glassy crystal state, similar to structural glasses.<sup>16</sup> As Raman scattering reflects lattice symmetry, temperature-dependent Raman spectra collected under similar heating and cooling conditions are shown in Figure 1D. The pattern at 300 K suggests an ordered crystal phase with a monoclinic structure, in which five strong peaks are observed at 529, 560, 779, 1,052 and  $1,176\text{ cm}^{-1}$ , corresponding to the C–C–N bending, O–C–C bending, C–N stretching, C–O vibration, and C–N stretching modes, respectively.<sup>27</sup> Upon heating to 363 K, most peaks disappear and only one strong peak is observed at  $765\text{ cm}^{-1}$ . Thus, it is suggested that the transition from phase II to phase I occurs. The essential profiles of the Raman spectra remain the same upon cooling to 200 K, which shows that the cubic lattice symmetry is retained. Hence, the Raman spectra underpin the XRD and NPD results.

### Microscopic spectral mechanism

To justify the frozen nature in where molecules distribute over such a BCC lattice without breaking the lattice symmetry. To this end, quasi-elastic neutron scattering (QENS) is a desirable tool for studying the molecular reorientation dynamics of hydrogen-containing systems because of the large, incoherent scattering cross-section of hydrogen atoms.<sup>28</sup> The QENS signal usually appears as a broad spectrum imposed underneath the elastic line. The strong quasi-elastic broadening suggests rapid motions of the molecules.<sup>29,30</sup> Figures 2A–2C show the dynamic structure factor  $S(Q, E)$  as a function of momentum transfer ( $Q$ ) and energy transfer ( $E$ ) with an incident neutron energy of  $E_i = 3.7\text{ meV}$  for these three states. The intense strips centered at  $E = 0$  represent the elastic line, which accounts for most of the scattering intensity, whereas a less intense signal spreading out from  $E = 0$  represents the QENS intensity. At 293 K, the compound crystallizes in the monoclinic phase, whose  $S(Q, E)$  is described by the elastic lines and suggests an ordered crystal state. At 363 K, the spectrum is typical of a plastic crystal state, in which a strong QENS signal is observed. However, the supercooled state exhibits a weak but visible QENS signal. These differences become clearer at the constant  $Q$  spectra at  $Q = 1.6\text{ Å}^{-1}$  (Figure 2D). The considerably weak quasi-elastic broadening of the ordered crystal phase indicates a lack of reorientation motion in the present frequency window, which agrees with the ordered crystal structure. In the plastic crystal phase, an intense



**Figure 2. Reorientation dynamics of AMP** (A–C) The dynamic structure factor  $S(Q, E)$  at (A) 293, (B) 363, and (C) 293 K (cooled back) at Pelican. (D)  $Q$ -integrated QENS spectra for the  $Q$  of  $1.6 \text{ \AA}^{-1}$  of the ordered crystal, plastic crystal, and supercooled plastic crystal, respectively.

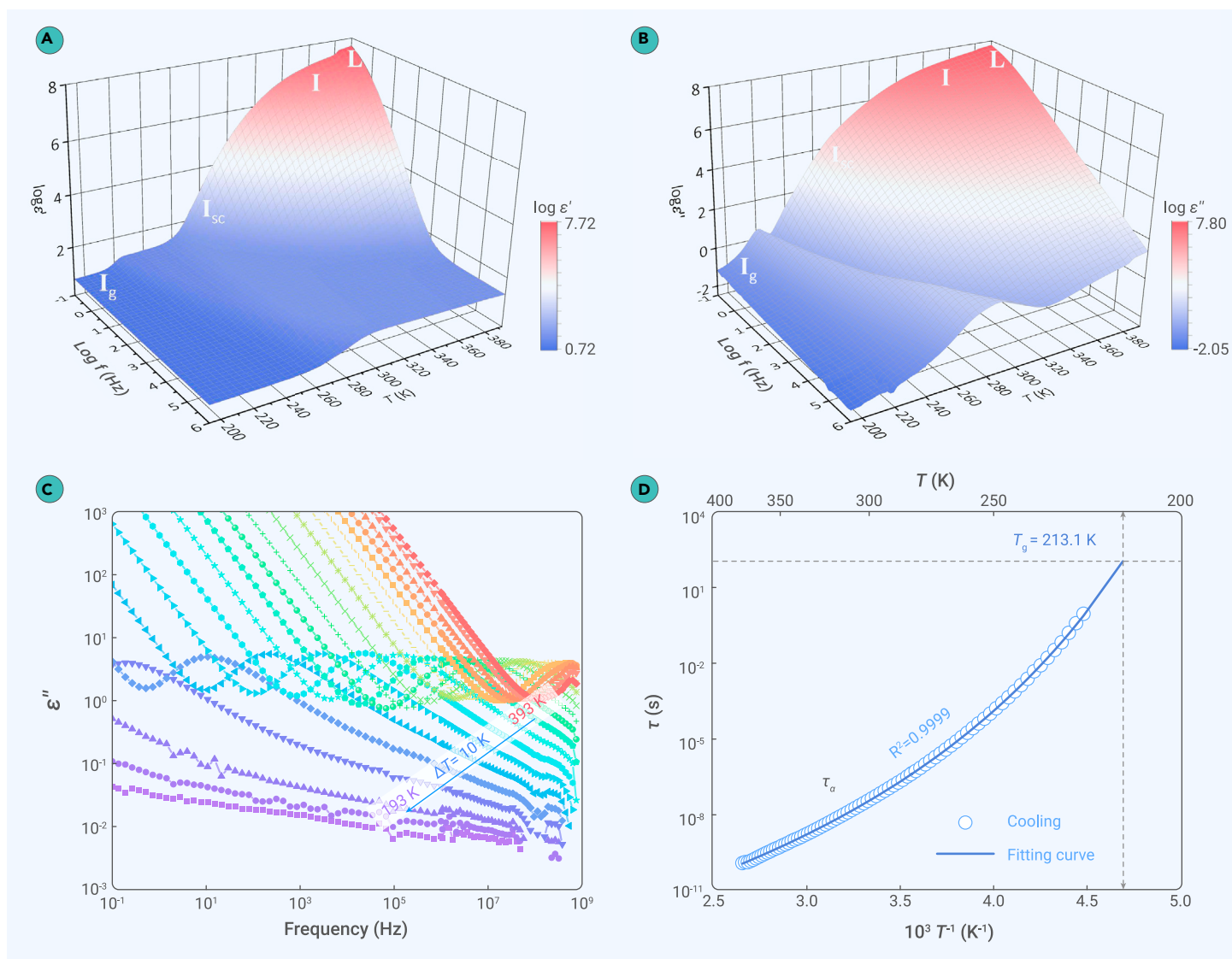
quasi-elastic broadening represents active reorientation motions. For the supercooled state, a one-order-of-magnitude weaker QENS suggests that most of the reorientation motions are slowed down to a dynamic regime slower than  $10^{10}$  Hz (defined by the energy resolution of Pelican,  $130 \text{ \mu eV}$ ). The distinct spectra of both the plastic crystal and supercooled states are impressive because they have identical lattice symmetry.

Broadband dielectric spectroscopy (BDS) is considered within a frequency range of several orders of magnitude in a bid to probe the dynamic freezing process over a wider timescale. Figures 3A and 3B show the surface plots of the real and imaginary parts of the complex dielectric permittivity, namely  $\epsilon'$  ( $f, T$ ) (dielectric constant) and  $\epsilon''$  ( $f, T$ ) (dielectric loss), respectively, measured upon cooling at frequencies from  $10^{-1}$  to  $10^6$  Hz. Both  $\epsilon'$  and  $\epsilon''$  exhibit a frequency-independent decrease at 382 K, corresponding to the transition from the liquid (L) to plastic crystal state (I), which is consistent with differential scanning calorimetry (DSC) data (Figure 1B). Further cooling results in monotonous decreases in  $\epsilon'$  and  $\epsilon''$  accompanied by a continuous shift of the dominant  $\alpha$ -relaxation down to the glassy crystal state. This scenario is also observed for the electrical conductivity  $\sigma'$  (Figure S2). To follow the dynamic glassy transition, shown by the  $\alpha$ -relaxation peak in Figure 3B, to shorter timescales, additional radiofrequency

dielectric spectra were obtained to bridge the gap between “standard” dielectric spectroscopy and the GHz timescale of the QENS data. Figure 3C shows dielectric loss spectra covering the extended frequency range from  $10^{-1}$  to  $10^9$  Hz at selected temperatures ranging from 393 to 193 K. Visual inspection of the curves confirms the expected continuous nature of the dynamic freezing over the entire frequency range, an observation qualitatively confirmed by the smooth temperature dependence of relaxation time  $\tau_\alpha$  upon cooling (Figure 3D). Moreover, all relaxation time data obey the Vogel-Fulcher-Tammann (VFT) law,  $\tau(T) = \tau_\infty \exp(E_V / R(T - T_V))$ , where  $E_V$ ,  $R$  and  $T_V$  denote the Vogel activation energy, gas constant, and Vogel temperature, respectively. Both the non-Arrhenius temperature dependence and the nonexponentiality in the dielectric response (peak shape) are striking evidence of cooperative reorientation dynamics in states I and  $I_{sc}$  as sensed by the dielectric  $\alpha$ -process.

#### Pressure control of heat

The existence of supercooled plastic and glassy crystal states is confirmed in AMP based on our extensive structural and dynamic data. Next, we explored their response to external pressure. The *in situ* pressure responses of AMP were studied via Raman scattering, XRD, and DSC. Figures 4A and 4B show



**Figure 3. Dielectric relaxation** (A) Surface plot of dielectric loss  $\epsilon''(f, T)$  (i.e., imaginary part of the complex dielectric permittivity) upon cooling at frequencies ranging from  $10^{-1}$  to  $10^6$  Hz. (B) Surface plot of dielectric loss  $\epsilon''(f, T)$  upon cooling at frequencies ranging from  $10^{-1}$  to  $10^6$  Hz. (C) Dielectric loss spectra in the extended frequency range from  $10^{-1}$  to  $10^9$  Hz at the selected temperatures. (D) Arrhenius diagram showing the relaxation time of the dominant  $\alpha$ -relaxation for cooling (blue symbols), fitted to the VFT law.  $E_V = 9.81$  kJ mol<sup>-1</sup> or 0.102 eV and  $T_V = 144$  K. The extrapolated temperature at  $\tau = 100$  s defines the glassy-crystal glassy transition temperature  $T_g$  from the dielectric relaxation data, which is 213.1 K, this is slightly different than 225 K obtained from the calorimetric data.

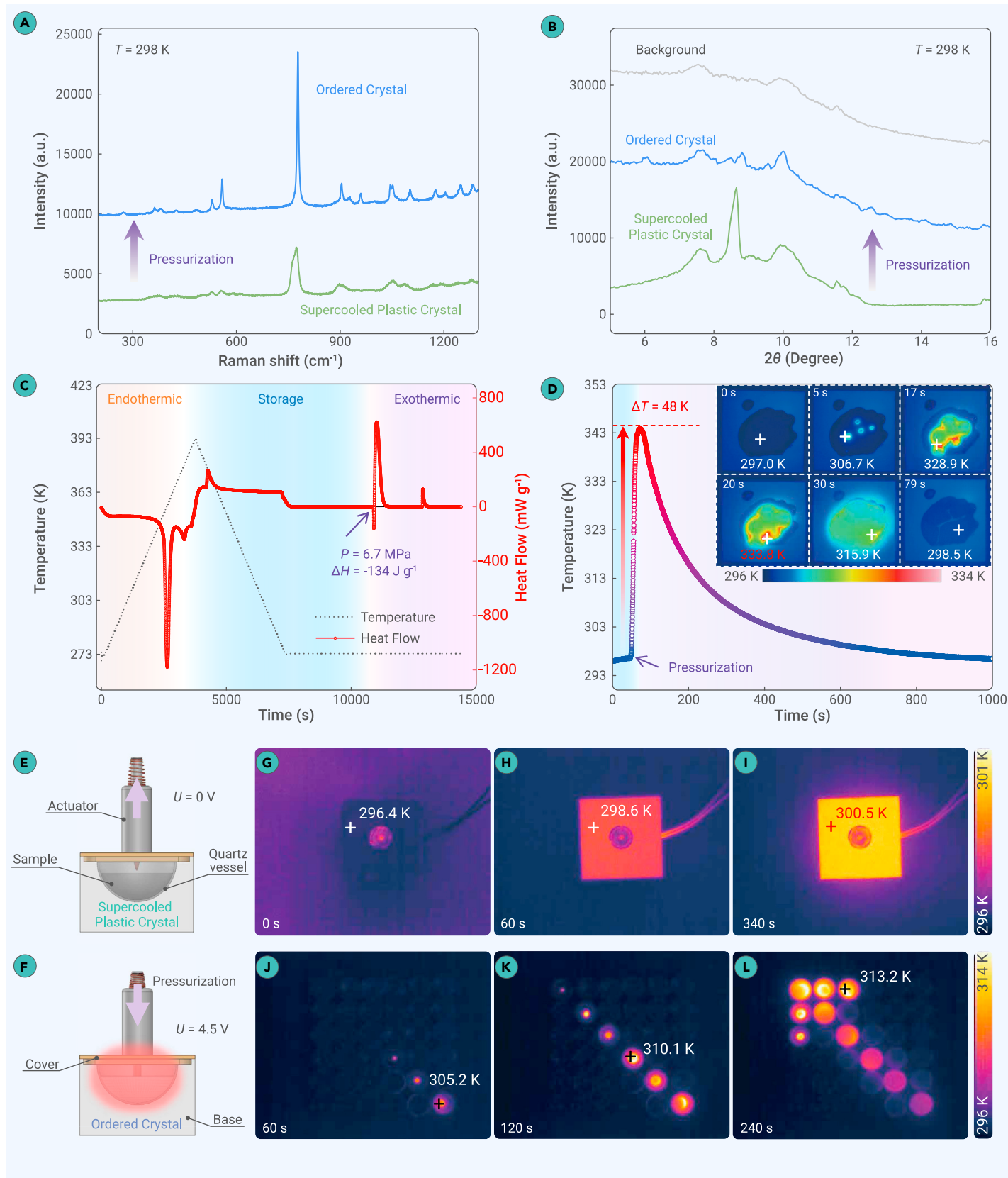
the pressure-dependent, *in situ* Raman and XRD spectra, respectively. Crystallization to the ordered crystal state occurs upon applying pressure, with signatures of five strong peaks in the Raman spectra (Figure 4A) and more Bragg peaks (Figure 4B). Figure 4C shows the heat flow data during a complete heating–cooling pressurization cycle. Initially, the compound is heated from 273 to 393 K at 0.1 MPa, and two endothermic peaks appear, corresponding to the ordered-to-plastic crystal phase transition and melting. Subsequently, the compound is cooled to 273 K; only a phase transition from the liquid to plastic crystal state occurs. At 273 K, the supercooled state is characteristic of an exothermic peak at a small pressure of 6.7 MPa. The latent heat associated with this peak is estimated to be  $134 \text{ J g}^{-1}$ . This value is similar to the latent heat of the temperature-induced transition from phase I<sub>sc</sub> to II (Figure 1B), suggesting the occurrence of a pressure-induced phase transition. In Figure S3, this temperature–pressure cycle has been repeated under varying conditions, indicating excellent reproducibility.

To take advantage of the enormous latent heat of crystallization, a pressure-controllable heat storage technology is proposed based on the joint temperature–pressure cycle (Figures 1A and 4C). Low-grade waste heat is harvested in the plastic crystal state, stored in the supercooled state, and then reused on demand upon pressure-induced crystallization to the ordered crystal state. The final step is directly demonstrated on a sample encapsulated with a

thermocouple using ethylene-vinyl acetate copolymer tapes. The real-time temperature change is recorded as a function of time. An enormous temperature increase of  $\sim 48$  K is achieved within 20 s upon the phase transition (Figure 4D). This process has also been visualized using an infrared camera, as shown in the inset in Video S1. In air, an as-prepared supercooled sample on a quartz glass plate is captured in dark blue at 297 K. A few bright spots immediately appear when the sample is needed, indicating an increase in temperature. The high-temperature zones emerge after a few seconds, and a maximum temperature of  $\sim 333.8$  K is reached at 20 s before the temperature decays to the original state in  $\sim 60$  s. Such performances are ranked as the optimum among those of all of the currently active thermal energy storage materials (Table S1).<sup>7–9,31,32</sup>

#### Application demonstration

We further demonstrated a proof-of-concept device (Figures 4E and 4F), which comprises an electrical actuator, a pellet of AMP, a vessel, and a cover. The stored heat is immediately released upon powering on the actuator (Figures 4G–4I). The work-to-heat conversion efficiency is as high as  $\sim 383$  (see materials and methods), which means that a thermal energy of 383 J is harvested at an estimated input energy of 1 J. A programmable heating system may be fabricated by taking this device as an element



**Figure 4. Pressure-induced crystallization of the supercooled state, and programmable taming heat via pressure** (A) *In situ* Raman spectra at room temperature. (B) *In situ* XRD patterns at ambient pressure and 8 MPa at 303 K. (C) Heat-flow variations as a function of time for the thermal battery cycle, including the endothermic, storage, and pressure-induced exothermic processes. The moment of applying pressure is indicated by an arrow. The small, negative heat-flow signal corresponds to the background from the gas pressurization process. Meanwhile, a positive heat-flow signal can be observed, which is attributed to the depressurization process. (D) Direct measurements of temperature increase at the pressure-induced crystallization of the supercooled plastic crystal. The inset highlights the temporal evolution of the temperature as monitored using an infrared camera upon applying pressure to the supercooled plastic crystal state. The bright spots appearing at 5 s represent the immediate changes in the needed zones. (E) The sample with supercooled plastic crystals corresponds to the heat storage state at no voltage. (F) The sample is induced to an ordered crystal state and releases heat through the actuator at 4.5 V applied voltage, as indicated in (G–I). (J–L) Heat release array comprising the heater units and their operation. A required heat release process is expected to be achieved by programmatically controlling the actuators of the heat release units in the array and independently controlling the heat release sequence of each unit, as shown by the arrow.

(Figures 4J–4L), from which schematic patterns can be observed. In addition to the thermal functionality, the distinct optical (Figures S4A–S4D) and electrical (Figure S4E) properties of the supercooled phase and ordered crystal phase allow for the fabrication of an ultrasensitive pressure sensor as well as a new-concept nonvolatile memory device (Figures S4F and S4G). Many applications with waste heat utilization would be realized via this device, such as recycling waste heat from thermal power plants, solar energy panels, and data center machine rooms, among others.

Reliability is a critical parameter for real applications, and it involves reproducibility and stability. The fabrication of the supercooled plastic crystal state was successfully tested 6 times in the temperature region from 273 to 393 K (Figure S5A). The sample dependence was also considered. The heating–cooling storage process was readily repeated in three different samples (Figures S5B–S5D). Because sensitivity and stability perform in a contradictory manner in general, the long-term aging stability of the prepared supercooled plastic crystal state of AMP samples was monitored by means of *ex situ* XRD, *in situ* Raman scattering, and with a camera. The supercooled state can survive for up to 6 months in a glove box (Figure S6).

## CONCLUSION

We delicately tune heat via pressure-induced crystallization of the supercooled plastic crystals of AMP. An enormous amount of heat as high as  $134 \text{ J g}^{-1}$  is released at small pressures of several megapascals, resulting in a temperature increase of 48 K. Moreover, we demonstrate a proof-of-concept device, which exhibits an extremely high work-to-heat conversion efficiency. This study considerably improves our ability to manipulate heat and, in particular, rationally reuse low-grade waste heat. This will undoubtedly guide emerging horizons for scientific research in thermal management.

## MATERIALS AND METHODS

### Materials

AMP (purity:  $\geq 99\%$ ; Chemical Abstracts Service no. 115-69-5) samples were purchased from Sigma-Aldrich. A partially deuterated sample was prepared by replacing the hydrogen atoms associated with the N and O sites via secondary deuteration using  $\text{D}_2\text{O}$  (99.9 atom % D, Sigma-Aldrich). A total of 4 g of the sample was added to a flask containing 3.6 mL of  $\text{D}_2\text{O}$  (99.9 atom % D, Sigma-Aldrich). The flask was then sealed and stirred at 313 K for 48 h. Thereafter, it was heated at 383 K for 2 h while purging with pure  $\text{N}_2$  gas (99.999%) to remove the solvent  $\text{D}_2\text{O}$ . The sample, together with the flask, was then frozen at  $\sim 254 \text{ K}$  in a refrigerator for 2 h, after which it was purified for 1 h on a Schlenk vacuum line at room temperature to remove the residual  $\text{D}_2\text{O}$ . The fine powders were again dried for 1 h on a Schlenk vacuum line at room temperature. The as-obtained product was again deuterated to enhance the purity. The final deuterated ratio of  $\sim 28.6\%$  was determined through proton nuclear magnetic resonance (Advance II-400 MHz, Bruker; solvent:  $\text{DMSO}-d_6$ ).

### Pressure-induced temperature changes

We directly measured the temperature change of AMP during a pressure-induced phase transition by means of thermography and a thermocouple. A needle was used to apply pressure to a supercooled sample. For a supercooled sample exposed to air, a  $\sim 1 \text{ mm}$  thick film sample was prepared *in situ* on a square silicon substrate (Length = 30 mm). The temperature evolution of the sample during the pressure-induced phase transition was recorded using an infrared camera (Fluke TiX580). For a supercooled sample under adiabatic conditions, an ellipsoid sample was prepared on the surface of the thermocouple and then encapsulated by ethylene-vinyl acetate copolymer tapes to avoid heat dissipation to the maximum possible extent. The pressure-induced temperature changes at room temperature were measured using a K-typed thermocouple inserted into the center of the sample.

### Calorimetric characterizations

Heat flow data for AMP at ambient pressure were collected using two differential scanning calorimeters ( $\mu\text{DSC7}$ , Setaram for scans at  $2 \text{ K min}^{-1}$  and NETZSCH DSC 200F3 for scans at  $10 \text{ K min}^{-1}$ ). The phase transition temperature was defined as that at which the heat flow peaked. Pressure-dependent heat flow data were collected using high-pressure DSC ( $\mu\text{DSC7}$ , Setaram). The sample was enclosed in a high-pressure vessel made of Hastelloy. The sample of the supercooled state was obtained using the  $\mu\text{DSC7}$  instrument at atmospheric pressure and was maintained at 273 K. For the constant-temperature process,

the AMP samples were pressurized from 0.1 to 8.7 MPa. Similar procedures have been applied to  $\text{NH}_4\text{SCN}$ <sup>7</sup> and  $\text{NH}_4\text{I}$ .<sup>33</sup>

### XRD

*Ex situ* XRD data were collected on states II and  $\text{I}_{\text{sc}}$  at room temperature using an X-ray diffractometer (Miniflex, Rigaku) with  $K_{\alpha 1}$  radiation of Cu. *In situ* XRD experiments were conducted using another X-ray diffractometer (Bruker D8) equipped with an HPC 900 chamber with  $K_{\alpha 1}$  radiation of Cu for temperature-dependent measurements and with  $K_{\alpha 1}$  radiation of Mo for pressure-dependent measurements. For the temperature-dependent experiments, the sample was heated from 303 to 363 K and then cooled to 303 K. For the pressure-dependent experiments, an as-prepared supercooled sample was measured at ambient pressure and  $\text{N}_2$  pressure of 8 MPa, respectively, at 303 K. The *ex situ* XRD data were analyzed using the Le Bail refinement method.<sup>34</sup>

### NPD

NPD experiments were conducted using the Multi-Physics Instrument (MPI), China Spallation Neutron Source (CSNS).<sup>35</sup> A total of 0.65 g of a partially deuterated sample was placed into a vanadium can ( $\phi = 9 \text{ mm}$  and  $L = 75 \text{ mm}$ ). The sample was heated from 300 to 363 K and then cooled to 200 K. Constant-temperature scans were conducted at 300, 363, 300 (cooled back), and 200 K. Counting persisted for 3 h at each temperature.

### Raman scattering

Raman spectra were collected using a commercial Raman system (Horiba Labram HR Evolution) under the normal incidence of a solid laser ( $\lambda = 532 \text{ nm}$ ). The laser beam was focused on the samples using a  $50\times$  objective lens (numerical aperture: 0.6). The beam diameter was  $\sim 1 \mu\text{m}$ . The sample was located in a continuous-flow, liquid-nitrogen cryostat. A calibrated Linkam heating–cooling stage was used to control the sample temperature via a thermocouple attached to the sample holder. High pressure was accessed through a membrane diamond anvil cell equipped with beryllium copper gaskets with holes of  $\sim 500 \mu\text{m}$  diameter serving as the sample chamber. Refer to previous results for details.<sup>36</sup>

### QENS

QENS experiments of AMP were conducted using the time-of-flight neutron spectrometer Pelican at the Australian Center for Neutron Scattering, Australian Nuclear Science and Technology Organisation.<sup>37</sup> The instrument was configured with an incident neutron wavelength of  $4.69 \text{ \AA}$ , affording  $3.72 \text{ meV}$  incident energy with  $0.135 \text{ meV}$  energy resolution at the elastic line. The AMP powder sample was placed into a quartz tube with 4 mm inside diameter and 0.5-mm wall thickness. The quartz tube was inserted into a sample can made of niobium sheet. The sample handling process was conducted in a glove box filled with dry  $\text{N}_2$  gas at atmospheric pressure. Measurements were performed at 293, 363, and 293 K during the heating–cooling sequence. The empty can was measured under the same conditions as for background subtraction. In addition, a standard vanadium sample was measured for detector normalization and determination of the energy resolution function. Data reduction, including background subtraction and detector normalization, was performed using the Large Array Manipulation Program.<sup>38</sup>

### Dielectric relaxation spectroscopy

The dielectric properties ( $\epsilon'$ ,  $\epsilon''$ , and  $\sigma'$ ) were measured using a broadband dielectric spectrometer (Novocontrol GmbH) with an active sample cell based on a high-resolution impedance analyzer (Novocontrol Alpha) at frequencies between  $10^{-1}$  and  $10^6 \text{ Hz}$ . The sample was placed in a stainless-steel liquid cell (diameter: 20.00 mm and electrode spacing: 1.560 mm) to realize a parallel plate geometry. For the upper-frequency range from  $10^6$  to  $10^9 \text{ Hz}$ , a Hewlett Packard HP 4291B network analyzer, in combination with a calibrated coaxial line and a Novocontrol RF cell (parallel plates of 5 mm diameter with  $100 \mu\text{m}$  electrode separation), was used. The sample temperature was controlled using a Novocontrol Quatro cryosystem, allowing for temperature control with  $\pm 0.01 \text{ K}$  accuracy via dry  $\text{N}_2$  gas flow derived from liquid nitrogen. To ensure complete filling of the cell, a fresh sample was first heated from room temperature to 393 K, followed by stabilization at this temperature for 15 min to eliminate any possible thermal history. The sample was then cooled to 193.15 K at a  $10 \text{ K min}^{-1}$  cooling rate. Thereafter, the sample was heated to 393 K and cooled to 193 K with 2 K temperature intervals (heating/cooling rate:  $10 \text{ K min}^{-1}$ ) for the dielectric spectroscopy measurements. More details can be found in references.<sup>39–41</sup>

## Design of the proof-of-concept heater unit

The basic unit of the heater includes a cover (square with 30 mm side length and 3 mm thickness), a quartz sample vessel (hemispherical with 2 mm diameter), an AMP sample, a base (length, width, and height are 30, 30, and 20 mm, respectively), and an electromagnetic spring actuator ( $\phi = 6$  mm and  $L = 30.6$  mm). Initially, an AMP sample in a supercooled plastic crystal state is obtained in the quartz vessel, and the actuator is in a nonworking state without voltage, which corresponds to the heat storage state. Upon applying a low voltage of 4.5 V to the electromagnetic spring actuator, the spring contracts and pushes the needle down to apply pressure to the sample. The AMP sample transitions to an ordered crystal state and releases heat to its surroundings. This heater unit with 1.2 g samples has extraordinary energy efficiency. The input electric energy is estimated to be 0.42 J (Resistance ( $R$ ) = 4.8  $\Omega$ , Voltage ( $U$ ) = 4.5 V and Time ( $t$ ) = 0.1 s). The heat energy released is  $\sim 160.8$  J.

## Optical measurement

Optical transmission spectra with light wavelengths ranging from 200 to 800 nm were obtained using an ultraviolet-visible spectrophotometer (Hitachi U-3010). A double-sided polished quartz substrate was used as the measurement reference.

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## ACKNOWLEDGMENTS

The work conducted in the Institute of Metal Research was supported by the Key Research Program of Frontier Sciences of the Chinese Academy of Sciences (grant no. ZDBS-LY-JSC002), the Liaoning Provincial Science Fund for Distinguished Young Scholars (grant no. 2023JH6/100500003), the Innovation Fund of Institute of Metal Research, Chinese Academy of Sciences, (grant no. 2021-ZD01), the CSNS Consortium on High-performance Materials of the Chinese Academy of Sciences, the Young Innovation Talent Program of Shenyang (grant no. RC210432), the Ministry of Science and Technology of the People's Republic of China (grant nos. 2021YFB3501201, 2022YFE0109900, and 2020YFA0406002), the National Natural Science Foundation of China (grant nos. 11934007, 52001101, and 61974147) and the International Partner Program of Chinese Academy of Sciences (grant no. 174321KYSB20200008). J.L. and M.W. are grateful for the Research Foundation Flanders (grant no. G0B3218N). J. Luo acknowledges Sichuan Science and Technology Program (grant nos. 2022ZYYD0016 and 2023JDR0013) and National Natural Science Foundation of China (grant nos. 21776120 and 22378270). The authors thank Sucheng Wang and Changji Li for their help with the *in situ* XRD experiments,

Shuai Huang for thermal infrared image measurements, and Bo Huang for sample deuteration. They also thank Prof. Jie Pan and Prof. Si Lan for valuable discussions.

### AUTHOR CONTRIBUTIONS

B.L. proposed the project. K.Z., Zhe Zhang, J.Q., Zhao Zhang, R.S., H.W., C.Y., and C.T. conducted the in-house structural, thermal, and Raman scattering experiments. Zhe Zhang was cosupervised by B.L. and Zhidong Zhang. X.Z., X.L., H.C., and W.Y. performed the neutron diffraction measurements. D.Y., Zhe Zhang, K.Z., and B.L. conducted the QENS measurements. J.L. and M.W. designed the BDS experiments. H.P., M.W., and J.L. performed the BDS measurements and analyzed the BDS data. J.L. and M.W. wrote the text related to BDS and revised the manuscript. J.L. supervised and analyzed the sample deuteration. B.H. and W.H. measured the optical transmittance. Zhao Zhang and K.Z. analyzed the diffraction data. Zhe Zhang and K.Z. analyzed the QENS data. K.Z. and

H.W. designed and demonstrated the devices. K.Z. and B.L. wrote the manuscript, with input from all of the authors.

### DECLARATION OF INTERESTS

B.L., K.Z., and Zhidong Zhang applied for a patent on heat storage and use of method-based supercooled plastic crystals on January 13, 2022. The authors declare no competing interests.

### SUPPLEMENTAL INFORMATION

It can be found online at <https://doi.org/10.1016/j.xinn.2024.100577>.

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