Colossal barocaloric effects with ultralow hysteresis in two-dimensional metal–halide perovskites

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Pressure-induced thermal changes in solids—barocaloric effects—can be used to drive cooling cycles that offer a promising alternative to traditional vapor-compression technologies. Efficient barocaloric cooling requires materials that undergo reversible phase transitions with large entropy changes, high sensitivity to hydrostatic pressure, and minimal hysteresis, the combination of which has been challenging to achieve in existing barocaloric materials. Here, we report a new mechanism for achieving colossal barocaloric effects that leverages the large volume and conformational entropy changes of hydrocarbon order–disorder transitions within the organic bilayers of select two-dimensional metal–halide perovskites. Significantly, we show how the confined nature of these order–disorder phase transitions and the synthetic tunability of layered perovskites can be leveraged to reduce phase transition hysteresis through careful control over the inorganic–organic interface. The combination of ultralow hysteresis and high pressure sensitivity leads to colossal reversible isothermal entropy changes (>200 J kg⁻¹ K⁻¹) at record-low pressures (<300 bar).
Early 4400 TWh of electricity—20% of the total consumed in the world—is used each year by refrigerators, air conditioners, and heat pumps for cooling. In addition to the 2.3 Gt of carbon dioxide emitted during the generation of this electricity, the vapor-compression-based devices that provided the bulk of this cooling emitted fluorocarbon refrigerants with a global warming potential equivalent to 1.5 Gt of carbon dioxide into the atmosphere. With population and economic growth expected to dramatically increase over the next several decades, the development of alternative cooling technologies with improved efficiency and reduced emissions will be critical to meeting global cooling needs in a more sustainable fashion.

Caloric materials, which undergo thermal changes in response to an applied magnetic, electric, or stress field, offer the potential for solid-state cooling with high energy efficiency and zero direct emissions, as well as faster start-up times, quieter operation, greater amenability to miniaturization, and better recyclability than conventional vapor-compression systems. Caloric effects are particularly strong in ferroic materials near first-order phase transitions, where small changes to the magnitude of an applied field can induce the large isothermal entropy and adiabatic temperature changes required for commercially viable cooling cycles.

Although magnetocaloric and electrocaloric effects have received the most attention for solid-state cooling, transitions between states with different magnetic ordering or electric polarization typically involve much smaller entropy changes than those that occur during the liquid–vapor transition of a hydrofluorocarbon refrigerant and can be complicated by the need to generate large magnetic fields or to avoid dielectric breakdown. Alternatively, the sensitivity of structural phase transitions to hydrostatic pressure and uniaxial strain can be leveraged to realize even larger entropy changes in barocaloric and elastocaloric materials, respectively. In particular, reversible structural transitions that are accompanied by a substantial change in volume can produce barocaloric effects with large entropy changes and high sensitivity to pressure.

An ideal material for barocaloric cooling would feature a phase transition with (i) a large isothermal entropy change (\(\Delta S_{\text{th}}\)) and adiabatic temperature change (\(\Delta T_{\text{ad}}\)), (ii) a large barocaloric coefficient (\(dT_{\text{rev}}/dP\)) that reflects a high sensitivity of the transition temperature, \(T_{\text{rev}}\), to pressure, \(P\), and (iii) a low reversible pressure, \(P_{\text{rev}}\), which represents the minimum pressure required to induce a reversible entropy change and is proportional, in part, to the thermal hysteresis of the phase transition. Among the limited range of compounds that have been investigated as candidate barocaloric materials, certain organic plastic crystals, such as neopentyglycol, have recently been shown to exhibit order–disorder phase transitions in the solid state that yield colossal barocaloric effects with entropy changes approaching those of commercial hydrofluorocarbon refrigerants. These transitions, however, often have large thermal hysteresis, occur away from ambient temperature, or have only moderate sensitivity to applied pressure. This highlights a longstanding challenge across all classes of caloric materials: field-induced phase transitions that lead to large isothermal entropy and adiabatic temperature changes are often accompanied by substantial hysteresis, which increases the magnitude of the applied field required to capture the full entropy of the transition and reduces the efficiency of each cooling cycle.

In pursuit of a new strategy to target barocaloric effects with low hysteresis, high sensitivity to pressure, and large entropy changes near ambient temperature, we sought a phase transition mechanism that would offer access to large volume changes and disordered states with high entropy but could take place within a microenvironment tailored to promote reversibility. To this end, we recognized that long-chain hydrocarbons undergo order–disorder transitions with far higher entropy changes than have ever been realized in a caloric effect. For instance, the entropy of n-decane (\(\text{C}_{10}\text{H}_{22}\)) increases by 829 J kg\(^{-1}\) K\(^{-1}\) (118 J mol\(^{-1}\) K\(^{-1}\)) upon melting, which is even larger than the 520 J kg\(^{-1}\) K\(^{-1}\) (53 J mol\(^{-1}\) K\(^{-1}\)) increase in entropy of the commercial refrigerant HFC-134a (CH\(_2\)FC\(_2\)) upon vaporization. These high entropy changes arise from increases in orientational, conformational, and positional entropy as molecules restricted in the crystalline state gain access to more rotational, vibrational, and translational degrees of freedom in the disordered—and expanded—melted state.

The entropy and latent heat changes associated with hydrocarbon melting transitions are already exploited for thermal energy storage in paraffin-based solid–liquid phase-change materials. Similar types of phase transitions are also known to occur in the solid state in several classes of layered materials, including two-dimensional (2-D) metal–halide perovskites of the form (R-NH\(_2\))\(_2\)MX\(_4\) (\(R = \text{C}2\text{H}_{3}\)), \(M = \text{Mn, Fe, Cu, Cd, Pb; } X = \text{Cl, Br, or I}\)). In these compounds, sheets of corner-sharing \(\text{MX}\(_4\)\) octahedra create anionic pockets—defined by the axial halides of four adjacent metal centers—that template the arrangement of bilayers of alkylammonium cations through charge-assisted hydrogen bonds. When long-chain hydrocarbon molecules (\(n > 3\)) are incorporated, many layered perovskites undergo thermally induced, first-order phase transitions between low- and high-entropy states driven by a partial disordering transition of the hydrocarbon bilayers (Supplementary Tables 1–3). These transitions are often referred to as “chain-melting” transitions because of the liquid-like conformational degrees of freedom associated with the hydrocarbon chains in the disordered phase, even though the transition occurs entirely in the solid state.

As such, we anticipated that 2-D perovskites would serve as a highly tunable solid-state platform to leverage the large changes in entropy and enthalpy that accompany hydrocarbon order–disorder transitions for barocaloric cooling. In addition, since the inorganic layers and organic bilayers of 2-D perovskites can be independently manipulated, we further expected that phase transition hysteresis could be minimized through confinement effects and careful control of the organic–inorganic interfaces. We note that 2-D perovskites were also independently identified as promising barocaloric materials by Lloveras and coworkers while our work was under peer review.

Here, we report a comprehensive study of barocaloric effects in two representative 2-D perovskites (DA\(_2\)MnCl\(_4\) (DA = decylammonium) and (NA\(_2\))CuBr\(_3\) (NA = nonylammomium)). Through a combination of high-pressure calorimetry and X-ray diffraction experiments, we show that these materials feature phase transitions with large entropy changes, high sensitivity to pressure, and minimal hysteresis, which collectively leads to outstanding barocaloric performance. Moreover, we demonstrate how the chemical tunability of 2-D perovskites and the decoupling of extrinsic and intrinsic factors that influence phase-change kinetics can be leveraged to drive reversible barocaloric effects with pressures approaching those used in vapor-compression cooling systems. These results are further supported by detailed crystallographic and spectroscopic characterizations, which provide molecular-level insights into barocaloric effects in 2-D perovskites, including compensation effects between entropy changes, hysteresis, and pressure sensitivity. Our work establishes hydrocarbon phase transitions in 2-D perovskites as a generalizable mechanism for achieving large and reversible barocaloric effects at low driving pressures.

**Results**

**Pressure dependence of phase transitions in (DA\(_2\))\(_2\)MnCl\(_4\).** The 2-D perovskite (DA\(_2\))\(_2\)MnCl\(_4\) was selected as a potential...
barocaloric material because of its large phase transition entropy ($\Delta S_{\text{tr}} = 230 \text{ J kg}^{-1} \text{ K}^{-1}$) and enthalpy ($\Delta H_{\text{tr}} = 71 \text{ kJ kg}^{-1}$), near-ambient phase transition temperature ($T_{\text{tr}} = 310 \text{ K}$), and lightweight, nontoxic elemental composition (Fig. 1b). At ambient temperature and pressure, (DA)$_2$MnCl$_4$ adopts an ordered monoclinic structure (low-temperature, LT, phase) with bilayers of hydrocarbon chains—each of which contains a single gauche C–C bond (C2–C3) and seven trans C–C bonds—aligned parallel to one another and tilted 48.3(1)$^\circ$ with respect to the Mn–Cl$_{\text{eq}}$ (equatorial chloride) plane (Fig. 2e)$.^{26}$ Upon heating above 310 K, the compound undergoes a first-order phase transition to an expanded orthorhombic lattice (high-temperature, HT, phase) with disordered hydrocarbon chains that have increased conformational and rotational degrees of freedom$.^{27}$ The large increase in entropy during the transition can be attributed to flipping of the alkylammonium cations between two favorable orientations within the Mn–Cl pockets, internal rotations of C–C bonds that create dynamically disordered conformational defects within the hydrocarbon chains, and a substantial increase in volume (Supplementary Notes 1–3)$^{24}$.

Differential scanning calorimetry (DSC) measurements at ambient pressure showed that the hydrocarbon order–disorder transition is sharp and fully reversible with a thermal hysteresis, $\Delta T_{\text{hys}}$, of just 1.4 K for a microcrystalline powder sample at a scan rate of 2 K min$^{-1}$ (Fig. 2a). Variable-temperature powder X-ray diffraction (PXRD) experiments at ambient pressure revealed that the phase transition is accompanied by an increase in interlayer distance of 1.88 Å (7.0%) as the alkylammonium cations tilt further away from the Mn–Cl$_{\text{eq}}$ plane to create additional space between disordered hydrocarbon chains in the HT phase (Supplementary Fig. 1). This expansion leads to an 8.0% overall increase in the volume of the compound ($\Delta V_n = 65.9 \text{ cm}^3 \text{ kg}^{-1}$; Fig. 2c). Based on the measured volume and entropy changes, the Clausius–Clapeyron relation, $dT/dp = \Delta V_p/\Delta S_{\text{tr}}$, can be used to predict a barocaloric coefficient for (DA)$_2$MnCl$_4$ of 28.7 K kbar$^{-1}$, which would represent one of the highest values reported for a barocaloric material (Supplementary Table 5). We note that select 3-D hybrid perovskites also exhibit similarly high barocaloric coefficients$^{28,29}$.

To directly evaluate the pressure dependence of the phase transition temperature, isobaric DSC experiments were performed under applied hydrostatic pressures of up to 150 bar using He as the pressure-transmitting medium (Fig. 3a). As expected, the phase transition shifts to higher temperatures as the pressure is increased, with a measured $dT/dp$ of 22.5 ± 0.3 K kbar$^{-1}$ during heating and 20.2 ± 1.1 K kbar$^{-1}$ during cooling (Fig. 3h, Supplementary Fig. 6). Importantly, the application of pressure does not lead to any significant changes to the phase transition width, and $\Delta S_{\text{tr}}$ remains within 96% of its ambient pressure value at 150 bar (Supplementary Fig. 10). Variable temperature and pressure PXRD experiments (performed at beamline 17-BM of the Advanced Photon Source at Argonne National Laboratory) confirm that similar order–disorder transitions still occur at pressures up to at least 360 bar (Fig. 3g, Supplementary Figs. 23–25), with small decreases in overall volume changes at higher pressures that are consistent with a higher compressibility for the HT phase relative to the LT phase (Supplementary Table 9).

Interestingly, the $dT/dp$ values for (DA)$_2$MnCl$_4$ determined by PXRD and HP-DSC are lower than those predicted using the Clausius–Clapeyron equation. One possible explanation for this is that the effective volume change in the presence of a pressure-transmitting medium is less than the crystallographic volume change$.^{30}$ This could occur if He was excluded from the dense, crystalline organic bilayer of the LT phase but could permeate into the disordered organic bilayer of the HT phase—owing to its increased free volume—which would reduce the amount of
Additional volume that was occupied by the expanded phase. Indeed, the volume change that is directly measured by He pycnometry is 17 cm$^3$ kg$^{-1}$ smaller than that determined by crystallography (Fig. 2c), and using this lower effective volume change in the Clausius–Clapeyron equation yields a predicted $dT/dP$ of 21.4 ± 1.5 K kbar$^{-1}$ that matches the HP-DSC and PXRD values (Supplementary Table 10). Although effects of the pressure-transmitting medium are not typically considered when evaluating barocaloric materials, this result provides a pathway to realizing a higher $dS_T/dfi$ that can be used to drive a Stirling-like cooling cycle$^{31}$, when cycling to and from ambient pressure. For a normal barocaloric effect, $P_{rev}$ corresponds to the pressure at which the onset temperature of the exothermic phase transition at applied pressure is equal to the onset temperature of the endothermic phase transition at 1 bar (ref. 11). As such, $P_{rev}$ is proportional to the thermal hysteresis at 1 bar and inversely proportional to the barocaloric coefficient for the exothermic transition, with $P_{rev} = \Delta T_{hys}/(dT/dP)_{cooling}$. In addition, the minimum pressure required to induce a reversible adiabatic temperature change, $P_{rev,ad}$, corresponds to the pressure at which the completion temperature of the exothermic phase transition at applied pressure is equal to the completion temperature of the endothermic phase transition at 1 bar (Supplementary Note 4). As such, $P_{rev,ad}$ is also affected by the transition peak width in addition to the thermal hysteresis and barocaloric coefficient, with smaller peak widths leading to lower $P_{rev,ad}$. During our isobaric DSC experiments, we found that the transition peak widths of powder samples of (DA)$_2$MnCl$_4$ were much broader than those of single-crystal samples (Fig. 4a, c). We attribute the narrower peak widths of the single-crystal samples to improved thermal contact between single crystals and the DSC sample pan, as poor thermal contact is
known to lead to thermal gradients that cause increased peak widths. Accordingly, single-crystal samples of (DA) 2MnCl 4 with high-quality thermal contact have a lower $P_{rev, ad}$ than powder samples (178 bar and 265 bar, respectively), even though powder samples have a slightly lower $P_{rev}$ because of their smaller thermal hysteresis (Supplementary Table 7, Supplementary Note 5). This demonstrates the importance of considering the influence of extrinsic factors, such as the quality of thermal contact between the sample and sample holder, when evaluating the intrinsic potential of new barocaloric materials.

Owing to its low $\Delta T_{hys}$ and high $d\Delta T/dP$, a single-crystal sample of (DA) 2MnCl 4 has a $P_{rev}$ of just 92 bar, which ranks among the lowest values reported for barocaloric materials (Supplementary Table 5). This low $P_{rev}$ was further confirmed by calculating reversible isothermal entropy changes ($\Delta S_{it}$) as a function of pressure from the difference between isobaric entropy changes.

**Fig. 3 Barocaloric effects in 2-D metal-halide perovskites.** DSC measurements under applied hydrostatic pressure for single-crystal samples of (a) (DA) 2MnCl 4 and (d) (NA) 2CuBr 4 with heating and cooling rates of 2 K min$^{-1}$. Isothermal entropy changes, $\Delta S_{it}$, are calculated by the quasi-direct method for (b) (DA) 2MnCl 4 and (e) (NA) 2CuBr 4 for compression from ambient pressure and for decompression to ambient pressure. The shaded area indicates the reversible $\Delta S_{it}$ within this pressure range. Isobaric entropy curves are shown in Supplementary Figs. 10 and 11. Direct evaluation of pressure hysteresis, $\Delta P_{hys}$, through quasi-isothermal DSC experiments for (c) (DA) 2MnCl 4 and (f) (NA) 2CuBr 4 at 311 K and 306 K, with pressure cycling from 1 to 150 bar and to 105 bar, respectively. $\Delta P_{hys}$ is calculated as the difference between the onset pressure for the compression-induced exotherm and the decompression-induced endotherm and is indicated by the horizontal green bar. Variable-temperature powder X-ray diffraction (PXRD) patterns for (g) (DA) 2MnCl 4 and (i) (NA) 2CuBr 4 at 360 bar and 300 bar of He, respectively, while cooling from 325 K to 280 K, with an X-ray wavelength of 0.45237 Å. The pressure dependence of the order-disorder transition temperature as determined by HP-DSC (diamonds) and PXRD (squares) is used to calculate the barocaloric coefficient, $dT/dP$, for (h) (DA) 2MnCl 4 and (j) (NA) 2CuBr 4. Red and blue symbols indicate the phase transition temperatures during heating and cooling, respectively. Barocaloric coefficients are summarized in Supplementary Table 8.
ΔS_{ib}, at ambient pressure and elevated pressures. Here, ΔS_{ib} values obtained from heating data correspond to the disordering transition induced by a decrease in pressure (ΔS_{ib} > 0), while ΔS_{ib} values from cooling data correspond to the ordering transition induced by an increase in pressure (ΔS_{ib} < 0) (Supplementary Fig. 10). Excitingly, these ΔS_{it} curves confirm that a non-zero reversible entropy change of 13 J kg⁻¹ K⁻¹ can be induced at 100 bar (Fig. 3b). Moreover, a reversible entropy change of 190 J kg⁻¹ K⁻¹ can be accessed at a driving pressure of 150 bar (Fig. 3b, Supplementary Fig. 17b, e). To the best of our knowledge, inducing a reversible entropy change of this magnitude through a pressure shift of only 150 bar is unprecedented in barocaloric materials (Supplementary Table 5). As a result, (DA)₂MnCl₄ displays a record-high barocaloric strength—defined as the reversible isothermal entropy change normalized by the driving pressure—of 1267 J kg⁻¹ K⁻¹ at 150 bar (Supplementary Table 6). Based on variable-temperature heat capacity, c_p, measurements at ambient pressure (Supplementary Fig. 31), a maximum adiabatic temperature change, ΔT_{ad, max} of 45 K can be estimated from the indirect calculation ΔT_{ad}(T) = - TΔS_{ib}/c_p, which also ranks among the highest values yet reported for barocaloric materials (Supplementary Table 6).

In order to evaluate reversible adiabatic temperature changes, we performed additional HP-DSC experiments at a higher pressure range of 300–500 bar for a powder sample of (DA)₂MnCl₄ (Fig. 5a–c). This data shows that the order–disorder phase transition persists to at least 500 bar of hydrostatic pressure while maintaining 94% of the ambient pressure entropy change (Supplementary Fig. 20). At a 500-bar operating pressure, (DA)₂MnCl₄ has a maximum reversible isothermal entropy change, ΔS_{ib, rev, max} of 248 J kg⁻¹ K⁻¹ and a maximum reversible adiabatic temperature change, ΔT_{ad,rev, max} of 7 K (Fig. 6a, Supplementary Fig. 22). We note that the single order–disorder phase transition splits into a major transition (93% of the total entropy change) and a minor phase transition (7% of the total entropy change) at pressures above 400 bar, with the minor transition occurring at a slightly higher temperature than the major transition (Fig. 5a, Supplementary Fig. 8a). This is consistent with similar splitting—albeit at much higher pressures—and entropy changes that were recently reported in an independent study of the barocaloric properties of (DA)₂MnCl₄ at pressures above 300 bar while this manuscript was under peer review.⁵

Although quasi-direct methods of calculating isothermal changes—and adiabatic changes—from isobaric experiments are commonly used to evaluate barocaloric materials due to the challenge of maintaining isothermality—or adiabaticity—during direct variable-pressure measurements, we also performed quasi-isothermal HP-DSC experiments to more directly evaluate P_{rev} by measuring pressure hysteresis. Specifically, we measured...
heat flow signals over three cycles of increasing and decreasing hydrostatic pressure between 1 bar and 150 bar at 311 K. By comparing the onset pressures for compression-induced exotherms and decompression-induced endotherms, we were able to directly measure a pressure hysteresis of $62 \pm 4$ bar for $\text{(DA)}_2\text{MnCl}_4$, which is in excellent agreement with the predicted value of 70 bar at 311 K (Fig. 3c, Supplementary Fig. 18, Supplementary Table 11).

Reversible barocaloric effects in $\text{(NA)}_2\text{CuBr}_4$. In an effort to target barocaloric materials with large reversible entropy and...
adiabatic temperature changes at even lower pressures, we searched for a 2-D perovskite that undergoes a hydrocarbon order–disorder transition near ambient temperature with a thermal hysteresis of less than 1 K. Unlike (DA)2MnCl4, however, the total entropy of the order–disorder transition in most 2-D perovskites is partitioned across one or more minor—lower entropy—phase transitions in addition to the principal transition (Fig. 1b, Supplementary Tables 1–3). Although not necessarily detrimental to barocaloric cooling performance, the presence of multiple successive transitions at different temperatures complicates the evaluation of barocaloric properties because each minor and major transition has an independent hysteresis loop—often greater than 1 K—with different pressure dependences (Supplementary Table 4). With a lack of suitable existing compounds, we endeavored to synthesize a new 2-D perovskite that features a sharp order–disorder transition near ambient temperature with ultralow hysteresis and a high sensitivity to pressure.

After screening different combinations of metal cations, halide anions, and alkylammonium chain lengths, we discovered a 2-D perovskite (NA)2CuBr4 (NA = n-amylyalammonium) that undergoes an order–disorder transition at 305 K with a high ΔSrev (76(1) K⋅kbar–1) and hysteresis of only 0.4 K for a powder sample (Fig. 2b) and 1.0 K for a single-crystal sample (Fig. 4e). Variable-temperature PXRD experiments, combined with single-crystal structures at 270 K and 335 K, revealed that the phase transition involves a 4.0% increase in volume (ΔVvol = 25.3 cm3 kg–1) and a 2.9% (0.67 Å) increase in interlayer distance (Fig. 2d, f; Supplementary Figs. 1 and 4). The crystallographic volume change yields a predicted barocaloric coefficient of 33.3 kbar–1, while the volume change determined by He pycnometry (ΔVHe = 20.0 cm3 kg–1)—which accounts for He permeation—yields a predicted barocaloric coefficient of 26.3 ± 2.5 kbar–1 (Supplementary Table 10).

Isobaric HP-DSC experiments confirmed that (NA)2CuBr4 features high barocaloric coefficients of 26.7 ± 0.4 kbar–1 during both heating and cooling (Fig. 3d, j; Supplementary Fig. 11, Supplementary Table 8). In fact, these values represent one of the highest sets of barocaloric coefficients ever measured (Supplementary Table 5). As a result of its high barocaloric coefficient, ultralow hysteresis, and extremely sharp transition, the powder sample of (NA)2CuBr4 has, to the best of our knowledge, the lowest reported Prev for a barocaloric material of 16 bar (Fig. 7b), which is within the pressure range already accessed during commercial vapor-compression refrigeration cycles.19 The low value of Pprev was further confirmed through quasi-isothermal pressure cycling experiments at 306 K, where we directly measured a pressure hysteresis of 18 bar (Fig. 3f, Supplementary Fig. 19). Moreover, a large reversible entropy change, with a maximum value of 68 J kg–1 K–1 (90% of ΔSrev at 1 bar), is accessible over the temperature range of 2 K at an operation pressure of 150 bar for the powder sample (Supplementary Fig. 16c, d). Through additional HP-DSC experiments conducted at higher pressures up to 500 bar, we demonstrated that a large reversible entropy change of 78 J kg–1 K–1—equivalent to the full transition entropy—is accessible over a wider temperature range of 5 K and 10 K at 300 bar and 500 bar, respectively (Figs. 5d–f, 6b; Supplementary Figs. 21 and 22). Note that the order–disorder transition over this extended pressure range is associated with a similar volume change (21–25 cm3 kg–1) as revealed by PXRD experiments (Supplementary Figs. 4, 26–29; Supplementary Table 12), and thus maintains a high sensitivity to pressure of 24 K kbar–1 (Fig. 3i, j; Supplementary Fig. 7; Supplementary Table 8).

Impact of thermal contact on low-pressure reversibility. Our results for single-crystal samples of (DA)2MnCl4 and (NA)2CuBr4 show how improved thermal contact can lead to even larger reversible barocaloric effects at lower pressures (Fig. 4, Supplementary Fig. 17). For instance, at a 150-bar driving pressure, the maximum value of ΔSadv increases from 75 J kg–1 K–1 (powder with poor thermal contact) to 190 J kg–1 K–1 (single crystal with improved thermal contact) for (DA)2MnCl4 and from 68 J kg–1 K–1 (powder) to 78 J kg–1 K–1 (single crystal) for (NA)2CuBr4 (Supplementary Table 7). At even lower pressures, (NA)2CuBr4 features a reversible isothermal entropy change of 4 J kg–1 K–1 and 11 J kg–1 K–1 at 20 bar and 40 bar, respectively, for a powder sample (Fig. 5f, Supplementary Fig. 16d) and of 5 J kg–1 K–1 and 49 J kg–1 K–1 at 40 and 60 bar, respectively, for a single-crystal sample (Fig. 3e, Supplementary Fig. 17d). Notably, the single-crystal sample of (NA)2CuBr4 exhibits a reversible adiabatic temperature change (ΔTadv) of 2.3 K at a 150-bar driving pressure (Supplementary Fig. 17g), which represents, to the best of our knowledge, the first demonstration of ΔTadv of a sizable magnitude—sufficient to create much wider temperature spans through regeneration—near room temperature at a more practically accessible pressure for a barocaloric material.

Relationships between entropy changes and reversibility. To provide additional insight into the structural and chemical factors that influence barocaloric effects in 2-D perovskites, we used X-ray crystallography and infrared (IR) spectroscopy to compare the nature of the hydrocarbon order–disorder transition in (NA)2CuBr4 and (DA)2MnCl4. In particular, we hypothesized that the increased size of the halide pocket in (NA)2CuBr4 (30.5 Å2) relative to (DA)2MnCl4 (26.3 Å2) coupled with weaker N–H–Br hydrogen bonds at the organic–inorganic interface—would lead to increased free volume in the organic bilayer of the Cu compound (Supplementary Figs. 34 and 35) and, as a result, greater disorder in the LT phase. As anticipated, the atoms in the NA chains of (NA)2CuBr4 have much larger atomic displacement parameters in the LT phase than those in the DA chains of the LT phase of (DA)2MnCl4 (Fig. 8). This is consistent with the LT phase of (NA)2CuBr4 having increased vibrational and conformational degrees of freedom, which would reduce the entropy difference between the LT and HT phases (Supplementary Notes 1 and 2).

The increased entropy of the alkylammonium chains of (NA)2CuBr4 prior to the phase transition is further corroborated by a broad feature in the heat capacity from 220–250 K that is consistent with a gradual activation of conformational degrees of freedom from the fully ordered organic bilayer that is present at 100 K (Supplementary Figs. 32 and 36). Variable-temperature IR spectra are also consistent with increased conformational entropy for the hydrocarbon chains in the LT phase of (NA)2CuBr4. Specifically, IR spectra show a band near 1360 cm–1, which can be assigned to CH2 wagging from g12h1-g12t-type kinks, that is present below the phase transition temperature for (NA)2CuBr4 but only above the phase transition temperature for (DA)2MnCl4 (Supplementary Fig. 37). As discussed in greater detail in Supplementary Note 6, the IR spectra also suggest that the local environment around the chain ends (CH3) and headgroups (NH2+) is more similar in the LT and HT phases of (NA)2CuBr4 than in those of (DA)2MnCl4 (Supplementary Table 13).

Although increasing the halide pocket size through Br substitution leads to a decreased entropy change (Fig. 7a), it also likely contributes to the enhanced reversibility of the (NA)2CuBr4 phase transition through two primary effects. First, the softer nature of Br anions—along with the higher degree of disorder in the alkylammonium chains in the LT phase—makes the (NA)2CuBr4 lattice more compressible than the (DA)2MnCl4 lattice (Supplementary Table 9). Since the barocaloric coefficient dTdP of a solid tends to increase with increasing compressibility,22,36 this causes...
the phase transition in (NA)\textsubscript{2}CuBr\textsubscript{4} to be more sensitive to pressure, which reduces the minimum pressure required to overcome hysteresis and induce a reversible phase transition. Indeed, $\frac{dT}{dP}$ for the ordering transition in (NA)\textsubscript{2}CuBr\textsubscript{4} is 29\% higher than for (DA)\textsubscript{2}MnCl\textsubscript{4} (Supplementary Table 7). Second, the increased free volume and presence of additional vibrational and conformational degrees of freedom in both the LT and HT phases should render the two phases more compatible, reducing the activation energy barrier for nucleation of a more ordered bilayer phase during cooling—or compression—and lowering both the isobaric and isothermal hysteresis\textsuperscript{37}.

Impact of hysteresis on thermodynamic efficiency. In addition to its influence on operating pressure, hysteresis adversely impacts the second-law efficiency and coefficient of performance...
(COP) of any caloric cooling cycle because of dissipative heat losses. The impact of hysteresis on efficiency can be quantified by calculating an idealized thermodynamic efficiency, \( \eta \)—relative to the Carnot efficiency—with a simple material model that accounts for dissipative losses due to hysteresis in a Carnot-like cycle:

\[
\eta = \frac{\text{COP}}{\text{COP}_\text{Carnot}} = 1 + \frac{\Delta T_{\text{hyst}}}{T_{\text{ad,max}}} \quad (1)
\]

Based on this model, caloric materials with \( \Delta T_{\text{hyst}}/T_{\text{ad,max}} \) of less than 10% will have idealized second-law efficiencies competitive with those of conventional vapor compression-based systems (~85%). Notably, (DA)\(_2\)MnCl\(_4\) and (NA)\(_2\)CuBr\(_4\) have the potential to reach the second-law efficiencies of 82 and 79%, respectively, based on their intrinsic barocaloric properties. Further, both compounds display large reversible refrigeration capacities (RCR) under easily accessible pressures (Fig. 5c, f).

**Discussion**

Overall, these results highlight exciting opportunities to exploit the tunability of 2-D perovskites to independently manipulate the hysteresis, sharpness, entropy, and sensitivity to pressure of hydrocarbon order–disorder phase transitions for improved barocaloric performance. For instance, it should be possible to realize phase transitions with even higher entropy changes through functionalization of the organic bilayers—such as by introducing hydrogen bond donor–acceptor pairs—and even lower hysteresis through modification of the organic–inorganic interface—such as by incorporating mixtures of different halide anions or introducing defects. Further, the modular nature and high tunability of 2-D perovskites can be leveraged to optimize, in addition to intrinsic barocaloric properties, a host of factors that are critical to realizing scalable and efficient solid-state cooling technologies, including safety, flammability, and thermal conductivity (Supplementary Figs. 39–42). In addition, the anisotropic nature of the order–disorder transition in (DA)\(_2\)MnCl\(_4\) and (NA)\(_2\)CuBr\(_4\)—as highlighted by variable-temperature atomic force microscopy (AFM) experiments on single crystals directly grown on a Si wafer (Fig. 9, Supplementary Fig. 43)—suggests that uniaxial stress, which can be readily applied through mechanical actuation, may be able to drive large elastocaloric effects in 2-D perovskites and that barocaloric effects should be accessible in 2-D perovskites with sub-micron thickness. More broadly, solid-state hydrocarbon order–disorder transitions are not unique to 2-D perovskites, and many other classes of layered materials—including di-n-alkylammonium salts, alkylammonium-modified layered silicates, and metal-alkylphosphonate salts—undergo reversible phase transitions near ambient temperature that should produce colossal barocaloric effects and have yet to be explored.

**Methods**

**Materials**

All compounds were synthesized and handled in air unless otherwise noted. Anhydrous diethyl ether was obtained from a Pure Process Technology anhydrous solvent system. Anhydrous methanol and ethanol were purchased from a commercial vendor and used as received. All other reagents were purchased from commercial vendors and used as received.

**Synthesis of (DA)\(_2\)MnCl\(_4\) (DA = decalammonium, C\(_9\)H\(_{19}\)NH\(_3\)).** Decalammonium (≥99.0% purity) and hydrochloric acid (HCl, 37 wt %) were purchased from Sigma Aldrich and used without further purification. Decalammonium chloride (C\(_9\)H\(_{19}\)NH\(_3\)Cl, (DA)Cl) was first synthesized by adding HCl (530 mL, 6.6 mmol) into a solution of decalammonium carbonate (C\(_9\)H\(_{19}\)NH\(_3\)CO\(_3\), (DA)CO\(_3\)) in ca. 5 mL ethanol in an ice water bath with stirring. After evaporating the solvent under reduced pressure, the resulting white powder of (DA)Cl was washed with diethyl ether and dried under vacuum at room temperature for 1 day. Crystalline powders of (DA)\(_2\)MnCl\(_4\) were prepared in a similar manner to previously reported syntheses. Specifically, (DA)Cl (96.9 mg, 0.5 mmol) was first dissolved in 4 mL of ethanol. After several minutes of stirring, MnCl\(_2\)·4H\(_2\)O (49.5 mg, 0.25 mmol) was added to the solution, and the solution was heated to 65 °C. Pale-pink crystals were obtained upon cooling the resulting solution to room temperature at a rate of 4 K h\(^{-1}\). The crystals were filtered, washed with diethyl ether (5 × 10 mL), and dried under vacuum for 6 h to afford 45.2 mg (35.2% yield) of product. Single crystals suitable for X-ray structure determination were obtained by cooling at a rate of 2 K h\(^{-1}\).

**Synthesis of (NA)\(_2\)CuBr\(_4\) (NA = decalammonium, C\(_9\)H\(_{19}\)NH\(_3\)).** Nonylammonium (≥99.5% purity) and hydrobromic acid (HBr, 48 wt %) were purchased from Sigma Aldrich and used without further purification. Nonylammonium bromide (C\(_9\)H\(_{19}\)NH\(_3\)Br, (NA)Br) was first synthesized by adding HBr (545 mL, 4.8 mmol) to a solution of nonylamine (0.33 mL, 4.0 mmol) in ca. 5 mL ethanol in an ice water bath with stirring. After evaporating the solvent under reduced pressure, the resulting white powder of (NA)Br was washed with diethyl ether and dried under vacuum at room temperature for 1 day. Crystalline powders of (NA)\(_2\)CuBr\(_4\) were prepared by dissolving of CuBr\(_2\) (402 mg, 1.8 mmol) and (NA)Br (807 mg, 3.6 mol) in 2 mL of ethanol at 65 °C. The solution was slowly cooled to room temperature at a rate of 4 K h\(^{-1}\) and then further cooled to 5 °C for 1 h. The resulting dark purple precipitate was filtered, washed with diethyl ether (5 × 10 mL), and dried under vacuum for 12 h to afford 705 mg (58.3% yield) of product. Single crystals suitable for X-ray structure determination were obtained by slow evaporation of a 1:1 solution of (NA)\(_2\)CuBr\(_4\) (202 mg, 0.3 mmol) in methanol. Anal. Calc. for (C\(_9\)H\(_{19}\)NH\(_3\))\(_2\)CuBr\(_4\): C: 31.84%, H: 6.69%, N: 4.43%, Br: 47.76%.

**Thermogravimetric analysis.** Samples were loaded into a TGA 550 from TA Instruments in open aluminum pans with a stainless-steel lid under air and heated at a rate of 4 K min\(^{-1}\) from ambient to 500 °C under a 10 mL min\(^{-1}\) N\(_2\) flow with an empty aluminum pan/stainless-steel lid used as a reference. The TGA measurements were conducted using a series of 3 reference masses, while the sample temperature was calibrated to the Curie temperature of nickel. The thermogravimetric analyses of (DA)\(_2\)MnCl\(_4\) and (NA)\(_2\)CuBr\(_4\) are shown in Supplementary Figs. 39 and 40.

**High-pressure differential scanning calorimetry (HP-DSC).** DSC measurements over the pressure range from 1 to 150 bar were conducted in a Setaram high-pressure DSC (Microcalvet) using microcrystalline powder samples. The calorimeter was calibrated based on the Joule effect, which does not require reference materials. For each set of measurements, 7 mg of sample was encapsulated in the high-pressure vessel of the calorimeter, and the pressure was generated by a compressing piston using Helium gas as a pressure-transmitting medium.

**Determination of \( T_{\text{tr}}, \Delta H_{\text{tr}}, \) and \( \Delta S_{\text{tr}} \).** Phase transition temperatures, \( T_{\text{tr}} \), and enthalpies, \( \Delta H_{\text{tr}} \), were determined using the TTRIOS software from TA Instruments. Peaks were selected for analysis by defining a temperature range containing the peak
Fig. 9 Phase transition of single crystals on a substrate. a Optical images of (DA)$_2$MnCl$_4$ single crystals directly grown on Si substrates through an anti-solvent vapor-assisted capping crystallization method. b Bright field (top) and dark field (bottom) images of a sub-micron thick single crystal. c Variable-temperature atomic force microscope (AFM) imaging experiments for a sub-micron thick (DA)$_2$MnCl$_4$ single crystal. d Height profiles of a sub-micron thick (DA)$_2$MnCl$_4$ single crystal in the low-temperature (LT, left) and high-temperature (HT, right) phases. e Thickness of a single crystal of (DA)$_2$MnCl$_4$ as a function of temperature. The heating-induced transition from the LT phase to HT phase gives rise to a 7.9% change in height, which agrees well with the 7.4% predicted from crystallographic data obtained from variable-temperature PXRD experiments at 30 °C and 45 °C. Error bars were obtained from the mean square difference between all data points in the scan region and the fitted step height. Thermal cycling AFM experiments are described in Supplementary Fig. 43.

Construction of isobaric entropy curves. Isobaric entropy changes, $\Delta S_{ib}$, were calculated as a function of temperature and pressure by integrating the HP-DSC heat flow signal $Q$, obtained at a scan rate of $\frac{\Delta T}{\Delta t}$ near the transition peak over the temperature range from $T_i$ to $T_f$ after baseline subtraction:

$$\Delta S_{ib} = \int_{T_i}^{T_f} \frac{1}{T} Q(T, P) dT$$

In a typical isobaric measurement with a scan rate of 2 K min$^{-1}$ at pressures up to 150 bar, the temperature range for peak integration, $\Delta T_{int} = T_f - T_i$, was set to 16 K for microcrystalline powder samples, for consistency, with $T_i = T_0 - 8$ K and $T_f = T_0 + 8$ K. For single-crystal samples, due to their sharper transition peak width, a narrower temperature range was chosen, with $\Delta T_{int}$ of 3 K and 2 K for (DA)$_2$MnCl$_4$ and (NA)$_2$CuBr$_4$, respectively. For isobaric measurements with a scan rate of 0.5 K min$^{-1}$ over the pressure range of 300 to 500 bar, $\Delta T_{int}$ of 12 K and 10 K were chosen for (DA)$_2$MnCl$_4$ and (NA)$_2$CuBr$_4$, respectively. Baselines for peak integration were generated using mutual tangent slopes, and the tangents before and after the transition peak were created from $T_i$ to $T_f$ on repeated measurements of the melting transition of an indium standard.

A positive slope in the isobaric entropy curves was introduced by adding the entropy contribution from heat capacity $S_c(T)$, calculated through Eq. (3), to the
induced cooling, for instance), the irreversible
independent of pressure,
\(\Delta S\) isobaric entropy changes associated with the phase transition.

\[
\Delta S(T) = \int_{T_0}^{T} \frac{\Delta C_P}{\Delta T} dT \quad \text{for} \quad T \leq T_0
\]

For both compounds, the reference temperature \(T_0\) was set to 290 K, with \(S(T_0) = 0\). The heat capacity values during the phase transition (between \(T_1\) and \(T_2\)) were obtained through \(c_p(x) = (1 - x)^2 a + x^2 b\) where \(x\) is the phase fraction of the material in the HT phase at the temperature \(T\).

The dependence of the heat capacity contribution \(S(T)\) on applied pressure can be estimated by calculating the pressure-induced changes in isothermal entropy that arises outside of the phase transition region. This entropy contribution, \(S_{\Delta T}\), is often referred to as the elastic heating contribution44 and can be calculated using the following formula derived from the Maxwell relation \((\partial V/\partial T)_p\) is zero:

\[
S_{\Delta T}(P) = \int_{P_0}^{P} \left( V \cdot \Delta P \right) dP
\]

where \(V\), \(\Delta P\), and \(\Delta S\) denote the specific volume, driving pressure \(\Delta P = P - P_0\), and thermal expansion coefficient at ambient pressure, respectively, with \(\Delta S = V^{-1}(\partial V/\partial P)_T\).

Equation (5) is commonly used to estimate \(S_{\Delta T}\) since high-pressure heat capacity measurements are difficult to perform accurately. At quasi-isothermal pressure, \(\Delta S\) entropy curves that include the contributions from heat capacity were obtained by adding \(S(T)\) to \(S_{\Delta T}\) and shifting the curves downward by \(S_{\Delta T}\) of the LT phase.

Although both (DA)\(_2\)MnCl\(_4\) and (NA)\(_2\)CuBr\(_4\) display large thermal expansion coefficients on the order of \(10^{-1}\) K\(^{-1}\), their estimated \(S_{\Delta T}\) values are small relative to their transition entropies at pressures up to 150 bar. For example, for a driving pressure of 150 bar, \(S_{\Delta T}\) in the LT phase of (DA)\(_2\)MnCl\(_4\) and (NA)\(_2\)CuBr\(_4\) is predicted to be just \(-3\) kg \(\cdot\) K\(^{-1}\) and \(-4\) kg \(\cdot\) K\(^{-1}\), respectively. We note, however, that \(S_{\Delta T}\) can become significant at higher driving pressures and can further enhance the barocaloric effect. The calculated \(S_{\Delta T}\) values are summarized in Supplementary Table 9.

**Evaluation of isothermal entropy changes.** Pressure-induced isothermal entropy changes, \(\Delta S_{\Delta T}\), were calculated by the quasi-direct method\(^{33}\) as the difference between \(S_{\Delta T}\) at ambient pressure \(P_0\) of 1 bar, \(S_{\Delta T}(T, P_0)\), and \(S_{\Delta T}\) at elevated pressure, \(S_{\Delta T}(T, P)\). For \(\Delta S_{\Delta T}\), corresponding to the endothermic, disordering transition induced by decompression \((P \rightarrow P_0)\), \(\Delta S_{\Delta T}\) values were obtained from heating data:

\[
\Delta S_{\Delta T}(P \rightarrow P_0) = \Delta S_{\text{heating}}(P, P_0) - \Delta S_{\text{heating}}(P_0, P_0)
\]

For \(\Delta S_{\Delta T}\) corresponding to the exothermic, order transition induced by compression \((P_0 \rightarrow P)\), \(\Delta S_{\Delta T}\) values were obtained from cooling data:

\[
\Delta S_{\Delta T}(P_0 \rightarrow P) = \Delta S_{\text{cooling}}(P, P_0) - \Delta S_{\text{cooling}}(P_0, P_0)
\]

For operations pressures above \(P_{\text{prev}}\), the reversible values of \(\Delta S_{\Delta T}\) were estimated from the overlap between compression-induced and decompression-induced \(\Delta S_{\Delta T}\) curves reflected across the temperature axis. From the reversible isothermal entropy curves, the reversible refrigeration capability values, \(R_{\text{rec}}\), were calculated as \(\Delta S_{\text{rec,max}} \times \Delta T_{\text{VTHM}}\), where \(\Delta S_{\text{rec,max}}\) is the maximum reversible isothermal entropy change for a given pressure and \(\Delta T_{\text{VTHM}}\) is the full width at half maximum of the reversible isothermal entropy peak at a given pressure (Fig. 5c, i).

**Evaluation of adiabatic temperature changes.** For evaluations of adiabatic temperature changes, two different methods were used: (i) the indirect method and (ii) the quasi-direct method. The DSC baseline of the simple relationship \(\Delta T_{\text{ad,indirect}} = -\Delta S_{\Delta T}/c_P\) (for specific values used for the calculation, see Supplementary Table 6). Although the indirect method is a useful way of evaluating an upper bound for the magnitude of an adiabatic temperature that could be achieved with a given material, this approach is not appropriate for calculating the dependence of \(\Delta T_{\text{ad}}\) on operating pressure or the magnitude of \(\Delta T_{\text{ad}}\) that can be accessed under reversible conditions. Moreover, the indirect method is accurate only when \(c_P\) is relatively independent of pressure and \(\Delta T_{\text{ad,indirect}}\) is sufficiently smaller than \(T\) (ref. 15). The magnitude of the adiabatic temperature change that can be accessed for a given pressure shift, however, can be evaluated through the so-called quasi-direct method by constructing two isobaric curves on a temperature (T) vs. entropy (S) plot at two different pressures (typically ambient pressure, \(P_0\), and applied pressure, \(P\)) (ref. 15). In such a plot, the width of horizontal—and adiabatic—lines between two isobaric entropy curves corresponds to the magnitude of the adiabatic temperature change that will be accessible for a given change in pressure. For the adiabatic temperature change that is induced by the first pressure change (decompression-induced cooling, for instance), the irreversible \(\Delta T_{\text{ad}}\) is calculated as

\[
\Delta T_{\text{ad,indirect}} = T(S, P_{\text{heating}}) - T(S, P_{\text{cooling}}) \quad \text{Supplementary Fig. 33).
\]
Therefore, when using the 14T heat flow, the pan mass matching criterion is not as stringent. Nevertheless, pan masses were selected here to be within ±0.1 mg, with the total empty pan mass being near 50 mg. Non-hermetic Tzero pans were used to allow for He gas to be present over the sample to be consistent with high-pressure DSC measurements and because the non-hermetic lids press directly on the sample, improving thermal contact. The DSC 2560 also features a robotic autosampler, which precisely and repeatably loads the sample and reference pans into the DSC. For all three temperature ranges, the reference pan remained in the cell and was not moved, with only the sample pan being exchanged by the autosampler. The cell purge gas was He at a flow rate of 30 mL min⁻¹. Samples were held under He for at least 30 min prior to the temperature ramp.

To examine the variability in our measurement and obtain a representative average heat capacity curve, the measurements of (DA)₂MnCl₄ and (NA)₂CuBr₄ were each conducted 8 times. The same reference pan and sapphire pan were used for all measurements, while a new sample pan with new sample was used for each measurement. All (DA)₂MnCl₄ and (NA)₂CuBr₄ heat capacity measurements were conducted between 230 and 360 K, and the averaged data is shown in Supplementary Fig. 31. After noticing a low-temperature feature in the heat capacity of (NA)₂CuBr₄, several additional runs were conducted down to 190 K, and an additional run of (DA)₂MnCl₄ was also conducted down to 190 K (Supplementary Fig. 32). The ASTm heat capacity was calculated using a feature in the TRIOS software (TA Instruments), which calculates the heat capacity from a set of three ASTm runs (the baseline, sapphire, and sample runs) with each heat capacity calculation representing a unique set of three runs. The heat capacity data was interpolated onto a common temperature axis and averaged at each temperature point to arrive at an average heat capacity curve for (DA)₂MnCl₄ and (NA)₂CuBr₄. The error was also calculated at each temperature point and is based on the ASTM recommendation, which specifies reporting an error of 2.8 times the standard deviation.

**Powder X-ray diffraction (PXRD).** PXRD data for (DA)₂MnCl₄ and (NA)₂CuBr₄ were collected on beamline 17-BM-B at the Advanced Photon Source (APS) at Argonne National Laboratory, with an X-ray wavelength of 0.45237 Å. For variable temperature and pressure experiments, approximately 10 mg of sample was loaded into a sapphire capillary (1.52 mm × 1.07 mm × 50.8 mm, Saint-Gobain Crystals). Each capillary was attached to a custom-designed flow cell equipped with a gas valve, which was mounted onto the goniometer head. A syringe pump (Teledyne ISCO 165) was then connected via a 1/16” gas line to the flow cell and used to control pressure of He gas (ultra-high purity, 99.9999%). During cooling, powder patterns were collected every 10–20 seconds at a temperature 5 °C away from the transition and every 0.5–1.0 °C close to the transition. For each measurement, the chamber volume was measured every 20 seconds by a pressure transducer (Thorlabs). In particular, the shoulder intensity as the emergence of the smaller unit cell of the LT phase. Note that the shoulder intensity is as small as 2% of the parental peak intensity was discernible. Since the sample temperature was varied continuously—similar to DSC experiments—the onset temperature for the emergence of the LT phase is reported as Tₛ. More specifically, the transition onset temperature was estimated to be just above the temperature at which the lower shoulder peak becomes visible in the pattern. This approach enabled the identification of transition temperatures with an estimated accuracy of 1–2 K.

To further improve the accuracy of Tₛ determination, we used data from the thermocouple embedded in the sample capillary that recorded the sample temperature every 2 s. During cooling, the thermocouple temperature trace features a shoulder, which we attributed to the LT phase. Despite the seemingly small signal, this feature can be clearly detected by monitoring the change in sample cooling rate over time. Specifically, the phase transition leads to a sudden spike in the first derivative of sample temperature with respect to time. The onset of the phase transition was assigned to the temperature at which the first sudden spike of the cooling rate curve appears, as this feature—which corresponds to the tangent of the onset transition peak—can be reliably identified across all datasets. Additionally, the uncertainty associated with the determination of the transition onset temperature was defined as the full width at half maximum of the cooling rate peak, which ranges from 1 to 2 K. Note that the Tₛ values were determined using the sample thermocouple temperature data. At ambient pressure, the onset transition temperatures, Tₛ, determined by these PXRD experiments were in excellent agreement with those determined by DSC, with a difference of less than 0.4 K. Since the goal of these experiments was to determine the pressure dependence of Tₛ, rather than the absolute values of Tₛ, the transition temperatures determined via PXRD were calibrated using the Tₛ value determined by DSC at ambient pressure for consistency.

**Determination of ΔV, from PXRD.** From the temperature dependence of unit cell volumes at ambient pressure, the specific volume change during the order–disorder transition, ΔVₛ, was calculated as the difference between the LT and HT phase volumes at the transition temperature (Tₛ): ΔVₛ = V_LT - V_HT (Supplementary Fig. 4). The volume at Tₛ for the LT and HT phases was extracted from unit cells determined below and above Tₛ, respectively, using thermal expansion coefficients for each phase determined at ambient pressure. Specific volume changes from 200 to 300 bar were determined using unit cell volumes measured as a function of pressure at constant temperature (273 K for both LT phases, 323 K for the HT phase of (DA)₂MnCl₄ and 314 K for the HT phase of (NA)₂CuBr₄). Thermal expansion coefficients were assumed to be independent of pressure over this pressure range, and the thermal expansion coefficients determined for each phase at 1 bar were used to extrapolate the isothermal specific volumes to Tₛ at each pressure.

**Helium pyknometry.** Scaled densities of the samples were determined using an Instron pressure and strain gauge helium pycnometer. In a typical measurement, a 150 mg of sample was transferred to the sample holder, and the sample mass was obtained. The holder was then placed into the instrument test chamber, and the headspace was evacuated and refilled five times with He. The sample was then cycled multiple times through the phase transition, with the chamber volume determined every 2–5 °C away from the transition and every 0.5–1.0 °C close to the transition. For a measurement of unknown volume in a sample holder, Vₛ, in the sample chamber with a known volume of Vₛ, at a temperature Tₛ, the sample chamber was first pressurized to ~200 kPa and the initial pressure (Pᵢ) was measured. A reference chamber of known volume (Vᵢ) was initially equilibrated with ambient pressure (Pᵢ) and the sample chamber was then connected to the reference chamber. After equilibration, the final pressure in the combined chamber, Pₗ, was measured. Since the system is closed when the two chambers are connected, the ideal gas law and conservation of moles can be used to provide the following relationship:

\[ \frac{P(Vₛ - Vᵢ)}{RTₛ} + \frac{PᵢVᵢ}{RTᵢ} = \frac{P(Vₛ - Vᵢ)}{RTₛ} + \frac{PᵢVᵢ}{RTᵢ} \]  \( \text{(8)} \)

where the left- and right-hand sides denote the moles of gas before and after connecting the sample and reference chamber, respectively. Solving for Vₛ gives:

\[ Vₛ = Vᵢ - Vᵢ \left( \frac{Pᵢ - Pₗ}{Pₛ - Pᵢ} \right) \]  \( \text{(9)} \)

Since Vᵢ includes the volume of the empty sample holder (Vₑ) that had been measured previously, sample volume (Vₛ) was determined by subtracting Vₑ from Vₛ. With Vₛ= Vₛ - Vₑ. For each volume measurement, the temperature was fully equilibrated until the temperature dropped by less than 0.2 °C. At each temperature, the chamber volumes were measured five times to obtain good statistics. Prior to measurement of the sample, a calibration run of the empty sample holder was performed over the same temperature range. The sample mass was re-determined after the measurement and found to have decreased by no more than 0.5 mg. Uncertainties of the reported densities were determined by propagation of the standard deviations of the empty and filled chamber volumes and the sample mass. ΔVₛ values for both compounds are tabulated in Supplementary Table 10.

**X-ray crystallography.** X-ray diffraction analyses were performed on single crystals coated with Paratone-N oil and mounted on MiTeGen microloops using...
Dow Corning high vacuum grease. The temperature during data collection was controlled from 100 to 335 K using an Oxford Cryostreams nitrogen flow apparatus. Crystals were first mounted at 270 K, and 270 K datasets were collected. Crystals were then cooled to 100 K for 100 K data collection. After 100 K datasets, high-temperature datasets were collected: 330 K for (DA₃MnCl₄ and 335 K for (NA₃CuBr₄). The temperature was manipulated at a rate of 60 K h⁻¹. The intensities of the reflections were collected by a Bruker D8 diffractometer with CMOS area detector (MoKα radiation, λ = 0.71073 Å). The collection method involved 0.5° scans in 2θ in 2θ with a detector distance of 9 cm for (DA₃MnCl₄ and 8 cm for (NA₃CuBr₄). Data integration down to 0.84 Å resolution was carried out using SAINT V8.37A with reflection spot size optimization. Absorption corrections were made with the program SADABS. All single-crystal structures were solved by the Intrinsic Phasing methods and refined by least-squares methods against F² using SHELXT-2014 and SHELXL-2018 with the OLEX2 interface. All non-H atoms, including all the disorder atoms, were located in difference-Fourier maps and then refined anisotropically. Hydrogen atoms were placed at idealized positions and refined using a riding model. The isotropic displacement parameters of all hydrogen atoms were constrained to be 1.2 times the parameters of the atoms they were linked to (1.5 times for methyl groups). Space groups were determined based on the systematic absences and the statistical indicators, such as the E-value and the CFOM values. The absence of higher symmetry was further confirmed by Platon/AdsymUnit cell information from ambient-pressure PXRD experiments was used to help select an appropriate data collection strategy. Atomic displacement parameter plots of alkylammonium cations are provided in Fig. 8 and Supplementary Fig. 36, and hydrogen bonding geometry of (DA₃MnCl₄ and (NA₃CuBr₄ are shown in Supplementary Figs. 34 and 35, respectively. Selected geometric parameters are tabulated in Supplementary Tables 16–20, and details of data collection and refinement are summarized in Supplementary Tables 21 and 22. We acknowledge that there are limitations with the use of X-ray single crystal diffraction to determine the geometry of small organic cations in a heavy element inorganic framework, especially at high temperatures and when substantial disorder is expected to be present.

Thermal conductivity measurements. The thermal conductivity of each sample was measured by the flash diffusivity method (ASTM E1461-13) using a Netzsch LFA 467 HyperFlash instrument (Supplementary Fig. 42). The samples were prepared in pellets of approximately 12.9 mm in diameter and 1 mm thickness. The measurements were carried out under a Helium atmosphere at 10°C below and 15°C above the transition temperature for the LT and HT phases, respectively, of (DA₃MnCl₄, and at 10°C below and above the transition temperature for the LT and HT phases, respectively, of (NA₃CuBr₄. The measurement results were not corrected for thermal expansion due to phase changes.

Data availability

The main data supporting the findings of this study are available within the paper and its Supplementary Information. Other data are available from the corresponding author upon request. Crystallographic data have been made available free of charge from the Cambridge Crystallographic Data Centre under reference numbers CCDC 2075108–2075113.

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Author contributions

J.S. and J.A.M. formulated the project. J.S., R.D.M., A.H.S., S.Z., and A.A.Y. collected and analyzed the powder X-ray diffraction data. J.S., R.D.M., A.H.S., and S.-L.Z. collected and analyzed single-crystal X-ray diffraction data. R.U. carried out AFM experiments. J.S. collected and analyzed the high-pressure calorimetry data. J.S. and J.A.M. wrote the paper, and all authors contributed to revising the paper.

Competing interests

J.S. and J.A.M. are inventors on a patent application related to this work held and submitted by Harvard University that covers barocaloric properties of two-dimensional perovskites and related compounds. The remaining authors declare no competing interests.

Additional information

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