Colossal Reversible Barocaloric Effects in Layered Hybrid Perovskite \((\text{C}_{10}\text{H}_{21}\text{NH}_3)_2\text{MnCl}_4\) under Low Pressure Near Room Temperature

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Barocaloric effects in a layered hybrid organic–inorganic compound, \((\text{C}_{10}\text{H}_{21}\text{NH}_3)_2\text{MnCl}_4\), that are reversible and colossal under pressure changes below 0.1 GPa are reported. This barocaloric performance originates in a phase transition characterized by different features: A strong disordering of the organic chains, a very large volume change, a very large sensitivity of the transition temperature to pressure and a small hysteresis. The obtained values are unprecedented among solid-state cooling materials at such low pressure changes and demonstrate that colossal effects can be obtained in compounds other than plastic crystals. The temperature-pressure phase diagram displays a triple point indicating enantiotropy at high pressure.

1. Introduction

In recent years, research on caloric effects induced by changes in applied hydrostatic pressure has experienced a significant growth,[1] boosted by the urgent need of replacing hydrofluorocarbon-based devices that currently cause around 8% of global greenhouse emissions.[2] A milestone has recently been achieved by the discovery of colossal barocaloric (BC) effects in plastic crystals.[3,4] While these materials seem to represent an upper limit for the isothermal entropy changes, there is still room for improvement in terms of reducing the required pressure changes to obtain reversible barocaloric effects useful for real devices. Other systems such as hybrid organic–inorganic perovskites (HOIPs)[5,6] and spin-crossover compounds[7] have revealed large reversible adiabatic temperature changes at moderate pressures along with giant isothermal entropy changes within large temperature spans, yielding excellent performance as BC agents thanks to phase transitions with small hysteresis and extreme sensitivity to pressure.

The extraordinary chemical flexibility in HOIPs allows a diversity of combinations that can be explored to tune their properties, seek optimal operational regimes and maximize performance. Indeed, HOIPs have raised great expectations in diverse areas of materials science due to their multifunctional properties, as used in photovoltaic technologies and optoelectronics.[8] Within such rich compositional and structural variety, an HOIP subfamily with the chemical formula \((\text{C}_n\text{H}_{2n+1}\text{NH}_3)_2\text{MCl}_4\) \((n = 1, 2, 3, \ldots)\), with \(M\) being a divalent metal, attracted particular interest in the 1970’s[9] as phase change materials for thermal energy storage applications. As in the case of plastic crystals,[10] this functionality emerges due to the occurrence of highly energetic, fully reversible first-order phase transitions with suitable transition temperatures. This feature, along with a large transition volume change, suggests that these compounds could be very suitable as barocaloric agents, as plastic crystals have already shown. Compounds with \(M = \text{Mn, Fe (and other very similar compounds)}\), awakened further interest due to their low-dimensional magnetic properties[11–16] whereas other layered HOIPs are being investigated for photoluminescence properties.[15–17]

As in plastic crystals, the huge latent heat originates in the dynamic structural disorder released across the transition. However, in contrast to the orientational disorder facilitated by globular or small molecules in plastic crystals, \((\text{C}_n\text{H}_{2n+1}\text{NH}_3)_2\text{MCl}_4\) compounds exhibit more complex structure and dynamical disorder. In particular, their structure has a 2D layered symmetry similar to lipid bilayers, displaying a perovskite-like structure of reduced dimensionality with \(\text{MCl}_6\) octahedra sharing their corners only between neighbors in the \((\text{ab})\) planes. Between these
planes there are two chains of alkylammonium \( \text{C}_n\text{H}_{2n+1}\text{NH}_3^+ \) cations arranged along the \( c \) direction, whose length prevents the 3D corner-sharing along this axis between octahedra belonging to different layers, as it does occur in true perovskites.\(^\text{[18,19]}\) These chains are linked at the ammonium end to the inorganic octahedra by electrostatic interactions and hydrogen bonds. The organic chain tails facing each other are stabilized by their van der Waals interactions.\(^\text{[20,22]}\)

Often, these compounds show rich polymorphism already at atmospheric pressure, typically displaying a sequence of two (sometimes more) transitions, one being significantly more energetic.\(^\text{[9,22,23]}\) At this major transition, while the organic chain remains ionically bonded to the inorganic part,\(^\text{[24]}\) some gauche conformations arise in the alkyl bonds, which show dynamic mobility along the chain. This so-called chain-melting process is at the origin of the huge entropy changes at the transition. The emergence of the gauche conformations causes the chains to shorten. However, this is more than compensated by the increase of the distance between the ends of the facing chains, leading to a significant positive net volume change. The minor transition is order–disorder, where the disorder was concluded to consist of the rigid chains rotating around the longitudinal chain axis between two equivalent orientations separated by 90°, and with neighboring chains rotating in opposite directions. While not as enormous as the major transition entropy change, the entropy change at the minor transition is still giant. The sequence of these transitions is not unique; it may vary from one composition to another. The transition temperatures increase with increasing \( n \), which is consistent with the enhancement of the stability regime of the ordered phase with the increasing chain length that will be more difficult to destabilize. From \( n = 9 \) to \( n = 17 \) the transition temperature varies from 287 to 373 K, thus offering a range of compositions with caloric effects near room temperature.

Here we choose the compound \( \text{C}_{90}\text{H}_{132}\text{NH}_3^+\text{MnCl}_4 \) \( (n = 10, \text{10-bis(alkylammonium) tetrachloromanganate(II), C}_{90}\text{Mn for short}) \) because in this material the disorder fully develops across a single phase transition and near room temperature and therefore exhibits a larger transition entropy change than compounds with larger \( n \) values. Using pressure-dependent calorimetry and X-ray diffraction, we demonstrate not only that colossal barocaloric effects can be obtained in compounds other than plastic crystals, such as this layered HOIP family, but also that an improved BC performance can be obtained at lower pressure than those reported so far in plastic crystals, due to a very small hysteresis and a very large sensitivity of the transition temperature to pressure. Raman scattering experiments explore changes in structure and dynamics across the transition.

2. Results and Discussion

2.1. Structural and Thermodynamic Properties at Atmospheric Pressure

The structure of \( \text{C}_{90}\text{Mn} \) was characterized using X-ray powder diffraction (XRPD) measurements at atmospheric pressure and at temperatures around its solid-to-solid first-order phase transition. The diffraction patterns of the low-temperature phase at 295 K and of the high-temperature phase at 330 K were refined by means of a Rietveld refinement procedure\(^\text{[25]}\) using TOPAS-Academic v.7.\(^\text{[26]}\) At low temperatures, a \( P2_1/a \) structure ( cif number: CCDC 2096682) was obtained, consistent with that reported in ref. \( \text{[27]} \), and in disagreement with the orthorhombic structure reported in ref. \( \text{[21]} \). For the high-temperature phase, which was previously undetermined, a \( C2/m \) structure was obtained (cif number: CCDC 2096683). From these refinements, pattern matching of the temperature dependent XRPD patterns was performed, to obtain the unit cell volume as a function of temperature \( V(T) \) (see Figure 1a). This revealed a very large increase in volume at the endothermic transition of \( \Delta V/V_0 \approx 7\% \). A thorough explanation of the refinement details, the crystallographic structures of the unit cell in the two phases and the dependence of the patterns and the lattice parameters on temperature can be found in the Supporting Information.

Isobaric temperature-dependent calorimetry at atmospheric pressure yielded positive and negative peaks in \( \delta Q/\delta T \) associated with endothermic and exothermic first-order phase transitions, respectively (see Figure 1b). The maxima of the peaks were obtained at \( T_{I\rightarrow II} = 312 \pm 1 \) K and \( T_{II\rightarrow I} = 303 \pm 1 \) K, whereas the onsets of the peaks at \( T_{II\rightarrow I} = 309 \pm 1 \) K and \( T_{I\rightarrow II} = 306 \pm 1 \) K. This shows a hysteresis of \( \approx 9 \) K as defined

![Figure 1](https://example.com/figure1.png)
from the peak maxima, and ≈3 K as defined from the peak onsets, which are both small. Integration over temperature of \( \frac{dQ}{dT} \) and \( \frac{1}{T} \frac{dQ}{dT} \) after baseline subtraction yielded transition enthalpy changes \( \Delta H_{II\rightarrow I} = 76 \pm 4 \text{ J g}^{-1} \) and \( \Delta H_{I\rightarrow II} = 79 \pm 4 \text{ J g}^{-1} \) and transition entropy changes \( \Delta S_{II\rightarrow I} = 241 \pm 12 \text{ J K}^{-1} \text{ kg}^{-1} \) and \( \Delta S_{I\rightarrow II} = 261 \pm 13 \text{ J K}^{-1} \text{ kg}^{-1} \), in very good agreement with the literature \([27,28]\). The integrated curve for \( \Delta S \) was used with the temperature-dependent heat capacity \( C_p \) obtained from modulated calorimetry (see Figure 1c) to calculate the temperature-dependent entropy with respect to a reference temperature \( T_0 = 213 \text{ K} \) (chosen arbitrarily below the transition) as:

\[
S(T, p_{\text{ atm}}) - S(T_0, p_{\text{ atm}}) = \int_{T_0}^{T} \left( C_p + \frac{dQ}{dT} \right) dT
\]

To understand the origin of such large entropy changes at the transition, we investigated the molecular disordering process by temperature-dependent Raman scattering in both low and high wavenumbers. Previous Raman studies on organic chains have described a peak at low frequency as corresponding to an accordion-like longitudinal acoustic mode (LAM) \([29-31]\). In our measurements, such a peak is obtained in the low

![Figure 2](image-url)

**Figure 2.** a–d) Temperature dependence of the Raman spectrum of \((\text{C}_{10}\text{H}_{21}\text{NH}_{3})_2\text{MnCl}_4\) at different wave number intervals. e,f) Schematic diagram for the probable conformation of the decylammonium chain under low and high temperature respectively, along with Newman projections for trans (T) and gauche (G) conformations corresponding to the positions indicated by numbers 1 and 2. \( R_1 \) stands for -CH\(_2\)-CH\(_2\)-CH\(_2\)-CH\(_2\)-CH\(_2\)-CH\(_2\)-CH\(_3\). \( R_2 \) stands for -CH\(_2\)-CH\(_2\)-CH\(_2\)-CH\(_2\)-CH\(_2\)-CH\(_2\)-CH\(_2\)-NH\(_3^+\). \( R' \) stands for -CH\(_2\)-CH\(_3\).
temperature phase near 235 cm\(^{-1}\) (see Figure 2a). In particular, this is higher than the value for all-trans (T) chain (209 cm\(^{-1}\)) or for chains of the same length engaged in hydrogen bonds, such as \(n\)-decylamine (213 cm\(^{-1}\)) or decylammonium chloride (217 cm\(^{-1}\))\(^{[32]}\) and corresponds to a conformational effect and the existence of a gauche (G) conformation near the NH\(_3\) polar head. In Figure 2b, the characteristic bands of the trans planar chains are observed at 1065, 1109, 1146 and 1174 cm\(^{-1}\). This indicates that the most intense bands in the Raman spectrum of the long alkyl chains correspond to the limiting \(k = 0\) modes of an infinite chain.\(^{[33]}\) Figure 2c,d shows the characteristic bands of the C–H twisting (1300 cm\(^{-1}\)), bending (1420–1480 cm\(^{-1}\)) and stretching (2830–3000 cm\(^{-1}\)) mode. It is worth noting that the scattering wing on the 2846 cm\(^{-1}\) line is due to intermolecular forces.\(^{[33]}\) Moreover, the Mn–Cl stretching mode band can be found at 186 and 236 cm\(^{-1}\) (overlapped with LAM at 235 cm\(^{-1}\)) and wavenumbers 300, 1040, and 1080 cm\(^{-1}\) correspond to the NH\(_3\) torsional band (overlapped with the trans bond stretching at 300 cm\(^{-1}\))\(^{[34,35]}\). Overall, the low-temperature study of these spectral regions indicates a typical ordered state of the low-temperature phase and gives further evidence for the existence of inter- and intramolecular coupling in an almost completely extended chain. In the high-temperature phase, the Raman spectra indicate the emergence of disorder. First, the LAM mode and the limiting \(k = 0\) mode bands disappear and only a broad and weak band is observed near 247 cm\(^{-1}\), which means the conformation of the long trans planar chains is changed. Further evidence of appearing of the gauche bond structure can be found in the decrease of the 1465 cm\(^{-1}\) shoulder, which is due to intramolecular coupling of trans structures.\(^{[31,32]}\) In order to fully understand the structure of the organic part, we schematically show the probable conformation of the decylammonium chain as reported in the literature from infrared spectra\(^{[27]}\) and incoherent neutron scattering.\(^{[36]}\) In Figure 2e,f we can see that the conformation for low temperature is T-G-T-T-T-T-T-T while the high temperature becomes T-T-T-G-T-G-T. As discussed previously, it is believed that the reorientation of the whole chain and the disorder of the hydrocarbon parts come from the increase of the G and G' conformations which is regarded as conformational disorder and contributes a large latent heat in the order–disorder first-order phase transition. Furthermore, the C–H stretching mode bands at 2870, 2883, and 2930 cm\(^{-1}\) merge into a broad scattering peak, indicating that the intermolecular forces were greatly changed. Finally, the Mn–Cl stretching mode bands become weak and broad at high temperature with the disappearing of the NH\(_3\) torsional mode band. This means a dramatic change for the layer, which is consistent with the increase of the \(c\)-axis length from the XRPD data (see Figure S4, Supporting Information).

2.2. Thermodynamic Properties at High Pressure

Isobaric temperature-dependent calorimetry performed at selected pressures (see Figure 3a; Figure S5, Supporting Information) below 0.1 GPa reveals single peaks associated with

![Figure 3](https://example.com/figure3.png)

**Figure 3.** a) Isobaric heat flow \(dQ/|dT|\) as a function of temperature at different applied pressures on heating (positive peaks) and on cooling (negative peaks). b–d) Transition temperatures as a function of pressure determined as the maximum of the peaks. For the sake of clarity, endothermic (b) and exothermic (c) data are shown separately. Panel (d) shows the fits for both endothermic and exothermic transitions. Shadowed areas show the equilibrium region for phase III. e) Transition entropy change as a function of the applied pressure, for the endothermic (red) and exothermic (blue) transitions. Filled symbols, top-half filled symbols and bottom-half filled symbols stand for II\(\rightarrow\)I, III\(\rightarrow\)I and II\(\rightarrow\)III transitions, respectively. Lines are fits to data.
the I\(\text{II} \rightarrow \text{I}\) transition, that shift strongly to higher temperatures with increasing pressure (see Figure 3b–d). This shift can be fitted by slightly convex second-order polynomials, yielding \(\frac{dT_{\text{II} \rightarrow \text{I}}}{dp} = 250 \pm 6 \text{ K GPa}^{-1}\) and \(\frac{dT_{\text{II} \rightarrow \text{III}}}{dp} = 280 \pm 20 \text{ K GPa}^{-1}\) for the endothermic and exothermic transitions, respectively, at atmospheric pressure. Above 0.15 GPa, the endothermic calorimetric signals clearly exhibit two consecutive peaks which indicate the appearance of a new phase (III) between the two peaks. The larger peak corresponds to the transition II\(\rightarrow\)III and is followed by the smaller peak corresponding to the III\(\rightarrow\)I. The exothermic transitions show the peak splitting at lower pressures. Two possible causes are, i) the occurrence of transitions between equilibrium phases, I–II–III, but with different hysteresis (i.e., a larger thermal hysteresis of the transition III\(\rightarrow\)I than that of the transition I\(\rightarrow\)II), for which the peak splitting can be more easily identified in exothermic peaks than in endothermic peaks because in the latter the overlap of the very close peaks prevents distinguishing them; ii) the occurrence of a metastable phase transition from the equilibrium phase I to the metastable phase III at temperatures and pressures below the triple point in equilibrium, followed by a phase transition from the metastable phase III to the stable phase II. Or a combination of (i) and (ii) is possible. The striking similarity between the \(\frac{dT}{dp}\) values of the different coexistence lines \(\left(\frac{dT_{\text{II} \rightarrow \text{I}}}{dp} = 180 \pm 1 \text{ K GPa}^{-1}\right), \frac{dT_{\text{II} \rightarrow \text{III}}}{dp} = 161 \pm 2 \text{ K GPa}^{-1}\), \(\frac{dT_{\text{III} \rightarrow \text{II}}}{dp} = 170 \pm 2 \text{ K GPa}^{-1}\), \(\frac{dT_{\text{III} \rightarrow \text{I}}}{dp} = 160 \pm 3 \text{ K GPa}^{-1}\) makes it even more difficult to determine the actual cause. Moreover, this behavior prevents an accurate determination of the coordinates of the triple point where phases I, II, and III coexist in equilibrium, \((T_{\text{TP}}, p_{\text{TP}})\), as cause (i) would lead the triple point to be at \((330 \text{ K}, 0.12 \text{ GPa})\) whereas cause (ii) would lead the triple point to be closer to \((337 \text{ K}, 0.14 \text{ GPa})\). On the other hand, notice that at the highest applied pressure \(p = 0.36 \text{ GPa}\) the exothermic peaks are observed in the inverse order, with the first the larger peak followed by the smaller peak. This behavior can only be explained if part of the material undergoes a phase transition from stable phase I toward a metastable phase II, which on further cooling becomes stable, while the rest of the material undergoes the transition sequence between stable phases I\(\rightarrow\)II–III.

Integration of the peaks in \((1/T)(dQ/dT)\) at different pressures reveals that the transition entropy change decays significantly with increasing pressure, at a rate of \(\approx 1.1 \times 10^3 \text{ J K}^{-1} \text{ kg}^{-1} \text{ GPa}^{-1}\) (see Figure 3e). Close to the triple point, we \(\Delta S_{\text{II} \rightarrow \text{III}}(p = -0.15 \text{ GPa}) = 144 \pm 14 \text{ J K}^{-1} \text{ kg}^{-1}\), \(\Delta S_{\text{II} \rightarrow \text{II}} = 102 \pm 10 \text{ J K}^{-1} \text{ kg}^{-1}\) and \(\Delta S_{\text{II} \rightarrow \text{I}} = 32 \pm 4 \text{ J K}^{-1} \text{ kg}^{-1}\). For the exothermic transitions we \(\Delta S_{\text{II} \rightarrow \text{I}}(p = 0.15 \text{ GPa}) = 196 \pm 20 \text{ J K}^{-1} \text{ kg}^{-1}\), \(\Delta S_{\text{II} \rightarrow \text{III}} = 134 \pm 14 \text{ J K}^{-1} \text{ kg}^{-1}\) and \(\Delta S_{\text{II} \rightarrow \text{I}} = 60 \pm 6 \text{ J K}^{-1} \text{ kg}^{-1}\). Notice that these values are consistent with the thermodynamic requirement at the triple point \(\Delta S_{\text{II} \rightarrow \text{I}} = \Delta S_{\text{II} \rightarrow \text{II}} + \Delta S_{\text{II} \rightarrow \text{III}}\). By comparison with the transition sequence exhibited by other compounds of the same family at atmospheric pressure, a\textsuperscript{(9,22,23)} and given that \(\Delta S_{\text{II} \rightarrow \text{III}}\) is significantly larger than \(\Delta S_{\text{II} \rightarrow \text{I}}\), we can assume that above the triple point the II\(\rightarrow\)III transition is the major transition involving the chain melting whereas the III\(\rightarrow\)I transition corresponds to the minor transition of the order–disorder type. On the other hand, given the inverse transition order obtained on cooling in a very few cases, to avoid any inconsistency in the determination of \(\Delta S_{\text{I} \rightarrow \text{II}}\) and \(\Delta S_{\text{I} \rightarrow \text{III}}\), we have omitted the integration values at high pressure when performing the fits to the data displayed in Figure 3e and when determining the BC effects. Also, it is worth noticing that the joint integration of the two peaks shows a smooth and monotonic behavior regardless of the transition order (see Figure S6, Supporting Information). This strongly indicates that the transitions order does not affect the thermodynamic properties associated with the overall transition path I\(\rightarrow\)II.

2.3. Determination of Entropy as a Function of Temperature and Pressure

To calculate the barocaloric effect via the quasi-direct method, the isobaric entropy as a function of temperature and for different pressures, \(S(T,p)\) was obtained with respect to a reference taken at temperature \(T_0\) and atmospheric pressure. The procedure to obtain \(S(T,p)\) consisted of integration of a \(d\Delta S/dT\) equation for an homogeneous system, extended to include a phase transition contribution, which can be expressed mathematically as:

\[
S(T,p) = S(T_0,p_{\text{ref}}) - \int_{T_0}^{T} \left( \frac{dV}{dT} \right)_p dp + \frac{1}{T} \int_{T_0}^{T} \left( C_p(T',p) + \frac{dQ}{dT}(T',p) \right) dT',
\]

At \(T = T_0\), the integral over temperature vanishes and we obtained \(S(T_0,p)\) through an isothermal path from \(S(T_0,p_{\text{ref}})\) via the integral over pressure in Equation (1), which was approximated to \(\left( \frac{dV}{dT} \right)_p \cdot p\). Above \(T_0\), \(S(T,p)\) was calculated through the integral over temperature. Here, \(\frac{dQ}{dT}(T',p)\) is the temperature- and pressure-dependent transition heat flow shown in Figure 3a and \(C_p(T,p)\) accounts for the isobaric heat capacity (shown in Figure S7, Supporting Information). The temperature dependence of \(C_p\) in the transition temperature interval was estimated as a weighted average of the two phases I and II, that is \(C_p(T',p) = (1 - x)C_p^\text{II}(T',p) + xC_p^\text{I}(T',p)\), where \(x(T,p)\) is the fraction of the system in phase I and is computed using the normalized cumulative integral for the transition entropy change. The former expression is also used for pressures above the triple point, where the \(C_p\) of phase III is experimentally inaccessibility. However, given the very narrow temperature range of stability of this phase, the error introduced in the entropy due to this approximation is expected to be insignificant.

The pressure dependence of \(C_p\) was evaluated from the temperature dependence of the volume by means of the thermodynamic relation \(\frac{dC_p}{dp} = -T \left( \frac{dV}{dT} \right)_p\). According to our data, \(V(T)\) is approximately linear in phase II below \(\approx 295 \text{ K}\) and in phase I in the measured interval (see red linear fit in Figure 1a), indicating that \(C_p\) is independent of pressure in these temperature intervals (red and blue lines in Figure 1c). Instead, \(V(T)\) is nonlinear in the temperature interval \((295 - 310) \text{ K}\) (see dashed line in Figure 1a), indicating a pressure dependence of
Cp in this temperature interval (see dashed lines in Figure 1c). Moreover, as the transition temperature increases with pressure, these Cp features must be translated to higher temperatures with increasing pressure an amount (dT/dp)(p−p_atm).

Calculated Cp(T, p) curves are shown in Figure S8, Supporting Information. A very detailed explanation of the procedure for the construction of the Cp(T, p) curves can be found in ref. [37]. The resulting functions S(T, p)−S(T, p_atm) are shown in Figure 4a,b for selected pressures.

2.4. Barocaloric Effects and Performance

BC effects were calculated from or to atmospheric pressure so that pressure changes will be approximated to |Δp| ≈ p. For phase transitions with dT/dp > 0, transitions on decompression (compression) are endothermic (exothermic) and therefore BC effects, ΔS and ΔT, on first decomposition (compression) must be computed from isobaric entropy functions on heating [S_H(T;p)] (cooling, [S_C(T;p)]), as displayed in Figure 4c.d. More importantly, this feature entails that the reversible ΔT usable in cooling devices that work in sequential compression–decompression cycles, are given by |ΔT_rev(S;p_atm→p)| = |T_C(S;p) − T_H(S;p_atm)|.

In turn, ΔS_rev can be determined as the overlapping between ΔS(T;p_atm→p) and ΔS(T;p→p_atm). The obtained results (shown in Figure 5a,b) reveal reversible values for ΔS_rev that exceed 100 J K⁻¹ kg⁻¹ under pressure changes as low as 0.03 GPa, and are colossal (>230 J K⁻¹ kg⁻¹) under p = 0.05 GPa. Under p = 0.1 GPa, we obtain colossal BC effects of ΔS_rev ≈ 250 J K⁻¹ kg⁻¹ and ΔT_rev ≈ 12 K, with a refrigerant capacity R_C ≈ |ΔS_revdT | = 3.5 kJ kg⁻¹ (see Figure 5c). Joint values for ΔS_rev and ΔT_rev are plotted in Figure 6a for different applied pressure changes as a function of temperature. The temperature span where these effects occur near room temperature are plotted as a function of the applied pressure change p in Figure 6b,c for ΔS_rev and ΔT_rev, respectively. For instance, at p = 0.1 GPa, at least ΔS ≈ 100 J K⁻¹ kg⁻¹ are obtained within an interval of ≈13 K.

Finally, we calculate the coefficient of refrigerant performance (CRP)[38,39] for comparison with other BC materials (see Figure 7). The set of values for this compound are comparable to or better than the best reversible BC effects reported so far (e.g., 1-Br-ada and 1-Cl-ada[1,40]). Particularly interesting is the low pressure change for which these excellent values are obtained, which brings BC materials closer to real applications, such as solid-state cooling or heat pumping. Our study paves the way for finding colossal BC effects in compounds beyond.

Figure 4. Isobaric entropy as a function of temperature for different values of applied pressure, a) on heating and b) on cooling. c) Isothermal entropy changes as a function of temperature and d) adiabatic temperature changes as a function of the starting temperature, for different values of pressure changes on first compression and on first decompression.

Figure 5. Reversible a) isothermal entropy changes and b) adiabatic temperature changes upon application and removal of pressure changes from or to atmospheric pressure, as a function of temperature. c) Reversible refrigerant capacity as a function of pressure change.
plastic crystals, thus widening the range of suitable materials and stimulating the research in similar compounds. This is especially appealing in this family of compounds because material properties can be sensitively tuned to match desired features by changing the chain length and/or by chemical substitution of the cation.

3. Conclusions

In this work we have demonstrated colossal barocaloric effects in a hitherto unexplored material family, the hybrid organic–inorganic layered perovskites. In particular, (C_{10}H_{21}NH_{3})_{2}MnCl_{4} undergoes reversible isothermal entropy changes of ≈ 230 J K^{-1} kg^{-1} under low pressure changes of 0.05 GPa, and reversible adiabatic temperature changes of ≈ 10 K under pressure changes of 0.08 GPa near room temperature, which are outstanding compared to other solid-state materials. The origin of this extremely good response is a very large increase in entropy and volume associated with the melting of the organic chain across a sharp and low-hysteresis first-order solid–solid phase transition. This compound not only widens the horizons for colossal barocaloric materials to include other compounds beyond the canonical plastic crystals but it also expands the limits for the barocaloric performance in solid-state materials. Our results suggest that this compound is among the best candidates to be exploited as a barocaloric agent in pressure-driven solid-state cooling.

4. Experimental Section

Preparation of the Sample: The (C_{10}H_{21}NH_{3})_{2}MnCl_{4} sample was prepared by using a two-step reaction method. Manganese(II) chloride tetrahydrate (MnCl_{2}·4H_{2}O, 99%, Sigma-Aldrich) was added into hydrochloric acid (HCl, 36.5–38.0%, Baker Analyzed) with magnetic stirring until MnCl_{2}·4H_{2}O was fully dissolved. Then, n-decylamine (C_{10}H_{21}NH_{2}, 99%, ACROS Organics) was added into this mixed solution with magnetic stirring for 3 h. Then, (C_{10}H_{21}NH_{3})_{2}MnCl_{4} powder was obtained by precipitation and washed with ethanol twice. The total yield of the compound is ≃ 72%.

X-Ray Diffraction: X-ray diffraction patterns were obtained using two diffractometers. A Siemens D5000 X-ray powder diffractometer using monochromatic Cu-K\(^{\alpha}\) radiation was employed to check the purity of the synthesized samples because impurities had been reported to modify thermodynamic transition data.\(^{[22]}\) An INEL diffractometer with Cu-K\(^{\alpha}\)\(_{1}\) = 1.5406 Å radiation, a curved position-sensitive detector (CPS120), a 0.5-mm-diameter Lindemann capillary and a 700 series Oxford Cryostream Cooler to control the temperature were used to perform temperature-dependent high-resolution X-ray powder diffraction measurements at atmospheric pressure and different temperatures.

Raman Spectroscopy: Raman spectra were obtained using an IK Series Raman spectroscopy system. A 532 nm He–Cd laser was used for excitation. A calibrated Linkam heating–cooling stage was utilized to control sample temperature, via a thermocouple attached to the sample holder.

Differential Scanning Calorimetry: Differential scanning calorimetry (DSC) at atmospheric pressure was performed using a Q100 DSC from TA Instruments. A few mg were hermetically encapsulated into the Al capsule sample-holders. Heating and cooling ramps were performed at ±2 K min^{-1}. Measurements of specific heat \(C_p\) were performed at atmospheric pressure in a commercial DSC (TA Q2000), at 5 K min^{-1},
using \(\approx 5\) mg samples of \((\text{C}_\text{10H}_{21}\text{NH}_3)\text{MnCl}_4\). The amplitude was 0.5 K and period was 60 s. The heating and cooling rate were 2 K min\(^{-1}\).

**High-Pressure Differential Thermal Analysis:** High-pressure differential thermal analysis was performed using three different bespoke variable-pressure calorimeters A, B, and C. Calorimeters A and B operated between atmospheric pressure and 0.3 GPa and used Bridge-type thermocouples as thermal sensors. Calorimeter C operated up to 0.6 GPa and used Peltier modules as thermal sensors. In calorimeter A, heating ramps within the temperature range from room temperature to 473 K were performed at 2 K min\(^{-1}\) using a resistive heater and cooling ramps were performed on average at \(-1\) K min\(^{-1}\) with an air stream system. In calorimeters B and C, the temperature was controlled by a thermal jacket connected to an external thermal bath (Lauda Proline 1290), within the range 200 to 800 K, with temperature rate on heating of \(\approx 2\) K min\(^{-1}\) and on cooling of \(\approx 2\) K min\(^{-1}\). The sample was mixed in powder form with an inert fluid (Galden Bioblock Scientist) to remove air and encapsulated inside tin capsules that were attached to the thermal sensors. The pressure transmitting fluid was DW-Term M90.200.02 (Huber) and the pressure was measured using a high-pressure transducer Model HP from Honeywell (0.5% accuracy).

**Supporting Information**
Supporting Information is available from the Wiley Online Library or from the author.

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**Conflict of Interest**
The authors declare no conflict of interest.

**Data Availability Statement**
The data that support the findings of this study are available from the corresponding author upon reasonable request.

**Keywords**
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[1] P. Lloveras, J.-L. Tamarit, *MRS Energy Sustain.* 2021, 8, 3.
[2] A. Kitanovski, *Adv. Energy Mater.* 2020, 10, 1903741.
[3] B. Li, Y. Kawakita, S. Ohira-Kawamura, T. Sugahara, H. Wang, J. Wang, Y. Chen, S. I. Kawaguchi, S. Kawaguchi, K. Ohara, K. Li, D. Yu, R. Mole, T. Hattori, T. Kikuchi, S.-I. Yano, Z. Zhang, Z. Zhang, W. Ren, S. Lin, O. Sakata, K. Nakajima, Z. Zhang, *Nature* 2019, 567, 506.
[4] P. Lloveras, A. Aznar, M. Barrio, P. Negrier, C. Popescu, A. Planes, L. Mañosa, E. Stern-Taulats, A. Avramenko, N. D. Mathur, X. Moya, J.-L. Tamarit, *Nat. Commun.* 2019, 10, 1803.
[5] J. M. Bermúdez-Garcia, M. Sánchez-Andújar, S. Castro-García, J. López-Beceiro, R. Artiaga, M. A. Señarís-Rodríguez, *Nat. Commun.* 2017, 8, 15715.
[6] M. Szafranski, W.-J. Wei, Z.-M. Wang, W. Li, A. Katrusiak, *APL Mater.* 2018, 6, 100701.
[7] M. Romanini, Y. Wang, K. Gürpinar, G. Ornelas, P. Lloveras, Y. Zhang, W. Zheng, M. Barrio, A. Aznar, A. Gracia-Condal, B. Emre, O. Atakol, C. Popescu, H. Zhang, Y. Long, L. Balicas, J.-L. Tamarit, A. Planes, M. Shatruk, L. Mañosa, *Adv. Mater.* 2021, 33, 2008076.
[8] W. Li, Z. Wang, F. Deschler, S. Gao, R. H. Friend, A. K. Cheetham, *Nat. Rev. Materials* 2017, 2, 16099.
[9] V. Busico, C. Carfagna, V. Salerno, M. Vacatello, F. Fittipaldi, *Sol. Energy* 2019, 24, 575.
[10] D. Benson, R. Burrows, J. Webb, *Sol. Energy Mater. Adv.* 2018, 13, 133.
[11] T. Nakajima, H. Yamauchi, T. Goto, M. Yoshizawa, T. Suzuki, T. Fujimura, *J. Magn. Magn. Mater.* 1983, 31–34, 1189.
[12] R. Willett, E. Riedel, *Chem. Phys.* 1975, 8, 112.
[13] H. van Kempen, F. H. Mischgofsky, F. Wyder, *Phys. Rev. B* 1977, 15, 4386.
[14] K. Lee, C. Lee, *Solid State Commun.* 2003, 126, 343.
[15] B. Zhou, D. Yan, *Angew. Chem., Int. Ed.* 2019, 58, 15128.
[16] R. Gao, M. S. Kodaimati, D. Yan, *Chem. Soc. Rev.* 2021, 50, 5564.
[17] Y. Qin, Z. Lv, S. Chen, W. Li, X. Wu, L. Ye, N. Li, P. Lu, *J. Phys. Chem. C* 2019, 123, 22491.
[18] D. B. Mitzi, *J. Chem. Soc., Dalton Trans.* 2001, 1, https://doi.org/10.1039/B007070J.
[19] L. Mao, C. C. Stoumpos, M. G. Kanatzidis, *J. Am. Chem. Soc.* 2019, 141, 1171.
[20] R. Blinc, M. Burgar, B. Lozzar, J. Seliger, J. Slak, V. Rutar, H. Arend, R. Kind, *J. Chem. Phys.* 1977, 66, 278.
[21] W.-W. Zhong, Y.-Y. Di, Y.-X. Kong, D.-F. Lu, J.-M. Dou, *J. Chem. Thermodynamics* 2014, 72, 100.
[22] G. F. Needham, R. D. Willett, H. F. Franzen, *J. Phys. Chem.* 1984, 88, 674.
[23] K. J. Schenk, G. Chapuis, *J. Phys. Chem.* 1988, 92, 7141.
[24] R. Kind, S. Plesko, H. Arend, R. Blinc, B. Zeks, J. Seliger, B. Lozar, J. Slak, A. Levstik, C. Filipic, V. Zagar, G. Lahanjnar, F. Milia, G. Chapuis, *J. Chem. Phys.* 1979, 71, 2118.
[25] H. M. Rietveld, *J. Appl. Crystallogr.* 1969, 2, 65.
[26] A. A. Coelho, *J. Appl. Crystallogr.* 2018, 51, 210.
[27] M. R. Ciajolo, P. Corradini, V. Pavone, *Gazz. Chim. Ital.* 1976, 106, 807.
[28] M. Vacatello, P. Corradini, *Gazz. Chim. Ital.* 1973, 103, 1027.
[29] R. F. Schauffele, T. Shimanouchi, *J. Chem. Phys.* 1967, 47, 3605.
[30] W. L. Peticolas, G. W. Hieber, J. L. Lippert, A. Peterlin, H. Olf, *Appl. Phys. Lett.* 1971, 18, 87.
[31] M. Soutzidou, A. J. Masters, K. Viras, C. Booth, *Phys. Chem. Chem. Phys.* 1999, 1, 415.
[32] J. R. Scherer, R. G. Snyder, *J. Chem. Phys.* 1980, 72, 5798.
[33] L. Ricard, R. Cavagnat, M. Rey-Lafon, *J. Phys. Chem.* 1985, 89, 4887.
[34] H. L. Casal, D. G. Cameron, H. H. Mantsch, *J. Phys. Chem.* 1985, 89, 5557.
[35] Y. Abid, M. Kamoun, A. Daoud, F. Romain, *J. Raman Spectrosc.* 1990, 21, 709.
[36] F. Guillaume, G. Coddens, A. Dianoux, W. Petry, M. Rey-Lafon, C. Sourisseau, *Mol. Phys.* 1989, 67, 665.
[37] J. Li, D. Dunstan, X. Lou, A. Planes, L. Mañosa, M. Barrio, J.-L. Tamarit, P. Lloveras, *J. Mater. Chem. A* 2020, 8, 20354.
[38] E. Brück, H. Yibole, L. Zhang, *Philos. Trans. A Math. Phys. Eng. Sci.* 2016, 374, 20150303.
[39] L. Mañosa, A. Planes, *Appl. Phys. Lett.* 2020, 116, 050501.
[40] A. Aznar, P. Negrier, A. Planes, L. Mañosa, E. Stern-Taulats, X. Moya, M. Barrio, J.-L. Tamarit, P. Lloveras, *Appl. Mater. Today* 2021, 23, 101023.