Solid-state refrigeration which is environmentally benign has attracted considerable attention. Mechanocaloric (mC) materials, in which the phase transitions can be induced by mechanical stresses, represent one of the most promising types of solid-state caloric materials. Herein, we have developed a thermodynamic phenomenological model and predicted extraordinarily large elastocaloric (EC) strengths for the (111)-oriented metal-free perovskite ferroelectric [MDABCO](NH4)I3 thin-films. The predicted room temperature isothermal $\Delta S_{EC}/\Delta \sigma$ (EC entropy change under unit stress change) and adiabatic EC $\Delta T_{EC}/\Delta \sigma$ (EC temperature change under unit stress change) for [MDABCO](NH4)I3 are $-60.0$ J K$^{-1}$ kg$^{-1}$ GPa$^{-1}$ and $17.9$ K GPa$^{-1}$, respectively, which are 20 times higher than the traditional ferroelectric oxides such as BaTiO3 thin films. We have also demonstrated that the EC performance can be improved by reducing the Young’s modulus or enhancing the thermal expansion coefficient (which could be realized through chemical doping, etc.). We expect these discoveries to spur further interest in the potential applications of metal-free organic ferroelectrics materials towards next-generation EC refrigeration devices.

To maximize the temperature change and improve the energy efficiency for the cooling cycle, materials with high EC strength are required. Previously, high EC strength with $\Delta T_{EC}/\Delta \sigma$ of 0.7 K GPa$^{-1}$ has been predicted for ferroelectric oxide heterostructures such as BaTiO3 thin films. One key factor limiting the EC performance of the oxide ferroelectrics is their low compressibility with strong ionic bonds. Even though a high adiabatic temperature change might be obtained by applying large external stress, the EC strength is quite small which gives rise to low energy efficiency for a refrigeration cycle.

Recently, Wang et al. predicted extraordinarily large EC strengths, 18 J m kg$^{-1}$ K$^{-1}$ MV$^{-1}$ for the isostructural $\Delta S_{EC}/\Delta E$ and 8.06 K m V$^{-1}$ for the adiabatic $\Delta T_{EC}/\Delta E$, of a metal-free pervoskite ferroelectric material [MDABCO](NH4)I3 (MDABCO stands for N,N-dimethyl-N'-diaza-bicyclo[2.2.2]octanium) which is superior to the prototype pervoskites such as BaTiO3 and PbTiO3. For instance, the EC strength of [MDABCO](NH4)I3 is three times higher than the largest reported values of BaTiO3, which could be attributed to the larger Curie-Weiss constant and smaller mass density of [MDABCO](NH4)I3. In addition to the smaller mass density, the molecular ferroelectric material has a much smaller elastic stiffness (~1 GPa) in comparison to typical ferroelectric oxides (~100 GPa). Therefore, it is rational to believe that large volume and entropy changes could be induced by applying external mechanical stimuli to [MDABCO](NH4)I3, which may generate a significant mC effect.

The very large BC effect was also reported in plastic crystals which are featured by the extensive disorder and giant compressibility. For example, The BC strength $\Delta S/\Delta \sigma$ for NPG plastic crystals can reach 961.5 J K$^{-1}$ kg$^{-1}$ GPa$^{-1}$ at 320 K. The metal-free organic pervoskite ferroelectric [MDABCO](NH4)I3 is...
principles calculations. Moreover, [MDABCO](NH₄)I₃ also has expansion effects, and have emerged as powerful tools to understand organic ferroelectric systems. The advantages of high polarization, mechanical flexibility, low weight, and low processing temperatures are, as compared to other ferroelectric systems.

Computational methods such as thermodynamic calculations have emerged as powerful tools to the understanding of eC effects, which has considerably large compressibility. Large piezoelectric response was also predicted in [MDABCO](NH₄)I₃ from first-principles calculations. Moreover, [MDABCO](NH₄)I₃ also has advantages of high polarization, mechanical flexibility, low weight, and low processing temperatures, as compared to other organic ferroelectric systems.

RESULTS

Phase transitions and phase diagram

The detailed procedure for developing a thermodynamic potential energy density function for (111)-oriented [MDABCO](NH₄)I₃ film is described in the Theoretical Method Section and Supporting Information. The parameters for this study are all taken from the previous report. We first calculate the analytical equilibrium polarization for the (111)-oriented [MDABCO](NH₄)I₃ thin film under different in-plane misfit strains and out-of-plane stresses at room temperature. Consider a single-domain (111)-oriented thin film epitaxially grown on a cubic substrate with in-plane coherency, the schematics is given in Fig. 2a. The stress and strain components in the global coordinate system satisfy the mixed mechanical boundary condition: \( \sigma_x = \sigma_y = 0, \sigma_z = \sigma \) and \( \varepsilon_x = \varepsilon_y = \varepsilon_z = 0 \). The calculated stress and strain intervals are 0.01 GPa and 0.001, respectively. Supplementary Fig. 2 shows the contour plots for the equilibrium polarization components \( P_x, P_y, \) and \( P_z \) in the pseudocubic system as a function of the misfit strain and external stress. It can be observed that the \( P_x, P_y, \) and \( P_z \) components have finite values at the low-stress region (see the R and M parts of the contour plot). In the high stress and high misfit strain regions, the cubic phase is stable where all polarization components vanish (the C-region in the phase diagram). In the O region (orthorhombic phase), the \( P_x, P_y, \) and \( P_z \) components are in the same magnitudes while \( P_x \) equals zero.

Figure 2b shows the stable phases for (111)-oriented [MDABCO](NH₄)I₃ thin films under different in-plane misfit strains and out-of-plane stresses at room temperature. There are four stable phases in total, depending on the misfit strain and applied stress. When the in-plane misfit strains are zero, the stable phase is orthorhombic O (\( P_x = P_y = P_z = 0 \)) for \( \alpha_{33} < -2.0 \) GPa, monoclinic M (\( P_x = P_y > P_z \neq 0 \)) for \( -2.0 \) GPa \( \leq \alpha_{33} \leq 0.0 \) GPa, and rhombohedral R (\( P_z = P_x = P_y \neq 0 \)) for \( \alpha_{33} > 0.0 \) GPa, respectively. In the region where both the in-plane misfit strain and the out-of-plane stress are highly negative, the cubic phase C (\( P_z = P_x = P_y = 0 \)) is stable. In this case, the mechanical condition applied to the material is similar to a hydrostatic pressure, which could favor the paraelectric cubic phase. Notably, no stable T-phase can be observed in the entire phase diagram. This can be understood since R-phase is the ground state for [MDABCO](NH₄)I₃ and the film is (111)-oriented. T-phase has much higher energy as compared to the O phase according to the calculations from Wang et al., which is difficult to stabilize via strain engineering in (111)-oriented [MDABCO](NH₄)I₃ thin films.

Elastocaloric effect

With the knowledge of the dependence of stress and epitaxial strain on the polarization, now we proceed to calculate the eC

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Temperature change $\Delta T_{ec}$ and the eC temperature change $\Delta T_{ec}$ under external stress for [MDABCO](NH$_4$)$_3$ thin film with a compressive misfit strains and b tensile misfit strains. The gray, white, and yellow regions mark different phases. The blue line shows the entropy change, while the red line indicates the temperature change. The pink dash line marks the maximum nonuniform directional stress $-1.28$ GPa above which the system undergoes plastic deformation.

**Table 1.** Comparison of elastocaloric properties for different materials from previous literature and [MDABCO](NH$_4$)$_3$ thin films in this study.

| Material          | $T$ (K) | $|\Delta \sigma|$ (GPa) | $|\Delta S_{ec}|$ (K) | $|\Delta T_{ec}|$ (K) | $|\Delta S_{ec}| / |\Delta \sigma|$ (K GPa$^{-1}$) | $|\Delta T_{ec}| / |\Delta \sigma|$ (K GPa$^{-1}$) | RC (J kg$^{-1}$) | COP (J kg$^{-1}$ K) | Method | Ref.
|-------------------|---------|--------------------------|----------------------|----------------------|---------------------------------|---------------------------------|-----------------|------------------|---------|---------|
| TiNiFe            | 293     | /                        | 4.8                  | /                    | /                               | /                               | 4.90            | 32               | Thermo            |         |
| PVDF              | 300     | 0.015                    | 2                    | 133                  | 11                             | 22                             | /               | /                | Ex.                | 38,39 |
| PbTiO$_3$         | 700     | 1                        | 20                   | 20                   | /                               | /                               | /               | /                | DFT                | 18      |
| PbZrO$_3$         | 950     | 2                        | 25                   | 12.5                 | /                               | /                               | /               | /                | DFT                | 46      |
| PMN-32PT          | 323     | 0.028                    | 0.36                 | 12.9                 | /                               | /                               | /               | /                | Ex.                | 20      |
| PbZr$_{0.2}$Ti$_{0.8}$O$_3$ | 298     | 2                        | 11                   | 5.5                  | /                               | /                               | /               | /                | PF                 | 47      |
| BaTiO$_3$         | 300     | 6.5                      | 4.6                  | 0.7                  | 8.7                             | 40                             | 0.003           | 1.21             | Thermo            |         |
| Ba$_{0.5}$Sr$_{0.5}$TiO$_3$ | 260     | 1                        | 9                    | 9                    | /                               | /                               | /               | /                | DFT                | 17      |
| BCZT              | 340     | 0.25                     | 1.5                  | 6                    | /                               | /                               | /               | /                | Ex.                | 48      |
| Bi$_4$Ti$_3$O$_{12}$ | 900     | 2                        | 8.8                  | 4.4                  | /                               | /                               | /               | /                | DFT                | 49      |
| [MDABCO](NH$_4$)$_3$ | 298     | 1.28                     | 22.9                 | 17.9                 | 76.85                           | 1760                           | 1.11            | this work        | Thermo            |         |

*Ex., DFT, PF, and Thermo stands for experimental, first principle calculations, phase-field simulations, and thermodynamic calculations, respectively.*

properties. Figure 3 shows the eC entropy change $\Delta S_{ec}$ and temperature change $\Delta T_{ec}$ versus the out-of-plane compressive stress for various [MDABCO](NH$_4$)$_3$ thin films under different misfit strains ($u_m$). To calculate the variations of the $\Delta S_{ec}$ and $\Delta T_{ec}$ with the phase change, compressive stress is applied on top of the thin film. With the increase of the applied stress, phase transitions from rhombohedral (R) to monoclinic (M) or cubic (C) and finally to orthorhombic (O) occur. According to the previous report, [MDABCO](NH$_4$)$_3$ undergoes a plastic deformation when the unidirectional compressive stress is above 1.28 GPa, which is set as the upper limit of the applied stress for the calculations in this study. Note that to sustain 1.28 GPa for the whole thin film device, one has to find either suitable oxide wafers or ductile metals as substrate, or even freestanding film without substrate. Assuming a constant heat capacity of 1000 J K$^{-1}$ kg$^{-1}$ for [MDABCO](NH$_4$)$_3$ at room temperature, the maximum adiabatic temperature change $\Delta T_{ec}$ ~18.7 K occurs with $u_m = -0.01$. In most cases, with the highest applied stress, the adiabatic temperature change can reach 10–20 K as shown in Fig. 3a, while the maximum adiabatic temperature change is 22.9 K with a tensile misfit strain of 0.01 as shown in Table 1. Interestingly, at the large compression side (e.g., $u_m = -0.05$ and $-0.03$), $\Delta S_{ec}$ ($\Delta T_{ec}$) shows a nonlinear relationship with the external stress while for all the other cases mainly linear dependency is observed.

Table 1 and Supplementary Fig. 4 summarize the eC properties for [MDABCO](NH$_4$)$_3$ and other ferroelectrics that has been reported recently. For the polyvinylidene fluoride (PVDF) based ferroelectric polymers, the polar to the nonpolar phase transition is very sensitive to external mechanical stresses. High eC effects have been reported and adiabatic temperature changes of ~2 K were measured directly in PVDF polymers near room temperature under uniaxial stresses of ~10 MPa. Meanwhile, some typical ferroelectric perovskite thin films also present finite eC effects at room temperature. For instance, BaTiO$_3$ thin films show a $\Delta T_{ec}$ ~5 K under huge uniaxial stress of 6.5 GPa. On the other hand, PbTiO$_3$ thin film exhibit a maximum adiabatic temperature change of ~20 K, which has been ascribed to the mixed ferroelastic and ferroelectric behaviors. However, such a giant eC effect can only occur at ~700 K, which is too high for practical applications. In comparison, [MDABCO](NH$_4$)$_3$ displays considerably high eC strength, which is much higher than traditional lead-free ferroelectric perovskites, as shown in the light gray area of Supplementary Fig. 4. Polymer-based ferroelectrics have been found to exhibit higher temperature change $\Delta T_{ec}$ but they have a very low refrigerant capacity (RC = $|\Delta T \Delta S|$). The calculated RC performance of [MDABCO](NH$_4$)$_3$ thin film is 1760 J kg$^{-1}$, much superior to other ferroelectrics as reported in the previous literature. The coefficient of performance (COP) is another commonly used metric to describe the efficiency of the cooling.
cycle, which is defined as the ratio of the cooling power (Q) to the input work (W) required to perform a thermodynamic cycle. As listed in Table 1, the calculated COP of [MDABCO](NH4)I3 thin film is about 1.11, which is much higher as compared to other ferroelectrics such as BaTiO3 and comparable to the widely used eC materials such as TiNiFe shape memory alloys.

Now we further turn to discuss the detailed underlying mechanisms for the superior eC performance of [MDABCO](NH4)I3 thin film. Figure 4 demonstrates the eC entropy change ΔS_eC, and the eC temperature change ΔT_eC for [MDABCO](NH4)I3 thin films under different in-plane misfit strains (\(\varepsilon_{lm}\)) and out-of-plane stresses. With the increasing of the out-of-plane stress, both the magnitudes of ΔS_eC and ΔT_eC increase. Figure 4c, d show the contributions of volume change and polarization change to the eC entropy change and eC temperature change, respectively. We choose a compressive stress of -1.28 GPa as an example, two contributions to ΔS_eC can be identified as follows. The ordering of the dipoles by the application of external stress under isothermal conditions leads to a reduction or increase in the dipole configurational entropy (ΔS^o), which is associated with the phase transitions. The other contribution is the volume change induced entropy change (ΔS^v) given by \(\frac{\rho}{V}(\sigma_1 + \sigma_2 + \sigma_3)\), where the thermal expansion coefficient \(\beta_i\) and the mass density \(\rho\) have both been evaluated in the previous paper. For [MDABCO](NH4)I3 film, these two parts compete with each other when compressive stress is applied but the ΔS^o dominates the total entropy due to its characteristic of low Young’s modulus, which is only one percent of the Young’s modulus for typical ferroelectric oxides. The low Young’s modulus prompts the high thermal expansion coefficient and thus results in the big entropy reduction when applying the compressive stress (see Fig. 4a, c).

Calculations of elastocaloric effect for inorganic oxide ferroelectrics

Moreover, the impact of physical properties in materials on the eC strength is investigated, by calculating some common (111)-oriented ferroelectric oxide films using the same method. Material parameters are taken from existing publications for BaTiO3 (BTO)40, PbTiO3 (PTO)40, PbZr0.52Ti0.48O3 (PZT-0.52)42, PbZr0.8Ti0.2O3 (PZT-0.8)42, K0.5Na0.5NbO3 (KNN)43,44, and KNbO3 (KNO)44 thin films, respectively. Figure 5a, b show the comparison of isothermal entropy change ΔS_eC and adiabatic temperature change ΔT_eC between [MDABCO](NH4)I3 and other typical ferroelectric materials. The predicted eC strengths, isothermal ΔS_eC/Δσ and adiabatic ΔT_eC/Δσ, for [MDABCO](NH4)I3 are ~60.0 J K\(^{-1}\) kg\(^{-1}\) and 17.9 K GPa\(^{-1}\), respectively, more than one order of magnitude higher than the largest value for oxide ferroelectric films. For example, the PTO film has the highest ΔT_eC = 24.70 K, but measured under a considerably high stress Δσ of 4.55 GPa. The calculated eC strength for PTO agrees well with the previous study by first principle calculation, in which the eC temperature change ΔT_eC is ~7 K under a stress Δσ of 1.4 GPa. Moreover, the calculated eC strength [ΔT_eC]/Δσ of 0.76 K GPa\(^{-1}\) for BaTiO3 film is consistent with Liu et al.41. Other ferroelectric oxides such as KNbO3 and K0.5Na0.5NbO3 thin films also show high ΔT_eC values under remarkably high compressive stress Δσ. In comparison, the [MDABCO](NH4)I3 thin film exhibits a high value of ΔS_eC (~76.85 J K\(^{-1}\) kg\(^{-1}\)) and ΔT_eC (22.9 K) under a lower Δσ of 1.28 GPa. The outstanding eC strength of [MDABCO](NH4)I3 film can be understood by separating the contributions from two parts. For the polarization change induced eC temperature change (ΔT/P), the value of [MDABCO](NH4)I3 is in the same order of magnitude as the value of the oxide perovskites. But for the volume change induced eC temperature change (ΔΔT/V), due to the high compressibility of [MDABCO](NH4)I3, it is one order of magnitude higher than the highest value of the other ferroelectric films. The specific value for the eC properties of the above ferroelectric films could be found in Supplementary Table 4 and Supplementary Figs. 5, 6.

DISCUSSION

Following the previous results, we further identify several intrinsic physical properties, namely the elastic compliance \(s_{ij}\) thermal expansion coefficient \(\beta_i\) on the eC effects of the metal-free

Fig. 4 Contributions of the eC performance of the [MDABCO](NH4)I3 thin film. a The eC entropy change ΔS_eC and b the eC temperature change ΔT_eC for [MDABCO](NH4)I3 thin film versus with misfit strain (\(\varepsilon_{lm}\)) under different external stresses. The contributions of polarization change and volume change under a compressive stress of 1.28 GPa for c the eC entropy change and d the eC temperature change ΔT_eC. The gray, white, and yellow regions mark different phases. The pink dash lines mark the maximum eC ΔS_eC and ΔT_eC at a stress of −1.28 GPa.
ferroelectrics, hoping to find design principles for high eC materials. The calculated eC temperature change $\Delta T_{ec}$ is plotted in Fig. 6 and Supplementary Fig. 6, by varying the values of the above-mentioned material properties. Figure 6a shows a two-dimensional plot of the evaluated eC temperature change $\Delta T_{ec}$ as a function of both elastic compliance and thermal expansion. It is indicated that generally, eC decreases with increasing of elastic compliance, while increases with increasing thermal expansion coefficient. A relatively stronger dependency on $\beta_l$ can be observed. For instance, $\Delta T_{ec}$ shows a dramatic increase to $\sim 100$ K with increasing of the $\beta_l$ to five times of $[\text{MDABCO}](\text{NH}_4)I_3$ with fixing of the elastic compliance (Supplementary Fig. 6).

Note that the elastic compliance and thermal expansion coefficient are not independent physical parameters for a certain material. We map out the elastic compliance and thermal expansion coefficient of several oxide ferroelectrics, PVDF, and $[\text{MDABCO}](\text{NH}_4)I_3$ in Fig. 6b. The thermal expansion coefficient $\beta_l$ and elastic compliance $s_{ij}$ for different ferroelectrics. The compressive stress and the misfit strain are fixed at 1.28 GPa and 0.01, respectively.

In summary, we have developed a thermodynamic description for (111)-oriented organic ferroelectric $[\text{MDABCO}](\text{NH}_4)I_3$ thin film and investigated its phase transition behavior and eC properties under different misfit strains and applied external stresses. We found that there are two contributions to the eC strength, namely the polarization changes induced entropy change ($\Delta S_P$) and the volume change induced entropy change ($\Delta S_V$), which competes with each other under compressive stress. For organic ferroelectric materials which are relatively soft, the entropy change $\Delta S_V$ dominates, which is an order of magnitude higher than traditional ferroelectric oxides. It
is demonstrated that an EC entropy change of $-65.4 \text{ J kg}^{-1} \text{ K}^{-1}$ and an adiabatic EC temperature change of 22.9 K are achieved for [MDABCO](NH₄)I₃ under a compressive stress of 1.28 GPa at a misfit strain of 0.01. This can be attributed to the low Young’s modulus of [MDABCO](NH₄)I₃, which is only one percent of Young’s modulus of conventional oxides. By analyzing the relationship of EC with thermal expansion coefficient and elastic compliance, we further discovered that the thermal expansion coefficient has a dominant role in determining the EC. Based on our theoretical analysis, we predict that it is possible to further improve the EC properties by enhancing the thermal expansion coefficient through chemical modification of the [MDABCO](NH₄)I₃. We envision this work will attract broad interest from the community of solid EC materials.

METHODS

Thermodynamic calculations of ferroelectric thin films

Based on the Landau-Devonshire theory, there are mainly four contributions to the total thermodynamic free energy density:

1. Polarization energy $G_{\text{polarization}} = a_1 P^2 + a_2 P^4 + P^6$.
2. Thermal energy $G_{\text{thermal}} = -c_e T \ln (1 + e^2) + P^2 (T - T_0)$.
3. Mechanical energy $G_{\text{mechanical}} = \frac{1}{2} C_{ijklmn} P_i P_j P_k P_l P_m$.
4. Electric energy $G_{\text{electric}} = -\varepsilon_0 E^2 (E - E_{\text{perm}}) E_{\text{perm}}$.

Where $a_1, a_2, c_e, C_{ijklmn}, \varepsilon_0, E_{\text{perm}}$, and $E_{\text{perm}}$ are the polarization, elastic modulus, parameters, dielectric constant, and permittivity of vacuum, respectively.

Under the reversible adiabatic condition, the total entropy is conserved and the COP can be evaluated by the following equation:

$$\Delta S' = \frac{W}{Q} = \frac{\int \frac{dQ}{T}}{\int \frac{dW}{T}}$$

(5)

where $Q$ represents the absorbed heat and $W$ is the specific mechanical work in the EC cooling cycle. The absorbed heat $Q$ is derived from $T dS$, in which $T$ and $S$ are the temperature and entropy, respectively. The specific mechanical work $W$ is calculated by $\int E dT$, in which the $p$, $\rho$, and $\varepsilon$ are the mass density, stress, and strain, respectively.

DATA AVAILABILITY

The raw data for the thermodynamic calculations in this paper and its supplemental information files are available from the corresponding author (hongzijian100@zju.edu.cn) upon reasonable request.

CODE AVAILABILITY

The code for the thermodynamic calculations in this paper and its supplemental information files are available from the corresponding author (hongzijian100@zju.edu.cn) upon reasonable request.
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AUTHOR CONTRIBUTIONS

Y.H.H., J.-J.W. and Z.H. conceived the idea and designed the project. C.L. and J.-J.W. performed the experiments. Y.H.H., J.-J.W., H.T. and Z.H. analyzed the data. L.-Q.C., Z.H., and Y.J.W. supervised the project. All authors contributed to the discussions and analyses of the data and results. Z.H. prepared the manuscript.

COMPETING INTERESTS

The authors declare no competing interests.

ADDITIONAL INFORMATION

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