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Large piezoelectric response in a family of metal-free perovskite ferroelectric compounds from first-principles calculations

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Metal-free organic perovskite ferroelectric materials have been shown recently to have a number of attractive properties, including high spontaneous polarization and piezoelectric coefficients. In particular, slow evaporation of solutions containing organic amines, inorganic ammoniums, and dilute hydrohalogen acid has been shown to produce several attractive materials in the MDABCO-NH₄-I₃ family (MDABCO is N-methyl-N'-diazabicyclo[2,2,2] octonium). In the present work, we study by first-principles calculations the origin of polarization, electronic density of state, piezoelectric response, and elastic properties of MDABCO-NH₄-X₃ (X = Cl, Br, I). We find that the dipole moments of the MDABCO and NH₄ groups are negligible, and the large spontaneous polarization of MDABCO-NH₄-I₃ mainly results from MDABCO and NH₄ being off-center relative to I ions. Although the piezoelectric response of organic materials is usually very weak, we observe large piezoelectric strain components, d_{x4} and d_{x5} ; the calculated d_{x5} is 119 pC/N for MDABCO-NH₄-Cl₃, 248 pC/N for MDABCO-NH₄-Br₃ and 178 pC/N for MDABCO-NH₄-I₃. The large value of d_{x5} is found to be closely related with the large value of elastic compliance tensor, s_{44} . These results show that MDABCO-NH₄-X₃ metal-free organic perovskites have large piezoelectric response with soft elastic properties.

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INTRODUCTION

The perovskite structures have been dubbed a “chameleon” due to their rich diversity of chemical compositions and physical properties.^{1–3} Searching for large piezoelectric perovskites has been the aspiration of science and engineering studies.⁴ Compared with inorganic perovskite, organic materials possess many advantages. For example, organic crystals can be synthesized at relatively low temperature.⁵ The easy reorientation of inorganic cations make them promising candidates for order–disorder ferroelectrics.^{6,7} By replacing Pb and other toxic ions with inorganic cations, they can be designed to toxic-metal-free materials. Therefore, organic materials have become an attractive topic not only due to the remarkable structural variability and highly tunable properties, but also due to their potential applications in light sources, photovoltaics, and electronics.⁸

Recently, a breakthrough of piezoelectric material was reported by Yu-Meng You, Ren-Gen Xiong, and colleagues.⁹ Based on molecular design strategy and elaborate organic cation selection, they successfully synthesized a family of metal-free organic perovskite ferroelectrics. This family contains 23 new compounds, in which 21 compounds have cubic perovskite structure and the other two have hexagonal perovskite structure. Among these cubic perovskite compounds, 14 compounds show paraelectric–ferroelectric transition and their Curie temperatures range from 355 to 493 K. This means all of them are ferroelectric at room temperature. The general formula of this family is A(NH₄)X₃, in which A is a divalent organic cation and X is halogen anion.

Despite their diversity, compounds of this family were obtained easily by a simple strategy: slow evaporation of solution containing organic amines, inorganic ammoniums, and dilute hydrohalogen acid. Not only the facile synthesis method but also their desirable properties make them are possible for application in flexible devices.

Among this metal-free organic perovskite family, MDABCO-NH₄-I₃ (MDABCO is N-methyl-N'-diazabicyclo[2,2,2]octonium) is an outstanding one. Its ferroelectric Curie temperature (T_0) is 448 K, spontaneous polarization (P_s) is 22 $\mu\text{C}/\text{cm}^2$ and piezoelectric coefficient d_{33} (along [1 1 1] direction) is about 14 pC/N⁹. Furthermore, second-harmonic generation response and dielectric permittivity were also measured as a function of temperature. Although a detailed investigation of MDABCO-NH₄-I₃ was made in experiment, some important physical properties were not reported. For example, except for the longitude piezoelectric stress coefficient d_{33} , other elements of piezoelectric stress tensor were not measured in experiment. Furthermore, the elastic tensor and piezoelectric strain tensor were not reported, too.

RESULTS AND DISCUSSION

In order to elucidate the piezoelectric and elastic properties of MDABCO-NH₄-I₃, we performed the density-functional theory (DFT) calculation using Perdew–Burke–Ernzerhof (PBE)¹⁰ and PBE-D3¹¹ methods as implemented in the Vienna ab initio simulation package (VASP).^{12–14}

The primitive and conventional unit cells of MDABCO-NH₄-I₃ in ferroelectric phase are depicted in Fig. 1. Herein, the MDABCO-

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Fig. 1 The ferroelectric structure of MDABCO-NH₄-I₃. **a** and **b** are NH₄ and MDABCO groups, **c** and **d** are the primitive unit cell viewed along [0 0 1] and [1 1 1] directions, **e** and **f** are the conventional unit cell viewed along [1 1 0] and [0 0 1] directions

NH₄-I₃ crystal is composed of three building blocks: NH₄, MDABCO, and I₆ octahedron. The NH₄ locates in the middle of I₆ octahedron, which shares corners with its six neighboring octahedra to form a three-dimensional (3D) network. The MDABCO locates in the middle of a cage defined by 12 iodine ions. It has a trigonal structure with space group *R*3̄. The three-fold axis passes through the two nitrogen atoms of MDABCO and the spontaneous polarization direction is parallel to this axis (z-axis). Similarly with K₃BO₁₀Cl^{15–17} and trimethylchloromethyl ammonium trichloromanganese,⁵ it is the ordered cation MDABCO that breaks the inversion symmetry and permits the occurrence of ferroelectric, piezoelectricity, second-harmonic generation, and other interesting phenomena. When temperature increases above 448 K, it turns to a cubic paraelectric phase.⁹ Besides MDABCO-NH₄-I₃, MDABCO-NH₄-Br₃ is also successfully synthesized with similar method.⁹ It has a similar structure with MDABCO-NH₄-I₃ and exhibits paraelectric-ferroelectric transition at 390 K.

So as to calculate the properties of these newly synthesized crystal, we relaxed their atomic positions and lattice parameters first. For MDABCO-NH₄-I₃ and MDABCO-NH₄-Br₃, we used the experimental data for their initial structures. Then, lattice parameters and atomic positions are relaxed without any symmetry constraint until calculated stresses and forces are less than the threshold. As MDABCO-NH₄-Cl₃ is not synthesized in experiment, we substitute the Br in MDABCO-NH₄-Br₃ to Cl as its initial structure.^{18,19} Then, we relaxed lattice parameters and atomic positions of MDABCO-NH₄-Cl₃ until they meet the threshold. So as to verify the calculated structure are stable, we calculated their zone center phonon frequencies and do not find unstable mode. Moreover, they all satisfy the mechanical stability criteria, namely, that the stiffness tensor is positive-definite.²⁰ The calculated lattice parameters of primitive unit cell are listed in Table 1 and are compared with available experimental data.

Because MDABCO-NH₄-X₃ are molecular materials, we use the DFT-D3 method to take the van de Waals interaction into consideration.⁹ Unfortunately, PBE + D3 does not give better result compared with PBE. As far as the angle is concerned, PBE functional is slightly better than PBE + D3. However, when it comes to the lattice length, PBE functional performs much better than PBE + D3. The PBE result overestimates the lattice parameter of MDABCO-NH₄-I₃ 1.5%, and PBE + D3 underestimates 1.9%. For

Table 1. Experimental and calculated lattice parameters of ferroelectric MDABCO-NH₄-X₃

Material		<i>a</i> (Å)	<i>a</i> (°)
MDABCO-NH ₄ -Cl ₃	PBE	6.84	84.30
	PBE + D3	6.64	84.22
MDABCO-NH ₄ -Br ₃	Exp.	7.1947	84.867
	PBE	7.04 (−2.1%)	84.59 (−0.3%)
	PBE + D3	6.82 (−5.2%)	84.63 (−0.3%)
MDABCO-NH ₄ -I ₃	Exp.	7.259	84.767
	PBE	7.37 (1.5%)	85.11 (0.4%)
	PBE + D3	7.12 (−1.9%)	85.16 (0.5%)

Deviations from experimental data are given in bracket

MDABCO-NH₄-Br₃, PBE underestimates lattice parameter 2.1%, while PBE + D3 underestimates it as large as 5.2%. This means PBE is more suitable than PBE + D3 in MDABCO-NH₄-X₃ calculation. The poor performance of PBE-D3 is due to the hydrogen bond in MDABCO-NH₄X₃. The total energy of DFT-D3 is $E_{KS-DFT} - E_{disp}$.¹¹ The first term E_{KS-DFT} is the usual self-consistent KS energy and the second term E_{disp} is the dispersion correction. This correction is a sum of two- and three-body energies, related with bond length, bond angle and etc. However, it has no relationship with the electronic band structure. Therefore, the developers of DFT-D3 says “the method is of molecular mechanics type in the sense that it is very fast and only geometric information is employed”.¹¹ It is pointed in refs. ^{21–24} that the long-range part of the exchange contribution is overestimated in PBE. This overestimation compensates the missing vdW interaction to some extent. Consequently, directly adding additional dispersion correction to PBE would lead to an unphysical ‘double-counting’ effect.²² As shown in ref. ¹¹, this unphysical effect in hydrogen bond is severe and results into the poor performance of PBE-D3. Therefore, we use the atom position and lattice parameters of PBE and calculate other properties with PBE functional as well.

So as to investigate the origin of large spontaneous polarization (22 μC/cm²) of MDABCO-NH₄-I₃, we calculate its Born effective

Fig. 2 The calculated structure and Born effective charges of MDABCO-NH₄-I₃. **a** The Born effective charges of MDABCO. **b** The Born effective charges and relative positions of MDABCO, NH₄, and I₃ groups. The dashed lines show hydrogen bonds between H⁺ and I⁻

charge (BEC). BEC is a second-order tensor and the component along the dipole direction is related with ferroelectric polarization. The calculated BEC components along the dipole direction are marked in Fig. 2.

As shown in Fig. 2a, MDABCO can be divide into three parts. The top hydrogen, the bottom CH₃ and the middle N₂C₆H₁₂ part. Their BECs are +0.84, +0.81, and +0.77, respectively. For MDABCO, all C and H show positive values, only N shows negative values. We calculate the positive and negative charge centers of MDABCO, and find the distance between the two centers is as small as 0.009 Å. They are almost overlap with each other. Therefore, the dipole moment of the MDABCO group is negligible. The total charge of MDABCO is +2.45 and the total charge center is marked as a red point in Fig. 2. The positive and negative charge centers of NH₄ are almost overlap with each other, too. Therefore, the dipole moment of the NH₄ group is negligible. The total charge of NH₄ is +1.15, centered at the N position. The charge of I is -1.2, similar to its formal charge -1. The relative positions of MDABCO, NH₄, and I₃ along the dipole moment direction are depicted in Fig. 2b. It is clear that the charge center of MDABCO (A-site of perovskite) shifts upward with the distance $d_A = (5.37 - 3.84)/2 = 0.765$ Å relative to the center of its nearest neighboring six I⁻ ions. At the same time, the charge center of NH₄ (B-site of perovskite) shifts upward, too, with the distance $d_B = (2.83 - 1.77)/2 = 0.53$ Å relative to the center of I₆ octahedron. As a comparison, the A-site and B-site displacements of rhombohedral BaTiO₃ are 0.10 and 0.19 Å, respectively. They are much smaller than the corresponding off-center distance of MDABCO-NH₄-I₃. Furthermore, d_A is larger than d_B for MDABCO-NH₄-I₃, similarly to the condition of PbTiO₃. This means that MDABCO-NH₄-I₃ is an A-site driven ferroelectricity. On the contrary, d_A is smaller than d_B for BaTiO₃, indicating a B-site driven ferroelectricity. Therefore, MDABCO-NH₄-I₃ is an A-site driven order-disorder ferroelectricity and its large polarization results from the large off-center distances of MDABCO and NH₄ relative to I.

As shown in the dashed lines of Fig. 2b, there are three hydrogen bonds between three hydrogens of CH₃ and three I⁻ anions. And there are also three hydrogen bonds between three hydrogens of NH₄ and its surrounding three I⁻ anions.⁹ When MDABCO-NH₄-I₃ turns from ordered ferroelectric phase to disordered paraelectric phase, much energy is needed to break

these six hydrogen bonds so as to make MDABCO and NH₄ rotating freely. In paraelectric phase, the rotating MDABCO must overcome a barrier, in which the two N atoms of MDABCO lines along the [1 1 0] direction. So as to get the barrier value, we calculate the total energy of two configurations. In the first configuration, lattice parameters are set to the experimental value of paraelectric phase and I ions forms a cubic network. Then we fix the positions of I and set the two N and two C atoms of MDABCO along the C₃ axis to move only along the [1 1 1] direction. Other atoms can move freely. In the second configuration, lattice parameters and positions of I ions are the same as configuration one. Then the selected two N and two C atoms of MDABCO in the first configuration are set to move only along the [1 1 0] direction. Other atoms can move freely. The energy difference between the above two configurations is $\Delta E = 0.156$ eV per primitive unit cell. As MDABCO is polyatomic molecules with six freedom (three translations and three rotations), the energy barrier corresponds to the temperature $T = \Delta E / (3 \times k_B) = 398$ K, which agrees with the experimental value 448 K.

The structure evolution with X ions is presented in four parts. Firstly, the structure parameters inner MDABCO are shown in Fig. 3a. The bond lengths (solid red symbol) refer to the left axis, while the bond angles (open blue symbol) correspond to the right axis. With halogen changing from Cl to I, the bond lengths change less than 0.01 Å and the bond angles change <0.2°. Therefore, the MDABCO group performs like a rigid body in MDABCO-NH₄-X₃ crystals.

Secondly, the structure parameters between MDABCO and its surrounding X ions are shown in Fig. 3b. There are two kinds of bond length between H and X ions. The first one is d_{HX-w} at the top of Fig. 3b inset, while the second one is d_{HX-s} at the bottom of Fig. 3b inset (the subscript 'w' and 's' represent 'relatively weak', and 'relatively strong'). The first bond length is larger than the second one, indicating the first hydrogen-halogen interaction is weaker than the second one. With the radius of X ion increases from Cl to I, the two hydrogen-X bond lengths increase. We also give the angles between H-X bond and the X₃ plane (inset of Fig. 3b). With halogen changing from Cl to I, the angle θ_{HX3-w} changes from 26.4° to 31.1°, increasing 4.7°. However, the angle θ_{HX3-s} changes from 46.4° to 44.4°, decreasing 2.2°. The opposite trends of θ_{HX3-w} and θ_{HX3-s} originate from the A-site space changing of

Fig. 3 The structure parameters **a** of inner MDABCO and **b** between MDABCO and its nearest neighboring X ions. The solid red symbols refer to the left vertical axis, while the open blue ones refer to the right vertical axis. The inset structures depict the bond lengths and angles

perovskite. With ion changing from Cl⁻ to I⁻, the lattice parameter of MDABCO-NH₄-X₃ increases from 6.84 to 7.37 Å. Then, the corresponding A-site space of perovskite increases. In MDABCO-NH₄-Cl₃, the MDABCO group is a little compressed as there is not enough room for it. When it comes to MDABCO-NH₄-I₃, there is spare room for MDABCO group. Because the hydrogen-halogen interaction at the bottom of Fig. 3b inset is stronger than the top one, the bottom hydrogen approaches its neighboring I, decreasing θ_{HX3_s} , while the top hydrogen leaves its neighboring I, increasing θ_{HX3_w} .

Thirdly, we give the structure parameters inner NH₄ in Fig. 4a. There are two N-H bond length: l_{NH_up} and l_{NH_dn} . The first bond almost points to the neighboring X ion, while the second bond points to the middle of three X ions. Therefore, the first N-H bond is enlarged by X ions relative to the second one, resulting into $l_{NH_up} > l_{NH_dn}$. Because NH₄ forms a tetrahedron, we calculate the Baur's distortion index D with the following equation^{17,25}:

$$D = \frac{1}{n} \sum_{i=1}^n \frac{|l_i - l_{av}|}{l_{av}} \quad (1)$$

where l_i is the distance from the central atom to the i_{th} coordinating atom, and l_{av} is the average bond length. For a regular tetrahedron, the distortion index equals zero. For NH₄ tetrahedron, the distortion index is very little, indicating that NH₄ performs like a rigid body in MDABCO-NH₄-X₃.

Fourthly, we show the structure parameters between NH₄ and its surrounding X ions in Fig. 4b. For a regular octahedron, N atom should locate at the center and ϕ_{XNX} should be 180°. Actually, the angle ϕ_{XNX} is about 157°, obviously deviating from the ideal value of 180°. With halogen changing from Cl to I, ϕ_{XNX} changes from 154.6° to 158.7°, increasing 4.1°. Similarly with MDABCO, we also give the angles between H-X bond and the X₃ plane (inset of Fig. 4b). With halogen changing from Cl to I, the angle ϕ_{HX3_w} changes from 36.0° to 33.8°, decreasing 2.2°. However, the angle ϕ_{HX3_s}

Fig. 4 The structure parameters **a** of inner NH₄ and **b** between NH₄ and its nearest neighboring X ions. The solid red symbols refer to the left vertical axis, while the open blue ones refer to the right vertical axis. The inset structures depict the bond lengths and angles

Fig. 5 The calculated electronic density of state of MDABCO-NH₄-X₃. Fermi level is set to zero. Some special points are label with arrows of different color

changes from 30.6° to 33.2°, increasing 2.6°. With halogen changing from Cl to I, the evolutions of ϕ_{HX3_s} (increasing) and ϕ_{HX3_w} (decreasing) are opposite to those of θ_{HX3_s} (decreasing) and θ_{HX3_w} (increasing). It originates from the B-site space changing of perovskite. With X ion changing from I⁻ to Cl⁻ (not Cl⁻ to I⁻), the B-site space of perovskite increases. In MDABCO-NH₄-I₃, the NH₄ group is a little compressed as there is not enough room for it. When it comes to MDABCO-NH₄-Cl₃, there is spare room for NH₄ group. Because the hydrogen-halogen interaction at the top of Fig. 4b inset is stronger than the bottom one, the top hydrogen approaches its neighboring Cl, decreasing θ_{HX_s} , while the bottom hydrogen leaves its neighboring Cl, increasing θ_{HX_w} .

Fig. 6 The calculated piezoelectric strain (a) and stress (b) tensor of MDABCO-NH₄-X₃. The experimental measured d_{z3} of MDABCO-NH₄-I₃ is also given

The calculated electronic density of state (DOS) of MDABCO-NH₄-X₃ are exhibited in Fig. 5. It can be clearly seen that these DOS are divided into three parts. The low energy part (below -2 eV) is mainly composed of occupied N-2p, C-2p, and H-1s states, the middle energy part (from -2 to 0 eV) is mainly composed of occupied Cl-3p, Br-4p, and I-5p states, and the high energy parts (above 3 eV) is unoccupied states of N, C, H, and halogen. By comparing Fig. 5a–c, we can see two obvious evolutions with anion changes from Cl[−] to I[−]. Firstly, the width of the occupied halogen p orbital increases from 0.8 (Cl[−]) to 1.1 (I[−]) eV. This width broadening originates from the X-N-X angle changing in Fig. 4b. With X ion changing from Cl[−] to I[−], the angle of X-N-X angle (φ_{XNX}) increases toward 180° , resulting into more electron interaction along the X-N-X line.²⁶ Secondly, there are obvious gap between the occupied halogen p state and the occupied states of C, N, and H. This characters indicate the halogen interactions with MDABCO and NH₄ are weak.^{16,27} It agrees with the analysis of Figs. 3a and 4a.

Piezoelectric effect allows interconversion between electric field and mechanical deformation. This property is important for applications of sensors, actuators, vibration reducer, and so on. Conventional perovskite ferroelectrics usually require high processing temperatures,¹⁸ have little mechanical flexibility, and even contain potential toxic elements.⁴ These drawbacks make scientists pay much attention to organic materials.^{5,9} Experiment shows that MDABCO-NH₄-I₃ is an organic piezoelectrics without metal element. The piezoelectric strain coefficient d_{z3} of MDABCO-NH₄-I₃ is measure to be ~ 14 pC/N at room temperature.⁹ However, other components of piezoelectric tensor are still unknown. Therefore, we calculated the piezoelectric strain and stress tensors of MDABCO-NH₄-X₃.

The crystallographic symmetry plays an important role in the piezoelectric phenomena.²⁸ According to the definition of the piezoelectric effect, in the matrix notation (with two indices), the piezoelectric strain tensor d_{ij} of MDABCO-NH₄-X₃ (space group $R3$) is

$$\begin{bmatrix} d_{x1} & -d_{x1} & 0 & d_{x4} & d_{x5} & -2d_{y2} \\ -d_{y2} & d_{y2} & 0 & d_{x5} & -d_{x4} & -2d_{x1} \\ d_{z1} & d_{z1} & d_{z3} & 0 & 0 & 0 \end{bmatrix}$$

The corresponding piezoelectric stress tensor e_{ij} is

$$\begin{bmatrix} e_{x1} & -e_{x1} & 0 & e_{x4} & e_{x5} & -e_{y2} \\ -e_{y2} & e_{y2} & 0 & e_{x5} & -e_{x4} & -e_{x1} \\ e_{z1} & e_{z1} & e_{z3} & 0 & 0 & 0 \end{bmatrix}$$

There are six independent coefficients in piezoelectric strain (stress) tensor.

The piezoelectric strain tensor is defined as the ratio of developed strain to the applied electric field.²⁸ Our calculated piezoelectric strain tensors are shown in Fig. 6a. The calculated d_{z3} of MDABCO-NH₄-I₃ is 14.4 pC/N, which agrees very well with the experimental value ~ 14 pC/N.⁹ This agreement proves the validity of our calculation.

The calculated d_{x4} and d_{x5} are much larger than d_{z3} . The largest components of piezoelectric strain tensor for the three crystals are all d_{x5} , which is 119 pC/N for MDABCO-NH₄-Cl₃, 248 pC/N for MDABCO-NH₄-Br₃, and 179 pC/N for MDABCO-NH₄-I₃. They are much larger than the largest component of inorganic crystals, such as lithium niobate ($d_{x5} = 68$ pC/N),²⁹ lithium tantalite ($d_{x5} = 26$ pC/N),²⁹ cadmium sulfide ($d_{x5} = -14$ pC/N),³⁰ barium sodium niobate ($d_{y4} = 52$ pC/N),²⁸ hexagonal zinc oxide ($d_{z3} = 12.4$ pC/N),³¹ and hexagonal zinc sulfide ($d_{z3} = 3.2$ pC/N).^{32,33} They are even comparable with that of barium titanate ($d_{x5} = 242$ pC/N)³⁴ and are almost one third of that of PZT-5H ($d_{x5} = 741$ pC/N).³⁴ The above comparison shows that MDABCO-NH₄-X₃ have large piezoelectric responds and are good candidate materials for a variety of piezoelectric applications.

Similarly with piezoelectric strain tensor, piezoelectric stress tensor is defined as the ratio of developed stress to the applied electric field.²⁸ Our calculated piezoelectric stress tensors are shown in Fig. 6b. Except for e_{x1} and e_{z3} , the other components change little with X anion. Furthermore, differently with the condition of d_{x5} , e_{x5} is not the largest component of piezoelectric stress tensor. It is well known that the piezoelectric strain tensor [d], piezoelectric stress tensor [e], and elastic compliance tensor [s] satisfy the relation [d] = [e][s].²⁸ This indicates that the large value of d_{x5} may originates from the large elastic compliance. In the matrix notation (with two indices), the elastic compliance tensor of MDABCO-NH₄-X₃ (space group $R3$) is

$$\begin{bmatrix} s_{11} & s_{12} & s_{13} & s_{14} & -s_{25} & 0 \\ s_{12} & s_{11} & s_{13} & -s_{14} & s_{25} & 0 \\ s_{13} & s_{13} & s_{33} & 0 & 0 & 0 \\ 0 & 0 & 0 & s_{44} & 0 & 2s_{25} \\ -s_{25} & s_{25} & 0 & 0 & s_{44} & 2s_{14} \\ 0 & 0 & 0 & 2s_{25} & 2s_{14} & 2(s_{11} - s_{12}) \end{bmatrix}$$

There are seven independent coefficients in elastic compliance tensor. The calculated values are shown in Fig. 7.

It is clear in Fig. 7 that the s_{44} is the largest component in MDABCO-NH₄-X₃. With X anion changes from Cl[−] to I[−], it firstly

Fig. 7 The calculated elastic compliance tensor of MDABCO-NH₄-X₃, in which s_{44} is the largest component

Fig. 8 The tolerance factor MDABCO-NH₄-X₃. **a** The evolution of tolerance factor with A ion radius (r_A). **b–d** The sketches of AX and BX planes for different tolerance factors. The arrows in **b** represent shear stress

increases from 449 to 658 and then decreases to $473 \times 10^{-12} \text{ m}^2/\text{N}$. This evolution is similar with that of d_{x5} in Fig. 6a. For MDABCO-NH₄-X₃, the piezoelectric strain tensor component $d_{x5} = e_{x5} \times s_{44} - 2e_{x1} \times s_{25} - 2e_{y2} \times s_{14}$. The last term $2e_{y2} \times s_{14}$ is about two orders smaller than the first term, and the second term $2e_{x1} \times s_{25}$ is about one-third of the first term. Because the e_{x5} difference for MDABCO-NH₄-X₃ is rather small, the d_{x5} evolution with halogen is dominated by s_{44} .

For MDABCO-NH₄-X₃, s_{44} equals $(c_{12} - c_{11})/(2c_{14}^2 + 2c_{25}^2 - c_{11}c_{44} + c_{12}c_{44})$, related with five parameters c_{12} , c_{11} , c_{14} , c_{25} , and c_{44} . No one dominates the others. Therefore, s_{44} is affected by many structure parameters. So as to give an intuitive explanation, we propose a model based on the tolerance factor of perovskite. For an inorganic perovskite ABX₃, the Goldschmidt tolerance factor (TF) is defined as below³⁵

$$TF = \frac{r_A + r_X}{\sqrt{2}(r_B + r_X)} \quad (2)$$

where r_A , r_B , and r_X are the ionic radii of the ions A, B, and X, respectively. In this model, all ions are assumed to be hard spheres. TF is widely used to analysis the structure of inorganic perovskite.³⁶ TF = 1 corresponds to an ideal cubic perovskite with A, B and X ions touching each other perfectly. TF > 1 implies that A cation is too large or B cation too small, while TF < 1 implies A cation is too small or B cation too large.

This concept is generalized to hybrid perovskites containing organic cations by Kieslich and Becker et al.^{37–39} It is found that the TF value of most hybrid perovskites lies in the range from 0.8 to 1. Hybrid perovskite structures with TF > 1 or TF < 0.8 are rarely observed.³⁹ So as to get the TF values of MDABCO-NH₄-X₃, ions radii are needed. The Shannon radius of Cl[−], Br[−], and I[−] are 1.81, 1.96, and 2.2 Å, respectively.⁴⁰ The radius of (NH₄)⁺ is proposed to be 1.46 Å³⁹. But the radius of MDABCO is difficult to define because it is not a hard sphere. Based on the available radii of X and NH₄, we calculate the TF value evolution with MDABCO radius (r_A). As shown in Fig. 8a, the TF value of MDABCO-NH₄-Cl₃ is the largest, while that of MDABCO-NH₄-I₃ is the smallest. In experiment, MDABCO-NH₄-Br₃ and MDABCO-NH₄-I₃ are successful synthesized, while MDABCO-NH₄-Cl₃ is not. Therefore, it is reasonable to assume that the TF values of MDABCO-NH₄-Br₃ and MDABCO-NH₄-I₃ is <1, while that of MDABCO-NH₄-Cl₃ is >1 (the middle light blue region of Fig. 8a). This assumption agrees with the angles analysis of Figs. 3b and 4b. We also give the sketch of AX plane and BX plane for different TF values in Fig. 8b–d. For

Table 2. Calculated elastic stiffness tensor c_{ij} , bulk modulus B , shear modulus G , and Young's modulus E (GPa) of MDABCO-NH₄-X₃

Material	c_{11}	c_{33}	c_{44}	c_{12}	c_{13}	c_{14}	c_{25}	B	G	E
MDABCO-NH ₄ -Cl ₃	17.3	21.5	3.3	9.1	5.7	−0.9	−1.9	10.7	3.9	10.5
MDABCO-NH ₄ -Br ₃	16.7	19.4	2.3	7.8	5.8	−0.7	−1.7	10.2	3.3	9.0
MDABCO-NH ₄ -I ₃	15.2	16.5	2.3	6.3	5.6	−0.5	−0.7	9.1	3.6	9.5

TF > 1, the A cation is too large, resulting into over compression between A and X ions. It is the condition of MDABCO-NH₄-Cl₃. For TF < 1, the B cation is too large, resulting into over compression between B and X ions. It is the condition of MDABCO-NH₄-I₃. The over compressions of MDABCO-NH₄-Cl₃ and MDABCO-NH₄-I₃ increase their shear resistance, reducing their s_{44} values. For MDABCO-NH₄-Br₃, its TF value is closer to 1 than that of MDABCO-NH₄-I₃. It implies there is less over compression between A and X ions or B and X ions in MDABCO-NH₄-Br₃. Consequently, its shear resistance is less than that of MDABCO-NH₄-Cl₃ and MDABCO-NH₄-I₃, resulting in large s_{44} value.

The large elastic compliance tensor in Fig. 7 suggests that MDABCO-NH₄-X₃ are soft materials.³² So as to investigate their elastic properties, Table 2 gives their bulk and shear moduli with Voigt-Reuss-Hill (VRH) approximation,⁴¹ which is a good estimation for mechanical properties of polycrystalline materials.^{16,20,42–44} Bulk modulus describes the resistance of a material to a change in volume and shear modulus describes the resistance to a change in shape. Although the crystal structures of MDABCO-NH₄-X₃ are similar with inorganic ABO₃ perovskite, their bulk moduli are only around 10 GPa. They are much smaller than that of inorganic perovskite CaTiO₃ (170.9 GPa),⁴⁵ BaTiO₃ (162 GPa),^{46,47} and PbTiO₃ (144 GPa).^{46,47} The Young's moduli of MDABCO-NH₄-X₃ are also around 10 GPa, even smaller than that of flexible metal-organic frameworks (MOFs): MIL-53(Al) (25.5 GPa), MIL-53(Ga) (19.2 GPa), MIL-47 (25.3 GPa), DMOF-1(lozenge) (11.2 GPa), and DMOF-1(square) (12.5 GPa).

Bulk modulus is an average value of all directions. Instead, directional Young's modulus characterizes uniaxial stiffness in different directions. As a reference, the directional Young's modulus of rhombohedral BaTiO₃ based on the calculated elastic

Fig. 9 The calculated directional Young's modulus. **a, b** are directional Young's modulus and crystal structure of BaTiO₃ viewed from different directions. **c–e** are directional Young's modulus of MDABCO-NH₄-Cl₃, MDABCO-NH₄-Br₃, and MDABCO-NH₄-I₃, respectively. They are represented as three-dimensional (3D) surfaces with axes tick labels in GPa

stiffness using PBE functional⁴⁸ are given in Fig. 9a, b. Similarly with MDABCO-NH₄-X₃, BaTiO₃ takes rhombohedral structure as its lowest energy phase. We set its polar direction along z-axis. The crystal structure and directional Young's modulus are shown in the same view point in Fig. 9a. It is clear that the directional Young's modulus has six local minimums and eight high value lobes. The local minimum clearly seen in Fig. 9a is along the **a**₁ direction (**a**₁, **a**₂ and **a**₃ are the lattice vectors of the primitive unit cell). The other five local minimums are along **-a**₁, **±a**₂, and **±a**₃ directions. They correspond to compression or stretching of O–Ti–O bonds. Owing to the Ti displacement from the center of oxygen octahedron, these six directions show low rigidity. The directional Young's modulus viewed along the polar direction is shown in Fig. 9b. It is clear that the view direction is perpendicular to the facet of oxygen octahedron. Similarly, the other seven high value lobes are perpendicular to the other seven facets of oxygen octahedron.

Similarly with BaTiO₃, the polar direction of MDABCO-NH₄-X₃ is parallel to z-axis in Fig. 9c–e. There are six local minimums and eight high-value lobes in the directional Young's modulus of MDABCO-NH₄-X₃. These local minimums are along the lattice vectors of their primitive unit cells. They correspond to compression or stretching of X–N–X bonds in octahedrons. The directions of these high value lobes are perpendicular to the facets of X₆ octahedron. Their directional Young's modulus can be described in the following equation⁴²:

$$E = 1/[s_{11}\sin^4\varphi + s_{33}\cos^4\varphi + (2s_{13} + s_{44})\sin^2\varphi\cos^2\varphi + 2(s_{14}\sin 3\theta - s_{25}\cos 3\theta)\cos\varphi\sin^3\varphi] \quad (3)$$

where θ is the azimuthal angle in the xy plane from the x-axis ($0 \leq \theta < 2\pi$), and φ is the zenith angle from the positive z axis ($0 \leq \varphi \leq \pi$). It can be derived from Eq. (3) that E equals $1/s_{33}$ with $\varphi = 0$. The s_{33} value of MDABCO-NH₄-X₃ (X = Cl, Br, I) is 52.3, 60.1, and $73.9 \times 10^{-12} \text{ m}^2/\text{N}$, respectively. Correspondingly, the highest value of the top lobe in Fig. 9c–e is 19.1, 16.6, and 13.5 GPa, respectively. When

it comes to xy plane, $\varphi = \pi/2$ and $E = 1/s_{11}$. Therefore, E value in the xy plane has no relationship with θ and becomes a circle with radius $1/s_{11}$. The s_{11} value of MDABCO-NH₄-X₃ (X = Cl, Br, I) is 110.8, 107.3, and $88.9 \times 10^{-12} \text{ m}^2/\text{N}$, respectively. Their corresponding circle radii in the xy plane are 9.0, 9.3, and 11.2 GPa. In Eq. (3), the only term related with angle θ is $(s_{14}\sin 3\theta - s_{25}\cos 3\theta)$, which means z-axis is a threefold axis. The maximum and minimum values of this term are $\sqrt{(s_{14}^2 + s_{25}^2)}$ and $-\sqrt{(s_{14}^2 + s_{25}^2)}$, respectively. Therefore, the anisotropy with angle θ is only related with $g = \sqrt{(s_{14}^2 + s_{25}^2)}$. The g value of MDABCO-NH₄-X₃ (X = Cl, Br, I) is 112.9, 134.1, and $46.1 \times 10^{-12} \text{ m}^2/\text{N}$, respectively. MDABCO-NH₄-Br₃ has the largest g value, and the g value of MDABCO-NH₄-I₃ is much lower than the others. That is why Fig. 9e looks much smoother than Fig. 9c, d.

In summary, we calculated the structure, electronic density of state, piezoelectric response, and elastic properties of metal-free organic perovskite MDABCO-NH₄-X₃. The MDABCO and NH₄ groups performs like a rigid body in MDABCO-NH₄-X₃, and they are linked to the I₆ octahedron network by H–X interaction. The high ferroelectric Curie temperature is closely related with the break of this H–X interaction. With halogen changing from Cl to I, the tolerance factor of MDABCO-NH₄-X₃ increases from lower than 1 to higher than 1. Based on Born effective charges, the calculated dipole moments of the MDABCO and NH₄ groups are negligible. Therefore, the large spontaneous polarization of MDABCO-NH₄-I₃ mainly results from the off-centers of MDABCO and NH₄ relative to X ions. Our calculated piezoelectric strain component d_{23} (14.4 pC/N) of MDABCO-NH₄-I₃ agrees very well with experimental value (~14 pC/N). Although most organic materials have a very weak piezoelectric response, we found that some piezoelectric strain components of MDABCO-NH₄-X₃ have large values. Among the six independent components, the largest one is d_{x5} . It is 119 pC/N for MDABCO-NH₄-Cl₃, 248 pC/N for MDABCO-NH₄-Br₃, and 179 pC/N for MDABCO-NH₄-I₃. The large value of d_{x5} is closely related with the large value of s_{44} . This means that the large piezoelectric strain

response of MDABCO-NH₄-X₃ is mainly originated from their softness. These unique properties of MDABCO-NH₄-X₃ make them good candidates as soft, low-density and bio-friendly piezoelectrics for various important applications, such as flexible devices, implantable systems, and micro robots.

METHODS

we performed the density-functional calculation using PBE¹⁰ and PBE-D3¹¹ methods as implemented in the Vienna ab initio simulation package (VASP).^{12–14} The projector-augmented wave method was used to represent the electron-ion interaction.⁴⁹ The valence-electron configurations were 2s²2p² for C, 2s²2p³ for N, and ns²np⁵ for halogen. The wave function was expanded in a plane-wave basis set with an energy cutoff of 650 eV and the first Brillouin zone of primitive unit cell was sampled on a 3 × 3 × 3 mesh. The lattice parameters and atomic positions were fully relaxed until stress and forces were <0.05 GPa and 10 meV/Å, respectively. The elastic stiffness is calculated with finite difference method.⁵⁰ It applies six finite strains (three normal and three shearing strains) to an optimized structure. All these six deformations correspond to strains of ±0.015, so as to keep strains in the elastic region. Then, the corresponding stress are calculated and the elastic stiffness constants are obtained by the strain-stress relationship. After that, the elastic compliance is obtained by inverting the elastic stiffness matrix directly. The piezoelectric constants, Born effective charges and zone center phonon frequencies are calculated by VASP package using density-functional perturbation theory.⁵¹ In order to obtain these values, three kinds of perturbations are applied to a crystal. They are atomic displacement away from equilibrium position u_i , strain S_j and electric field E_k . The corresponding responses to these three perturbations are force F_i , stress T_{mj} and polarization P_n . Based on these perturbations and their responses, one can obtain force-constant matrix dF_i/du_i , Born effective charge dP_n/du_i and piezoelectric response dP_n/dS_j .

DATA AVAILABILITY

The data that support the findings of this study are available from the corresponding author (Hui Wang) upon reasonable request.

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AUTHOR CONTRIBUTIONS

H.W., H.H.L., Z.Y.Z., and Z.H.L. did the PBE calculations, Z.L.L., T.W.L., and H.H. did the PBE + D3 calculations. W.W.J., H.S.L., and X.W.C. provided valuable comments and suggestions to the work. H.W. and H.H. wrote the paper. All authors have given approval to the final version of the manuscript.

ADDITIONAL INFORMATION

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