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Pressure-induced reversible framework rearrangement and increased polarization in the polar $[\text{NH}_4][\text{Cd}(\text{HCOO})_3]$ hybrid perovskite

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In this work, we study the structural changes of the polar $[\text{NH}_4][\text{Cd}(\text{HCOO})_3]$ hybrid perovskite under external hydrostatic pressure. We report a reversible framework rearrangement as a function of pressure characterized by: (i) a gradual modification of one formate ligand, which changes its coordination mode from a bridging *syn-anti* mode at atmospheric pressure (LP-phase) to a *chelating-anti* mode at high-pressure (HP-phase); and (ii) a change in the coordination of the Cd^{2+} cations from six-coordinated (LP-phase) to hepta-coordinated (HP-phase). Very interestingly, this unprecedented framework arrangement displays a large electrical polarization. For instance, the polarization value observed at $p = 17.7$ GPa is about four times the polarization at atmospheric pressure. Therefore, we report that the external pressure induces a novel framework rearrangement in the polar $[\text{NH}_4][\text{Cd}(\text{HCOO})_3]$ hybrid perovskite with enhanced electrical polarization. This structure-property relation offers new insights for designing novel ferroelectric materials based on pressure-responsive hybrid perovskite materials.

Introduction

Hybrid organic-inorganic perovskites (HOIPs) are an emerging class of materials with (multi)functional properties of interest for technological applications. They have been found to display a large variety of physical properties^{1,2} (*i.e.* magnetism, ferroelectricity, multiferroicity, photoconductivity), which were traditionally associated to transition metal oxides with perovskite structure (pure inorganic perovskites).^{3,4} Similar to the pure inorganic perovskites, HOIPs also display a general formula ABX_3 . Nevertheless, in this case the A-site

and/or the X-site are occupied by organic cations and/or organic ligands, respectively. Specially well-known are the families with $\text{A} =$ organic cations and $\text{X} =$ halides (hybrid halide perovskites)⁵ or those with $\text{A} = \text{NH}_4^+$ or organic cations and $\text{X} =$ organic anions, such as the hybrid formate perovskites with $\text{X} = \text{HCOO}^-$.²

An important consequence of the incorporation of molecular components to these compounds is the emergence of new structural degrees of freedom for which there is no analogue in conventional perovskites, such as the so-called “forbidden” tilts and the columnar shift degree of freedom.⁶ More importantly, their large structural and chemical diversity offers substantial opportunities for tuning their physical properties by suitable chemical modification.^{7,8} In addition, HOIPs can also respond to different types of physical and chemical stimuli, such as light,¹ pressure,⁹ temperature,¹⁰ electric^{11,12} and magnetic fields.¹³

Since HOIPs are rather soft and flexible materials, the application of external hydrostatic pressure can induce different distortions within the framework. Therefore, these materials can display different types of transformations,^{14,15-16} such as amorphization,^{17,18} metallization,¹⁹ as well as non-reversible^{20,21} and reversible phase transitions.^{22,23-24} Very interestingly, the external pressure can enhance functional properties, such in the case of photovoltaic perovskites,^{25,26} which have been recently rather intensively studied in this regard. Moreover, pressure can induce completely new properties,

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Electronic Supplementary Information (ESI) available: Detail of PXRD patterns and Le Bail refinement of $[\text{NH}_4][\text{Cd}(\text{HCOO})_3]$ upon compression at room temperature. Diagram showing the main changes on the crystal structure caused by applied external pressure. See DOI: 10.1039/C9QI00749K

such as the barocaloric effects²⁷ recently reported for the [TPrA][M(dca)₃] perovskites (TPrA = tetrapropylammonium cations, M = Mn²⁺ and Cd²⁺, dca = dicyanamide ligands).^{28,29} Nevertheless, and at difference with halide perovskites, fundamental high-pressure studies on hybrid perovskites remain relatively much more scarce, probably due to their intrinsic structural complexity. And as it is well-known, such studies would be very useful for gaining insights into the origin of pressure-structure-property relationships. Eventually, they could even lead to the discovery of new polymorphs or to shed light into new materials with improved properties.³⁰

With this aim, in this work we have focused on the hybrid organic-inorganic compound with X = formate [NH₄][Cd(HCOO)₃] with perovskite-like structure. As we had previously reported,³¹ this compound is polar and external pressure markedly increases its polarization (observed by second harmonic generation SHG studies) and induces several phase transitions around 2.5, 6, 10 and 14 GPa (as observed by Raman spectroscopy),³¹ whose nature and characteristics remain to be clarified. At room temperature and ambient pressure, this compound displays a [Cd(HCOO)₃]⁻ framework showing a 4¹²-6³ topology and a perovskite-like architecture with a combination of different structural distortions, which are responsible of the polar nature of this compound.^{31,32} Moreover, this compound is singular and unique (among all the up-to-date reported hybrid metal formates with perovskite structure) because the Cd²⁺ cations are connected by bridging HCOO⁻ anions, where all display only a *syn-anti* coordination mode.³¹ In that context, it should be remembered that even if the bidentate bridge is the usual coordination mode between two metal cations in HOIPs,³³ the *anti-anti* coordination mode is by far the predominant one, even if there are a couple of examples of coexistence of *syn-anti* and *anti-anti* formate bridges in other compounds.³¹

In addition, as recently reported, the coordination of the formate ligand can be switched by an external stimulus (*i.e.* temperature and pressure), thus inducing relevant changes in the crystal structure of the given compound.^{34,35}

Taking into account this background, in this work, we try to shed light on the structural changes and polarization enhancement driven by the application of hydrostatic pressure in the polar [NH₄][Cd(HCOO)₃] compound, previously suggested by SHG and Raman studies.

To achieve this aim, we have made combined efforts to address this challenge from two new approaches, namely by high-pressure powder X-ray diffraction (PXRD) experiments carried out using a conventional X-ray radiation source together with density functional theory (DFT) calculations.

Experimental

Caution! Compounds containing cadmium are highly toxic. Care must be taken when handling the samples, and appropriate disposal procedures are required.

Synthesis

Cd(ClO₄)₂·xH₂O (Aldrich), HCOONH₄ (99.995%, Panreac), absolute methanol (99.5% Panreac) and formic acid (98%, Fluka) were commercially available and used as purchased without further purification.

For the synthesis, 4 mL of a methanol solution containing 0.1 M Cd(ClO₄)₂·xH₂O were placed at the bottom of a glass tube. Upon the Cd²⁺ solution, 4 mL of a methanol solution containing 0.8 M HCOONH₄ and 0.4 M HCOOH were carefully layered. The tube was sealed and kept undisturbed, and colourless crystals with plate morphology were obtained after 2 weeks. They were washed with ethanol and dried at room temperature.

High-pressure powder X-ray diffraction (PXRD) studies

High-pressure powder X-ray diffraction measurements have been carried out with a modified Merrill-Bassett Diamond Anvil Cell (DAC), coupled to an Xcalibur diffractometer. PXRD patterns were collected on a 135-mm Atlas CCD detector, placed at 90 mm from the sample using Kα₁:Kα₂ molybdenum anode. The X-ray beam was collimated to a diameter of 300 μm. A stainless-steel gasket pre-indented to a thickness of 80 μm was used. A 250 μm diameter hole was drilled in the gasket, in which the sample was located. The diamond anvils used have 600 μm culets. Finally, silicone oil was used as pressure-transmitting medium and several ruby chips were distributed in the pressure chamber for measuring the pressure through the ruby fluorescence method. CRYCALIS software was used for data collection and preliminary data reduction.

The obtained PXRD patterns were analyzed by Le Bail profile analysis using the GSAS³⁶ and EXPGUI³⁷ software.

Density functional theory (DFT) calculations

The density functional theory (DFT) method have been used for studying the structural properties and for estimating the electric polarization. The ion-electron interaction is described by the projector augmented wave (PAW) method^{38,39} as implemented in the Vienna *ab-initio* simulation package (VASP).^{40,41} For the exchange-correlation potential we used the PBE⁴² approximation. The plane-wave cut-off energy is set to 550 eV, and all the atoms are allowed to relax until atomic forces are smaller than 0.01 eV/Å on any ion. The electric polarization is computed with the Berry phase method^{35,43-45} by building an appropriate antiferroelectric (AFE) reference state and considering a suitable path in the configurational space connecting to the ferroelectric (FE) state.⁴⁶ In order to save computational time and to simplify the path, after atomic optimization the NH₄⁺ were replaced by K⁺ atoms at the same atomic position of the N atom of the organic cation, while all the other atoms are frozen at previously relaxed atomic positions.

For each structure under different pressures, we studied the pressure-induced phase transitions using the swarm-intelligence CALYPSO method,^{47,48} which enables a global minimization of free-energy (reduced to enthalpy at 0 K) surface merging first-principles total-energy calculations. The method is specially designed for global search of ground-state

structures at given chemical composition and external condition (*i.e.* pressure) unbiased by any known structural information, and it has been successfully applied to predictions of high-pressure phases of various system.⁴⁹⁵⁰⁵¹⁵²⁻⁵³

The Raman spectra have been simulated at the DFT level for the cluster unit $[\text{Cd}(\text{HCOO})_6]^{4-}$, mimicking either ambient pressure or high pressure atoms arrangements. The computations have been performed with the B3LYP⁵⁴ functional including D3(BJ)^{55,56} dispersion correction, which allows good reproduction of vibrational spectra in the solid state by cluster models.⁵⁷ The basis set 6-31+G(d,p) has been used for H, C and O atoms in conjunction with the Stuttgart-Dresden electron core pseudopotential⁵⁸ for the Cd⁵⁹. These computations employed the Gaussian suite of programs.⁶⁰

Results and discussion

High-pressure PXRD experiments

We have studied the crystal structure evolution of $[\text{NH}_4][\text{Cd}(\text{HCOO})_3]$ perovskite under pressure by in situ high-pressure PXRD experiments. The obtained patterns of $[\text{NH}_4][\text{Cd}(\text{HCOO})_3]$ from atmospheric pressure (p_{atm}) to 17.7 GPa are shown in Figure 1.

A smooth evolution of the PXRD patterns with applied pressure is observed, without any dramatic change in response to external pressure, not even at the pressures for which Raman spectroscopy under pressure suggested the existence of phase transitions.³¹ Nevertheless, a more careful look at the obtained patterns (whose limited resolution is due to the complexity of DACs experimental setup), reveals several pressure-driven phase transitions. These transitions are evidenced by the splitting of some peaks, the broadening of other peaks, and the appearance of new diffraction peaks under the applied pressure. It should be noted that such pressure-driven structural modifications are reversible, and the atmospheric pressure crystal structure is recovered after decompression (see Fig. S1 of ESI).

In order to study the evolution of the crystal structure with applied pressure, we carried out Le Bail refinement of the obtained high-pressure PXRD patterns (see Fig. S2-24 of ESI).

In this context, and from the evolution of the PXRD patterns as a function of pressure, we concluded that the clearest phase transition occurs around 9.0 GPa, pressure at which Raman spectroscopy also detects a sharp change. Therefore, we focus our studies on such phase transition, even if other weaker changes are also observed at 2.2, 6.3 and 14.3 GPa (also in agreement with our previous Raman spectroscopy results³¹).

According to the Le Bail fitting of the PXRD patterns at around 9.0 GPa, the low-pressure phase (LP-phase) with orthorhombic symmetry (space group $Pna2_1$) transforms into a high-pressure phase (HP-phase) with monoclinic symmetry. It should also be noted that in the proposed HP-phase, the a - and c -axes are swapped with respect to those of the LP-phase (see Figure 2 and 3).

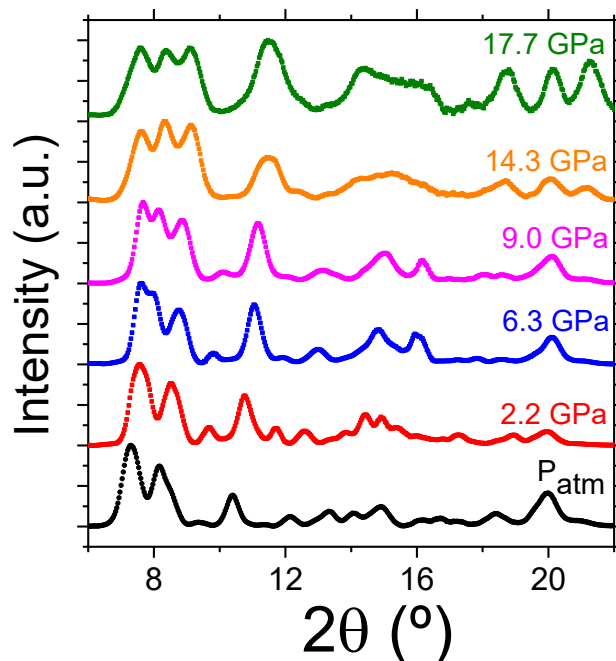


Figure 1. Representative examples showing the evolution of the PXRD patterns of $[\text{NH}_4][\text{Cd}(\text{HCOO})_3]$ with pressure, from P_{atm} up to 17.7 GPa, at room temperature

The evolution of lattice parameters of these two crystal structures under pressure is shown in Figure 2 and table S1 of ESI. As it can be seen, a sharp decrease of cell parameters and cell volume takes place upon application of pressure around $p \sim 9.0$ GPa (the volume of the HP-phase is around 5.5 % smaller than the LP-phase), which indicates a first order phase transition with substantial changes in the atomic arrangement. In addition, the HP-crystal structure shows an anisotropic compressibility for pressures above 9.0 GPa, where the cell parameter c increases with pressure while the a and b parameters decrease. As a result, the cell volume remains finally almost constant for $p > 9.0$ GPa. It worth noting that this unusual phenomenon has also been reported -among framework materials- in $[\text{C}(\text{NH}_2)_3][\text{Cd}(\text{HCOO})_3]$ and $\text{Ag}_3[\text{Co}(\text{CN})_6]$.^{61,62,63}

The volume-pressure (V - P) data for the LP-phase were fitted (see Fig. S25 of ESI) with second-order Birch-Murnaghan (BM) equations of state (EoS) and the isothermal bulk modulus for LP-phase was found to be 32(1) GPa, which lies in the range of values for dense MOFs (~ 30 – 58 GPa).^{64,65-66} This value is very similar to the values reported for $[\text{tmenH}_2^{2+}][\text{Er}(\text{HCOO})_4]_2$ ($\text{tmenH}_2^{2+} = \text{N,N,N',N'}$ -tetramethylethylenediammonium), which is about 13.8(4) GPa and 31.5(6) GPa for phases I and II, respectively.³⁵ The isothermal axial compressibility (β) of the LP-phase was estimated as $\beta_a = 7.2(2) \times 10^{-3} \text{ GPa}^{-1}$, $\beta_b = 4.5(2) \times 10^{-3} \text{ GPa}^{-1}$ and $\beta_c = 6.1(2) \times 10^{-3} \text{ GPa}^{-1}$. The a and c axes display the greatest degree of compressibility, which confirms that the structure is more easily deformable along these axes.

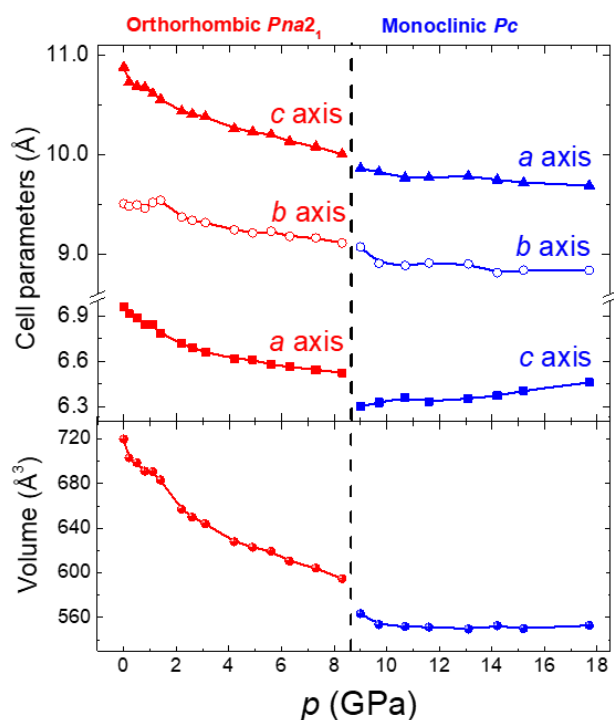


Figure 2. Unit cell parameters (top) and volume (bottom) of $[\text{NH}_4][\text{Cd}(\text{HCOO})_3]$ as a function of pressure as obtained from Le Bail fitting of the PXRD-patterns.

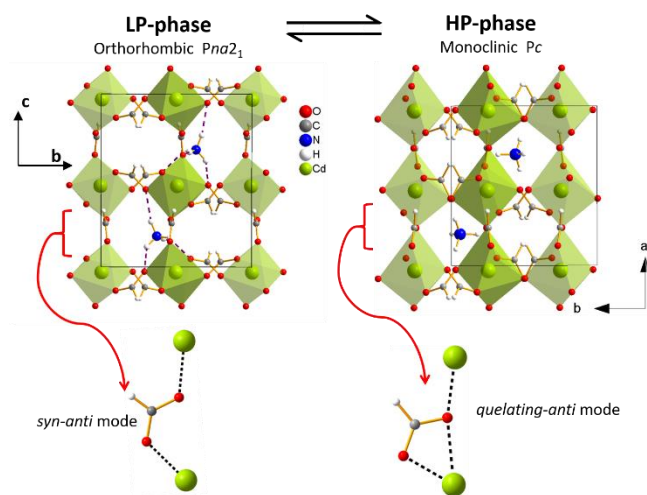


Figure 3. (Top) crystal structures of LP- and HP-phases of $[\text{NH}_4][\text{Cd}(\text{HCOO})_3]$. (Bottom) . Detail of the coordination mode of the formate ligand, which changes from an *syn-anti* bridging mode in the LP-phase to a *chelating-anti* mode in the HP-phase.

Crystal structure at high-pressure from DFT calculations

In order to elucidate the microscopic mechanism of the structural changes under pressure, the atomic coordinates of the $[\text{NH}_4][\text{Cd}(\text{HCOO})_3]$ compound at p_{atm} , 1.4, 4.2, 8.3, 11.6 and 17.7 GPa were refined by first-principles geometry optimization (CALYPSO method) based on the experimental cell parameters. The previously reported crystal structure³¹ at p_{atm} was employed as starting structural model.

Once the geometry optimization of the atomic coordinates and cell parameters was reached without the restraint of a space group, taking into account the atomic positions inside the unit cell, we could determinate the space group of the obtained crystal structure, which turned out to be Pc in the case of the HP-phase. The obtained HP-phase (see table S2 of ESI) can adequately simulate the experimental data obtained from the High-Pressure X-ray diffraction experiments (see Figure S26 of ESI).

The crystal structure of the HP-phase in comparison with the LP-phase, as well as the structural details of the formate ligand in both phases, are shown in Figure 3.

According to our results, the HP-phase is described by a polar space group Pc and it has an anionic $[\text{Cd}(\text{HCOO})_3]^-$ framework with a perovskite-like topology, even if it is very distorted, and where the NH_4^+ cations are located inside the resulting and also very distorted cavity.

Surprisingly, in this HP-phase the Cd^{2+} cations are no longer six-coordinated (as in the case of the LP-phase and the “conventional” perovskite structure) but is hepta-coordinated, as shown in Figure 4. As shown there, in the HP-Phase each Cd^{2+} cation is connected to its six nearest neighbour metal cations through six formate bridges, where four of them exhibit a *syn-anti* configuration (within the bc plane) whereas another two show a *chelating-anti* mode (along the a axis), thus finally resulting in a coordination number of 7 in a “pseudo” pentagonal bipyramid environment. Therefore, the most prominent differences between LP-phase and HP-phase are: (i) the change of coordination of part of the formate bridges from *syn-anti* mode in the LP-phase to *chelating-anti* mode in the HP-phase (see Fig. 3), and (ii) the change of coordination of the Cd^{2+} cations from six-coordinated in the LP-phase to hepta-coordinated in the HP-phase (see Figure 4).

Even if it is well-known that the formate ligand can display different coordination modes⁶⁷ (*i.e.* mono- and bidentate bridging and chelating modes), and the *chelating* mode is observed in lanthanide metal-formate systems, this is the first time that such coordination is found in transition metal-formate systems.⁶⁸ Moreover, it should be noted that the here observed pressure-induced bond rearrangements is different from those reported in the literature (*i.e.* $[\text{EtNH}_3][\text{Cu}(\text{HCOO})_3]$,³⁴ and $[\text{tmenH}_2][\text{Er}(\text{HCOO})_4]$ ³⁵) where a change of coordination of the formate ligand from *chelating*

mode in the LP-phase to *anti-anti* mode in the HP-phase was reported. Even more, the number of examples reporting seven-coordinated Cd^{2+} compounds are very scarce, and none of these compounds are mononuclear or involves monodentate ligands.⁶⁹

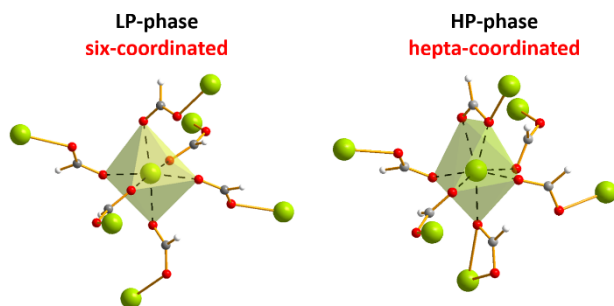
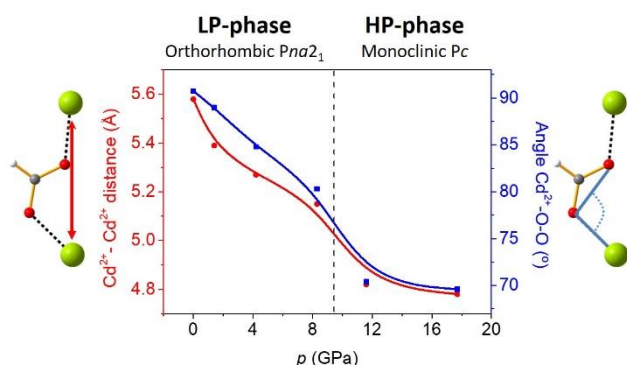


Figure 4. Detail of the coordination environment of Cd^{2+} cations, namely six-coordinated in the LP-phase (left), and hepta-coordinated in the HP-phase (right).

From a deeper structural point of view, this complex pressure-driven phase transition, is related to the presence of the unusual *syn-anti* bridging coordination mode in the formate ligands of this hybrid organic-inorganic perovskite. In fact it is the rotation of two of these *syn-anti* formate ligands which are along the *c*-axis which gives rise to the modifications observed in this compound upon application of pressure, namely the high deformation of the framework structure, the change of the coordination environment of the Cd^{2+} cations and the change of the coordination mode of part of the formate ligands (see Fig. 4 and sketch in Fig. S27 of ESI). In addition, the mentioned rotation of such formate ligands upon compression induces a notable decrease in the Cd^{2+} - Cd^{2+} distance along the *c* axis of the LP-phase and along the *a* axis of the HP-phase (see Fig. S27 of ESI). The evolution of this distortion can be observed through the variation of the Cd^{2+} -O-O angle of the formate ligand and the Cd^{2+} - Cd^{2+} distance with applied pressure. As shown in Figure 5, both parameters exhibit a marked decrease upon compression in the LP-phase and display a sharp change at the phase transition. Additionally, both parameters remain almost constant under compression



in the HP-phase

Figure 5. Evolution of Cd^{2+} - Cd^{2+} distance and Cd^{2+} -O-O angle (showing the rotation of formate ligand) as a function of pressure.

In order to gain more insight and support for the proposed HP-crystal structure, we have also performed DFT calculations to see if such changes would have a direct and clear reflection in the vibrational spectra of this compound under pressure.

For this purpose, we have carried DFT calculations to estimate the vibrational frequencies of the ambient pressure phase and the HP-phase at $P = 17.7$ GPa, and obtain a more detailed assignment of the vibration modes. It is worth noting that due to the large amount of atoms at both phases, the theoretical studies have been performed in a cluster unit $[\text{Cd}(\text{HCOO})_6]^{4-}$, solution which allows to carry the calculations without compromising the reliability of obtained results.²³

Also, taking into account that pressure-induced changes bring about a strong distortion of the anionic framework, and a change in the coordination mode of some of the formate ligands we specially focused on vibrational modes related to HCOO^- , such as, the O-C-O bending mode [$\nu_3(\text{HCOO}^-)$] and the out-of-plane H-C mode [$\nu_6(\text{HCOO}^-)$].

According to DFT simulations of the Raman spectrum at ambient pressure, where all formate ligands form *syn-anti* bridges, both [$\nu_3(\text{HCOO}^-)$] and [$\nu_6(\text{HCOO}^-)$] modes are Raman active give and give rise to single peaks at 760 cm^{-1} and 1060 cm^{-1} , respectively, in full agreement with the experimental Raman results, see reference 31 and Fig. S28 of ESI

Very interestingly, DFT Raman simulations show a different situation in the HP phase. In this context DFT results predict that the coexistence of *syn-anti* bridging formate ligands together with *chelating-anti* formate ligands will give rise to the appearance of more signals corresponding to new O-C-O bending modes. And that the vibration related to the bending of the *chelating-anti* bridging ligand will appear at higher wavenumbers than those of the *syn-anti* ones, see Fig. S28 of ESI. The reason relies on the stronger constrains of the *chelating-anti* bridging ligand (linked through three Cd-O bonds with two different Cd^{2+} cations), which results in a more hindered O-C-O bending vibration than in the case of the *syn-anti* ligands (linked through two bonds to two different Cd^{2+} cations).

On the other hand, for the out-of-plane H-C mode [$\nu_6(\text{HCOO}^-)$] the DFT calculations also predict that it will no longer appear as a signal peak in the Raman spectrum of the HP phase, but splitted, with a new wavenumber vibrations related to the *chelating-anti* bridging ligand and presence of several inequivalent *syn-anti* ligands. Such softening of the H-C bending mode experienced by the *chelating-anti* ligands in turn implies that the increase in the coordination number of this type of ligand results in a weakening of this internal bond compared to the case of the rest of the *syn-anti* formate ligands.

In addition, the general shortening of the C-H bonds under pressure also result in a slight blue shift of the *syn-anti* bending vibrations compared to the ambient pressure phase.

As shown in Fig. S28 of ESI, the experimental high pressure Raman data can be interpreted with the DFT predictions, supporting the here reported HP-phase, where the coexistence of two coordination modes in the formate ligands induce the

presence of novel Raman peaks with the expected shifts in their wavenumbers.

Polarization at high-pressure from DFT calculations

As we already mentioned, both the LT- and HP-phases display a polar structure. Furthermore, the previously reported experimental SHG results suggest a marked increase in polarization upon application of pressure.³¹ In this work, to confirm that the proposed high-pressure crystal structure supports an increase of polarization, we have performed DFT calculations.

For a given pressure, the optimized structure obtained by CALYPSO has been used to compute the ferroelectric polarization. For a given structure, we introduce a computational reference centric structure which allows us to build an appropriate path for evaluating the polarization. The centric structure has been constructed using a computational crystallographic approach as implemented in the software PSEUDO.⁷⁰⁷¹⁻⁷²

As an example, Figure 6 shows the calculated polarization (P) at 17.7 GPa. The $\lambda = 0$ represents the centric reference structure, and $\lambda = 1$ represents the optimized ferroelectric structure. A smooth variation of the polarization is obtained along the interpolating path, which assures that no polarization quanta is included in the calculation.

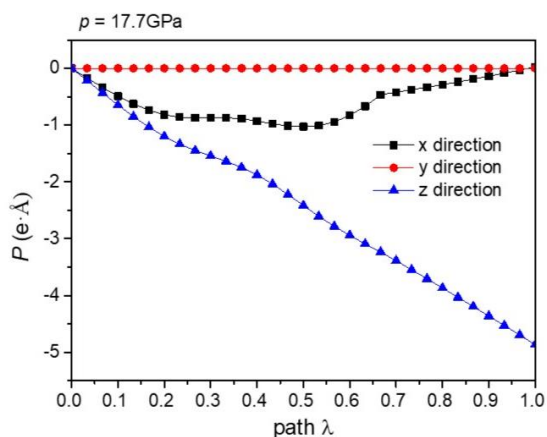
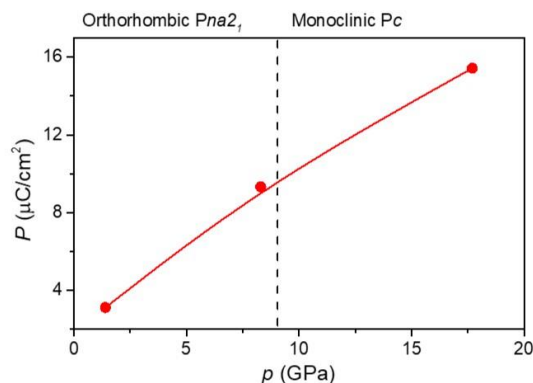


Figure 6. Calculated polarization for 17.7 GPa structure along the main directions as a function of path λ , where the $\lambda = 0$ represents the centric structure and $\lambda = 1$ represents the optimized FE structure.

We have performed the same type of calculation for each different structure corresponding to three different pressure. The calculated polarization as a function of pressure is reported in Figure 7. From the obtained results it is clear that the pressure-driven polarization is around four times the polarization at p_{atm} , with a saturated value of $P \sim 16 \mu\text{C}/\text{cm}^2$ along the z direction. Our calculations clearly show that the polarization increases as the pressure increases, in very good agreement with the experimental data.³¹

Figure 7. Calculated polarization (P) for different crystal structures as a function of



pressure (p) along the z direction.

Therefore, the unprecedented framework arrangement of the HP-phase induces a large polarization in the $[\text{NH}_4][\text{Cd}(\text{HCOO})_3]$ perovskite, mainly due to the cooperative tilting of one formate ligand under high pressure. In particular, the cooperative tilting of one formate ligand under external pressure could be related to a large polarization. In order to gain more insights into this phenomena we performed a *functional group analysis* of the polarization.⁷³ Considering the path connecting the centrosymmetric to the polar structure in the configuration space and starting from the centrosymmetric reference structure, one can activate the atomic displacements corresponding to a particular functional group and evaluate the electric polarization (P). For the ABX_3 perovskite framework topology, this means that one can calculate P_A and P_{BX_3} as the induced polarization due to the atomic displacements at the A site keeping the BX_3 framework at centrosymmetric position, or viceversa. The two contributions usually add linearly to give approximately the total polarization calculated by considering all the correlated atomic displacements (as shown in Figure 6). In our case, we used such approach, but the sum of two contributions significantly differs from the total polarization. This suggests that the structure is significantly distorted under high-pressure, so that the linearity in the functional group analysis of the polarization does not hold anymore. However, we have observed that the high-pressure induces correlated atomic distortions, which, collectively, give rise to an increase of polarization. We can conclude here that high-pressure and high-polarization are “positively correlated”. Last, but not least, a comment is in order. It is very well-known that the effects of the external pressure can also be driven by internal chemical pressure within the perovskite crystal structure.⁷⁴ For this reason, our work opens the door to future challenges for designing novel FE hybrid perovskites with singular crystal structure and large polarization (as here reported) induced by internal chemical pressure.

Conclusions

This work shed a new light on the structural transformations and polarization increase driven by the application of hydrostatic pressure in the polar $[\text{NH}_4][\text{Cd}(\text{HCOO})_3]$ hybrid perovskite.

This compound displays a reversible framework rearrangement as a function of the applied external pressure, which mainly involves: (i) a change in the coordination mode of one formate ligand from a bridging *syn-anti* mode to a *chelating-anti* mode, and (ii) a change in the coordination of the Cd^{2+} cations, from six-coordinated to hepta-coordinated. Very interestingly, this unprecedented framework arrangement induces a large polarization, $P \sim 16 \mu\text{C}/\text{cm}^2$.

Therefore, the external pressure is responsible for a singular framework arrangement and a large polarization in the $[\text{NH}_4][\text{Cd}(\text{HCOO})_3]$ hybrid perovskite.

This novel crystal structure highlights the interest for designing novel ferroelectric materials based on pressure-responsive formate ligands. Moreover, this work encourages future studies on similar structural rearrangement and polarization enhancement induced not only by hydrostatic pressure, but also by internal chemical pressure.

Conflicts of interest

There are no conflicts to declare. All authors have contributed equally to the work.

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