Properties and mechanism of strain and piezoelectricity of hybrid molecular ferroelectrics

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2020

Hu, Y. (2020). Properties and mechanism of strain and piezoelectricity of hybrid molecular ferroelectrics. Doctoral thesis, Nanyang Technological University, Singapore.

<https://hdl.handle.net/10356/145124>

<https://doi.org/10.32657/10356/145124>

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**PROPERTIES AND MECHANISM OF STRAIN AND
PIEZOELECTRICITY OF HYBRID MOLECULAR
FERROELECTRICS**

HU YUZHONG

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PIEZOELECTRICITY OF HYBRID MOLECULAR
FERROELECTRICS**

HU YUZHONG

SCHOOL OF PHYSICAL AND MATHEMATICAL SCIENCES

A thesis submitted to the Nanyang Technological
University in partial fulfilment of the requirement for the
degree of Doctor of Philosophy

2020

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Authorship Attribution Statement

This thesis contains materials from 1 accepted paper, in which I am listed as an author.

Chapter 3-5 is published as Yuzhong Hu, Lu You, Bin Xu, Tao Li, Samuel Alexander Morris, Yongxin Li, Yehui Zhang, Xin Wang, Pooi See Lee, Hong Jin Fan and Junling Wang, Nature materials, accepted

The contributions of the co-authors are as follows:

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- I performed all the laboratory work and analyzed the data at School of Materials Science and Engineering, and School of Physical and Mathematical Sciences with assistance from Lu You and Tao Li.
- I prepared the manuscript drafts. The manuscript was revised by Lu You, Prof. Junling Wang and Prof. Hong Jin Fan.
- The density function theory (DFT) calculations were conducted by Yehui Zhang, Xin Wang and Prof. Bin Xu.
- The crystal structure X-ray diffraction (XRD) measurement were performed and analyzed by Samuel Alexander Morris and Yongxin Li.

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Acknowledgements

Great gratitude to my supervisors Prof. Fan Hong Jin and Prof. Wang Junling, for their guidance and patience, which not only cultivate me into a researcher but also lead me to a mature individual. They corrected tons of my mistakes in research strategy, data analysis, English writing and communication skills. And many thanks for their full support in access to central facility and building collaborations. Without their helps, it is impossible for me to finish this journey.

Sincere thanks to Prof. You Lu for his invaluable guidance on experimental skill, theoretical knowledge and English writing, which are the real treasure for me. Special appreciation to Prof. Yong Ee Hou, who conducted entry exam and interview in Sichuan University and chose me as the PhD candidate among all applicants.

Many thanks to collaborators and my group mates, including Prof. Xu Bin, Prof. Lee Pooi See, Prof. Yu Ting, Prof. Sum Tze Chien, Prof. Gao Weibo, Prof. Dong Shuai, Dr. Li Tao, Dr. Samuel Alexander Morris, Dr. Li Yongxin, Dr. Pio. John. S. Buenconsejo, Mr. Zhang Hongbo, Mrs Zhou Xinran, Dr. Chong Wee Kiang, Dr Ke Yujie, Dr. An Hongjie, Dr. Zheng Shoujun, Dr. He Haiyong, Mr. Zhang Zhaowei, Dr. Zhang Yongqi, Dr. Chao Dongliang, Dr. Zhu Changrong, Dr. Xu Kun, Dr. Nguyen Huy Tiep, Dr. Tang Shasha, Dr. Jia Guichong, Dr. Shen Chao, Dr. Hu Songbo, Dr. Zhou Shuang, Dr. Chang Lei, Mr. Amr Abdelsamie, Dr. Zhou Yang and Prof. OuYang Bo for the discussions and assistance during my PhD study.

Last but not least, I would like to give my deepest gratitude to my family for their love and support in this journey.

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Summary

Ferroelectrics are materials with spontaneous polarization that can be reversed by external electric field. Because of the polarized structure and electrically driven domain reversibility, ferroelectrics possess numerous electronic applications, including memory devices, sensors, and energy conversion device. Based on their structural and composition differences, ferroelectrics can be divided into different categories including oxide perovskite, inorganic salt, organic ferroelectrics and organic-inorganic hybrid systems. Among all these material families, oxide perovskites are so far the most intensively studied ferroelectrics in both fundamental research and industrial fields. For instance, lead zirconate titanate (PZT) is used as translation actuator in various micropositioning applications due to its fast response speed and high stiffness. However, the future perspectives of electronic devices require materials to be lightweight, thin, and bio-friendly, while most of these traditional oxide ferroelectrics have low mechanical flexibility, high temperature synthesis requirement and contain toxic elements.

Organic-inorganic hybrid ferroelectrics (OIHF) possess the unique organic and inorganic mixed composition. The organic part grants this hybrid system with advantages of organic ferroelectrics such as easy processing, lightweight, and mechanical flexibility, while the inorganic framework brings in high mechanical strength and semiconductor properties including photoluminescence, photovoltaics and other photo-electronic effects. With this hybrid composition and high structure flexibility, OIHFs receive great attention as electromechanical materials and multifunctional materials in recent years. Since 2014, more than forty new OIHFs have been successfully discovered. Their structures vary from 0D to 3D and applications cover optical, ferroelectric and electrostrictive fields. Particularly, with rational molecule design, the piezoelectric responses of some hybrid structures have even outperformed traditional oxide ceramics such as bismuth titanate and PZT.

In Chapter 3, we report the discovery of a new OIHF and investigate the influence of the halide part on its ferroelectricity. In previous reports, OIHFs were found to lose their ferroelectricity even with a very low level of halide substitution, making the investigation to the role of halide part in OIHFs ferroelectric mechanism quite challenging. In this chapter,

the structure and ferroelectric properties of a new solid solution, $\text{C}_6\text{H}_5\text{N}(\text{CH}_3)_3\text{CdBr}_{3x}\text{Cl}_{3(1-x)}$ ((PTMA) $\text{CdBr}_{3x}\text{Cl}_{3(1-x)}$) are systematically investigated. Different with other OIHF, the ferroelectricity of this hybrid structure is well preserved throughout bromide to chloride substitution. This enables us to disclose the role of halide part in OIHF ferroelectricity. Through systematic characterization, we find Br substitution has obvious softening effect, which leads to faster switching speed, lower switchable temperature and lower coercivity (E_c). The crystallography results indicate that this softening effect should originate from strength weakening on hydrogen and Cd-halide (Cd-X) bonds.

In Chapter 4, the design strategy and discovery of the colossal shear strain in this OIHF will be presented. Materials with controllable strain is highly desirable in shape memory devices, sensors and actuators. So far, great efforts have been made to realize and optimize strain output in various material systems, including shape memory alloy, electrostrictive polymer and ferroelectrics. However, few of them can achieve high output in both stress and strain. In this chapter, we discuss the properties and origin of the colossal shear strain (21.5%) in (PTMA) $\text{CdBr}_{3x}\text{Cl}_{3(1-x)}$, which is two orders of magnitude higher than general ferroelectrics and much larger than all shape memory alloys. The giant strain stems from non-180°ferroelastic switch induced by special structure confinement effect, while its decent stress output should come from its strong inorganic backbone.

Chapter 5 discusses the piezoelectric properties and relevant mechanism in this solid solution. The Br substitution in this OIHF effectively softens its lattice and leads to this giant piezoelectric response. In Br rich sample, d_{35} can reach 4800 pm/V, which is much larger than other hybrid structures (up to 2560 pm/V) and is comparable to top-performance Pb based relaxor (5000 pm/V).

In summary, this thesis presents the discovery of a new OIHF (PTMA) $\text{CdBr}_{3x}\text{Cl}_{3(1-x)}$ which gets both colossal shear strain and piezoelectric responses. The mechanism of these giant electromechanical properties and the role of the halide part in the ferroelectricity of this solid solution are systematic investigated. These outstanding strain output and piezoelectric performances make this OIHF a good candidate as flexible devices, microelectromechanical systems and wearable electronics. In addition, our design strategy for high strain output crystal structure and insights to the soften mechanism in hybrid ferroelectric system should

shed light on the discovery of new OIHF_s with excellent electromechanical and ferroelectric properties.

List of Abbreviation

0, 1, 2, 3D: Zero, one, two, three dimension
DFT: Density function theory
XRD: X-ray diffraction
PZT: Lead zirconate titanate
OIHF: Organic-inorganic hybrid ferroelectric
PTMA: Trimethylphenylammonium, $\text{C}_6\text{H}_5\text{N}(\text{CH}_3)_3^+$
Cd-X: Cd-halide bond
E: Electric field
P: Polarization
PE: Polarization-Electric field
Ec: Coercivity
 P_r : Remnant polarization
 P_s : Saturation polarization
AC: Alternating current
SE: Strain-electric field
MPB: Morphotropic phase boundary
FeRAM: Ferroelectric random access memory
PVDF: Polyvinylidene fluoride
MOF: Metal organic framework
HT: High temperature
HTP: High temperature phase
LT: Low temperature
LTP: Low temperature phase
PFM: Piezoresponse force microscopy
PMN-Pt: $(1-x)\text{Pb}(\text{Mg},\text{Nb})\text{O}_3-x\text{PbTiO}_3$
IR: Infrared

PL: Photoluminescence
FET: Field effect transistor
HPF: Hybrid perovskite ferroelectric
RT: Room temperature
DSC: Differential scanning calorimetry
T_P: Phase transition temperature
SMA: Shape memory alloys
MSMA: Magnetic shape memory alloys
FSMA: Ferromagnetic shape memory alloys
TSMA: Temperature driven shape memory alloys
SMM: Shape memory materials
SMP: Shape memory polymer
VRMSMA: Variant reorientation magnetic shape memory material
SMC: Shape memory composite
TGA: Thermogravimetric analysis
PUND: Positive-up-negative-down method
DFT: Density functional theory

Chapter 1: Introduction

1.1 Ferroelectric materials

1.1.1 Basic concepts and properties

Ferroelectricity and piezoelectricity

Ferroelectrics are materials with spontaneous polarization that can be reversed by external electric field (E). Ferroelectric states at different polarization (P) directions are thermally equivalent (Fig. 1.1). In atomic scale, polarization can be regarded as array of long-range ordered unit cells at the same polar state. A ferroelectric material should possess at least two spontaneous polarization states with absence of E . A region of crystal sitting on the same P state is called domain.

Figure 1.1 (a) Energy-atomic displacement diagram of a ferroelectric system with two polarization states. (b) Up- and downward polarization in PbTiO_3 unit cell. The figure is adapted from reference 1.

Piezoelectricity is the phenomenon of electric charge induction at material surface under external stress. The invert piezoelectric effect is the straining of materials with applied

electric field. Ferroelectrics are all naturally piezoelectric due to the existence of spontaneous electric dipole in unit cell. The deformation and polarization of piezoelectrics can be expressed in two forms, stress-charge and strain-charge. For the convenience of discussion in later chapters, here I introduce piezoelectric concepts in strain-charge form.

The strain and charge in materials can be characterized as:

$$\mathbf{S} = s_E \mathbf{T} + d \mathbf{E}$$

$$\mathbf{D} = d \mathbf{T} + \varepsilon \mathbf{E}$$

Where $\mathbf{S}$, $\mathbf{T}$, $\mathbf{E}$, $\mathbf{D}$ are strain, stress, electric field and electric displacement in vector form, respectively. s_E , d and ε are the matrix of compliance, piezoelectric coefficient and permittivity, respectively.

In invert piezoelectric effect, external stress is zero, electric field induced strain and electric displacement can be written as:

$$\begin{pmatrix} S_1 \\ S_2 \\ S_3 \\ S_4 \\ S_5 \\ S_6 \end{pmatrix} = \begin{pmatrix} d_{11} & d_{21} & d_{31} \\ d_{12} & d_{22} & d_{32} \\ d_{13} & d_{23} & d_{33} \\ d_{14} & d_{24} & d_{34} \\ d_{15} & d_{25} & d_{35} \\ d_{16} & d_{26} & d_{36} \end{pmatrix} \begin{pmatrix} E_1 \\ E_2 \\ E_3 \end{pmatrix}$$

Figure 1.2 Tensor directions of strain and piezoelectric effect.

The direction of S_i and d_{ij} tensor are illustrated in fig. 1.2. In ferroelectric and piezoelectric systems, direction 3 should be the poling direction. Direction 4, 5, 6 are the

planes parallel to the normal plane of axis 1, 2, 3, respectively. The subscript i of piezoelectric coefficient d_{ij} indicates the direction of E , while j indicates the direction of triggered strain.

Strain-electric field (SE) and polarization-electric field (PE) behavior

Switching between different ferroelectric states induces polarization-electric field hysteresis loop (PE loop), which are characterized by following parameters:

Coercivity (E_c): The electric field where net polarization is zero.

Remnant polarization (P_r): The magnitude of polarization at zero electric field.

Saturation polarization (P_s): The polarization at the intersection of polarization axis and tangent of P versus E line at linear region.

Figure 1.3 A typical PE loop of a PZT film. Circles with arrows indicate polarization state of the material at indicated E . The figure is adapted from reference 2.

To illustrate the polarization switching mechanism, here I take the PE behavior of a (111) oriented PZT thin film (fig.1.3) as an example. The PE loop is obtained by using

Sawyer–Tower circuit³. Under small Alternating current (AC) field (AB segment), the E is not strong enough to switch the domains with unfavorable polarization directions. P and E thus has linear relationship according to $P = \epsilon_r \epsilon_0 E$, where ϵ_0 is vacuum permittivity and ϵ_r is dielectric constant. In BC segment, E keeps increase and unfavorable polarization starts aligning with electric field. With the contribution of P from these switched domains, PE relationship becomes highly nonlinear. After all polarization are reversed (C point), the linear relation becomes valid again (CD). Electric field then starts to decrease (DE part), some domains (pinned because of influences such as from defect) will switch back. Because of the hysteresis effect, the polarization at E point would be non-zero. Its magnitude is remnant polarization. The zero-polarization point is at E_c in reversed direction (point F). Keep E increasing will lead to new alignment and finally meet saturation (G point) again. Electric field then decreases and complete the cycle.

However, it is noteworthy that the hysteresis effect of PE behavior is necessary but not sufficient to establish ferroelectricity. Non-intrinsic hysteresis effect such as homocharging can also lead to similar PE behavior. Typical materials with this effect are electrets like carnauba wax⁴, which gets high density of charged defects. Under electric field, these mobile defects can be driven to top and bottom surface of the samples. Nevertheless, the polarized and initial states are not equivalent, so these driven charges will inevitably, relax back to ground state. Due to this polarization instability, electrets can not be used in ferroelectric applications such as memory device.

In addition to hysteresis in polarization, switching between polarization states would simultaneously induces strain-electric field (SE) hysteresis effect. Here we use a reported instructive description⁵ to illustrate strain behavior during an E cycle. Fig. 1.4 (a) shows an idealized SE loop with assumption that ferroelectric domain can be instantly switched. Here the zero strain point is set as the strain at zero electric field. First, electric field increases to its maximum while strain increases (trace A-B-C) according to piezoelectric effect $S_3 = d_{33}E_3$. E then starts to decrease to zero and increase in negative direction. The strain traces back to zero at point A and then contracts with respect to zero E point. At point E, electric field is large enough to switch polarization after which P is parallel to electric field and strain becomes positive again. Next, electric field increases to point F and decrease to zero while

strain expands and contracts according to piezoelectric effect. After E decreases to zero and goes to opposite direction again, switch of polarization happens again at G point, leading to the sudden change in strain. Then follow piezoelectric effect, strain will expand and decrease again along G-C-A trace and finishes the cycle.

Figure 1.4 (a) Idealized SE curve in ferroelectrics. (b) Actual PE and SE loop in monodomain $\text{Pb}(\text{Zr}_{0.53}\text{Ti}_{0.47})\text{O}_3$ thin film. The figure is adapted from reference 2.

The case of experimental SE curve is more complicated. Here polarization switch is a gradual but not sudden process, leading to obvious nonlinear S behavior (fig. 1.4b). In addition, effects such as non-180°ferroelastic switch and domain pinning also make the curve behaves differently to the ideal case. Specifically, non-180°polarization switch is associated with dimension change in lattice thus may induce additional strain other than intrinsic piezoelectricity. Fig. 1.5 illustrates a ferroelastic switch between crystallographic **a** and **c** axis corresponding to 90°dipole rotation. The corresponding straining in the lattice is $1-c/a$, where c and a are dimension of unit cell along **c** and **a** axis. The theoretical strain of BaTiO_3 ($a = 3.994 \text{ \AA}$, $c = 4.034 \text{ \AA}$) and PbTiO_3 ($a \sim 3.902 \text{ \AA}$, $c \sim 4.156 \text{ \AA}$) are 1%² and 6%⁶, respectively, which is one order of magnitude higher than the strain induced by piezoelectric effect. However, no recoverable strain has been realized at this scale in these two ferroelectrics so far because all ferroelastic states are identical in energy. Consequently, there is no force to re-establish the ferroelastic state after removing electric field⁷. The largest strain achieved in most ferroelectrics are still below 1%⁸.

Figure 1.5 Ninety degree ferroelastic switching in tetragonal ferroelectrics. The figure is adapted from reference 9.

Phase transition property

Most ferroelectrics undergo structural phase transitions with temperature change. The transition can be ferro- to paraelectric, ferro- to piezoelectric or successive transitions between different ferroelectric phases. In the perspective of energy structure, these phase changes are attributed to increasing in kinetic energy of particle (usually oxygen, hydrogen or fluorine) hopping over state energy barriers. For example, ferroelectric-paraelectric phase transition in ferroelectrics with two polarization states can be regarded as the thermal process where particle obtains enough energy to overcome the energy barrier in double-wall structure (see fig. 1.1a). The particle would consequently move around in an energy region centering at zero atomic displacement position. With time averaging, the polarization of unit cell becomes zero and thus induces paraelectric phase in bulk crystal. There are two types of phase transitions varying energy structure change. The first is order-disorder type, where the double wall structure is independent to temperature while only the kinetic energy changes during the phase transition. Another case is displacive transition, where potential energy shows obvious shift with temperature change. Particularly, the energy structure of this type would change dramatically near transition temperature, with its minimum energy positions merging to the midpoint and lead to paraelectric phase. This process may finish with only minor change in ion kinetic energy.

Phase transitions in ferroelectrics can also be classified regarding the derivative discontinuity of Gibbs free energy near phase transition temperature (T_P). First order transition refers to structure change with discontinuous derivative at first order. Second order transition means this first order derivative is continuous while the second order is not¹⁰. At ferro-paraelectric phase transition, P decreases to zero with discontinuous change in first order ferroelectrics and continuous change in second order ferroelectric (Fig.1.6 a and b). Curie temperature (T_c) are defined as the temperature of ferroelectric to paraelectric phase transition. Around T_c , the dielectric constant-temperature curve for both first and second order ferroelectrics follow Curie-Weiss law $\varepsilon = \frac{C}{T-T_c}$, where C is Curie constant. Ferroelectric relaxers, however, do not follow this rule and have more complicated behaviors. Their phase transition properties such as T_c and peak width may be influenced by AC frequency and sample preparation process (see Fig.1.6c).

Figure 1.6 Permittivity- and spontaneous polarization-temperature curves for ferroelectrics with first order (a), second order (b) phase transition and relaxor behavior (c). Adapted from reference 10.

1.1.2 Ferroelectrics of different material systems

Oxide perovskite

The most intensively studied ferroelectric system so far is oxide perovskite

ferroelectrics, which drives its name from the mineral CaTiO_3 . The chemical formula of this material family is ABO_3 , where A and B represents cation or mixed elements and O is oxygen anion. Because of the large variety of elements for A and B, this type of material possesses highly diverse physical and chemical properties. Ferroelectric oxide perovskite is a subgroup of this material family. Figure 1.7 shows the two types of cubic structures for oxide ferroelectrics. The first type (fig. 1.7a) gets the structure with its cubic center occupied by B atom while A locates at the corners and O at each plane center. If A cation is at the center (Fig. 1.7b), B would locate at the corners while O are positioned at the midpoints of edge. Fig. 1.8 is the structure of BaTiO_3 unite cell with up- and downward spontaneous polarization. The displacement of Ti cation with respecting to central position leads to ferroelectric polarization. Since the discovery of BaTiO_3 ¹¹, oxide perovskite ferroelectrics with different elements in A and B site, such as PbTiO_3 , BiFeO_3 and SrTiO_3 have been reported and intensively studied. Because of their good thermal stability, excellent ferroelectric/piezoelectric performance and fast response speed, oxide ferroelectrics are so far the most intensively studied ferroelectric system and has the widest range of commercial applications¹¹, which will be discussed in detail in Chapter 1.1.4.

Figure 1.7 Two types of ABO_3 unit cell structures with B (a) and A (b) cation at the cubic center. Circle with dashed, grilled and white pattern are A, B and O sites, respectively. Adapted from reference 12.

In oxide perovskite ferroelectric, doping of A and B sites may lead to dramatic structural and property changes. One typical case is PZT, the benchmark piezoelectric material (d_{33} around 500 pC/N^{13}) which has Zr and Ti mixed cations as B site. The piezoelectric constant of its Ti doping endpoint PbTiO_3 is only around 100 pC/N^{14} , while another end PbZrO_3 ¹⁵ is

an antiferroelectric material. As Fig 1.9 indicates, from Zr to Ti side, a sequence of phase transitions are induced with the increase in Ti amount. At the boundary of rhombohedra and tetragon (50% vertical) structure, the application of electric field can easily induce structure transition between these two states and achieves large strain, leading to the ultrahigh piezoelectric coefficient in PZT. The barrier of these two phases is called morphotropic phase boundary (MPB).

Figure 1.8 Up- (a) and downward (b) polarization states of BaTiO₃ unit cell. Adapted from reference 16.

Figure 1.9 Phase diagram of PZT. Adapted from reference 17.

Organic and polymer ferroelectrics

Oxide perovskite ferroelectrics have dominated superiority in applications such as actuator, memory device and capacitor. However, practical electronic devices for the next generation require ‘triple E’ features- environmentally friendly, energy efficient and economically inexpensive¹⁸. This is undoubtedly conflict with the situation in PZT materials, which contain lead and require high energy synthesis methods such as pulsed laser deposition¹⁹. Organics are low cost, structurally and mechanically flexible, light weight and easy to process²⁰. These unique properties bring in strong research impetus to organic ferroelectrics.

The most obvious superiority for organic ferroelectrics is their structure variety. Due to the large amount of available molecular building blocks and various types of intermolecular interactions, the ferroelectricity origin of organic materials is more diverse than oxide perovskite²¹. First, though rarely to be seen, the ferroelectricity of organic materials can also arise from ionic displacement like the case in oxide perovskite. This type of organic ferroelectrics generally have much faster switching speed than other molecular ferroelectrics since no large molecular movement or chemical bond rebuilding is involved in *P* switching process. 4-(cyanomethyl) anilinium perchlorate, as an example, shows high switching frequency around 10 kHz, which makes it a promising candidate material for ferroelectric random access memory (FeRAM) devices²².

The second type is donor (D)-acceptor (A) ferroelectric system. The structure of this material family is generally one-dimension D-A chain (see Figure 1.10). The donor and acceptor molecules are neutral at paraelectric phase. When temperature goes below phase transition point, a valence transformation called neutral-ionized transition occurs, which dimerizes D^0A^0 to D^+A^- pairs and induces spontaneous polarization. Ferroelectricity would be induced if this 1D structure can be inverted between ...DA DA... and ...AD AD... states under electric field. Tetrathiafulvalene-p-chloranil as an example, exhibits a large *Pr* ($6.3 \mu\text{C}/\text{cm}^2$, compared with other organic ferroelectrics) with low-energy-cost electronic response, which makes it affordable to be electro-optics devices²³. In addition, piezoelectric structure with high dielectric constant (~ 2000) was also discovered in DA system²⁴, which stems from the unique DA ionization near Curie temperature.

Figure 1.10 Schematic neutral-ionized transition of DA system. Adapted from reference 20.

The third ferroelectricity origin is transfer of proton in hydrogen bond, which is commonly exists in O, N and halide containing compounds. Materials with this type of ferroelectricity origin get the greatest in number and have the longest history among organic ferroelectrics. With the discovery of classic ferroelectric structures such as KH_2PO_4 and Rochelle salt, hydrogen bond was once thought to be necessary for ferroelectricity. The phase transitions of this material family are generally order-disorder type (may coexist with displacive type). Because of the large diversity in chemical bond and strength, modulations towards bond interaction are always used to adjust ferroelectric properties such as band gap and T_P ²⁵. Recently, hydrogen bonds with halogen bonding are suggested to be the reason of the giant piezoelectric response in hybrid structures²⁶.

Polymer ferroelectrics possess similar features to organic ferroelectrics, such as lightweight, flexible and environmental-friendly. The drawbacks of polymer ferroelectrics are smaller polarization and slower switching speed compared with other ferroelectric systems²⁷. Since the discovery of polyvinylidene fluoride (PVDF) in early 1970s, various polymer ferroelectrics including odd-numbered polyamides²⁸, vinylidene cyanide²⁹ and poly-L-lactic acid³⁰ have been synthesized and intensively studied. Among all these materials, PVDF and relevant composites are the most studied system because of its good processability, high mechanical strength and excellent thermal stability³¹. These superior properties make

PVDF have the widest applications among ferroelectric polymers, which includes filtration membrane, acid gases absorption and high energy capacitor^{32,33}.

Hybrid systems

In recent years, the most intensively studied hybrid ferroelectric systems are organic-inorganic hybrids and metal organic frameworks (MOFs). The former will be discussed in chapter 1.3, here I give a brief introduction to MOF ferroelectrics.

MOFs are molecular structures consisted of metallic cluster linked by molecules in ordered manner. Different with perovskite-like OIHFs, MOFs possess even higher structural freedom that enables them to integrate several exclusive properties³⁴. This enormous structure flexibility may open the avenue towards multiferroic properties, which means material is both ferroelectric and ferromagnetic. Such fascinating properties will lead to great developments in both applications and fundamental physics. For example, if ferromagnetic states can couple with ferroelectricity, data in memory device can be written by electric pulse and read by magnetic signal. This will improve storage lifetime tremendously since the reading process will not disturb memory state. Through efforts have been put in oxide perovskites in past tens of years, practical multiferroic device still has not been achieved due to both experimental and theoretical difficulties³⁵. In MOF structure, ferroelectric poling is always associated with movement or rotation of organic cluster linked with metal element contained polyhedron. This component mixed structure provides another design freedom to correlate ferroelectric dipole with the distortion of magnetic inorganic part and leads to multiferroic effect^{36,37}. With this strategy, though multiferroics has not been achieved, several magnetoelectric MOF ferroelectrics have been successfully synthesized and characterized in recent years³⁶⁻³⁹.

However, the research of MOF ferroelectrics is still in its embryo. Though more than ten structures have been discovered, room temperature ferroelectricity still has not be achieved⁴⁰. In addition, their P_r are generally very small (less than $0.5 \mu\text{C}/\text{cm}^2$), which limits their ferroelectric application³⁴.

Other material systems

2D chalcogenide-based ferroelectric is another system exhibiting tantalizing future in both fundamental research and application. It has superiorities in several aspects. First, its no-organic-contain composition ensures its good thermal stability, which expands its application territory to high temperature (HT) region, such as HT pyroelectrics and transducer. Second, the 2D structure makes this ferroelectrics can be exfoliated to atom thickness (see figure.1.11). This shines light on the realization of ultrahigh density data storage and may lead to new nanoscale phenomenon, such as special interfacial effects in heterostructure and layer dependent T_p ⁴¹. In addition, compared with hybrid materials, the structure of chalcogenide 2D ferroelectrics is much simpler. This enables reliable predication towards new ferroelectric structure and advanced functionality based on first-principle calculation, which largely accelerates its research process⁴². Through only few ferroelectric structures have been discovered and characterized, with all these unique properties, the research of chalcogenide 2D ferroelectrics may have its blooming stage in near future⁴³.

Figure 1.11 Piezoresponse force microscopy (PFM) diagrams of CuInP_2S_6 . Topography (a) amplitude (b) and phase (c) PFM diagrams. The scale bar is 500 nm. (d) Height and amplitude profile along the dash line in (a) and (b). Adapted from reference 44.

Besides perovskite structure, ferroelectricity has also been discovered in other oxides materials. Layered perovskites, as an example, are oxides with Ruddlesden–Popper structure⁴⁵ ($\text{Sr}_{n+1}\text{Ti}_n\text{O}_{3n+1}$, in fig. 1.12) or stacking of perovskite-like $\text{A}_{n-1}\text{B}_n\text{O}_{3n+1}$ molecules and other oxide building blocking⁴⁶. There are other ferroelectric systems such as Tungsten Bronze group, Aurivillius compounds and salt like Triglycine Sulphate, which I will not go into details due to their small number and relatively lower research interest.

Figure 1.12 Ruddlesden–Popper structure of $\text{Sr}_{n+1}\text{Ti}_n\text{O}_{3n+1}$, with n vary from 1,2,3,4,5 and ∞ . Adapted from reference 45.

Table 1.1 summarizes the advantages and disadvantages of aforementioned main ferroelectric systems. Overall, oxide perovskite is still the material family with the best performance in various aspects of ferroelectricity/piezoelectricity, yet polymer and hybrid systems possess superiority in structural and mechanical flexibility, which makes them promising as the next generation smart electronic materials.

Table 1.1| Comparisons among different ferroelectric systems

	Oxide perovskite	Polymer	OIHF's
Advantages	Superior overall ferro/piezo performance Large polarization Excellent stability Fast operation speed Large stress output Low fatigue effect High curie temperature	Environmental-friendly Economically inexpensive Mechanically flexible Easy process	Structure/composition flexibility Multifunctionality Easy process Light weight Good piezo/strain performance Exfoliable (for 2D structures) Mechanical flexible
Disadvantages	Synthesis requires high energy Toxicity Low mechanical flexibility	Inferior stability Small polarization Low multifunctionality	Low operation frequency Inferior stability Small polarization

1.1.3 Applications of ferroelectrics

Ferroelectrics possess a great number of applications and have become the leading material in several industrial areas. Ferroelectric structures are all piezoelectric and pyroelectric. Here I give a brief review covering the major applications based on all these properties.

Pyroelectrics

There is increasing research interests to pyroelectric based energy harvesting devices in recent years (see figure 1.13). Among different kinds of harvesters, the flexible type receives

the most attention due to its unlimitedly wide applications in wearable devices⁴⁷. So far, different materials have been used as wearable harvesters, including $(1-x)\text{Pb}(\text{Mg}, \text{Nb})\text{O}_3-x\text{PbTiO}_3$ (PMN-Pt)⁴⁸, PZT⁴⁹, PVDF⁵⁰ etc. Among these pyroelectrics, PVDF gets the most intensive study due to its lightweight, biocompatible, flexible nature and high sensitivity for small deformation/geometrical effects. Another type of energy conversion device is nano-generator (hybrid harvester). Since piezoelectrics are all pyroelectric, these two electromechanical effects can be combined to enhance the energy output. So far, different design strategies have been realized in several polymer composite systems such as PVDF/tin oxide⁵¹ and Polydimethylsiloxane/carbon nanotube systems⁵².

Figure 1.13 Number of papers on pyroelectric energy harvesting published since the year of 2000. Adapted from reference 47.

Pyroelectrics can also be used in infrared (IR) detection. Here IR is detected by the heat converted from its photon energy. Compared with optoelectronics, pyroelectric detectors have following advantages⁵³: 1. Sensitive in a wide wavelength range; 2. Applicable to wide temperature range and no requirement for cooling; 3. Low energy consumption; 4. Fast response; 5. Lower cost. With these superiorities, several practical applications have been

successfully achieved based on pyroelectric IR detectors, including fire alarm, intruder detector and pollution monitor^{54,55}. Enlighted by the development of IR detector, pyroelectrics 2D arrays was recognized to be a good candidate as imaging device. In early stage, Whatmore proposed that pyroelectric detector can be used to build up as imaging device by employing rotation mirror system to scan its scene⁵⁶. With further developments in device design and property optimization, practical applications such as vidicon camera and imagine array have been successfully commercialized⁵³.

Figure 1.14 Pictures taken by pyroelectric based vidicon camera (a) and $\text{PbSc}_{0.5}\text{Ta}_{0.5}\text{O}_3$ imaging array (b). Adapted from reference 53.

Another application is photopyroelectric spectroscopy, which is used to measure photothermal effect and thus characterize the material. Here, characterized sample is first placed on a pyroelectric holder and then exposed under short pulse or continuous beam. Due to nonradioactive deexcitation effect, heat would be produced and diffuse to the pyroelectric holder acting as thermal sensor. From the detected pyroelectric signal, sample's properties such as thermal conductivity, diffusivity, optical transmission, absorption and nonradiative deexcitation efficiencies can be determined^{57,58}. Based on this working principle, photopyroelectric spectroscopy have been used in a number of scientific measurements such as quantum efficiency and phase transition test⁵³.

Piezoelectrics

Based on piezoelectric effect, industrial applications such as gas igniter, accelerator and pressure sensor have been successfully achieved. The voltage produced under stress can cause spark and ignite flammable gas. The stimuli of piezoelectric gas igniter can be both rapid pulse and signal produced by continuous mechanical loading⁵⁹. In the application of smart electrotonic, various smart structures such as 3D stress sensor and acceleration sensor in both linear and rotational direction can be achieved by depositing piezoelectrics on quartz with electrodes^{60,61}.

Vibrator and transducer are important applications of piezoelectrics. Because of the resonance effect, both vibrational mode and material size should be considered in the practical device. For example, in buzzer and speaker, low resonance frequency is required (100 to 2000 Hz). Piezoelectrics in these devices are thus adjusted to centimeter-level, where the resonance frequency is generally around 100 ~ 1000 Hz. In industrialized piezoelectric buzzer, the size is only around 0.7 mm in thickness and 0.4 g in weight, with power consumption 1/5 to 2/3 to electromagnetics device⁶². Another important application of piezoelectric vibrator are resonator and filter. When vibrate at resonance frequency, piezoelectrics absorb much higher energy, leading to a sharp decrease in impedance. This phenomenon makes piezoelectrics good candidate for wave filter. Varying from the sizes of piezoelectrics, filters with different working frequencies have been successfully achieved, which are used as radio receiver and transmitter in different electronic systems⁶³. In transducer applications, piezoelectric based devices are so far the main ultrasonic generator beside magnetostrictive materials. Compared with magnetics-based devices, piezoelectric ceramic has superiorities in size, efficiency, power generation and low heat producing. In transducer, materials are required to possess high mechanical quality factor rather than high piezoelectric coefficient. Hard ferroelectrics like ceramic materials are consequently preferable. With intensive studies conducted on oxide piezoelectrics in last few decades, various industrialized devices have been achieved, including ultrasonic microphones, sonar, underwater detection, fish finding, ultrasonic washers, etc⁶⁴. Finally, piezoelectrics can also

be used in ultrasonic detection such as imaging⁶⁵ and in sonochemistry⁶⁶, which play important roles in clinical application in therapy, diagnosis and surgery.

Piezoelectric and electrostrictive materials can be used as smart actuator devices in adaptive mechanical dampers, precision positioners and miniature ultrasonic motors. Compared with traditional actuator such as magnetostrictors and shape memory alloys, piezoelectrics output much smaller strain but has superiorities in several aspects: 1. Considerable faster operating speed and smaller noise signal⁶⁷, leading to high work efficiency. 2. Lower energy consumption⁶⁴. 3. Advantages in material miniaturization. With synthesis method such as PLD, the thickness of piezoelectric ceramic device can go to nanometer level⁶⁸. Piezoelectric actuators can be classified into three categories (fig. 1.15) with different requirements. The first is servo displacement positioner, which is driven by feedback signal from position detection and requires piezoelectrics have small hysteresis effect. The second is pulse-controlled motor with on/off signal as its stimuli. This class of actuator prefers materials with small permittivity, fast respond speed and low energy cost. The last is resonating actuator. Devices for this type output altering strain triggered under AC field at mechanical resonance frequency. Piezoelectrics with large Young's modulus and high quality factor are preferred for lower heat generation.

Figure 1.15 Three classes of piezoelectric/electrostrictive actuators. Adapted from reference 64.

Piezoelectrics can be used as energy harvester, where the energy transfer process is inverted to actuator. Here mechanical movement is converted to electrical energy for power generation. Due to the huge variety of possible stimuli sources including industrial machinery vibration⁶⁹, movement of air flow⁷⁰, action of walking⁷¹ and even heartbeat⁷², piezoelectric harvester have potential to provide enormous amount of energy for human society. Compared with other energy devices such as battery, piezoelectric energy harvester does not require installation labor from complex system or extra cost/time for maintenance, which makes the future of this application super tantalizing⁷³. The piezoelectric modes used in most of practical harvesting application are d_{33} and d_{31} . There are also a large number of harvesting devices using shear mode, but are still in research stage⁷⁴⁻⁷⁶. Regarding the type of mechanical energy sources, piezoelectric energy harvesters can be classified into two groups, ‘inertial’ and ‘kinematic’ type devices. As its name suggests, inertial harvester extracts mechanical energy by the inertia of a mass. In this system, piezoelectric device is connected to a base by a single point. With the movement of this base, vibration would be triggered in mass-spring system, which acts as mechanical energy source. With proper base drive frequency, piezoelectric resonance effect can be induced and enhances the vibration amplitude considerably, leading to high electrical energy output. In kinematic system, harvester device is directly coupled with relative movement between different parts of source base. For example, energy can be produced from bending of monitor tire pressure to tire wall⁷⁷, and extension-flexing cycle of limb⁷⁸.

Ferroelectrics

Ferroelectrics have been regarded as candidate of next-generation nonvolatile memory for around 30 years⁷⁹. Compared with other materials such as static-, dynamic random access memory and flash memory, ferroelectric devices have superiorities in better scalability, faster write-read speeds, better nonvolatility, less power dissipation, higher radioactivity tolerances and higher resistances to temper⁸⁰. Ferroelectric nonvolatile memories can be classified into two structures. The first is field effect transistor (FET) with capacitor consisting ferroelectric

film (figure 1.16a). Memory state in this type of device is written by applying pulse with amplitude exceeding coercivity. In reading process, pulse is applied and ON/OFF states (as stored data) can be identified by current difference induced by possible polarization switch. Nevertheless, this means a re-write pulse is always required to preserve the initial memory state, leading to faster fatigue effect and hinders its application. The best device lifespan achieved is around 10^{12} cycles⁸¹. The second type of ferroelectric memory device is ferroelectric gate FET system (figure 1.16b). The ferroelectric film here is used to adjust the energy structure of the N-P-N junction by its polarization. The memory state here is written by applying voltage on gate and read out by drain current. Thus, different with the first type of memory, the reading operation does not disturb memory state and no re-write pulse is required. However, fatigue effect can still be induced from deterioration of the ferroelectric film and degradation of the ferroelectrics-insulator interface. Due to all these issues, commercial ferroelectric memory devices are still limited in very niche applications.

Fig. 1.16 The structures of ferroelectric capacitor (a)⁸² and gate type (b) FET memory devices. Figure (a) and (b) are adapted from reference 82 and 80.

1.2 Organic-inorganic hybrid ferroelectric

1.2.1 Research background

Overview

The last few decades witness the changing development trend of ferroelectric and piezoelectric materials, which is from “single to multifunctional”, “macro to nano”, “hard to soft”, “homo to hetero” and “performance to reliability”. In addition, the worldwide regulation in toxicity gradually drives more and more attention from PZT dominated oxide materials to new lead-free ferroelectric structures⁶⁴. OIHF are molecular ferroelectrics that have both organic and inorganic components. The inorganic part acts as structural backbone and organic part induces additional functionalities and modulates material properties. Hybrid system thus takes advantages from both sides. The great chemical and structural diversity of organic molecule offer substantial opportunities to modulate structural and physical properties. In addition, the organic composition grants hybrid structures with the superiority of molecular ferroelectrics such as flexibility, lightweight and environmental-friendly. The inorganic part consisted by metal-molecule polyhedron provides hybrid structure with excellent optical and mechanical properties, such as robust opto-electron activity, large Young’s modulus and good fracture toughness^{83,84}. These unique features make OIHF ‘the chosen one’ for next generation ferroelectrics. After the year of 2010, the breakthrough of hybrid perovskite solar cell^{85,86} leads enormous interests to the exploration of new hybrid structure. This opens up the ‘Age of Discovery’ for OIHF and largely accelerates its research progress in both fundamental characterization and device design. Since 2014, more than forty new OIHF have been reported with structure varying from 0D to 3D⁸⁷. Particularly, great strides were made in piezoelectric⁸⁸ and electrostrictive properties⁸⁹. The piezoelectric coefficients of some OIHF have outranked benchmark oxide perovskites such as bismuth barium titanate⁸⁸ and PZT²⁶. Research also blooms in device applications including light⁹⁰

and X-ray⁹¹ detection, high efficient photoluminescence (PL)⁹², polarized light emission⁹³, energy harvester⁹⁴ and photoferroelectricity switching device⁹⁵.

Through several works have been reported in device design^{90,91,94}, most HOIFs researches so far are still in molecule design strategy and new ferroelectric structures discovery. Due to the volume diversity on the organic part, 1D, 2D, 2D-3D mixed, 3D, anti-perovskite and 0D structure molecular ferroelectrics have all be successfully design and characterized⁸⁷. Here I give a brief review firstly on the features of hybrid structure, then go to molecule modification strategies and finally cover the specific research progress of OIHF in different structural dimensions.

Structure of OIHF

OIHF can be classified into two groups. The first is perovskite structures, which are consisted by corner-sharing metal-molecule octahedron (figure 1.17a-b) or face-sharing 1D hexagonal (figure 1.17c-d) chain. The second is hybrid molecular ferroelectrics, with non-perovskite-type inorganic framework consisting face- or corner-sharing polyhedron or organic-inorganic hybrid discrete clusters (0D) (figure 1.18).

Figure 1.17 Perovskite structures in hybrid and oxide systems. Corner sharing octahedron structure of (MeHdabco)RbI₃ (a)⁹⁶ and PbTiO₃ (b)¹ and face sharing hexagonal 1D structures of (CH₃)₄PCdCl₃ (c)⁹⁷ and LiNbO₃ (d)⁹⁸. Figure (a), (b) and (c) are adapted from reference 96, 97, 98 respectively.

Figure 1.18 Structures of hybrid molecular ferroelectrics. (a) Non-perovskite-type 1D OIHF (CH₃)₄NZnCl₃. (b) 0D molecular ferroelectric (N-methylpyrrolidinium)₃Sb₂Br₉. Figure (a) and (b) are adapted from reference 99 and 100.

Similar to oxide perovskite, the chemical formula of hybrid perovskite ferroelectrics (HPFs) is ABX₃, where A is organic cations, B is metal elements and X are anions such as

halogen ions, HCOO^- and NO_2^- . With different components at A, B and X sites, the structure of HPFs can be led to different symmetries and dimensions. A tolerance factor is proposed by Goldschmidt to predict its structure properties¹⁰¹: $t = (R_A + R_X)/[\sqrt{2}(R_B + R_X)]$, where R_A , R_B and R_X are the radii of A, B and X site, respectively. Ideal cubic perovskite structure occurs in the range of $0.85 < t < 1.11$, where ferroelectricity may be impossible to exist since the lack of symmetry breaking¹⁰². When $t < 1$, compression will occur in B-X bond and tension will be induced in A-X to compensate excess void in unit cell. The stress in metal-halide octahedron will consequently result in tilt and reduce in symmetry. If a large A site or small B site is employed and makes $t > 1$, 2D or 3D structure may occur¹⁰³.

The doping of HPFs make this type of ferroelectrics possess even more structural flexibility and composition diversity. To date, A¹⁰⁴, B¹⁰⁵ and X²⁵ sites doping have all been successfully realized. Among these molecule modulations, the doping of A site was found to have function in dimension engineering. In oxide perovskite, the component of A site can only vary in different single metal atoms with limited size difference. HPFs however, have highly diverse organic molecules for A position. Recently, even organic-inorganic mixed A site has been successfully achieved¹⁰⁴. In addition, the two composition at A site can be molecules with volume difference that is large enough to result in dimension variety. This leads to 2D-3D mixed HPFs^{90,106} (fig. 1.19). Unlike Ruddlesden–Popper oxide perovskites, the bonding between each hybrid layer is Van der Waals force, which enables the materials to be exfoliated to nanometer-level thin film.

Fig.1.19 Crystal structures of $(\text{CH}_3(\text{CH}_2)_3\text{NH}_3)_2(\text{CH}_3\text{NH}_3)_{n-1}\text{PbIn}_{3n+1}$, with n from 1 to ∞ . Adapted from reference 106.

1.2.2 Strategies of inducing ferroelectricity

There are 32 point groups in crystallography. Among these structures, 11 have centrosymmetry, which exclude the possibility for crystal to have polar structure or be ferroelectric. For the remaining 21 non-centrosymmetric structures, 20 point groups have piezoelectric effect within which 10 possess spontaneous polarization and thus be pyroelectric. Among these pyroelectrics, only materials with switchable polarization under electric field are ferroelectrics. Figure 1.20 illustrates the relationship of dielectric, piezoelectric, and pyroelectric materials¹⁰⁷. Because of this structural uniqueness, only around 40 structures are found to be ferroelectric among hundreds of discovered hybrid compound since the year of 2014. Exploring new ferroelectrics by just trying new molecule in A, B and X sites is material and time consuming. Consequently, smart ferroelectricity inducing strategy attracts enormous attention. To date, several successful molecule modulation strategies have been reported in hybrid system. The core of these molecular

engineering is to break the symmetry in the organic part, which increases the possibility of the crystal falling into non-centrosymmetric space groups. In the meanwhile, molecule size is another important factor that need to be handled carefully. A too small organic part coupled with large B site may lead to small t , which results in high symmetry unit cell or disordered phase. Here, I review some successful examples.

Fig. 1.20 Relationship between the point groups of dielectric (with centrosymmetry point groups), piezoelectric and pyroelectric materials. Adapted from reference 107.

(MeHdabco)RbI₃: H₂dabco²⁺ (fig. 1.21a, left) is a building block for several molecular ferroelectrics with a highly symmetric point group of D_{3h} ⁹⁶. Ferroelectrics containing this molecule cluster, e.g. (Hdabco)ReO₄, (Hdabco)BF₄ and (Hdabco)ClO₄, always possess multiaxial-polar nature, which is desired for both research and application⁹⁶. Through tens of OHIFs have been successfully designed, only few of them have 3D structure. The discovery of alkali perovskite (Hdabco)ReCl₃ by Harrison et al shines light on achieving multiaxial OHIF with 3D structure¹⁰⁸. Unfortunately, the structure of (Hdabco)ReCl₃ is in centrosymmetric D_{3h} point group thus impossible to be ferroelectric. In 2017, Xiong et al successfully designed a new dabco based 3D ferroelectric structure with molecule modulation schematic shown in figure 1.21. First, a methyl is added on Hdabco to remove its mirror symmetry. The resulting (MeHdabco)RbCl₃ is in polar structure with point group of C_{3v} . However, no ferro- to paraelectric phase transition is observed, which means a super large E (generally above decomposition electric field) may be required to reverse its polarization. This indicates a more loosen structure may needed to reduce its switching

barrier. Consequently, iodide is employed to expand the inorganic backbone. As expected, ferroelectric phase transition is induced at 430 K and the polar structure is preserved with point group of C_3 . This work illustrates a typical molecule engineering process of inducing ferroelectricity in OIHF, where adjustments are made in the size and symmetry property of building blocks.

Figure 1.21 Molecular modulation schematic of inducing methyl on organic part (a) and corresponding change triggered in hybrid structures (b). Adapted from reference 96.

For a more complex system, multiple modulation strategies are required. The discovery of (FMeTP)Ni(NO₂)₃ (FMeTP=N-fluoromethyl tropine)¹⁰⁹ is a typical instance. N(CH₃)₄⁺ is a sphere-geometry cation with centrosymmetric group of $P6_3/m$. As indicated in figure 1.22, to reduce the symmetry of this hybrid structure, different halogens were firstly added on the organic molecule. However, breaking in symmetry has not been triggered even with the largest halide atom iodide. Considering halogen-hydrogen bonding has an important role in ferroelectricity generation^{110,111}, hydroxy is then added on another methyl to act as hydrogen

bond donor while nitrite acts as acceptor. Unfortunately, the non-ferroelectric structure is persisted. Engineering strategy is then switched to reducing symmetry through increasing structure stress, which was conducted by employing a large molecule azabicyclic N-methyl tropine (MTP). However, the obtained structure still crystalizes in a high symmetry space group $P2_1/n$. In previous report, H to F substitution is proposed to be capable of adjusting molecule physical properties while largely maintain initial structure^{112,113}. With this strategy employed, ferroelectric Cc structure is finally triggered in this hybrid compound.

Figure 1.22 Schematic of molecule tailoring from $N(CH_3)_4N(NO_2)_3$ to $(FMeTP)Ni(NO_2)_3$. Adapted from reference 109.

Bond enhancement is another modulation strategy of inducing ferroelectricity in disordered crystals. In most hybrid structures, organic cations and inorganic framework are linked by hydrogen bond. During polarization reversal, these organics flip to the equivalent positions by hydrogen bond break and rebuild. Too weak hydrogen bond strength or too small inorganic framework may result in disordered phase at room temperature, where cations jump freely among equivalent sites, leading to high-symmetry point group. Fortunately, the flexibility of organic molecule provides the possibility to tailor these building blocks. The modulation employed in the discovery of $N(CH_3)_3CH_2PbI_3$ indicates a good example of

triggering room temperature (RT) ferroelectricity by enhancing cation-anion bond strength. In $\text{N}(\text{CH}_3)_4\text{PbI}_3$, the bond between organic and inorganic parts is weak C-H-I bond, which results in an order-disorder phase transition at low temperature 184 K. Consequently, the crystal is in centrosymmetric space group ($P6_3/m$) at RT. To enhance cation-anion bonding strength and induce ferroelectricity at room temperature, highly electronegative halogen atoms was added on the organic part¹¹⁴. With substitution from fluoride to iodide, the tailored organics becomes larger and heavier (see figure 1.23), which leads to a smooth increase in Curie temperature up to 312 K. In the iodide substitution counterpart $\text{N}(\text{CH}_3)_3\text{CH}_2\text{IPbI}_3$, RT polar structure is finally successfully induced. The simulation result indicates a consistent monotonously increasing trend of bond strength from fluorine to iodide tailored structures. This confirms the T_c promotion effect of the halide engineering schematic (see figure 1.24).

Fig. 1.23 Space groups and Curie temperatures of hybrid systems consisted by PbI_3^- chain and $\text{N}(\text{CH}_3)_3\text{CH}_2\text{X}^+$. Adapted from reference 114.

Fig. 1.24 Differential scanning calorimetry (DSC) (a) and simulation results of bond energy in $N(\text{CH}_3)_3\text{CH}_2\text{X-I}$, with $\text{X}=\text{F}, \text{Cl}, \text{Br}, \text{I}$ (b). Adapted from reference¹¹⁴.

Finally, employing chiral organic cation is another strategy to trigger ferroelectricity. Chirality is the symmetry property that molecule can be distinguished with its mirror image. Chiral materials have various unique properties such as chiroptical nonlinear optical effect, circularly polarized PL, circular dichroism and spintronic effect, which enable chiral materials own great potential in spintronic and optical applications^{115,116}. Because of the lack of chiral molecule, chirality is very difficult to be induced in oxide and inorganic halide perovskites. However, the organic-inorganic component of hybrid system enables perovskite structure to embrace chirality, which may lead to new phenomenon in ferroelectrics. Some chiral molecules are naturally in polar structures (figure 1.25a). This makes incorporation of chiral organic a possible way to induce ferroelectricity. Following this strategy, several ferroelectrics (see figure 1.2b, (R- and S-FMQ)Ni(NO₂)₃ as an example) have been successfully achieved. Additionally, chiral properties such as polarized PL have been reported to coexist with ferroelectricity, which may lead to the discovery of new coupling phenomenon and multifunctional devices⁹³.

Fig. 1.25 (a) The relationship among different properties and corresponding space groups. (b) Crystal structures of (R- and S-FMQ)Ni(NO₂)₃ (left and right). Figures are adapted from reference 115 and 116.

1.2.3 1D OIHF

One dimensional OIHF are the most intensively studied hybrid ferroelectrics in recent years due to their outstanding properties in piezoelectricity^{26,88,117}, photoluminescence^{92,93,97} and switchable photovoltaic effect⁹⁵. The crystal structure of this type OIHF are generally arranged in 1D corner- or face-sharing metal-molecule polyhedron, with organic cations occupying the space enclosed by discrete inorganic chains. Ferroelectricity in this structure is generally originated from flip-flop motion of organic cations under electric bias.

The greatest discovery in 1D OIHF is the giant piezoelectric response that outranks the performance of classic perovskite ceramics. Molecular piezoelectrics have several advantages such lightweight, flexible and environmental friendly. Yet for tens of years, their

piezoelectric coefficients are still largely inferior to oxide perovskites⁸⁸. This is recently changed by the continuous discoveries of OIHF with record-high piezoelectric coefficient. In 2017, You et al reported the large piezoelectricity ($d_{33}=185$ pC/N) in (TMCM)MnCl₃ (TMCM: Trimethylchloromethyl ammonium) that outperform the classic piezoelectric ceramic BaTiO₃ (figure 1.26). The large d_{33} is proposed to come from its special halogen-decorated organic cation. However, solid proof is lacking considering such large piezoelectricity have not be reported in other halogen bond based OIHF^{109,114,116}.

Figure 1.26 (a) Crystal structure of (TMCM)MnCl₃ at ferroelectric phase. (b) d_{33} comparison with other piezoelectrics. Adapted from reference 88.

Two years later, piezoelectric responses with d_{33} larger than PZT were discovered in (TMFM)_x(TMCM)_{1-x}CdCl₃ ($0 \leq x \leq 1$), where TMFM is trimethylfluoromethyl ammonium and TMCM is trimethylchloromethyl ammonium²⁶. Similar to oxide perovskite, doping triggers a sequence of structure and property changes (figure. 1.27) in this hybrid structure. At room temperature, the crystal is in ferroelectric space group for $x \leq 0.5$. Above this ratio, the solid solution crystallizes in a centrosymmetric group of $6/m$. The giant d_{33} (1540 pC/N) is discovered at the MPB between the monoclinic (m) and hexagonal ($6mm$) region, which is two order of magnitude higher than general molecular piezoelectric such as PVDF (~30 pC/N)¹¹⁸ and is even larger than PZT (~500 pC/N)¹³. Additionally, the hybrid component nature makes this OIHF an easy processing piezoelectrics, which is largely different with PLD-required oxide ceramic materials. With simple drop-casting method, piezoelectric thin

film can be easily obtained. This easy proceeding feature is also found in other high piezoelectric performance OIHFs^{88,117}. These breakthrough undoubtedly make hybrid ferroelectrics one of the most promising candidates as next-generation electronic materials with both high piezoelectric performance and low cost proceeding feaatures²⁶.

Figure 1.27 Structure projections and phase diagram of $(\text{TMFM})_x(\text{TMCM})_{1-x}\text{CdCl}_3$ ($0 \leq x \leq 1$). Crystal structures with $0 \leq x \leq 0.25$ (a) and $0.3 \leq x \leq 0.5$ (b). (c) Space group- x diagram. Adapted from reference 26.

High-efficient PL has also been reported in 1D OIHFs. Luminescent ferroelectrics, where ferroelectricity coupling with photoluminescence, have attracted great attention for tens of years. The polarization in ferroelectrics may provide a new method to manipulate light-matter interactions, which may lead to next-generation optoelectronic devices^{92,119}. For instance, Dipak et al reported an electric field triggered PL in an Eu^{3+} doped $\text{NaBi}_{0.5}\text{Ti}_{0.5}\text{O}_3$ - BaTiO_3 (figure 1.28a)¹¹⁹, while Hao et al discovered the phenomenon of enormous enhancement in PL emission in Yr^{3+} and Er^{3+} doped BaTiO_3 under electric field (Figure 1.28b)¹²⁰. Conventional luminescent ferroelectrics are rare earth-doped oxide perovskites, which suffer from poor luminescence efficiency and low stability because of the size difference between the foreign and substituted cations¹²¹. Hybrid system however, has a natural mixed structure of PL active inorganic backbone and flexible organic parts as ferroelectricity inducer. It consequently becomes a perfect platform for new luminescent

ferroelectrics design, which not only spears complicate doping produces but also avoids the side effects coming from doping.

Figure 1.28 (a) *E* triggered PL emission in NaBi_{0.5}Ti_{0.5}O₃-BaTiO₃. (b) Intensity tunable luminescent ferroelectric Yr³⁺/Er³⁺ co-doped BaTiO₃. Figures (a) and (b) are adapted from reference 119 and 120.

With all these superiorities in luminescent ferroelectrics, several hybrid ferroelectrics with highly efficient PL have been successfully designed and characterized. In 2015, Zhang et al discovered an OIHF (pyrrolidinium)MnCl₃, which exhibits ferroelectricity and PL with considerably high quantum yield of 56% (figure 1.29)⁹². The ferroelectric polarization stems from the flip-flop motion of pyrrolidinium⁺ under electric field, while the red phosphorescence arises from electronic (t_{2g})³(e_g)²–(t_{2g})⁴(e_g)¹ transition in MnCl₆²⁻ hexagon¹²². However, the below RT Curie temperature limits its application. This issue was solved by substituting pyrrolidinium by 3-pyrrolinium¹²³, which may lead to decrease in electronegativity in cation thus enhances the organic-inorganic bonding. The curie temperature is then successfully promoted to 376 K. In other OIHFs, doping induced PL was also discovered in a Cd base 1D ferroelectrics doped with Sb³⁺, which enriches the PL inducing strategy of OIHF⁹⁷.

Fig. 1.29 Ferroelectric (a) and PL properties (b) of (pyrrolidinium) MnCl_3 . Adapted from reference 92.

Good progress has also been made in circularly polarized luminescence (CPL). As discussed before, employing chiral organics in hybrid system may not only lead to ferroelectricity but also induces chiral properties. In practical optical system, CP light is generally produced by polarized light source coupling with filters and polarizer. Materials with tunable CPL is highly desired because they may potentially simplify the CP light generation process by application of outer stimuli such as electric or magnetic field. Recently, Gao et al reported the synthesis and characterization of (R)- and (S)-3-(fluoropyrrolidinium) MnBr_3 , a luminescence ferroelectric with excellent CPL generation⁹³. The chiral structures of R and S phases can be easily identified from crystallography (see figure 1.30a-b). With MnBr_6^{2-} hexagon as inorganic part, this material exhibits similar absorption and emission spectra to (pyrrolidinium) MnCl_3 (figure 1.30c). Interestingly, with chiral structure, different circular PL are obtained from R- and S- structures (see figure 1.30d). This work indicates that by smart molecular engineering, more OIHF with special chiral properties may be achieved. This make hybrid ferroelectrics have great potential in chiral materials applications such as biological probe, spintronic device, asymmetric photosynthesis, molecular switch device and information storage^{115,124}.

Figure 1.30 Structure and optical property of (S)- and (R)-3-(fluoropyrrolidinium)-MnBr₃. Crystal structures of S- (a) and R-structure (b). Absorption/PL (c) and CPL spectra (d) for these hybrid structures at different chiral states. Adapted from reference 93.

Finally, switchable photovoltaic effect was recently achieved in a Pb-based OIHF. With the stunning rise of CH₃NH₃PbI₃ solar cell, hybrid structure is recognized as an excellent platform that may spark new materials with outstanding electron mobility, high absorption coefficient and active photovoltaic effect¹⁰³. The inner electric field of polar structure can effectively adjust the energy potential of the photovoltaic device^{125,126}. Combined with ferroelectricity and active light-matter interaction feature, OIHF is regarded as candidate for switchable photovoltaic materials. Shi et al reported the tunable photocurrent in a chiral ferroelectrics R- and S- CYHEAPbI₃⁹⁵. Apart from ferroelectricity and chiral optical properties, this material also exhibits excellent switchable photovoltaic effect (see figure 1.31). This work expands the application territory of OIHF and provides a new method to manipulate the light-matter interaction in hybrid system.

Fig. 1.31 Switchable photovoltaic effects and relevant mechanism in CYHEAPbI₃. (a) Photocurrent of polarized ferroelectrics under positive and negative voltages. (b) Band structures under different bias. Adapted from reference 95.

1.2.4 2D and 2D-3D mixed OIHFs

The emergence of 2D materials triggers tons of intriguing discoveries in nanometer-level and interfacial phenomena. Ferroelectrics with exfoliable structure have great research significance in fundamental mechanism and applications. On the one hand, ultrathin thickness may lead to new ferroelectric phenomenon such as polarization destabilization, dramatic increase in depolarization field and various interfacial effects due to crystal mismatch¹²⁷⁻¹²⁹. Discover and disclose these new phenomena can improve the understanding of ferroelectricity and help researchers to dig out new applications for ferroelectric materials. On the other hand, nanometer thickness shine light on the realization of ultrahigh density storage and enables ferroelectrics to combine with other 2D materials, where ferroelectrics act as optical and electrical properties manipulators. This largely broaden the application of ferroelectric materials¹³⁰. With the highly flexible organic part, OIHF is an excellent system

for new 2D ferroelectrics design. To date, more than ten 2D and 2D-3D mixed ferroelectrics have been smartly designed and characterized. Progress have been made in unit-cell-thick ferroelectricity discovery¹³¹, rare earth doping¹³², band gap narrowing¹³³, vortex domain characterization¹³⁴ and visible light⁹⁰/X-ray detection⁹¹.

Through PFM measurements, great strides have been made in nanoscale characterization including the discovery of nanometer level ferroelectric thin film and vortex domain. Ferroelectricity is hard to survive in ultrathin film because of dramatically increasing destabilization field and thermal fluctuation. The thickness where materials lose their ferroelectricity is call ‘critical thickness’, which is generally several unit-cell level (2-5 nm) for oxide perovskites¹²⁷. This size limitation largely prohibits ferroelectrics in nanometer-level applications such as high-density memory device. You et al, reported the discovery of ferroelectricity in single unit-cell thick (benzylammonium)PbCl₄¹³¹. As indicated in figure 1.32, with sample orientation reversed, the phase signal of PFM diagrams exhibits typical up- to downward rotation while amplitude remain the same, indicating the well-preserved ferroelectricity. This robust nano-level polarization may be attributed to the weak van der Waals bonding between the thin film and substrate, which avoids the disturbance issue coming from lattice mismatch in oxide ferroelectrics¹³¹.

Figure 1.32 AFM characterizations. (a) Topology diagram. (b) PFM amplitude and height profile along the red line in (a). (c) and (d) Amplitude diagrams (lateral mode) with 0° and 180° sample rotation. Adapted from reference 131.

Another discovery is the existence of vortex ferroelectric domain. A flux-closure pattern, such as vortex, indicates low cross-talking properties in ferroelectric system, which is highly desired for high-density storage applications. Characterization of vortex domain have been intensively studied in oxide perovskite systems such as BaTiO_3 ¹³⁵ and BiFeO_3 ¹³⁶. Zhang et al, discovered the vortex ferroelectric domain in $(4,4\text{-difluoropiperidinium})_2\text{PbI}_4$ (see figure 1.33), which fills the blank in OIHFs and may lead to more hybrid-based vortex devices.

Figure 1.33 Amplitude (a) and phase (b) diagrams at different rotation angles, indicating the obvious vortex configuration. Adapted from reference 134.

Several OIHF s with narrow band gap have been recently reported in 2D¹³³ and 2D-3D mixed systems¹⁰⁵. Ferroelectrics with small bandgap is of great importance in optical applications such as visible light emission and photovoltaic devices. In OIHF s, the metal-halide polyhedron can induce high light absorption in ferroelectrics system. For visible light optical applications, materials with band gap in ultraviolet region is unfavorable. Fortunately, the high flexibility of halide and organic sites enables molecule engineering towards realization of narrow band gap ferroelectrics. To date, several OIHF s with band gap down to 2.25 eV have been successfully designed and characterized (see fig. 1.34).

Fig. 1.34 Optical spectra of (n-propylammonium)₂CsAgBiBr₇ (a) and (4,4-DFHHA)₂PbI₄ (b). Figure (a) and (b) are adapted from reference 105 and 133.

Taking advantaged from high absorption coefficient and extra electron-hole separation force of polar structures, various OIHF's devices have been reported as highly sensitive light and X-ray detectors. For example, Liu et al successfully designed a self-powered photodetector based on (EA)₂(MA)₂Pb₃Br₁₀ (EA: ethylammonium, MA: methylammonium)⁹⁰. As shown in figure 1.35, this photodetector possess excellent figure of merits including high on/off ratio (10⁶), fast response (96 and 123 μ s for rise and fall), nanosecond level response time ($\sim$ 1 ns) under transient laser (width $\sim$ 2 ns) and polarization dependent photocurrent.

Figure 1.35 Photodetection properties of $(\text{EA})_2(\text{MA})_2\text{Pb}_3\text{Br}_{10}$. (a) Electric-field dependent photocurrents under periodic 405 nm illumination. (b) Detail photoresponse behavior without E application. (c) Response under nanosecond 305 nm illumination. (d) Switchable photodetection identified from I - V curves at different polarization states. Adapted from reference 90.

Progress have also been made in X-ray detection. Currently, the dominated commercial detectors are based on inorganic materials such as Si^{137} , CdZnTe^{138} and PbI_2^{139} . Nevertheless, large-scale application of these materials is prohibited by complicated device fabrication and high temperature required synthesis process. These issues can be easily solved in hybrid materials. Based on a 2D-3D mix OIHF $(\text{butylaminium})_2(\text{ethylaminium})_2\text{Pb}_3\text{Br}_{10}$, a X ray detector with both high sensitivity ($6.8 \times 10^3 \mu\text{C Gy}_{\text{air}}^{-1} \text{cm}^{-2}$) and low energy cost ($E_{\text{min}}=1\text{V/mm}$) was successfully achieved by Ji et al⁹¹. As illustrated in fig. 1.36a, producible photoresponse with decent on/ff ratio was obtained under periodic X ray illumination. The neglectable attenuation indicates good stability of this device. Its high sensitivity can be reflected in fig. 1.36b. With ultraweak signal as $5.5 \mu\text{Gy s}^{-1}$, a distinguishable photoresponse can still be obtained under low voltage (10V). Additionally, with its unique 2D structure, nanometer device is expectable. These discoveries undoubtably shine light on the realization

of highly sensitive, low energy consuming and easy processing nanodevice for photodetection.

Figure 1.36 (a) Photocurrent-time plot under X-ray lamination. (b) Dose rate dependent photoresponse. Adapted from reference 91.

1.2.5 3D, antiperovskite and molecular hybrid ferroelectrics

A dozen of OIHF's with 3D perovskite, antiperovskite and molecular ferroelectric structures have been discovered in recent years. Through their properties are so far not as remarkable as 1D and 2D hybrids, these discoveries largely enrich OIHF's family and may possess potential advanced applications. Decent progress have been made in piezoelectric mechanism¹⁴⁰ study and energy harvester design⁹⁴.

Although stunning discoveries have been made in the piezoelectricity of OIHF's, the origin of their giant d_{33} is still unclear. Recently, Ye et al report two new 3D OIHF's with insight to their ferroelastic switches, which may explain the large piezoelectric response in some 1D OIHF's¹⁴⁰. The crystals of $(RM_3HQ)_2RbLa(NO_3)_6$ and $(RM_3HQ)_2NH_4La(NO_3)_6$ (RM_3HQ : RN-methyl-3-hydroxylquinuclidinium) are in $P2_13$ space group at low temperature and switches to $R3$ after phase transition. At LT, these two crystals are in a special structure where half cations are in disorder phase while another half are aligned to

different direction. This produces a large unit cell containing dozen of $\text{Rb}(\text{LA})_8(\text{NO}_3)_{12}$ octahedron (like the one in figure 1.37) with dipoles largely offsetting each other. Yet a weak net polarization with P_s of 0.3 C/cm^2 still remains. According to Aizu rule, this phase transition corresponds to 23F3 Aizu notion, which allows HT structure to have four equivalent states with polarizations along four C_3 axes. This means the ferroelectric dipole is possible to have 109° ferroelastic switch under outer stimuli. With piezometer measurement, large d_{33} up to 105 pC/N are discovered at HT phase. The author attributes the piezoelectric origin to the possible ferroelastic switch. However, it is noteworthy that this ferroelastic switch is different with the classic model, where non- 180° dipole switch can directly lead to obvious deformation on unit cell. In this hybrid structure, non- 180° switch only happens on some dipole inside the large unit cell, which contains dozens of anion-cation pairs aligned at different directions or even in disordered states. It is consequently difficult to see how the octahedron framework or unit cell will deform when some cations make such ferroelastic switch. In addition, since PE loop is not obtainable at HT, it is also hard to understand why dipoles can be switched by mechanical force but not by electric field. Consequently, more direct proves of dipole rotation are required to explain the active piezoelectric response in these two structures.

Figure 1.37 Crystal structure (left) and ferroelastic switch under stress (right). Adapted from reference 140.

Efforts have also been made in energy application. Vijayakanth et al designed an energy harvester based on a new molecular ferroelectric (phosphonium-P-methyl)₄Ni(NCS)₆ embedded in polymer matrix⁹⁴. The device shows excellent energy conversion efficiency with highest voltage output of 19.29 V, power density of 2.51 mWcm⁻³ and largest storage energy of 198.8 μ J for 200 μ F. This work indicates hybrid ferroelectric possess great potential as energy conversion device.

Figure. 1.38 Energy harvester performance of (phosphonium-P-methyl)₄Ni(NCS)₆ composite. (a) Voltage output of samples with different wt% of OIHF. (b) Voltage- and power density-resistance plot. (c) Charge traces of capacitor. (d) Accumulated charge with different capacitances employed on the 15 wt% harvester with 17 N mechanical force under frequency of 8 Hz. Adapted from reference 94.

Recently, ferroelectricity has been discovered in antiperovskite, which has inverted ionic site as X₃BA. Here A and B site are anions and X is cation. Research on this materials family start as early as 1930s, focusing on metallic compound such as Ni₃NZn, Mn₃NCu and

Li_3OBr . Outstanding properties such as giant magnetostriction, superionic conductivity and giant magnetoresistance have been intensively studied in this material system¹⁴¹. However, the ferroelectric properties remain to be puzzle. Recently, Xiong et al gave solid proves on its ferroelectricity with the discovery of OIHF s of $(\text{CH}_3)_3\text{NH}_3(\text{MnBr}_3)(\text{MnBr}_4)$ ¹⁴¹ and $(\text{C}_3\text{H}_7\text{FN})_3(\text{SnCl}_6)\text{Cl}$ ¹⁴². Considering its perovskite-like flexible structure, these works may open a new high-performance material family for ferroelectrics.

Figure 1.39 PE loop for $((\text{CH}_3)_3\text{NH})_3(\text{MnBr}_3)(\text{MnBr}_4)$ (a)¹⁴¹ and $(\text{C}_3\text{H}_7\text{FN})_3(\text{SnCl}_6)\text{Cl}$ (b)¹⁴². Figure (a) and (b) are adapted from reference 141 and 142.

1.3 Controllable strain materials

1.3.1 Overview

Materials with controllable strain have a wide range of applications including actuators¹⁴³⁻¹⁴⁵, sensor^{146,147}, dampener^{148,149}, aerospace applications¹⁵⁰ and energy harvester¹⁵¹. In this material family, strain can be driven by various outer stimuli in different systems, such as electric field (piezoelectrics, ferroelastic ferroelectrics and electroactive polymers), magnetic field (magnetostrictive materials and magnetic-driven shape memory alloys), temperature change (temperature-driven shape memory alloys) and pH difference

(shape memory polymer). In these strain materials and their relevant devices, output strain, stress and operating frequency are commonly seen as figure of merits (FOMs). Materials from different systems all get superiority in certain FOM but few can achieve high performance in all aspects (see table 1.2). For instance, temperature driven shape memory alloys (TSMAs), which is the most intensively studied shape memory materials, have high stress but suffered from slow speed and phase transition hysteresis effect⁶⁷. Magnetic shape memory alloys (MSMAs) get slightly higher strain, but much lower stress. Piezoelectrics are superior in speed and stress output while their strain are one to two magnitudes lower than other systems. Shape memory polymers (SMPs) on the contrary, produce the highest strain but much lower stress with slow speed. In addition, due to their chemical-method stimuli such as pH and moisture difference, some SMPs are not suitable for electronic or mechanical applications. A comparison of different materials classes can be seen in table 1.2 and figure 1.40¹⁵². Here I give a brief introduction to the background of each system.

Table 1.2| Properties of different material systems. SMA: Shape memory alloys, FSMA: ferromagnetic shape memory alloys (field induced variant reorientation)

	SMA	FSMA	Polymer (non-piezoelectric)	Ferro/piezoelectric ceramic
Stimuli method	Thermal	Magnetic	Thermal, electric, magnetic, light...	Electric
Strain output (%)	2-14	1-10	MAX 1000	0.01-1
Stress output (MPa)	10-1000	1-10	0.1-10	1-100
Work frequency	Generally below 1 Hz	~kHz	Very slow, operation period varies from second to minute	Up to GHz

Advantages	Excellent stress output	Good strain output	Large strain	Good stress output
	Low fatigue	Decent work frequency	Bio-friendly	Excellent work frequency
			Environment friendly	Electric stimuli
			Easy process	
Disadvantages	Thermal stimuli	Low stress output	Low stability	Poor strain output
		Require large magnetic field	Poor stress output	Some are lead-contained

Fig. 1.40 Strain-stress performance of different material systems. Adapted from reference 152.

1.3.2 Piezoelectric strain materials

Among all strain materials, piezoelectrics possess great superiority in high operation speed and large stress response. Taking electric field as the mainly stimuli, piezoelectrics have wide applications in electronic and optical devices⁶⁴. Materials working in linear strain

mode have been reviewed in previous chapter. The strain response for this type of piezoelectrics are generally below 0.5%⁸ with very few exceptions such as poly(vinylidene fluoride-trifluoroethylene) (~4%) exceeding 1%. The origin of linear-strain is piezoelectric effect and fast-response ferroelastic domain reorientation. Nonlinear strain, however, are deformation with hysteresis effect produced by non-180° ferroelastic switch¹⁵³, pinning effect¹⁵⁴ or electric field induced phase transition^{155,156}. The magnitude of this type of strain is relatively larger but generally are still lower than 1%.

Fig. 1.42 Non-180°(a) and 180°(b) ferroelastic switch and their induced strains.

Non-180° ferroelastic switch are common found in perovskite ceramics, which leads to potentially giant strain yet is irrecoverable in most ferroelectrics. One landmark work on strain enhancement is achieved in aged BaTiO₃ by Ren⁷. As shown in figure 1.43, in aging process, defects were formed because of ion diffusion under inner electric field. These defects induce an additional bias with the same direction to the ferroelectric polarization, which does not disappear during polarization reversal. This inner electric field drives ferroelectric dipole back to their initiate states after remove of E . Consequently, a recoverable 0.75% large strain can be induced in this aged system, which is several times large than the

strain in general BaTiO₃ (0.2%)¹⁵⁷. To date, the largest strain been achieved is 5% in BiFeO₃ film¹⁵⁵. However, this strain is produced by phase conversion at nanoscale, which may relate to special epitaxial strain of thin film. Strain at this level have never be observed in bulk materials. Consequently, this giant response is difficult to be used in practical strain applications. For non-nanoscale device, the strains output of piezoelectric material are still one to two orders of magnitude smaller than those of SMAs and SMPs, which is the biggest disadvantages of piezoelectric based strain output devices.

Figure 1.43 Mechanism of the large strain in BaTiO₃. (a) Initial cubic state. (b) Multidomain structure formed after cooling. Black arrows indicate inner electric field originating from polarization. (c) After-aging state. Small arrows illustrate electric field induced by defects after diffusing. (d) Material state under upward bias. (e) *PE* loop before and after aging. (f) *SE* loop of aged BaTiO₃. Bottom diagrams indicate the stable and unstable states in aged sample. Adapted from reference 7.

1.3.3 Temperature driven shape memory alloys

The first alloy with shape memory effect was reported in a Cd-Au structure by Arne in 1932¹⁵⁸. The name “shape memory alloy” was proposed in 1941¹⁵⁹ but had not get much attention until their excellent shape memory effect was disclosed in 1962¹⁶⁰. Classified by their stimuli, SMAs can be divided into temperature and magnetic field SMAs. From strain generation mechanism, magnetic shape memory alloys can be further classified into materials with domain reorientation and phase transition. Among all these SMAs, NiTi dominated TSMAs are the most intensively studied system due to its high ductility and strength¹⁶¹. However, TSMAs also suffer from disadvantages such as relatively small strain output, slow actuation speed, low energy efficiency and heating transfer issues⁶⁷.

Figure 1.44 Different phases and working cycles of SMAs. Adapted from reference 67.

There are two phases, three crystal structures and six transformations in all SMAs working cycles (see figure. 1.44). SMAs is in Martensite structure at LT and transfer to Austenite phase at HT. The temperatures where this phase change begins and finishes are A_s and A_f , while M_s and M_f correspond to the temperature where the invert transition starts and completes. These temperatures can be largely influenced by outer stress. M_d designate the temperature in which heat input can no longer induce additional stress. Based on these phase changes properties, three shape memory cycles have been built: The first is one-way shape memory effect. As indicated in figure 1.44, SMAs first go through twinned to detwinned Martensite transition under force loading. After the removal of stress, materials would maintain at deformed states and then recover to initial shape after one heating-cooling cycle. The second is two-way shape memory effect. Here SMAs can memory both its high and low temperature shape through simply heating and cooling. However, this working mode is less favorable in commercial devices due to halved strain output and faster fatigue effect referring to one-way effect^{162,163}. The third are pseudoelasticity or superelasticity. This effect requires a temperature range between A_f and M_d but does not need thermal activation. With simply force loading and unloading, SMAs can transfer between initial Austenite and detwinned Martensite states and produced strain output. These shape memory effects provide diverse working cycles that are preferable in different situations. With features of high stress output and relatively low fatigue effect, TSMAs have wide applications in different area, including automotive devices, aerospace applications, robotic systems and biomedical materials⁶⁷.

1.3.4 Magnetic shape memory alloys

MSMAs have attracted great attention since the discovery of the large strain output of NiMnGa in 1996¹⁶⁴. There are two mechanisms of strain generation. The first, also the dominating one in applications, originates from variant reorientation triggered by twin interface motion under magnetic field. The second is magnetic field induced phase transition. Due to mechanism difference, materials working in these two modes possess different mechanical properties and are employed for different applications.

Variant reorientation MSMA (VRMSMA)

Magnetocrystalline anisotropy energy (MAE) is defined as the energy required to switch the magnetic moment from easy to hard axis in single crystal. Strain will be induced when MAE of favorable variant is larger than the energy needed for twin boundary movement. Figure 1.45a and b are the MAE and boundary motion of the archetype MSMA NiMnGa^{152,165}. Due to its variant reorientation nature, the strain/stress output are independent to magnetic field once surpassing the saturation value. Compared with traditional SMAs such as NiTi, variant reorientation MSMA get slightly higher strain (maximum around 12%) and much faster operation speed (up to 1k Hz) but two orders of magnitudes lower stress (2-5M Pa)¹⁵². These features make VRMSMA a good candidate for micro-actuation system, where large travel per length and fast speed are highly desired¹⁶⁶. In addition, this type of MSMA fills the gap between piezoelectric materials (low strain/work output with high frequency) and conventional SMA (high work output and low frequency), providing new solution in various actuation systems¹⁶⁶. However, the small stress output still prohibits their applications in some traditional actuator fields. The requirement of single crystal form also increases the cost of relevant devices.

Figure 1.45 Magnetization-magnetic field diagrams and domain change with applied magnetic field in VRMSMA (a and b) and PTMSMA NiMnGa (c and d). Figure (a) and (c) are adapted from reference 152, (b) and (d) are from reference 167.

Phase transition MSMA (PTMSMAs)

The strain in PTMSMAs stems from magnetic field triggered martensitic phase transformation due to the change in Zeeman energy. Zeeman energy comes from the saturation magnetization difference between different phases and Zeeman energy is thus dependent to magnetic field (see figure 1.45c)¹⁶⁸. Since magnetization is also found to have strong influence on the phase transition temperature, it can be used as the on/off switch of the phase transition and accompanied strain change at high temperature. For instance, application of magnetic field is found to have suppressing effect to Martensite-Austinite phase transition in alloys such as NiMnCoIn, NiMnCoSn and NiMnIn¹⁶⁷. Under magnetic field, these materials would maintain at Martensite state even above phase transition temperature. Removing of magnetic field in this case will suddenly induce structure change and trigger a large strain output (figure 1.45d). This working principle leads to magnetic

actuator. Compared with VRMSMAs, PTMSMA have much higher stress output (few hundred M Pa) but lower actuation strain (1-4%)¹⁶⁷. Because the Zeeman energy related phase transition mechanism, strain along a certain direction is dependent to the magnitude of magnetic field. This makes polycrystal form PTMAMs possible to be used in practical devices, leading to a large reduce in cost. However, the magnetic field required in PTMAMs devices can be as high as tens of tesla, which severely prohibits its commercial application¹⁶⁹.

1.3.5 Shape memory polymers

SMPs are polymers with elastic recovery force that stabilize its shape under a certain physical/chemical condition. This force stems from elastic entropy related to the expansion of polymer chain and associated conformational entropy¹⁷⁰. Since the elastic entropies of polymers are sensitive to various forms of condition changes, the outer stimuli of SMPs are more diverse than those of other SMMs. Reported stimuli so far include change in temperature, moisture, light, pH, magnetic/electric fields and being exposed to certain solvent¹⁷⁰. Figure 1.46 are examples of light and pH driven SMPs. Among all these stimuli, thermal change is still the most common triggering method¹⁷¹. Because of the full organic component, SMPs possess superior features such as lightweight, low cost, biocompatibility and environmental friendly¹⁷². In addition, these polymers can produce giant strain up to 800%, which is the highest among all SMMs⁶⁷. However, SMPs have the lowest stress output (~3 MPa) and very slow response time (maximum ~1 Hz). Stimuli mechanism such as pH, moisture and solvent change also makes these materials almost impossible to be used in practical electronic systems. Due to these features, SMPs are more employed in biomedical applications including tissue engineering, tightening systems, drug deliver and self-deployable surgical devices. Progress on traditional SMMs applications have also been made such as actuator, sensor and flexible electronic devices¹⁷².

Fig. 1.46 Light and pH driven SMPs with examples of multiblock polyesterurethane (a)¹⁷³-(b)¹⁷⁴ and β -CD-DETA (c)¹⁷⁵. (a) Pictures of SMP in permanent (1), temperature (2) and recovered states (3). (b) Molecule origin of the light induced shape memory effect in multiblock polyesterurethane. (c) Working cycle of pH driven shape memory effect in multiblock polyesterurethane. Figure (a), (b) and (c) are adapted from reference 173, 174 and 175, respectively.

Compared with SMAs, SMPs are more often to incorporate with other nano systems (nanotube, nanoparticle, nanoribbon, etc) to overcome its disadvantages such as low strength and low thermal conductivity. Due to the inherent high stiffness and functionalities of these agents, the obtained shape memory composites (SMCs) always show obvious improvements in mechanical, thermal or electrical properties¹⁷⁶. For instance, by incorporating styrene-based nanopaper with multiwall carbon nanotube, the electroconductivity and recover speed can be largely improved¹⁷⁷. Because of these conferred functionalities and fast research development, SMCs are regarded as multi-stimuli-responsive materials and the SMPs for the next generation¹⁷⁸.

Chapter 2: Experiment Methods

This chapter includes synthesis, characterization and theoretical simulation details of the research in chapter 3, 4 and 5.

2.1 Synthesis and basic characterizations

Synthesis of $\text{C}_6\text{H}_5\text{N}(\text{CH}_3)_3\text{CdBr}_{3x}\text{Cl}_{3(1-x)}$ ($0 \leq x \leq 1$)

Chemicals were purchased from Sigma-Aldrich and used without further purification. Stoichiometric $\text{C}_6\text{H}_5\text{N}(\text{CH}_3)_3\text{Cl}$, $\text{C}_6\text{H}_5\text{N}(\text{CH}_3)_3\text{Br}$, CdCl_2 and $\text{CdBr}_2 \cdot 4\text{H}_2\text{O}$ were dissolved in acetonitrile/deionized water mixed solution with stirring (volume ratio = 3:2 for $0 \leq x \leq 0.67$ and 4:1 for $0.67 < x \leq 1$). The solution was then left for slow evaporation at room temperature. Centimeter level single crystals with branch shape were obtained after 3 weeks. With increasing Br ratio, the color of single crystals gradually changes from transparent to slight blue. $(\text{PTM})\text{CdBr}_{3x}\text{Cl}_{3(1-x)}$ crystals with $x = 0.15, 0.29, 0.45, 0.63, 0.7, 0.77, 0.8$ and 0.9 were synthesized from precursors with Br molar ratios = 0.2, 0.33, 0.5, 0.67, 0.73, 0.8, 0.87, 0.96, respectively. For example, crystal with $x = 0.8$ is synthesized by dissolving $\text{CdBr}_2 \cdot 4\text{H}_2\text{O}$, $\text{C}_6\text{H}_5\text{N}(\text{CH}_3)_3\text{Br}$ and $\text{C}_6\text{H}_5\text{N}(\text{CH}_3)_3\text{Cl}$ with weight of 688.56 mg (2 mmol), 259.344 mg (1.2 mmol) and 137.336 mg (0.8 mmol) into acetonitrile/DI water mix solution with volume ratio of 4:1. The halide ratio x of crystals with different precursors were calculated by the mass fraction of C, H, and N measured by elemental analyzer (PerkinElmer model 2400 Series II). The crystals are stable in air. No obvious change was observed after months in air or during high temperature (up to 150°C) measurements.

XRD measurements

Powder XRD: Powder were obtained by grinding single crystals. XRD measurements were performed at room temperature by a Panalytical XRD with Cu K α radiation ($\lambda=1.540598$ Å, 30 mA and 40 kV).

Single crystal XRD: XRD data were recorded by a Bruker APEX II diffractometer. Bruker SHELXTL Software Package was used to solve crystal structures with refinement on all data by Full-matrix least-squares based on F^2 . All nonhydrogen atoms were solved using anisotropic refinement. All hydrogen atoms were generated on their geometrical positions and allowed to ride in their respective parent atoms with appropriate isotropic thermal parameters. Structure factor calculations include all these atoms.

DSC and thermogravimetric analysis (TGA) measurements

Differential scanning calorimetry measurements were carried out on a TA Q10 with nitrogen atmospheric pressure in aluminum pans. Data were collected from single crystal samples in heating and cooling with a rate of 5 K min⁻¹. TGA was performed on single crystal samples under air using a TGA/ Q500 V6.7 Build 203 instrument with heating rate of 10 K min⁻¹.

2.2 Electrical measurements

Dielectric and ferroelectric properties measurements

Temperature dependent dielectric/ferroelectric measurements were conducted in a cryogenic micromanipulator probe station with a heating stage. Dielectric data were recorded

by Agilent E 4980A with 1 V AC voltage and conductive tips on probe station on bulk single crystal specimens. Crystals were carefully cut and polished to plate form. Silver paste were evenly deposited on crystals as top and bottom electrodes. *PE* loops and PUND properties were measured along *c*-axis on single crystal samples by a commercial ferroelectric tester (Precision LC, Radiant technologies) equipped with voltage amplifier (Precision 4kV HVI, Radiant technologies). Due to the low dielectric constant and ferroelastic switch in polarization reversal, full-surface-covered depositions of silver paste were required. Otherwise would lead to inaccurate capacitance and much larger E_c .

PFM measurements

PFM scanning were performed on a $x=0.77$ single crystal with a commercial atomic force microscope (Asylum Research MFP-3D). A soft conductive Au-coated silicon tip (Budget Sensor, ContGB-G, spring constant of $\sim 0.2 \text{ N m}^{-1}$, free air resonance frequency of 13 kHz) was used for PFM measurements to avoid surface damage. With the advantages in signal-to-noise ratio improvement, resonance-enhanced dual AC resonance tracking (DART) mode¹⁷⁹ (500 mV tip driven voltage, $\sim 220\text{kHz}$ frequency) was used in angular PFM study for accurate amplitude comparison among sample at different rotated orientations.

Shear strain and piezoelectricity measurements

As shown in fig. 2.1, crystals were aligned with (100) crystallographic direction perpendicular to the bottom slide and fixed by epoxy and double side tape. Right and left side were first carefully cut along *c* axis normal plane and were polished to make the edge

surface being parallel to each other. Silver pastes were then deposited on both sides as electrodes. An aluminum foil was fixed on top of each crystal by epoxy as reflective mirror with its plane perpendicular to laser beam and crystals top surface. With application of electric field (by Precision ferroelectric tester), strain with following movements would be induced, which is recorded by a commercial photonic sensor (MTI-2100 fotonic sensor). Shear strain (S) can be calculated with $S_5=d/H$ ¹⁸⁰, where d is induced displacement and H is the height of crystal. Same setup was used for piezoelectric measurements. Samples were first pole to a certain polarization and small electric field in polarization direction was then applied. The shear piezoelectric coefficient (d_{35}) is obtained through $d_{35}=S_5/E_3$.

Figure 2.1 Experimental setup for the shear strain and d_{35} measurements. The solid and dash line present the sample outline before and after electric field application. The coordinate on bottom left indicates the crystallographic orientation of the sample.

2.3 Computational simulation

Density functional theory (DFT) were performed to simulate Young's moduli, ferroelectric switch barriers and chemical bond strengths of (PTMA)CdBr₃ and (PTMA)CdCl₃ crystals. The calculations were conducted by exchange-correlation functionals of projected augmented wave (PAW) method¹⁸¹ and the Perdew-Burke-Ernzerhof (PBE)¹⁸², which is implemented in the Vienna ab-initio simulation package (VASP)¹⁸³. A 2×2×4 Monkhorst-Pack k-mesh is employed and 500 eV is set as the cutoff energy for plane wave expansion. Treated valence electrons includes Br (4s²4p⁵), Cl (3s²3p⁵), H (1s¹), N (2s²2p³), C (2s²2p²) and Cd (4d¹⁰5s²). Optimized structures were based on experimental crystallographic data with adjustment carried out until atomic force below 0.002 eV/Å. Van der Waals (vdW) effects¹⁸⁴ were included in structural and electronic relaxations and all the subsequent calculations. We use Berry phase approach to calculate ferroelectric polarizations^{185,186}, and generalized solid-state nudged elastic band (GSSNEB) method to simulate polarization switching path with the minimum energy¹⁸⁷. The elastic constants were obtained from the strain-stress relationship. LOBSTER package with a 3×3×5 Monkhorst-Pack k-mesh were used to compute the crystal orbital hamiltonian populations (COHP)¹⁸⁸⁻¹⁹⁰.

The calculated polarization vectors for (PTMA)CdCl₃ and (PTMA)CdBr₃ are $(7.8 + nP_{\text{Cl}}, 0, -3.7) \mu\text{C}/\text{cm}^2$ and $(9.5 + mP_{\text{Br}}, 0, -2.8) \mu\text{C}/\text{cm}^2$, respectively. Here n and m are undetermined integers. The polarization quantum $P_{\text{Cl}} = 15.8$ and $P_{\text{Br}} = 14.8 \text{ mC}/\text{cm}^2$ are defined as $\frac{1}{\Omega}ea$, where a is the lattice length along a axis, e is polarization charge, and Ω is the volume of unit cell. The absolute polarization magnitude along a cannot be fully determined since no HTP structure is available.

The elastic matrix is calculated by strain-stress curve with finite differences¹⁹¹. Specifically, ISIF=3, IBRION=6, and NFREE=4 were used in VASP simulation. The elastic constants are obtained by conducting six finite lattice distortion and calculating their corresponding stress. Calculation with ENCUT varied from 500 to 800 eV was performed to test the convergence with respect to cut-off energy. Many elastic constants are dependent to

the cut-off energy. The shear modulus $C_{55}=5.8$ Gpa, which is used in stress and work output calculation, is obtained under high energy cut-off.

Four-point method with NFREE=4 is used to calculate the elastic constants from the strain-stress relationship. Strain elements was obtained considering 4 unit-cell distortions. Distortions of $-2d$, $-d$, d , and $2d$ are performed with $d=1.5\%$. The elastic constant is extracted by:

$$C_{ijkl} = \frac{-\sigma_{ij}(-2\delta_{kl}) + 8\sigma_{ij}(-\delta_{kl}) - 8\sigma_{ij}(\delta_{kl}) + \sigma_{ij}(2\delta_{kl})}{12\delta_{kl}}$$

Here, δ_{kl} is the 1.5% strain change and σ_{ij} is the obtained stress. The tensor C_{ijkl} was reduced to second rank by inducing Voigt notation.

Chapter 3: Insight into the Modulation Role of Halide Part in Organic-inorganic Hybrid Ferroelectric System

3.1 Introduction and motivation

Since the first HPF be reported in 2014¹⁹², more than forty OIHF s have been successfully design and characterized. Like hybrid perovskite, the structure diversity of OIHF s (with general chemical formula of AB_nX_m , n and m vary regarding the structure), stems from its composition flexibility in A and B sites. To date, site doping have been successful induced among all A, B, and X positions, which were found to have large tunability in their structure, optical and ferroelectric properties^{26,91,105}. For example, A site doping may induce sequent structure change and morphotropic phase boundary effect, leading to giant piezometric response ($d_{33}=1540$ pC/N) in several OIHF s (see fig 1.27c and fig. 3.1)²⁶. In addition, site doping was reported to have structure tailoring effect, which is rarely to be seen in oxide perovskite^{193,194}. This effect enables 3D hybrids transfer to 2D structure, which leads to the discovery of various 2D-3D OIHF s with great potential as nano-optical devices^{90,193,194}.

Figure 3.1 Change of piezoelectric response induced by A site doping in $(\text{TMFM})_x(\text{TMCM})_{1-x}\text{CdCl}_3$. Figure adapted from reference 26.

Figure 3.2 Structure tailoring effect of A site doping in $(\text{C}_4\text{H}_9\text{NH}_3)_2(\text{CH}_3\text{NH}_3)_2\text{Pb}_3\text{Br}_{10}$ (a) and $(\text{CH}_3(\text{CH}_2)_3\text{NH}_3)_2(\text{CH}_3\text{NH}_3)\text{Pb}_2\text{Br}_7$ (b). Figure (a) and (b) are adapted from reference 193 and 194.

However, different with the stunning progress made in A site doping, the effect of halide site modulation is still obscure. Unlike A and B sites, the modification towards the halide part can directly change the metal-halide polyhedron, such as its volume and halide-metal-halide tilt angle, which may induce obvious change in materials energy structure¹⁹⁵. In organic-inorganic perovskite, halide doping has robust modulating ability to various optical and electrical properties, such as photoluminescence peak position, photovoltaic effect and carrier density^{195,196}, which are high desired in ferroelectrics for both fundamental research and applications. For example, by halide substitution, OIHF with ultrasmall energy bandgap may be achieved, which would be a huge breakthrough in ferroelectric photovoltaic device. Or with the tuning effect of halide substitution on emission bandwidth, white light PL with high quantum efficiency may be realized in luminescent ferroelectrics. All these may lead to superior optical-electronic materials and multifunctional devices for the next generation.

Nevertheless, in previous reports, OIHF are found to lose their ferroelectricity with even minor halide substitution, which makes the investigation to the role of halide site very difficult to be conducted²⁵. Here, we report the halide doping mechanism study based on a

new OIHF $\text{C}_6\text{H}_5\text{N}(\text{CH}_3)_3\text{CdBr}_{3x}\text{Cl}_{3(1-x)}$ ((PTMA) $\text{CdBr}_{3x}\text{Cl}_{3(1-x)}$), $0 \leq x \leq 1$). The ferroelectricity of this solid solution is well preserved throughout two halide sides. With systematic characterization on its crystallographic and ferroelectric properties, we found the halide site has strong soften effect and possesses large influence on ferroelectric switching barrier making halide substitution an effective method in tuning various ferroelectric properties such as coercivity, phase transition temperature and polarization switching speed. This mechanism studied provide great insight into the role of halide part in OIHF ferroelectricity, which should inspire hybrid ferroelectric design and property optimization. In addition, ((PTMA) $\text{CdBr}_{3x}\text{Cl}_{3(1-x)}$) possess outstanding flexibility on various ferroelectric properties. This unique composition dependent ferroelectricity makes this solid solution have great potential in wide range of ferroelectric and electric semiconductor applications.

3.2 Result and discussion

3.2.1 Crystallography and basic characterizations

As mentioned in Chapter 2, bulk crystals with different halide compositions were obtained by slow evaporation of DI water/acetonitrile mixed solution containing corresponding precursors. TGA and DSC measurements were first conducted to investigate decomposition and phase transition temperatures. As shown in Fig 3.3a, this solid solution has good stability up to 180°C. DSC is a thermoanalytical technique which measures the amount of heat required to increase sample temperature. Because of latent heat, heat flow changes dramatically during phase transition of the sample. The peak of heat flow can consequently mark the phase transition temperature. With this technique, composition dependent DSC measurements were conducted to investigate the phase transitions properties of this solid solution under heating (lower lines) and cooling (upper lines) cycles. As illustrate in Fig. 3.3b, with increasing Br ratio, the transition temperature decreases from above decomposition temperature (180°C) to 19°C (pure Br composition). Additionally, thermal

hysteresis effect becomes more obvious with higher Br amount, which increases from $\sim 7^\circ\text{C}$ to $\sim 30^\circ\text{C}$ following the Br ratio increasing from 63 % to 100 %.

Figure 3.3 Thermal properties of $(\text{PTMA})\text{CdBr}_{3x}\text{Cl}_{3(1-x)}$. TGA (a) and DSC (b) analysis on crystals with selected compositions. (c) Phase transition temperatures of this solid solution with different Br amount.

Powder XRD were performed to study the structure properties of this solid solution. Fig. 3.4 shows the powder XRD pattern at room temperature. The highly similar XRD pattern indicates no structure transition is induced by halide substitution. The Br doping otherwise brings in unit cell expansion in all dimensions (Fig. 3.5). The refinement (see table 3.1) on these XRD data further specifies this expansion effect and indicates no phase transition was involved. Crystals with different Br ratio are all in Cc space group at LTP.

Figure 3.4 Powder XRD measurements. (a) XRD patterns of $(\text{PTM})\text{CdBr}_{3x}\text{Cl}_{3(1-x)}$ with x varying from 0 to 0.9 at room temperature. (b) Indexed of selected peaks of $(\text{PTM})\text{CdBr}_{2.7}\text{Cl}_{0.3}$. Information of full peak indexes is available in submitted crystallography data in Cambridge Crystallographic Data Centre (CCDC).

Figure 3.5 Lattice expansion along [100], [010] (a) and [001] directions (b) with increasing Br amount.

Table 3.1 Structural information of (PTMA) $\text{CdBr}_{3x}\text{Cl}_{3(1-x)}$ in LTP.

Br amount (%)	0	15	29	45	63	70	77	80	90
a / Å	12.7541(2)	12.8262(1)	12.8497(2)	12.8960(1)	12.9338(3)	12.9763(2)	12.9909(2)	13.0015(2)	13.0465(2)
b / Å	14.5035(1)	14.5961(1)	14.6257(2)	14.6785(1)	14.7126(4)	14.7458(3)	14.7443(2)	14.7601(1)	14.7827(1)
c / Å	7.1515(1)	7.2275(1)	7.2554(1)	7.31681(6)	7.3650(1)	7.4153(3)	7.4261(1)	7.4567(1)	7.5058(1)
β / °	96.3069(9)	95.910(1)	95.823(1)	95.5064(7)	95.282(1)	94.985(2)	95.035(1)	95.000(1)	94.841(3)
Vol / Å³	1314.86(3)	1345.89(3)	1356.50(3)	1378.63(2)	1395.54(5)	1413.54(6)	1416.92(4)	1425.52(3)	1442.43(3)
Space Group	<i>Cc</i>	<i>Cc</i>	<i>Cc</i>	<i>Cc</i>	<i>Cc</i>	<i>Cc</i>	<i>Cc</i>	<i>Cc</i>	<i>Cc</i>

Crystallography XRD measurements were then performed on selected compositions (fig. 3.6). For the mixed-halide crystal (fig 3.6d-e), Br and Cl atoms randomly occupy the halide sites, leading to different Cd-X bond lengths in fig. 3.6d. All structures undergo monoclinic (*Cc*) to orthorhombic (*Ama2*) phase transition. Given that this solid solution is isostructural, structure with low Br amount should have similar structural phase transitions at high enough temperature, which of course, do not available because corresponding T_p are higher than decomposition temperatures.

Figure 3.6 Crystallographic structures of pure Br (a-b), pure Cl (c) and 76% Br crystals (d-e). The LTP (a, c and d) are all in *Cc* space group, while HTP (d and e) are crystalized in *Ama2* group.

Here, I make a detail discussion of structural change during phase transition with the example of pure Br structures. In LTP, the crystal is consisted by 1D CdBr_5^- hexahedron and PTMA cation. The edge sharing metal-halide polyhedron form the 1D network while PTMA cations occupy the space between inorganic chains and link with CdBr_5^- by hydrogen bond between H in methyl group and Br in metal halide hexahedron. Within the one-dimension chain, each cadmium atom is surrounded by five bromide atoms, where four edge sharing Br atoms link Cd atoms in two nearby CdBr_5^- polyhedron. A simple polarization analysis can be made by regarding N and Cd as the centers of cation and anion. As shown in Fig. 3.7a, there is a net long-rang-order polarization along **c** direction, while in **b** direction, each dipole's projection is offset by its upper and lower dipole. Polarization along **a** direction can be identified in Fig. 3.7b. However, due to the too large organic cation, polarization along this direction is not switchable, which is confirmed by $\text{mm}2\text{Fm}$ Aizu rule¹⁹⁷ and our experiment result, that no polarization reversal was realized until crystals decomposed because of too high electric field.

Figure 3.7 Ferroelectric polarizations in (PTMA)CdBr₃ along **a** (a) and **b** (b) axis at LTP.

As temperature increase above 19° C, obvious structure changes occur in 1D metal-halide chains and organic cations. With higher thermal energy, the longest Cd-Br bond (3.2 Å, blue dash lines in Fig. 3.8a) is broken. Following this bond change, Br1 and Br3 now get same attraction force from upward and downward directions inside metal-halide hexahedron and thus move to the new lowest energy position-the plane that has the same distance to two Br2 atoms (denoted by red dash line). The 1D inorganic chain is now consisted by mirror-symmetric corner sharing CdBr₄⁻ tetrahedron. Following the inorganic framework change, organic cations get corresponding movement and mirror symmetry. As the result, order-disorder transition occurs on organic parts and mirror symmetry is finally induced in this hybrid system. With cation and anion moving to the same plane, ferroelectric polarization along **c** direction disappears.

Figure 3.8 (PTMA)CdBr₃ crystal structures at LTP (A) and HTP (B). The blue dash lines indicate the broken Cd-Br bond at HTP while the red arrows indicate corresponding Br movement. As the consequence of these structure changes, mirror symmetry (red dash line as one of the symmetry planes) is induced in this crystal system.

Temperature dependent dielectric measurement was conducted on a 77%-Br single crystal to investigate dielectric property across the phase transition. As shown in Fig. 3.9, there is an anomaly with mixture of step-like and peak-like character at around 86°C along **c** axis, which is consistent with DSC data. The small peak along **a** axis is attributed to ionic movement during phase transition. No significant change was observed in **b** axes.

Figure 3.9 Temperature dependent dielectric behavior of 77% Br sample along different crystal directions in heating process at frequency of 1k Hz.

To test stability in air condition, powder XRD measurements were carried out on pure Cl and 90% Br samples at the 1, 2, 4 and 7th day (fig. 3.10). The unchanged XRD peak positions and intensities indicate the excellent air stability of this solid solution.

Figure 3.10 Powder XRD pattern of pure Cl (a) and 90% Br (b) samples at the 1, 2, 4 and 7th day.

3.2.2 Ferroelectric properties

The polarization reversal studies were first carried out by PFM measurement. A 77% Br crystal was orientated with [001] direction parallel and [010] direction perpendicular to the scanning face. From crystallography measurement, switchable polarization is along [001] direction, so lateral PFM tip was employed and positioned with cantilever perpendicular to [001] direction (condition described in PFM part of chapter 2). By scanning along the green line in figure 3.11, the upper and lower part of crystal were switch into different polarization states (second column). Electric field was then applied again to lower position, part of previous $\odot$ domain was switched to another direction, while the $\otimes$ domain showed further expansion. These PFM results indicate the robust ferroelectricity of this crystal.

Figure 3.11 PFM diagrams of polarization switching on 77% thin film. The first, second and third column indicate the states before and after the first and second voltage applications (the 7V switching electric field is applied by tip scanning along the green line).

Ferroelectric behaviors were then investigated in detail by hysteresis loop and PUND measurements. 63% Br sample was chosen due to its relatively high phase transition temperature (150° C) and ease in polarization switching, which leaves a wide range of temperature to study the ferroelectric behaviors. Hysteresis loops were first measured under different electric fields with frequency of 2 Hz (Fig. 3.12 a) at 55° C. Polarization is very difficult to be fully switched below this temperature because of too large coercivity. With E increasing to 5.10 kV/cm, PE loop gradually becomes saturated with a remnant polarization (P_r) of $\approx 3.19 \mu\text{C}/\text{cm}^2$, which fits the typical behaviors of E dependent hysteresis loop. Polarization reversal was then measured at different temperatures. With increasing T , P_r

shows no obvious change while *PE* loops become narrower, indicating the reduction of energy switching barrier between equivalent polarization states^{198,199}. The frequency dependent behavior was then studied at 100° C (fig. 3.12c). The polarization was found difficult to be fully switched at higher frequency (*F*). As *F* increases from 1 to 40 Hz, coercivity increase dramatically from 3.8 to 5.5 kV/cm while *P_r* show an obvious drop from ~3.2 to 1.9 $\mu\text{C}/\text{cm}^2$. The lack of saturation polarization region at high frequency also indicates incomplete polarization reversal. We think the reasons for the low frequency feature and highly *F* sensitive *PE* behavior comes from the structure confinement condition and the large-volume/weight cation in this OIHF. In oxide perovskite, the cations are generally single atoms that possess large freedom of small movement under electric field. In this OIHF, cations are large molecules confined by rigid inorganic frameworks. The large-weight cations and structure confinement condition thus require higher driven energy, which can be understand as driven force multiple application time. Consequently, electric field here needs more time to make full polarization switch in this. This *F* sensitive behavior can also be seen in other OIHF^{111,123,200}.

To measure remnant polarization (*P_r*), the conventional positive-upnegative-down (PUND) measurements were performed on the crystal. Here *P_r* is obtained by subtracting the non-remnant part (*P[^]*) from the total reversed polarization (*P^{*}*) (see fig. 3.12d). Fig. 3.12e and f indicate this material has typical *T* and *E* dependent ferroelectric behaviors. *P_r* keeps increasing at larger electric field and longer long pulse width. As temperature goes up, the switching-start onset keeps decreasing while no obvious change happens in *P_r* value. These results show good consistence with *PE* loop measurements.

Figure 3.12 Detail ferroelectricity characterizations of 63% Br sample. (a) Hysteresis loops under different electric field at 55°C. (b) Temperature dependent *PE* loops. (c) *PE* loops with different frequencies at 100°C. (d) Working mechanism of PUND measurement. Pulses and polarizations measured within one PUND cycle. (e) Pund measurements at different temperatures with $E = 6.19$ kV/cm. (f) E dependent pund responds at 95°C under various pulse widths.

3.2.3 Modulation effects of halide part

Halide substitution was found to have major influence on this OIHF's ferroelectric properties including saturation polarization, coercivity, phase transition and the lowest polarization switching temperature (see in fig. 3.13). The reason for most of these modulation effects is the decrease in ferroelectric switching energy barrier induced by Br substitution.

Figure 3.13 The influence of halide substitution on ferroelectric properties. (a) *PE* loops of selected compositions. Measurement frequency is 2Hz. (b) P_r and unit cell volume change throughout Br substitution. (c) Br ratio dependent polarization switch temperature and coercivity. (d) Br amount dependent phase transition temperature.

Fig. 3.13a shows the *PE* loops of this solid solution with different halide compositions. P_r show decreasing trend with higher Br amount (fig. 3.13b). Given the condition that there is only minor polarization change within each unit cell (calculated by regarding N and Cd atom as the center of cation and anion), this decrease should be mainly attributed to the

expansion of unit cell, leading to less amount of ferroelectric dipoles contained in per unit volume. The most obvious change induced by Br substitution is the soften effect, which is associated with the decrease of ferroelectric switch energy barrier. As shown in fig. 3.13 a and c, with Br ratio increase from 0 to 90%, coercivity drops from 7.3 to 3.9 kV/cm and the lowest switching temperature decrease from 145 to 35 °C. These changes indicate less electric and thermal energy are required for polarization reversal as Br increasing. The soften effect can also be reflected by the decrease in phase transition temperature (figure 3.13d), as the temperature of order-disorder phase transition can reflect the thermal energy required for dipole to overcome the potential height among polarization states in this OIHF⁷⁹.

Figure 3.14 Comparison between the polarization reversal in this solid solution (a) and oxide perovskite (b). Red arrows in (a) illustrate molecule movement during polarization switch. Figure (b) is adapted from reference 1.

The origin of this soften effect is the expansion of unit cell and decrease in chemical bond strength. Different with oxide perovskite, where electric field only induce small movement on single atom cation, polarization reversal in this OIHF is involved with both shear deformation of inorganic backbone and rotation of the large molecular cation (fig. 3.14). The ferroelectric potential height is thus directly related to the energy required to change the

strength of Cd-X and X-H bonds (X is the halide element). In this solid solution, Br substitution can directly expand Cd-X and hydrogen bond length and consequently reduces the energy barrier (see table 3.2). This results in obvious soften effect, and tunable ferroelectric properties including phase transition temperature, coercivity and switchable temperature.

Table 3.2| Chemical bond lengths of the mainly involved chemical bonds during polarization reversal. The Cd-X here is the longest cadmium halide bond of inorganic framework and X-H1, X-H2 are the first and second strongest hydrogen bonds. These bonds are broken and rebuilt during polarization reversal.

Composition	(PTMA)CdBr ₃			(PTMA)CdCl ₃		
Bond	Cd-Cl	Cl-H1	Cl-H2	Cd-Br	Br-H1	Br-H2
Bond length (Å)	2.8186	2.6113	2.7170	3.0299	2.6973	2.8417

3.2.4 Reference table

Table S1| Crystallography data of (PTMA)CdBr_{3x}Cl_{3(1-x)} with different Br amounts.

Br amount (%)	0	76		100	
Empirical formula	(PTMA)CdCl ₃	(PTMA)CdBr _{2.3} Cl _{0.7}		(PTMA)CdBr ₃	
Temperature (K)	299(2)	296(2)	393(2)	253(2)	308(2)
Space group	Cc	Cc	Ama2	Cc	Ama2
a (Å)	12.7404(4)	12.9705(15)	12.9801(13)	13.0388(5)	13.0309(9)
b (Å)	14.4928(6)	14.7252(17)	14.7100(14)	14.7738(6)	14.7328(9)
c (Å)	7.1432(3)	7.4093(8)	7.6583(6)	7.4720(3)	7.7137(4)

β (°)	96.3055(14)	95.121(4)	90	95.2538(10)	90
Volume (Å ³)	1310.97(9)	1409.48	1462.25	1433.3	1480.89
Z	4	4	4	4	4
F (000)	696	861	859	912	912
R factor (%)	3.29	3.8	3.15	3.71	3,88
Goodness-of-fit	1.029	1.036	1.009	1.072	1.064

3.3 Conclusion

To summarize, we discovered the soften effect of halide substitution and a new OIHF with tunable ferroelectric properties. Different with oxide perovskite ferroelectrics, the polarization reversal in this new OIHF involves with break and rebuild of metal-halide bond. Tailoring this bond strength through halide substitution thus becomes an effective method to tune ferroelectric switching barrier and consequently change various ferroelectric properties including coercivity and phase transition temperature. This mechanism discovery shines light on new OIHF design and their property optimization. In addition, a new OIHF with highly tunable ferroelectric properties and high phase transition temperature at its high Cl region is successfully designed and characterized. From pure Cl to high Br crystals, the coercivity changes from 7.3 kV/cm at 140° C to 3.8 kV/cm at 35° C, while the phase transition temperature decreases from 180°C above to 19°C. To the best of our knowledge, this solid solution should be the first OIHF with tunable and preserved ferroelectricity throughout Cl to Br substitution. This outstanding property tunability makes this OIHF possess broad applications in ferroelectric and semiconductor devices.

Chapter 4: Colossal shear strain in (PTMA) $\text{CdBr}_{3x}\text{Cl}_{3(1-x)}$, properties and mechanism studies

4.1 Introduction and motivation

Materials with giant controllable strains have wide applications in actuators^{201,202}, shape memory devices²⁰³ and sensors²⁰⁴. Intensively studied have been made in the discovery of new strain materials and properties optimization in various materials systems including shape memory alloy²⁰⁵, piezoelectrics⁷ and electrostrictive materials²⁰⁶, where different stimuli are employed to trigger strain output, such as change in temperature, magnetic and electric fields. For instance, NiTi, as the archetype of SMA, can produce shear strain up 8 % from thermal energy induced phase transition²⁰⁷. NiMnGa, the most intensively studied MSMA, shows ~10 % shear strain coming from twin boundary movement under magnetic field²⁰⁴. The general strain for ferroelectric perovskite oxides are about 0.3 %⁸. With optimization strategy such as point-defect inducing and ferroelastic switching, their strain can be increased to 0.75 %⁷. Polymer system possess more diverse stimuli, including change in temperature, pH, moisture, light, electric and magnetic fields¹⁷¹. Because of their structural flexibility, the strain output of some SMPs, for instance, elastomers, can even surpass 100 %²⁰⁸.

However, although various materials systems are available for different device applications, very few of them can satisfy the requirements of high work output, high speed and large strain simultaneously. As shown in figure 1.40, shape memory alloys have good stress and medium strain output, but the actuation is always limited by low speed and is accompanied with phase transition hysteresis effect⁶⁷. Piezoelectric oxides perovskites generate good force output with high speed, but produce much lower strain than other systems. Polymers on the opposite, possess the largest strain response but one to two orders of magnitude lower stress (2 MPa on average)¹⁵².

OIHF's are consisted by both inorganic frameworks and organic molecules. They consequently take advantages from both organic ferroelectrics such as lightweight, good flexibility and from inorganics materials such as good mechanical strength. This makes them possible to provide both large strain and high stress output^{83,84}. The cations in OIHF's are large organic molecular linking with the inorganic frameworks through hydrogen bond and van der Waals interaction. During polarization switch, these organic cations rotate or flip to other energy equivalent positions. This is largely different with oxide ferroelectrics, where only small displacements of single-atom ions are get involved (see figure 4.2). With a large organic cation and limited space enclosed by rigid inorganic backbone, it is thus possible to suppress the strain-equivalent 180° dipole rotation. Structure like this may result in structure confinement effect that induce large energy barrier along a certain direction and blocks the 180° rotation path, leading to giant shear strain. Following this thought, we design and investigate the strain properties of (PTMA)CdCl₃, which was found to produce colossal shear strain about two orders of magnitude higher than typical oxide perovskite ferroelectrics and around two times larger than top-performance shape memory alloys. The giant strain in this OIHF is attributed to ferroelastic switch associating with lattice distortions under electric field. Additionally, we found Br substitution leads to lower strain output (~12.5% for 90% Br sample) but much higher operation speed, which are attributed to their smaller unit cell tile angle and soften effect of Br substitution.

Figure 4.2 Polarization switch in OIHF and oxide perovskite. (a) (Pyrrolidinium)MnCl₃⁹². (b) (PTMA)CdBr₃ (c) PbTiO₃. Black arrows in (a) and (b) indicate molecular movement during polarization reversal. Figure (a) and (c) are adapted from reference 92 and 1.

4.2 Result and discussion

4.2.1 Strain property

Figure 4.3 Experiment and strain response of (PTMA)CdBr_{2.7}Cl_{0.3} at 35 °C. (a) Experiment set up for strain measurement, the coordinate on the right illustrate crystal orientation of the sample. (b) E dependent strain-electric field (SE) loops. (c) SE loops at different driven frequency. (d) Fatigue effect.

Strain properties were first systematically studied on 90% Br sample with experiment setup in fig. 4.3a. As discussed in Chapter 3, the structure confinement effect restrains the flip of organic cation across 1D inorganic chain, the polarization along **a** axis consequently can not be successfully switched till material breaks down under large electric field. E was then applied along **c** axis. Shear strain is angular deformation. When the rotation angle β is smaller than 25°, the difference among $\sin(\beta)$, $\tan(\beta)$ and β is neglectable, the change in height is thus negligible. In condition, shear strain can be calculated by $S = \tan(d/H) \approx d/H$, where d and H are the shear movement and height of the sample^{180,209}. As shown in fig. 4.3b, the obtained SE curves get PE loop like shape with the maximum strain going up to 12.5%, which is two orders of magnitude higher than general piezoelectric ceramic (0.3%) and larger than all temperature driven shape memory alloys (9%)^{8,207}. Working frequency is another important factor that determinate power output in applications such as actuator. Next we

studied F dependent strain behavior. As indicated in fig. 4.3c, SE loop with good shape can be obtained with frequency up to 10 Hz, which is much higher than most of NiTi based actuators (generally below 1 Hz)²¹⁰. Fatigue measurement was carried out by applying repeatable electric field (fig. 4.3d). The strain output is almost unchanged till 20 cycles, while obvious deterioration starts to appear after 30 cycles. This result indicates this strain response is highly reversible, yet more optimization work on fatigue-resist is required for practical applications.

Composition dependent strain response were then conducted on samples with different Br ratios. As illustrated in fig. 4.4a, strain shows monotonous increasing trend with decreasing Br amount. The largest response 22.15% was obtained in (PTMA)CdCl₃, which is the record high strain for non-polymer materials. Taking a 5.8 GPa Young's modulus from simulation result, we get a blocking stress output of 29 MPa and volumetric work of 3.7×10^6 J/m³ within one working cycle. This work value is higher than most of electrostrictive polymers, all magnetic shape memory materials and piezoelectrics^{152,211}. Fig. 4.4a compares actuation strain and volumetric work density for different material systems (see references table in chapter 4.2.3). The strain of (PTMA)CdCl₃ surpasses all the shape memory alloys and is two orders of magnitude higher than them of traditional ferroelectrics. To provide solid prove for this colossal strain, we take pictures of crystals that are poled to different polarized states (fig. 4.5). The angular deformation obtained from 90% Br and pure Cl samples pictures are 8.21° (14.43%) and 12.72° (22.57%), respectively, which show good consistence to our photonic sensor results (12.58% and 21.4%).

Figure 4.4 (a) Composition dependent strain response. (b) Comparison of volumetric actuation work and strain of materials from different systems. The position of (PTMA)CdCl₃ is marked by red star (see Chapter 4.2.3 for reference table).

Figure 4.5 Pictures of crystals at two strain states with crystals with composition of 90% Br (a and b) and pure Cl (c and d).

4.2.2 Mechanism analysis

Obviously, this shear strain comes from ferroelastic switch accompanied with polarization reversal. This can be reflected by the similar behavior between *SE* and *PE* loop (fig. 3.13a and 4.4a). The structure switch during polarization reversal can be understood as dipole rotating to mirror symmetric position, which is consist of shear deformation of inorganic framework and accompanied angular movement of organic cation. The sequent change of structure and shear deformation of inorganic chain during polarization reversal can be shown by our simulation result (fig. 4.6). The monotonous shear strain increase with higher Cl ratio is attributed to the larger dipole rotation in polarization reversal, which is consistent with the change of tilt angle β with different composition obtained by powder XRD results (table 3.1).

Figure 4.6 Sequential structure change of (PTMA)CdCl₃ during polarization switch.

Except for the structure confinement effect triggered by the large volume of organic cation, the inorganic 1D chain also plays an important role in shear strain origin, which acts as the fixer for the organic part. During polarization reversal, shear deformation is induced on inorganic chain with its position in real space only show negligible movement. This enables the 1D chain act as the fixer for the large organic moiety. The rotation of large molecular chain under electric field is actually a common phenomenon for organic ferroelectric. PVDF, for example, have giant 60° step rotation during polarization switch (fig.4.7b). However, the lack of unmoved fixer makes the organic chain rotate freely, leading to non-ferroelastic switch, which is prohibited by the inorganic fixer in this OIHF.

Figure 4.7 Comparison of polarization switch among (a) (PTMA)CdCl₃, (b) PVDF and (c) General oxide perovskite ferroelectric.

4.2.3 Reference table

Table 4.1| Actuation performance of different materials system.

Material system	Compound	Strain (%)	Stress (MPa)	Strain type	Work per volume J/m ³	Reference
Hybrid ferroelectric	(PTMA)CdCl ₃	21.5	29	Shear	3.7×10^6	This work
Ferro/Piezoelectric oxides	Soft PZT	0.1	20	Shear	2×10^4	212
	PMN-0.3PT	0.4	35	Normal	7×10^4	213
	BNT-BT-KNN	0.22	120	Normal	1.3×10^5	214

	PMN-0.38PT	0.66	20	Normal	6.6×10^4	215
	BTO	0.93	6	Normal	3.7×10^4	215
Shape memory alloy	NiTi	8	700	Shear	2.8×10^7	216
	NiTiHf	3.5	150	Shear	5.25×10^6	217
	CuZnAl	4	550	Normal	1×10^7	218,219
	CuAlNi	4	450	Normal	9×10^6	218,219
MAMAs	NiMnGaCoCu	12	2	Normal	1.7×10^5	220
	14M NiMnGa	9.5	1.8	Normal	1.45×10^5	221
	NiFeGaCo	8.5	8.5	Normal	7.225×10^5	222
Shape memory polymer	Polyurethane	80	0.05	Normal	2×10^4	223
	Styrene resin	30	0.236	Shear	3.5×10^4	224
	Semicrystalline oligome	50	0.5	Shear	1.2×10^5	225
	Nylon 66	10	22	Normal	1×10^6	226
Electroactive polymers	Graft elastomer	4	22	Normal	4.4×10^5	227
	Polyurethane	11	2	Normal	1.1×10^5	227
	VHB 4910 acrylic	68	2.4	Normal	1.36×10^6	208
	HS3 silicone	54	0.4	Normal	1.6×10^5	208
	CF19-2186	39	0.8	Normal	2×10^5	208
	Liquid crystal	4	0.12	Normal	2.4×10^3	228
	Polypyrrole	5	1.2	Normal	3×10^4	229
Piezoelectric polymer	PVDF	1.6	35	Normal	2.8×10^5	230
	PVDF+CuPc	2	15	Normal	1.5×10^5	231
	Irradiated PVDF	4	15	Normal	3×10^5	206

4.3 Conclusion

In summary, we demonstrate that by molecular design, it is possible to manipulate the polarization switching pathways and achieve colossal strain in OIHF. The new discovered hybrid ferroelectric (PTMA)CdCl₃ shows record-high shear strain (~21.5%) among ferroelectrics and shape memory alloys. As Br amount increase to 90%, this strain output shows monotonous decrease to around 13% because of the smaller tilt angle β . The colossal strain in this solid solution comes from non-180° ferroelastic switch induced by structure confinement effect-the limited space encapsulated by rigid 1D metal-halide chain limits the motion of the large organic cation and block its 180° rotation path. This demonstrates that with a careful chose of organic and inorganic parts, the volume ratio between these two moieties can be used to manipulate the freedom level of cation. With a tight structure, non-180°ferroelastic switch can be realized to achieve giant shear strain. The material and design strategy described should enlighten the development of OIHF based strain controllable materials and relevant devices.

Chapter 5: Giant shear piezoelectricity in (PTMA) $\text{CdBr}_{3x}\text{Cl}_{3(1-x)}$, properties and mechanism studies

5.1 Introduction and motivation

Piezoelectrics are materials without inversion symmetry in unit cell. The polar structure enables them to make mechanical to electrical energy conversion and vice versa, leading to a wide range of commercial and industrial applications such as transducer, actuator and energy harvester⁶⁴. Piezoelectric coefficients describe material volume change under electric field, which is one of the most important figure of merits for all piezoelectric devices. Based on the strain direction, piezoelectric coefficients can be classified into normal (such as d_{11} , d_{33}), transverse (d_{13} , d_{31}) and shear (d_{15} , d_{35}) mode. Each of these mode can be employed in different electrical devices with corresponding structure design. Materials with larger shear piezoelectric coefficient have always attracted great attention since the first discovery of piezoelectric material in 1880²³². The most widely used piezoelectrics so far are oxide perovskite ferroelectrics such as PZT and PMN-Pt. With MPB effect, the shear piezoelectric coefficients of these ferroelectric relaxor can go up to 5000 pm/V²³³.

The last few decades witness the changing development trend of ferroelectric and piezoelectric materials: from “single to multifunctional”, “macro to nano”, “hard to soft”, “homo to hetero” and “performance to reliability”. In addition, the worldwide regulation in toxicity gradually drives more and more attention from PZT dominated oxide piezoelectrics to new ferroelectric structures⁶⁴. Molecular ferroelectrics have distinct features such as soft, lightweight, environmental friendly and thus be regarded as one of the potential solution for these issues⁸⁸. However, their low piezoelectric response severally limits their applications. Before 2019, the molecular ferroelectric with the largest shear response (d_{16}) was 178 pm/V (beta-glycine), which is one order of magnitude smaller than those of top performance perovskite ceramics (see table 5.1)²³⁴.

Table 5.1| Comparison of piezoelectric constant of different materials. Figure is adapted from reference 235.

Piezoelectric Biomaterial	Material Type	Piezoelectric Constants
PZT-5H	Anisotropic (Orthotropic), Ceramic	$d_{33}= 593$ [pC/N], $d_{31}= -274$ [pC/N]
AlN	Anisotropic, Ceramic	$d_{33}= 3-6$ [pC/N], $d_{31}= -2$ [pC/N]
Quartz	Anisotropic (Orthotropic), Single Crystal	$d_{11}= 2.3$ [pC/N], $d_{14}= -0.67$ [pC/N]
ZnO	Anisotropic, Crystal	$d_{33}= 6-13$ [pC/N], $d_{31}= -5$ [pC/N]
BaTiO ₃	Anisotropic (Orthotropic), Ceramic	$d_{33}= 190$ [pC/N], $d_{31}= -78$ [pC/N]
LiNbO ₃	Anisotropic (Orthotropic), Ceramic	$d_{33}= 16$ [pC/N], $d_{31}= -1$ [pC/N]
PMN-PT	Anisotropic, Single Crystal	$d_{33}= 2000-3000$ [pC/N]
GaN	Anisotropic, Crystal	$d_{33}= 2-4$ [pC/N], $d_{31}= -1.5$ [pC/N]
PVDF	Anisotropic, Polymer	$d_{33}= -33$ [pC/N], $d_{31}= 23$ [pC/N]
PLLA	Anisotropic (Transversely Isotropic), Polymer	$d_{14}= 6-12$ [pC/N]
β -Glycine	Anisotropic, β -Crystal	$d_{16}= 195$ [pm/V]
Collagen	Anisotropic, Non-oriented	$d_{14}= 0.1$ [pm/V]
Silk	Anisotropic, Semi-crystalline, Draw Ratio=2.7	$d_{14}= -1.5$ [pC/N]
Peptide Nanotubes	Self-assembly process of diphenylalanine	$d_{15}= 60$ [pm/V]
Graphene	Single-layer	$d_{33}= 1.4$ [nm/N]

OIHF s are molecular ferroelectrics with both organic and inorganic composition where the inorganic part builds their backbone and organic cations occupy the space enclosed by inorganic framework. This hybrid structure makes OIHF s possess superiority from both organic ferroelectrics, such as soft and high structure flexibility, and traditional inorganic ferroelectric such as high mechanical strength^{83,84}. Recently, great stride has been made in the research of OIHF s piezoelectricity. With smart structure design and MPB effect, d_{15} of 2560 pm/V have been achieved in a 1D OIHF (TMFM)_x(TMCM)_{1-x}CdCl₃, which outperformances most of PZT materials²⁶. Giant piezoelectric responses with d_{33} surpassing BaTiO₃ have also been reported in other OIHF s^{88,111,117}. The multiaxial ferroelectric nature of these hybrid ferroelectrics implies their giant piezoelectricity may originate from ferroelastic switch²³⁶. Nevertheless, direct proof is still lacking.

These heart-stirring progresses suggest OIHF s system is a structure that possibly leads to high performance piezoelectrics. In chapter 3 and 4, we discussed the soften effect of Br substitution and the colossal shear strain in solid solution, which suggests high Br ratio crystals may potentially possess giant d_{35} . Encouraged by these discoveries, we investigate the shear piezoelectric property of (PTMA)CdBr_{3x}Cl_{3(1-x)}. As expected, a large shear piezoelectric response of 4800 pm/V is discovered in high Br amount region, which surpasses most of shear piezoelectricity in Pb based ferroelectric relaxor and all other OIHF s. With systematic characterization and simulation result, we confirm this giant d_{35} comes from the

giant strain associated ferroelastic switch and the soften effect of halide substitution. The superior piezoelectric properties and soften mechanism should enrich piezoelectricity optimization strategies of OIHFs and inspire the development of the next-generation piezoelectric materials.

5.2 Result and discussion

Figure 5.1 Angular PFM study of a 77%-Br single crystal. PFM images are collected with the crystal oriented at different azimuthal angles with regard to the cantilever axis. The average PFM amplitude of each image is plotted in polar coordinate. Initial and final crystallographic orientations are indicated beneath the PFM images, with red arrow denotes the polarization vector.

The in-plane piezoelectric response was first studied by angular PFM measurement. A bulk crystal with 77% Br composition was investigated by PFM with [010] axis perpendicular to the basal plane and [001] parallel to AFM cantilever, that is, the polarization vector lies in the scanning plane. Lateral PFM measures the torsional motion of the cantilever caused by shear piezoelectricity arising from in-plane polarization (P). The magnitude of the torsion (PFM amplitude) is proportional to the polarization component perpendicular to the cantilever axis, namely, $P \cdot \cos\theta$, where θ is azimuthal angle between the cantilever axis and P vector. Angular-resolved PFM study can then be conducted by rotating the sample in the basal plane to determine its P direction. To increase the signal-to-noise ratio, resonance-enhanced DART mode was used. Since the contact resonance and quality factor remain almost unchanged throughout the experiment, the raw amplitude data (A) were used to estimate the magnitude of piezoelectric response. Fig. 5.1 shows the PFM images and corresponding average amplitude data at sequential azimuthal angles. By fitting these phase and amplitude signals, P axis can be determined as denoted by red arrows. Particularly, A maximum is obtained at $\sim 160^\circ$ rather than at 0° or 180° , which is consistent with the non-zero polarization components along both **a** and **c** axes.

Shear piezoelectric property was then investigated by photonic sensor with the same experiment setup in Fig. 4.3a. All samples were preploded before applying unipolar electric field. Shear piezoelectric coefficient d_{35} was calculated by $d_{35} = S_5/E_3$. Fig. 5.2a illustrates the composition dependency of d_{35} in (PTMA) $\text{CdBr}_{3x}\text{Cl}_{3(1-x)}$. Obviously, piezoelectric response shows monotonous increasing tendency with higher Br amount, which becomes even more dramatic with Br ration above 63%. In 90% Br crystal, a giant $d_{35} = 4800$ pm/v is obtained, which is comparable to top-performance oxide perovskite piezoelectric and is higher than all other molecular ferroelectrics (see fig. 5.2e). However, there is a strong hysteresis effect and nonlinear feature in SE curves, which are similar to the piezoelectric behaviors of BZT-BCT and BNT-BT-KNN systems^{237,238}. Meaning more engineering work may be required for commercial applications. These special piezoelectric behaviors drive us to conduct systematic characterization to understand the origin of this giant piezoelectric response and the hysteresis effect.

Figure. 5.2 Piezoelectric properties of (PTMA)CdBr_{3x}Cl_{3(1-x)}. (a) *SE* curves of samples with selected compositions. (b) Electric dependent unipolar *SE* behavior of 90% Br sample. (c) *SE* curves at different frequencies for 90% Br sample. (d) d_{35} map of 90% Br crystal at different electric field and frequencies. (e) Comparison of shear piezoelectric coefficients of different materials (see references in table 5.2).

Next, we conducted electric field and frequency dependent piezoelectricity measurement in 90% Br sample. As indicated in fig 5.2b-d, the shear piezoelectric performance shows obvious increase with higher E and lower F . Such strong dependency is rarely to be seen in perovskite ceramics. The frequency range where piezoelectric response shows dramatic increasing coincides with the switching frequency of its PE loop. This indicates the origin of the giant piezoelectricity may come from back-switched ferroelastic domain, which is just in our expectation. This piezoelectric mechanism is also consistent to its E dependent behavior, where more domain switch/strain would be triggered under larger electric field.

To confirm our hypothesis that this giant d_{35} is attributed to ferroelastic switch, we conducted E and F dependent dielectric behavior measurements on crystals with different compositions. Here, PE curves were measured under small electric field and dielectric constants were calculated by PE slopes. As shown in fig 5.3c-d, the polarization curves of 90% Br samples show much more ‘blow up’ behavior than those of pure Cl, indicating a more typical PE response of lossy capacitor (see comparison between fig 5.3a and b). This indicates the increase in piezoelectric constant and amount of domain switch with higher Br composition are synchronous effect. Additionally, dielectric constant show similar behavior to piezoelectricity in E and F dependence. As illustrated in fig. 5.2e and f, compared with pure Cl sample, 90% Br crystal shows much stronger dielectric increase under higher E and lower F , which is highly consistent with the corresponding changes in their piezoelectric responses. This further indicates that the piezoelectricity comes from ferroelastic switch, while d_{35} dependence on E and F stem from the difference in the amount of switched ferroelastic domain. The large hysteresis effect in unipolar SE curve is thus attributed to the slow polarization switching nature in this OIHF, which is reflected by the low F feature of polarization reversal.

Figure 5.3 Dielectric behavior of (PTMA)CdBr_{3x}Cl_{3(1-x)}. (a-b) PE curves of ideal and lossy capacitor²³⁹. (c-d) PE properties of 90% Br and pure Cl sample under small electric field. (e-f) E and F dependent dielectric constants for samples with 90% and pure Cl compositions. Figure (a) and (b) are adapted from reference 239.

The simulation result confirms that the energy barrier for ferroelastic switch is much lower in high Br composition, which, leads to the soften effect of Br substitution and robust piezoelectric response in high Br sample. Here, ab initio DFT calculations was carried out for the minimum energy paths of polarization switch in these two compositions. As

illustrated in fig. 5.4a, the switching barrier of pure Br compound is much smaller and flattened compared to the pure Cl counterpart. This can be explained by the special polarization reversal process in this solid solution. The intermediate state of the inorganic chain during *P* switch is consisted by mirror-symmetric corner-sharing CdX^{4-} tetrahedra, which is a reminiscence of the high temperature phase structure. This indicates the switching process in inorganic backbone can be visualized as breaking and reformation of the bonds between Cd and its two adjacent apex halide atoms. Consequently, the switching barrier in this OIHF is highly related to the bond strength of the longest Cd-X and rebuilt hydrogen bond during polarization reversal. Crystal orbital Hamilton populations (COHPs) was then employed for bond strength calculation. Fig. 5.4b indicate the simulation results of the longest Cd-X and two shortest hydrogen bonds in pure Br and Cl systems. As expected, stronger bonds were found in pure Cl structure by integrating COHPs to the Fermi energy. This is consistent with the stronger electronegativity in pure Cl composition.

Figure 5.4 Simulation results of the switching energy barriers of (PTMA)CdCl₃ and (PTMA)CdBr₃. (a) Minimum energy paths of polarization switch. Generalized solid-state nudged elastic band (GSSNEB) method was employed for calculation. (b) Integrated crystal orbital Hamilton populations (ICOHPs) of the two shortest hydrogen bonds and the broken Cd-X bond during polarization switching.

5.3 Photonic sensor calibration and reference table

PMN-0.3PT single crystal were used to confirm the reliability of the photonic sensor (see fig. 5.5). The obtain butterfly loop, d_{33} and d_{15} value show good consistence to previous reports²⁴⁰⁻²⁴².

Figure 5.5 SE curve of PMN-0.3 Pt and (PTMA)CdBr_{3x}Cl_{3(1-x)} single crystal (a) Repetitive SE curves (33 mode) of PMN-0.3PT (100) crystal. (b) Electric dependent SE response of PMN-0.3PT (100) crystal in d_{33} mode. (c) Comparison of the bipolar SE loops between (PTMA)CdCl₃ and PMN-0.3 PT. (d) A comparison of the unipolar SE responses between (PTMA)CdBr_{2.7}Cl_{0.3} and (111) PMN-PT (d_{15}).

Table 5.2| Comparison of shear piezoelectric coefficient of different materials.

Compound	Piezoelectric coefficient (pm/V)	Piezoelectric mode	Reference
(PTMA)CdBr _{2.7} Cl _{0.3}	4800	d ₃₅	This work
KH ₂ PO ₄	23.2	d ₃₆	13
LiNbO ₃	68	d ₁₅	13
PbTiO ₃	68	d ₁₅	243
Glycine amino acid (β)	178	d ₁₆	234
BaTiO ₃	260	d ₁₅	13
PZT-5A	584	d ₃₅	244
BZT-BCT	1586	d ₃₆	245
(TMFM) _{0.26} (TMCM) _{0.74} CdCl ₃	2560	d ₁₅	26
Pb Based relaxor	1300-5000	d ₁₅	233

5.4 Conclusion

In summarize, we discovered a record high $d_{35}=4800$ pm/V among OIHF_s in Br rich (PTMA)CdBr_{3x}Cl_{3(1-x)}. This giant piezoelectric response comes from back-switched ferroelastic domain and the soften effect of Br substitution, which is confirmed by four features: 1. The relatively low linearity of *SE* curve. 2. Highly electric field and frequency dependent piezoelectric constant. 3 The similar electric field and frequency dependence of *PE*, *SE* and dielectric behaviors. 4. Increase of piezoelectric constant and the soften effect (reflected by decreasing coercivity of *PE* loops) induced by higher Br ratio. In addition, with computer simulation, we demonstrate that this soften effect comes from the weakening of

cadmium-halide bond with Br substitution. The discovered giant shear piezoelectric response is comparable to those of top-level Pb relaxors and higher than those of other OIHF, which makes this OIHF an excellent candidate for the next generation piezoelectric material. In the meanwhile, the discovered soften effect and bond weakening mechanism open a new avenue for piezoelectricity optimization in hybrid system.

Chapter 6 Conclusion and Outlook

6.1 Conclusion

The research described in this thesis covers two major parts. The first part is about the insight to the role of halide ion in the ferroelectricity of OIHF. The second part provides a precise molecular design towards large piezoelectric/strain response for molecular ferroelectrics. We prove that in hybrid perovskite, colossal strain can be induced through ferroelectric dipole movement under structure confinement condition. This thesis work enriches the understanding to OIHF's ferroelectric mechanism and provides a new molecular engineering strategy to effectively promote their electrostrictive property. More specific details are provided below.

In Chapter 3, we report the discovery of a new OIHF structure and the tuning of ferroelectricity by its halide part. Through systematic characterizations and theoretical simulation, it is found that the halide site directly influences the potential energy barrier through its modulation effect on chemical bond strength, which further determines the ferroelectric properties including coercivity and phase transition temperature. This outstanding tuning effect comes from the special polarization reversal process of this molecular ferroelectrics, where polarization switch involves the breaking and rebuilding of hydrogen and metal-halide chemical bonds. With an obvious difference in atom size and electronegativity between different halide ions, the halide composition has a determinative role in the ferroelectric properties of this OIHF. These discoveries provide mechanistic understanding of the ferroelectric mechanism and also further expand the composition/structure diversity of OIHF. Hence, the result opens a new avenue to both ferroelectric property manipulation and new ferroelectricity mechanism. This may lead to the discovery of a large number of new OIHF structures. For example, due to the generally large size of organic cations, the polarization of many hybrid structures cannot be switched under external electric field. With the conclusion described in Chapter 3, one may reduce the energy barrier through halide doping.

In Chapter 4, we demonstrate that controllable ferroelastic switching can be achieved by structure confinement in OIHF system. The colossal strain response comes from the

unique coupling effect between the organic and inorganic parts. First, the organic cation induces large-angle molecule rotation under electric field in this hybrid structure, which is the base for the giant strain output. Second, the discrete 1D inorganic chains act as fixers and confine the rotation of organic cations. These two factors lead to the colossal strain in PTMACdCl₃. More importantly, Chapter 4 indicates that the mixed composition in hybrid not only can trigger dual properties, such as PL emission and reversible polarization in luminescent ferroelectrics, but can also result in unique coupling phenomenon in polar structures.

With the discovery of the halide substitution induced softening effect (Chapter 3) and the polarization switching triggered colossal strain output (Chapter 4), a large piezoelectric response is expectable in the high Br region of PTMABr_{3x}CdCl_{3(1-x)}. In Chapter 5, we report the large d_{35} discovered in this hybrid structure. The unique and highly electric field/frequency dependent piezoelectric response originates from the increasing amount of ferroelastic domain switching under stronger outer stimuli. This piezoelectric mechanism may also explain the giant d_{33} discovered in other OIHFs with similar 1D structures.

6.2 Outlook

Piezoelectricity is the most widely used application for ferroelectric materials, and OIHF is the first material family that shows piezoelectric performance comparable to Pb relaxor dominated oxide perovskite ferroelectrics. The large structure and composition flexibilities render OIHF with enormous possibility of performance improvement, while its organic-inorganic hybrid nature may simplify the synthesis and reduces the cost. For the future research on OIHF, I would like to propose the following points.

(1) Structure discovery towards new phenomenon and multifunctionality. The large-molecule organic cation brings three inferiorities to OIHF: (i) Slow polarization reversal speed compared with oxide ferroelectrics; (ii) Smaller polarization because of larger unit cell; and (iii) Inferior thermal stability. These disadvantages may make OIHF difficult to compete with perovskite ceramics in the aspect of performance in traditional ferroelectric applications. Consequently, new OIHF molecular design should not be limited to ferroelectricity enhancement but instead make better use of their intrinsic superiority, viz., structure and

composition flexibility. These unique features may lead to discovery of new coupling phenomenon and multifunctionality in hybrid structures, and putting OIHF's on a unique position in the ferroelectrics family.

(2) More study on understanding piezoelectricity mechanism and performance optimization. Obviously, the most promising property for OIHF's so far is their outstanding piezoelectric and strain responses. However, the origin of the giant d_{33} in several reported OIHF's are still not clear. Understanding the mechanism behind these hybrid ferroelectrics will undoubtedly benefit the rational molecule and device designs. In addition, the giant piezoelectric coefficient reported in this thesis is accompanied with large hysteresis effect and featured with low operation speed, which limits its piezoelectric applications. Considering the cations of $\text{PTMABr}_{3x}\text{CdCl}_{3(1-x)}$ and other hybrid piezoelectrics are all large-molecule organics, these piezoelectric behaviors may be common to OIHF's. Hence, more research on performance optimization is required for practical piezoelectric applications.

(3) OIHF's based devices. Since 2014, more than 40 types of hybrid ferroelectric structures have been successfully fabricated. They possess superior physical properties and functions in several aspects, including high piezoelectric response, high-efficient PL, high-sensitivity light detection and chiral light emission. The great variety in structure dimension of OIHF's also creates applications on both nanometer and bulk scale. However, currently most of the research are still focused on synthesis and basic characterizations. More research on devices should be conducted to uncover the potential of OIHF's in practical applications. Considering their flexible, lightweight and excellent piezoelectricity features, it is proposed that wearable electronics and nanogenerators be viable applications for which OIHF's own advantages over pure inorganic perovskites.

(4) It is observed that many excellent-function perovskite materials contain toxic elements including Pb or Cd. However, with increasing concern on environment protection, pushing the performance may be no longer the top priority in searching new materials to serve the community in near future. A good balance between performance and less-toxicity should be pursuit in materials research. Indeed, more attentions should be paid to candidates with low cost, toxicity free and easy processing features.

Publication list

- (1) **Yuzhong Hu**, Hongbo Zhang, Wee Kiang Chong, Yongxin Li, Yujie Ke, Rakesh Ganguly, Samuel Alexander Morris, Lu You, Ting Yu, Tze Chien Sum, Yi Long, and Hong Jin Fan, Molecular engineering toward coexistence of dielectric and optical switch behavior in hybrid perovskite phase transition material, *The Journal of Physical Chemistry A* 122.31 (2018): 6416-6423;
- (2) **Yuzhong Hu**, Lu You, Bin Xu, Tao Li, Samuel Alexander Morris, Yongxin Li, Yehui Zhang, Xin Wang, Pooi See Lee, Hong Jin Fan and Junling Wang, Ferroelastic-switching-driven large shear strain and piezoelectricity in a hybrid ferroelectric; *Nature Materials*, accepted.
- (3) Lu You, Fucui Liu, Hongsen Li, **Yuzhong Hu**, Shuang Zhou, Lei Chang, Yang Zhou, Guoliang Yuan, Shuai Dong, Hongjin Fan, Zheng Liu, Junling Wang, In - Plane Ferroelectricity in Thin Flakes of Van der Waals Hybrid Perovskite, *Advanced Materials* 30.51 (2018): 1803249;
- (4) Shuang Zhou, Lu You, Apoorva Chaturvedi, Samuel Alexander Morris, Jason S. Herrin, Na Zhang, Amr Abdelsamie, **Yuzhong Hu**, Jieqiong Chen, Yang Zhou, Shuai Dong and Junling Wang, Anomalous polarization switching and permanent retention in a ferroelectric ionic conductor, *Materials Horizons* 7.1 (2020): 263-274.

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