1. Introduction

Discovered in 1921, ferroelectricity was initially called Seignette electricity because Seignette or Rochelle Salt was the first material that was found to exhibit ferroelectric properties. From a crystallographic point of view, ferroelectric materials are characterized by the breaking of inversion symmetry, that is, they are non-centrosymmetric. As a result, each ferroelectric material exhibits a macroscopic polarization that can be switched by an external electric field. Many well-known inorganic ferroelectrics possess perovskite structure and can be described with the general chemical formula of ABO₃, where A and B represent cations of different sizes and B is a transition metal (e.g., BaTiO₃ and PbTiO₃).

Perovskite oxide ferroelectrics have been extensively used in capacitor, sensor, actuator, memories, energy storage, surface acoustic wave devices, optoelectronics, and microelectromechanical systems applications, which are critical components for modern technologies. For example, BaTiO₃ has been widely used in capacitor applications since 1950. Many ferroelectrics also have high dielectric constant, low dielectric loss, and high breakdown electric field, showing high electric energy density and storage efficiency during energy storage as capacitors. PbZrₓTi₁₋ₓO₃ (PZT) has been incorporated in automobiles as piezoelectric sensors, and it is also used in actuators for the direct conversion of electrical energy to mechanical energy which are especially important for robotics, optical fiber switches and optical displays. Ferroelectric random-access memories (RAMs) are another application of perovskite oxide ferroelectrics such as PZT and doped Bi₄₋ₓAₓTi₅O₁₂ (A = La, Nd, et al.) which have the merits of their high speed, nonvolatility, low power requirements, anti-radiation, physical robustness, and high density. Besides, LiNbO₃ and LiTaO₃ have been widely used as surface acoustic wave devices, which are the key components of wireless communication devices such as TV and mobile phone. Nevertheless, perovskite oxide ferroelectrics, although have been used in various applications, present some disadvantages. For instance, most of them may contain heavy metals which are not environmentally friendly and are usually processed at high temperatures. In addition, most perovskite oxide ferroelectrics are brittle, hence they cannot be exploited in flexible devices.

Perovskite oxides such as PbZrₓTi₁₋ₓO₃ (PZT) and BaTiO₃ show excellent dielectric, piezoelectric, pyroelectric, and ferroelectric properties simultaneously and have been widely used in capacitor, sensor, actuator, motor, surface acoustic wave devices, and energy storage applications. Recently, a variety of solution-processed halide perovskite materials have been discovered to exhibit fascinating properties such as high charge mobility, strong light absorption, and even ferroelectricity. In this review, the recent progress on two classes of halide perovskite ferroelectrics is summarized. The first class is organo-lead halide perovskite semiconductor such as MAPbI₃ (MA = CH₃NH₃⁺), which is intensively pursued for solar cell and light emitting diode applications. Dynamic ferroelectric polarization is believed to be one of the essential factors to protect carriers from being scattered by charged defects in these halide perovskites. The second class is normal/multilayered halide perovskite ferroelectrics with large polarization or strong piezoelectricity. The piezoelectric coefficient of these latter perovskites can be as high as ≈1540 pC N⁻¹, comparable to those of PZT-based ferroelectrics. Multiaxial polarizations and morphotropic phase boundaries are also demonstrated in such halide perovskites. Overall, the fast development of halide perovskite ferroelectrics opens a new avenue for not only advancing fundamental materials science but also designing novel electronic and photoelectric devices.
Halide perovskites, with general chemical formulas of 3D ABX$_3$ and layered 2D A$_{n+1}$B$_n$X$_{3n+1}$ ($X = F, Cl, Br,$ or I), consist of inorganic BX$_6$ octahedra, with A, an organic/inorganic cation (e.g., Cs or MA $=$ CH$_3$NH$_3$) and B usually a metal cation with smaller size (e.g., Pb$^{2+}$ or Sn$^{2+}$). Halide perovskites exhibit many unique properties that cannot be observed in perovskite oxide ferroelectrics, such as structural softness, lightweight, and low synthesis temperatures (Table 1). On the other hand, the existence of ferroelectricity in halide perovskites remains controversial and a long-lasting theme of research. For example, whether CH$_3$NH$_3$PbI$_3$ (MAPbI$_3$) truly exhibits ferroelectricity or not remains contentious. Piezoelectric force microscopy (PFM) and scanning electron microscopy studies reported polar domains in tetragonal MAPbI$_3$, and a weak ferroelectricity was demonstrated by dielectric and piezoelectric measurements as well as second harmonic generation (SHG). However, most traditional methods which are effective to identify ferroelectric insulators cannot effectively characterize the ferroelectricity of a typical semiconductor like MAPbI$_3$. It is not easy to differentiate ferroelectric domains from ferroelastic domains, and a standard saturated polarization versus electric field ($P$–$E$) loops has not been achieved in MAPbI$_3$ until now. It was reported by macroscale polarization and temperature-dependent dielectric measurements that MAPbI$_3$ thin films cannot be ferroelectric under solar cell measurement conditions. Obviously, there is a vast space for researchers to develop new characterization techniques and to prepare reliable ferroelectric semiconductors.

Clarifying the possibility of existence of ferroelectricity in halide perovskites is not just a question of fundamental interest, it may also have important technological consequences. For example, some theoretical works have shown that ferroelectric nanodomains can reduce the recombination of light-excited electron–hole pairs, extend the carrier lifetime and promote the charge separation and collection. This unique merit of MAPbI$_3$ contributes to its promising optoelectronic properties such as high carrier mobility, tunable light absorption, long charge diffusion lengths, and high power conversion efficiency (PCE) of >20% in the corresponding solar cells.

On the other hand, a series of halide perovskite ferroelectrics with Curie temperature above 373 K have been discovered recently, and some of them show excellent ferroelectric and piezoelectric properties (Table 1). For example, Liao et al. synthesized the molecular perovskite (TF)$_{0.26}$(TC)$_{0.74}$CdCl$_3$ with morphotropic phase boundaries (MPB) of monoclinic and hexagonal phases. It shows the maximum piezoelectric coefficient $d_{33}$ of $\approx$1540 $\mu$C N$^{-1}$ at room temperature, which is even higher than most conventional ferroelectrics, thus possessing the potential to be used in flexible piezoelectric applications.

In this progress report, we will first discuss briefly the fundamentals of ferroelectric materials, and then we introduce several organo-lead halide perovskite semiconductors with a focus on the elusive ferroelectricity and the impact of such a ferroelectric-like property on the photovoltaic applications, particularly solar cells. Moreover, a series of halide perovskite ferroelectrics with strong piezoelectricity and poor semiconducting properties are reviewed and compared to the organo-lead halide perovskites. Finally, we present perspectives on future research directions to advance halide perovskite ferroelectrics.

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2. Brief Introduction of Ferroelectric Materials

2.1. Basic Physics of Ferroelectricity

Ferroelectric materials are a subclass of pyroelectric materials, which are a subclass of piezoelectrics and they are all a group of dielectric materials (Figure 1a). Therefore, ferroelectrics possess both the pyroelectric and piezoelectric properties and are known as wide-bandgap polarizable semiconductors. According to the definition, ferroelectric compounds must adopt symmetry-breaking space groups belonging to the 10 polar point groups, that is, triclinic 1 (C1), monoclinic m (C2), 2 (C2), orthorhombic mm2 (Cmmm), trigonal 3 (C3v), 3m (C3h), tetragonal 4 (C4v), 4mm (C4mm), hexagonal 6 (C6v), and 6mm (C6h) (Table 1 and Figure 1b). Although ferroelectricity is believed to be a property of crystalline solid compounds according to the conventional wisdom, it was also discovered in liquid crystals. For example, it was shown that chiral molecules can possess spontaneous polarization.

Table 1. Basic physical properties of halide perovskite materials, and some representative ferroelectric oxides are also shown for comparison. Here, MD is N-phenylethylenediamine (2,2,2)-pyridine, TF is triethylammonium, TC is trimethylammonium, PE is potassium, EA is ethylammonium, R2PbI4 is [4-(4-chlorophenyl)ethylammonium]2PbI4, S2PbI4 is [1-(4-chlorophenyl)-diazabicyclo[2.2.2]octonium, TF is trimethylfluoromethyl ammonium, TC is trimethylchloromethyl ammonium, MD is methylammonium, and FA is formamidinium. Here, MD is methylenediamine, TF is trimethylfluoromethyl ammonium, TC is trimethylchloromethyl ammonium, PE is potassium, EA is ethylammonium, R2PbI4 is [4-(4-chlorophenyl)ethylammonium]2PbI4, S2PbI4 is [1-(4-chlorophenyl)-diazabicyclo[2.2.2]octonium, TF is trimethylfluoromethyl ammonium, TC is trimethylchloromethyl ammonium, MD is methylammonium, and FA is formamidinium. Here, MD is methylenediamine, TF is trimethylfluoromethyl ammonium, TC is trimethylchloromethyl ammonium, PE is potassium, EA is ethylammonium, R2PbI4 is [4-(4-chlorophenyl)ethylammonium]2PbI4, S2PbI4 is [1-(4-chlorophenyl)-diazabicyclo[2.2.2]octonium, TF is trimethylfluoromethyl ammonium, TC is trimethylchloromethyl ammonium, MD is methylammonium, and FA is formamidinium.
exclusive and some ferroelectric crystals show both displacive and order-disorder characteristics.\textsuperscript{[34c]}

2.2. Techniques of Measuring Ferroelectric Materials

In the past decades, ferroelectric insulators have been studied extensively and several effective methods were developed to identify whether a new material shows ferroelectricity or not. In addition to an asymmetrical crystal structure, a ferroelectric material shows ferroelectricity, piezoelectricity, and pyroelectricity simultaneously. Thus, these four properties can be characterized to identify ferroelectricity of a new material. First, all ferroelectrics have the asymmetric crystal structures with 10 polar point groups, which can be characterized by techniques such as XRD, SHG, TEM, and other advanced microscopies.\textsuperscript{[8,34c]} These methods are quite effective if the polarization of the specimen is larger than 1 \( \mu \text{C cm}^{-2} \). Second, ferroelectricity is commonly characterized by \( P–E \) hysteresis loop. When an \( E \) over \( E_c \) is applied on an insulating ferroelectric material, polarization can switch its orientation, which introduces the change of positive and negative bound charges at two opposite surfaces. As a result, there are free charges to neutralize the new bound charges. For a ferroelectric insulator, nearly all free charges go through an external circuit and thus a commercial ferroelectric tester can integrate the external current and time to calculate the bound charges and the corresponding polarization. Third, a \( d_{33} \) meter is commonly applied to characterize the piezoelectric effect with a unit of \( \text{pC N}^{-1} \). The mechanical force can introduce a change in the surface-bound charges of two opposite surfaces as well as the corresponding external current. Furthermore, a strain meter is commonly used to characterize the inverse piezoelectric effect with a unit of \( \text{pm V}^{-1} \) when an external \( E \) induces the nonlinear strain of a material. Both Doppler instrument and PFM as strain meters are widely applied to identify strain with an accuracy of \( \text{pm} \) or better.\textsuperscript{[9,38]} and different kinds of domains have recently been discovered by PFM.\textsuperscript{[12,15,21–33]} Finally, the bound

![Figure 1. a) Relationship of dielectric, piezoelectric, pyroelectric, and ferroelectric materials. b) Crystal systems and point groups of ferroelectrics.](image1)

![Figure 2. a) \( P–E \) hysteresis loops and the domain evolution during polarization switching. b) Schematic illustrations for the displacive-type and order-disorder-type ferroelectric–paraelectric phase transition.](image2)
charges of two opposite surfaces will vary with the temperature changing in a pyroelectric material, and thus there are free charges to neutralize these new bound charges. Through integrating the pyroelectric current and time, the total free charges and the corresponding polarization can be calculated. In fact, this method has successfully discovered many new multiferroic materials with narrow bandgaps and polarizations as small as \(10^{-5} \text{ C cm}^{-2}\).\(^{[39]}\)

Although these traditional characteristic methods are effective for ferroelectric insulators, it is still a big challenge to exactly identify some ferroelectric semiconductors with halide perovskite structure such as MAPbI\(_3\). Indeed, MAPbI\(_3\) and many halide perovskites do not show large polarization. Besides, there is just slight difference between their asymmetric and symmetric crystal structures which makes it difficult to identify this difference by normal XRD, TEM, SHG, and so on. Moreover, many halide perovskite materials are not stable enough during TEM measurements.\(^{[8,34c]}\) Most importantly, when there is a change in polarization and the corresponding surface bound charges induced by the varying \(E\), strain, and/or temperature, the free charges inside semiconductor can replace the free charges in external circuit to neutralize the new bound charges. As a result, polarization cannot be exactly calculated through integrating external current and time. Besides, the inner current inside semiconductor may produce heat which is large enough to break the semiconductor itself. Recently, the domains of halide perovskites such as MAPbI\(_3\) have clearly been observed by PFM,\(^{[32,36,18–21,38]}\) however it is not easy to switch their polarization by an external \(E\). In fact, an \(E\) may induce a large current to break semiconductor before reaching above \(E_C\) to switch the polarization. In this case, it is not easy to differentiate ferroelectric domains from ferroelastic domains due to inhomogeneous strain. Although there are many obstacles, a great deal of work has already been performed and it is possible to clearly switch and manipulate polarization in most of the ferroelectric semiconductors.

3. Lead-Halide Perovskite Semiconductors with Weak Ferroelectricity

3.1. Ferroelectric Large Polaron

Lead-halide perovskite materials can be prepared with the aqueous solution method at room temperature, and some of them have been extensively applied in solar cells and light emitted diodes (LED).\(^{[40]}\) The crystal structure of halide perovskites is presented in Figure 3a. Recently, extensive efforts have been devoted to improving the efficiency of perovskite solar cells, especially by composition engineering and optimizing the material processing (Figure 3b). Despite of having high defect densities, prototype halide perovskites such as MAPbI\(_3\), CH\(_3\)NH\(_3\)PbI\(_3\), Pb\(_2\)(I\(_3\))\(_2\)_Cl\(_2\) (i.e., FAPbI\(_3\)), and CsPbBr\(_3\) exhibit excellent charge transport properties like conventional semiconductors with 7N or higher purity (e.g., Si and GaAs).\(^{[41]}\) First, the temperature (\(T\)) dependence of charge carrier mobility (\(\mu\)) follows a simple power law (\(\mu \propto T^{-3/2}\)), thus indicating the hindrance of coherent transport by acoustic phonon scattering in the halide perovskites.\(^{[40]}\) Second, halide perovskites possess a modest charge carrier mobility (\(\mu = 1–100 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}\)), a high carrier diffusion length (up to \(10^7 \mu\)m), and a long carrier lifetime (\(\geq 1\) ms) simultaneously.\(^{[42]}\) Third, the electron–hole recombination rate constant (\(10^{-10} \text{ cm}^3 \text{ s}^{-1}\)) is as low as those of the purest crystalline semiconductors such as GaAs.\(^{[43]}\) These properties of hybrid organic–inorganic lead halide perovskites indicate that there are few scatterings of charge carriers by charged defects, optical phonons, or other interferences.

Recently, Zhu and Podzorov et al. proposed that the screened Coulomb potential created in the crystal by large polarons can reduce the carrier scattering by charged defects, other charge carriers, and phonons.\(^{[44b,44]}\) There are two kinds of large polaron that can protect charge carriers from scattering, that is, Fröhlich large polaron and ferroelectric large polaron. For the Fröhlich large polaron, the polarization of the ionic lattice (i.e., the dipole moment due to atomic displacement from their equilibrium position) shows a linear response to the applied electric field or generated by charged defects. As a result, the dipole moment in a unit cell decreases with increasing the distance from the injected charge (Figure 3c). For the ferroelectric large polaron model (Figure 3d), there is an enhanced local electric field of 0.1–1 MV cm\(^{-1}\) in the proximity of a charge, which can induce collective polarization and polar nanodomains (PND) in the ferroelectric-like materials. These nanodomains may be dynamic and transient and vanish when the charge is removed and there is just a local microscopic ordering with radial symmetry centered on the charge, which is different from the conventional ferroelectric phenomenon.\(^{[46]}\) Compared with a conventional Fröhlich large polaron, much larger Coulomb potential screening is caused by the ferroelectric large polaron. Furthermore, there is a chance for inducing a potential barrier against charge recombination due to the collective polarization of nanodomains. Ferroelectric large polaron model provides a new platform for hybrid perovskite-based defect-tolerant semiconductor devices.

3.2. Impact of Ferroelectricity on Optoelectronic Performance

Ferroelectric properties of halide perovskites can lead to advantageous applications in optoelectronic devices. The impact of ferroelectricity on the performance of energy-conversion devices such as high-performance ferroelectric solar cells has been intensively investigated.\(^{[45]}\) In addition, by utilizing ferroelectric semiconductors, photocatalytic activities can be improved with a permanent internal polarization to effectively separate photexcited carriers.\(^{[46]}\) Recently, Singh et al. reported improved photoelectrochemical properties by growing Ag, Nb-doped SrTiO\(_3\) (Ag/Nb:STO) with ferroelectric nanoporous/nanocolumnar structure.\(^{[47]}\) By applying external electrical bias, the photocurrent was increased from 40 to 130 \(\mu\)A \(\cdot\) cm\(^{-2}\) followed by a decrease in flat-band potential from \(0.55\) to \(-1.13\) V, resulting in an enhanced charge transfer. In addition, Wang et al. reported EA\(_3\)Pb\(_3\)Cl\(_{10}\) (EA = ethylammonium) as a 2D trilayered hybrid perovskite ferroelectric, presenting a high Curie temperature of 415 K and \(P_0\) of \(\approx 4.5\) \(\mu\)C \(\cdot\) cm\(^{-2}\) as well as a wide bandgap of 3.39 eV, suitable for applications such as self-powered photodetection.\(^{[48]}\) In another work, (EA)\(_2\)(MA)\(_2\)Pb\(_3\)Br\(_{10}\) was shown to have ferroelectric behavior with a high Curie
temperature of 375 K, $P_s$ of 3.7 $\mu$C · cm$^{-2}$, and a high photocurrent density of 4.1 $\mu$A · cm$^{-2}$,[25] superior to some ferroelectric oxides such as BiFeO$_3$.[49] In general, hybrid organic–inorganic perovskites with ferroelectric or ferroelectric-like properties have been widely pursued in many applications. Because of their unique low temperature process ability and low manufacture cost, these halide perovskites could be good candidates for future applications, such as flexible and wearable devices.

Among different organic–inorganic perovskites, MAPbI$_3$ and its compositional variants have been widely investigated in photovoltaic (PV) applications due to its promising optical and electronic properties, such as high carrier mobility, strong light absorption, reduced charge recombination, and optimized charge diffusion length. MAPbI$_3$ undergoes two phase transitions, that is, from orthorhombic (space group Pna2$_1$) to tetragonal ($\beta$ structure, space group I4/mcm) at 162 K and from tetragonal to cubic ($\alpha$ structure, space group Pm3m) at 327 K.[50] Figure 4a shows the phase transitions of MAPbI$_3$ in comparison to MAPbBr$_3$ and MAPbCl$_3$, depicted from anomalous changes in temperature-dependent dielectric permittivity.

Stong evidences of ferroelectricity have been shown for MAPbI$_3$. First, Monte Carlo model simulations suggest the existence of ferroelectricity due to the orientation of the molecular cations following ferroelectric domains.[51] Second, noncentrosymmetry and pyroelectricity of the tetragonal MAPbI$_3$ film were confirmed by SHG and the abnormal pyroelectric current, respectively. Third, dependence of real ($\varepsilon'$) and the imaginary ($\varepsilon''$) relative permittivity as a function of temperature shows a dielectric anomaly around $T_c \approx 327$ K for polycrystalline MAPbI$_3$ films, which suggests the tetragonal MAPbI$_3$ film is ferroelectric. Fourth, exotic dielectric properties are derived in this material due to the presence of MA$^+$ cations with a large dielectric constant on the order of $10^1$–$10^3$ in the frequency range of $10^1$–$10^3$ Hz.[52] It is believed that MA$^+$ ions undergo order-disorder phase transition at $T_c$ and mainly introduce the weak ferroelectric polarization along [001] orientation in the tetragonal MAPbI$_3$. At last, the dielectric response is dominated by $\varepsilon''$ in this ferroelectric semiconductor. Rakita et al. obtained a $P$–$E$ hysteresis loop from integration of $\varepsilon''$ over the bias electric field ($E_{DC}$) at 204 K (Figure 4b).[4,12,53] Even so, reliable remnant polarization has not yet been experimentally observed in MAPbI$_3$ semiconductor at room temperature until now due to the relatively high electrical conductance and low stability under high applied bias voltage.[54]

Ferroelectric domains were observed in the tetragonal MAPbI$_3$ films with different methods. By chemical etching of the crystal with acetone, Rakita et al. observed polar domains periodically stacked along the polar axis of the crystal.[55] Furthermore, Röhm et al. observed ferroelectric domains by PFM.[56] Ferroelectric domains of alternating polarization with a width of 90 nm were identified (Figure 4c). The polarized...
domains in one grain with parallel stripes of polarization are able to self-organize to reduce the mechanical strain during cubic to tetragonal or orthorhombic phase transformation. A continuation of the polarization pattern within one grain is observed occasionally. The high-resolution photo-conductive atomic force micrographs under illumination also show alternating charge carrier extraction patterns which are due to the local vertical polarization components within the ferroelectric domains (Figure 4d). On the other hand, it was observed that the ferroic domains in MAPbI$_3$ may include alternating polar and nonpolar orders. These domains cannot be switched under an electrical field due to the blockage of polar switchable domains by nonpolar ones. Later, first-principle calculations reveal that ferroelectric domain walls can reduce the bandgaps significantly, as well as promote the charge separation. Polarized ferroelectric domains in β-MAPbI$_3$ films can act as small internal p-n junctions, which may accelerate the separation of photoexcited electron-hole pairs. To further improve the cell performance of MAPbI$_3$-based solar cells, Zhang et al. integrated P(VDF-TrFE), a ferroelectric polymer, into the light absorption layer of MAPbI$_3$ and/or between MAPbI$_3$ and the hole-transporting layer of Spiro-OMeTAD. These composite materials effectively improve the crystallization of MAPbI$_3$, enhance the built-in electric field $(E_{bi})$ and decrease the nonradiative recombination of electron–hole pairs in perovskite solar cells. The P(VDF-TrFE)-doped MAPbI$_3$ shows an orderly arrangement of MA$^+$ cations, resulting in a preferred growth orientation of polycrystalline perovskite films with reduced trap states. In addition, the depletion region is widened and $E_{bi}$ is enhanced in the device. The photovoltaic performance and polarization of P(VDF-TrFE) was obviously affected by the applied electric field, as shown in Figure 4e. The up-polarization had a positive effect on the cell efficiency, while the down-polarization showed an opposite effect. Most importantly, P(VDF-TrFE) as an interfacial dipole layer plays a critical role in increasing $E_{bi}$ which enhances the open circuit voltage $(V_{OC})$ from 1 to 1.14 V due to efficient suppression of nonradiative recombination. Consequently, the resulting perovskite solar cells present a power conversion efficiency of 21.38% (Figure 4f).

3.3. Ferroelectricity of Composition-Tailored Hybrid Perovskite Films

In general, there are several composition-based routes to tuning the ferroelectricity of MAPbI$_3$. By incorporation of Br in MAPbI$_3$, the band gap of iodide-based hybrid perovskites can be adjusted as a result of structural distortion of Pb–I bonds. Furthermore, the improvement of diffusion lengths, carrier lifetimes, and better stability can be achieved by tuning the percentage of PbBr$_2$ in mixed hybrid perovskites. In a recent work, the ferroelectricity of MAPbI$_3$–Br$_x$ $(x = 0–1.5)$ was confirmed by PFM. Fully polarization switching was demonstrated by a phase angle difference of 180° in the phase hysteresis loops (Figure 5a) and the butterfly-like shape observed in the amplitude loops at the bias-off state. Then the $J–V$ characteristics of glass/ITO/PEDOT:PSS/MAPbI$_3$Br$_{1.5}$/PCBM solar cells were studied, showing that the polarization switching can change the power conversion efficiencies.
(Figure 5b). Besides, Chen et al. investigated a ferroelectric TiO$_2$/MAPb$_{1-x}$Cl$_x$/Au solar cell and observed a high PCE of 19%.[64] Furthermore, the partial replacement of Pb$^{2+}$ with Fe$^{2+}$ improved both the morphology and crystallinity of MAPb$_{1-x}$Fe$_x$I$_3$ (0 ≤ x ≤ 0.50) films that undergo a tetragonal-cubic phase transition with a specific Fe$^{2+}$ concentration of x > 0.07.[18] The MAPb$_{1-x}$Fe$_x$I$_3$ (x = 0.07) films exhibited the saturated ferroelectric P–E hysteresis loops and a remnant polarization of $\approx$ 1.6 $\mu$C cm$^{-2}$ (Figure 5c). The flexible PET/ITO/MAPb$_{0.93}$Fe$_{0.07}$I$_3$/PDMS/Au/PI piezoelectric generators have an output voltage of $\approx$ 7.29 V and a current density of $\approx$ 0.88 $\mu$A cm$^{-2}$ through the piezoelectric effect of MAPb$_{0.93}$Fe$_{0.07}$I$_3$ during its repetitive stretching and bending (Figure 5d).

### 3.4. Ferroelectricity of FAPbBr$_3$ and Its Derivatives

FAPbBr$_3$ perovskite could be a promising ferroelectric material in high performance energy harvesting applications.[65] PFM measurements revealed that FAPbBr$_3$ nanoparticles contain well-developed ferroelectric properties with high piezoelectric charge coefficient (d$_{33}$) of 25 pm V$^{-1}$.[19a] The FAPbBr$_3$/PDMS/ITO/PDMS/ITO/PDMS/ITO composite film was grown onto an ITO-coated PET substrate, and then an Al film was deposited as the top electrode on the FAPbBr$_3$/PDMS layer to prepare the flexible piezoelectric generator (Figure 6a). The piezoelectric effect generates a positive voltage signal from the nanogenerator under a vertical compression, and the accumulated charges transport back in a reverse direction when the vertical compression is released, as shown in Figure 6b. The flexible device exhibits high performance with a piezoelectric output voltage of 8.5 V and current density of 3.8 $\mu$A cm$^{-2}$ under periodically vertical compression and release operations (Figure 6c).[19a] Furthermore, a ferroelectric FAPbBr$_3$ perovskite-based nanogenerator was optimized by using piezoelectric polymer of poly vinylidene fluoride (PVDF), and the nanogenerator with PET/Cr/Au/FAPbBr$_3$+PVDF/Au/Cr/PET configuration showed the current density of 6.2 $\mu$A cm$^{-2}$ and output voltage of 30 V (Figure 6d).[65] In another report, Zhang et al. applied FAPbBr$_3$ nanocrystals (NCs) into perovskite LEDs and piezoelectric nanogenerators. They found that the power produced by these nanogenerators can be collected in capacitors and then drive LEDs.[66]

According to the calculations, CsPbBr$_3$ can be transformed to a ferroelectric phase with tetragonal P4mm symmetry and a $P_s$ of 23 $\mu$C cm$^{-2}$ under a pressure of 15 GPa and CsPbF$_3$ may be ferroelectric with rhombohedral R3c symmetry (Table 1).[67] Recently, Kim and Stroppa et al. predicted in theory that FASnI$_3$ is also ferroelectric phase with an orthorhombic A$\text{mm}_2$ structure. Furthermore, in principle the reversal of the polar axis with an external electric field can switch spin texture in tetragonal MAPbI$_3$, MASnI$_3$, orthorhombic MASbBr$_3$, and FASnI$_3$ ferroelectrics through the existence of a strong spin-orbit coupling effect.[53,68] These predictions are very relevant to further study of the functionality of ferroelectric large polaron...
on CsPbBr$_3$ and FASnI$_3$ semiconductors, which show excellent semiconducting properties and PCE as high as 8.9% and 7.78%, respectively.

4. Halide Perovskite Insulators with Strong Ferroelectricity

4.1. Ferroelectricity of MD–NH$_4$I$_3$ Crystal

As summarized in Table 1, several halide perovskite ferroelectrics have emerged with strong ferroelectric characteristics but poor semiconductor properties (e.g., low carrier mobility and short diffusion length). Halide perovskite materials that possess robust ferroelectric and piezoelectric properties have lots of potential for flexible and wearable electronic applications. In fact, the order-disorder transitions of cations in these halide perovskites around the BX$_6$ octahedra are responsible for symmetry breaking and ferroelectricity of these materials. The possibility of ferroelectric–paraelectric phase transition can be recognized by at least a twofold increase in dielectric constant with increasing the temperature. Moreover, the compound can be considered as either piezoelectric or pyroelectric if no dielectric anomaly is observed.[69] Ye et al. prepared N-methyl-N’-diazabicyclo[2.2.2]octonium–NH$_4$I$_3$ (i.e., MD–NH$_4$I$_3$) crystal with a relatively simple 3D structure (Figure 7a).[26] The crystal has rhombohedral R3 structure with crystal parameters of $a = b = c = 7.259$ Å and $\alpha = \beta = \gamma = 84.767^\circ$ at room temperature. MD is positioned at the center in the unit cell, NH$_4^+$ groups stand at vertexes and I$^-$ ions are at the centers of the edges. The high-level ferroelectric performance of (111) MD–NH$_4$I$_3$ crystal renders a $P_s$ of 22 $\mu$C cm$^{-2}$ at 448 K according to the $P$–$E$ loops shown in Figure 7b and a piezoelectric $d_{33}$ of $\approx$14 pC N$^{-1}$ at room temperature. Such $P_s$ value is comparable to barium titanate and much higher than PVDF.[10] Furthermore, both $P_s$ and the effective second-order nonlinear optic susceptibility $\chi^{(2)}$ show the same trend with increasing temperature (Figure 7c), which is in accordance with the Landau relationship $\chi^{(2)} = 6\varepsilon_0\beta P_s$ where, $\beta$ denotes an almost temperature independent coefficient.[70] There is an abrupt change in both $P_s$ and $\chi^{(2)}$ near $T_c$ due to the ferroelectric–paraelectric phase transition. MD–NH$_4$I$_3$ crystals have potential to be applied in biomedical devices, soft robotics, energy transduction, and other fields in the future.[71]

4.2. Ferroelectricity and Piezoelectricity of TC–MnCl$_3$ Crystal

Halide perovskite ferroelectric materials possess the advantages of flexible design, light weight, easy processing, and being environmentally friendly. Ferroelectrics are naturally piezoelectrics, because of lacking inversion center in their structures. However, the weak piezoelectric effect of these molecular ferroelectrics has remained a shortcoming for a long time. You et al. prepared trimethylchloromethyl ammonium (TC) trichloromanganese (II) (TC-MnCl$_3$) in aqueous solution at room temperature.[27] It has a centrosymmetric structure above $T_c$, that is, $\approx$405 K due to the orientational disorder of the organic cation. The crystal loses its centrosymmetry below $T_c$ as a result of the "freezing" of cations, which induces the appearance of a spontaneous polarization in the monoclinic $Cc$ phase (Figure 8a). The $P_s$ is of 4.0 $\mu$C cm$^{-2}$ according to their $P$–$E$ loops in Figure 8b, in which the corresponding current density-bias voltage curves are illustrated as well. Polarization of TC-MnCl$_3$ only decreases less than 10% after 10$^7$ cycles of polarization switching. Besides, TC-MnCl$_3$ also presents a piezoelectric $d_{33}$...
value of 185 pC N\(^{-1}\) along the proximity of the [102] direction of the crystal (Figure 8c), which is superior to most of the weak piezoelectric coefficients measured in organic materials.\(^{[72]}\) The inset shows the \(d_{33}\) with fluctuation as little as <10 pC N\(^{-1}\) when the frequency of driving force ranges from 30 to 300 Hz. These high performances pave the path for the application of TC-MnCl\(_3\) in micromechanical and biomechanical industries such as flexible devices and nanogenerators.

### 4.3. Ferroelectricity and Piezoelectricity of (TF)\(_x\)(TC)\(_{1-x}\)CdCl\(_3\) Crystal

Based on the organic TC group, Liao et al. synthesized the molecular perovskite (TF)\(_x\)(TC)\(_{1-x}\)CdCl\(_3\) (TF, trimethylfluoromethyl ammonium; 0 \(\leq x \leq 1\)).\(^{[15]}\) As shown in Figure 9a, with increasing of TF content (\(x\)) from 0.25 to 0.3, (TF)\(_x\)(TC)\(_{1-x}\)CdCl\(_3\) stays in MPB region where the ferroelectric monoclinic phase (point group m, 0 \(\leq x < 0.25\)) and the ferroelectric hexagonal phase (point group 6\(\bar{m}\), 0.3 \(< x \leq 0.5\)) coexists. The hexagonal phase (point group 6\(\bar{m}\)) lies in the region of 0.55 \(\leq x \leq 1\) at room temperature.\(^{[15]}\) The MBP of monoclinic and hexagonal phases optimized their piezoelectric property. Piezoelectric coefficient \(d_{33}\) was obtained by PFM and the abrupt change at \(x = 0.26\) verified the piezoelectricity near the MPB (Figure 9b).

Besides, the Berlincourt method further confirmed the giant \(d_{33}\) of \(\approx 1540\) pC N\(^{-1}\) in (TF)\(_{0.26}\)(TC)\(_{0.74}\)CdCl\(_3\) solid solution, which is as high as PZT piezoelectric ceramics. This makes it potentially useful for flexible piezoelectric applications. The maximum dielectric constant (\(\varepsilon''\)) of (TF)\(_{0.26}\)(TC)\(_{0.74}\)CdCl\(_3\) value is of \(\approx 1500\) at \(T_c \approx 370\) K (Figure 9c). Moreover, (TF)\(_x\)(TC)\(_{1-x}\)CdCl\(_3\) demonstrates well-saturated \(P-E\) hysteresis loops at \(x \leq 0.4\). Both \(P_s\) and remnant polarization (\(P_r\)) present the same tendency to increase slightly as \(x\) increases, showing the maximum values at \(x = 0.26\) in the MPB region and then decreasing monotonously with \(x\) (Figure 9d).\(^{[15]}\)

### 4.4. Ferroelectricity of 2D Lead Halide Perovskites

Some 2D multilayered lead halide perovskite ferroelectrics not only show strong ferroelectricity but also have a narrow band gap. In a multilayered lead halide perovskite \((A2)_2(A1)_{n-1}Pb_nX_{3n+1}\), \(A1\) cation is the “perovskitizer” that occupies the central cavity of corner sharing PbX\(_6\) octahedra and \(A2\) cation is the “spacer” that is confined in the interlayer space of the inorganic sheets. In a representative work, Yang, et al. prepared 2D lead iodide perovskite ferroelectrics \([R-1-(4-chlorophenyl) ethylammonium]_2PbI\(_4\) (i.e., R\(_2\)PbI\(_4\)), [S-1-(4-chlorophenyl)ethylammonium]_2PbI\(_4\) (i.e., S\(_2\)PbI\(_4\)), and (4,4-difluorocyclohexylammonium)_2PbI\(_4\) (i.e., D\(_2\)PbI\(_4\)).\(^{[28]}\) The enantiomorphic structure of R\(_2\)PbI\(_4\) is shown in Figure 10a. Similar to the structure of typical 2D perovskites such as (C\(_6\)H\(_3\)NH\(_3\))\(_2\)PbI\(_4\) and (C\(_6\)H\(_3\)C\(_2\)H\(_4\)NH\(_3\))\(_2\)PbI\(_4\), corner-sharing PbI\(_6\) octahedron
layers are separated by 1-(4-chlorophenyl)ethylammonium cationic bilayers. Besides, these 2D perovskites possess semiconductor characteristics with a direct bandgap of 2.34 eV. The ferroelectric phases of S$_2$PbI$_4$ and R$_2$PbI$_4$ appear below 483 and 473.2 K, respectively. Figure 10b presents the PFM phase image of R$_2$PbI$_4$ film, indicating that the herringbone-shaped ferroelectric domains are formed by four kinds of domains that have different polarization directions, revealing its multiaxial ferroelectric nature.\[27\] Besides, there is an 180° change of phase angle in the bias dependence data. In fact, such switchable polarization is a compelling evidence of ferroelectricity (Figure 10c). Most importantly, R$_2$PbI$_4$ possesses a direct bandgap of 2.38 eV.\[28\] Furthermore, the ferroelectric polarization switching can change the direction of photovoltaic current. Owing to their unique properties, 2D lead iodide perovskite ferroelectrics are expected to be utilized in high-performance applications in future.\[74\]

4.5. Other Halide Perovskite Ferroelectrics

Recently, it was reported that hexagonal stacking perovskite-type complex (3-pyrrolinium)(CdCl$_3$) shows $P_r = 5.1$ μC cm$^{-2}$ below its $T_c$ of 316 K.\[75\] The 1 mm-thick bulky crystal shows a $V_{OC}$ as high as 32 V. Besides, (Pyrrolidinium)MnBr$_3$ and (3-aminopyrrolidinium)RbBr$_3$ are molecular pyrrolinium-based materials exhibiting attractive ferroelectric properties.\[76\] (Pyrrolidinium)MnBr$_3$ belongs to the 2-H stacking perovskite structure which is tunable through tailoring some templating cations or bridging atoms. It possesses intense red luminescence under UV excitation and 640 nm photoluminescence emission with a quantum efficiency around 28.5%. Moreover, (3-aminopyrrolidinium)RbBr$_3$ is a thermally stable ferroelectric candidate with a $T_c$ as high as 440 K. More importantly, the compound has multiple polar axes, resulting in a large macroscopic polarization in the polycrystalline sample. As another attractive feature, the fast polarization reversal of >20 kHz is favorable for high-speed devices.\[77\]

Besides 3D and 2D halide perovskites, 1D halide perovskites, consisting of chains of metal halide octahedra surrounded by insulating organic cations, have presented remarkable properties due to site isolation and quantum confinement effects. Some 0D perovskites with the chemical formula of $A_4BX_6$ (A = monovalent organic cations, $BX_6$ = metal halide octahedra) have also shown ferroelectric properties due to the rotation of organic cations, making them suitable for electronic applications such as switchable memory devices.\[78\] However, the issue of low conductivity as a result of the existence of insulating organic cations between separated metal-halide octahedra have to be addressed in order to improve the utilization of low-dimensional halide perovskites.\[79\] Seo et al. reported that (C$_3$H$_5$NH$_3$)$_n$(MA)$_{1-n}$Pb$_n$I$_{3n+1}$ exhibited resistive switching behavior,\[80\] and they claimed that there was a decrease in device performance with increasing the dimension of the structures due to the change of bandgap. Clearly, in order to further advance this field, potential design rules should be developed to engineer the molecular structure, particularly the organic cations since they are strongly correlated to the ferroelectric
dipoles. The dynamic domain nucleation and polarization switch should also be investigated, as reported on some organic and oxide ferroelectrics.\[81\]

There have been few studies on the ferroelectric properties of halide perovskites when the materials are fabricated down to nanoscale. There is a possibility of disappearing of ferroelectricity in small scales as a result of decreasing long-range ordering of dipoles.\[82\] In fact, the existence of vortex domains followed by a toroidal ordering of dipoles may lead to zero net polarization in small ferroelectric nanoparticles.\[83\] Moreover, ferroelectricity can be limited by other parameters such as mechanical and electrical boundary conditions or the quality of nanomaterials.\[84\] On the other hand, DFT calculations have indicated that some absorbates such as carboxylates and OH can stabilize ferroelectricity in nanowires by screening polarization charges on the surfaces and therefore reducing the depolarization field.\[85\] Generally, it is important to obtain a complete understanding of the molecular structure design and ferroelectric behavior of these novel materials in order to promote halide perovskites in future electronic and electromechanical applications.

5. Conclusions and Future Perspectives

In summary, two types of halide perovskite ferroelectrics have been reviewed, that is, perovskite semiconductors with weak ferroelectricity and insulating ferroelectrics with strong piezoelectricity. For the first type of halide perovskites prepared in aqueous solution near room temperature, the ferroelectric large polaron model is employed to explain how carriers are protected from scattering by charged defects. MAPbI$_3$, Fe- or Br-doped MAPbI$_3$, and FAPbBr$_3$ are the most representatives of halide perovskite ferroelectrics. As ferroelectricity is difficult to be recognized by macroscopic methods in these...
typical semiconductors, most of researches characterized ferroelectric properties of these perovskites using microscopic methods such as PFM.\textsuperscript{[9,12,15]} The second type of ferroelectric halide perovskites also have great potential for applications and are fundamentally interesting. MD-NH$_4$I, TC-MnCl$_3$ and (TF)$_3$(TC)$_{-3}$CdCl$_3$ show large ferroelectric polarization and high piezoelectric $d_{33}$ coefficient according to recent reports.\textsuperscript{[15,26,27]} Especially, the (TF)$_{0.26}$(TC)$_{0.74}$CdCl$_3$ solid solution has MPB of monoclinic and hexagonal phases, which contributes to a giant $d_{33}$ value of $\approx 1540$ pC N$^{-1}$, being as high as that of PZT piezoelectric ceramics. Furthermore, there are ferroelectrics which belong to the family of multilayered halide perovskites with formula of (A$_2$)$_n$(AI)$_{n-1}$Pb,X$_{3n+1}$ such as R$_2$PbI$_4$, S$_2$PbI$_4$, D$_2$PbI$_4$, EA$_4$Pb$_3$Br$_{10}$ and (EA)$_4$(MA)$_3$Pb$_3$Br$_{10}$.\textsuperscript{[25,28]} Some of them have a relatively narrow bandgap and the photovoltaic current can be reversed by switching their ferroelectric polarization. Their unusual ferroelectricity and piezoelectric properties can be exploited in optical, mechanical, and energy transduction applications. As a great advantage, halide perovskite ferroelectrics provides plenty of room for exploration and engineering in terms of material design.

Although extensively studied, the development of halide perovskite ferroelectrics is still at its infancy stage compared to their inorganic perovskite counterparts. In future, researchers should pay more attentions to at least five directions of advancing halide perovskite ferroelectrics regarding theoretical mechanisms, material properties, chemical and electrical stability, environmental friendliness, and new high value-added applications. 1) The mechanisms of these halide perovskite ferroelectrics still need to be elucidated. It is still not very clear how carriers are protected from scattering in halide perovskite semiconductors, which have much higher density of charged defects than those of conventional semiconductors such as high-purity Si and GaAs. Design rules are also needed to engineer the molecular structure, particularly the organic cations, to enhance ferroelectric dipoles and stability for practical applications. Insights on the mechanisms will facilitate the design of halide perovskites with high carrier mobility, wide band gap, and large polarization coexisting simultaneously. 2) It is necessary to design and prepare more halide perovskite materials with excellent semiconductor and ferroelectric properties. More systems of these materials should be explored with a focus on trying different organic groups with rationally selected metal ions and halogens to obtain a better device performance. 3) Most of the halide perovskites can be prepared in aqueous solution near room temperature. Some of them are not stable and even decompose in humid environment, high-temperature ambiance, and/or under high light illumination. It is very important to further improve the chemical and electrical stability of halide perovskite ferroelectrics in order to use these materials widely in industries. 4) Pb element is not environmentally friendly and Pb-acid cells are pollutant sources. To substantially decrease or completely avoid the use of Pb element should be the precondition for new solar cells to be commercially viable, thus it would be desirable to develop high-performance solar cells on the base of Pb-free halide perovskite materials. 5) In addition to solar cells, LEDs, optical detectors, piezoelectric sensors, some high-value and high-quality cost-effective devices such as ferroelectric transistors, ferroelectric tunnel junctions, and multiferroic devices should be developed as urgent tasks.\textsuperscript{[86]} As the range of applications expands, halide perovskites can find some niche areas with the possibility of substantial cost reduction and product recycling. Furthermore, these halide perovskite ferroelectrics are soft and flexible enough to be applied in wearable sensors and photoacoustic devices.\textsuperscript{[87]} By leveraging on the rapid achievements recently achieved, researchers will be able to improve the mechanical and electrical properties of halide ferroelectric perovskites to further advancing their applications.

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Conflict of Interest
The authors declare no conflict of interest.

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