Re-Entrant Relaxor Ferroelectricity of Methylammonium Lead Iodide

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Abstract

We have performed a piezoresponse force microscopy (PFM) study on methylammonium lead iodide (MAPbI₃) thin films in normal (non-resonance, non-band-excitation) contact mode. In contrast to the ferroelectric Pb_{0.76}Ca_{0.24}TiO₃ (PCT) control sample, a typical ferroelectric response was not observed. However, a nonlinear electric field dependence of the local PFM amplitude was found in MAPbI₃, similar to PCT. An analysis combining results on structure, dielectric dispersion, and weak ferroelectricity demonstrates that MAPbI₃ is actually a re-entrant relaxor ferroelectric which, upon cooling, enters into a relaxor phase below its ferroelectric phase transition at ~327 K, due to the balance between the long range ferroelectric order and structural methylammonium group orientational disorder. The ferroelectricity at room temperature is compromised due to the re-entrant relaxor behavior, causing the poor polarization retention or weak ferroelectricity. Our findings essentially conciliate the conflicting experimental results on MAPbI₃'s ferroelectricity and are beneficial both for basic understanding as well as for device applications.

Keywords: Electronic materials; Atomic force microscopy; Ferroelectrics; Relaxor; Piezoresponse force microscopy

1. Introduction

Solar cells based on the perovskite methylammonium lead iodide (MAPbI₃) have received wide interest due to their high efficiency, easy fabrication, and the abundant constituent elements [1-3]. Ferroelectricity in MAPbI₃ has been proposed to be closely related to both its high device performance and current-voltage hysteresis [4-6]. However, there is conflicting evidence for this property both macroscopically and microscopically [7-10]. Microscopically, some have claimed a very weak ferroelectric response while others have reported a hysteresis loop with piezoresponse force microscopy (PFM) in resonance-enhanced or band excitation (BE) modes. The ferroelectricity is weak because it cannot be easily observed using normal (non-resonance, non-BE) PFM [11]; the reported local properties are mainly from resonance-enhanced [12, 13], BE PFM [10] or at a fast rate [14]. As is well known, for a conventional ferroelectric, microscopic PFM domains and/or local hysteresis loops can be usually obtained, even though macroscopic properties may vary depending on sample quality. However, this is not the case for MAPbI₃. For example, while Fan *et al.* [8] and Xiao *et al.* [11] found no PFM domain contrast, domain structure and/or d_{33} ~V loops were observed through resonance-enhanced PFM [12, 13, 15] and BE PFM by Kim *et al.* [10]. Recently, Coll *et al.* [14] attributed the frequency-dependent local hysteresis loop of MAPbI₃ (which can only be observed at a very fast rate) to poor polarization retention.

With so much attention to the ferroelectricity in MAPbI₃, further investigation may lead to a clearer understanding of this intriguing material. *Via* the inverse piezoelectric effect, PFM piezoresponse (the local dielectric constant d_{33}) is related to polarization. The dimensions of a ferroelectric sample will change with the external voltage, giving rise to the observed domain pattern and/or local hysteresis loop. Furthermore, as a microscopic method, PFM is less affected by leakage current [8]. Therefore, we performed PFM measurement on MAPbI₃ films in normal (non-resonance) mode. Our observations corroborate the reported weak PFM amplitude and phase contrast [11]. After careful analysis of the electric field dependence of the PFM amplitude and the reported temperature-dependent dielectric dispersion, we demonstrate that MAPbI₃ is an unconventional ferroelectric: a re-entrant ferroelectric relaxor.

2. Experimental

The MAPbI₃ samples were prepared by a solution method; for details of preparation and characterization, see the Supplementary Information.

Before discussing MAPbI₃, we first present the PFM result on the conventional ferroelectric Pb_{0.76}Ca_{0.24}TiO₃ (PCT). Fig. 1 shows typical ferroelectric domain images

[Figs. 1(b) and (c)] and local ferroelectric switching curve [Fig. 1(d)]. To compare with the following MAPbI₃'s case, we also measured the initial part of local hysteresis loop by scanning the DC field with a constant AC field superimposed on. Fig. 1(e) shows that at two chosen locations (A and B), where there is no pre-existing domain, the PFM amplitude changes with external field nonlinearly.

Fig. 1. Typical ferroelectric response of a PCT film: (a) Topography, (b) PFM amplitude (A), (c) PFM piezoresponse ($A \cos \theta$), and (d) Local hysteresis loop with PFM amplitude and phase. (e) Initial field-dependence of piezoresponse amplitude at the two marked locations in (b).

At locations A and B, instead of pre-existing domains, we presume that there are only randomly-oriented domains smaller than our PFM spatial resolution. During initial domain nucleation, the polarization changes slowly with the external field (a small slope in the $d_{33} \sim V$ curve). Afterwards, the ferroelectric domain grows fast, resulting in a nonlinear initial amplitude field-dependence curve [Fig. 1(e)]. Similar initial curves have been observed in ferroelectrics as shown in Fig. 1(a) of Ref. [17] and Fig. 2 of Ref. [18].

From PFM measurement on MAPbI₃, we found a weak domain contrast [Fig. 2(c)]. Instead of two polarities of typical ferroelectrics, the histogram of PFM phase (Fig. S2 of Supplementary Information) shows only one polarization direction. No typical

ferroelectric local hysteresis loop was found. These results are largely consistent with Refs. [8] and [11]. However, the initial field-dependence of the PFM amplitude is nonlinear, which can be fitted to the polynomial function of Eq. (1) [Table 1 and the red curves in Fig 2(c)]:

$$y = B_0 + B_1x + B_2x^2 \quad (1)$$

where y , x are the sample's dimensional change and the external field, while B_0 , B_1 and B_2 are the coefficients. Such nonlinear dependence can be explained by the initial domain nucleation and growth, as for afore-mentioned PCT case. To add to the complexity, because of the hydrophilic property of MAPbI_3 , the electrostatic contribution cannot be completely excluded, even efforts were taken to minimize it during the measurements: e.g. with stiff NSG10 probes ($\sim 11 \text{ N/m}$).

Fig. 2. Piezoresponse of MAPbI_3 as a re-entrant ferroelectric relaxor. PFM images of MAPbI_3 film: (a) Topography, (b) PFM amplitude (A), and (c) PFM piezoresponse ($A \cos \theta$), respectively; (d) Topographical image. A and B are two selected locations for measuring the initial field-dependence of the PFM amplitude in (e). (e) The initial field-dependent PFM amplitude curves at sites A and B in (d). (Other measurements were carried out at the sites marked with small white crosses. The measurements at A and B are representative.)

Table 1. Fitting result of field-dependent PFM amplitude curves in Fig. 2c

	Curve A		Curve B	
	Value	Standard Error	Value	Standard Error
B_0	4.47368	0.01078	5.12565	0.01224
B_1	-0.16664	0.0083	-0.41202	0.00942
B_2	0.19479	0.00134	0.16889	0.00152

In contrast, for dielectric Al_2O_3 film there is no nonlinear field dependence of the amplitude (Fig. S3 of the Supplementary Information). Comparing the measurement results for the ferroelectric PCT, the dielectric Al_2O_3 , and MAPbI_3 , it is very likely that MAPbI_3 exhibits nanoscopic weak ferroelectricity. This result is consistent with the reported ferroelectricity of MAPbI_3 [12-14].

3. Discussion

In general, ferroelectric relaxors exhibit structural disorder arising from different ions occupying equivalent lattice sites (i.e. compositional, chemical, ionic disorder). A typical example is $\text{Pb}(\text{Mg}_{1/3}\text{Nb}_{2/3})\text{O}_3$ with ions of different valences (Mg^{2+} and Nb^{5+}) on crystallographically equivalent sites [19]. In MAPbI_3 , the orientation of the CH_3NH_3^+ cation cannot be fixed by symmetry [20, 21]. Both Poglitsch *et al.* and Weller *et al.* [20, 22] found that upon cooling, this disorder persists through the first cubic-to-tetragonal phase transition at ~ 150 K. Furthermore, Stoumpos *et al.* found that cooling through this transition, the CH_3NH_3^+ cations were frozen into different orientations, rendering 50% of the structure unable to be indexed [21]. The low-temperature orthorhombic phase stays disordered, consistent with the nature of a (re-entrant) relaxor.

In addition, a ferroelectric relaxor has characteristic dielectric frequency dispersion, namely an increase of the temperature of maximum-permittivity (T_m) with frequency, which follows Vogel-Fulcher law [19, 23]. Indeed, such dielectric dispersion has been observed in MAPbI_3 by Onodayamamuro *et al.* using dielectric spectroscopy at frequencies from 20 Hz to 1 MHz, in a temperature range between 50 and 100 K (Fig. 6 of Ref. [24]). Furthermore, we have found this dispersion can be fitted with Vogel-Fulcher law (Fig. 3). It is worth noting that dielectric property from bulk samples as in Ref. [24] is usually more repeatable and reproducible than the thin film samples because they are less affected by leakage problem, especially for such a material like MAPbI_3 .

Hence structurally and dielectrically, the perovskite MAPbI₃ has the characteristics of a ferroelectric relaxor below its Curie temperature, i.e. behaviors of a re-entrant type ferroelectric relaxor. For a re-entrant relaxor, the ferroelectricity is compromised because of the disorder in the material: In re-entrant relaxor 0.99BaTiO₃–0.01AgNbO₃, the disorder introduced by only 1% of AgNbO₃ in BaTiO₃ causes a sizable loss of polarization [25, 26]. Therefore, as a re-entrant relaxor, MAPbI₃ has characteristics of poor polarization retention and weak ferroelectricity. However, ferroelectricity can be induced in a re-entrant relaxor by excitation, *e.g.* an electrical field, as in the case of (1-*x*)BaTiO₃-*x*BiScO₃ [27]. Thus, we propose that the ferroelectricity in MAPbI₃ is originated from the delicate balance of ferroelectric long-range order and the relaxor's disorder.

Fig. 3. Fitting the dielectric dispersion of Ref. [24] to Vogel-Fulcher law. Data were obtained from the dielectric maximums extracted from Fig. 6 of Ref. [24].

Because grain size and grain orientation largely affect the ferroelectricity [28], further study along this line may shine light on relaxor-ferroelectricity of MAPbI₃. Domain structures as well as switching-related domain nucleation and activation energy are susceptible to external influences *e.g.* surface charges and defects. Studies with Kelvin probe force microscopy (KPFM) have shown that contact potential differences behave differently in grain and grain boundary of MAPbI₃ [29-32]. Further investigation combining PFM and KPFM on grain and grain boundary may reveal detailed structure-property relationship in MAPbI₃.

4. Conclusions

By measuring the field-dependent PFM amplitude as well as analyzing the reported structural and dielectric behaviors, we have found that MAPbI₃ is a re-entrant type ferroelectric relaxor, not a conventional ferroelectric. Its polarization has been compromised by the local disorder, resulting in characteristics of poor polarization retention and weak ferroelectricity. Our findings accommodate the local and

macroscopic experimental results on MAPbI₃'s ferroelectricity as well as its structure and dielectric dispersion, and pave the way for a fundamental understanding of this promising perovskite material.

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Figure 1

Figure 2

Figure 3