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ABSTRACT
Tetramethylammonium bromotrichloroferrate(III) ([N(CH₃)₄][FeBrCl₃]) is a plastic crystal ferroelectric with small dielectric constant <20 and piezoelectric coefficient as high as 110 pC/N. Here, super-coercive hysteresis and dielectric properties under direct current (DC) bias fields up to 260 and 120 kV/cm, respectively, were studied to shed light on the polarization switching [N(CH₃)₄][FeBrCl₃] and the related family of plastic crystal and supramolecular ferroelectrics. [N(CH₃)₄][FeBrCl₃] exhibited peak-to-peak strains of 0.1% and saturated ferroelastic switching at fields of 170 kV/cm. Above 170 kV/cm, rates of field increase were too fast for domain switching, resulting in reduced strain rates during the switching cycle. Leakage currents had larger contributions at higher field amplitudes. This was also reflected in the switching behavior at higher frequencies, 100 Hz, in which hysteresis was asymmetric and switching incomplete. The dielectric constant and loss exhibited a butterfly-like shape during application of DC bias electric fields indicative of domain switching, but showed a small dielectric tunability of 0.038 and no signs of dielectric stiffening, with the relative permittivity from 16.9 to 17.3 at fields from 0 to 120 kV/cm. The present findings provide insight into the domain switching kinetics and dielectric properties of [N(CH₃)₄][FeBrCl₃] that will assist with further development of plastic crystal ferroelectrics.

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Ferroelectric materials with low dielectric constants and high piezoelectric coefficients are uniquely suited for applications like sensing and energy harvesting, where the figure of merit is inversely proportional to the dielectric constant. Demand for these applications will increase as the Internet of Things (IoT), smart buildings, self-driven electric vehicles, and energy autonomous devices become more prevalent in society. Many commercial ferroelectrics, such as BaTiO₃ and PbZr₀.₅₂Ti₀.₄₈O₃ (PZT) however, have high dielectric constants, brittle mechanical properties, and face a number of synthesis challenges, which can make them less than ideal for many applications in this growing area. The investigation of materials with small dielectric responses and greater mechanical flexibility, such as supramolecular and organic–inorganic hybrids, is therefore a useful avenue of investigation for the development of alternative sensor and energy harvester devices.

[N(CH₃)₄][FeBrCl₃] is a supramolecular hybrid organic–inorganic plastic crystal that was recently identified with useful dielectric and electromechanical properties, such as a low dielectric constant (relative permittivity <20) and a strong piezoelectric coefficient (d₃₃) of 110 pC/N. [N(CH₃)₄][FeBrCl₃] has a noncentrosymmetric orthorhombic Ammm2 crystal structure at room temperature [Fig. 1(a)] and four temperature dependent polymorphs between 0 and 110 °C, with a ferroelectric to paraelectric transition between 70 and 90 °C. Above 110 °C, the material forms a cubic mesophase, in which the molecular ions rotate freely in the crystal lattice and allow the material to be plastically deformed. The mesophase provides a pathway for low temperature synthesis of polycrystalline materials, making [N(CH₃)₄][FeBrCl₃] appealing from an environmental perspective, and for compatibility with other polymeric materials. Despite the potential of [N(CH₃)₄][FeBrCl₃] and the wider family of plastic crystal ferroelectrics, critical aspects of the ferroelectric properties, such as switching dynamics, electric field dependence, and leakage currents, have not yet been thoroughly characterized. To help rectify this, we report on the characteristics of electric field dependent switching of polycrystalline [N(CH₃)₄][FeBrCl₃].
Polycrystalline \([\text{N}(\text{CH}_3)_4]_2[\text{FeBrCl}_3]\) was prepared by separately dissolving methylammonium bromide (99%, Sigma Aldrich) and iron trichloride hexahydrate (98%, Sigma Aldrich) in de-ionized water and mixing 1:1 molar ratios of each solution. Crystallization occurred at room temperature during slow evaporation of water over 7 days. Crystals were vacuum filtrated and dried in vacuum at 60 °C for 6 h. The largest crystal agglomerates, averaging 15 mm in diameter [Fig. 1(b)], were hot pressed at 140 °C and 10 MPa into flat 380 μm thick 30 mm diameter disks [Fig. 1(c)]. The disks were cut into 10 mm² pieces and sputter coated with 4 mm diameter Au electrodes [Fig. 1(d)]. The whole synthesis process therefore involved only aqueous solvents and temperatures no higher than 140 °C.

The orthorhombic \(\text{Amm2}\) crystal structure [Fig. 1(a)] was confirmed by x-ray diffraction (XRD) using a D8 focus x-ray diffractometer with a Cu source and Rietveld refinement, fitted to the Cambridge crystallographic data center (CCDC) file 1574204 from Harada et al. using the Topas® software package (data not shown). All bipolar electric field hysteresis and dielectric measurements of \([\text{N}(\text{CH}_3)_4]_2[\text{FeBrCl}_3]\) were measured with an Axilact ferroelectric tester, trek 10 kV amplifier, and a laser interferometer. A triangular wave form at a frequency of 10 Hz was used for hysteresis measurements at field amplitudes up to 260 kV/cm. Samples were stored in a desiccator and were typically hot pressed and electroded within one week of their electrical measurements. Measurements conducted several weeks or months after processing confirmed that leakage currents did increase but that ferroelectric behavior was qualitatively comparable. The single most influential factor on electrical leakage was the process of drying of crys-
tals after synthesis. Poorly dried samples, for example, those dried on a hot plate, resulted in electrical leakage 1000 times larger than those dried in vacuum at 60 °C. Measurements conducted several weeks or months after processing confirmed that leakage currents did increase but that ferroelectric behavior was qualitatively comparable. The single most influential factor on electrical leakage was the process of drying of crystals after synthesis. Poorly dried samples, for example, those dried on a hot plate, resulted in electrical leakage 1000 times larger than those dried in vacuum at 60 °C.

Critical parameters of the P–E, I–E, and S–E hysteresis loops were analyzed as a function of the driving electric field amplitude [Figs. 2(d)–2(g)]. The \(P_r\) increased linearly up to 170 kV/cm and the polarization at maximum electric field \(E_{\text{max}}\) increased linearly with two distinct gradients above and below 170 kV/cm [Fig. 2(d)]. The current density peaks \(I_{\text{peak}}\) correspond with the greatest number of domains switching during the electric field cycle, and also exhibited different linear gradients as a function of field amplitude above and below 170 kV/cm [Fig. 2(e)]. The peak-to-peak strain \(S_{\text{pp}}\), which is a measure of the total strain generated during the domain switching, increased from 0.014% to 0.109% between field amplitudes 80 and 170 kV/cm and plateaued at fields above 170 kV/cm [Fig. 2(f)].

Two physical explanations can be used to understand the behavior observed for \(P_r\), polarization at \(E_{\text{max}}\), and \(S_{\text{pp}}\). Below 170 kV/cm, the number of domains being switched for the first time increases with the increasing field amplitude, but above 170 kV/cm, this number decreases with increasing field amplitude.7,10–11 The constant \(S_{\text{pp}}\) above 170 kV/cm indicates that the total number of ferroelastic domains being switched saturates, as only the ferroelastic domains will contribute to strain and there is no direct contribution from leakage current. The smaller gradients seen above 170 kV/cm in \(P_r\), polarization at \(E_{\text{max}}\), and \(I_{\text{peak}}\) all suggested that ferroelectric domain switching may also begin to saturate, but domains and leakage current contributions cannot be separated in these data.

The difference between \(E_c\) in positive \((E^+\text{c})\) and negative \((E^-\text{c})\) field directions determined from the I–E loop peak positions were plotted together with the internal bias fields \((E_{\text{bias}} = E^+\text{c} - E^-\text{c})\) and indicated preferential switching of domains [Fig. 2(g)].12,15,16 Both \(E^+\text{c}\) and \(E^-\text{c}\) increased with field amplitude at a decreasing rate, while the \(E_{\text{bias}}\) decreased from 9 to 2 kV/cm between 80 and 170 kV/cm above which it fluctuated. The \(E_{\text{bias}}\) of \([\text{N}(\text{CH}_3)_4]_2[\text{FeBrCl}_3]\) at lower electric fields suggests the presence of oriented defect complexes [Fig. 2(g)].16 V\(^{++}\)\([\text{FeBrCl}_3]\) (lattice vacancy in Kröger–Vink notation) and...
Br\textsubscript{[FeBrCl3]} were previously identified as likely charged point defects that could form a complex.\textsuperscript{10} Orientation of these defects could result from hot pressing, as complex defects can have both an electrical and mechanical dipole.\textsuperscript{17} The reduction of $E_{\text{bias}}$ up to 170 kV/cm implies that the preferred orientation was destroyed by the bipolar electric field or that the defects were mobile.\textsuperscript{15,16} The instability of the $E_{\text{bias}}$ at fields $>170$ kV/cm may relate to the leakage current.

Strain rate hysteresis curves are a plot of the first derivative of the strain ($\frac{ds}{dt}$) as a function of electric field, thus the relationship between strain and strain rate is analogous to that of the polarization and current hysteresis [Fig. 2(g)].\textsuperscript{14} Among other useful features, the peaks in the strain rate signify where the largest amount of ferroelastic domain reorientation took place during an electric field cycle. To understand the strain rate hysteresis of [N(CH$_3$)$_4$][FeBrCl$_3$] in terms of switching kinetics, we first analyzed the loop with field amplitude 170 kV/cm [Fig. 2(i)]. The strain rate hysteresis at 170 kV/cm was highly symmetrical with a total of four distinct peaks corresponding to inflection points of the S–E loops. The strain loop had two minima and two maxima, indicating two consecutive and reproducible steps of ferroelastic domain switching in each field direction.\textsuperscript{14} Notably, the strain rate hysteresis loops bore significant qualitative similarities to that of commercial soft PZT ceramics (PZT 5H) and so an over-simplified model of domain switching with domains approximately parallel, perpendicular, and anti-parallel to the electric field (as if the structure had tetragonal symmetry) was useful to qualitatively describe the two-step switching process.

As the electric field first increased the material shrank, indicated by the negative strain rate [points 1–2, Fig. 2(i)]. This was associated with depoling the sample from the remanent polarization state left by the previous electric field cycle.\textsuperscript{14} The shrinkage rate reached a sharp maximum at point 2 (90 kV/cm), indicating the field at which most ferroelastic domains switched from approximately anti-parallel to...
approximately perpendicular to the electric field. From point 2 to 3, the strain rate increased rapidly from \(-0.002\%\) to \(0\%\, s^{-1}\), with \(0\%\, s^{-1}\) strain rate corresponding with the minimum in the S–E loop. When the strain rate became positive, the material was expanding and reached a maximum rate at point 3 (130 kV/cm), where the most domains were switching from approximately perpendicular to parallel to the electric field. The strain rate then decreased to near \(0\%\, s^{-1}\) at the maximum electric field (point 4). After maximum electric field strain loops exhibited minor strain recovery from 0.02% to zero during which time the strain rate first went slightly negative, suggestive of back switching but was then effectively \(0\%\, s^{-1}\) until point 5 at 0 kV/cm. This near \(0\%\, s^{-1}\) strain rate signified that very little back switching of domains occurred until the electric field direction was reversed. Due to the high degree of symmetry in the loop, the behavior described between points 1 and 5 is also reflected by the loop between points 5 and 9 in Fig. 2(i).

Two notable observations were made in the strain rate hysteresis as a function of field amplitude. First, for field amplitudes between 100 and 170 kV/cm the strain rate intensity increased, indicating that an increasing portion of ferroelastic domains was being switched with each successive field increase. Second, at field amplitudes from \(\geq 170\), the strain rate peaks remained at approximately the same electric field position (130 kV/cm) and the intensities decreased. This indicated that the bulk of ferroelastic domains switched at 130 kV/cm, but that less domains switched at that field as the amplitude was increased. As the \(S_{pp}\) \(\geq 170\) kV/cm was constant [Fig. 2(f)], the conclusion is that approximately the same total number of ferroelastic domains must switch but distributed over fields between 170 and 260 kV/cm. Such a distribution of switching must result from the rate of electric field increase, which increased with field amplitude, thus revealing a kinetic limit to ferroelastic domain switching.

The hysteresis behavior at a field amplitude of 200 kV/cm observed at field frequencies between 1 and 100 Hz provided further insight into the switching kinetics (Fig. 3). The leakage current contribution to P–E hysteresis increased almost exponentially as the frequency decreased [Fig. 3(a)], and the \(E_r\) decreased markedly [Fig. 3(b)]. The \(E_r\) reduction was also seen in the S–E hysteresis loops, but most notable was the asymmetry in the S–E loop at 100 Hz which indicated incomplete domain switching [Fig. 3(c)]. This indication of incomplete switching at 100 Hz correlated well with the kinetic limit revealed by the strain rate analysis. Similarly prepared \([N(CH_3)_4][FeBrCl_3]\) followed domain growth limited-switching described by the Kolmogorov–Avrami–Ishibashi model and was heavily influenced by the presence of charge defect complexes that resulted in a reversible asymmetrical hysteresis at 100 Hz. Similarly, defect complexes are considered to play an important role here and evidence for this was also seen in the \(E_{bias}\) behavior.

The dielectric response of the material was studied as a function of direct current (DC) bias field to observe the dielectric properties and gain further insight into the domain switching. For these measurements, a small alternating current (AC) signal of 5 kV/cm and 1 kHz frequency was used to measure the dielectric permittivity (relative permittivity, \(\varepsilon_r\)) and loss, while a sample was subject to a direct current (DC) electric field bias. The bias was increased and decreased in increments first in the positive, and then negative field directions so that the data can be plotted as a permittivity hysteresis loop (Fig. 4). The cycle was repeated several times, increasing the maximum electric field by 10 kV/cm with each successive cycle, but the maximum DC bias field was limited to 120 kV/cm due to sample arcing. For DC bias fields up to 50 kV/cm, the \(\varepsilon_r\) vs DC bias field loop had a V-like shape and increased linearly from 16.9 at 0 kV/cm in both positive and negative field directions [Fig. 4(a)]. As the DC bias field was increased above 50 kV/cm, peaks in \(\varepsilon_r\), occurring below the maximum DC bias field emerged. The intensity of \(\varepsilon_r\) peaks increased as the maximum DC bias field was increased, likely arise from coincidental switching of ferroelectric (180°) and ferroelastic (non-180°) domains, analogously with metal oxide ferroelectrics such as PZT. This \(\varepsilon_r\) peak, while corresponding to domain switching, just like the \(E_r\) from the hysteresis

![Figure 3](image-url) Figure 3. Hysteresis loops with an electric field amplitude of 200 kV/cm and frequencies of 1, 3, 10, 30, and 100 Hz. (a) Polarization, arrows highlight increasing leakage contributions. (b) Current density, dashed lines mark \(E_{bias}\) at 1 and 100 Hz and arrows show the increase. (c) Strain, dashed lines mark \(E_{bias}\) at 1 and 100 Hz and arrow shows increase. Curved arrow highlights asymmetry at 100 Hz.

![Figure 4](image-url) Figure 4. (a) Relative permittivity and (b) loss tangent, as a function of DC electric field bias up to 120 kV/cm. Dashed lines mark the \(E_{bias}\) in the 120 kV/cm DC bias field cycle.
The mechanism for the underlying V-shape behavior observed in the $[\text{N(CH}_3\text{)}_4][\text{FeBrCl}_3]$ is unknown and warrants further investigation, but does bare some similarities with the dielectric response of the classic molecular piezoelectric material Rochelle salt. The corresponding loss tangents had a similar w i t h the electric response of the classical piezoelectric material. 

In total, the $\varepsilon_r$ varied between 16.9 and 17.5 for DC bias up to 120 kV/cm, revealing a low dielectric tunability of 0.035% or 3.5%. By comparison, commercial metal oxide ferroelectric PZT can show tunability of 0.68 over the same field range, thus the plastic crystals $[\text{N(CH}_3\text{)}_4][\text{FeBrCl}_3]$ seem to exhibit rather high dielectric stability as a function of electric field bias.21-23

Polycrystalline plastic crystal ferroelectric $[\text{N(CH}_3\text{)}_4][\text{FeBrCl}_3]$ was driven with bipolar electric field amplitudes up to 260 kV/cm, demonstrating a maximum peak-to-peak strain of 0.1%. The hysteresis behavior suggested that ferroelastic domain switching saturated at 170 kV/cm. However, at higher field amplitudes, the rate of electric field increase was too fast for domain switching to keep up, producing a ferroelastic domain switching lag that distributed the strain over higher fields and reduced the maximum strain rate. This kinetic limit of switching was confirmed by hysteresis measurements at 100 Hz that were asymmetric due to incomplete switching. High leakage currents were evident in the polarization and current density hysteresis and were thus expected to play a role in the switching behavior. The dielectric constant and loss tangents under DC bias also were expected to play a role in the switching behavior. The dielectric constant and loss tangents under DC bias after the maximum $\varepsilon_r$ is reached, due to reduced domain wall contributions and internal stress.24

The observed domain switching dynamics of $[\text{N(CH}_3\text{)}_4][\text{FeBrCl}_3]$ suggest that electric field conditions play an important role in the electromechanical response of these materials. Further detailed studies of additional plastic crystals are needed to reveal universal traits of their ferroelectricity as well as the key differences from metal oxides and will be beneficial to the development of the wider family of supramolecular ferroelectrics.

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DATA AVAILABILITY

The data that support the findings of this study are available within the article and upon request from the corresponding author.

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