This review summarizes dielectric studies and related experiments on ferroelectrics and multiferroics about which there has been considerable controversy in the literature, sometimes at unusually impolite and unprofessional levels. In addition it focuses attention on a new anomalous phenomenon – that of ferroelectric hysteresis loops P(E) that are parallelograms with straight sides. In some cases materials have been considered to be multiferroic when the data can be interpreted more simply via other well-known mechanisms. In some cases the systems truly are multiferroic, despite X-ray crystallographic data implying that this is not possible; some properties arise only from the domain walls. And in some cases authors get different results from previous work, simply because they used bulk ceramics instead of very thin films, or epitaxial films instead of randomly oriented ceramics; it is of course preferable if groups exchange specimens before they claim the work of others is simply wrong. Emphasis is on newly discovered lozenge-shaped hysteresis loops, whose parallelepiped geometries are found in four unrelated materials. This review has intentionally not discussed ferroelectric artifacts that appear in atomic force microscopy, since that is actually more extensive in variety and well reviewed this year by Kalinin’s group [1].

Introduction
There has been a rapid growth in the studies of ferroelectrics and especially multiferroics in the past decade. This has attracted many newcomers to the field, and it is important to give them a review which carefully discriminates between interesting new discoveries and artifacts. Many new materials have been found [2], but often the ferroelectricity is small, as measured by polarization (nC/cm² rather than μC/cm²) or of unusual “lozenge” or “hummingbird” shape, or the dielectric anomalies (isothermal electric susceptibilities) as a function of temperature ε’(T) are weak or very different from the expected Curie-Weiss behavior. These anomalies have often been reported by leading, highly experienced researchers, and so in specifying them in the present review we do not wish to suggest that they arise from naivete or carelessness. In fact it is specifically because the mistakes are often made by experts that new researchers from different backgrounds in solid state chemistry, magnetism, and materials science are warned.

A separate problem is that most researchers in this field no longer build their own test equipment. Commercial apparatus is of high quality in this field, but ferroelectric testers always assume that the specimen examined is a pure capacitance. As discussed in the standard text by Jonscher [3], this is never true. Unlike measurements of magnetization, polarization requires leads and electrodes, and since no sample has infinite resistivity, there is always some charge injection. Charge injection acts like an inductance, and so even the best parallel-plate capacitor structure will give an LCR circuit, which necessarily implies a magnetic field dependence.

Examples of a charge injection artifact in BiFeO₃ [4] are a close duplicate of the illustration of a “dead short” in the equipment instruction manual (last figure, p.37 of the instructions for the...
Radiant tester). Unfortunately, if you put a metal paper clip into such test equipment, you get a loop that looks like an American football, or a lemon lying on its side; and the software will label the height of this artifact as $P_r$, the remanent polarization, and the width of each side as $E_c$, the coercive field. It will also center the loop at $V = 0$, even if in reality there is a large asymmetric bias field.

In addition to these artifacts, there is the question of electrets [5–7]. Electrets exhibit extremely square hysteresis loops (Figure 1 below [8]), but they are not ferroelectrics. The switched charge $Q = 2PA$, where $A$ is the electrode area on one face, arises entirely from mobile charged impurities and defects (such as oxygen vacancies). Electrets differ from ferroelectrets in that the switched charge is generally smaller ($\text{nC/cm}^2$) and much slower (so that good loops are observed at 50–60 Hz but not 1–100 kHz). Additionally, they are not truly stable, typically relaxing back to their unpoled state in minutes or hours (although may persist for years in some polymer electrets). They are not always easy to discriminate from real ferroelectrics, because the hysteresis loops go with time in a counterclockwise path, like real ferroelectric hysteresis, and not clockwise like most charge injection. Carina wax and Teflon are classic electrets [5,7]. More recently electret effects involving small highly mobile interstitial Li-ions have been misinterpreted as true ferroelectricity in ZnO:Li [9–12], but whether these ZnO:X systems are truly ferroelectric is still moot. Such electret effects are of course not limited to oxide films: the new development of a PVDF (polyvinylidenefluoride) thin-film memory at Intel has been delayed by severe impractical problems which arise from electret effects. It took many years to show that PVDF is a ferroelectric and not an electret. The most recent example [14] of a square electret hysteresis is in an amorphous room-temperature material. However, the squareness of the observed loop leaves some question as to the nanocrystallinity of that sample, and it remains possible that YbCrO$_3$ has some ferroelectric qualities. Note that electrets need not be crystals! Good electret effects are shown recently for non-ferroelectric Al$_2$O$_3$ [15]. These authors found that the polarization state disappeared in 77 s, orders of magnitude shorter than in real ferroelectrics.

Several papers are already well known to alert readers to such artifacts: [6,16–20]. Readers are asked to keep in mind that “artifact” (or “artefact” in the UK) is a term like “weed” to gardeners: Neither has a precise definition and generally they refer to anything undesirable in the eye of the beholder. In this review we term “artifact” a phenomenon that arises from the choice of measuring apparatus. But we do not term leakage currents “artifacts” because, although their magnitude may depend upon electroding, they are intrinsic to the material and its finite conductivity. As a result, we expect bulk ceramic samples to have different ferroelectric properties from epitaxial thin films or single crystal specimens. In this sense it is probably not fair to say that a substance (formula) is ferroelectric or not, only that certain specimens are. Historically this perhaps first arose with the question of ferroelectricity in GeTe [21,22]. Since ferroelectricity is an empirical engineering definition (the sample must switch below break-down voltage) and not a symmetry property, GeTe “became ferroelectric” when it was first made in high-resistivity samples. We note that GeTe ferroelectricity remains an extremely subtle question [21–25].

Paradoxically and conversely, there are also a number of materials in which very suspicious ferroelectric properties are quite real, although nominally forbidden in bulk by symmetry. We shall see examples in the following sections in which these may arise, for example, at domain walls, including antiferromagnetic walls and/or ferroelastic twin walls, as first emphasized by Darakchiev et al. [25,26].

**The general case of transition or no transition: SrSnO$_3$ family**

As a kind of preface to the ferroelectric and multiferroic controversies discussed below, it is useful to examine a simpler question concerning the disagreement over whether a substance exhibits a phase transition or not. A recent example is afforded by ferroelastic SrSnO$_3$. Here a series of different measurements (Raman, specific heat, etc.) showed [27,28] that there were two phase transitions near 160 K and 260 K. These were confirmed by groups in Cambridge, Puerto Rico, and Korea [29]. A subsequent paper [30] claimed that there was no transition at 260 K and none at all near 160 K. This was based on the apparent lack of an $a$-axis anomaly in their neutron diffraction data at the supposed upper transition. We note parenthetically that there are phase transitions in other perovskite oxides [31] with no measurable lattice constant anomalies. This inconsistency may be attributed to sample differences between the powder specimens used by the authors of Ref. [30] and samples used in other studies from three different sources (Korea, Cambridge and Puerto Rico) – see [28,29].

A separate problem is that the reported series of phase transitions in [30] violate Glazer’s Rule in that an in-plane octahedron rotation transition in a perovskite cannot be order–disorder, since adjacent octahedral share oxygen ions.

![Figure 1](image)

**Figure 1**


(NbSe$_4$)$_3$I, CdCr$_2$S$_4$ and HgCr$_2$S$_4$: Magneto resistance misinterpreted as magnetoelectricity

Within a short period of time reports of magnetoelectric properties in three materials were presented in two very high-impact journals [32,33].
In (NbSe₄)₃I they found that below the structural phase transition close to 270 K, which is accompanied by complex charge-order processes, colossal dielectric constants (see Figure 2).

**CdCr₂S₄ and HgCr₂S₄**

The same group reported magnetoelectric-like properties in CdCr₂S₄ and HgCr₂S₄ [35]. However, these data were shown by Catalan and Scott [34,36] to arise possibly from Maxwell-Wagner effects, Figure 3.

Subsequent work [38] showed that the anomalies disappeared in samples subject to vacuum anneal. That study also showed that HgCr₂S₄ is definitely not multiferroic, but CdCr₂S₄ might be. The original authors later found [39] that their samples had anomalous dielectric properties with or without contamination with Cl; however, Cl presence strongly affected magnitudes. µSR does not confirm a ferroelectric transition [40]. See also the original study by Baltensperger [41].

**Lead zirconate-titanate/lead iron tungstate**

Beginning in 2008 the San Juan group headed by R. Katiyar [42–45] began a series of publications on PZT mixed with lead iron tungstate to produce a homogeneous single-phase room-temperature ferroelectric magnet. They also collaborated with Blinc and Pirč, to publish some theoretical models of the effects measured [46,47]. Soon after, however, it was suggested that this material was not multiferroic [48].

Very recently this complete discrepancy seems to have been resolved in favor of the San Juan group, with data from Seoul [49] showing unambiguous albeit weaker multiferroic properties at room temperature. However, Noh’s group found [49] a very much smaller (5% or less) – albeit nonzero – magnetoelectric coefficient than did Kumar et al. This is rather important because the original San Juan reports showed that a modest magnetic field of <1 Tesla was sufficient to shift the relaxor-type dielectric response to peak at much lower frequencies. The reason for this large effect of magnetic field on some samples but not others

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**FIGURE 2**


**FIGURE 3**

probably arises from inductance. Later unpublished work showed that this does not arise from connecting wires and test equipment, but it seems likely that it is due to inductance in the ceramic PZT-PFW samples in San Juan. Although this is in principle a simple parallel-plate capacitor, in fact it has significant leakage current, only slightly mitigated by electrode choice.

As Jonscher emphasizes [50] and Feynman elaborates upon [51], all dielectric capacitors have some nonzero inductance. Most of this arises from injected charge, which has a finite delay time from the applied voltage; hence, it acts as a phase lag or inductance in the equivalent circuit. In the presence of an applied magnetic field, this inductance decreases the resonant frequency. As proof of this, close inspection of Kumar’s original figure (below) shows that the dielectric constant actually decreases to zero at a specific frequency, indicating an LCR circuit (pure RC-circuits do not exhibit zero permittivity).

PFTW-PZT has a very nonlinear magnetization. When it is put into a circuit to measure susceptibilities (electrical or magnetic) and the circuit is subject to an external magnetic field, the magnetization M changes with field; the system acts like a nonlinear transformer with a magnetic core.

To convert the measured magnetization M(H) to an inductance in an LC or LCR circuit at very low fields H, the relationship \( \mu H = B + \mu_0 M \) is normally used together with

\[
L = (N^2 A/\lambda) \frac{d|B|}{dH}\text{(average)}
\]  

for an ordinary magnetic iron-core solenoid transformer, where the symbols have their usual definitions (N turns of area A and total length \( \lambda \)); however, at high magnetic fields (0.70–0.85 T in the present case), dB/dH(average) must be replaced by the slope dB/dH at the applied field H. This is called the incremental permeability \( \mu'(\text{inc}) \) and can be several orders of magnitude larger than the ordinary (average) permeability, especially near the coercive field. (Figures 7–47 of Ref. [53]) Since the resonance frequency \( f \) varies as (LC)\(^{-1/2} \), this produces a large decrease (factor of order \( \times100 \)) in \( f \), as observed in Figure 4 below.

\[
\lim_{H \to H_c} f = (\text{DM/dH})^{-1/2} = 0.
\]

This analysis is quantitative, because the LC-resonant frequency \( f \) in Figure 4 occurs for \( H \) slightly >0.85 Tesla, whereas the critical field \( H_c \) in this family of multiferroics is known to be slightly less than 1.0 Tesla (switching was observed with a 1.0 T bar-magnet) Refs. [54,55].

This is not an artifact, in the sense that it is not due to the equipment used. However, it is not a property of all samples, and it is not a “magneto-electric” effect; rather, it is a “magneto-inductive Maxwell-Wagner effect.” It can nevertheless, if reproducible, be used for tunable devices [52,53].

**SmFeO\(_3\) family**

Samarium orthoferrite is a paradigm of the large orthoferrite family of magnetic materials. It has space group symmetry Pbnm which does not permit ferroelectricity [56]. Nevertheless, Lee et al. found ferroelectricity in it and interpreted that as due to spin-canting [57]. Their conclusion regarding the algebraic form of coupling was quickly dismissed by a group at Oxford [58] as incompatible with symmetry requirements. In reply, the Pohang group agreed with the Oxford theoretical criticism but reasserted the correctness of the experimental data [59].

But to add to the skepticism, an experimental group failed to find any ferroelectricity in their samples, using the ALBA synchrotron TLS beamline 08B1 [60]. However, more recently the theory group of Bellaiche in Arkansas [61] showed unambiguously that SmFeO\(_3\) is indeed multiferroic, but that this arises from the ferroelectricity at the antiferromagnetic domain boundaries, and that multidomains with even number of layers possess an electric polarization aligned along \( b \)-axis and multiferroic Pmc\(_2\) ground state [61]. This polarization is of the improper type, and originates from an exchange striction mechanism that drives a polar displacement of the oxygen ions located at the magnetic domain walls. [Note that the synchrotron study [60] does not permit detection of polarizations that arise from domain walls; it measures only structures within domains.] And experimentally, Su et al. showed that the magnitude of the dielectric anomalies depends upon sample dimensions [62].

Most recently, in agreement with the initial report by Jang’s group, SmFeO\(_3\) is indeed multiferroic experimentally [63]. Sahoo et al. found that the temperature dependence of the observed dielectric peaks corresponds to two distinct phase transitions——
one electric and the other magnetic. The value of the magneto-electric voltage-coupling coefficient $\alpha$ of their SmFeO$_3$ ceramics was found to be 2.2 mV cm$^{-1}$ Oe$^{-1}$.

This was also confirmed by [64]; see also W.-Z. Si et al. [65], whose ferroelectric hysteresis loops are illustrated below:

They find ferroelectricity up to $T_C = 480$ K, close to the spin reorientation temperature at $460$ K, with polarization $P = 2 \mu$C/cm$^2$ and no leakage current, and magnetism up to $T_N = 655$ K, and hence multiferroic behavior at room temperature. They conclude that the space group has lowered from centric Pbnm to ferroelectric Pna$_2$1 (a different labeling from the Pmc$_2$1 of Yang et al. above).

However, work in Australia [66] indicates that the multiferroic behavior is biggest in epitaxial thin films and hence presumably arises at least in part from strain. This has been confirmed very recently [67] by S. Chaturvedi et al. who studied size effects from 55 to 500 nm crystallites. Another Chinese group has shown that TbFeO$_3$ is also multiferroic at room temperature [68].

The conclusion in the present review is that, despite the synchrotron study, the theoretical work by Bellaiche’s group is convincing and that SmFeO$_3$ and other orthoferrites are indeed multiferroic at room temperature, but only by virtue of their domain walls. Hence, it is not an artifact but neither is it a bulk property. In retrospect, this probably should have been obvious from the work of Tokura’s group on GdFeO$_3$ [69].

Very recently Garg and Bhattacharya from India have found ferroelectric polarization at the magnetic transition in LuFeO$_3$, Figure 5b [70]. This probably arises from the same magnetic domain wall mechanism as described above by Y. Yang et al. for SmFeO$_3$.

In addition to having ferroelectricity at magnetic domain walls, it is well established that ferroelectricity occurs at ferroelastic twin walls. This was best shown by the Cambridge group for CaTiO$_3$ [71]. Most recently it has apparently also been observed in Pb-halide perovskites at their cubic-tetragonal ferroelastic phase transitions.

Hummingbird hysteresis loops: tris-sarcosine calcium chloride (TSCC)

Figure 6 shows the polarization-electric field hysteresis loop obtained from an undoped tris-sarcosine calcium chloride (TSCC) crystal. Such loops with a “hummingbird” shape were measured along the b-axis from $T_C$ (c.a. 130 K) down to approximately 48 K (the lowest temperature attainable by the sample environment). As is typical of TSCC [72], the loop is highly biased, resulting in an offset in the electric field axis. Additionally, TSCC displays switching in only one polarity. The software of some commercial P-E hysteresis testers balances the measured change in polarization so that the loop is re-centered with respect to the ordinate axis. In Figure 6 this would have the effect of displacing the loop vertically as with the loops in Ref. [72].

The origin of this loop morphology is unclear; reports of similar “triple” hysteresis loops near phase transitions, including in compounds which have been suggested to be ferrielectric [73,74], are typically only observed over narrow temperature ranges close to phase transitions.

Ferroelastic loops of this shape also exist as shown in Figure 7 – see [75,76] for further details. This loop additionally displays jumps which have been attributed to an effect which is the...
elastin analogy of Barkhausen pulses observed in ferroelectric switching [76].

**Negative differential resistivity**

Negative differential resistivity is an older problem that is still debated. In materials such as BST or PZT sometimes the current I(V) saturates at high voltage, and sometimes it actually decreases. [Figure 8 below.]

This was first observed in ferroelectric BST thin films by Melnick et al. [77] and later by Dawber et al. [78]. It is important to note that these sol–gel spin-on films were not extremely pure and had defect densities that produced rather fast dielectric relaxation (seconds). Later a multi-group effort over several years at North Carolina State, IMEC in Belgium, Phillips in Eindhoven, and especially Aachen produced higher purity epitaxial films with much longer relaxation times.

The resulting controversy lingers on. The higher-purity films exhibit such long relaxation times that the dielectric response is still relaxing while additional data are taken. This can be hours and causes the current J(V) to decrease as data are taken (always with increasing voltage). Waser’s group designed equipment to eliminate this artifact [79].

However, it is easily demonstrated that this is not the source of decreasing J(V) in the earlier data from Melnick or from Dawber, because data were taken for both increasing and decreasing V, and they were nearly the same, showing clearly that the J(V) values were in quasistatic equilibrium. The quantitative analyses by Sigov’s group yield a very small depletion width w = 7–9 nm, a donor concentration of ND = (5.1 ± 0.1) × 10¹⁹ cm⁻³, compatible with independent experimental measurements, and a modification of the original Dawber–Scott equation for current density J versus applied electric field $E$

$$J/E = (σ/d)Eexp[-cE^2]$$

(3)

to

$$J/E = (σ/d)Eexp[-c(E - E_0)^2] + b(E - E_0)^n,$$

(4)

where n is the exponent for space-charge-limited current in a particular field regime (n = 2 or 3) and Eo is an additional threshold parameter that is measured independently at the field at which the space charge limited current J/E changes from quadratic to cubic. Eq. (4) fits all data to a correlation coefficient of 0.97 and yields a region of negative differential resistivity in PZT of 50–60 kV/cm. The depletion width of w = 7–9 nm agrees with the value w < 10 nm from Scott [81] and disagrees qualitatively with that from Dietz et al. (Ref. [69]) that w > 200 nm (fully depleted).

Thus it would appear in hindsight that both groups were correct, and it is unfortunate that commercial financial issues prevented a simple exchange of samples. The verdict in hindsight is that negative differential resistivity probably does occur, but readers should view the recent review on this topic by Li et al. [20] as well as the detailed simulation models of Sigov’s group [80,82]. The latter derive realistic donor/acceptor concentrations from their model (see Figure 8).

**Lozenge-shaped hysteresis**

The most probable explanation of these lozenge-shaped polarization curves with rounded corners and no sharp points near the saturation values, Figure 9, has been given by Su et al. [83] who found that frequency dependence of ferroelectric hysteresis is a result of direct competition between the speed of polarization switching and the speed of the voltage ramp rate employed. A similar dependence was first reported by Poul Larsen et al. at Eindhoven many years ago [85], and is known to be due to a current-limited (source-limited) voltage source for fast switching. The calculated low-frequency phenomena of Su and Liu are widely supported by old experiments, but the high-frequency ones were not commonly found in the literature until the present review. Their new physics clearly shows a complete 180° polarization reversal at low frequencies, but switching stopping mostly at 90° at high frequencies. We believe that the dominance of 90-degree switching helps explain the straight, slanted sides on our lozenge hysteresis loops, since that is what one
always finds in stress/strain hysteresis and/or ferroelastics (which involve 90-degree domains).

In order to show clearly the origin of lozenge-shaped ferroelectric hysteresis loops, we show three cases in Figure 10 of hysteresis in the same PMN-PT (lead magnesium niobate-lead titanate) sample under different conditions detailed in the figure caption. These show that the lozenge shapes are just a case of unsaturated switching. However, the lack of saturation does not always come from too small an applied voltage: Especially in materials with large polarization, such as ultra-tetragonal PbTiO$_3$, it can arise from a current-limited power supply or too slow a ramp rate. In this case the induced polarization relaxes away before the film is completely saturated. This current-limited case was first demonstrated in PZT by Poul Larsen [86]. Figure 10(b) (right hand panel) shows that a fully saturated loop with sharp corners can be restored.

**Misleading faceting symmetry**

Another possible source of misinterpretation is not a true artifact, but the fact that nanocrystals and microcrystals can display an apparent symmetry that is different from the true crystallographic symmetry, as shown experimentally in Figure 11 above [88] and theoretically in Figure 12(a) and (b) below [89]. These facets arise as the domains eject accumulated space charge. Lukyanchuk et al. [90] show with a very quantitative model how polygonal domain structures with $n = 3, 4, 5, 6$ sides can appear. This is a case where good TEM microscopy can actually mislead researchers.

A full theory explaining how low-symmetry crystals can form high-symmetry domains is given by Lukyanchuk I, Sharma P, Nakajima T, Okamura S, Scott J F, Gruverman A, High-Symmetry Polarization Domains in Low-Symmetry Ferroelectrics, Nano Lett. 14, 6931–6935 (2014) [90]. Table 1 illustrates additional geometrical requirements to make multiferroics magnetoelectric [87].

**Ghost domains**

The coupling between ferroelasticity and ferroelectricity can be very subtle and lead to confusions of interpretation. This is best illustrated in the tetragonal tungsten bronzes. There are three qualitatively different possibilities: first, the ferroelasticity and ferroelectricity can be completely separate and independent. An example is Ba$_2$NaNb$_5$O$_{15}$, which has two separate transitions (complicated further by incommensurate modulations), from ferroelectric-ferroelastic mm$^2$ to ferroelectric-paraelastic 4mm to paraelectric-paraelastic 4/mmm. The crystal has four stable states, two polarization states (along the $b$-axis) and two strain states. However the application of either stress or electric field changes the magnitude of size or polarization but does not couple ferroelectricity and ferroelasticity [91]. Second, the opposite case of strong coupling: K$_3$Fe$_5$F$_{18}$ [92]. Here there is an orthorhombic distortion that has two polarization states and two strain states. But unlike barium sodium niobate, in this case the inversion of the strain states along the $x$-axis and the $y$-axis necessarily causes an inversion of the polarization along $z$. Hence the ferroelectric and ferroelastic transitions occur simultaneously – they are locked together – and a single symmetry
change mm2 to 4/mmm occurs, with the intermediate 4mm phase completely gone! In a different context, Janovec [93] has referred to such missing states as “ghost phases” and points out that domains and domain walls can indeed exist that mimic the structures expected for this pseudo-phases, even when conventional crystallography does not reveal them as stable bulk phases. In this sense domain walls can provide new information, independent of bulk characterizations, a point not often recognized [93].

This comparison illustrates the complexity of ferroelastic-ferroelectric transitions very clearly. A third, intermediate case also exists: In Pb2KNb5O15 the ferroelasticity and ferroelectricity are only weakly coupled, and there is a single phase transition. The coupling strength is sufficient to lock the ferroelastic and ferroelectric distortions together. It would be an interesting yet unsolved theoretical problem to calculate the threshold coupling constant to lock strain and polarization together in these materials; will any nonzero value suffice?

Thus we see that a knowledge of group-subgroup relations is insufficient to sort out ferroelectric-ferroelastic phases, and intermediate phases (which might be narrow in temperature or occur only in some samples due to off-stoichiometry or strain) need not be artifacts. For example, if new work should discover an intermediate 4 mm phase in some K3Fe5F15 specimens, it might not be a complete surprise. Work by Reisinger et al. already shows that how’s that the phases separate in K2.90Fe5F15 [94].

A full DFT theory of K3Fe5F15 has been given by Piccozzi, [95] and the effects of substitution by Morrison et al. and by Blinc’s
**TABLE 1**

<table>
<thead>
<tr>
<th>Geometrical requirements of magnetoelastics (after [87]).</th>
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<td>Magnetic point group</td>
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<td>3. 3m', 4. 4m', 6. 6m'</td>
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* Table 1 reveals some subtleties in multiferroics that can alert researchers to possible artifacts. In particular, magnetoelasticity is strictly forbidden in crystals with symmetry 2 or m|2, because polarization P must be parallel to magnetization M, with both along the twofold axis. This is the case in BaCoF, which is a ferromagnetic and ferroelectric, but not magnetoelectric. Consequently, a report of a magnetoelastic coupling in BaCoF would be regarded with suspicion. In contrast, BaMnF or BaNiF are magnetoelectric. The other constraints shown in Table 1 alert us to the fact that there are additional symmetry requirements for multiferroics to be magnetoelectric, and these are not always satisfied, differing even among materials with the same crystallographic (nonmagnetic) space group symmetry. In BaMnF, the addition of even 2% Cu substitutional for Mn is sufficient to cause spin-flop and make the magnetoelasticity disappear.

**Atomic/piezoforce microscopy**

Observation of domains using atomic/piezoforce microscopy (AFM/PM) has led to greater study of domains and domain wall behavior, however, artifacts arising from the use such techniques has been intentionally omitted, since they are actually more extensive in variety and well reviewed this year by Kalinin's group [1].

**Acknowledgements**

We thank C. D. Tan for assistance in obtaining the hysteresis data shown in Fig. 10 and Prof. Dwight Viehland of Virginia tech for the PMN sample used.

**Appendix A. Supplementary data**

Supplementary data associated with this article can be found, in the online version, at https://doi.org/10.1016/j.mattod.2017.12.003.

**References**