Review Article
Prospects for Ferroelectrics: 2012–2022

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A review is given of more than a dozen subtopics within the general study of ferroelectrics, with emphasis upon controversies, unsolved problems, and prospects for the next decade, including pure science and industrial applications. The review emphasizes work over the past two years, from 2010 to 2012.

1. Introduction

Ferroelectrics have undergone a minor renaissance in the past twenty years with the development of high-quality thin (<300 nm) oxide films, capable of performing switching at the 5 V standard logic level for silicon transistors [1, 2]. The general field of integrated ferroelectrics is not limited to memory devices entailing polarization reversal but includes such things as electrically controlled tunnel junctions, [3, 4] which are much more demanding in their thickness requirements (<7 nm), or electrocaloric cooling devices [5, 6], THz emitters [7, 8], resistive random access memories (RRAMS) [9, 10], photochromics [11], domain nanoelectronics [12, 13], flexible polymeric ferroelectrics [14, 15], and photovoltaics [16, 17]. At present there are perhaps 500 laboratories worldwide with R and D interests in ferroelectric films, and the present review is a rather personal viewpoint of what the most promising lines of investigation will be over the next decade.

2. Mott Field Effect Transistors (MOTTFETs) and Ferroelectric-Gated FETs

In a typical computer memory the area of the chip is taken up primarily by the capacitors. Historically the capacitance was provided by a very thin silicon-oxide layer grown by exposing the Si chip to oxygen during processing. However, silicon oxide (mostly quartz) has a rather small dielectric constant (ca. 6.0), and hence the capacitance is small even for very thin films. Even using a high-dielectric material (most of which are ferroelectric oxides), the capacitors in a memory

take up most of the chip area; in the jargon of the trade, the capacitors leave a large footprint [1]. A possible solution to this problem is to make the active memory element a programmable gate. For example, a ferroelectric gate (FE-FET) can exhibit a very small footprint [18, 19]. Although such FE-FETs have been actively researched for a decade or more, with noticeable progress in Tokyo, their defect is that the gate must be grounded during the READ operation, so that the gate charge is eventually dissipated. This problem can be circumvented by designing logic cells that are large (six transistors per bit—a so-called "6T" design) but have not been commercialized.

A promising new direction in this area is to use the FET gate in materials such as rare earth nickelates [20, 21]. These materials exhibit a phase transition from semiconducting to metallic as a function of temperature or applied electric field. Hence they can be used as a bistable memory element in the gate of an FET. Their problems are primarily related to optimizing growth; no one has reported a commercially viable CVD (chemical vapor deposition) process, for example; Figure 1.

Prospects for the next decade are very high, due to the breakthrough (Zubko et al.) in achieving a Mott transition with applied voltage and not just with temperature change.

3. Multiferroics and Magnetoelectrics

3.1. Introduction and Oxides. There are several hundred compounds that exhibit magnetic ordering and ferroelectricity (multiferroics) at the same time [22, 23]. Although most
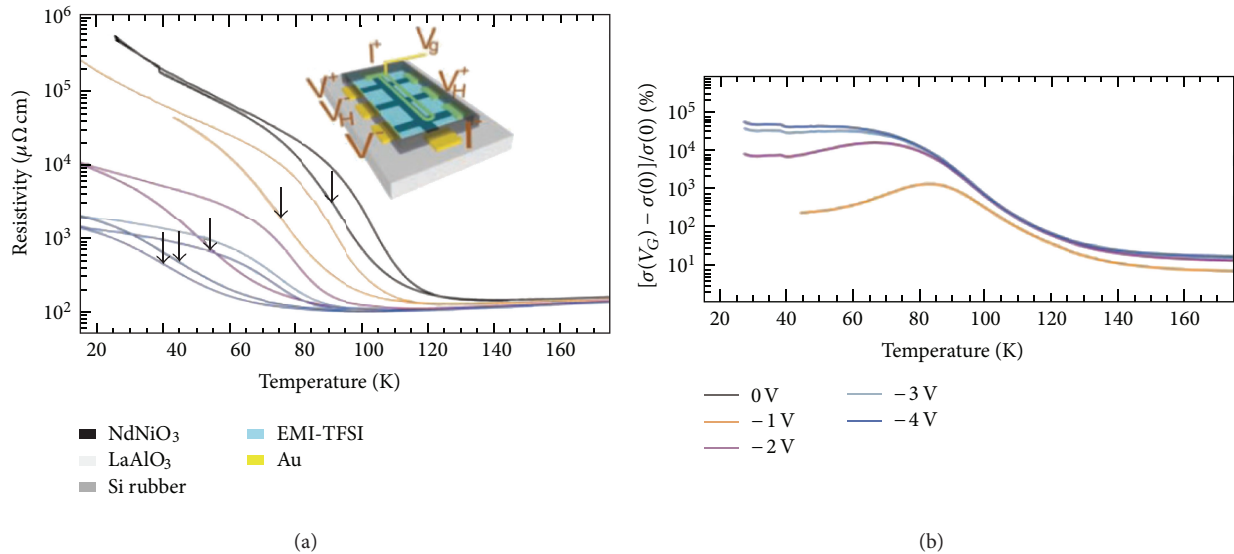
(a)

(b)

FIGURE 1: Electric Field Control of the Metal-Insulator Transition in Ultrathin NdNiO$_3$ Films [20]. (Inset): schematic of the MIT-FET or Metal-Insulator Transition Field Effect Transistor. In this example, the gate is an ionic liquid, capable of providing more surface charge than conventional solid state dielectrics. The channel is NdNiO$_3$, a perovskite with a first metal-insulator transition. (a) The electric field suppresses the metal insulator transition—notice the gradual lowering of the MI temperature as voltage is increased—causing orders of magnitude change in the conductivity: up to 100000% electroconductivity was measured (b).

of these are oxides, there are many fluorides, oxyfluorides, chlorides, phosphates, and so forth. Rather rare, however, are those which exhibit magnetization and spontaneous polarization at room temperature or above. The most studied of these is bismuth ferrite (BiFeO$_3$), discovered by Smolensky's group in 1959 [24–26]. Very recently two other materials have been observed to be multiferroic at or near room temperature—copper oxide [27] and a double-perovskite oxide [28]. However, these have extremely small switched polarization (nC/cm^2 rather than μC/cm^2) and hence offer a more limited range of potential applications.

A different family of multiferroic is exemplified by PbFe$_{1/2}$Ta$_{1/2}$O$_3$ [29] and PbFe$_{1/2}$Nb$_{1/2}$O$_3$ [30]. When mixed with PZT—PbZr$_{1-x}$Ti$_x$O$_3$—it produces a wide range of single-phase compounds with quaternary occupation at the B-site. For 60–70% PZT these materials are multiferroic (ferromagnetic) up to ca. 100°C, due to Fe clustering, although the long-range magnetic ordering is antiferromagnetic and sets in at ca. 50 K [31, 32].

Magnetoelectricity is a linear combination of polarization P and magnetization M in the free energy of a crystal, with a coupling coefficient α_{ij}. Multiferroicity is neither necessary nor sufficient for magnetoelectricity: Cr$_2$O$_3$ is neither ferromagnetic nor ferroelectric, but bilinear antiferroic coupling is allowed. For BaCoF$_4$ linear coupling is forbidden in its crystal structure since P and M are parallel, and yet α_{ij} has no diagonal terms for this lattice symmetry.

The related compounds of PbFe$_{2/3}$W$_{1/3}$O$_3$-PZT are also multiferroic at temperatures near ambient, but their magnetoelectric coupling is not bilinear; since both the cluster ferromagnetism and the spontaneous polarization are only short range, it is biquadratic through strain via magnetostriction and electrostriction [33, 34].

3.2. Ferromagnetic Ferroelectric Fluorides.
Most work on ferroelectrics is on oxides, because these are easy to grow, and there is a long history of ceramic devices driving the science and funding. More recently experts on oxides from the high-T_c superconductivity community and/or magnetism have also gravitated to oxide ferroelectrics in the search for increased funding. However, ferroelectrics and multiferroics include numerous families of fluorides, chlorides, and phosphates.

Soon after their experimental proof [35, 36] of linear magnetoelectric coupling in Cr$_2$O$_3$, Astrov et al. made related measurements [37–41] in BaMnF$_4$ and BaCoF$_4$. But these results differed qualitatively from those in chromia: the BaMF$_4$ effect is a frequency-dependent ac response, not a dc electrostatic response. In fact these data have never been explained, although the role of domain walls has been suggested. A detailed frequency dependent bulk response was calculated for this family of multiferroic by Tilley and Scott [42], but that did not include domain walls and does not correspond closely to the data of Astrov et al. [37–41]. The structure of these compounds consists of MF$_6$ octahedra linked at corners (Figure 2) and forming zig zag chains [42, 43]. Note that the magnetic Mn (Ni or Co or Fe) ions do not move in the ferroelectric soft-mode eigenvector, rather the motion consists of Ba-ion displacements coupled to nearly rigid rotation of MF$_6$ octahedra. This makes it less than obvious why there should be strong coupling between polarization P and magnetization M. That understanding required a more detailed recent ab initio model [44, 45]. The basic mechanism is that of Dzyaloshinskii-Moriya anisotropic exchange, but the models and experiments are both subtle. In 1975 Venturini and Morgenthaler at MIT showed [46] that BaMnF$_4$ has weak ferromagnetism (3 mrad canting angle), and that the
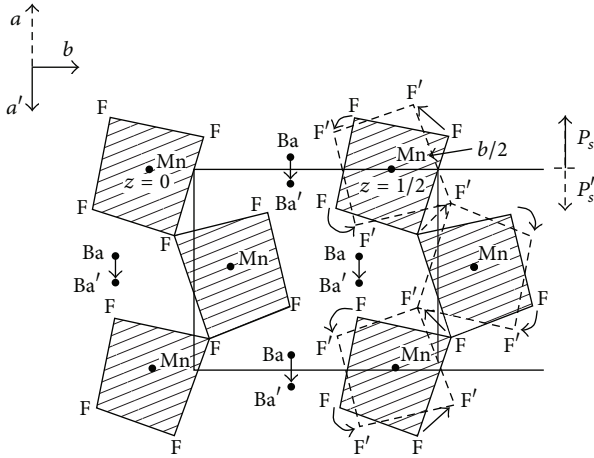
FIGURE 2: Structure of BaMnF$_4$.

○ Decreasing T
● Increasing T

FIGURE 3: Dielectric anomaly at T (Neel) in BaMnF$_4$ [56].

axis of sublattice magnetization is also tilted (9 degrees of the b-axis), but both of these results remained controversial, with both Kizhaev and Prozorova in Leningrad and Moscow, respectively [47–49] finding no ferromagnetism, presumably due to the spatial averaging of domains in their specimens. However, recently another Russian work [50] confirmed the data of Venturini, including the 9-degree tilt.

It is especially puzzling that BaMnF$_4$ and BaCoF$_4$ exhibit similar magnetoelectric data [37–41], because as shown in Table 1 [51, 52] and the more detailed model of Fox et al. [53], the Mn compound manifests ferroelectrically-induced (weak) ferromagnetism [54], whereas the Co isomorph cannot, since its spins and polarization are collinear, yielding magnetic point group $2'$ rather than 2, as in BaMnF$_4$. Moreover, BaMnF$_4$ is incommensurately modulated, whereas BaCoF$_4$ is not.

Other magnetoelectric effects in BaMnF$_4$ arising from coupling of polarization P and magnetization M are the dielectric anomalies illustrated in Figures 3 and 4. The anomaly shown in Figure 3 is the dielectric susceptibility along the polar a-axis. This change in dielectric constant $\varepsilon(T)$ near $T_N = 29$ K is small (<1%), negative, and proportional [55, 56] to the sublattice magnetization squared $M^2(T)$, in accord with the general theory of Gehring [57]. All of these characteristics are expected for intrinsic effects, whereas extrinsic Maxwell-Wagner space charge effects are usually much larger, often positive, and not proportional to any power of $M(T)$ [58–60]. Although these interpretations have remained contentious [61–66], recent studies discriminate carefully between intrinsic and extrinsic effects [58, 67, 68]. Note that an earlier theory by Albuquerque and Tilley [69] incorrectly predicted that the change in $\varepsilon(T)$ near T_N must be positive definite. This was due to neglect of higher-order terms in the free energy they used; these terms are necessarily positive definite and can be larger than the lowest-order negative term. A very similar model was independently published by Glass et al. [70] and by Negran [71] to fit data on BaNiF$_4$. However, a more comprehensive model was detailed by Fox et al., [53] which explains the magnitude,
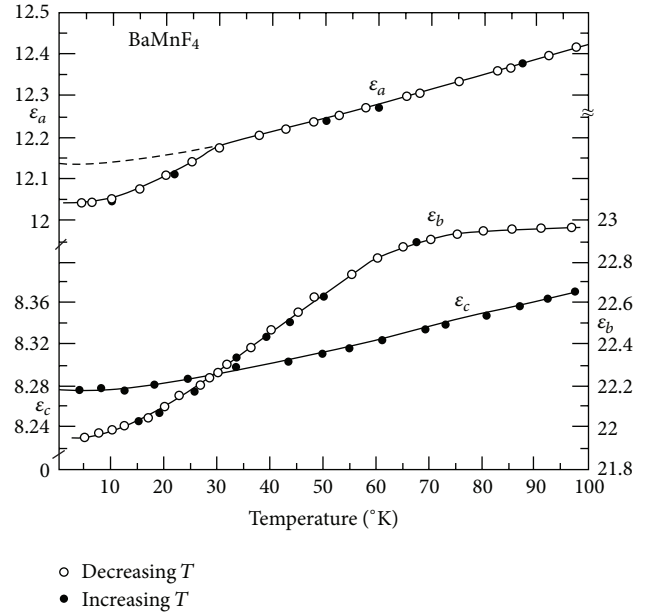
temperature dependence, and rather importantly, the signs of the dielectric constant changes at both T_N in BaMF$_4$ and also at T_{2D} (the higher temperature ca. 90 K at which the spins order in-plane. The latter is a larger magnetoelectric effect on the nonpolar b-axis electric susceptibility; this occurs at approximately $3T_N$, where the magnetic spins order in-plane in two dimensions, and is proportional to the magnetic energy. This is an early study of magnetoelectric effects well above the temperature of long-range (3D) ordering, and recently we see something similar (discussed in the following sections) for PbFe$_{1/2}$Ta$_{1/2}$O$_3$ compounds, where $T_N =$ ca. 150 K, but magnetoelectric effects persist up to ca. 400 K due to short-range spin ordering (clustering).

The dielectric data discussed above that are shown in Figure 4 are for the magnetic b-axis in BaMnF$_4$. Here the anomaly is larger, still negative, and goes well above $T_N = 29$ K. It is maximal near 90 K, which the temperature at which magnetic in-plane ordering sets in Zorin et al. [39, 41]. It arises from the linear-quadratic term in the free energy $\langle P_i M_j M_k \rangle$, which is nonzero well above T_N in any antiferromagnet, since $\langle M^2 \rangle > 0$, but is very large (nearly equal to $\langle M \rangle^2$ in-plane) in any magnet that orders in two dimensions.

This is a particularly fine example of the linear-quadratic magnetoelectric coupling first discovered by Hou and Bloembergen [72] because it permits very quantitative analysis of $\langle M^2 \rangle$ in-plane. This quadratic magnetoelectric effect is also strong in BaMnF$_4$ [73, 74].

Ferroelectrically-induced ferromagnetism: in 1979 Scott showed [52] that it is plausible that the weak ferromagnetism in BaMnF$_4$ measured by Venturini and Morgenthaler [46] arises from the ferroelectricity. The key term in the free energy developed explicitly by that group [51] is of form

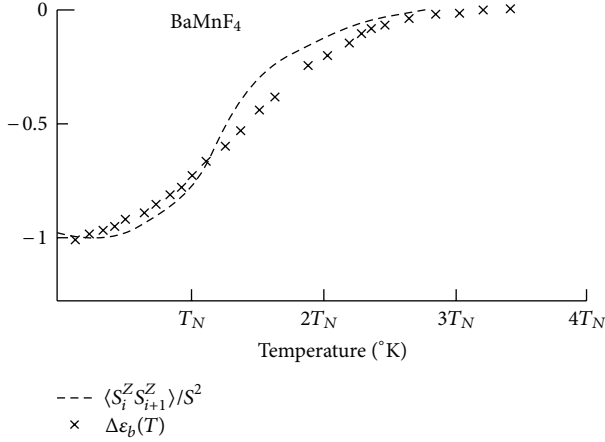$$G(P, M, L, T) = b_1 P(T) \cdot (M \times L), \qquad (1)$$

FIGURE 4: Dielectric anomaly at the temperature at which in-plane magnetic ordering sets in for BaMnF$_4$ [56].

TABLE 1: Requirements for ferroelectrically-induced ferromagnetism (after Birss [51]); see also Ederer and Fennie [78].

Magnetic point group symmetry	Relationship required between P and M	Spin canting via ferroelectricity
1	None	Allowed
m'	P parallel m'; M parallel m'	Allowed
m	P parallel m; M perpendicular m	Allowed
$2'$	P perpendicular M; P parallel $2'$	Allowed
$m'm2'$	P parallel $2'$; M perpendicular m	Allowed
2 or $m'm'2$	P parallel M parallel 2	Forbidden
3 or $3m'$ or 4; $4m'm'$ or 6 or $6m'm'$	P parallel M parallel principal axis	Forbidden

where P is the polarization; L is the sublattice magnetization; and M is the weak ferromagnetic moment. b_1 is a Dzyaloshinskii-Moriya anisotropic exchange term; it signifies physically that the ferroelectric displacement of the magnetic ion will modify the quantum mechanical exchange in particular directions. More recently Perez-Mato [75] and Benedek and Fennie [76] have independently shown that an interaction of this algebraic form is generic and is required for ferroelectrically-induced ferromagnetism in all crystals, and not just the BaMF$_4$ family. Fennie and Benedek have extended the treatment of such trilinear coupling to ferroelectrics in which all three parameters X, Y, and P are structural (nonmagnetic), so that polarization P arises from coupling of form PXY rather than PLM. We can see from (1) why such a ferroelectric canting of spins is favored in BaMnF$_4$, since P is along the a-axis; L is along the b-axis; and M is along c. However, in BaCoF$_4$, P and L are both along the a-axis, and this spin flop makes the interaction term vanish. The space group requirements for ferroelectrically induced (weak, canted) ferromagnetism are given in Table 1, from Scott [52], based upon the original theory of Birss [51].

Using the definition of the magnetoelectric tensor a'_{ij}, Fox and Scott write

$$M_c = 4\pi a'_{ac} P_a \qquad (2)$$

for the magnetization along the c-axis. But by the usual model of spins with spin $S = 5/2$ for Mn^{+2} and g approximately 2.0, with $N = 1.1 \times 10^{22}$ cm^{-3} [77] and $P = 11.5\ \mu$C/cm^2 [77], we can also express M_c as

$$M_c = \mu_B g N S \sin\phi, \qquad (3)$$

where ϕ is the canting angle of the spins. Solving (2) and (3) together for ϕ, using the known values of off-diagonal a' magnetoelectric tensor components for other Mn^{+2} systems, Venturini and Morgenthaler estimated ϕ as 2.1 ± 1.0 mrad, in good agreement with the measured value of 3.0 mrad [46].

In addition to explaining the induced ferromagnetism, a magnetoelectric theory of BaMnF$_4$ should be able to explain the dielectric anomalies. The assumed free energy of Fox et al. was

$$
\begin{aligned}
G(P, M, L) ={}& \frac{1}{2}AL^2 - \frac{1}{2}aL_z^2 + \left(\frac{1}{4}\right)B'L^4 \\
&+ \frac{1}{2}BM^2 + \left(b_0 + b_1 p + b_2 p^2\right)M_x L_z \\
&- \gamma M_z L_x + \frac{1}{2}D(L \cdot M)^2 \\
&+ \varepsilon p^2 - P \cdot E - M \cdot H,
\end{aligned}
\qquad (4)
$$

where P (total) $= P_r + p$; P_r is the remnant polarization; and p is the part of the polarization induced by applied magnetic field H.

Note that this is a mean-field (Landau) theory; this is quite allowed for weak ferromagnets, because the order parameter (the canting) is small at all temperatures. Single-ion anisotropy (originally favored by Rado in some materials) has been ignored. More importantly, no electrostriction or magnetostriction has been included; these are of paramount importance in the discussion of PbFe$_{2/3}$W$_{1/3}$O$_3$ on sections of this review that follow.

Minimizing this free energy showed that the dielectric anomaly at the Neel temperature is of form

$$\Delta\varepsilon(T) = \frac{\left(b_1^2 + b_0 b_2\right) L^2(T)}{\left(B\varepsilon_0 \varepsilon^2\right)}. \qquad (5)$$

This shows several important things. Firstly, the dielectric anomaly varies as magnetization squared; secondly, it can be positive or negative, depending upon the sign of $b_0 b_2$; thirdly, it is not very large (numerically of order 1% of the background dielectric constant). Therefore when we see publications about other materials in which the dielectric anomaly is 20–30% of the background value and is not proportional to the magnetization or its square, we can be skeptical [24, 26–31].

The theory of Fox et al. explains very well the small negative anomaly in the a-axis dielectric constant in BaMnF$_4$

at and below T_N = 29 K, but it cannot explain the larger dielectric anomaly along the b-axis near T_{2D} = ca. 90 K. As discussed above, this anomaly arises (Figure 4) because of the Hou-Bloembergen linear-quadratic term $\langle P_i M_j M_k \rangle$ and is due to the in-plane ordering up to ca. T = $3T_N$. Two-dimensional systems *cannot* be modeled via mean-field theories, simply because integrating overall three dimensions gives zero. In this particular case, the correct details are given elsewhere [53, 68, 69], but the main conclusion is that the dielectric anomaly in this case is proportional not to $L^2(T)$, but to the magnetic energy. In other systems [60–66] the observed dielectric anomaly is not proportional to either; hence it may arise from extrinsic Maxwell-Wagner space charge. The work in [61] is especially suspicious and has never been reproduced or discussed further by the original authors.

A general ab initio theory of ferroelectricity in this $BaMF_4$ family has been published by Ederer and Spaldin [79].

There is an added complication for careful analysis of $BaMnF_4$, which is that it is structurally incommensurate below its antiferroelectric phase transition [80] near 254 K. Cox et al. reported [81] that the initial value of the wave vector for the soft mode is at q = $(1/2, 1/2, 0.39)a^*$ and that the incommensurate 0.39 value remains independent of temperature down to 4 K. This is perhaps true only in their specimen, however, and probably due to incommensurate antiphase boundary pinning by defects (perhaps fluorine vacancies). In other samples several transitions are found via dielectric studies [82], by piezoelectric resonance [83], a double peak in specific heat [84], and most importantly, neutron scattering [85, 86], and it would appear that a Devil's staircase of wave vectors of probable form $q_n = (5+2n)/(13+5n)$ exists, starting at $5a^*/13 = 0.385a^*$ and asymptotically reaching a lock-in at q = $(1/2, 1/2, 2/5)a^*$, that is with a unit cell of ten MnF_6 octahedra, compared with two in the paraelectric phase. Some modelling of this has been done [87].

3.3. Ferrimagnetic Ferroelectrics [88, 89].

The study of ferroelectric magnetic fluorides has recently been centered at two locations: Groningen [90] and Ljubljana [91–95]. The Ljubljana effort has emphasized the family $K_3Fe_2^{+3}Fe_3^{+2}F_{15}$ whose structure is diagrammed in Figure 5. This is in fact an unusual ferromagnetic ferroelectric, with two Fe^{+3} ions and three Fe^{+2} ions per formula group ($4Fe^{+3}$ and $6Fe^{+2}$ ions per primitive unit cell). It is possible to substitute separately for the Fe^{+2} ions, giving for example $K_3Fe_2^{+3}Cu_3F_{15}$, and for the Fe^{+3} ions, giving $K_3Fe_3^{+2}Cr_2F_{15}$. All of these are magnetoelectric, and the latter exhibits two-phase transitions at low temperatures, possibly signifying the spin ordering of Fe (higher T) and Cr (lower T) ions. A more general discussion of the possibility of magnetoelectricity in the wider family of $A_3Fe_5F_{15}$ has been given by Abrahams [96, 97]. Here the A-ion can be Na, Li, K, and so forth. No lattice dynamical modelling of these structures has been published.

Models: Picozzi's group has published [98] an ab initio model for $K_3Fe_2^{+3}Fe_3^{+2}F_{15}$ with certain predictions of electronic character for its magnetoelectric transition. Unfortunately she had been unaware of the fact that the
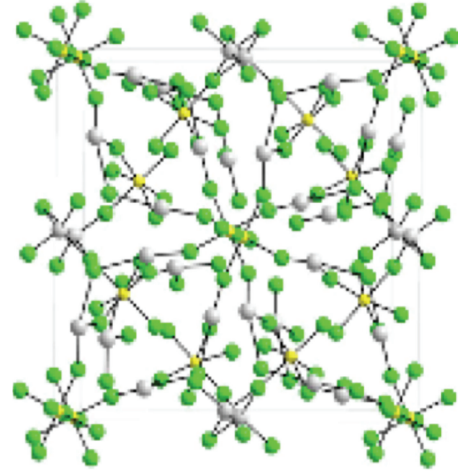

FIGURE 5: Structure of $K_3Fe_5F_{15}$.

pertinent experimental results had been published several years before and did not agree with her postfacto predictions. It is sometimes difficult to get theoreticians to do literature searches at present. A similar example is the recent ab initio model for the family BaClF [99] where the authors were unaware of the Raman phonon experiments [100].

3.4. Magnetoelectric Fluoride Relaxors.

General view: the idea of materials that are simultaneously ferroelectric relaxors and magnetic relaxors was initiated by Levstik et al. who developed the basic idea [88] and also showed a specific example [89] involving $PbFe_{1/2}Nb_{1/2}O_3$ and $PbMg_{1/2}W_{1/2}O_3$.

A large amount of research has been carried out on three lead-ferrite-based relaxors: $PbFe_{2/3}W_{1/3}O_3$ [101–109]; $PbFe_{1/2}Ta_{1/2}O_3$ [110]; and $PbFe_{1/2}Nb_{1/2}O_3$ [111–116] and on their solid solutions with PZT (lead zirconate titanate). The Ta and Nb compunds have high Neel temperatures (ca. 150 K) and ferroelectric T_c well above ambient (310 K and 380 K, resp.) and when combined with PZT are both ferroelectric and somewhat magnetic at room temperature, with evidence of coupling between the polarization and magnetization. The mechanisms are somewhat unclear yet, and spin clustering may be involved. The PZT-mixed compounds are good single-phase materials, generally with the tetragonal $BaTiO_3$ structure.

Many multiferroic relaxor materials exhibit glassy magnetic phases. In this regard it is important to recognize, as emphasized by Fischer and Hertz in their text, [117] that published spin-glass theories generally do not apply to crystals such as ferroelectrics that lack inversion centers. In particular, they stress that such systems cannot be Ising like. Since some multiferroics exhibit properties resembling spin glasses [118], this means that existing theories are apt to be inapplicable [119]. Theorists should take note. This may be the cause of unusually low values for the critical exponent zv reported in the magnon cross sections of $BiFeO_3$ [120]; however, we note that cluster models also give very low values ca. 1-2.

3.5. $PbFe_{2/3}W_{1/3}O_3$ ("PFW") and Its Solid Solutions with PZT.

Lead iron tungstate has been known since the days of Smolensky are to be a multiferroic with a "diffuse" phase transition (now termed a "relaxor"). Very recently a theory has been developed that gives very specific predictions for magnetic field dependence of electrical properties in such materials [121]. Based upon the earlier work of Pirc and Blinc, in their newer paper Pirc et al. calculate that for systems like PFW that are both magnetic relaxors (nanoregions of oriented spins) and ferroelectric relaxors (polar nanoregions) the coupling of magnetization and polarization through strain s, that is, via magnetostriction sM^2 and electrostriction sP^2 can be very large—much larger in fact than the direct biquadratic coupling P^2M^2. This kind of indirect strain-coupled magnetoelectric effect is not subject to the mathematical limit on magnetoelectric susceptibilities imposed by the Hornreich-Shtrikman constraint, that is, $\chi_{ME} < [\chi_{elec}\chi_{mag}]^{1/2}$. We note parenthetically that the Hornreich-Shtrikman constraint is not rigorous in any event, as shown recently by Dzyaloshinskii [122]; it is based upon linear response theory, which fails, for example, if there is a ferromagnetic phase transition at a temperature below the magnetoelectric transition (e.g., if Cr_2O_3 were to become ferromagnetic at low temperatures).

The conclusion of this theory [121] is that materials near the instability limit between short-range electric relaxor ordering and long-range ferroelectricity can be driven to the relaxor state by application of a magnetic field H. This occurs as a continuous dynamic process in which the polarization relaxation time τ is increased with applied field H. The explicit dependence of $\tau(H)$ is given by

$$\tau(H) = \text{constant} \times \exp\left[\frac{-H_c^2}{(H_c^2 - H_2)}\right], \qquad (6)$$

where the critical field H_c is estimated to be $0.4T < H_c < 4T$ using averages of magnetostriction and electrostriction tensor components from related compounds (those for PFW/PZT are yet unmeasured; Figure 6). Readers will recognize the unusual algebraic dependence in (6) as that of a Vogel-Fulcher equation (known to fit ordinary ferroelectric relaxors) in which the freezing temperature T_f has been replaced with a critical magnetic field H_c. As shown in Figures 6 and 7, this formula fits the observed data in PFW/PZT very well, and the critical field H_c is evaluated as $H_c = 0.92T$, rather close to the theoretical estimate. The drive of a long-range ferroelectric to become a relaxor in this model requires that the product of magnetostriction tensor and electrostriction tensor is to be negative; for a positive product, the applied magnetic field will conversely drive the relaxor to long-range ferroelectric ordering.

When the applied magnetic field H becomes close to H_c, the hysteresis loop becomes unmeasurable, and the material exhibits only a small extrinsic (space-charge) loop of a very lossy linear dielectric [123]. If the time constant of the measuring apparatus were unlimited, this would occur at H_c, but in reality it will occur at a slightly lower field, as the polarization relaxation time moves of the frequency range of the detector. In the data shown in [123] $H_c = 0.92T$, and
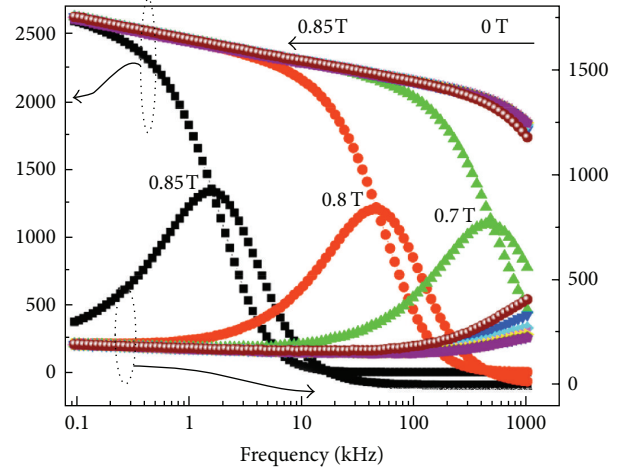

FIGURE 6: Real (left axis and upper curves) and imaginary (right axis and lower curves) dielectric responses in lead iron tungstate/lead zirconate-titanate at ambient temperatures and different magnetic field H, showing shift in peak frequency versus H.
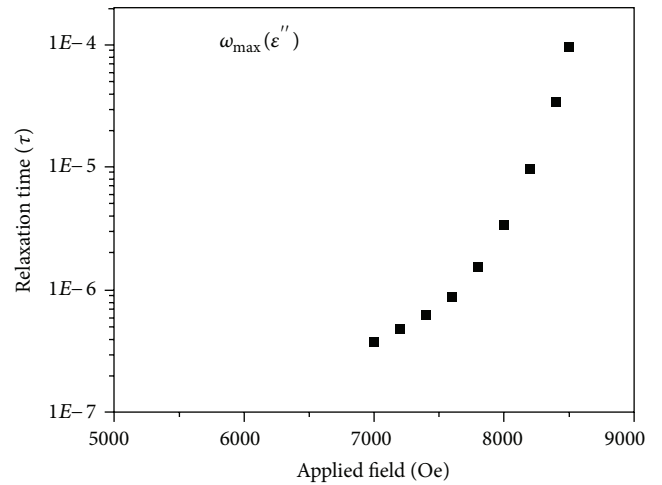

FIGURE 7: Dielectric (ferroelectric) polarization relaxation time in $PbFe_{2/3}W_{1/3}O_3$/PZT as a function of applied magnetic field. There are no adjustable parameters except for the time at $H = 0$ and the value H_c. The curve is a least squares fit to (6).

the polarization relaxation time increases from ca. 200 ns at $H = 0$ to $100\,\mu s$ at $H = 0.5T$. Longer relaxation times exceed the measuring window of the apparatus employed, but independent of the kit used, the hysteresis loop should vanish before $H = 0.92T$.

Other Models: Inductance due to Charge Injection. Despite the excellent agreement between theory and experiment for these data, there are nagging worries because the experiments were not reproducible in Seoul (Noh, [124]) or Prague [125] and in our own lab were highly sensitive to substrates, electroding, and wire bonding. The electrode sensitivity suggests an extrinsic possibility, namely, that of inductance. A ferroelectric capacitor is normally assumed to function as a pure capacitance without inductance, but in these leaky

semiconducting materials there is always some charge injection, and charge injection produces an inductance [126–128]. Such a "negative capacitance" (not in the very recent sense of the phrase) would explain why the dielectric data at high H appear to drop to zero in the graph of [123]. Hence there is a possibility that the H-dependence of polarization arises from an LCR resonance. This is also supported somewhat by similar observations [129] by Martínez et al. in LSMO which is known to exhibit strong negative magnetoresistance at small magnetic fields, making charge injection in that material very H dependent.

These PFW/PZT films also exhibit positive temperature coefficients of resistivity (PTCR) [130]. The data fit the model of Dawber and Scott [131]. PTCR is of commercial device importance because it eliminates the problem of thermal-runaway shorts.

3.6. Other Fluoride and Oxyfluoride Magnetoelectrics. In addition to the $Pb(Fe,W)O_3$, $Pb(Fe,Ta)O_3$, and $Pb(Fe,Nb)O_3$ families [132], there are a number of other fluoride magnetoelectrics and some oxyfluoride crystals that are probably magnetoelectric. The latter are reviewed by Ravez [133]. Most of these are magnetic and ferroelectric below 100 K as follows:

(a) $Pb_5Cr_3F_{19}$ family [134, 135],

(b) $Sr_3(FeF_6)_2$ family [136],

(c) $(NH_4)_2FeF_6$ family [137, 138],

(d) Oxyfluorides.

Of these $Pb_5Cr_3F_{19}$ has received the most recent attention. It exhibits long-range magnetic ordering at $T = 11$ K and ferromagnetic clustering at higher temperatures [139].

Prospects for development are high for basic physics (including copper oxide); modest to good for quaternary perovskite oxides. Switching of ferroelectric domains in PFT/PZT at 300 K by a weak magnetic field of $H = 0.3$ Tesla is shown in Figure 8.

4. Nanodomains and Surface Phase Transitions

4.1. Nanodomains . Unlike domains in magnets, which can have complicated Bloch walls, Neel walls, and vortex structures, the domains in ferroelectrics were thought for many years to be very abrupt (one or two unit cells, compared with hundreds in magnets) and Ising like, with straight rectilinear boundaries. However, recently a plethora of nanostructures has been revealed in ferroelectrics, including complex vortex structures, of which some are vortices [140, 141] (having winding number 1 is not sufficient to make a vortex; div P—an explosion—also has winding number +1 but lacks a curl $\times P$) and some are not. In the past domains were generally a nuisance, although their wall motion contributes a great deal to their effective dielectric constant [142, 143]. Now, however, we see that domain walls can be conducting [144] or even superconducting [145] in insulators, and the walls can be ferromagnetic even though the domains outside the walls are not [146, 147]. Note that Privratska and Janovec [148, 149]
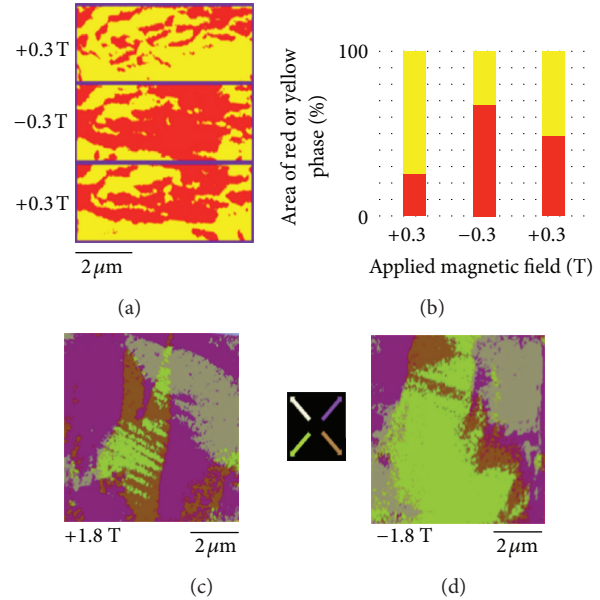

(a) (b)

(c) (d)

Figure 8: Ferroelectric domains (white = $+P$; dark = $-P$) at $T = 295$ K for + and -0.3 Tesla applied magnetic fields [33].

list all cases in which the domain walls can be ferromagnetic when the surrounding domains are not. A detailed microscopic theory of magnetic walls in nonmagnetic multiferroics has been developed by Daraktchiev et al. [150, 151].

One of the most profound differences between magnetic domain walls and ferroelectric domain walls has to do with inertia and momentum. Ferroelectric walls satisfy Newton's equations of motion, which have mass and momentum. These are second order in time, and hence domain walls coast a long distance (up to ca. 50 microns) after large fields E are turned off. In contrast, magnetic walls satisfy the Landau-Lifshitz-Gilbert equations, which are first order in time. Equations that are first order in time lead to motion that stops instantly when the driving field H (or B) is terminated. This problem has been discussed in the literature, but not clearly resolved. It leads to apparent paradoxes, such as the experimentally long coasting of magnetic domain walls in race-track memory devices. It also makes it complicated to write down equations of motion for domain walls in magnetoelectric multiferroics.

This failure to differentiate between magnetic domain walls and ferroelectric domain walls has occasionally led authors to ignore how far ferroelectric walls can coast after the external field E is cut off. This produces, in my opinion, errormeous models of domain wall dynamics in high fields, [152, 153], where Molotskii et al. ignore the momentum of ferroelectric walls and assume that they stop the instant when the field E is terminated.

The theory of such nonrectilinear domains was stimulated by the model calculation of Naumov et al. [154] and Fu et al. [155], but the idea of circular or toroidal domains is deeper and goes back to Ginzburg et al. [156, 157] or to Zeldovich before that, with a good recent review by Van Aken et al. [158].

Domain wall dynamics are as fascinating as their statics. Paruch has quantitatively analyzed creep [159], and some
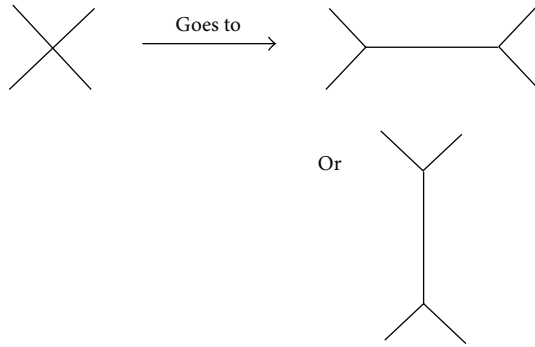
FIGURE 9: Threefold and fourfold vertex structures in ferroelectrics [161]. Reference [160] reports the coalescence of the threefold vertex pairs into a single fourfold vertex, shown to be theoretically possible by Srolovitz and Scott, followed by reseparation st 90 degrees. For a more general skyrmion-based theory, see Komineas [162].
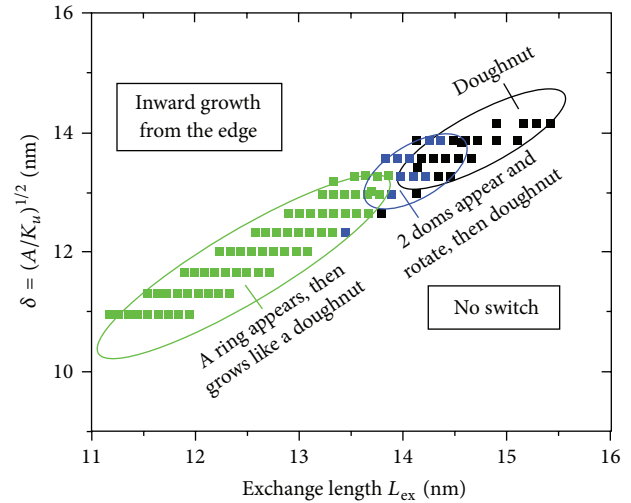

FIGURE 10: Parameter-space diagram showing the dependence of the occurrence of doughnut shaped concentric domains in thin films upon film disk diameter for circular specimens (H-J Fan and J. F. Scott, unpublished).

FIGURE 11: Regular polygons that do or do not produce concentric domain structures, from a MAGPAR-like simulation (H-J Fan and J. F. Scott, unpublished).

vertex dissociations and recombinations have been studied in detail by McQuaig [160], following the early Srolovitz-Scott model [161]. The latter is illustrated in Figure 9. Such adjacent pairs of threefold vertices have been reported by Jia et al. [141] and their collision to form a single fourfold vertex, and subsequent reseparation has been observed by McQuaid and Gregg. A skyrmion theory is given by Komineas [162].

In circular thin-film 1-micron diameter disks of PZT De Guerville et al. find domains form concentric circles whose aperiodic diameters resemble second-order Bessel functions [163]. These are absent in square films of the same size, indicating an unexpectedly strong role for boundary conditions. For skyrmion theory of such ring domains, see Axenides et al. [164]. Figure 10 shows a graph in parameter space showing how the presence or absence of such concentric domains depends upon sample diameter; the horizontal axis is a material parameter. Figure 11 illustrates just how sensitive the existence of such domains is to boundary conditions. These domains in our simulation occur for disks, octagons, hexagons, and not for squares or triangles; pentagons are an intermediate situation. No analytic theories explain this critical dependence on the number of sides, but Baudry et al. [165] have derived such patterns from a nonlinear model, and his group [166] has further shown that a kind of surface tension in the film is involved; Figure 12 illustrates data.

Prospects for 2012–22: excellent for pure physics. Since devices in which the operation is entirely via domain wall motion exist in both magnets [167, 168] and ferroelectrics [169], the application prospects for industry are also outstanding.

Particularly interesting from the physics point of view are the fractal domains reported by Catalan et al. [170].

4.2. Surface Phases.
Surface phases are lumped together in the present review because domains are usually studied on surfaces (via atomic force microscopy AFM and in particular in the polarization mode, PFM). Several important materials have had surface phases discovered in them, particularly in BiFeO$_3$.

In the initial study of BiFeO$_3$, Smolensky et al. reported [171] many temperatures at which anomalies were observed and suggested that this might be due in each case to a phase transition. Although other scientists generally expressed skepticism over the years, it appears now that her inferences were correct. BiFeO$_3$ exhibits at least three bulk phases (R3c, Pbnm (insulating), Pbnm (metallic), and possibly Pm3m (cubic) very near to its melting point [172–176]. But it also exhibits several anomalies that appear to be surface phase transitions: 548 K [177], 458 K [178–180], 201 K, and 140.3 K [181–183]. A variety of techniques have been used to elucidate these transitions, including EPR, in-plane interdigital electrode dielectric studies, neutron scattering [184], and both film and nanotube geometries (the latter to maximize surface/volume ratio).

Prospects: the surface studies show that the spin waves in BiFeO$_3$ are propagating modes well above ambient temperatures, making them useful for THz devices. The use of
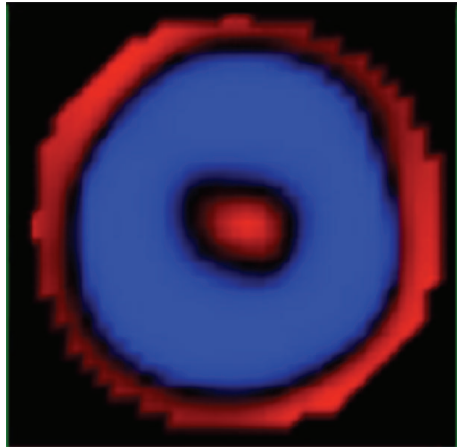
FIGURE 12: Experimental domain structure, resembling second-order Bessel function, in a PZT 1-micron diameter thin film [12].

FIGURE 13: Structure of $BaTiO_3/SrTiO_3$ superlattices [195].

$BiFeO_3$ surfaces for picosecond THz emitters was developed in beautiful detail by Tonouchi's group [185].

5. Artificially Grown Superlattices

Superlattices of alternating slices a few lattice constants thick have been made by several groups with two (or three) different kinds of ferroelectrics [186, 187], of a ferroelectric and paraelectric (e.g., $SrTiO_3$) [188, 189], or of a ferroelectric and a magnet [190, 191]. In many cases there is new physics learned from these geometries and combinations. For example, when $BaTiO_3$ with P along [001] is interlaced with $SrTiO_3$, it is expected [192] that the strontium titanate develops a polarization along [001] also. However, accurate second harmonic generation (SHG) data show P in $SrTiO_3$ develops along [110] [193, 194], as shown in Figure 13. This involves a high cost in energy due to Poisson's equation for electrostatic charge at the interfaces, but Johnston et al. were able to show [195] that this is more than compensated by the savings in elastic energy. Some similar effects may be involved in O-18 $SrTiO_3$ at very low temperatures (<35 K) because the apparent symmetry [196, 197] is lower than that predicted from the Ti-O soft mode [198].

Rather more profound physical effects are observed in $SrTiO_3/PbTiO_3$ superlattices, for which a good review is given by Dawber et al. [199].

Prospects: this is a very hot topic, particularly in oxide perovskites, because it is a precise way of analyzing interface oxide physics, which relates closely to the superconductivity in $LaAlO_3/SrTiO_3$ interfaces [200]. In this regard the studies of oxygen vacancies and conduction in pure $LaAlO_3$ [201] have new importance.

6. Photovoltaics

6.1. Basic Idea. The basic idea of photovoltaics is that in the presence of above-bandgap-energy light electron-hole pairs are formed in a crystal, and the absence of an inversion center in the crystal la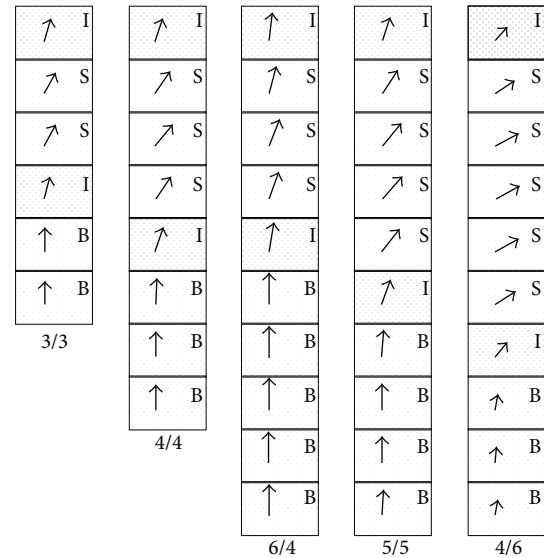ttice will electrically cause these e-h pairs to diffuse away from the illuminated spot. This produces a photovoltage, and in a conducting material, a photocurrent. Generally the photovoltage peaks at the bandgap energy (wavelength), although Fridkin's text [202] describes other possibilities.

This phenomenon has undergone a minor renaissance recently with the report by Seidel et al. [203] that voltages of order 500% of the bandgap Eg (13 eV in a 2.7 eV material, $BiFeO_3$) are observed in thin-film specimens with many small domains. This immediately suggests that the observed process is one of series voltage connections among (ca. 5) domains, such that the total voltage generated is 5 Eg/e. Various theoretical models have been used recently to describe the photovoltaic effect in detail [204], of which a "shift model" is perhaps most popular [205]. Some authors have argued that the electrode-dielectric interaction plays a dominant role [206], but this seems impossible based upon earlier optical measurements by the present author of photovoltaic effects in $LiNbO_3$ with no electrodes [207, 208]. The photovoltaic effect is in general not along the polar axis of ferroelectric crystals, so that it is a morphic symmetry-breaking perturbation. Since the photovoltaic tensor is third rank, large (40 kV/cm) fields can be produced perpendicular to the polar axis and be modest laser illumination (e.g., 500 mW of Argon-ion light focussed to ca. 50 micron diameter spots). This shows up dramatically in the phase-marching conditions for small-angle Raman scattering, as shown in Figure 14 [207].

Impact: renewed interest in the theory (e.g., Rappe et al.). Significant funding for new improved devices (e.g., NASA).

7. Phase Transitions

Phase transitions will always be popular among physicists because they represent a pathological state of matter, and among chemists in part because of the complexity and
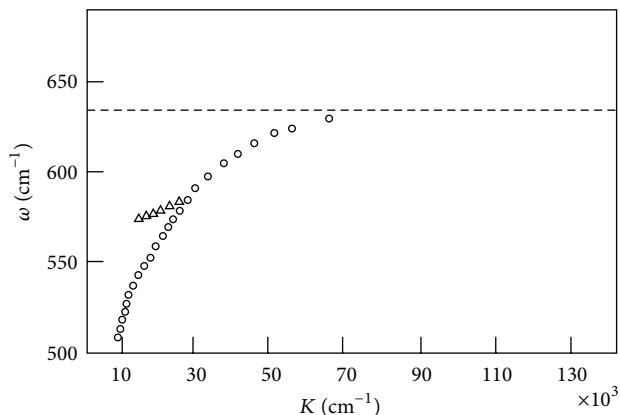
FIGURE 14: Small-angle Raman spectra in optically illuminated lithium niobate; the large photovoltaic effect transverse to the polar axis in this unelectroded specimen changes the phase-matching conditions strongly, such that the spectra differ significantly with and without illumination [207].

dynamics of phase diagrams. Phase transitions in ferro-electrics have traditionally been modeled using simple mean-field theory, following Landau [209] and Devonshire [210]. Attempts to fit more sophisticated exponents to Heisenberg or Ising models have in general raised skepticism. The main problem in fitting any critical exponents is first to show that the temperature range fitted is not arbitrary, and second that alternative models such as the "defect exponent" model of Sigov et al. [211, 212] are not better choices. The defect model gives success for unusually large exponents, such as that for ultrasonic attenuation, in systems such as incommensurates (e.g., $BaMnF_4$ [213, 214]) and relaxors such as PMN-PT [215, 216] or SBN [217] where discommensurations or stoichiometric boundaries serve as extended defects. In particular Bobnar measures a very unusual exponent of 2.50 ± 0.02 for in several PMN-PT samples, whereas the Sigov defect theory predicts exactly 5/2 in mean field [218, 219]. We note that SBN is now known to be a first-order phase transition [220, 221], which makes the critical exponents claimed for it suspicious.

7.1. Stress/Temperature Diagrams. Early in the studies of the cubic-tetragonal and cubic-rhombohedral phase transitions in $SrTiO_3$ and $LaAlO_3$ very nice phase diagrams were calculated and measured by Burke and Pressley in 1969 [222, 223], which showed in detail the critical stresses required to change phase on a uniaxial stress-temperature graph.

Many years later this form of presentation became popular with the calculations of Pertsev et al. [225] for situations in which the stress/strain in ferroelectric perovskite oxides was controlled by the lattice mismatch with the underlying substrate. Although not all of the latter phase diagrams were qualitatively correct, these graphs became known in some circles as "Pertsev diagrams." In view of the 1969 work by Burke and Pressley on perovskite oxides, this seems to be an inappropriate misnomer. Even if one favors the "cult of personality," a fairer label might be "Burke-Pressley diagrams." The present author prefers "strain/temperature" or "stress/temperature" diagrams. In general it is not a good idea

to name things after folks who rediscover them; not reading the literature should not be rewarded.

Phase diagrams are often pedagogically interesting in ferroelectrics. Figures 15 and 16 show [224, 227] in incommensurate sodium nitrite a triple point, a tricritical point, a critical end point, and something that extrapolates to a Lifshitz point where phase boundaries "kiss." Tris-sarcosine calcium chloride (TSCC) has a number of newly discovered yet unexplained phase transitions under both temperature and pressure [226, 228, 229]. Rather remarkably, the one at 185 K detected via NMR [228] and probably isosymmetric neither is observable in any specific heat measurements, nor is the transition at 64 K [229]. Figure 17 illustrates the use of resonant ultrasonic spectroscopy (RUS) to reveal such subtle phase transitions; here the acoustic phonon response to ac driving frequencies changes slope or exhibits new resonances at the phase transition temperatures of 185 K and 64 K in TSCC. Surprisingly, very precise specific heat measurements (Figure 18) reveal nothing at these temperatures.

7.2. Quantum Critical Points. When superconductors or magnets have phase transitions exactly at $T = 0$, there exist peculiar phenomena. This situation is referred to as a Quantum Critical Point (QCP). Reviews discuss in some detail the interesting new physics at such points [230–232]. It is possible to prepare several ferroelectrics, such that $T_c = 0$. Examples are $SrTiO_3$ with 30% O-18 [233], TSCC with 18% Br or iodine [234], or $TmVO_4$ (a quantum ferroelastic) [235]. Studies of these three materials are underway in our group [236], and some work has been published [237] or submitted.

Prospects are scientifically interesting, especially for multiferroics. Applications are nil.

7.3. Phase Transitions without Domains. Landau and Lifshitz pointed out long ago that it is quite possible for a ferroelectric to reverse individual polarizations all at once without forming or moving any domain walls. Each local polarization would simply flip 180 degrees simultaneously. However, the Landau-Devonshire free energy shows that in general this requires about 1000x as much field E as is required for the usual domain-wall controlled coercive field E_c. So the problem experimentally is not to show that it happens, but to show why the domain-wall process does not happen first; that is, any applied field E has a finite rise time, and authors need to show unambiguously that the domain wall mechanism is somehow suppressed.

Such claims have been made occasionally over the years, such as by Ducharme Fridkin et al. [238, 239]. At present the best case has been argued by Zhang [240] and Scott [241]. A slightly weaker case has been made by the Argonne group [242].

Prospects: more experiments need to be done. Probably no industrial application for devices will exist.

8. Flexoelectricity

Flexoelectricity is the creation of a voltage via an inhomogeneous strain in a crystal (or vice versa). It was probably
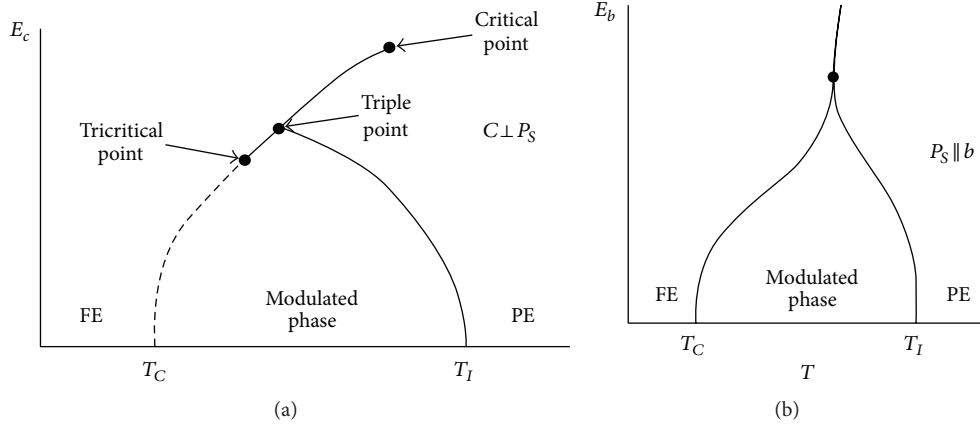
FIGURE 15: Schematic phase diagram in sodium nitrite $NaNO_2$ for field E: (a) along the polar axis; (b) transverse to the polar axis [224].
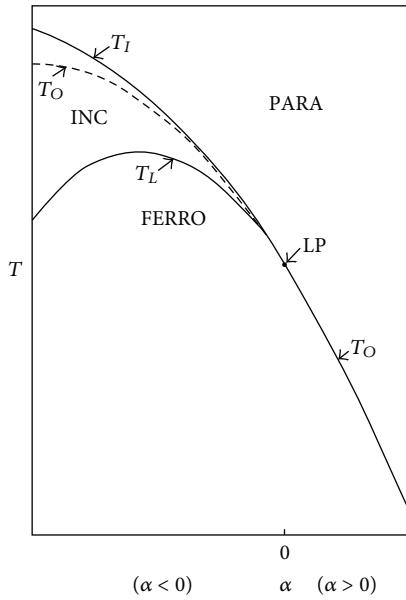

FIGURE 16: Detailed phase diagram for sodium nitrite $NaNO_2$ for field transverse to the polar axis; here the graph is in the temperature-wave vector plane and shows that the Lifshitz point is not quite reached; since the transition is first-order, the Lifshitz point is slightly extrapolated [225].

FIGURE 17: Resonant ultrasonic spectra of TSCC revealing phase transitions at 185 K, 130 K, and 64 K [226].

first analyzed by the present author in 1968 [243] in the Scheelite crystals represented by $CaWO_4$, $CaMoO_4$, $SrWO_4$, $BaMoO_4$, and so forth. As shown in Figure 1, these materials crystallize in a centric tetragonal structure with even and odd parity phonon modes that are, respectively, Raman and infrared active. However, the B_u symmetry vibrations are "silent," forbidden in both infrared and Raman spectroscopy. The presence of an inhomogeneous shear strain of symmetry E_u makes the nominally forbidden B_u mode(s), such as that at $360\, cm^{-1}$, appear in the Raman spectra with apparent symmetry A_g, since the product $B_u \times E_u$ contains the representation A_g.

When single crystals of these compounds are prepared for laser Raman studies they are mechanically polished to minimize reflections from the incident and transmitted laser beam. Unfortunately such polishing creates inhomogeneous strains. By considering which A_u and B_u modes occur in each Raman tensor component, we can infer the symmetry of the perturbation. An example is given below. The inferred perturbation transforms as xyz and in the case studied corresponds

FIGURE 18: Specific heat data in TSCC showing no evidence of phase transitions at 185 K and 64 K (Zdravko Kutnjak and J. F. Scott, unpublished).

FIGURE 19: Giant flexoelectric effect [18]; upper curve shows X-ray Bragg peaks at different stresses; lower figure, schematic diagram of atomic displacements.

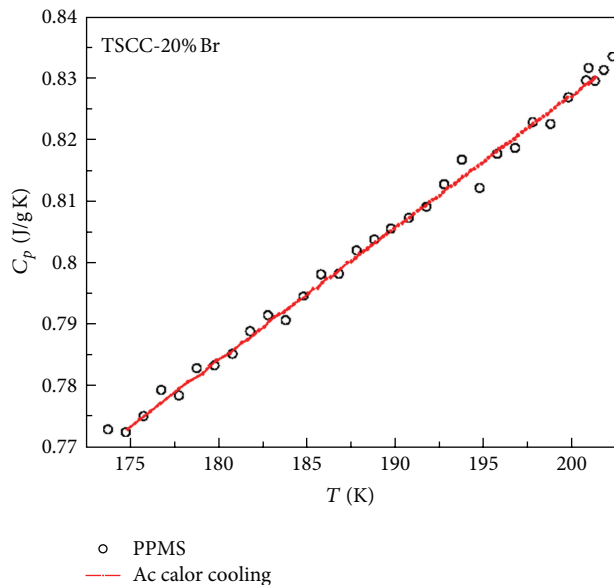to a surface shear strain of symmetry xy, with depth gradient along z, that is, $d(xy)/dz$. In present-day terminology this would be termed a flexoelectric perturbation. This analysis permitted the identification of the silent modes in the Scheelites and the explanation of their splittings according to the model diagrammed in Figure 1, which implies that theinternal vibrational modes of the WO_4 ions are split into A and E symmetries by the tetragonal crystal field and further into gerade (g) and ungerade (u) symmetry pairs by Davidov interaction of the two WO_4 ions per primitive unit cell [244]. The fact that these splittings in energy are proportional to the inverse sixth power of the W-W interionic distance implies that the interaction is dipole-dipole. This use of Raman spectroscopy to study flexoelectricity should be exploited further.

In the 1960s this sort of flexoelectricity was generally considered a nuisance, not the basis for devices. In bulk it is a small effect and was carefully studied by the Penn State group [245, 246] and by Tagantsev [247]. More recently the first studies of oriented single crystals were reported [248], together with ab initio calculations [249]. There remain some unresolved controversies, with Resta maintaining that there are not separate bulk and surface flexoelectric effects [250], but Tagantsev argues that there are [251]. Some unpublished work by Zhou et al. [252] may resolve this question. In the interim, Lee et al. report [253] giant flexoelectric effects in very thin films, as shown in Figure 19, and Lu et al. [254] show flexoelectric switching as a memory device, Figure 20.

9. Relaxors and Birelaxors

9.1. Relaxors. Relaxor ferroelectrics are oxide compounds with large dielectric anomalies at phase transition temperatures but no long-range order or spontaneous polarization
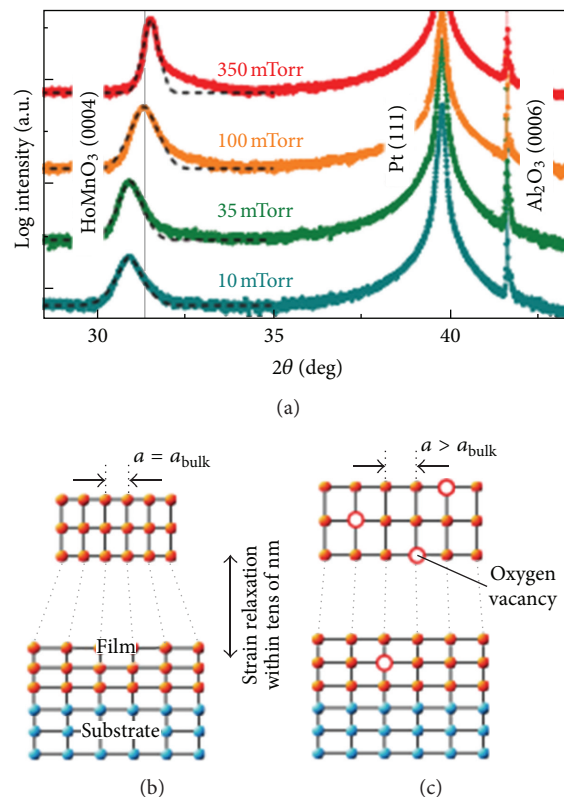
[255, 256]. It is important that the temperature at which the dielectric constant peaks varies strongly with probe frequency. They are of commercial importance as transducers and actuators because they exhibit large piezoelectric strain without fracture. The most important families are probably PMN (lead magnesium niobate), including PMN mixed with lead titanate (PMN-PT) and SBN (strontium barium niobate).

These materials exhibit large local deviation from stoichiometry, such that PMN of nominal formula $PbMg_{1/3}Nb_{2/3}O_3$ may have local Nb : Mg ratios of as little as 1 : 1 rather than 2 : 1. This implies that the systems are not in mechanical or thermal equilibrium, and hence that equilibrium statistical mechanics may not give a wholly accurate description of their dynamics. One should be particularly cautious in fitting subtleties such as critical (fluctuation-dominated) exponents. Generally a good model for relaxors is the random-bond, random-field model of Pirc and Blinc [257, 258], which gives a quantitative description of most of their properties, including a critical end point [259].

However, a specific discrepancy in their modeling occurs in the area of critical exponents. Generally the application of critical phenomena requires that the phase transition in question is continuous (second order). In the contrary case of a phase transition with a small discontinuity (first order), no critical exponents technically exist, but erroneous fitting
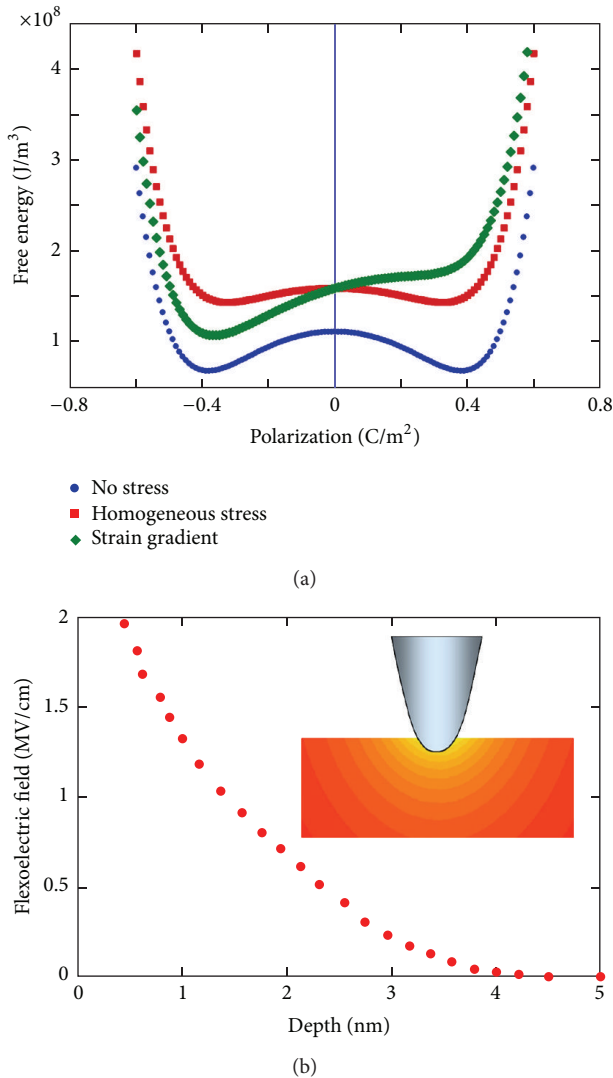
(a)

(b)

Figure 20: Switching of polarization P without electric fields, via floexoelectric stress [254].

attempts will give small numerical values near 0.0–0.1 for the order parameter (polarization) exponent beta (1/2 in mean field) and equally erroneous values for isothermal susceptibility exponent gamma (1.0 in mean field). We emphasize that fitting critical exponents to a first-order phase transition is usually physically nonsense [260–262].

The first suggestion that SBN had a first-order phase transition was by J. Dec (EMF conference, Lake Bled, Slovenia, 2007), but this was strenuously rejected by his coauthor, W. Kleemann, in the discussion following Dec's invited talk. However, this year it was shown conclusively that the transition in SBN is first order [220, 221].

Although true critical exponents are not applicable to first-order phase transitions such as that in SBN, there is an approximate theory that fits very well because it is not asymptotically valid at T_c. This is the defect exponential theory of Sigov et al. In general it gives large exponents such as 2.5 for the divergence with temperature of ultrasonic attenuation [260], and these have been measured very precisely

experimentally by Fritz in $BaMnF_4$ [215, 216] and by Bobnar and Kutnjak in PMN-PT [218].

Our general conclusion regarding SBN is that the critical exponents published by Kleemann et al. are not physically meaningful because the transitions are first order (ironically as first suggested by Dec), and that more generally the defect theory of Sigov et al. is more applicable to relaxors due to their large local deviations from stoichiometry, which act as extended defects. However, the specific heat data of Kutnjak et al. [259] seem quite precise and suggest that real exponents characteristic of precursor fluctuations near Tc might give valid numbers, despite the discontinuous jump.

More work is required.

9.2. Birelaxors. Magnets with short-range order have been called magnetic relaxors or sometimes micromagnets. When this short-range magnetic ordering is combined with short-range polarization ordering, the term birelaxor is used. Polarizations P and magnetizations M can couple bo-quadratically via electrostriction and magnetostriction, as shown schematically in Figure 21.

The theory of birelaxors has been given by Pirc et al. [33] with experiments from Kumar et al. [34]; good recent work was added from Ljubljana [263].

10. Composites

A general discussion of composites is beyond the scope of this review, but it would be remiss not to mention the exciting work of Viehland et al. on multilayer magneto-electric composites, for example, of terfenol-d and PZT, which have reached the level of commercial devices for weak magnetic field sensors, competitive with some respects to SQUID superconducting devices [264, 265]. It is worthy to note that multiferroic composites were unintentionally made in extremely large numbers by the cost-saving process if replacing Pt with Ni in multilayer capacitors, as illustrated in Figure 22 [266].

Prospects are basic physics—modest; applications—excellent.

11. Polymer and Flexible Ferroelectrics

Led by extensive studies of polyvinylidene and its fluoroethylene copolymers, flexible ferroelectrics, usually polymeric, have new basic physics in them yet and a host of applications, including switched capacitor RAMs, [267] and resistive RAMs (RRAMs) [268–270]. The field is led by Blom's group in Groningen and Ducharme in Nebraska.

The only drawback is that it can be difficult to discriminate electret (mobile defect charge) effects from true ferroelectricity. This is an even greater problem with materials such as ZnO : Li. Wurtzite ZnO is pyroelectric but definitely cannot be ferroelectric; electrical hysteresis in ZnO : Li probably comes from electret transport of small Li ions and is not related to ferroelectricity, although there are numerous erroneous claims. The wurtzite structure ZnO is a good
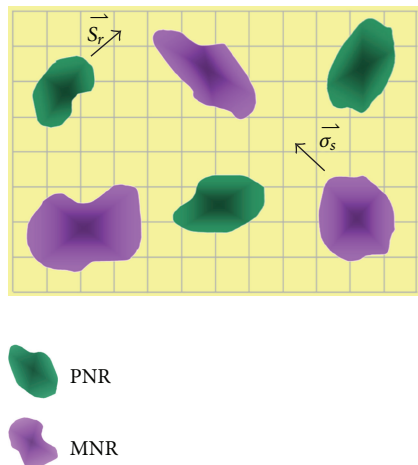
Figure 21: Cartoon illustrating the stress interaction of magnetic domains and ferroelectric domains in a multiferroic birelaxor [33].

Figure 22: One-cent multiferroic multilayer device [266].

pyroelectric, but switching would require breaking Zn-O bonds.

Prospects for PVDF basic physics—very good; devices—outstanding.

Ferroelectricity in ZnO : Li is unproven and very unlikely.

12. Electrocalorics

The electrocaloric effect was discovered by Kobeko and Kurtschatov [271]. This is the same man who led the development of the Soviet atomic bomb, although the German transliteration of his name in the electrocaloric paper as J. Kurtschatov renders that nonobvious.

It is the easiest to describe Carnot-like heat cycles for electrocalorics with T, E and S, T diagrams, where T is temperature; S is entropy, and E is applied electric field. Figure 23 illustrates for (T, E) the case for a first-order ferroelectric, where T_0 is the actual phase transition temperature, and T_1 is the higher temperature above which ferroelectricity cannot be induced by an applied field. Heating cycles of maximum interest cross the phase boundary as isotherms, at constant
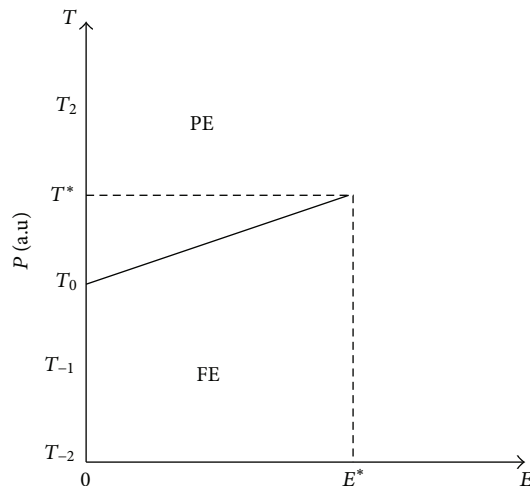

Figure 23: (E, T) diagram for electrocaloric ferroelectrics, for a first-order phase transition.

field E or adiabatically at constant S. Figure 24 illustrates the (S, E) graph, with numerical values appropriate for $BaTiO_3$.

It is well known that an electrocaloric effect (cooling under an electric field) exists. The author discusses this in an early encyclopedia article [227]. Usually the effect (measured as cooling degrees per volt K/N) is very small, $\ll 1$ K/V in bulk. However, since the actual physics involves cooling per unit electric field, the effect is very large in thin films [272, 273] and can even be "giant" [274]. However, making the samples thin dramatically decreases the amount of heat removed (calories). That is, the temperature change remains large, but the cooling load becomes very small. Nevertheless, values of 660 J/kg have been reported at room temperature [275]. Fully integrated prototypes have been made by Kar-Narayan [276]. The leading material is the PVDF family of polymers (polyvinyldifluoride) [277, 278]. Fundamental ab initio theory of electrocalorics has also been published [279].

13. Biological Ferroelectrics

There has been a recent flurry of papers on biological ferroelectrics, with exaggerated claims about their relevance to human physiology. [280–282]. These follow many piezo-electric studies in soft tissue and not just bone and teeth [281]. The new works include measurements of dessicated tissue from a human aorta, but experts in this technique have expressed skepticism about the results. A different problem is the paper on n-glycine Oak Ridge and Aveiro [282]. Here the data are good, but crystalline n-glycine is not found in the human body (or any other living creatures). Therefore too much hyperbole has been invoked. Readers should keep in mind that crystalline ferroelectrics are not known to exist in humans, and no in vitro or even in situ work has been reported. Showing electrical artifacts in a piece of dead aorta is a debatable beginning, and certainly no relevance to human physiology or evolution is established.

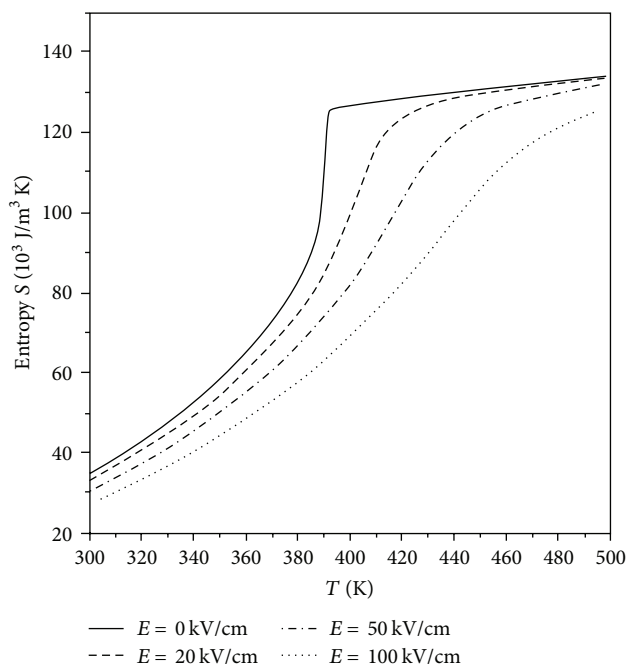Prospects are disappointing and slightly exaggerated claims in publications.

Figure 24: (S, E) diagram for electrocaloric ferroelectrics, for a first-order phase transition, with numerical values for barium titanate [283].

14. Resistive Random Access Memories (RRAMs)

There are two kinds of resistive memories. The first involves a dendritic short ("moving cathode") and was first discovered by Plumlee at Sandia in 1967 [284]. See also Lou et al. [285, 286]. This process is highly reversible in some materials and has reached prototype development stage in a number of Asian and European corporations, with 10^{10} cycle performance shown in Korea. Very good reviews have been published of this work [287, 288]. It seems likely that some commercialization will occur within five years. The favorite material is rutile TiO_2.

A second kind of ferroelectric resistive RAM utilizes the Schottky barrier change at electrode-ferroelectric interfaces. This was first analyzed by Blom et al. in 1994 [289]. His device switched only a small amount of charge in PZR, but ×1000 in current switched was recently reported by Jiang et al., using semiconducting $BiFeO_3$ [290]. Very recently Noheda has confirmed [291, 292] Jiang's result and shown that the bandgap lowers from the 2.7 eV bandgap of unbiased $BiFeO_3$ to ca. 0.2 eV with voltage bias, and hence the Schottky barrier height decreases dramatically with forward bias.

Prospects: For reversible microshortsm as in TiO_2—some commercialization within five years. For Schottky-type RRAM, excellent physics for five years; commercialization within ten.

15. Combinations with Graphene and with Carbon Nanotubes

It is of recent interest to fabricate functional ferroelectrics as end units onto both carbon nanotubes and graphene sheets [291–295]. The latter can serve as an FET gate, replacing the conventional Si/SiO_2 (see "carbon-ferroelectric gates") [296]. There is a longer history, reviewed elsewhere, of ferroelectric nanowires and nanotubes [297], with recent ab initio theory [298].

16. Second Sound

Since the early theoretical proposal by Gurevuch and Tagantsev [299] for second sound in $SrTiO_3$ at low temperatures, there have been several experimental claims [300–302]. These are generally based upon the observed splitting of certain acoustic phonon branches in Brillouin spectra. Based upon the assumption that $SrTiO_3$ is tetragonal below 105 K [303], such splitting is forbidden. However, recent work by Blinc et al. [304] and by Scott et al. [305] shows that $SrTiO_3$ below ca. 60 K has Sr-ion disorder along [111], which convoluted with the TiO_6 rotation about [001], renders $SrTiO_3$ triclinic. The observed Brillouin splitting is required for this triclinic symmetry. The paradox observed spectroscopically between Takesada et al. and Shigenari et al. is thereby resolved. In addition, the crystal symmetry of O-18 $SrTiO_3$, which is now known to be lower than orthorhombic [306, 307] is also resolved.

Prospects: second sound in crystal is very hard to observe, requiring exquisite perfection and no isotopic variation (as in NaF). It is highly unlikely in oxide ferroelectrics.

17. Electrically Controlled Magnetic Tunnel Junctions

Beyond the scope of this review. See [308–312].

18. Summary

I have given a rather personal perspective on more than a dozen subtopics withing the general area of ferroelectrics, with predictions of short-term progress and impact. In the area of memory applications they may still be competitive with phase change memories, magnetic RAMs, and FLASH. Ferroelectrically gated FETs (including MOTTFETs) look promising as do magnetic tunnel junctions that are electrically controlled.

I have emphasized the magnetoelectric properties of fluorides because they lack the covalent bonding of oxide perovskites that Cohen showed [313] to be important and contradict the oxide-based view of Spaldin [314] that there are few multiferroic/magnetoelectrics in nature. These offer new insights in physics, but alas, have no examples of magnetoelectric effects above ca. 123 K.

In general, the game has moved away sharply from the single crystal and bulk ceramics work of 196-80. Future devices will undoubtedly be thin films, and operating voltages will be low (<5 V). Interfacial physics and chemistry will be emphasized. Emphasis will still be on oxides, and folks will be referring to "oxide electronics." As we understood the role of grain boundaries over the past generation, the next decade will find analogous physics and chemistry in domain walls,

albeit on a smaller length scale. Domain walls in ferroelectrics exhibit effects not seen in magnetic analogs. It should be fun.

References

[1] M. Dawber, K. M. Rabe, and J. F. Scott, "Physics of thin-film ferroelectric oxides," *Reviews of Modern Physics*, vol. 77, pp. 1083–1130, 2005.

[2] O. Auciello, J. F. Scott, and R. Ramesh, "The physics of ferroelectric memories," *Physics Today*, vol. 51, no. 7, pp. 22–27, 1998.

[3] V. Garcia, M. Bibes, L. Bocher et al., "Ferroelectric control of spin polatization," *Science*, vol. 327, no. 5969, pp. 1106–1119, 2010.

[4] A. Chanthbouala, A. Crassous, V. Garcia et al., "Solid-state memories based on ferroelectric tunnel junctions," *Nature Nanotechnology*, vol. 7, pp. 101–104, 2012.

[5] A. S. Mischenko, Q. Zhang, J. F. Scott, R. W. Whatmore, and N. D. Mathur, "Giant electrocaloric effect in thin-film $PbZr_{0.95}Ti_{0.05}O_3$," *Science*, vol. 311, no. 5765, pp. 1270–1271, 2006.

[6] A. S. Mischenko, Q. Zhang, R. W. Whatmore, J. F. Scott, and N. D. Mathur, "Giant electrocaloric effect in the thin film relaxor ferroelectric 0.9 Pb $Mg_{1/3}Nb_{2/3}O_3$-0.1 $PbTiO_3$ near room temperature," *Applied Physics Letters*, vol. 89, no. 24, Article ID 242912, 2006.

[7] K. Takahashi, N. Kida, and M. Tonouchi, "Terahertz radiation by an ultrafast spontaneous polarization modulation of multiferroic $BiFeO_3$ thin films," *Physical Review Letters*, vol. 96, no. 11, Article ID 117402, pp. 1–4, 2006.

[8] J. F. Scott, H. J. Fan, S. Kawasaki et al., "Terahertz emission from tubular Pb(Zr, Ti)O_3 nanostructures," *Nano Letters*, vol. 8, no. 12, pp. 4404–4409, 2008.

[9] D. S. Jeong, R. Thomas, R. S. Katiyar et al., "Emerging memories: resistive switching mechanisms and current status," *Reports on Progress in Physics*, vol. 75, no. 7, Article ID 076502, 2012.

[10] R. Waser and M. Aono, "Nanoionics-based resistive switching memories," *Nature Materials*, vol. 6, no. 11, pp. 833–840, 2007.

[11] J. Seidel, W. Luo, S. J. Suresha et al., "Prominent electrochromism through vacancy-order melting in a complex oxide," *Nature Communications*, vol. 3, article 799, 2012.

[12] A. Gruverman, D. Wu, H. J. Fan, and J. F. Scott, "Vortex ferroelectric domains," *Journal of Physics Condensed Matter*, vol. 20, no. 34, Article ID 342201, 2008.

[13] G. Catalan, J. Seidel, J. F. Scott, and R. Ramesh, "Domain wall nanoelectronics," *Reviews of Modern Physics*, vol. 84, pp. 119–156, 2012.

[14] A. V. Bune, V. M. Fridkin, S. Ducharme et al., "Two-dimensional ferroelectric films," *Nature*, vol. 391, no. 6670, pp. 874–877, 1998.

[15] T. Furukawa, "Ferroelectric properties of vinylidene fluoride copolymers," *Phase Transitions*, vol. 18, pp. 143–211, 1989.

[16] D. Daranciang, M. Highland, H. Wen et al., "Ultrafast photovoltaic response in ferroelectric nanolayers," *Physical Review Letters*, vol. 108, no. 8, Article ID 087601, 8 pages, 2012.

[17] R. M. Swanson, "Photovoltaics power up," *Science*, vol. 324, no. 5929, pp. 891–892, 2009.

[18] J. F. Scott and C. A. Paz De Araujo, "Ferroelectric memories," *Science*, vol. 246, no. 4936, pp. 1400–1405, 1989.

[19] E. Tokumitsu, R. I. Nakamura, and H. Ishiwara, "Nonvolatile memory operations of metal-ferroelectric-insulator-semiconductor (MFIS) FET's using PLZT/STO/Si(100) structures," *IEEE Electron Device Letters*, vol. 18, no. 4, pp. 160–162, 1997.

[20] R. Scherwitzl, P. Zubko, I. G. Lezama et al., "Electric-field control of the metal-insulator transition in ultrathin $NdNiO_3$ films," *Advanced Materials*, vol. 22, no. 48, pp. 5517–5520, 2010.

[21] C. Girardot, S. Pignard, F. Weiss, and J. Kreisel, "$SmNiO_3$/$NdNiO_3$ thin film multilayers," *Applied Physics Letters*, vol. 98, Article ID 241903, 2011.

[22] M. Lines and A. M. Glass, *Theory and Application of Ferroelectrics and Related Materials*, Clarendon Press, Oxford, UK, 1979.

[23] M. Fiebig, "Revival of the magnetoelectric effect," *Journal of Physics D*, vol. 38, no. 8, pp. R123–R152, 2005.

[24] G. A. Smolensky, V. A. Isupov, and A. I. Agranovskaya, "A new group of ferroelectrics (with layered structure)," *Soviet Physics Solid State*, vol. 1, no. 1, pp. 149–150, 1959.

[25] G. A. Smolensky, V. A. Isupov, and A. I. Agranovskaya, "Ferroelectrics of the oxygen-octahedral type with layered structure," *Soviet Physics Solid State*, vol. 3, no. 3, pp. 651–655, 1961.

[26] G. A. Smolensky, V. A. Isupov, and A. I. Agranovskaya, "New Ferroelectrics of a complex composition: 4," *Soviet Physics Solid State*, vol. 2, no. 11, pp. 2651–2654, 1961.

[27] T. Kimura, Y. Sekio, H. Nakamura, T. Siegrist, and A. P. Ramirez, "Cupric oxide as an induced-multiferroic with high-TC," *Nature Materials*, vol. 7, no. 4, pp. 291–294, 2008.

[28] T. Kimura, "A room-temperature multiferroic," Nature conference, Aachen, Germany, June 2012.

[29] W. Peng, N. Lemee, M. Karkut et al., "Spin-lattice coupling in multiferroic Pb ($Fe_{1/2}Nb_{1/2}$)O_3 thin films," *Applied Physics Letters*, vol. 94, no. 1, Article ID 012509, 2009.

[30] R. Martinez, R. Palai, H. Huhtinen, J. Liu, J. F. Scott, and R. S. Katiyar, "Nanoscale ordering and multiferroic behavior in Pb ($Fe_{1/2}Ta_{1/2}$)O_3," *Physical Review B*, vol. 82, no. 13, Article ID 134104, 2010.

[31] D. Sanchez, N. Ortega, A. Kumar, R. S. Katiyar, and J. F. Scott, "Symmetries and multiferroic properties of novel room-temperature magnetoelectrics: lead iron tantalate—lead zirconate titanate (PFT/PZT)," *AIP Advances*, vol. 1, Article ID 042169, 2011.

[32] D. N. Evans, J. N. Gregg, A. Kumar, D. Sanchez, R. S. Katiyar, and J. F. Scott, "Magnetoelectric switching at room temperature in a new multiferroic," *Nature Communications*. In press.

[33] R. Pirc, R. Blinc, and J. F. Scott, "Mesoscopic model of a system possessing both relaxor ferroelectric and relaxor ferromagnetic properties," *Physical Review B*, vol. 79, no. 21, Article ID 214114, 2009.

[34] A. Kumar, G. L. Sharma, R. S. Katiyar, R. Pirc, R. Blinc, and J. F. Scott, "Magnetic control of large room-temperature polarization," *Journal of Physics Condensed Matter*, vol. 21, no. 38, Article ID 382204, 2009.

[35] D. N. Astrov, "The magnetoelectric effect in antiferromagnets," *Soviet Physics JETP*, vol. 11, pp. 708–709, 1960.

[36] D. N. Astrov, "Magnetoelectric effect in chromium oxide," *Soviet Physics JETP*, vol. 13, pp. 729–733, 1961.

[37] B. I. Alshin, D. N. Astrov, and A. V. Tischen, "Magnetoelectric effect in $BaCoF_4$," *JETP Letters*, vol. 12, pp. 142–145, 1970.

[38] D. N. Astrov, B. I. Alshin, R. V. Zorin, and L. A. Drobyshe, "Spontaneous magnetoelectric effect," *Soviet Physics JETP*, vol. 28, pp. 1123–1127, 1969.

[39] R. V. Zorin, A. V. Tischen, and D. N. Astrov, "2-dimensional magnetic ordering in $BaMnF_4$," *Fizika Tverdovo Tela*, vol. 14, pp. 3103–3107, 1972.

[40] B. I. Alshin, D. N. Astrov, and R. V. Zorin, "Low-frequency magnetoelectric resonances in $BaMnF_4$," *Zhurnal Eksperimenti Teoretische Fizik*, vol. 63, pp. 2198–2204, 1972.

[41] R. V. Zorin, D. N. Astrov, and B. I. Alshin, "Low-frequency magnetoelectric resonances in $BaCoF_4$," *Zhurnal Eksperimenti Teoretische Fizik*, vol. 62, pp. 1201–1120, 1972.

[42] D. R. Tilley and J. F. Scott, "Frequency dependence of magneto-electric phenomena in $BaMnf_4$," *Physical Review B*, vol. 25, no. 5, pp. 3251–3260, 1982.

[43] E. T. Keve, S. C. Abrahams, and J. L. Bernstein, "Crystal Structure of pyroelectric paramagnetic barium cobalt fluoride, $BaCoF_4$," *Journal of Chemical Physics*, vol. 53, pp. 3279–3283, 1970.

[44] C. Ederer and N. A. Spaldin, "Recent progress in first-principles studies of magnetoelectric multiferroics," *Current Opinion in Solid State and Materials Science*, vol. 9, no. 3, pp. 128–139, 2005.

[45] C. Ederer and N. A. Spaldin, "Electric-field-switchable magnets: the case of $BaNiF_4$," *Physical Review B*, vol. 74, no. 2, Article ID 020401, 2006.

[46] E. L. Venturini and F. R. Morgenthaler, "AFMR versus orientation in weakly ferromagnetic $BaMnF_4$," *AIP Conference Proceedings*, vol. 24, pp. 168–169, 1975.

[47] S. A. Kizhaev, Ioffe Institute, private communication, 1981.

[48] S. A. Kizhaev and R. V. Pisarev, "Dielectric and magnetic properties of $BaMnF_4$ at low temperatures," *Fizika Tverdogo Tela*, vol. 26, pp. 1669–1674, 1984.

[49] L. A. Prozorova, Kapitza Institute, private communication, 1981.

[50] A. K. Zvezdin and A. P. Pyatakov, "Symmetry and magnetoelectric interactions in $BaMnF_4$," *Low Temperature Physics*, vol. 36, no. 6, Article ID 006006LTP, pp. 532–537, 2010.

[51] R. R. Birss, "Magnetic symmetry and forbidden effects," *Americam Journal of Physics*, vol. 32, no. 2, Article ID 142150, 1964.

[52] J. F. Scott, "Phase transitions in $BaMnF_4$," *Reports on Progress in Physics*, vol. 42, no. 6, pp. 1055–1084, 1979.

[53] D. L. Fox, D. R. Tilley, J. F. Scott, and H. J. Guggenheim, "Magnetoelectric phenomena in $BaMnF_4$ and $BaMn_{0.99}Co_{0.01}F_4$," *Physical Review B*, vol. 21, no. 7, pp. 2926–2936, 1980.

[54] D. L. Fox and J. F. Scott, "Ferroelectrically induced ferromagnetism," *Journal of Physics C*, vol. 10, no. 11, pp. L329–L331, 1977.

[55] J. F. Scott, "Mechanisms of dielectric anomalies in $BaMnF_4$," *Physical Review B*, vol. 16, no. 5, pp. 2329–2331, 1977.

[56] G. A. Samara and J. F. Scott, "Dielectric anomalies in $BaMnF_4$ at low temperatures," *Solid State Communications*, vol. 21, no. 2, pp. 167–170, 1977.

[57] O. Bonfim and G. Gehring, "Magnetoelectric effect in crystals," *Advances in Physics*, vol. 29, pp. 731–769, 1980.

[58] G. Catalan, "Magnetocapacitance without magnetoelectric coupling," *Applied Physics Letters*, vol. 88, Article ID 102902, 2006.

[59] J. F. Scott, "Electrical characterization of magnetoelectrical materials," *Journal of Materials Research*, vol. 22, no. 8, pp. 2053–2062, 2007.

[60] G. Catalan and J. F. Scott, "Magnetoelectrics: is $CdCr_2S_4$ a multiferroic relaxor?" *Nature*, vol. 448, no. 7156, pp. E4–E5, 2007.

[61] D. Staresinić, P. Lunkenheimer, J. Hemberger, K. Biljaković, and A. Loidl, "Giant dielectric response in the one-dimensional charge-ordered semiconductor $(NbSe_4)_3I$," *Physical Review Letters*, vol. 96, no. 4, Article ID 046402, 2006.

[62] P. Lunkenheimer, R. Fichtl, J. Hemberger, V. Tsurkan, and A. Loidl, "Relaxation dynamics and colossal magnetocapacitive

[effect in $CdCr_2S_4$," *Physical Review B*, vol. 72, no. 6, Article ID 060103, 2005.

[63] J. Hemberger, P. Lunkenheimer, R. Fichtl, H. A. Krug Von Nidda, V. Tsurkan, and A. Loidl, "Relaxor ferroelectricity and colossal magnetocapacitive coupling in ferromagnetic $CdCr_2S_4$," *Nature*, vol. 434, no. 7031, pp. 364–367, 2005.

[64] S. Krohns, F. Schrettle, P. Lunkenheimer, V. Tsurkan, and A. Loidl, "Colossal magnetocapacitive effect in differently synthesized and doped $CdCr_2S_4$," *Physica B*, vol. 403, no. 23-24, pp. 4224–4227, 2008.

[65] J. Hemberger, P. Lunkenheimer, R. Fichtl, H. A. K. Von Nidda, V. Tsurkan, and A. Loidl, "Magnetoelectrics: is $CdCr_2S_4$ a multiferroic relaxor? (Reply)," *Nature*, vol. 448, no. 7156, pp. E5–E6, 2007.

[66] S. Weber, P. Lunkenheimer, R. Fichtl, J. Hemberger, V. Tsurkan, and A. Loidl, "Colossal magnetocapacitance and colossal magnetoresistance in $HgCr_2S_4$," *Physical Review Letters*, vol. 96, no. 15, Article ID 157202, 2006.

[67] H. Kliem and B. Martin, "Pseudo-ferroelectric properties by space charge polarization," *Journal of Physics Condensed Matter*, vol. 20, no. 32, Article ID 321001, 2008.

[68] N. Ortega, A. Kumar, R. S. Katiyar, and J. F. Scott, "Maxwell-Wagner space charge effects on the $Pb(Zr,Ti)O_3$—$CoFe_2O_4$ multilayers," *Applied Physics Letters*, vol. 91, no. 10, Article ID 102902, 2007.

[69] E. L. Albuquerque and D. R. Tilley, "Mode mixing and dielectric function," *Solid State Communications*, vol. 26, no. 11, pp. 817–821, 1978.

[70] A. M. Glass, M. E. Lines, M. Eibschutz, F. S. L. Hsu, and H. J. Guggenheim, "Observation of anomalous pyroelectric behavior in $BaNiF_4$ due to cooperative magnetic singularity," *Communications on Physics*, vol. 2, no. 4, pp. 103–107, 1977.

[71] T. J. Negran, "Measurement of the thermal diffusivity in $BaMnF_4$ by means of its intrinsic pyroelectric response," *Ferroelectrics*, vol. 34, pp. 285–289, 1981.

[72] S. L. Hou and N. Bloembergen, "Paramagnetoelectric effects in $NiSO_4 \cdot 6H_2O$," *Physical Review*, vol. 138, pp. A1218–A1226, 1965.

[73] P. Sciau, M. Clin, J. P. Rivera, and H. Schmid, "Magnetoelectric measurements on $BaMnF_4$," *Ferroelectrics*, vol. 105, pp. 201–206, 1990.

[74] A. K. Zvezdin, G. P. Vorob'ev, and A. M. Kadomsteva, "Quadratic magnetoelectric effect and the role of the magnetocaloric effect in the magnetoelectric properties of multiferroic $BaMnF_4$," *Journal of Experimental and Theoretical Physics*, vol. 109, pp. 221–226, 2009.

[75] J. M. Perez-Mato, *Summer School on Multiferroics*, Girona, Spain, 2008.

[76] N. A. Benedek and C. J. Fennie, "Hybrid improper ferroelectricity: a mechanism for controllable polarization-magnetization coupling," *Physical Review Letters*, vol. 106, no. 10, Article ID 107204, 2011.

[77] E. T. Keve, S. C. Abrahams, and J. L. Bernstein, "Crystal structure of pyroelectric paramagnetic barium manganese fluoride, $BaMnF_4$," *The Journal of Chemical Physics*, vol. 51, no. 11, Article ID 4928, 9 pages, 1969.

[78] C. Ederer and C. J. Fennie, "Electric-field switchable magnetization via the Dzyaloshinskii-Moriya interaction: $FeTiO_3$ versus $BiFeO_3$," *Journal of Physics Condensed Matter*, vol. 20, no. 43, Article ID 434219, 2008.

[79] C. Ederer and N. A. Spaldin, "Origin of ferroelectricity in the multiferroic barium fluorides $BaMF_4$: a first principles study," *Physical Review B*, vol. 74, Article ID 024102, 2006.

[80] J. F. Scott, "Phase transitions in BaMnF$_4$," *Reports on Progress in Physics*, vol. 42, no. 6, Article ID 1055, 1979.

[81] D. E. Cox, S. M. Shapiro, R. J. Nelmes et al., "X-ray- and neutron-diffraction measurements on BaMnF$_4$," *Physical Review B*, vol. 28, no. 3, pp. 1640–1643, 1983.

[82] A. Levstik, R. Blinc, P. Kadaba, S. Cizikov, I. Levstik, and C. Filipic, "Multiple phase transitions in BaMnF$_4$," *Ferroelectrics*, vol. 4, pp. 703–707, 1976.

[83] M. Hidaka, T. Nakayama, J. F. Scott, and J. S. Storey, "Piezo-electric resonance study of structural anomalies in BaMnF$_4$," *Physica B+C*, vol. 133, no. 1, pp. 1–9, 1985.

[84] J. F. Scott, F. Habbal, and M. Hidaka, "Phase transitions in BaMnF$_4$: specific heat," *Physical Review B*, vol. 25, no. 3, pp. 1805–1812, 1982.

[85] M. Barthes-Regis, R. Almairac, P. St-Gregoire et al., "Temperature dependence of the wave vector of the incommensurate modulstion in two BaMnF$_4$ crystals—neutron and X-ray measurements," *Journal de Physique Lettres*, vol. 44, no. 19, pp. 829–835, 1983.

[86] P. St. Gregoire, M. Barthes, R. Almairac et al., "On the incommensurate phase in BaMnF$_4$," *Ferroelectrics*, vol. 53, pp. 307–310, 1984.

[87] B. B. Lavrencic and J. F. Scott, "Dynamical model for the polar-incommensurate transition in BaMnF$_4$," *Physical Review B*, vol. 24, no. 5, pp. 2711–2717, 1981.

[88] A. Levstik, V. Bobnar, C. Filipič et al., "Magnetoelectric relaxor," *Applied Physics Letters*, vol. 91, no. 1, Article ID 012905, 2007.

[89] A. Levstik, C. Filipič, V. Bobnar et al., "0.3Pb(Fe$_{1/2}$Nb$_{1/2}$)O$_3$-0.7Pb (Mg$_{1/2}$W$_{1/2}$)O$_3$: a magnetic and electric relaxor," *Journal of Applied Physics*, vol. 104, no. 5, Article ID 054113, 2008.

[90] G. Nénert and T. T. M. Palstra, "Prediction for new magneto-electric fluorides," *Journal of Physics Condensed Matter*, vol. 19, no. 40, Article ID 406213, 2007.

[91] R. Blinc, G. Tavčar, B. Zemva, and J. F. Scott, "Electron paramagnetic resonance and Mossbauer study of antiferromagnetic K$_3$Cu$_3$Fe$_2$F$_{15}$," *Journal of Applied Physics*, vol. 106, Article ID 023924, 2009.

[92] R. Blinc, G. Tavčar, B. Žemva et al., "Weak ferromagnetism and ferroelectricity in K$_3$Fe$_5$F$_{15}$," *Journal of Applied Physics*, vol. 103, Article ID 074114, 2008.

[93] R. Blinc, B. Zalar, P. Cevc et al., "^{39}K NMR and EPR study of multiferroic K$_3$Fe$_5$F$_{15}$," *Journal of Physics Condensed Matter*, vol. 21, no. 4, Article ID 045902, 2009.

[94] A. Levstik, C. Filipic, and V. Bobnar, "Polarons in magnetoelectric (K$_3$Fe$_3$Cr$_2$F$_{15}$)," *Journal of Apploed Physics*, vol. 106, Article ID 073720, 2009.

[95] R. Blinc, B. Zalar, P. Cevc et al., "^{39}K NMR and EPR study of multiferroic K$_3$Fe$_5$F$_{15}$," *Journal of Physics Condensed Matter*, vol. 21, no. 4, Article ID 045902, 2009.

[96] S. C. Abrahams, "Systematic prediction of new inorganic ferroelectrics in point group 4," *Acta Crystallographica Section B*, vol. 55, no. 4, pp. 494–506, 1999.

[97] S. C. Abrahams, "Structurally based predictions of ferroelectricity in 7 inorganic materials with space group Pba2 and two experimental confirmations," *Acta Crystallographica B*, vol. 45, pp. 228–232, 1989.

[98] K. Yamauchi and S. Picozzi, "Interplay between charge order, ferroelectricity, and ferroelasticity: tungsten bronze structures as a playground for multiferroicity," *Physical Review Letters*, vol. 105, no. 10, Article ID 107202, 2010.

[99] N. Yedukondalu, K. R. Babu, C. Bheemalingam, D. J. Singh, G. Vaitheeswaran, and V. Kanchana, "Electronic structure, optical properties, and bonding in alkaline-earth halofluoride scintillators: BaClF, BaBrF, and BaIF," *Physical Review B*, vol. 83, no. 16, Article ID 165117, 7 pages, 2011.

[100] J. F. Scott, "Raman spectra of BaClF, BaBrF, and SrClF," *The Journal of Chemical Physics*, vol. 49, no. 6, pp. 2766–2769, 1968.

[101] A. Kumar, R. S. Katiyar, R. N. Premnath, C. Rinaldi, and J. F. Scott, "Strain-induced artificial multiferroicity in Pb(Zr$_{0.53}$Ti$_{0.47}$)O$_3$/Pb(Fe$_{0.66}$W$_{0.33}$)O$_3$ layered nanostructure at ambient temperature," *Journal of Materials Science*, vol. 44, no. 19, pp. 5113–5119, 2009.

[102] A. Kumar, N. M. Murari, and R. S. Katiyar, "Investigation of dielectric and electrical behavior in Pb(Fe$_{0.66}$W$_{0.33}$)$_{0.50}$Ti$_{0.50}$O$_3$ thin films by impedance spectroscopy," *Journal of Alloys and Compounds*, vol. 469, no. 1-2, pp. 433–440, 2009.

[103] W. Peng, N. Lemee, J. L. Dellis et al., "Epitaxial growth and magnetoelectric relaxor behavior in multiferroic 0.8Pb (Fe$_{1/2}$Nb$_{1/2}$)O$_3$-0.2Pb (Mg$_{1/2}$W$_{1/2}$)O$_3$ thin films," *Applied Physics Letters*, vol. 95, no. 13, Article ID 132507, 2009.

[104] J. F. Scott, R. Palai, A. Kumar et al., "New phase transitions in perovskite oxides: BiFeO$_3$, SrSnO$_3$, and Pb(Fe$_{2/3}$W$_{1/3}$)$_{1/2}$Ti$_{1/2}$O$_3$," *Journal of the American Ceramic Society*, vol. 91, no. 6, pp. 1762–1768, 2008.

[105] A. Kumar, I. Rivera, R. S. Katiyar, and J. F. Scott, "Multiferroic Pb (Fe$_{0.66}$W$_{0.33}$)$_{0.80}$Ti$_{0.20}$O$_3$ thin films: a room-temperature relaxor ferroelectric and weak ferromagnetic," *Applied Physics Letters*, vol. 92, no. 13, Article ID 132913, 2008.

[106] R. N. P. Choudhary, D. K. Pradhan, C. M. Tirado, G. E. Bonilla, and R. S. Katiyar, "Effect of la substitution on structural and electrical properties of Ba(Fe$_{2/3}$W$_{1/3}$)O$_3$ nanoceramics," *Journal of Materials Science*, vol. 42, no. 17, pp. 7423–7432, 2007.

[107] A. Kumar, N. M. Murari, R. S. Katiyar, and J. F. Scott, "Probing the ferroelectric phase transition through Raman spectroscopy in Pb (Fe$_{2/3}$W$_{1/3}$)$_{1/2}$Ti$_{1/2}$O$_3$ thin films," *Applied Physics Letters*, vol. 90, no. 26, Article ID 262907, 2007.

[108] R. N. P. Choudhary, D. K. Pradhan, C. M. Tirado, G. E. Bonilla, and R. S. Katiyar, "Impedance characteristics of Pb(Fe$_{2/3}$W$_{1/3}$)O$_3$-BiFeO$_3$ composites," *Physica Status Solidi*, vol. 244, no. 6, pp. 2354–2366, 2007.

[109] A. Kumar, N. M. Murari, and R. S. Katiyar, "Diffused phase transition and relaxor behavior in Pb(Fe$_{2/3}$W$_{1/3}$)O$_3$ thin films," *Applied Physics Letters*, vol. 90, no. 16, Article ID 162903, 2007.

[110] R. N. P. Choudhury, C. Rodríguez, P. Bhattacharya, R. S. Katiyar, and C. Rinaldi, "Low-frequency dielectric dispersion and magnetic properties of La, Gd modified Pb(Fe$_{1/2}$Ta$_{1/2}$)O$_3$ multiferroics," *Journal of Magnetism and Magnetic Materials*, vol. 313, no. 2, pp. 253–260, 2007.

[111] W. Peng, N. Lemée, J. Holc, M. Kosec, R. Blinc, and M. G. Karkut, "Epitaxial growth and structural characterization of Pb(Fe$_{1/2}$Nb$_{1/2}$)O$_3$ thin films," *Journal of Magnetism and Magnetic Materials*, vol. 321, no. 11, pp. 1754–1757, 2009.

[112] W. Peng, N. Lemee, and M. Karkut, "Spin-lattice coupling in multiferroic thin films," *Applied Physics Leters*, vol. 94, Article ID 012509, 2009.

[113] A. Kumar, R. S. Katiyar, C. Rinaldi, S. G. Lushnikov, and T. A. Shaplygina, "Glasslike state in PbFe$_{1/2}$Nb$_{1/2}$O$_3$ single crystal," *Applied Physics Letters*, vol. 93, no. 23, Article ID 232902, 2008.

[114] M. Correa, A. Kumar, and R. S. Katiyar, "Observation of magnetoelectric coupling in glassy epitaxial Pb(Fe$_{1/2}$Nb$_{1/2}$)O$_3$ thin films," *Applied Physics Leters*, vol. 93, Article ID 192907, 2008.

[115] D. Varshney, R. N. P. Choudhary, C. Rinaldi, and R. S. Katiyar, "Dielectric dispersion and magnetic properties of Ba-modified $Pb(Fe_{1/2}Nb_{1/2})O_3$," *Applied Physics A*, vol. 89, no. 3, pp. 793–798, 2007.

[116] D. Varshney, R. N. P. Choudhary, and R. S. Katiyar, "Low frequency dielectric response of mechanosynthesized $(Pb_{0.9}Ba_{0.1})(Fe_{0.50}Nb_{0.50})O_3$ nanoceramics," *Applied Physics Letters*, vol. 89, no. 17, Article ID 172901, 2006.

[117] K. H. Fischer and J. A. Hertz, *Spin Glasses*, Cambridge University Press, Cambridge, UK, 1991.

[118] M. K. Singh, W. Prellier, M. P. Singh, R. S. Katiyar, and J. F. Scott, "Spin-glass transition in single-crystal $BiFeO_3$," *Physical Review B*, vol. 77, no. 14, Article ID 144403, 2008.

[119] M. M. Parish and P. B. Littlewood, "Magnetocapacitance in nonmagnetic composite media," *Physical Review Letters*, vol. 101, no. 16, Article ID 166602, 2008.

[120] M. K. Singh, R. S. Katiyar, W. Prellier, and J. F. Scott, "The Almeida-Thouless line in $BiFeO_3$: is bismuth ferrite a mean field spin glass?" *Journal of Physics Condensed Matter*, vol. 21, no. 4, Article ID 042202, 2009.

[121] I. E. Dzyaloshinskii, "Magnetoelectric to multiferroic phase transitions," *Europhysics Letters*, vol. 96, no. 1, Article ID 17001, 2011.

[122] R. Pirc, R. Blinc, and J. F. Scott, "Mesoscopic model of a system possessing both relaxor ferroelectric and relaxor ferromagnetic properties," *Physical Review B*, vol. 79, no. 21, Article ID 214114, 2009.

[123] A. Kumar, G. L. Sharma, R. S. Katiyar, and J. F. Scott, "Magnetic control of large roomtemperature polarization," *Journal of Physics Condensed Matter*, vol. 21, Article ID 382204, 2009.

[124] M. Kempa, S. Kamba, M. Savinov et al., "Bulk dielectric and magnetic properties of PFW-PZT ceramics: absence of magnetically switched-off polarization," *Journal of Physics Condensed Matter*, vol. 22, no. 44, Article ID 4453002, 2010.

[125] D. Lee, Y. A. Park, S. M. Yang et al., "Suppressed magnetoelectric effect in epitaxially grown multiferroic $Pb(Zr_{0.57}Tix_{0.57})O_3$-$Pb(Fe_{2/3}W_{1/3})O_3$ solid-solution thin films," *Journal of Physics D*, vol. 43, no. 45, Article ID 455403, 2010.

[126] K. S. A. Butcher, T. L. Tansley, and D. Alexiev, "An instrumental solution to the phenomenon of negative capacitances in semiconductors," *Solid-State Electronics*, vol. 39, no. 3, pp. 333–336, 1996.

[127] P. Zubko, University of Geneva, Private Communication.

[128] M. Ershov, H. C. Liu, L. Li, M. Buchanan, Z. R. Wasilewski, and A. K. Jonscher, "Negative capacitance effect in semiconductor devices," *IEEE Transactions on Electron Devices*, vol. 45, no. 10, pp. 2196–2206, 1998.

[129] R. Martínez, A. Kumar, R. Palai, J. F. Scott, and R. S. Katiyar, "Impedance spectroscopy analysis of $Ba_{0.7}Sr_{0.3}TiO_3/La_{0.7}Sr_{0.3}MnO_3$ heterostructure," *Journal of Physics D*, vol. 44, no. 10, Article ID 105302, 2011.

[130] A. Kumar, R. S. Katiyar, and J. F. Scott, "Positive temperature coefficient of resistivity and negative differential resistivity in lead iron tungstate-lead zirconate titanate," *Applied Physics Letters*, vol. 94, Article ID 212903, 2009.

[131] M. Dawber and J. F. Scott, "Negative differential resistivity and positive temperature coefficient of resistivity effect in the diffusion-limited current of ferroelectric thin-film capacitors," *Journal of Physics Condensed Matter*, vol. 16, no. 49, pp. L515–L521, 2004.

[132] A. Levstik, C. Filipič, and J. Holc, "The magnetoelectric coefficients of $Pb(Fe_{1/2}Nb_{1/2})O_3$ and $0.8Pb(Fe_{1/2}Nb_{1/2})O_3 -0.2Pb(Mg_{1/2}W_{1/2})O_3$," *Journal of Applied Physics*, vol. 103, no. 6, Article ID 066106, 2008.

[133] J. Ravez, "The inorganic fluoride and oxyfluoride ferroelectrics," *Journal de Physique III*, vol. 7, no. 6, pp. 1129–1144, 1997.

[134] S. C. Abrahams, J. Albertsson, and C. Svensson, "Structure of $Pb_5Cr_3F_{19}$ at 295K," *Acta Crystallographica B*, vol. 46, pp. 497–502, 1990.

[135] S. Sarraute, J. Ravez, R. Von Der Mühll, G. Bravic, R. S. Feigelson, and S. C. Abrahams, "Structure of ferroelectric $Pb_5Al_3F_{19}$ at 160 K, polarization Reversal and Relationship to Ferroelectric $Pb_5Cr_3F_{19}$ at 295 K," *Acta Crystallographica Section B*, vol. 52, no. 1, pp. 72–77, 1996.

[136] E. Kroumova, M. I. Aroyo, J. M. Perez-Mato, and M. R. Hundt, "Ferroelectric-paraelectric phase transitions with no group-supergroup relation between the space groups of both phases?" *Acta Crystallographica B*, vol. 57, pp. 599–601, 2001.

[137] M. Lorient, R. VonderMuhll, J. Ravez, and A. Tressaud, "Etude de la transition de phase de $(NH_4)_3FeF_6$ par mesures dielectriques et de thermocourant," *Solid State Communications*, vol. 36, no. 5, pp. 383–385, 1980.

[138] M. Lorient, R. Von der Mühll, A. Tressaud, and J. Ravez, "Polarisation remanente dans les varietes de basse temperature de $(NH_4)_3AlF_6$ ET $(NH_4)_3FeF_6$," *Solid State Communications*, vol. 40, no. 9, pp. 847–852, 1981.

[139] R. . Blinc, P. Cevc, G. Tavcar, Z. Trontelj, V. V. Laguta, and J. F. Scott, "Magnetism in $Pb_5Cr_3F_{19}$," *Physical Review B*, vol. 85, Article ID 054419, 2012.

[140] C. T. Nelson, P. Gao, J. R. Jokisaari et al., "Domain dynamics during ferroelectric switching," *Science*, vol. 334, no. 6058, pp. 968–971, 2011.

[141] C. L. Jia, K. W. Urban, M. Alexe, D. Hesse, and I. Vrejoiu, "Direct observation of continuous electric dipole rotation in flux-closure domains in ferroelectric $Pb(Zr, Ti)O_3$," *Science*, vol. 331, no. 6023, pp. 1420–1423, 2011.

[142] A. Fousková, "Increase in permittivity of ferroelectrics as a consequence of polarization reversal," *Journal of the Physical Society of Japan*, vol. 20, no. 9, pp. 1625–1628, 1965.

[143] A. Fouskova and V. Janousek, "Permittivity of rochelle salt during switching," *Czechoslovak Journal of Physics*, vol. 12, no. 5, pp. 413–416, 1962.

[144] J. Seidel, L. W. Martin, Q. He et al., "Conduction at domain walls in oxide multiferroics," *Nature Materials*, vol. 8, no. 3, pp. 229–234, 2009.

[145] A. Aird and E. K. H. Salje, "Sheet superconductivity in twin walls: experimental evidence of WO_{3-x}," *Journal of Physics Condensed Matter*, vol. 10, no. 22, pp. L377–L380, 1998.

[146] J. Guyonnet, I. Gaponenko, S. Gariglio, and P. Paruch, "Conduction at domain walls in insulating $Pb(Zr_{0.2}Ti_{0.8})O_3$ thin films," *Advanced Materials*, vol. 23, no. 45, pp. 5377–5382, 2011.

[147] S. Farokhipoor and B. Noheda, "Conduction through 71 degrees domain walls in $BiFeO_3$ thin films," *Physical Review Letters*, vol. 107, no. 12, Article ID 127601, 2011.

[148] J. Privratska and V. Janovec, "Pyromagnetic domain walls connecting antiferromagnetic non-ferroelastic magnetoelectric domains," in *Proceedings of the 3rd International Conference on Magnetoelectric Interaction Phenomena in Crystals (MEIPIC '96)*, Novgorod, Russia, September 1996.

[149] J. Privratska and V. Janovec, "Pyromagnetic domain walls connecting antiferromagnetic non-ferroelastic magnetoelectric domains," *Ferroelectrics*, vol. 204, no. 1–4, pp. 321–331, 1997.

[150] M. Daraktchiev, G. Catalan, and J. F. Scott, "Landau theory of ferroelectric domain walls in magnetoelectrics," *Ferroelectrics*, vol. 375, no. 1, pp. 122–131, 2008.

[151] M. Daraktchiev, G. Catalan, and J. F. Scott, "Landau theory of domain wall magnetoelectricity," *Physical Review B*, vol. 81, no. 22, Article ID 224118, 2010.

[152] M. Molotskii, Y. Rosenwaks, and G. Rosenman, "Ferroelectric domain breakdown," *Annual Review of Materials Research*, vol. 37, pp. 271–296, 2007.

[153] A. Agronin, M. Molotskii, Y. Rosenwaks et al., "Dynamics of ferroelectric domain growth in the field of atomic force microscope," *Journal of Applied Physics*, vol. 99, no. 10, Article ID 104102, 2006.

[154] I. I. Naumov, L. Bellaiche, and H. Fu, "Unusual phase transitions in ferroelectric nanodisks and nanorods," *Nature*, vol. 432, no. 7018, pp. 737–740, 2004.

[155] I. I. Naumov and H. X. Fu, "Vortex-to-polarization phase transformation path in lead zirconate-titanate nanoparticles," *Physical Review Letters*, vol. 98, Article ID 077603, 2007.

[156] V. L. Ginzburg, A. A. Gorbatsevich, and Y. V. Kopaev, "On the problem of super diamagnetism," *Solid State Communications*, vol. 50, pp. 339–343, 1984.

[157] A. A. Gorbatsevich and Y. V. Kopaev, "Toroidal order in ferroelectric crystals," *Ferroelectrics*, vol. 161, pp. 321–330, 1994.

[158] B. B. Van Aken, J. P. Rivera, H. Schmid, and M. Fiebig, "Observation of ferrotoroidic domains," *Nature*, vol. 449, no. 7163, pp. 702–705, 2007.

[159] P. Paruch, T. Giamarchi, T. Tybell, and J. M. Triscone, "Nanoscale studies of domain wall motion in epitaxial ferroelectric thin films," *Journal of Applied Physics*, vol. 100, no. 5, Article ID 051608, 2006.

[160] R. McQuaig, *Atomic force microscopy of ferroelectric domains [Ph.D. thesis]*, Queens University Belfast, 2012.

[161] D. J. Srolovitz and J. F. Scott, "Clock-model description of incommensurate ferroelectric films and of nematic-liquid-crystal films," *Physical Review B*, vol. 34, no. 3, pp. 1815–1819, 1986.

[162] S. Komineas, "Scattering of magnetic solitons in two dimensions," *Physica D*, vol. 155, no. 3-4, pp. 223–234, 2001.

[163] F. De Guerville, M. E. Marssi, I. Lukyanchuk, and L. Lahoche, "Ferroelectric domains in thin films and superlattices: results of numerical modeling," *Ferroelectrics*, vol. 359, no. 1, pp. 14–20, 2007.

[164] M. Axenides, S. Komineas, L. Perivolaropoulos, and M. Floratos, "Dynamics of nontopological solitons: Q balls," *Physical Review D*, vol. 61, no. 8, Article ID 085006, pp. 1–11, 2000.

[165] L. Baudry, I. A. Lukyanchuk, and A. Sene, "Inhomogeneous polarization switching in finite-size cubic ferroelectrics," *Ferroelectrics*, vol. 427, pp. 34–40, 2012.

[166] L. Baudry, I. A. Lukyanchuk, and A. Sene, "Switching properties of nano-scale multi-axial ferroelectrics: geometry and interface effects," *Integrated Ferroelectrics*, vol. 133, pp. 96–102, 2012.

[167] D. A. Allwood, G. Xiong, C. C. Faulkner, D. Atkinson, D. Petit, and R. P. Cowburn, "Magnetic domain-wall logic," *Science*, vol. 309, no. 5741, pp. 1688–1692, 2005.

[168] S. S. P. Parkin, M. Hayashi, and L. Thomas, "Magnetic domain-wall racetrack memory," *Science*, vol. 320, no. 5873, pp. 190–194, 2008.

[169] G. Catalan, J. Seidel, R. Ramesh, and J. F. Scott, "Domain wall nanoelectronics," *Reviews of Modern Physics*, vol. 84, pp. 119–156, 2012.

[170] G. Catalan, H. Béa, S. Fusil et al., "Fractal dimension and size scaling of domains in thin films of multiferroic $BiFeO_3$," *Physical Review Letters*, vol. 100, no. 2, Article ID 027602, 2008.

[171] G. A. Smolensky, V. A. Isupov, and A. I. Agranovskaya, "Ferroelectrics of the oxygen octahedral type with layered structure," *Soviet Physics*, vol. 3, no. 3, pp. 651–655, 1961.

[172] R. Palai, R. S. Katiyar, H. Schmid et al., "β phase and γ-β metal-insulator transition in multiferroic $BiFeO_3$," *Physical Review B*, vol. 77, no. 1, Article ID 014110, 2008.

[173] G. Catalan and J. F. Scott, "Physics and applications of bismuth ferrite," *Advanced Materials*, vol. 21, no. 24, pp. 2463–2485, 2009.

[174] D. C. Arnold, K. S. Knight, F. D. Morrison, and P. Lightfoot, "Ferroelectric-paraelectric transition in $BiFeO_3$: crystal structure of the orthorhombic β phase," *Physical Review Letters*, vol. 102, no. 2, Article ID 027602, 2009.

[175] D. C. Arnold, K. S. Knight, G. Catalan et al., "The β-to-γ transition in $BiFeO_3$: a powder neutron diffraction study," *Advanced Functional Materials*, vol. 20, no. 13, pp. 2116–2123, 2010.

[176] X. Martí, P. Ferrer, J. Herrero-Albillos et al., "Skin layer of $BiFeO_3$ single crystals," *Physical Review Letters*, vol. 106, no. 23, Article ID 236101, 2011.

[177] M. Polomska, W. Kaczmarek, and Z. Pajak, "Electric and magnetic properties of $(Bi_{1-X}La_X)FeO_3$ solid solutions," *Physica Status Solidi A*, vol. 23, no. 2, pp. 567–574, 1974.

[178] A. Kumar, J. F. Scott, R. Martinez, G. Srinivasan, and R. S. Katiyar, "In-plane dielectric and magnetoelectric studies of $BiFeO_3$," *Physica Status Solidi*, vol. 309, pp. 1207–1212, 2012.

[179] A. Kumar, J. F. Scott, and R. S. Katiyar, "Magnon raman spectroscopy and in-plane dielectric response in $BiFeO_3$: relation to the polomska transition," *Physical Review B*, vol. 85, Article ID 224410, 2012.

[180] M. K. Singh, R. S. Katiyar, and J. F. Scott, "New magnetic phase transitions in $BiFeO_3$," *Journal of Physics Condensed Matter*, vol. 20, no. 25, Article ID 252203, 2008.

[181] M. Cazayous, Y. Gallais, A. Sacuto, R. De Sousa, D. Lebeugle, and D. Colson, "Possible observation of cycloidal electromagnons in $BiFeO_3$," *Physical Review Letters*, vol. 101, no. 3, Article ID 037601, 2008.

[182] J. F. Scott, M. K. Singh, and R. S. Katiyar, "Critical phenomena at the 140 and 200 K magnetic phase transitions in $BiFeO_3$," *Journal of Physics Condensed Matter*, vol. 20, no. 32, Article ID 322203, 2008.

[183] R. Jarrier, X. Marti, J. Herrero-Albillos et al., "Surface phase transitions in $BiFeO_3$ below room temperature," *Physical Review B*, vol. 85, Article ID 184104, 2012.

[184] J. Herrero-Albillos, G. Catalan, J. A. Rodriguez-Velamazan, M. Viret, D. Colson, and J. F. Scott, "Neutron diffraction study of the $BiFeO_3$ spin cycloid at low temperature," *Journal of Physics Condensed Matter*, vol. 22, no. 25, Article ID 256001, 2010.

[185] M. Tonouchi, "THz radiation by optically controlled depolarization in $BiFeO_3$," in *Proceedings of the 35th International Conference on Infrared, Millimeter, and Terahertz Waves (IRMMW-THz '10)*, Rome, Italy, September 2010.

[186] L. Esaki and R. Tsu, "Superlattice and negative differential conductivity in semiconductors," *IBM Journal of Research and Development*, vol. 14, no. 1, pp. 61–65, 1970.

[187] K. M. Rabe, M. Dawber, C. Lichtensteiger, C. H. Ahn, and J. M. Triscone, "Modern physics of ferroelectrics: essential background," *Topics in Applied Physics*, vol. 105, pp. 1–30, 2007.

[188] M. Dawber, C. Lichtensteiger, M. Cantoni et al., "Unusual behavior of the ferroelectric polarization in PbTiO$_3$/SrTiO3 superlattices," *Physical Review Letters*, vol. 95, no. 17, Article ID 177601, 4 pages, 2005.

[189] J. Y. Jo, P. Chen, R. J. Sichel et al., "Nanosecond dynamics of ferroelectric/dielectric superlattices," *Physical Review Letters*, vol. 107, no. 5, Article ID 055501, 2011.

[190] R. Martínez, A. Kumar, R. Palai, R. S. Katiyar, and J. F. Scott, "Study of physical properties of integrated ferroelectric/ferromagnetic heterostructures," *Journal of Applied Physics*, vol. 107, no. 11, Article ID 114107, 2010.

[191] P. Zubko, S. Gariglio, M. Gabay, P. Ghosez, and J. M. Triscone, "Interface physics in complex oxide heterostructures," *Annual Review of CondensedMatter Physics*, vol. 2, pp. 141–165, 2011.

[192] S. M. Nakhmanson, K. M. Rabe, and D. Vanderbilt, "Predicting polarization enhancement in multicomponent ferroelectric superlattices," *Physical Review B*, vol. 73, no. 6, Article ID 060101, 2006.

[193] A. Q. Jiang, J. F. Scott, H. B. Lu, and Z. Chen, "Phase transitions and polarizations in epitaxial BaTiO$_3$/SrTiO$_3$ superlattices studied by second-harmonic generation," *Journal of Applied Physics*, vol. 93, pp. 1180–1185, 2003.

[194] S. Ríos, A. Ruediger, A. Q. Jiang, J. F. Scott, H. Lu, and Z. Chen, "Orthorhombic strontium titanate in BaTiO3-SrTiO$_3$ superlattices," *Journal of Physics Condensed Matter*, vol. 15, no. 21, pp. L305–L309, 2003.

[195] K. Johnston, X. Y. Huang, J. B. Neaton, and K. M. Rabe, "Unusual behavior of the polarization in BaTiO$_3$/SrTiO$_3$ superlattices," *Physical Review B*, vol. 71, no. 10, Article ID 100103, 2005.

[196] T. Shigenari, K. Abe, T. Takemoto et al., "Raman spectra of the ferroelectric phase of Sr Ti$_{18}$O$_3$: symmetry and domains below Tc and the origin of the phase transition," *Physical Review B*, vol. 74, no. 17, Article ID 174121, 2006.

[197] J. F. Scott, J. Bryson, M. A. Carpenter, J. Herrero-Albillos, and M. Itoh, "Elastic and anelastic properties of ferroelectric SrTi^{18}O$_3$ in the kHz-MHz regime," *Physical Review Letters*, vol. 106, no. 10, Article ID 105502, 2011.

[198] M. Takesada, M. Itoh, and T. Yagi, "Perfect softening of the ferroelectric mode in the isotope-exchanged strontium titanate of (SrTiO$_3$)-^{18}O studied by light scattering," *Physical Review Letters*, vol. 96, no. 22, Article ID 227602, 2006.

[199] M. Dawber, N. Stucki, C. Lichtensteiger, S. Gariglio, and J. M. Triscone, "New phenomena at the interfaces of very thin ferroelectric oxides," *Journal of Physics Condensed Matter*, vol. 20, no. 26, Article ID 264015, 2008.

[200] N. Reyren, S. Thiel, A. D. Caviglia et al., "Superconducting interfaces between insulating oxides," *Science*, vol. 317, no. 5842, pp. 1196–1199, 2007.

[201] S. A. Hayward, F. D. Morrison, S. A. T. Redfern et al., "Transformation processes in LaAlO$_3$: neutron diffraction, dielectric, thermal, optical, and Raman studies," *Physical Review B*, vol. 72, no. 5, Article ID 054110, 2005.

[202] V. M. Fridkin, *Photoferroelectrics*, Springer, Berlin, Germany, 1979.

[203] J. Seidel, P. Maksymovych, Y. Batra et al., "Domain wall conductivity in La-doped BiFeO$_3$," *Physical Review Letters*, vol. 105, no. 19, Article ID 197603, 2010.

[204] D. Daranciang, M. Highland, H. Wen et al., "Ultrafast photovoltaic response in ferroelectric nanolayers," *Physical Review Letters*, vol. 108, no. 8, Article ID 087601, 2012.

[205] N. Laman, M. Bieler, and H. M. Van Driel, "Ultrafast shift and injection currents observed in wurtzite semiconductors via emitted terahertz radiation," *Journal of Applied Physics*, vol. 98, no. 10, Article ID 103507, 8 pages, 2005.

[206] M. Alexe and D. Hesse, "Tip-enhanced photovoltaic effects in bismuth ferrite," *Nature Communications*, vol. 2, no. 1, article 256, 2011.

[207] A. Anikiev, L. G. Reznik, B. S. Umarov, and J. F. Scott, "Perturbed polariton spectra in optically damaged LiNbO$_3$," *Ferroelectrics Letters*, vol. 3, pp. 89–96, 1985.

[208] L. G. Reznik, A. A. Anikiev, B. S. Umarov, and J. F. Scott, "Studies of optical damage in lithium niobate in the presence of thermal gradients," *Ferroelectrics*, vol. 64, pp. 215–219, 1985.

[209] L. Landau, "The theory of phase transitions," *Nature*, vol. 138, no. 3498, pp. 840–841, 1936.

[210] A. F. Devonshire, "Theory of BaTiO$_3$," *Philosophical Magazine*, vol. 40, no. 309, pp. 1040–1063, 1949.

[211] A. F. Ermolov, A. P. Levanyuk, and A. S. Sigov, "Anomaly of high frequency sound absorption near the point of structurakl phase transitions in crystals with defects," *Fizika Tverdogo Tela*, vol. 21, no. 12, pp. 3628–3633, 1979.

[212] A. P. Levanyuk and A. S. Sigov, "The influence of defects on the properties of ferroelectrics and related materials near the point of a 2nd kind of phase transition," *Izvestia Akademii Nauk SSSR*, vol. 45, no. 9, pp. 1640–1645, 1981.

[213] A. I. Morozov and A. S. Sigov, "Point defect near the displacive phase transition," *Fizika Tverdogo Tela*, vol. 25, no. 5, pp. 1352–1356, 1983.

[214] Y. M. Kishinets, A. P. Levanyuk, A. I. Morozov, and A. S. Sigov, "Absorption coefficient and sound velocity anomalies in the vicinity of phase transitions of the 2nd kind in crystals with dislocations," *Fizika Tverdogo Tela*, vol. 29, no. 2, pp. 601–604, 1987.

[215] I. J. Fritz, "Ultrasonic attenuation and mechanism for the 250˚K antiferrodistortive transition in BaMnF$_4$," *Physical Review Letters*, vol. 35, no. 22, pp. 1511–1514, 1975.

[216] I. J. Fritz, "Ultrasonic velocity measurements near the 250˚K phase transition in BaMnF$_4$," *Physics Letters A*, vol. 51, no. 4, pp. 219–220, 1975.

[217] T. Chen, S.-J. Sheih, and J. F. Scott, "Temporal dependence of thermal self-focussing in ferroelectric Ba$_2$NaNb$_5$O$_{15}$ and Ce^{+3}:SrXBa$_{1-X}$Nb$_2$O$_6$," *Ferroelectrics*, vol. 120, pp. 115–129, 1991.

[218] V. Bobnar and Z. Kutnjak, "High-Temperature dielectric response of (1-x)PbMg$_{1/3}$Nb$_{2/3}$O$_3$ -(x)PbTiO$_3$: does burns temperature exist in ferroelectric relaxors?" *Journal of Applied Physics*, vol. 107, Article ID 084104, 2010.

[219] J. F. Scott, "Comment on 'High-Temperature dielectric response of (1-x)PbMg$_{1/3}$Nb$_{2/3}$O$_3$ –(x)PbTiO$_3$: does burns temperature exist in ferroelectric relaxors?'," *Journal of Applied Physics*, vol. 108, no. 8, Article ID 086107, 2010.

[220] K. Samanta, A. K. Arora, T. R. Ravindran, S. Ganesamoorthy, K. Kitamura, and S. Takekawa, "Raman spectroscopic study of structural transition in Sr$_x$Ba$_{1-x}$Nb$_2$O$_6$," *Vibrational Spectroscopy*, vol. 62, pp. 273–278, 2012.

[221] J. Dec, private communication.

[222] W. J. Burke, R. J. Pressley, and J. C. Slonczewski, "Raman scattering and phase transitions in stressed SrTiO$_3$," *Solid State Communications*, vol. 9, no. 2, pp. 121–124, 1971.

[223] W. J. Burke and R. J. Pressley, "Stress induced ferroelectricity in SrTiO$_3$," *Solid State Communications*, vol. 9, no. 3, pp. 191–195, 1971.

[224] S. L. Qiu, M. Dutta, H. Z. Cummins, J. P. Wicksted, and S. M. Shapiro, "Extension of the Lifshitz-point concept to first-order phase transitions: incommensurate NaNO$_2$ in a transverse electric field," *Physical Review B*, vol. 34, no. 11, pp. 7901–7910, 1986.

[225] N. A. Pertsev, A. G. Zembilgotov, and A. K. Tagantsev, "Effect of mechanical boundary conditions on phase diagrams of epitaxial ferroelectric thin films," *Physical Review Letters*, vol. 80, no. 9, pp. 1988–1991, 1998.

[226] S. P. P. Jones, D. M. Evans, M. A. Carpenter et al., "Phase diagram and phase transitions in ferroelectric tris-sarcosine calcium chloride and its brominated isomorphs," *Physical Review B*, vol. 83, no. 9, Article ID 094102, 2011.

[227] J. F. Scott, "Dielectrics," *Encyclopedia of Applied Physics*, vol. 5, pp. 25–35, 1993.

[228] K. Lee, M. Lee, K. S. Lee, and A. R. Lim, "^{1}H NMR study of the phase transitions of trissarcosine calcium chloride single crystals at low temperature," *Journal of Physics and Chemistry of Solids*, vol. 66, no. 10, pp. 1739–1743, 2005.

[229] H. Haga, A. Onodera, H. Yamashita, and Y. Shiosaki, "New phase transition in ferroelectric tris-sarcosine calcium chloride at low temperature," *Journal of the Physical Society of Japan*, vol. 62, pp. 1857–1859, 1993.

[230] R. B. Laughlin, G. G. Lonzarich, P. Monthoux, and D. Pines, "The quantum criticality conundrum," *Advances in Physics*, vol. 50, no. 4, pp. 361–365, 2001.

[231] E. Fradkin and S. A. Kivelson, "Electron nematic phases proliferate," *Science*, vol. 327, no. 5962, pp. 155–156, 2010.

[232] S. Rowley, R. Smith, and M. Dean, "Ferromagnetic and ferroelectric quantum phase transitions," *Physica Status Solidi B*, vol. 247, pp. 469–475, 2010.

[233] J. F. Scott, R. Pirc, A. Levstik, C. Filipic, and R. Blinc, "Resolving the quantum criticality paradox in O-18 isotopic SrTiO$_3$," *Journal of Physics Condensed Matter*, vol. 18, no. 16, pp. L205–L208, 2006.

[234] W. Windsch, H. Braeter, U. Gutteck, B. Malige, and B. Milsch, "The concentration dependence of the ferroelectric transition temperature of the solid solution of TSCC and TSCB," *Solid State Communications*, vol. 42, no. 12, pp. 839–842, 1982.

[235] H. Suzuki, S. Naher, T. Shimoguchi, M. Mizuno, A. Ryu, and H. Fujishita, "X-ray diffraction measurement below 1 K," *Journal of Low Temperature Physics*, vol. 128, no. 1-2, pp. 1–7, 2002.

[236] S. E. Rowley, L. J. Spalek, R. P. Smith et al., "Ferroelectric quantum criticality," *Nature*. In press.

[237] S. E. Rowley, R. Smith, M. L. Sutherland, P. Alireza, S. S. Saxena, and G. G. Lonzarich, "Quantum criticality and unconventional order in magnetic and dielectric material," *Journal of Physics: Conference Series*, vol. 400, Article ID 032048, 2012.

[238] A. V. Bune, V. M. Fridkin, S. Ducharme et al., "Two-dimensional ferroelectric films," *Nature*, vol. 391, no. 6670, pp. 874–877, 1998.

[239] R. Gaynutdinov, S. Yudin, S. Ducharme, and V. Fridkin, "Homogeneous switching in ultrathin ferroelectric films," *Journal of Physics Condensed Matter*, vol. 24, no. 1, Article ID 015902, 2012.

[240] L. Zhang, "Field induced phase transition and dielectric energy density in PVDF terpolymers," *Europhysics Letters*, vol. 91, Article ID 47001, 2010.

[241] J. F. Scott, "Switching of ferroelectrics without domains," *Advanced Materials*, vol. 22, no. 46, pp. 5315–5317, 2010.

[242] M. J. Highland, T. T. Fister, M. I. Richard et al., "Polarization switching without domain formation at the intrinsic coercive field in ultrathin ferroelectric PbTiO$_3$," *Physical Review Letters*, vol. 105, no. 16, Article ID 167601, 2010.

[243] J. F. Scott, "Lattice perturbations in CaWO$_4$ and CaMoO$_4$," *The Journal of Chemical Physics*, vol. 48, no. 2, pp. 874–878, 1968.

[244] J. F. Scott, "Dipole-dipole interactions in tungstates," *The Journal of Chemical Physics*, vol. 49, no. 1, pp. 98–100, 1968.

[245] W. Ma and L. E. Cross, "Flexoelectricity of barium titanate," *Applied Physics Letters*, vol. 88, Article ID 232902, 2006.

[246] W. Ma and L. E. Cross, "Flexoelectric effect in ceramic lead zirconate titanate," *Applied Physics Letters*, vol. 86, no. 7, Article ID 072905, 2005.

[247] A. K. Tagantsev, "Piezoelectricity and flexoelectricity in crystalline dielectrics," *Physical Review B*, vol. 34, no. 8, pp. 5883–5889, 1986.

[248] P. Zubko, G. Catalan, P. R. L. Welche, A. Buckley, and J. F. Scott, "Strain gradient induced polarization in SrTiO$_3$," *Physical Review Letters*, vol. 99, Article ID 167601, 2007.

[249] J. Hong, G. Catalan, J. F. Scott, and E. Artacho, "The flexoelectricity of barium and strontium titanates from first principles," *Journal of Physics Condensed Matter*, vol. 22, no. 11, Article ID 112201, 2010.

[250] R. Resta, "Towards a bulk theory of flexoelectricity," *Physical Review Letters*, vol. 105, no. 12, Article ID 127601, 2010.

[251] J.-W. Hong and D. Vanderbilt, "First-principles theory of frozen-ion flexoelectricity," *Physical Review B*, vol. 84, no. 18, Article ID 180101, 2011.

[252] H. Zhou, J. Hong, Y. Zhang, F. Li, Y. Pei, and D. Fang, "External uniform electric field removing flexoelectric effect in epitaxial ferroelectric thin films," *Europhysics Letters*, vol. 99, no. 4, Article ID 47003.

[253] D. Lee, A. Yoon, S. Y. Jang et al., "Giant flexoelectric effect in ferroelectric epitaxial thin films," *Physical Review Letters*, vol. 107, no. 5, Article ID 057602, 2011.

[254] H. Lu, C. W. Bark, D. E. De los Ojos et al., "Mechanical writing of ferroelectric polarization," *Science*, vol. 336, no. 6077, pp. 59–61, 2012.

[255] L. E. Cross, "Relaxor ferroelectrics," *Ferroelectrics*, vol. 76, no. 3-4, pp. 241–267, 1987.

[256] M. D. Glinchuk, "Relaxor ferroelectrics: from cross superparaelectric model to random field theory," *British Ceramic Transactions*, vol. 103, no. 2, pp. 76–82, 2004.

[257] R. Pirc and R. Blinc, "Spherical random-bond-random-field model of relaxor ferroelectrics," *Physical Review B*, vol. 60, no. 19, pp. 13470–13478, 1999.

[258] R. Pirc and R. Blinc, "Vogel-Fulcher freezing in relaxor ferroelectrics," *Physical Review B*, vol. 76, no. 2, Article ID 020101, 2007.

[259] Z. Kutnjak, J. Petzelt, and R. Blinc, "The giant electromechanical response in ferroelectric relaxors as a critical phenomenon," *Nature*, vol. 441, no. 7096, pp. 956–959, 2006.

[260] J. Dec, W. Kleemann, and V. V. Shvartsman, "From mesoscopic to global polar order in the uniaxial relaxor ferroelectric Sr$_{0.8}$Ba$_{0.2}$Nb$_2$O$_6$," *Applied Physics Letters*, vol. 100, no. 5, Article ID 052903, 2012.

[261] J. F. Scott, "Absence of true critical exponents in relaxor ferroelectrics: the case for defect dynamics," *Journal of Physics Condensed Matter*, vol. 18, no. 31, pp. 7123–7134, 2006.

[262] W. Kleemann, J. Dec, V. V. Shvartsman, Z. Kutnjak, and T. Braun, "Two-dimensional ising model criticality in a three-dimensional uniaxial relaxor ferroelectric with frozen polar nanoregions," *Physical Review Letters*, vol. 97, no. 6, Article ID 065702, 2006.

[263] D. Pajic, Z. Jaglicic, M. Jagodic et al., "Low temperature magnetic behaviour of PZT-PFW bulk multiferroic ceramics," *Journal of Physics Conference Series*, vol. 303, Article ID 012065, 2011.

[264] H. Zheng, J. Wang, S. E. Lofland et al., "Multiferroic $BaTiO_3$-$CoFe_2O_4$ nanostructures," *Science*, vol. 303, no. 5658, pp. 661–663, 2004.

[265] C. W. Nan, M. I. Bichurin, S. Dong, D. Viehland, and G. Srinivasan, "Multiferroic magnetoelectric composites: historical perspective, status, and future directions," *Journal of Applied Physics*, vol. 103, no. 3, Article ID 031101, 2008.

[266] C. Israel, N. D. Mathur, and J. F. Scott, "A one-cent room-temperature magnetoelectric sensor," *Nature Materials*, vol. 7, no. 2, pp. 93–94, 2008.

[267] Z. Hu, M. Tian, B. Nysten, and A. M. Jonas, "Regular arrays of highly ordered ferroelectric polymer nanostructures for non-volatile low-voltage memories," *Nature Materials*, vol. 8, no. 1, pp. 62–67, 2009.

[268] K. Asadi, H. J. Wondergem, R. S. Moghaddam et al., "Organic ferroelectric opto-electronic memories," *Materials Today*, vol. 14, no. 12, pp. 592–599, 2011.

[269] T. J. Reece, S. Ducharme, A. V. Sorokin, and M. Poulsen, "Nonvolatile memory element based on a ferroelectric polymer Langmuir-Blodgett film," *Applied Physics Letters*, vol. 82, no. 1, pp. 142–144, 2003.

[270] M.-Y. Li, N. Stingelin, J. Jasper et al., "Processing and low voltage switching of organic ferroelectric phase-separated bistable diodes," *Advanced Functional Materials*, vol. 22, no. 12, pp. 2750–2757, 2012.

[271] P. Kobeko and J. Kurtschatov, "Pielectric (sic) properties of Rochelle salt crystals," *Zeitschrift für Physik*, vol. 66, no. 3-4, pp. 192–205, 1930.

[272] Y. Liu, X.-P. Peng, X.-J. Lou, and H. Zhou, "Intrinsic electrocaloric effect in ultrathin ferroelectric capacitors," *Applied Physics Letters*, vol. 100, Article ID 192902, 2012.

[273] C. Israel, S. Kar-Narayan, and N. D. Mathur, "Eliminating the temperature dependence of the response of magnetoelectric magnetic-Field sensors," *IEEE Sensors Journal*, vol. 10, no. 5, pp. 914–917, 2010.

[274] S. Kar-Narayan and N. D. Mathur, "Direct and indirect electrocaloric measurements using multilayer capacitors," *Journal of Physics D*, vol. 43, no. 3, Article ID 032002, 2010.

[275] S. Kar-Narayan and N. D. Mathur, "Predicted cooling powers for multilayer capacitors based on various electrocaloric and electrode materials," *Applied Physics Letters*, vol. 95, no. 24, Article ID 242903, 2009.

[276] C. Israel, S. Kar-Narayan, and N. D. Mathur, "Converse magnetoelectric coupling in multilayer capacitors," *Applied Physics Letters*, vol. 93, no. 17, Article ID 173501, 2008.

[277] Q. M. Zhang, V. Bharti, and X. Zhao, "Giant electrostriction and relaxor ferroelectric behavior in electron- irradiated poly(vinylidene fluoride-trifluoroethylene) copolymer," *Science*, vol. 280, no. 5372, pp. 2101–2104, 1998.

[278] S. G. Lu, B. Rožič, Q. M. Zhang et al., "Organic and inorganic relaxor ferroelectrics with giant electrocaloric effect," *Applied Physics Letters*, vol. 97, no. 16, Article ID 162904, 2010.

[279] S. Prosandeev, I. Ponomareva, and L. Bellaiche, "Electrocaloric effect in bulk and low-dimensional ferroelectrics from first principles," *Physical Review B*, vol. 78, no. 5, Article ID 052103, 2008.

[280] Y. Liu, Y. Zhang, M.-J. Chen, Q. N. Chen, and J. Li, "Biological ferroelectricity discovered in aorta walls by piezo force microscopy," *Physical Review Letters*, vol. 108, Article ID 078103, 2012.

[281] T. Li and K. Zeng, "Piezoelectric properties and surface potential of green abalone shell studied by scanning probe microscopy techniques," *Acta Materialia*, vol. 59, no. 9, pp. 3667–3679, 2011.

[282] A. Heredia, V. Meunier, I. K. Bdikin et al., "Nanoscale ferroelectricity in crystalline γ-glycine," *Advanced Functional Materials*, vol. 22, no. 14, pp. 2996–3003, 2012.

[283] J. F. Scott, "Electrocaloric materials," *Annual Review of Materials Research*, vol. 41, pp. 229–240, 2011.

[284] R. Plumlee, Sandia Laboratories Report SC-RR-67-730, 1967.

[285] X. Lou, X. Hu, M. Zhang, S. A. T. Redfern, E. A. Kafadaryan, and J. F. Scott, "Nano-shorts," *Reviews on Advanced Materials Science*, vol. 10, no. 3, pp. 197–204, 2005.

[286] X. Lou, X. Hu, M. Zhang, F. D. Morrison, S. A. T. Redfern, and J. F. Scott, "Phase separation in lead zirconate titanate and bismuth titanate during electrical shorting and fatigue," *Journal of Applied Physics*, vol. 99, no. 4, Article ID 044101, 2006.

[287] R. Waser, R. Dittmann, C. Staikov, and K. Szot, "Redox-based resistive switching memories nanoionic mechanisms, prospects, and challenges," *Advanced Materials*, vol. 21, no. 25-26, pp. 2632–2663, 2009.

[288] D. S. Jeong, R. Thomas, R. S. Katiyar et al., "Emerging memories: resistive switching mechanisms and current status," *Reports on Progress in Physics*, vol. 75, Article ID 076502, 2012.

[289] P. W. M. Blom, R. M. Wolf, J. F. M. Cillessen, and M. P. C. M. Krijn, "Ferroelectric Schottky diode," *Physical Review Letters*, vol. 73, no. 15, pp. 2107–2110, 1994.

[290] A. Q. Jiang, C. Wang, K. J. Jin et al., "A resistive memory in semiconducting $BiFeO_3$ thin-film capacitors," *Advanced Materials*, vol. 23, no. 10, pp. 1277–1281, 2011.

[291] B. Noheda, private communication.

[292] P. Paruch, A. B. Posadas, M. Dawber, C. H. Ahn, and P. L. McEuen, "Polarization switching using single-walled carbon nanotubes grown on epitaxial ferroelectric thin films," *Applied Physics Letters*, vol. 93, no. 13, Article ID 132901, 2008.

[293] S. Kawasaki, G. Catalan, H. J. Fan, and J. F. Scott, "Conformal oxide coating of carbon nanotubes," *Applied Physics Letters*, vol. 92, Article ID 053109, 2008.

[294] A. Kumar, S. G. Shivareddy, M. Correa et al., "Ferroelectric-carbon nanotube memory devices," *Nanotechnology*, vol. 23, no. 16, Article ID 165702, 2012.

[295] F. Mendoza, A. Kumar, R. Martinez et al., "Conformal coating of ferroelectric oxides on carbon nanotubes," *Europhysics Letters*, vol. 97, no. 2, Article ID 27001, 2012.

[296] Y. Zheng, X. N. Guang, C.-T. Toh, C.-Y. Tan, K. Yao, and B. Özyilmaz, "Graphene field-effect transistors with ferroelectric gating," *Physical Review Letters*, vol. 105, Article ID 166602, 2010.

[297] F. D. Morrison, Y. Luo, I. Szafraniak et al., "Ferroelectric nanotubes," *Reviews of Advances in Materials Science*, vol. 4, pp. 114–122, 2003.

[298] J. Hong, G. Catalan, D. N. Fang, E. Artacho, and J. F. Scott, "Topology of the polarization field in ferroelectric nanowires from first principles," *Physical Review B*, vol. 81, no. 17, Article ID 172101, 2010.

[299] V. L. Gurevuch and A. K. Tagantsev, "Second sound in ferroelectrics," *Journal of Experimental and Theoretical Physics*, vol. 67, no. 1, pp. 206–212, 1988.

[300] B. Hehlen, L. Arzel, A. K. Tagantsev et al., "Brillouin-scattering observation of the TA-TO coupling in SrTiO$_3$," *Physical Review B*, vol. 57, no. 22, pp. R13989–R13992, 1998.

[301] A. Koreeda, R. Takano, and S. Saikan, "Second sound in SrTiO$_3$," *Physical Review Letters*, vol. 99, no. 26, Article ID 265502, 2007.

[302] E. Courtens, B. Hehlen, E. Farhi, and A. K. Tagantsev, "Optical mode crossings and the low temperature anomalies of SrTiO$_3$," *Zeitschrift fur Physik B-Condensed Matter*, vol. 104, no. 4, pp. 641–642, 1997.

[303] P. A. Fleury, J. F. Scott, and J. M. Worlock, "Soft phonon modes and the 110°K phase transition in SrTiO$_3$," *Physical Review Letters*, vol. 21, no. 1, pp. 16–19, 1968.

[304] R. Blinc, V. V. Laguta, B. Zalar, M. Itoh, and H. Krakauer, "^{17}O quadrupole coupling and the origin of ferroelectricity in isotopically enriched BaTiO$_3$ and SrTiO$_3$," *Journal of Physics Condensed Matter*, vol. 20, no. 8, Article ID 085204, 2008.

[305] J. F. Scott, M. A. Carpenter, and E. K.-H. Salje, "Domain wall damping and elastic softening in SrTiO$_3$, evidence for polar twin walls," *Physical Review Letters*, vol. 109, no. 18, Article ID 187601, 2012.

[306] M. Bartkowiak, private communication.

[307] M. Bartkowiak, G. J. Kearley, M. Yethiraj, and A. M. Mulders, "Symmetry of ferroelectricphase of (SrTiO$_3$)-^{18}O determined by ab initio calculations," *Physical Review B*, vol. 83, no. 6, Article ID 064102, 2011.

[308] E. Y. Tsymbal, A. Gruverman, V. Garcia, M. Bibes, and A. Barthelemy, "Ferroelectric and multiferroic tunnel junctions," *MRS Bulletin*, vol. 37, no. 2, pp. 138–143, 2012.

[309] M. Bibes and A. Barthélémy, "Multiferroics: towards a magnetoelectric memory," *Nature Materials*, vol. 7, no. 6, pp. 425–426, 2008.

[310] A. Chanthbouala, A. Crassous, V. Garcia et al., "Solid-state memories based on ferroelectric tunnel junctions," *Nature Nanotechnology*, vol. 7, no. 2, pp. 101–104, 2012.

[311] M. Gajek, M. Bibes, S. Fusil et al., "Tunnel junctions with multiferroic barriers," *Nature Materials*, vol. 6, no. 4, pp. 296–302, 2007.

[312] L. E. Hueso, J. M. Pruneda, V. Ferrari et al., "Transformation of spin information into large electrical signals using carbon nanotubes," *Nature*, vol. 445, no. 7126, pp. 410–413, 2007.

[313] R. E. Cohen, "Origin of ferroelectricity in perovskite oxides," *Nature*, vol. 358, no. 6382, pp. 136–138, 1992.

[314] N. A. Hill, "Why are there so few magnetic ferroelectrics?" *Journal of Physical Chemistry B*, vol. 104, no. 29, pp. 6694–6709, 2000.