

## 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 Magnetolectrics

*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

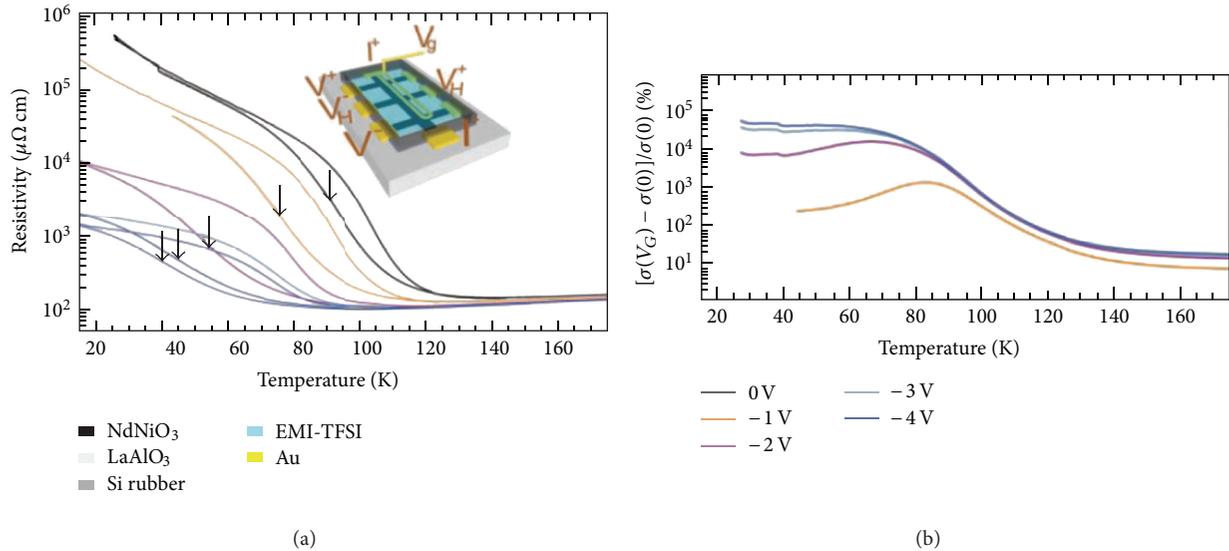


FIGURE 1: Electric Field Control of the Metal-Insulator Transition in Ultrathin  $\text{NdNiO}_3$  Films [20]. (Inset): schematic of the MIT-FET or Metal-Insulator Transition Field Effect Transistor. In this example, the gate is an ionic liquid, capable of providing more surface charge than conventional solid state dielectrics. The channel is  $\text{NdNiO}_3$ , 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 ( $\text{BiFeO}_3$ ), 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 ( $\text{nC/cm}^2$  rather than  $\mu\text{C/cm}^2$ ) and hence offer a more limited range of potential applications.

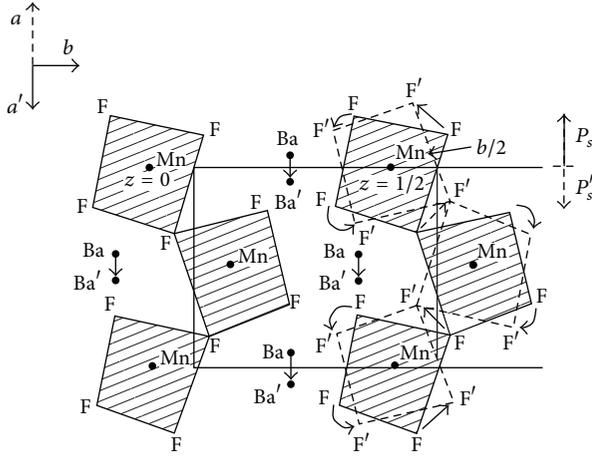
A different family of multiferroic is exemplified by  $\text{PbFe}_{1/2}\text{Ta}_{1/2}\text{O}_3$  [29] and  $\text{PbFe}_{1/2}\text{Nb}_{1/2}\text{O}_3$  [30]. When mixed with PZT— $\text{PbZr}_{1-x}\text{Ti}_x\text{O}_3$ —it produces a wide range of single-phase compounds with quaternary occupation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

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

The related compounds of  $\text{PbFe}_{2/3}\text{W}_{1/3}\text{O}_3$ -PZT are also multiferroic at temperatures near ambient, but their magnetolectric 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.

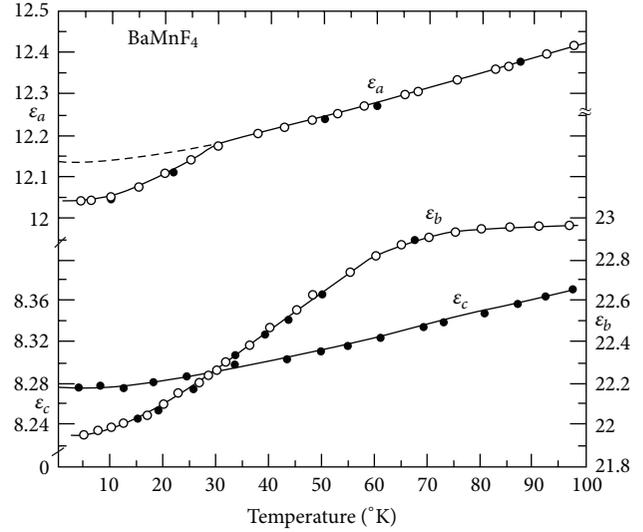
Soon after their experimental proof [35, 36] of linear magnetolectric coupling in  $\text{Cr}_2\text{O}_3$ , Astrov et al. made related measurements [37–41] in  $\text{BaMnF}_4$  and  $\text{BaCoF}_4$ . But these results differed qualitatively from those in chromia: the  $\text{BaMF}_4$  effect is a 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  $\text{MF}_6$  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  $\text{MF}_6$  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  $\text{BaMnF}_4$  has weak ferromagnetism (3 mrad canting angle), and that the

FIGURE 2: Structure of BaMnF<sub>4</sub>.

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<sub>4</sub> and BaCoF<sub>4</sub> 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<sub>4</sub>. Moreover, BaMnF<sub>4</sub> is incommensurately modulated, whereas BaCoF<sub>4</sub> is not.

Other magnetoelectric effects in BaMnF<sub>4</sub> 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  $\epsilon(T)$  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  $\epsilon(T)$  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<sub>4</sub>. However, a more comprehensive model was detailed by Fox et al., [53] which explains the magnitude,



○ Decreasing  $T$   
● Increasing  $T$

FIGURE 3: Dielectric anomaly at  $T$  (Neel) in BaMnF<sub>4</sub> [56].

temperature dependence, and rather importantly, the signs of the dielectric constant changes at both  $T_N$  in BaMnF<sub>4</sub> 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<sub>1/2</sub>Ta<sub>1/2</sub>O<sub>3</sub> 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<sub>4</sub>. 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<sub>4</sub> [73, 74].

Ferroelectrically-induced ferromagnetism: in 1979 Scott showed [52] that it is plausible that the weak ferromagnetism in BaMnF<sub>4</sub> 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

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

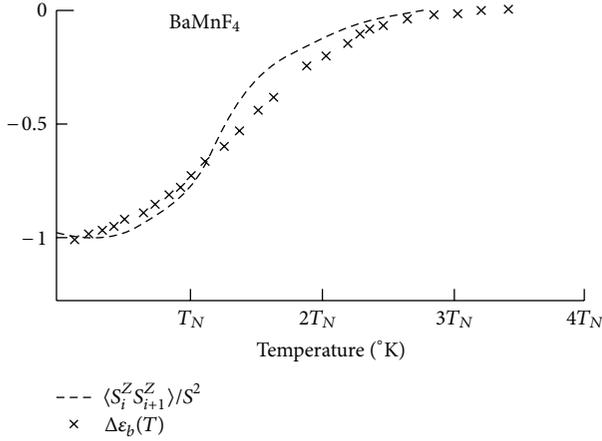


FIGURE 4: Dielectric anomaly at the temperature at which in-plane magnetic ordering sets in for BaMnF<sub>4</sub> [56].

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<sub>4</sub> 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<sub>4</sub>, since  $P$  is along the  $a$ -axis;  $L$  is along the  $b$ -axis; and  $M$  is along  $c$ . However, in BaCoF<sub>4</sub>,  $P$  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

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

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

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

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

In addition to explaining the induced ferromagnetism, a magnetoelectric theory of BaMnF<sub>4</sub> should be able to explain

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 $m'$ ;<br>$M$ parallel $m'$     | Allowed                           |
| $m$  | $P$ parallel $m$ ;<br>$M$ perpendicular $m$  | Allowed                           |
| $2'$   | $P$ perpendicular $M$ ;<br>$P$ parallel $2'$ | Allowed                           |
| $m'm'2'$   | $P$ parallel $2'$ ;<br>$M$ perpendicular $m$ | Allowed                           |
| $2$ or $m'm'2$                                     | $P$ parallel $M$ parallel $2$                | Forbidden                         |
| $3$ or $3m'$ or $4$ ;<br>$4m'm'$ or $6$ or $6m'm'$ | $P$ parallel $M$ parallel principal axis     | Forbidden                         |

the dielectric anomalies. The assumed free energy of Fox et al. was

$$G(P, M, L) = \frac{1}{2}AL^2 - \frac{1}{2}aL_z^2 + \left(\frac{1}{4}\right)B'L^4 + \frac{1}{2}BM^2 + (b_0 + b_1p + b_2p^2)M_xL_z - \gamma M_zL_x + \frac{1}{2}D(L \cdot M)^2 + \epsilon p^2 - P \cdot E - M \cdot H, \quad (4)$$

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<sub>2/3</sub>W<sub>1/3</sub>O<sub>3</sub> on sections of this review that follow.

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

$$\Delta\epsilon(T) = \frac{(b_1^2 + b_0b_2)L^2(T)}{(B\epsilon_0\epsilon^2)}. \quad (5)$$

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  $b_0b_2$ ; 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<sub>4</sub>

at and below  $T_N = 29$  K, but it cannot explain the larger dielectric anomaly along the  $b$ -axis near  $T_{2D} = \text{ca. } 90$  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  $\text{ca. } T = 3T_N$ . 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  $\text{BaMF}_4$  family has been published by Ederer and Spaldin [79].

There is an added complication for careful analysis of  $\text{BaMnF}_4$ , 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  $\text{MnF}_6$  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  $\text{K}_3\text{Fe}_2^+\text{Fe}_3^+\text{F}_{15}$  whose structure is diagrammed in Figure 5. This is in fact an unusual ferromagnetic ferroelectric, with two  $\text{Fe}^{+3}$  ions and three  $\text{Fe}^{+2}$  ions per formula group (4 $\text{Fe}^{+3}$  and 6 $\text{Fe}^{+2}$  ions per primitive unit cell). It is possible to substitute separately for the  $\text{Fe}^{+2}$  ions, giving for example  $\text{K}_3\text{Fe}_2^+\text{Cu}_3\text{F}_{15}$ , and for the  $\text{Fe}^{+3}$  ions, giving  $\text{K}_3\text{Fe}_3^+\text{Cr}_2\text{F}_{15}$ . 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  $\text{A}_3\text{Fe}_5\text{F}_{15}$  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  $\text{K}_3\text{Fe}_2^+\text{Fe}_3^+\text{F}_{15}$  with certain predictions of electronic character for its magnetoelectric transition. Unfortunately she had been unaware of the fact that the

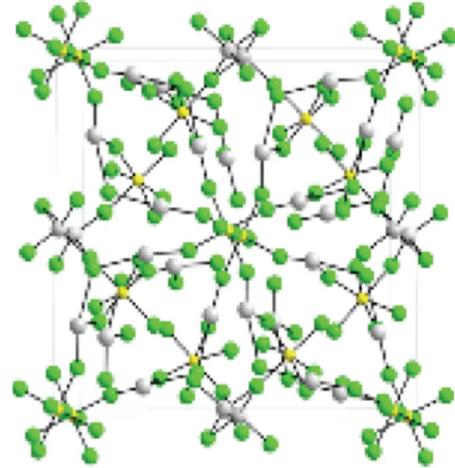


FIGURE 5: Structure of  $\text{K}_3\text{Fe}_5\text{F}_{15}$ .

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  $\text{BaClF}$  [99] where the authors were unaware of the Raman phonon experiments [100].

**3.4. Magnetolectric 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  $\text{PbFe}_{1/2}\text{Nb}_{1/2}\text{O}_3$  and  $\text{PbMg}_{1/2}\text{W}_{1/2}\text{O}_3$ .

A large amount of research has been carried out on three lead-ferrite-based relaxors:  $\text{PbFe}_{2/3}\text{W}_{1/3}\text{O}_3$  [101–109];  $\text{PbFe}_{1/2}\text{Ta}_{1/2}\text{O}_3$  [110]; and  $\text{PbFe}_{1/2}\text{Nb}_{1/2}\text{O}_3$  [111–116] and on their solid solutions with PZT (lead zirconate titanate). The Ta and Nb compounds 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  $\text{BaTiO}_3$  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  $z\nu$  reported in the magnon cross sections of  $\text{BiFeO}_3$  [120]; however, we note that cluster models also give very low values ca. 1–2.

3.5.  $\text{PbFe}_{2/3}\text{W}_{1/3}\text{O}_3$  (“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,  $\chi_{\text{ME}} < [\chi_{\text{elec}}\chi_{\text{mag}}]^{1/2}$ . 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  $\text{Cr}_2\text{O}_3$  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  $\tau$  is increased with applied field  $H$ . The explicit dependence of  $\tau(H)$  is given by

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

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 out of the frequency range of the detector. In the data shown in [123]  $H_c = 0.92T$ , and

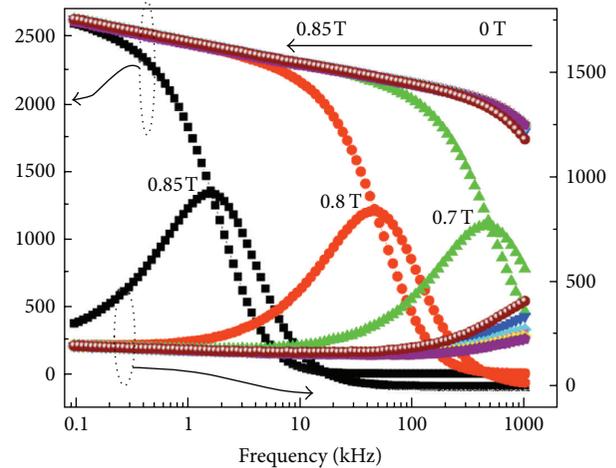


FIGURE 6: Real (left axis and upper curves) and imaginary (right axis and lower curves) dielectric responses in lead iron tungstate/lead zirconate-titanate at ambient temperatures and different magnetic field  $H$ , showing shift in peak frequency versus  $H$ .

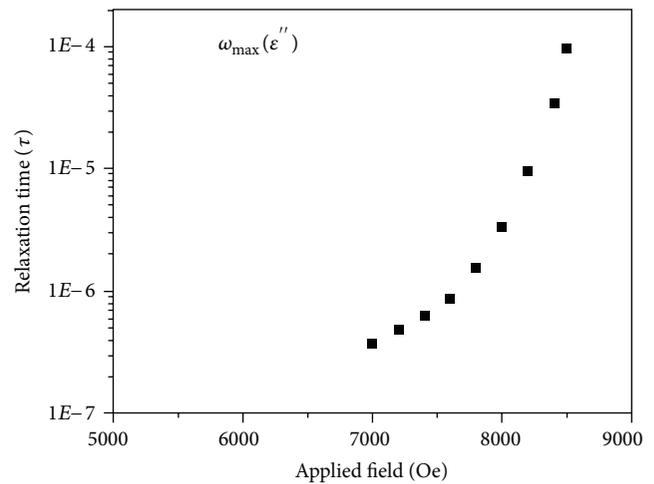


FIGURE 7: Dielectric (ferroelectric) polarization relaxation time in  $\text{PbFe}_{2/3}\text{W}_{1/3}\text{O}_3/\text{PZT}$  as a function of applied magnetic field. There are no adjustable parameters except for the time at  $H = 0$  and the value  $H_c$ . The curve is a least squares fit to (6).

the polarization relaxation time increases from ca. 200 ns at  $H = 0$  to 100  $\mu\text{s}$  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  $\text{Pb}(\text{Fe,W})\text{O}_3$ ,  $\text{Pb}(\text{Fe,Ta})\text{O}_3$ , and  $\text{Pb}(\text{Fe,Nb})\text{O}_3$  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)  $\text{Pb}_5\text{Cr}_3\text{F}_{19}$  family [134, 135],
- (b)  $\text{Sr}_3(\text{FeF}_6)_2$  family [136],
- (c)  $(\text{NH}_4)_2\text{FeF}_6$  family [137, 138],
- (d) Oxyfluorides.

Of these  $\text{Pb}_5\text{Cr}_3\text{F}_{19}$  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 vertex structures, of which some are vortices [140, 141] (having winding number 1 is not sufficient to make a vortex;  $\text{div } P$ —an explosion—also has winding number +1 but lacks a  $\text{curl } \times P$ ) 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]

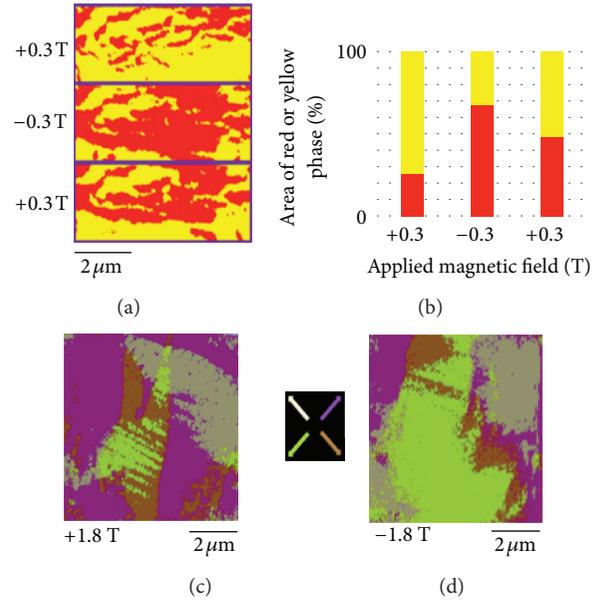


FIGURE 8: Ferroelectric domains (white =  $+P$ ; dark =  $-P$ ) at  $T = 295$  K for + and  $-0.3$  Tesla applied magnetic fields [33].

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, erroneous 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

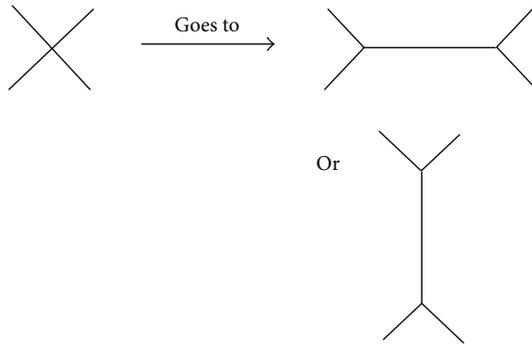


FIGURE 9: Threefold and fourfold vertex structures in ferroelectrics [161]. Reference [160] reports the coalescence of the threefold vertex pairs into a single fourfold vertex, shown to be theoretically possible by Srolovitz and Scott, followed by reseparation at 90 degrees. For a more general skyrmion-based theory, see Komineas [162].

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 McQuaig 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<sub>3</sub>.

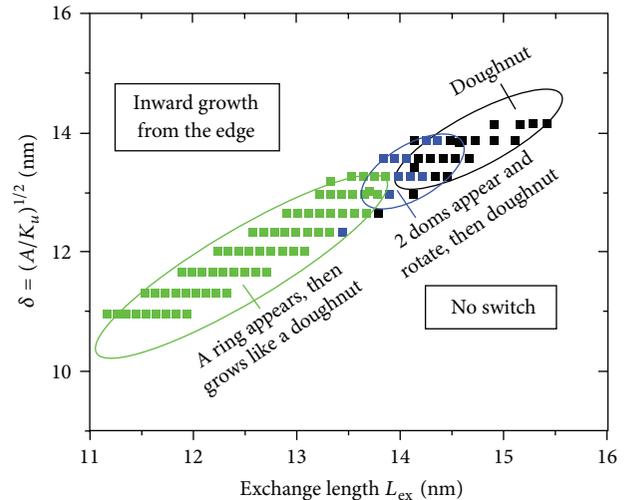


FIGURE 10: Parameter-space diagram showing the dependence of the occurrence of doughnut shaped concentric domains in thin films upon film disk diameter for circular specimens (H-J Fan and J. F. Scott, unpublished).

| Effect of shape                       |   |  |                     |                          |
|---------------------------------------|---|--|---------------------|--------------------------|
| Negative field<br>( $\times 10^3$ Oe) | All shapes have similar volumes                           |  |                     | Larger squares           |
| 6.2                                   |   |  |                     |                          |
| 6.5                                   |   |  |                     |                          |
| 7                                     |   |  |                     |                          |
| 7.5                                   |   |  |                     |                          |
| 8                                     |   |  |                     |                          |
| 8.2                                   |   |  |                     |                          |
| $\geq 8.4$                            |   |  |                     |                          |
|                                       |   |  | Single-domain grows | Multi-domain no doughnut |
|                                       | Starts with a narrow ring-shaped domain, which then grows |  |                     |                          |

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).

In the initial study of BiFeO<sub>3</sub>, 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<sub>3</sub> 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<sub>3</sub> are propagating modes well above ambient temperatures, making them useful for THz devices. The use of

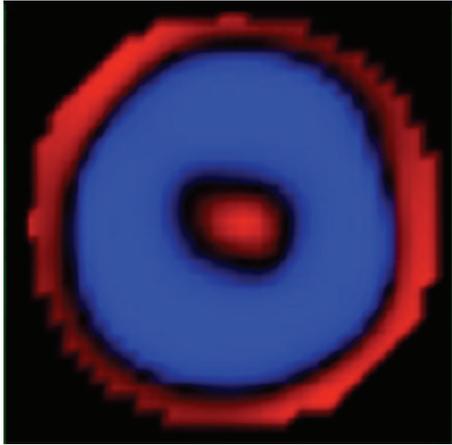


FIGURE 12: Experimental domain structure, resembling second-order Bessel function, in a PZT 1-micron diameter thin film [12].

BiFeO<sub>3</sub> 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<sub>3</sub>) [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<sub>3</sub> with  $P$  along [001] is interlaced with SrTiO<sub>3</sub>, 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<sub>3</sub> 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<sub>3</sub> 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<sub>3</sub>/PbTiO<sub>3</sub> 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<sub>3</sub>/SrTiO<sub>3</sub> interfaces [200]. In this regard the studies of oxygen vacancies and conduction in pure LaAlO<sub>3</sub> [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 lattice will electrically cause these e-h pairs

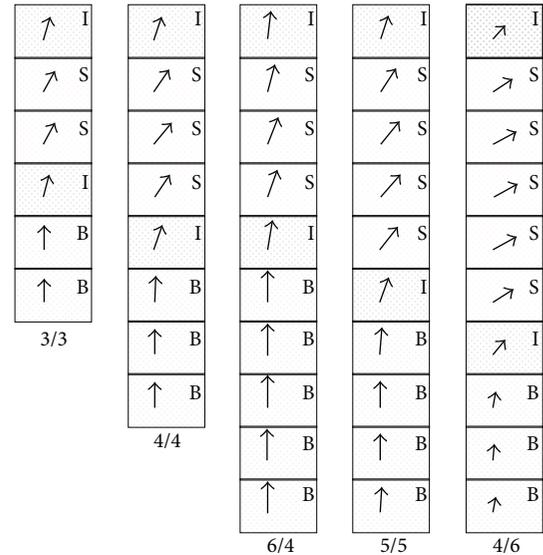


FIGURE 13: Structure of BaTiO<sub>3</sub>/SrTiO<sub>3</sub> superlattices [195].

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  $E_g$  (13 eV in a 2.7 eV material, BiFeO<sub>3</sub>) 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  $E_g/e$ . 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<sub>3</sub> 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

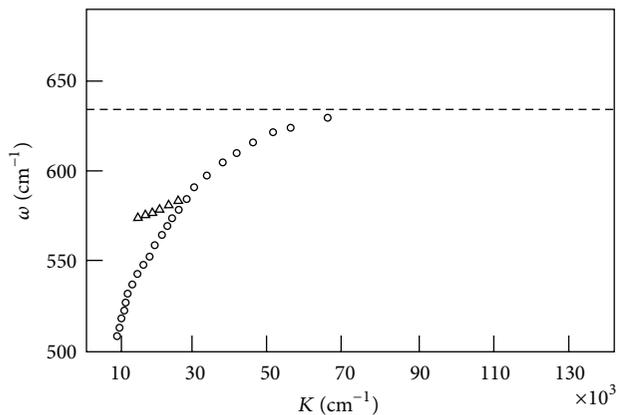


FIGURE 14: Small-angle Raman spectra in optically illuminated lithium niobate; the large photovoltaic effect transverse to the polar axis in this unelectroded specimen changes the phase-matching conditions strongly, such that the spectra differ significantly with and without illumination [207].

dynamics of phase diagrams. Phase transitions in ferroelectrics 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.,  $\text{BaMnF}_4$  [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  $2.50 \pm 0.02$  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  $\text{SrTiO}_3$  and  $\text{LaAlO}_3$  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  $\text{SrTiO}_3$  with 30% O-18 [233], TSCC with 18% Br or iodine [234], or  $\text{TmVO}_4$  (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

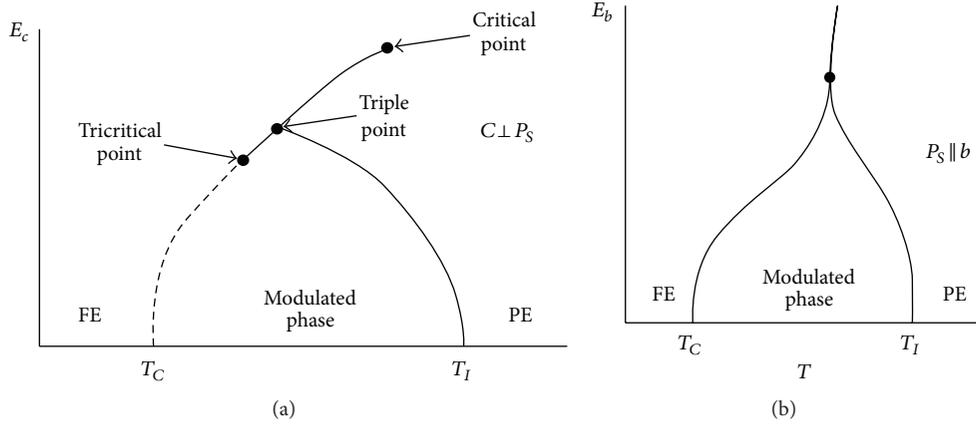


FIGURE 15: Schematic phase diagram in sodium nitrite  $\text{NaNO}_2$  for field  $E$ : (a) along the polar axis; (b) transverse to the polar axis [224].

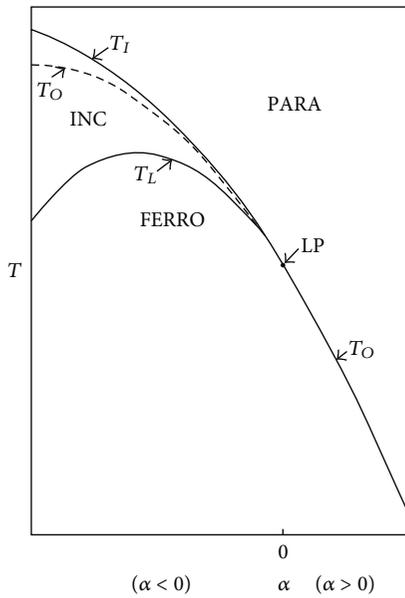


FIGURE 16: Detailed phase diagram for sodium nitrite  $\text{NaNO}_2$  for field transverse to the polar axis; here the graph is in the temperature-wave vector plane and shows that the Lifshitz point is not quite reached; since the transition is first-order, the Lifshitz point is slightly extrapolated [225].

first analyzed by the present author in 1968 [243] in the Scheelite crystals represented by  $\text{CaWO}_4$ ,  $\text{CaMoO}_4$ ,  $\text{SrWO}_4$ ,  $\text{BaMoO}_4$ , 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  $360 \text{ cm}^{-1}$ , 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

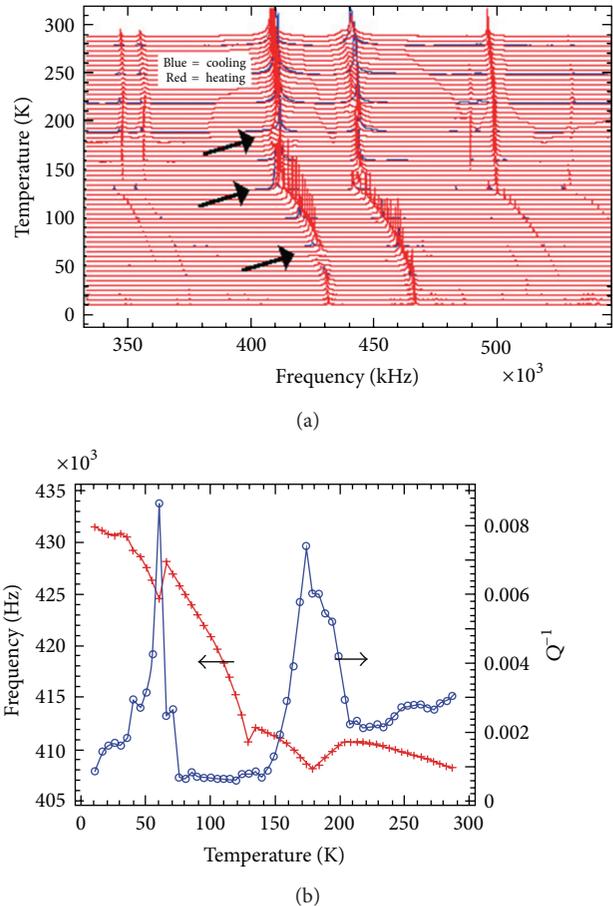


FIGURE 17: Resonant ultrasonic spectra of TSCC revealing phase transitions at 185 K, 130 K, and 64 K [226].

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

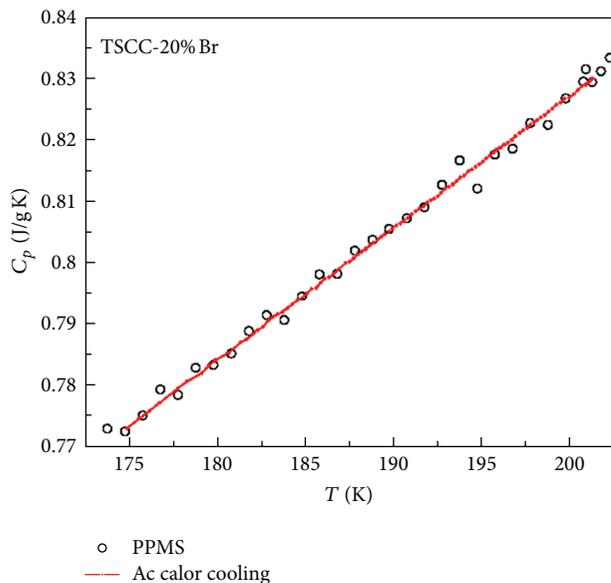


FIGURE 18: Specific heat data in TSCC showing no evidence of phase transitions at 185 K and 64 K (Zdravko Kutnjak and J. F. Scott, unpublished).

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 the internal 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 Davydov 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

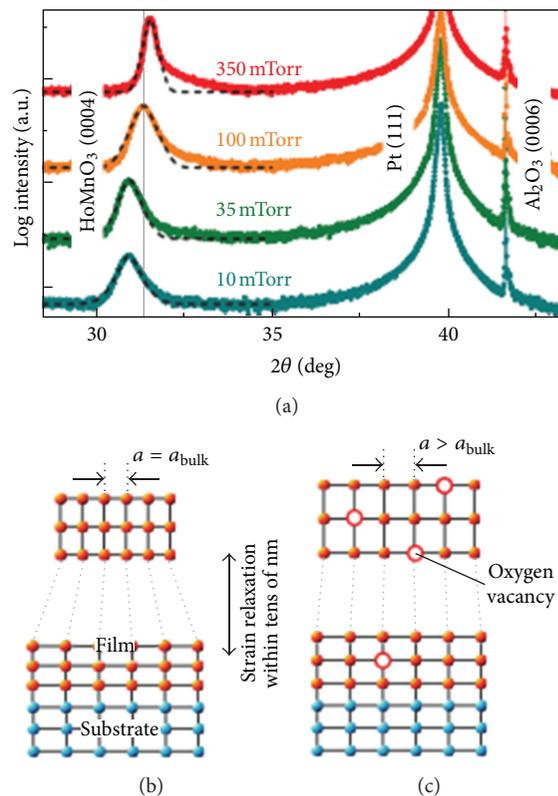


FIGURE 19: Giant flexoelectric effect [18]; upper curve shows X-ray Bragg peaks at different stresses; lower figure, schematic diagram of atomic displacements.

[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 endpoint [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

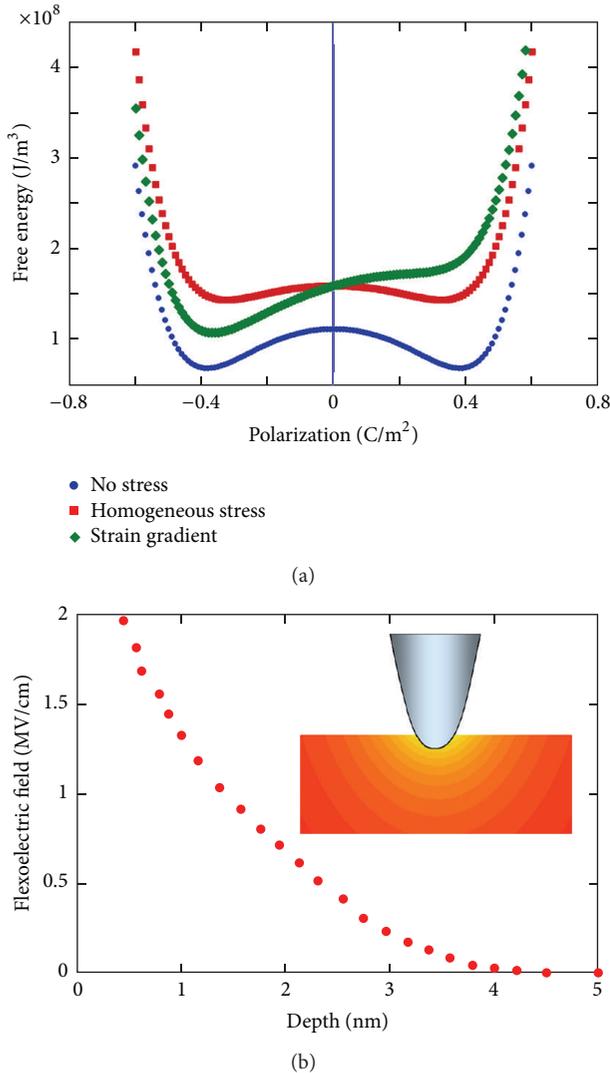


FIGURE 20: Switching of polarization  $P$  without electric fields, via flexoelectric stress [254].

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<sub>4</sub> [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  $T_c$  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 bi-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 of 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

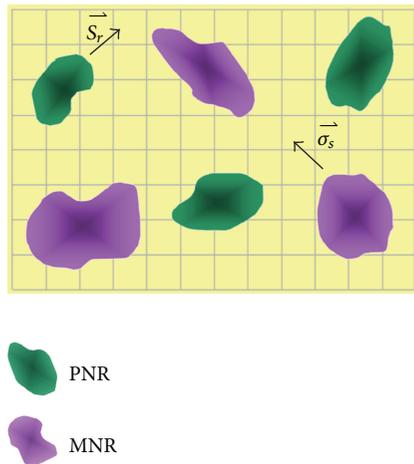


FIGURE 21: Cartoon illustrating the stress interaction of magnetic domains and ferroelectric domains in a multiferroic birelaxor [33].



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

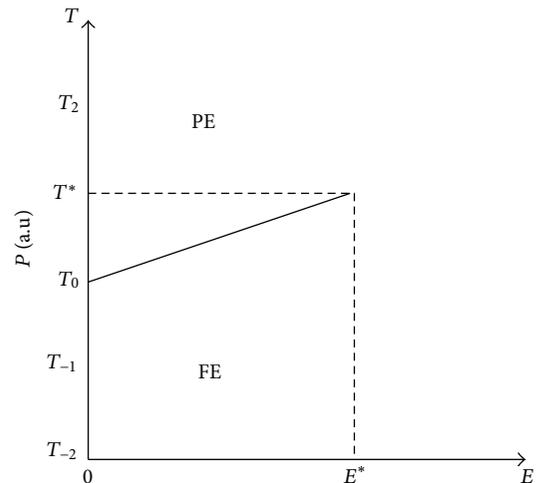


FIGURE 23:  $(E, T)$  diagram for electrocaloric ferroelectrics, for a first-order phase transition.

field  $E$  or adiabatically at constant  $S$ . Figure 24 illustrates the  $(S, E)$  graph, with numerical values appropriate for  $\text{BaTiO}_3$ .

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,  $\ll 1\text{K/V}$  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  $660\text{J/kg}$  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 (polyvinylidene fluoride) [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 piezoelectric studies in soft tissue and not just bone and teeth [281]. The new works include measurements of desiccated 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.

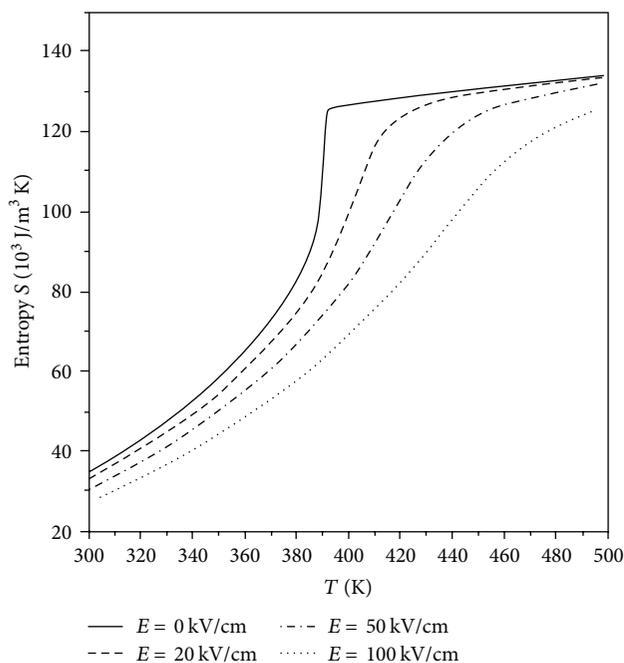


FIGURE 24:  $(S, E)$  diagram for electrocaloric ferroelectrics, for a first-order phase transition, with numerical values for barium titanate [283].

#### 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  $\text{TiO}_2$ .

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  $\times 1000$  in current switched was recently reported by Jiang et al., using semiconducting  $\text{BiFeO}_3$  [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  $\text{BiFeO}_3$  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  $\text{TiO}_2$ —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  $\text{Si}/\text{SiO}_2$  (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 Gurevich and Tagantsev [299] for second sound in  $\text{SrTiO}_3$  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  $\text{SrTiO}_3$  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  $\text{SrTiO}_3$  below ca. 60 K has Sr-ion disorder along [111], which convoluted with the  $\text{TiO}_6$  rotation about [001], renders  $\text{SrTiO}_3$  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  $\text{SrTiO}_3$ , 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 within 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 MOTTFFETs) 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.

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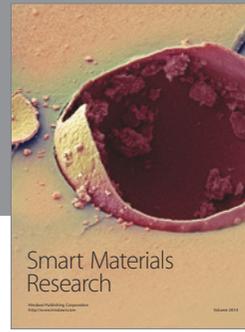
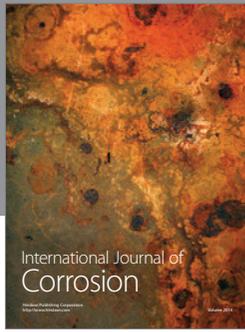
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