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Antiferroelectrics: History, Fundamentals, Crystal Chemistry, Crystal Structures, Size Effects, and Applications

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Abstract

Antiferroelectric (AFE) materials are of great interest owing to their scientific richness and their utility in high energy density capacitors. Here, the history of AFEs is reviewed, and the characteristics of antiferroelectricity and the phase transition of an AFE material are described. AFEs are energetically close to ferroelectric (FE) phases, and thus both the electric field strength and applied stress (pressure) influence the nature of the transition. With the comparable energetics between the AFE and FE phases, there can be a competition and frustration of these phases, and either incommensurate (INC) and/or a glassy (relaxor) structures may be observed. The phase transition in AFEs can also be influenced by the crystal/grain size, particularly at nanometric dimensions, and may be tuned through the formation of solid solutions. There have been extensive studies on the perovskite family of AFE materials, but many other crystal structures host AFE behavior, such as $\text{CuBiP}_2\text{Se}_6$. AFE applications include DC-link capacitors for power electronics, defibrillator capacitors, pulse power devices, and electromechanical actuators. The paper concludes with a perspective on the future needs and opportunities with respect to discovery, science, and applications of AFE.

1.0 Introduction of the AFE:

Antiferroelectric materials have identifiable spontaneously ordered dipole moments that are arranged antiparallel so as to cancel out on a unit-cell basis at zero field, but for which an electric field of sufficient magnitude can induce a phase transition to a ferroelectric phase with parallel dipole ordering, as

illustrated in Figure 1(a). The AFE phase is typically a consequence of a structural phase transition from a higher temperature phase known as the prototype and/or paraelectric (PE) phase.¹⁻³ It takes place through either a displacive soft-mode transition or an order-disorder process that involves the ordering of pre-existing dipoles that were disordered in the high temperature PE phase. The phase transition between PE-AFE occurs at a critical temperature, T_C . On the application of an electric field of sufficient strength, the material can switch from the low temperature AFE phase to a ferroelectric phase (FE) with a polar space group (Fig. 1a).^{4,5}

In a phenomenological description, a phase transition is typically described by an order parameter or a set of order parameters.⁶ In the case of the AFE, there are two sublattices with the same magnitude of spontaneous polarization but in opposite directions, leaving a net zero macroscopic polarization within the crystal structure at zero field. Figure 1(b) shows a typical double hysteresis curve measured in $\text{Pb}_{0.98}\text{La}_{0.02}(\text{Zr}_{0.66}\text{Ti}_{0.10}\text{Sn}_{0.24})_{0.995}\text{O}_3$.⁷ Associated with antiferroelectric-ferroelectric switching, there is a critical forward coercive field, E_F , that is the field induced AFE-to-FE phase transition. Then, on reducing the forward field, there is a switch back to the AFE phase at a different coercive field, E_A . On reversing the field direction, similar transitions are observed at $-E_F$. After saturation of the FE polarization at high fields, on reducing electric field strength to $-E_A$, the FE reverts to the AFE phase. As will be discussed below, observation of double hysteresis alone does not provide conclusive proof of a phase being AFE, as double hysteresis can also arise from randomly oriented defect dipoles in an aged FE and/or switching of a FE with a first order phase transition temperature above the Curie temperature (T_C). Below, the experimental characteristics of AFE phases are described which collectively aid in identifying a material as AFE. Before considering these characteristics, the history of the first twenty years of AFE materials is discussed.

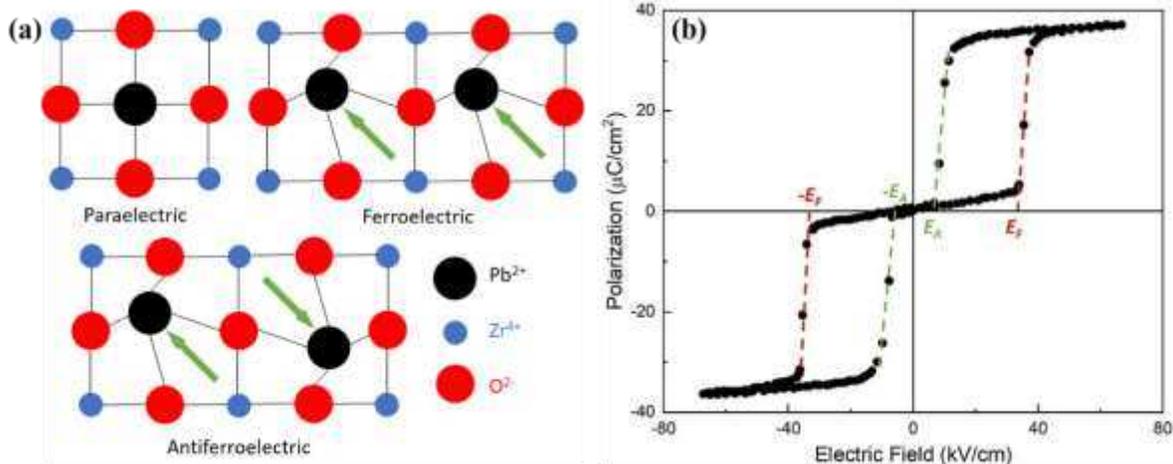


Figure 1. (a) Schematic representation of Paraelectric (PE), Antiferroelectric (AFE) and Ferroelectric (FE) states in PbZrO_3 (oxygen octahedral tilting not shown). (b) Typical double hysteresis loop measured in $\text{Pb}_{0.98}\text{La}_{0.02}(\text{Zr}_{0.66}\text{Ti}_{0.10}\text{Sn}_{0.24})_{0.995}\text{O}_3$ (replot from Ref. 7).

2.0 Early AFE Pioneers and Key Discoveries from the First Twenty Years.

2020 was the hundred-year anniversary of the discovery of ferroelectricity by Valasek (1920) in Rochelle salt. In that work, the polarization – electric field (P-E) hysteresis invited analogies to ferromagnetic materials, and hence the use of the word “ferro” as a prefix to the dielectric analog.⁸ Anti-ferromagnetism has been known as a phenomenon since the work of Louis Néel, in the 1930’s.⁹ Following the discovery of ferroelectricity in the perovskite BaTiO_3 – in various locations, including USA, Russia, and Japan (and possibly Germany), during WWII, as scientists looked for alternative dielectric materials to replace mica for capacitor applications – antiferroelectricity was discovered.¹⁰⁻¹⁴ Figure 2 shows photos of some of the critical pioneers in AFE materials from 1951-1970.

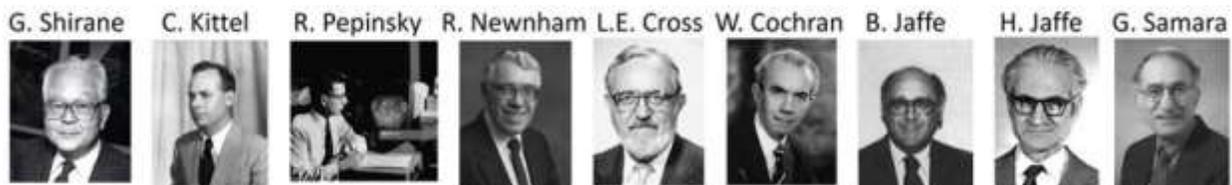


Figure 2. Key pioneers in the first 20 years of AFE’s discovery and development (1951 to 1970)

The first reports on AFEs were from the Tokyo Institute of Technology (Tokyo Tech), on the perovskite AFE PbZrO_3 , in two publications from Shirane, Sawaguchi, Takeda, (1950) and Sawaguchi, Maniwa, and Hoshino (1951).¹⁵⁻¹⁷ Kittel, at Bell Labs in 1951, provided the first theoretical justification, suggesting that antiferroelectricity should exist.¹⁸ Shirane came to Penn State and joined the X-ray structural group of Pepinsky, who at that time had a very advanced structural refinement laboratory and used diffuse scattering to aid structural determinations of polar symmetries and calculate the electron density maps around atoms. He used structural analytics to discover ferroelectric and related materials across many different crystal structures. By 1953, the second AFE phase was published and refined; this was the perovskite, PbHfO_3 .¹⁹ At that time, Newnham was a student at Penn State working in the Pepinsky group, and he published with Shirane and Pepinsky (1954) the crystal structure of the AFE NaNbO_3 .^{20,21}

Meanwhile, in the United Kingdom at University of Leeds, Cross and Nicholson were also working on NaNbO_3 crystals and were able to show double hysteresis.²² Simultaneous to the experimental work, and inspired by the recent power of the Devonshire phenomenological modelling of the BaTiO_3 ferroelectric materials, Cross utilized the postulates in the Kittel publication and introduced a model to account for the double hysteresis observations in NaNbO_3 .²³

Outside of the perovskites, Keeling and Pepinsky (1955) studied the low temperature (148K) behavior of Ammonia Di-Hydrogen Phosphate (NH_4) H_2PO_4 (ADP) and determined the order-disorder H-displacement with AFE sublattice symmetry breaking.²⁴

Another important step came with Cochran (following work of Frohlich, Ginzburg, Landau, Anderson, and Landauer and colleagues) with the elucidation of the soft mode theory for displacive phase transitions (1959).²⁵ Although it was initially introduced for ferroelastics, it was generally applicable to many displacive phase transitions, including ferrodistortive and antiferrodistortive ones. This theory drove many important fundamental studies coupling phonon dispersions and structural transitions.²⁶

In parallel to the fundamental work, there were important advances in development of the $\text{PbZrO}_3\text{-PbTiO}_3$ (PZT) solid solution phase diagram. While many groups contributed, the most extensive and comprehensive work came from the Clevite Corporation in Cleveland USA, and the work of Jaffe, Cook, Jaffe, Cmolik, and Berlincourt in the early 1960s.²⁷ This produced interest in the AFE-FE boundary of the PZT phase diagram for critical defense applications. Fundamental work at the defense national laboratories was also conducted to probe the physical parameters controlling the AFE phase transition behavior. Excellent work by Samara (1970) at Sandia National Laboratories reported on the hydrostatic pressure effects on the AFE transitions.^{28,29} The results correlated the empirical observations within the soft mode theory of Cochran. So, seventy years after the discovery of AFE in PbZrO_3 , there have been many other important contributions beyond the first twenty years. Nonetheless, those first twenty years underpinned many of the important characteristics that guide current understanding.

3.0 Empirical Property Characteristics Associated with an AFE Phase

There are several empirical observations that aid the determination and verification of an AFE phase. Below, a number of these properties, ranging from the double hysteresis, crystallographic structure, unit cell volume, stress dependence of the transition temperature, field dependence of the permittivity, low thermal conductivity, and negative electrocaloric coefficient, are considered.

3.1 Polarization-Electric Field Switching in the Form of Double Hysteresis Loops

Antiferroelectricity is characterized by the ability to induce a phase transition between a non-polar antiferroelectric phase and a polar ferroelectric phase, producing remarkable changes in properties. To observe the switching, the dielectric material must have the appropriate crystallographic structure with antiparallel spontaneous polarizations; the coercive fields for the transformation must be sufficiently low as to minimize conductivity and/or dielectric breakdown. So, in order to permit the field forcing the

switching and thereby observe the dielectric double hysteresis response, it is imperative to minimize the extrinsic dielectric loss associated with conductivity of ionic or electronic space charge contributions that can screen and limit the energy necessary to drive AFE-FE transitions. Other than composition, external conditions can affect the AFE performance. Figure 3(a) is the double hysteresis in the AFE material $\text{Pb}(\text{Lu}_{0.5}\text{Nb}_{0.5})\text{O}_3$, and (b) shows the linear proportionality between the E_F and temperature.³⁰ As already implied from the historically important work of Samara, the mechanical boundary conditions can also influence the properties. So, in the double hysteresis experiments, the applied stresses, and/or the ability for the material to undergo the shape changes in the AFE-FE switching, and even the electrode configuration can partially clamp the transition and should be considered.³¹ The multi-polymorphic AFE phases can also influence the nature of the hysteresis loops; this is very nicely demonstrated in single crystals of PbZrO_3 , by Fesenko et al., Figure 3(c).³² Generally speaking, for a particular composition, $E_F > E_A$, while the sign of E_A depends on the phase. If the testing condition is away from phase boundary, E_A has the same sign as E_F (classic double loop). However, AFE and FE phases often coexist when close to the phase boundary. Under such circumstance, the P-E loop can possess a pinched shape owing to the negative E_A (assuming positive E_F). In those materials, the electric field can not only induce FE out of an AFE, but also trigger the opposite transition.³³⁻³⁵

Double hysteresis is an important observation, but is not a sufficient condition for experimental verification of an AFE. Double hysteresis can also be seen in the case of ferroelectrics that have randomly oriented defect dipoles, or strong aging that induces pinning of the spontaneous polarization.³⁶⁻³⁸ In this case, when a large enough electric field is applied, the driving force overcomes the local fields associated with the defect dipoles or aged domain state, and the polarization can be switched. However, if the time scale of the hysteresis loop is too short to allow the local fields to be reoriented, they will act to provide a strong restoring force when the field is removed that will reduce the remanent polarization. Figure 4 shows such double hysteresis in aged KNbO_3 with acceptor doping.^{39,40} Aged ferroelectrics can be de-aged

by heating the materials to higher temperatures to either redistribute and/or realign defect dipoles, thereby remove the pinning. For example, running the sample through multiple hysteresis loops, with heating and realignment of defects, can also de-age and remove the double hysteresis in ferroelectrics. An approach that can be used to quickly discern whether aging or antiferroelectricity is responsible for observed double hysteresis is to check the loops under different frequencies. If the double loop originates from aging, it tends to "open up" at a sufficiently low frequency switching and transition to a ferroelectric hysteresis loop. In contrast, real antiferroelectrics exhibit much weaker frequency dependence, and presumably, the double loop remains stable under switching.

Another source of a double hysteresis is in first order ferroelectrics, at temperatures in the window between the Curie temperature and the Curie-Weiss temperature. From a free energy perspective, in such a case there are energy minima at $P=0$, and metastable minima at finite polarizations for such a FE; an external electric field can drive a double hysteresis under these special conditions. Double hysteresis can also be observed in a narrow temperature window above the Curie temperature, when the ferroelectric phase can be field-induced.

Experimentally, double hysteresis can be missed in samples with high background conductivity, or in cases where mechanical clamping obscures the behavior of a true AFE material. Therefore, identification of an AFE phase should rely on more than the electrical analysis.

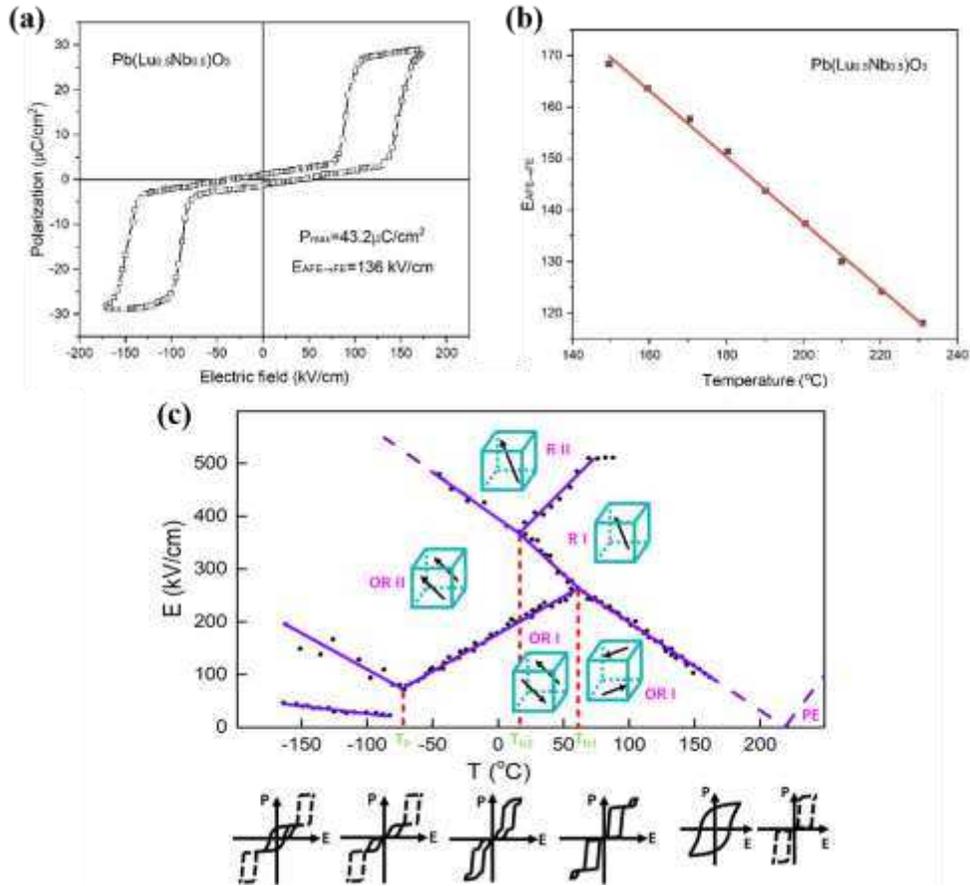


Figure 3: Antiferroelectric double hysteresis loops in (a) $\text{Pb}(\text{Lu}_{0.5}\text{Nb}_{0.5})\text{O}_3$ and (b) the temperature dependent critical field in it (replotted from Ref. 30). (c) shows the phase diagram of PbZrO_3 as a function of temperature and electrical field (replotted from Ref. 32).

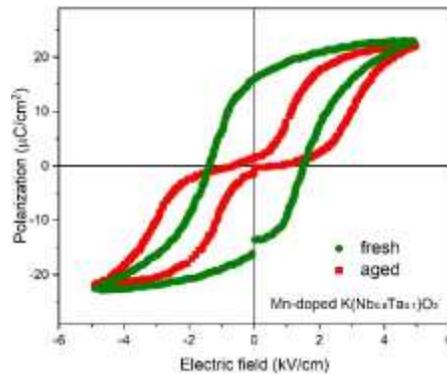


Figure 4: Double Hysteresis loops observed in ferroelectric Mn-KNbO₃-based materials (replotted from Ref. 39).

3.2 Superlattice Diffraction Between the High Temperature PE and Low Temperature AFE Phases

As briefly described above, the structural phase transition between the nonpolar PE and an antipolar AFE involves formation of two antiparallel polarization sublattices. This necessitates changing the translational

symmetry of the structure of the AFE relative to the PE to account for the need for multiple prototype cells to reach a true repeat unit in the AFE phase. One consequence of this is that the AFE phase has additional diffraction spots/lines relative to the PE diffraction pattern. As an example, in PbZrO_3 , the local dipoles orient along $\langle 110 \rangle$ directions and form an antiparallel arrangement with two by two alternation; this will be described further below. Consequently, the net polarization is cancelled to zero, while the lattice parameter is quadrupled along $\langle 110 \rangle$, which gives rise to the $\frac{1}{4}\{110\}$ type superlattice diffraction reflections and necessitates defining a new unit cell comprised of eight prototype cells.⁴¹ However, it is essential to be very careful when using the superlattice diffraction to determine the phase. First, $\frac{1}{4}\{110\}$ spots could be invisible if the observation direction is not perpendicular to the modulation, hence a systematic investigation is needed. Second, many other superlattice diffractions are potentially confounding, for instance, those owing to an anti-distortive phase transition, such as the antiphase octahedral tilting associated with the AFE/FE phase that typically leads to α ($\frac{1}{2}\{110\}$) and F ($\frac{1}{2}\{111\}$) superlattice spots.⁴² So, a translational symmetry signature is an important and necessary property, but again, extra care is demanded for an appropriate analysis.

3.3 Unit Cell Volume Changes Relative to PE-AFE Phases

AFE–PE phase transitions can be first or second order, although many cases are first order with all of the related characteristics. That is, transitions of this type show a discontinuous onset of the order parameters at the transition temperature, a thermal hysteresis, a discontinuous change of the unit cell volume, and a latent heat anomaly associated with the volume change in accordance with the Clausius-Clapeyron relationship. The change in the unit cell volume is a noteworthy parameter that aids in the determination of the AFE relative to a FE phase. PE-AFE transitions lead in perovskites, in general, to a lower unit cell volume relative to the PE unit cell; in contrast, the opposite is true for the PE-FE transition. (Note that this is not generally true for other structure types). So, there is a contraction in volume for the AFE, and an expansion in volume for the FE on cooling through the transition temperature. This has important

consequences on both the hydrostatic pressure effects and the electrocaloric effect. Figure 5 (a) and (b) contrasts the PE-AFE lattice parameters for PbZrO_3 , and the PE-FE-FE (cubic-tetragonal-orthorhombic) phase transitions in the BaTiO_3 perovskites.^{43,44}

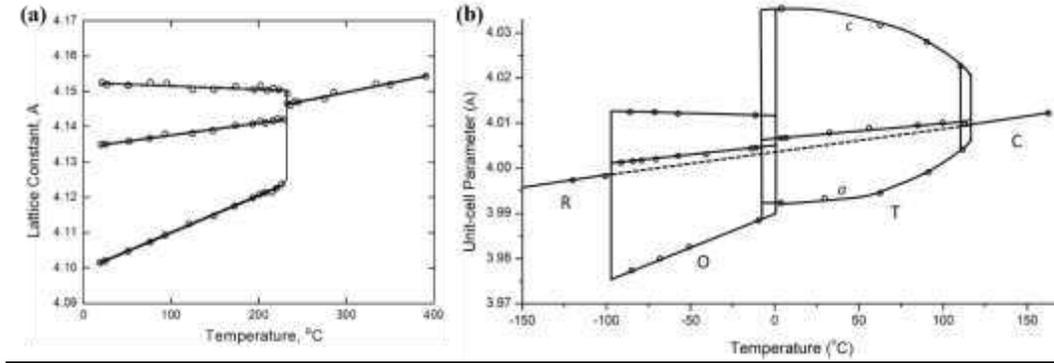


Figure 5: Lattice parameters as a function of temperature for (a) antiferroelectric PbZrO_3 , showing the decrease in lattice volume on cooling through the phase transition temperatures (replotted from Ref. 43), and (b) ferroelectric BaTiO_3 , showing the expansion in the lattice volume on cooling into the tetragonal ferroelectric phase; C is the cubic paraelectric phase, T is tetragonal, O is orthorhombic, and R is rhombohedral ferroelectric phase, the dashed line is the cube root of the unit volume of the cell as a function of temperature (replotted from Ref. 44).

3.4 Hydrostatic Pressure Dependence of Phase Transition Behavior

The differences in volume change between AFE and FE phases relative to the volume of the PE phase induces consequences on the stability of these phases as a function of the applied external pressure. As higher hydrostatic pressures favor higher densities (and hence smaller prototype unit cell volumes) pressure increases the stability of perovskite AFE phases to a higher temperature, whereas the FE phase stability is suppressed to lower transition temperatures. Thus, a PE-AFE has a $dT_C/dp > 0$, and the PE-FE is $dT_C/dp < 0$. If the pressure is applied near the AFE/FE phase boundary, pressure-induced FE to AFE phase transitions can take place (Figure 6a).⁴⁵ Samara also showed the effects of pressure on the magnitude of the permittivity and the diffuseness of the phase transition; these are discussed later in context with the soft mode theory. Figure 6(b) shows Samara's experimental data of the hydrostatic pressure dependence on the dielectric anomaly for PbZrO_3 ceramics.²⁸

Uniaxial stress also alters the phase transition behavior in AFEs; this becomes more complicated when an electric field is applied simultaneously. In general, isostatic stress also favors the AFE phase over FE, which leads to an increase of the critical field E_F .⁴⁶ Moreover, the polarization of the induced FE phase is suppressed via the piezoelectric effect. It was found that, when subjected to a compressive stress, the $\langle 001 \rangle_c$ axis of the AFE lattice (the dipoles are along $\langle 110 \rangle_c$) tends to align with stress, resulting in a remanent strain.⁴⁷ Moreover, an electric field can also texture the AFE domains, but in a different way. Prior to the field exposure, AFE domains are randomly oriented. After one AFE—FE—AFE cycle, however, the $\langle 001 \rangle_c$ axis rotates towards the plane perpendicular to the field direction.⁴⁸

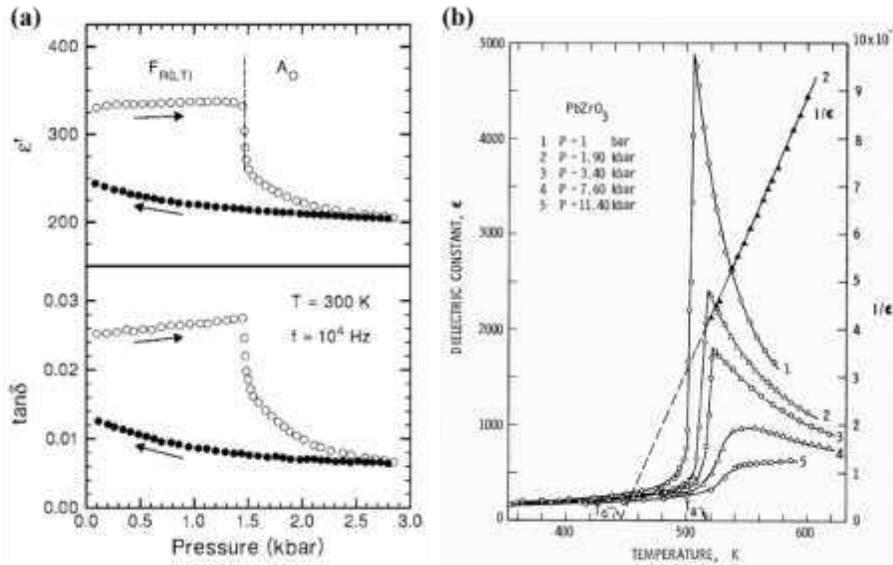


Figure 6: (a) Variations of ϵ' and $\tan\delta$ for increasing and subsequent decreasing pressure in PZT 95/5; (reproduced by permission from Ref. 45) (b) Isobaric hydrostatic pressures (1 bar to 11.4 Kbar) and temperature dependence of the phase transition behavior of AFE PbZrO_3 , and the Curie-Weiss plot of the dielectric permittivity in the PE regime. (reproduced by permission from Ref. 28)

In the cases of compressive and tensile stresses, these stresses the situation is more complex as often in the experimental set up there can be local deviatoric stress gradients that breaks the symmetry that in turn then favors the polarized regions and the ferroelectric phase. So, the volume change can be compromised with these gradients, hence most studies on the phase transitions are performed with hydrostatic pressure applications.

3.5 Electric Field Dependent Permittivity in AFE

The field-induced transition of the AFE phase to the FE phase changes the polarizability of the dielectric, and so increases the permittivity (ϵ) with increasing field strength, $d\epsilon/dE > 0$.² This is the opposite trend from ferroelectrics, where $d\epsilon/dE < 0$. That is, high fields reduce the permittivity of ferroelectric materials; that process is often referred to as voltage saturation behavior. This field dependence of the dielectric permittivity can provide additional evidence for a phase being an AFE or FE. In addition, the phase transition temperatures vary with external fields. Normally, both AFE-FE and AFE-PE transition temperature shift towards the AFE side under a DC field (i.e. DC fields reduce the stability of the AFE phase).⁴⁹

3.6 Thermal Conductivity in AFE's

In general, ferroelectrics with long range order, such as normal ferroelectrics, have relatively higher thermal conductivities due to the comparatively long phonon mean free path. Relaxor ferroelectrics, with their nano-polar domains, have a polar glassy behavior that strongly reduces the thermal conductivity (due to phonon scattering from the nanoscale heterogeneities). Likewise, under zero electric field, AFE also have very low thermal conductivities. There is a lot of disorder in the antipolar ordering that leads to scattering of phonons and thereby suppresses the thermal conductivity. Figure 7 shows experimental data of the temperature dependence of the thermal conductivity in ferroelectric and related materials, with AFE NaNbO_3 having phonon glass behavior. At 100K, there is about an order of magnitude between the thermal conductivities with paraelectric and normal ferroelectric perovskites such as KTaO_3 , BaTiO_3 , PbTiO_3 and KNbO_3 where $\kappa \sim 10 \text{ Wm}^{-1}\text{K}^{-1}$ and in an AFE such as NaNbO_3 $\kappa \sim 1 \text{ Wm}^{-1}\text{K}^{-1}$. It is also noted that relaxor ferroelectrics such as $\text{Pb}(\text{Mg}_{1/3}\text{Nb}_{2/3})\text{O}_3$ have nanoscale polar regions also show extremely low thermal conductivities, $\kappa \sim 1 \text{ Wm}^{-1}\text{K}^{-1}$.⁵⁰

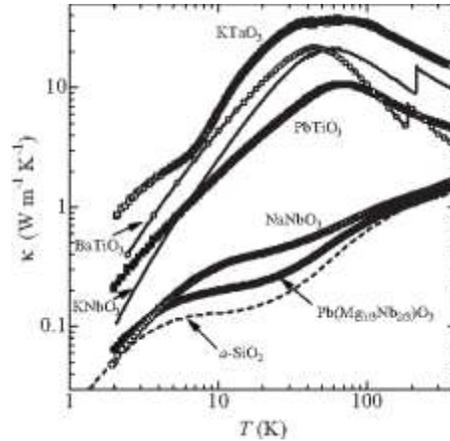


Figure 7: Thermal conductivity of various perovskite materials with different ferroic structures ranging from PE (KTaO_3), FE (BaTiO_3 , KNbO_3 , PbTiO_3), AFE (NaNbO_3), and relaxor ferroelectricity ($\text{Pb}(\text{Mg}_{0.33}\text{Nb}_{0.67})\text{O}_3$). All of these are contrasted with amorphous silica (reproduced by permission from Ref. 50).

3.7 Electrocaloric Coefficients in AFE's and FE's.

The electrocaloric effect (ECE) is of interest for potential applications in solid state cooling.^{51,52} The operating premise is that the entropy of dipole alignment can be changed under an applied electric field. This, in turn, can be used to provide a temperature change under an electric field. Both AFE and FE materials are of interest for this phenomenon. Figure 8(a) shows a series of temperature changes that can be induced by applied electric fields. In FEs, the applied field aligns the polarization, and hence reduces the dipole entropy associated with an originally partially random domain configuration. Under the adiabatic condition, the material is therefore heated, $dT > 0$. In contrast, AFE show a negative ECE, where the isothermal entropy change, ΔS , is positive (Figure. 8b) and the adiabatic temperature change, ΔT , is negative under an increasing electric field.⁵³⁻⁵⁵ The negative ECE sign in AFEs was suggested to originate from the dipole disruption by moderate field, but may also be associated with the phase transition sequence and the presence of commensurate/incommensurate ordering.

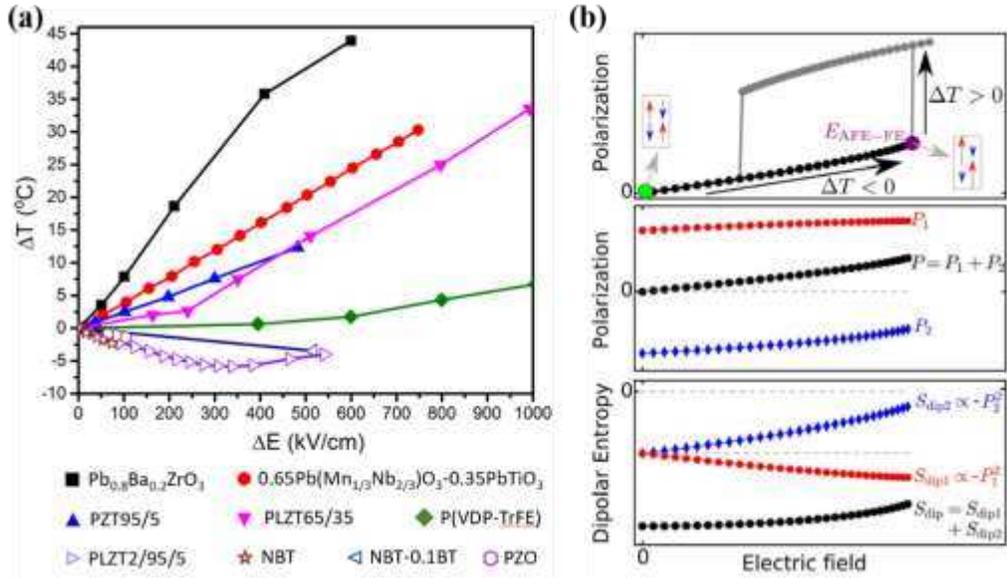


Figure 8. (a) Electrocaloric responses in FE (solid symbol) and AFE (unfilled symbol) materials (replotted from Ref. 53); (b) Schematic illustration of the inverse electrocaloric effect in AFE phases based on the different responses of the two sublattices (reproduced by permission from Ref. 54).

The above experimental observations, combined with structural refinement diffraction data or high-resolution transmission electron microscope images of antiparallel atomic displacements, can be used to identify AFE unambiguously.

3.8 Soft modes, Structural Phase Transition and Flexoelectricity

Lattice dynamics and the associated phonon spectra control the thermal properties of a material. In addition, in the case of special lattice vibration modes that soften (i.e. the frequency drops to zero), the phonon mode signals structural phase transitions. While the theory was first developed for displacive transitions, it was later extended also to order-disorder transformations.⁵⁶⁻⁵⁸ The soft mode describes the atomic displacements within the unit cell and the phase modulation of the relative displacement amplitudes from one unit cell to another with the wavevector of the lattice vibration. One common case is that of a ferroelectric phase transition driven by a soft mode. Here, there is a transverse optic phonon mode with relative displacements between the anions and cations. It has an angular frequency, ω_s , at $K=0$,

or $\lambda \rightarrow \infty$; this is the Brillouin zone center. The soft mode frequency, ω_s , varies with temperature according to $\omega_s^2 = A(T - T_c)$. Thus, as the temperature approaches T_c , the frequency approaches zero, and then the material freezes in the new structure. The optic transverse soft mode also accounts for the dielectric anomaly around T_c , the so-called the Curie Law. The Curie Law can be correlated to the temperature dependence of the soft mode frequency via the so-called Lydanne-Sachs-Teller (LST) relations. The LST equation describes the low and high frequency dielectric responses as being a function of the longitudinal and transverse frequencies of the optical phonon modes. Figure 9(a) illustrates the concept of the optical soft mode freezing in and driving the PE-FE phase transition.⁵⁹

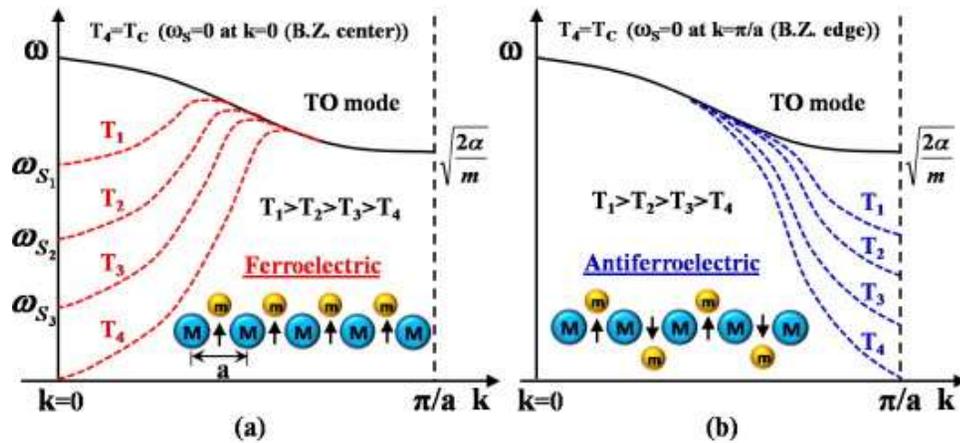


Figure 9. A schematic of soft mode condensation of a transverse optical phonon for (a) ferroelectrics and (b) antiferroelectric phase transitions (reproduced by permission from Ref.59).

The soft mode theory can also describe the case in which the optical phonon freezes at the Brillouin zone edge. Here the critical wave vector is $k = \pi/na$, and this produces a vibrational mode that has a wavelength of two-unit cells for $n=1$. Given that the displacements are antiparallel in the adjacent unit cells, this would constitute the AFE superlattice cell. There are other positions that lead to more complex situations, for example one in which the critical wave vector, $k = \pi/na$ with $n=2$, leads to polarization sequences with two up and two down, somewhat akin to the PbZrO_3 case where along $\langle 110 \rangle_c$, there are two up and down polar displacements; these are simplified and shown in Figures 9(b). In addition to the temperature dependence of the soft mode freezing, hydrostatic pressure can also impact the condensation process.

In the cases where n is not an integer, the soft mode may condense at irrational positions in the Brillouin Zone. This induces incommensurate (INC) phase transitions, in which the superlattice structures and frozen-in vibration modulations have wavelengths that may be extremely large and have symmetries that cannot be classified under the constraints of the 3-dimensional basis and symmetry operations with the 230 space groups. The superlattices are also not at rational positions that correspond to simple multiplicities of the PE unit cell. The wavelength of these modulations can be temperature dependent and can converge with lower temperatures toward a rational multiplicity for the superlattice. The temperature evolution from the INC to the commensurate phase is often pinned by defects; if these defects are not limited, the critical temperature from INC to Commensurate is the lock-in transition. The INC structures are often associated with competing phase transitions, and therefore it is natural to see a close correlation with INC with FE and AFE phase being close in energy, and/or through coupled soft modes within the Brillouin Zone.⁶⁰

Flexoelectricity is the induction of a polarization that is possible in all insulating materials when subjected to an inhomogeneous strain or stress, i.e. a strain or stress gradient.⁶¹⁻⁶³ Most of the historical discussion around electromechanical behavior was linked to electrostriction, and in the case of non-centrosymmetric materials, piezoelectricity. But in some cases, particularly when the relative permittivity is large, flexoelectricity must be considered when there are strong gradients within a material. This is particularly true in the case of AFEs, as they have high local polarization gradients both at the domain level where there is large strain mismatch at complex domain configurations and large polarization gradients on the lattice level with antipolar ordering. In both ferroelectrics and AFEs which pair local polar order with low or zero net polarization, and a high permittivity, flexoelectric contributions are large, and not obscured by piezoelectricity. Hence, flexoelectricity is discussed in this AFE review. Vales-Castro et al. has experimentally determined the flexoelectric coefficients in both PbZrO_3 and AgNbO_3 , as shown in Figure 10).⁶⁴ In that work, it was pointed out that the flexoelectricity and flexocoupling coefficients show a sharp

peak at the antiferroelectric phase transition. While these coefficients are not as high as in materials such as $\text{Ba}_{1-x}\text{Sr}_x\text{TiO}_3$, most antiferroelectrics lack the nanopolar regions (as in $\text{Ba}_{1-x}\text{Sr}_x\text{TiO}_3$) that significantly increase the reported flexoelectric coefficients.^{65,66}

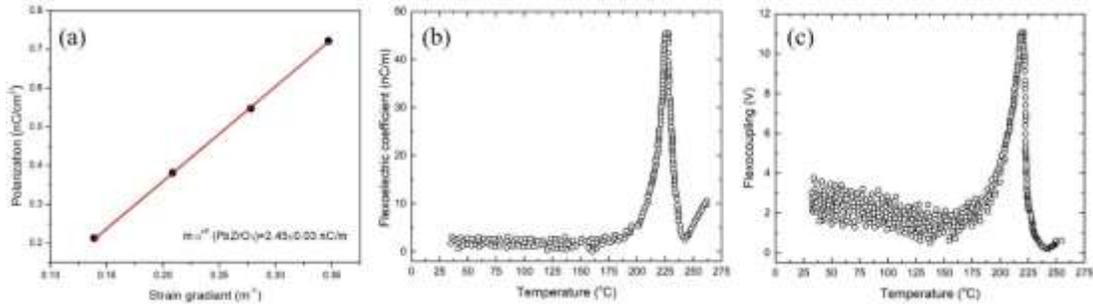


Figure 10. (a) Flexoelectric coefficient at RT, (b), (c) flexoelectric coefficients, flexocoupling as a function of temperature in PbZrO_3 (replot from Ref.64).

Tagantsev et al. point to the possibility that flexoelectric coupling is essential to the development of antiferroelectric behavior in PbZrO_3 .⁶⁷ In their work, the gradient terms in Landau-Ginzburg-Devonshire phenomenology (the same terms that determine the domain wall energies in ferroelectrics and/or the modulations that are inherent to the INC phase) coupled with high dynamic flexoelectric coefficients are shown to influence the phase transition. The result is that a ferroelectric-like lattice instability is interrupted by incommensurate modulations as described by Axe et al.⁶⁸ Specifically, the dynamic flexoelectric effect that underpins the coupling between the acoustic and transverse optic modes drives a phonon frequency softening at the Brillouin zone center. An Umklapp interaction then leads to bypass of the incommensurate state and produces the locked-in polar order of PbZrO_3 . Within the soft mode theory, these large flexoelectric couplings between the optical branch push the acoustic branch to zero frequency at a certain point with $q=0$ in the Brillouin zone, leading to a soft mode condensation at an irrational point in the Brillouin Zone, and this then leads to the INC antipolar modulations. This model is also consistent with the work of Borisevich et al. on Sm-doped BiFeO_3 antiferroelectrics.⁶⁹ It is clear,

though, that additional experimental and modeling work in this area would benefit the field, and would help test the universality of the role of flexoelectricity in AFE materials.

3.9 Size Effects in AFEs

As with many ferroic phase transitions, the materials properties can change with either the dimensions or size of the coherent crystal; moreover, the relative stability of the various phases can also change.⁷⁰⁻⁷⁴

There are two major types of size effects, namely intrinsic and extrinsic. Intrinsic size effects are related to changes that are associated with the nature of the phase transition, including the transition temperature, diffuseness of the transitions, and magnitudes of the anomalous properties related to the phase transition. Eliseev et al. has considered phenomenological calculation for AFEs and predicted the loss of double hysteresis loops with thin film thickness.⁷⁵ An alternative prediction was made using first principles calculation by Mani et al, where a size driven phase transition from AFE (PbZrO_3) to a FE phase in nanoscale epitaxial thin films under short circuit conditions. These predictions at this time have not been experimentally verified, as sufficiently thin films to test this prediction have not been produced to sufficient quality, and free of strain effects.⁷⁶

There are also extrinsic properties in the size or field induced ferroelectric phase that are impacted by the ferroic domains and their contributions to properties. Material properties, such as permittivity and the piezoelectric coefficients, are affected by the movement of the domain walls.^{77,78} In the case of AFEs, there are no major extrinsic contributions associated with mobile domain boundaries, and hence the dielectric losses are often lower in the case of AFE. This assumes that under an electric field, the movement of a domain wall separating two AFE variants, there is no net polarizability as a consequence of the antipolar alignment limits such contributions. Only polarizability and extrinsic properties contributions are possible with a transition to a nucleating FE phase. Further discussions on the nature of the structure of AFE domain walls are discussed below. Also, in the case of ferroelectrics, the need for continuity of the polarization

in the absence of incomplete screening can drive the size effect. However, the AFE phase can be perturbed by symmetry breaking at the surface. The surface energy can significantly contribute to the structural phase transition at nanoscale and drive the phase transition temperature lower; this also increases the diffuseness of the transition anomalies and the structural distortion strain relative to prototype and the magnitude of the permittivity maxima. These trends are experimentally shown for the AFE PbZrO_3 by Chattopadhyay et al.⁷⁹ The extrinsic size effects that are often found in the case of the FE may well be important, but at this time there is a lack of reported evidence with the high field size effects when the field drives the AFE to the FE phase. One would hypothesize that there should be extrinsic size effects under such conditions.

4.0 Antiferroelectric Phenomenological Theoretical Perspectives

The very first theoretical model to describe an antiferroelectric phase transition was proposed by Kittel, who employed a two sublattice model with each sublattice having its independent spontaneous polarization \vec{P}_a and \vec{P}_b .¹⁸ In such a two-sublattice model, the different ferroelectric states of a crystal are distinguished by the relative values of \vec{P}_a and \vec{P}_b (Table 1 below). For example, $\vec{P}_a = -\vec{P}_b \neq 0$ corresponds to the antiferroelectric state.

Table 1 Distinguishing different polar states based on a two sublattice description of polarization (\vec{P}_a and \vec{P}_b) and ferroelectric and antiferroelectric order parameters (\vec{p} , \vec{q})

Phases	Sublattice Polarization	Order Parameters
Paraelectric Phase	$\vec{P}_a = \vec{P}_b = 0$	$\vec{p} = 0, \vec{q} = 0$
Ferroelectric Phase	$\vec{P}_a = \vec{P}_b \neq 0$	$\vec{p} \neq 0, \vec{q} = 0$
Ferrielectric Phase	$\vec{P}_a \neq \vec{P}_b \neq 0$	$\vec{p} \neq 0, \vec{q} \neq 0$
Antiferroelectric Phase	$\vec{P}_a = -\vec{P}_b \neq 0$	$\vec{p} = 0, \vec{q} \neq 0$

Kittel discussed the possibility of both second and first-order antiferroelectric phase transitions and their characteristics by writing down a Landau potential as a function of the sublattice polarization \vec{P}_a and \vec{P}_b .

Such a sublattice model is a mixed microscopic description of polarization at the unit cell scale and a continuum description of the thermodynamics.

Cross and Okada formulated a consistent continuum phenomenological description of antiferroelectric phase transitions by introducing an antiferroelectric vector order parameter (\vec{q}) in addition to the ferroelectric vector order parameter (\vec{p}), which can be related to the two-sublattice spontaneous polarizations, i.e., $\vec{p} = (\vec{P}_a + \vec{P}_b)/2$ and $\vec{q} = (\vec{P}_a - \vec{P}_b)/2$.^{80,81} Such a formulation has been applied by Haun *et al.* to study the antiferroelectricity in bulk PbZrO_3 and Eliseev *et al.* in antiferroelectric films.⁸²⁻⁸⁴ A similar model was presented by Balashova and Tagantsev by coupling a structural and ferroelectric order parameter to describe the FE to AFE phase transition and corresponding dielectric responses under applied electric fields.⁸⁵

It should be emphasized that it is entirely possible there might exist antiferroelectric phases in which there are more than two sublattices that have finite spontaneous polarization values. Furthermore, the polarizations associated with the sublattices of antiferroelectric phase are usually different from those of the ferroelectric phase within the same crystal in the absence of an applied electric field, i.e. the antiferroelectric state and the corresponding ferroelectric states may not be simply related by flipping the polarization on one of the two sublattices. For example, in the Sm-doped BFO system, the spontaneous polarization is orientaed along the [111] direction for the ferroelectric state while it is along [110] for the antiferroelectric state.⁶⁹ Xue and Chen recently extended the phenomenological theory for antiferroelectricity by defining two independent ferroelectric and antiferroelectric order parameters, which allow the ferroelectric polarization directions to be entirely different from the antiferroelectric state.⁸⁶ Using the unpolarized and unstressed state at the same temperature as the reference, the general free energy density of a crystal g can be expressed as

$$g(p_i, q_i, E_i, \sigma_{ij}) = a_{ij}p_i p_j + a_{ijkl}p_i p_j p_k p_l + a_{ijklmn}p_i p_j p_k p_l p_m p_n \\ + b_{ij}q_i q_j + b_{ijkl}q_i q_j q_k q_l + b_{ijklmn}q_i q_j q_k q_l q_m q_n$$

$$+t_{ijkl}p_i p_j q_k q_l - E_i p_i - \frac{\epsilon_b}{2} E^2$$

$$-\frac{1}{2} s_{ijkl} \sigma_{ij} \sigma_{kl} - Q_{ijkl} p_i p_j \sigma_{kl} - \Lambda_{ijkl} q_i q_j \sigma_{kl}$$

where the Einstein summation convention is adopted. In the above equation, p_i and q_i represent the i^{th} components of ferroelectric and antiferroelectric order parameters, respectively; a_{ij} , a_{ijkl} , and a_{ijklmn} are the second and higher order ferroelectric dielectric stiffnesses with their non-zero components determined by the crystalline symmetry of the reference crystal; b_{ij} , b_{ijkl} , and b_{ijklmn} are the AFE dielectric stiffnesses with their non-zero components determined by symmetry; t_{ijkl} are coupling coefficients between the ferroelectric and antiferroelectric order parameters; s_{ijkl} is the mechanical compliance tensor; σ_{ij} is stress; and Q_{ijkl} and Λ_{ijkl} are ferroelectric and antiferroelectric electrostrictive coefficients, respectively. The free energy density is written as a sixth order to allow the possibility of either a second-order or a first-order phase transition, depending on the values of the coefficients. Typically, all the free energy coefficients are assumed to be independent of temperature except the second-order stiffness coefficients a_{ij} and b_{ij} , which are assumed to be linearly dependent on temperature. Here only the coupling term between p_i and q_i is included for simplicity. With a given set of coefficients, the stability regions of different states can be obtained by minimizing the free energy with respect to p_i and q_i under a given stress or strain and electric field, and temperature-strain-electric-field phase diagrams can be constructed.

5.0 Crystal Structures and Crystallography of AFEs

This section will cover some of the important crystal structures that host antiferroelectricity.

5.1 Perovskite Structure and AFE

The ABO_3 perovskite structure has a B-cation site that is octahedrally coordinated and an A-site cation site that is twelve-fold coordinated. The prototype cubic perovskite structure is shown in Figure 11(a). Various cooperative displacements of cations develop through the phase transition and can lead to lower symmetry phases: polar or non-polar. There are many different perovskite compounds that have an AFE

phase; these include PbZrO_3 (PZ), PbHfO_3 (PH), $(\text{Na}_{0.5}\text{Bi}_{0.5})\text{TiO}_3$ (NBT), $\text{Pb}(\text{Yb}_{0.5}\text{Nb}_{0.5})\text{O}_3$ (PYN), $\text{Pb}(\text{Lu}_{0.5}\text{Nb}_{0.5})\text{O}_3$ (PLN), $\text{Pb}(\text{Co}_{0.5}\text{W}_{0.5})\text{O}_3$ (PCW), $\text{Pb}(\text{Mg}_{0.5}\text{W}_{0.5})\text{O}_3$, (PMW) and $\text{Pb}(\text{In}_{0.5}\text{Nb}_{0.5})\text{O}_3$ (PIN).⁸⁷⁻¹¹⁰ Also, there are many solid solutions between each of these compounds and other solid solutions with AgNbO_3 , NaNbO_3 , and doped BiFeO_3 ; these will be discussed in more detail later.

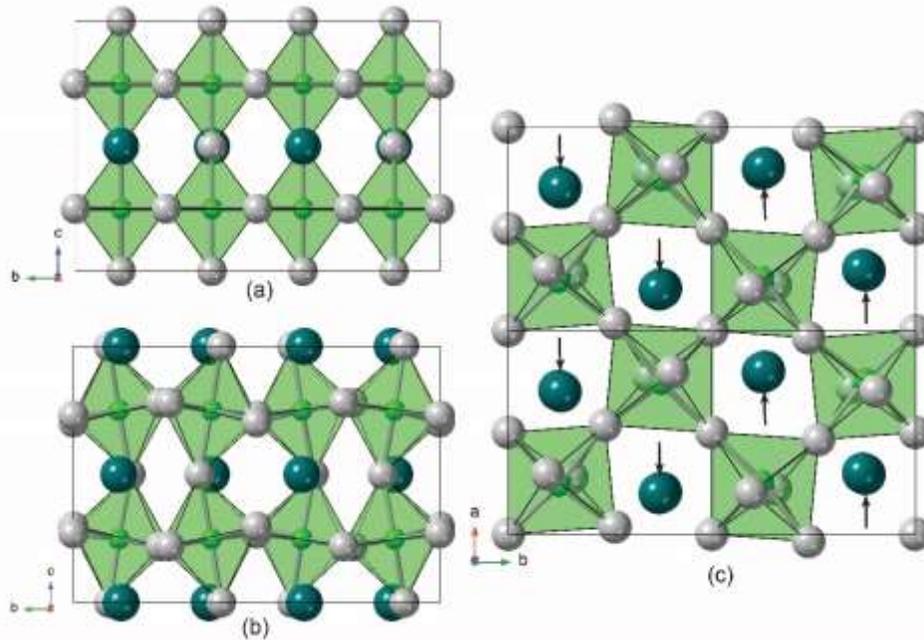


Fig. 11: Crystallography of PbZrO_3 , after Corker et al.¹¹¹ Pb are the large dark green colored atoms, Zr is light green, and O is grey. The ZrO_6 octahedra are shown. (a) View of the prototype cubic structure along the a axis of an orthorhombic cell (to facilitate the comparison to the antiferroelectric phase). View of the antiferroelectric polymorph viewed along (b) the a axis and (c) the c axis. The arrows in (c) show the orientation of the local polarization due to Pb displacements; it is clear that the polarization cancels at a unit cell level.

Some of the details of the nature of the AFE state and the structures of many AFE are controversial, and in recent times, first principle calculations have added a clearer understanding of the energetics of the phases and structures. Many AFEs within the perovskite structures are complex, and this is related to associated octahedral tilt transitions, impurities, and non-stoichiometric perturbations. As described above, through a lattice dynamics investigation, Tagantsev et al. point out that incommensurate phase transitions are an important factor influencing the AFE state. The phase transition of PbZrO_3 is $T_c \sim 505$ K.

PbZrO₃ has an orthorhombic structure (Pbam) on cooling from the paraelectric phase. Figure 11(b),(c) show the basic AFE structure of PbZrO₃.

In the case of the PbHfO₃, there is a different phase sequence; on cooling below the cubic phase, at 493 K, the structure is tetragonal, but with the $c/a < 1$; from $441 < T \text{ (K)} < 493$, a lower temperature orthorhombic AFE phase is isomorphous with PbZrO₃.¹¹² Figure 12(a) shows the dielectric –temperature data and (b) incommensurate modulation for PbHfO₃.⁹⁷ It was recently reported that this system also has an INC structural transition (Fig. 12b,c).¹¹³

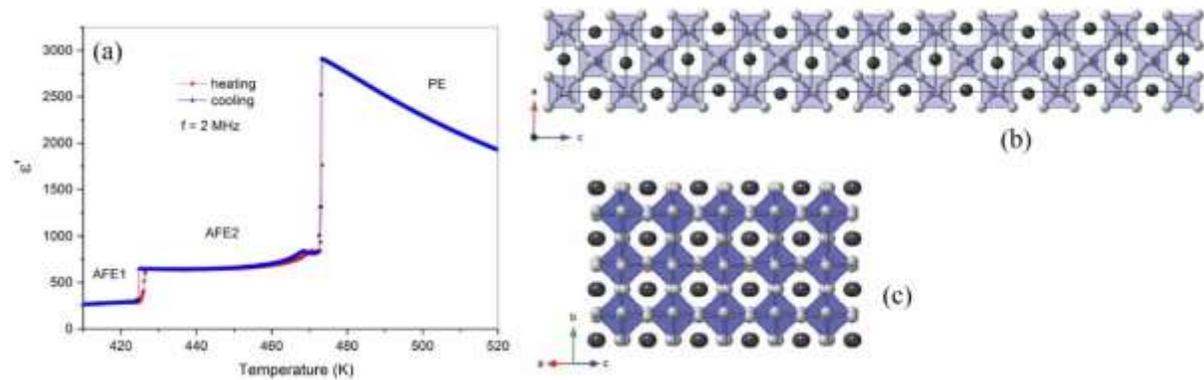


Fig. 12: (a) Phase transition sequence in PbHfO₃ (Reproduced by permission from Ref. 97). (b),(c) Representation of the incommensurate modulations in the structure of PbHfO₃, after Bosak et al.¹¹³ (b) The Pb atoms (shown as dark circles) are modulated predominantly in the [110] of the cubic prototype group. (c) the structure also has octahedral tilt.

Niobate perovskites such as NaNbO₃ and AgNbO₃ have multiple octahedral tilt transitions. Near room temperature, there is an AFE phase that has the orthorhombic space group Pbcm, with the antipolar distortions coming from the Nb-O bonds. In the case of NaNbO₃, there are two phases that are very close in energy; these are the so-called P and Q phases that are antipolar Pbma and polar phase P2₁ma, as shown in Figure 13. This manifests itself in co-existence of both these phases in the NaNbO₃, and these can limit the observation of the double hysteresis loops.¹¹⁴⁻¹¹⁶ However, as will be discussed below, strategic solid solutions can stabilize the AFE phase over the FE phase.^{117,118}

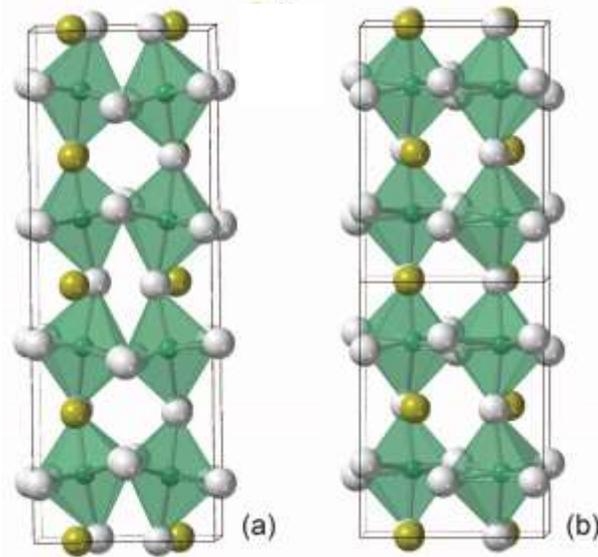
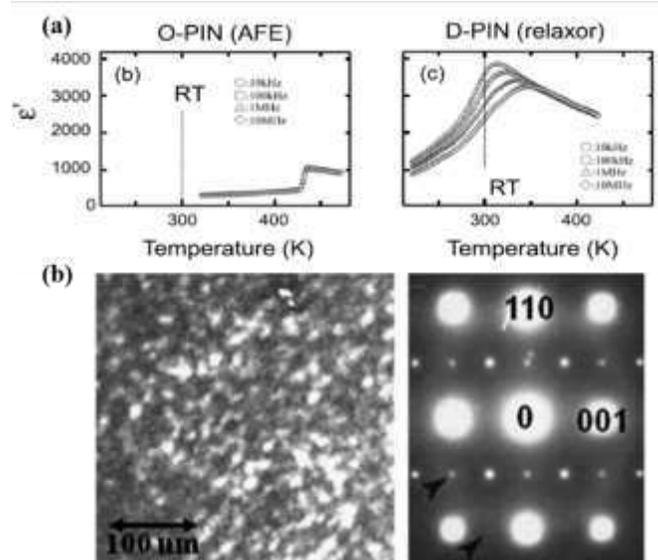


Fig. 13. Crystal structures of NaNbO_3 , after Johnston et al.¹¹⁹ (a) antipolar P phase, (b) polar Q phase with Na^+ gold, Nb^{+5} green, O^{-2} white.

AFE also occurs in double perovskites, $\text{Pb}(\text{B}'_{0.5}\text{B}''_{0.5})\text{O}_3$, that have two cations which can experience ordered occupancy on the B-site. This produces a unit cell with a $2a_o \times 2a_o \times 2a_o$ cell (relative to the prototype cubic cell), with a superlattice structure associated with the F-centered ordering of the respective B'-cations. At low temperatures, $\text{Pb}(\text{Lu}_{0.5}\text{Nb}_{0.5})\text{O}_3$, $\text{Pb}(\text{Yb}_{0.5}\text{Nb}_{0.5})\text{O}_3$, $\text{Pb}(\text{Lu}_{0.5}\text{Ta}_{0.5})\text{O}_3$, $\text{Pb}(\text{Yb}_{0.5}\text{Ta}_{0.5})\text{O}_3$, $\text{Pb}(\text{Co}_{0.5}\text{W}_{0.5})\text{O}_3$, $\text{Pb}(\text{Mg}_{0.5}\text{W}_{0.5})\text{O}_3$ and $\text{Pb}(\text{In}_{0.5}\text{Nb}_{0.5})\text{O}_3$ have been found to be antiferroelectric. The electrostatic energy and strain difference between the B' and B'' cations induce long-range order at the high temperatures of crystal growth and/or conventional sintering.

In $\text{Pb}(\text{In}_{0.5}\text{Nb}_{0.5})\text{O}_3$, an order-disorder transformation for the In and Nb ions can be controlled with appropriate thermal annealing and/or quenching. B-site order with intermediate length scales yields relaxor ferroelectric response, whereas the ordered state is AFE.^{109,110,120-122} Figures 14(a) contrasts the dielectric permittivity versus temperature for intermediate and long-range B-site ordered $\text{Pb}(\text{In}_{0.5}\text{Nb}_{0.5})\text{O}_3$; (b) shows the dark field imaging of the $\frac{1}{2}\{\text{hh}0\}$ superlattice reflections.¹²³



Figures 14: (a) Dielectric permittivity in the double perovskite $\text{Pb}(\text{In}_{0.5}\text{Nb}_{0.5})\text{O}_3$ with relaxor and AFE order (Reproduced by permission from Ref.122). (b) Transmission electron microscopy images of $\text{Pb}(\text{In}_{0.5}\text{Nb}_{0.5})\text{O}_3$ with nanopolar ordering in the disordered materials as imaged through a dark field image of a $\frac{1}{2}\{110\}$ superlattice, the [011] zone axis pattern shows the $\frac{1}{2}\{hh0\}$ dipole superlattice and the $\frac{1}{2}\{hhh\}$ B-site chemical ordering superlattice reflections (Reproduced by permission from Ref. 123).

There are extensive studies in $(\text{Na}_{0.5}\text{Bi}_{0.5})\text{TiO}_3$ and its' solid solutions, due to its potential interest as a lead-free piezoelectric, building from the initial work of Takenaka et al. The double hysteresis at higher temperatures in $[(\text{Na}_{0.5}\text{Bi}_{0.5})_{1-x}\text{Ba}_x]\text{TiO}_3$ solid solutions has variously been described as an AFE response or an ergodic relaxor behavior. Tan et al. combined the two models and proposed a "relaxor AFE" concept characterized by nano-antipolar regions.¹²⁴ However, with careful HRTEM and Rietveld neutron powder analysis structural analysis, it is shown that there are inequivalent cation displacements that are coupled with the octahedral tilts. In fact, at temperatures between 593K to 813 K, the Na/Bi and Ti cations are displaced in opposite directions along the [001] axes, and these are coupled to an in-phase $a^+a^+c^+$ octahedral tilt.^{124,125} The displacements are not equal and opposite, and therefore the material is not strictly an AFE. So, as pointed out above, even indications such as superlattices and double hysteresis loops are not necessarily definitive proof of an AFE.

5.1.1 Crystal Chemistry, Solid Solutions, and AFE Stability in Perovskites

The most extensive crystal chemical investigations of AFE have been in the perovskite crystal structure. Great insight into the trends of perovskites and their solid solutions have been guided by the Goldschmidt tolerance factor (t). It is based on a simple idea of the assumption of ionic packing in the perovskite ABX_3 compounds, The Goldschmidt tolerance factor is a dimensionless quantity that considers the geometric packing, where $t = (R_A + R_X)/\sqrt{2}(R_B + R_X)$, and where R_A , R_B , and R_X are the ionic radii of A, B, and X (for the appropriate coordinations). An extremely useful ionic radii base is supplied in the classic work of Shannon and Prewitt.¹²⁶ When $t=1$, the geometry is consistent with an ideal cubic perovskite; as the t factor differs from 1, the perovskite structure distorts (often through tilt or ferroelectric distortions). At large deviations, the crystal structures changes to structures such as ilmenite, $FeTiO_3$, $t \sim 0.71$, and hexagonal perovskite, $t \sim 1.06$. Goldschmidt, Megaw, Evans, Galasso, Fesenko, Isupov, and Navrotsky all noted the useful thermodynamic property trends correlating with tolerance factor, t , such as heat of formation, and antidistortive versus ferrodistoritive phase stability trends within the perovskites.^{1,127-132} Later, others identified that many different electric property trends in perovskites correlate with the tolerance factor, including the temperature dependence of the permittivity in microwave dielectrics, morphotropic phase boundary temperatures, and of interest here, the stability of AFE over FE phases.^{133,134}

There are several examples of the use of tolerance factor to stabilize an AFE phase in a perovskite, as detailed below. AFE in perovskites requires $t < 0.97$:¹¹⁷

(i) $(Bi,Re)FeO_3$: Re is a rare earth cation substitution in the end member $BiFeO_3$ is an extremely high temperature ferroelectric material, with a T_C of $\sim 820^\circ C$ and a large distortion due to the large displacement of its cations relative to ideal positions (~ 0.66 Å for Bi and 0.26 Å for Fe at $\sim 100^\circ C$).¹³⁵ Given the high temperature stability of FE phase, it is not intuitive that it can be transitioned into an AFE material. It does, however, have a tilt transition, and it also has a low tolerance factor, $t \sim 0.96$. The group of Takeuchi first reported the double loop in $(Bi_{1-x}Sm_x)FeO_3$ thin film beyond the MPB while attributed such AFE-type behavior to a low symmetry pseudo-orthorhombic phase.¹³⁶ Later, assisted by the electron

diffraction pattern, they revised that argument to, the PbZrO_3 -like symmetry is responsible for the AFE ordering, which was then reproduced in Gd and Dy doped BFO as well.^{137,138} Corresponding to different doping amount/tolerance factor, the paraelectric symmetry is Pnma , the AFE phase is Pbma (isostructural with PbZrO_3), and at lower temperature, a FE R3c phase appears. Figure 15(a) shows the phase fields as a function of temperature and composition in rare earth doped BiFeO_3 .¹³⁸

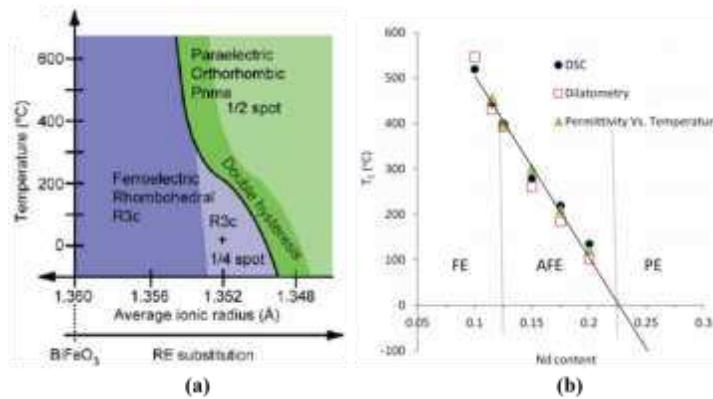


Figure 15. Effect of rare earth doping on the crystallography of BiFeO_3 . The phase fields in RE doped BiFeO_3 (Reproduced by permission from Ref. 138). (b) T_c vs Nd content obtained from differential scanning calorimetry (DSC), dilatometry and dielectric measurements. The phase boundaries are shown (Reproduced by permission from Ref. 143).

Reaney and co-workers investigated in detail the crystal chemistry of $(1-x)\text{BiFeO}_3-x\text{REFeO}_3$.¹³⁹⁻¹⁴¹ The PbZrO_3 (Pbam , a^0b^0b') structured AFE phase was stable for a certain range of RE doping, below which an R3c ($a^-a^-a^-$) dominates and above which compounds adopted the classic orthoferrite (Pnma) structure with an $a^-a^-c^+$ tilt system.¹⁴² Although the structural refinement in $(1-x)\text{BiFeO}_3-x\text{REFeO}_3$ $0.13 < x < 0.22$ using XRD data is conducted with the same symmetry (Pbam , $\sqrt{2}a, 2\sqrt{2}a, 2a$) as the PbZrO_3 structure, electron diffraction reveals extra, weak $\frac{1}{4}\{h00\}$ superstructure reflections which suggest Pnma symmetry with a $\sqrt{2}a, 2\sqrt{2}a, 4a$ cell.¹³⁹

The phase transition from PE to FE/AFE is associated with a large volume change driven by an expansion along the b-axis. As a result, phase transitions in Nd-doped BiFeO₃ can be readily followed by DSC and dilatometry as well as in conventional permittivity temperature plots, Figure 15(b).¹⁴³

The driving force for the formation of an AFE phase in RE doped BiFeO₃ can be rationalized by comparing this system to the PbZrO₃-PbTiO₃ phase diagram. In the PZT phase diagram, as the PZ end member is approached, the tolerance factor and average ionic polarizability decrease in an R3c/R3m phase field. Doping BiFeO₃ with Nd also decreases the tolerance factor and polarizability, leading to similar structural instabilities.^{140,141}

However, there are subtle differences in behavior between the onset of antiferroelectricity in the PZT phase diagram and that of Nd-doped BiFeO₃. In PZT, at room temperature, the amplitude of octahedral rotations increases in the R3c phase field as Zr concentration increases but then decreases to zero (R3m) as the PZ phase field is approached. This anomalous tilt behavior is not reproduced in the Nd doped BiFeO₃ and suggests complex coupling between the Pb displacements and the octahedral rotations which force a gradual composition transformation, $a^-a^-a^-$ to $a^0a^0a^0$ to $a^0b^-b^-$ rather than the abrupt change in RE doped BiFeO₃ from $a^-a^-a^-$ to $a^0b^-b^-$.¹³⁹⁻¹⁴¹ Electron diffraction patterns from compositions in between the $a^-a^-a^-$ and $a^0b^-b^-$ phase fields in PZT also exhibit superstructure reflections consistent with a cell doubling rather than quadrupling. The cell doubling was confirmed by Woodward et al.;¹⁴⁴ these reflections violate the Weiss zone law in $\langle 110 \rangle$ zone axes for in phase tilting and, therefore, are more likely associated with cation rather than anion displacements. However, XRD studies of this region of the phase diagram have not, to date, unambiguously identified an intermediate structure of this nature.

One of the main problems associated with BiFeO₃ has been to control the electrical conductivity, generally considered to be p-type as a result of Bi-loss compensated by the oxidation of Fe³⁺ to Fe⁴⁺.¹⁴⁵ In principle, the substitution of a donor dopant such as Ti⁴⁺ on the B-site should, therefore, significantly decrease

conductivity. Kalantari et al. doped AFE- RE doped BiFeO₃ with TiO₂ in an attempt to decrease the conductivity and establish whether a double AFE P-E loop could be obtained.¹⁴⁶ Although they were successful in decreasing conductivity by several orders of magnitude, only a linear dielectric P-E loop could be obtained, suggesting that AFE-FE switching in RE doped BiFeO₃ may only be achieved at fields far greater than in PbZrO₃. However, Ti doping yielded unexpected phenomena within the matrix arising from an unusual ionic compensation mechanism such that $Ti_{Fe}^{\bullet} \equiv 1/3V_{Nd}'''$. As a result of this ionic compensation mechanism, Nd₂O₃ was expelled from solid solution at high temperature in the form of coherent nano-rods a few unit cells wide.^{147,148} A number of other unusual planar defects were observed, some of which force a local FE rather than a AFE configuration.¹⁴⁹

(ii) NaNbO₃: The earliest experimental results on AFE in NaNbO₃ were reported by Nicholson and Cross.²² It proved to be very challenging to reproduce the results, most likely due to differences in impurity contents of the samples which led to small changes in the relative stability of AFE and FE phases. The structure of NaNbO₃ was also challenging to unravel; there is now a consensus that NaNbO₃ has two low temperature phases of almost identical energetics, namely the **P** (AFE) and **Q** (FE) phases.¹¹⁵ Experimental studies are prone to uncertainty, as material impurities and/or non-stoichiometry can affect the relative stability of these two phases. DFT investigations verified the iso-energetics between the **P** and **Q** phases.¹⁵⁰ As NaNbO₃ had a tolerance factor t of $t \sim 0.967$, Guo et al. examined a wide variety of solid solutions that would lower this tolerance factor, and in doing so, favor the **P** phase.¹¹⁸ Among the compositions that were experimentally determined to be AFE were $x\text{CaZrO}_3-(1-x)\text{NaNbO}_3$ and $x\text{BiScO}_3-(1-x)\text{NaNbO}_3$.^{117,151} TEM analysis of the domain configurations associated with the coexistence of **P** and **Q** phases confirmed that on lowering the tolerance factor, the **Q** phase systematically disappears, and a single **P** phase can be stabilized. Although not fully understood, INC phases also are involved as an intermediate in the electric field driven phase transitioning from AFE to FE.¹⁵² In NaNbO₃ stabilized with doping, the incommensurate phase in the **P** phase region can be inferred from the polarization current density and differential dielectric

permittivity anomalies; it provides the bridge structure during the electric field-induced polarization reversal and antiferroelectric-to-ferroelectric transition in NaNbO_3 solid solutions.^{153,154}

(iii) AgNbO_3

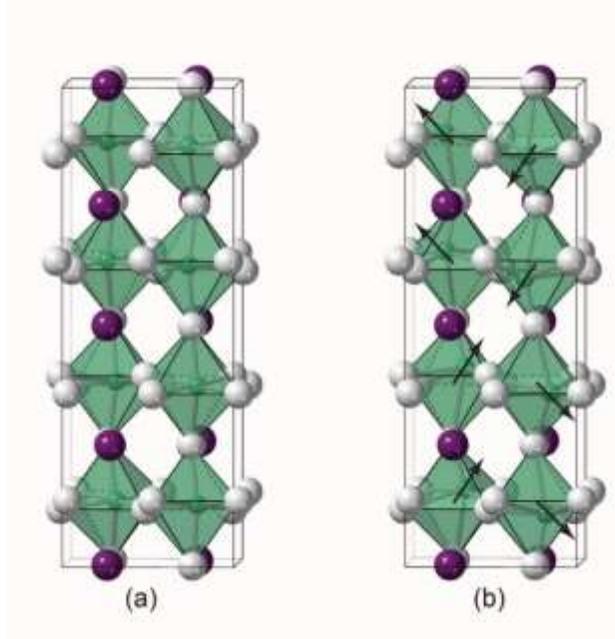


Fig. 16: AgNbO_3 crystal structure at room temperature, after Levin et al.¹⁵⁵ (a) Shows the average structure, illustrating quadrupling along the c lattice parameter due to a complex tilt structure. In the so-called **M** phases, the Nb atoms displace in the octahedron over short length scales. (b) A schematic of one possible displacement pattern that would account for the observation of antiferroelectric hysteresis loops; the local polarization is shown with arrows. However, it is important to note that the best structure refinements available suggest that the displacements do not correlate over long length scales, and indeed may not appear in the same unit cell.

The crystal structure of AgNbO_3 undergoes a series of polymorphic phase transformations as a function of temperature, from a high temperature cubic prototype perovskite structure to progressively more complex tilt patterns, through two antiferroelectric orthorhombic phases, and finally to a ferroelectric phase. Octahedral tilt transitions are driven, in this material, by the fact that the Ag is too small for the 12-coordinated A-site; as a result, it displaces from the center of its coordination polyhedron, driving coupled puckering of the octahedral framework. The magnitude of the tilt angles and the phase transition temperatures can be modulated by applied strains.^{119,156-158}

In the antiferroelectric phases, tilting of the NbO_6 octahedra favors a locally ordered antipolar arrangement of the Nb displacements. These Nb displacements occur predominantly along the $[110]$ direction of the prototype cubic unit cell, with a finite displacement in the crystallographic “c” direction of the unit cell. This is illustrated schematically in Fig. 16, where the average and a potential local structure are shown. However, it is important to note that Fig 16(b) is a simplification – the cancellation may not occur in the length scale of a single unit cell (as shown) but may occur elsewhere in the structure. In either case, the antiferroelectric behavior is presumably observed because a high enough electric field can induce a more ordered phase, where a net polarization is field-induced.

The general rationale adopted for the M phase transitions suggested that they occur as a result of a gradual increase in the amplitude of tilting on cooling from the O-**M3** transition which drives displacement of the cations from their average positions in the **M3** phase. The displacements occur initially such that they do not break the $Pbcm$ symmetry (**M3–M2**), but finally a ferroelectric phase occurs (**M2–M1**) in which there are inequivalent cation antipolar displacements within the quadrupled tilted framework (Figure 17). This mechanism explains why the Curie maxima are so broad, since the cation displacements which contribute to permittivity are coupled to the amplitude of octahedral rotation. It should be noted that the FE and AFE phases all refine well with $Pbcm$ symmetry, and it is only the appearance of weak polarization in the M1 phase that suggest that it is non-centrosymmetric ($Pmc2_1$).¹⁵⁶⁻¹⁶⁰

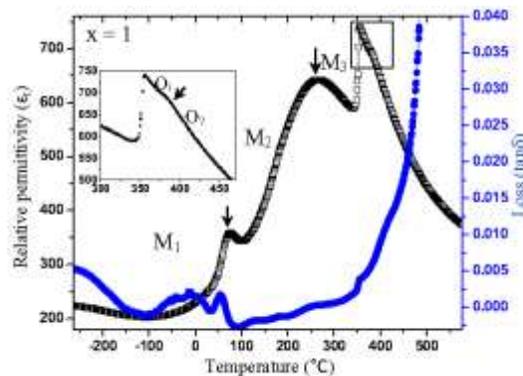


Fig. 17: Relative permittivity (open circles) and loss tangent (filled circles) for AgNbO_3 showing some of the multiple phase transitions (Reproduced by permission from Ref. 160).

Khan *et al.* studied the effect of Li doping on AgNbO_3 and observed a transformation from a 4x to a 6x cell in electron diffraction patterns at $\sim 10\% \text{Li}$ (Figure 18),¹⁶¹ which was accompanied by a dramatic change in the Raman spectra. Rietveld refinement was not undertaken by these authors but the formation of a 6x cell is analogous to the transitions observed in NaNbO_3 .

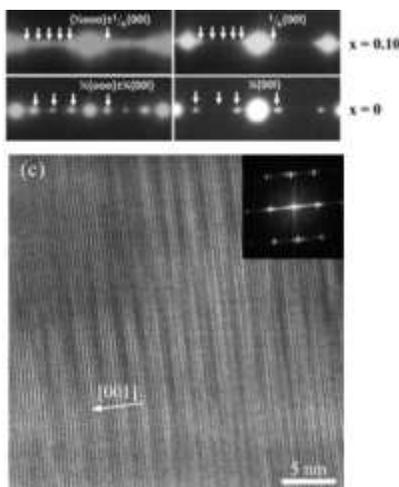


Figure 18. Systematic rows in $\langle 310 \rangle$ electron diffraction showing the formation of the 6x supercell for 10% Li doped AgNbO_3 and high-resolution image obtained parallel with $\langle 110 \rangle$ zone axis. Inset is the associated Fourier transform further illustrating the $1/6(001)$ spacing (Reproduced by permission from Ref. 161).

5.1.2 Other AFE Solid Solutions:

A typical phase diagram of the solid solution formed between an AFE end member and a FE end member is the $(1-x)\text{PbZrO}_3-x\text{PbTiO}_3$. The phase boundary between the AFE (Pbam) and FE (R3C) is at 95/5. Dopants such as La, Ca, Sn, Nb, etc. drive the material to a more diffuse phase transition. The resulting AFE structures are often INC and/or frustrated, inducing relaxor-like behavior.¹⁶²⁻¹⁶⁸ Figure 19 shows examples of phase boundary with La doping batched according to ionic compensation in the form $\text{Pb}_{1-3x/2}\text{La}_x(\text{Zr}_{1-y}\text{Ti}_y)\text{O}_3$.¹⁶⁹ Many of the AFE-FE materials within the perovskites with PbTiO_3 have Morphotropic Phase Boundaries associated with enhanced piezoelectric properties; PYN-PT has noteworthy piezoelectric properties at its MPB. The AFE-FE MPB can be tuned or even created by applying electric field and/or pressure, as shown in Figure 20.¹⁶⁹

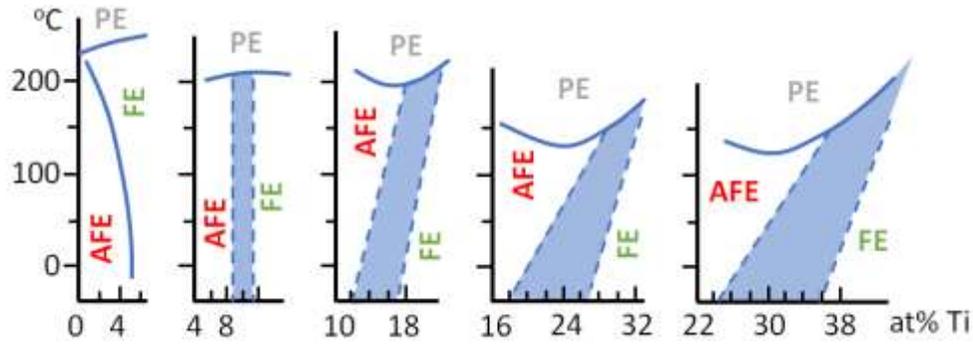


Figure. 19: Phase boundaries as a function of Ti content in PZT doped with 0% - 8% La (left to right) (replotted from Ref. 169).

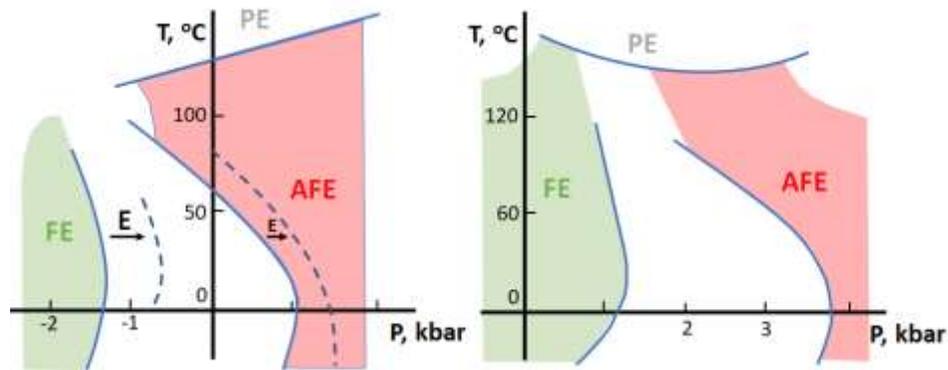


Figure 20. Pressure-Temperature phase diagram for PLZT solid solution with 6% La, and Zr/Ti of 80/20 (left) and 65/35 (right), the E field applied is 500 V/cm (replotted from Ref. 169).

6.0 Other Possible Crystallographic Families with Antiferroelectric Behavior

6.1. H-bonded ADP AFE

After the discovery of AFE in perovskites, the H-bonded KH_2PO_4 (KDP) family that had been found to host ferroelectricity was shown to have chemistries that host AFE, such as with ammonium di-hydrogen phosphate $(\text{NH}_4)_2\text{H}_2\text{PO}_4$. The PO_4 tetrahedra are hydrogen bonded to other parts of the structure, and order-disorder in the position of the H-ion influences the dipoles within the tetrahedra. In the high temperature phase, the H position is statistically averaged between the two oxygens in respective minima with no spatial repeating of the occupancies of those minima. In the case of ferroelectrics such as KDP

(KH_2PO_4) below T_c , there is a cooperative occupancy, and the PO_4 dipole moments are aligned in chains. The hydrogen bonds do not directly contribute to the spontaneous polarization, but the ordering of the H atoms act as a trigger to the phase transition. In the case of ADP, the rotation of the $(\text{NH}_4)^+$ complexes drive adjacent chains with antiparallel dipole alignments to form an AFE phase. Figures 21 show a comparison between the paraelectric and AFE phases of ADP and the FE KDP.^{24,170-172}

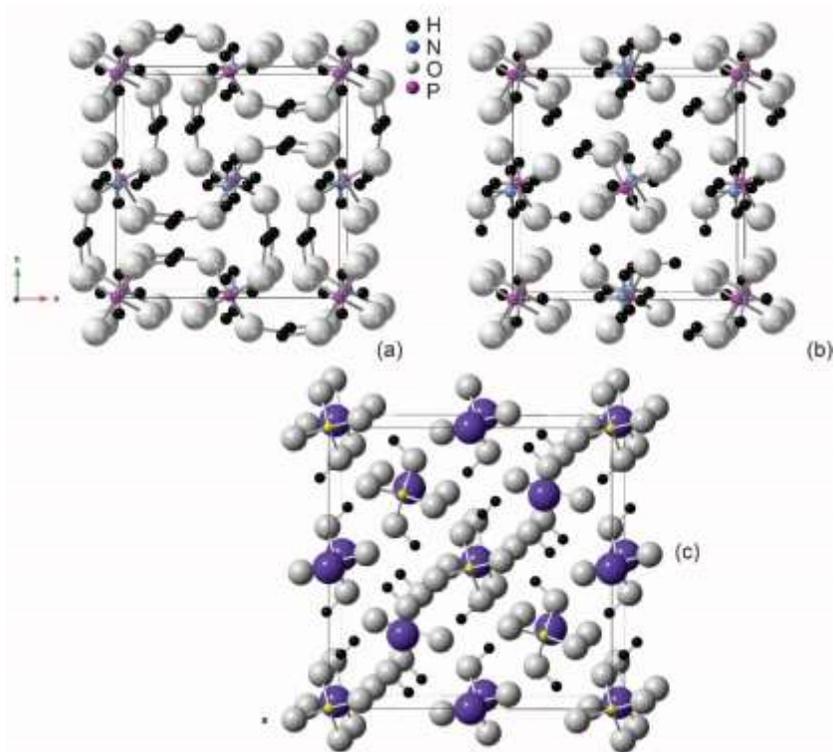


Figure. 21: Crystal structures of $\text{NH}_4\text{H}_2\text{PO}_4$, after Fukami et al.,¹⁷² in the (a) paraelectric phase at 152 K and (b) the antiferroelectric phase at 143 K. (c) Ferroelectric phase of $\text{K}_2\text{H}_2\text{PO}_4$ (K is the large dark sphere).

Solid solutions have also been explored with ADP (AFE) as an end member and FE compounds such as KDP and RDP, $\text{RbH}_2(\text{PO})_4$. In these order-disorder solid solutions, FE and AFE order compete, resulting, at intermediate compositions, in relaxor-like behavior typical of dipolar glasses.¹⁷³ This arises because the solid solution induces frustration that limits the long-range ordering. The ordering is, therefore, short range and highly disordered, giving rise to glassy behavior and highly dispersive dielectric responses. In regions near the end members there are FE and AFE phase fields, and there is a systematic decrease of

the phase transition temperature in solid solution with other end members. The region between these phase boundaries is characterized by a random local freezing-out of the dipoles owing to the frustration of the parallel and antipolar ordering (Figure 22).¹⁷⁴⁻¹⁷⁶

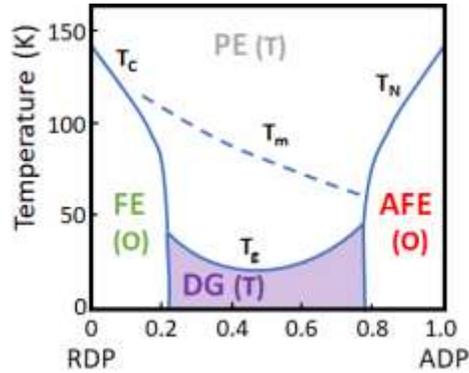


Figure 22: Show the binary solid solution between the FE KDP and the AFE ADP, the nature of the polarization changes to a dipolar glass in the central compositions (replotted from Ref. 173).

6.2 M-type Hexaferrite Structure and AFE:

The M-type hexaferrites are based on the chemical formula $MFe_{12}O_{19}$ ($M = Ba, Sr$ or Pb); these are important ferrimagnetic oxides with high values of magneto-crystalline anisotropy and saturation magnetization. Recently, the M-type hexaferrites, such as $PbFe_{12}O_{19}$ and $SrFe_{12}O_{19}$, were reported to have large ferroelectric polarization and large magnetic properties coexisting at room temperature.^{177, 178} $La_{0.2}Sr_{0.7}Fe_{12}O_{19}$ has been postulated to have an AFE phase. There are some anomalies in the loops that bear future exploration, such as the polarization saturation that is physically difficult to explain. Nonetheless, this is an interesting result, given the magnitude of the polarization reported. More work needs to be done on this family of materials to fully verify the potential AFE phase.

6.3 HfO₂-ZrO₂ Thin Films:

There is double hysteresis observed in the new HfO₂-ZrO₂ thin film systems, especially for the ZrO₂ rich compositions.¹⁷⁹ At this time there are no additional experiments to point to a true antiferroelectric behavior, as opposed to an aging or domain pinning effect. However, a detailed DFT calculation has shown

that there are optical phonon instabilities in the cubic phase at the Brillouin zone edges, and these also are coupled to a zone center mode.¹⁸⁰ So it is quite possible that there is either an AFE structure or INC structure in these new systems, but the field awaits the important structure details in this interesting ferroelectric binary system.

6.4 Alkali Earth Sulfoaluminate Structure and AFE

Calcium sulfoaluminate is of interest for cements, as well as its luminescent properties. The structure is built up of $[\text{AlO}_2]_{12}^-$ anionic framework, and the spaces between are filled by M^{2+} cations and X^{2-} anions. The $[\text{AlO}_2]_{12}^-$ framework of corner-shared AlO_4 tetrahedra can undergo a variety of distortion modes. Recently the $(\text{Ca}_{1-x}\text{Sr}_x)_8 [\text{AlO}_2]_{12}(\text{SO}_4)_2$ with $x = 0.8-1.00$ has dielectric properties that has been proposed to be due to AFE and relaxor dielectric properties. The basic crystal structure is shown in Figure 23.¹⁸¹ The high temperature phase is $\text{Im}\bar{3}m$. On cooling, the material undergoes a series of transitions from $\text{Im}\bar{3}m \rightarrow I\bar{4}3m \rightarrow P\bar{4}c2$. At lower temperatures, an AFE phase is speculated to occur for $x > 0.95$; for higher Ca-doping, the $P\bar{4}c2$ phase field is lost. In this case, the transition is believed to be to a low temperature relaxor AFE, from the cubic $I\bar{4}3m$. Further work is required to fully confirm these materials to be members of the AFE family.

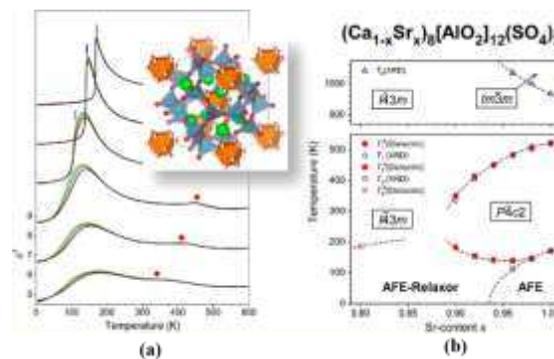


Figure 23. (a) Temperature dependent dielectric constant in $(\text{Ca}_{1-x}\text{Sr}_x)_8 [\text{AlO}_2]_{12}(\text{SO}_4)_2$. (b) Phase diagram of $(\text{Ca}_{1-x}\text{Sr}_x)_8 [\text{AlO}_2]_{12}(\text{SO}_4)_2$ (Reproduced by permission from Ref.181).

6.5 Ruddlesden-Popper Structures

Recently a new Ruddleden–Popper compound, $\text{Sr}_3\text{Zr}_2\text{O}_7$, was reported as having a first order ferroelectric to paraelectric phase transition.¹⁸² The tilt transitions drive this system to a room temperature ferroelectric. There is an unusual a sequence of coupled and uncoupled octahedral rotation and tilt transitions making this a hybrid improper ferroelectric. DFT calculations and structural analysis successfully explain the phase transitions. In addition to the ferroelectric and tilt transitions, it is noteworthy that there is an antipolar P_{nab} high temperature phase that is classed as a hybrid improper antiferroelectric. At this time, the DFT calculations are not experimentally verified, but they point to a broader concept of tilt and soft mode instabilities, especially in materials with small chemical driving forces for polar modes.

6.6 2-D Antiferroelectrics

2-D materials have emerged as a new family of optoelectronic materials. Depending upon the number of layers and the composition, a wide variety of properties from superconductors, metals, semiconductors, and insulators have been reported.¹⁸³ More recently, there have been a limited number of reports that 2-D materials such as $\text{AgBiP}_2\text{Se}_6$, CuInP_2S_6 and $\text{CuBiP}_2\text{Se}_6$ can have FE, ferrielectric, or AFE phases.^{184,185} As shown in Fig. 24(a), in $\text{AgBiP}_2\text{Se}_6$, the chalcogenide framework has octahedral voids filled by Ag (Bi) and P-P pairs. The bulk crystals are made from stacks of these layers. It is apparent that the Ag^+ and Bi^{3+} positions show AFE-like ordering. Recently, Xu et al. mapped out the in-plane antiparallel dipole arrangement with the modulation wavelength of $8d_{1100}$ in the single layer $\beta\text{-In}_2\text{Se}_3$ (Fig. 24b). The domain boundary is observed at both nano- and micron-scale.¹⁸⁶ Unfortunately, perhaps due to the relatively low band gap of the compounds, clear AFE double hysteresis loops have not been reported. Van der Waals interactions bond the adjacent layers, and the weakness of the Van der Waal bonds allows for the material to be exfoliated into 2-D layers. A detailed DFT investigation points to the balance of ionic and Van der Waal interactions that can control the ferroelectric and/or the AFE ordering of these materials.¹⁸⁷

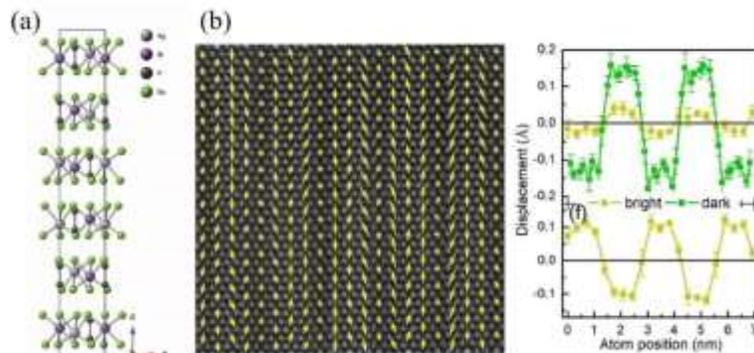


Figure 24. (a) Crystal structure of CuBiP₂Se₆ at room temperature, after Gave et al. The positions of the Ag and the Bi show an antiferroelectric-like arrangement.¹⁸⁴ (b) ADF-STEM mapping of the dipoles in β-In₂Se₃ and the measured atomic displacements (Reproduced by permission from Ref. 186).

6.7 Antiferroelectric Liquid Crystals

Liquid crystals are between two states of matter, i.e. liquids and solid crystalline phases. Meyer (1975) discovered FEs in a tilted chiral smectic C* (SmC*) liquid crystalline phase.¹⁸⁸ These materials had very fast electrooptic switching, as shown by Clark and Lagerwall (1980),¹⁸⁹ that at that time was highly appealing for computer monitors. This, in turn, applied a technological pull to explore more chemistries that could form tilted SmC* materials. SmC* chiral molecules naturally are non-centrosymmetric. In the tilted chiral form, molecules are arranged with an orientational order in smectic layers, and in each layer, there can be a dipole-dipole ordering that overrides the thermal disordering of the paraelectric phase.¹⁹⁰ The low temperature phase then has several cooperative forms ranging from parallel or antiparallel dipoles. So, this not only led to the discovery of liquid crystal ferroelectrics, but also to ferrielectric, incommensurate, and AFEs. The AFE SmC*_A phase was discovered by Chandani (1989).¹⁹¹ Figure 25 shows the spontaneous polarization pointing upward and downward in alternative layers in SmC*_A phase and the double loop measured from 4'-Octyloxy-biphenyl-4-carboxylic acid 4-(1-methyl-heptyloxycarbonyl)-phenyl ester (MHPOBC).¹⁹² There are several antiferroelectric variants classified into four major groups; alternative layers with antipolar orthogonal ordering SmA_P, tilted polar case that can be synclinic or anticlinic leaning, and combinations of the tilting and leaning alternatives, sometimes called double tilted or general tilted.

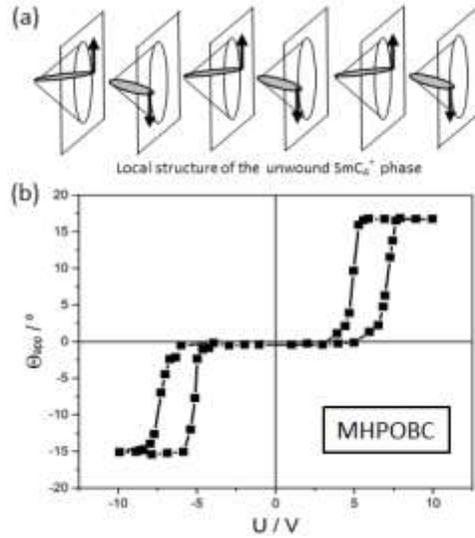


Figure 25. (a) Schematic illustration of the structure of an antiferroelectric smectic liquid crystal (without the helical superstructure); (b) corresponding double hysteresis loop (replotted from Ref.192).

7.0 Hierarchical Domain Structures and Switching in Antiferroelectric Materials

For either order-disorder or displacive PE-AFE phase transitions, there is a crystallographic symmetry change. In general, if the high temperature or PE point group symmetry is called G , then the symmetry of the lower temperature phase, F , is a subgroup of G . In this case, the number of domain states can be determined from the ratio of the order of point group G , divided by the order of point group, F .^{193,194} In the case of antidistortive phase transitions, because of the superlattice structure, the translational symmetry and the space group need to be considered. The number of formula units per unit cell in both the PE and AFE phases are Z_G and Z_{AFE} . So, for the case of AFE, the number of domain states is then given by¹⁹⁵

$$q = \frac{|G| Z_G}{|F| Z_{AFE}}$$

When there are more than 2 domain states in the absence of external fields (such a magnetic, electric, and stress), and these domains can be moved by external fields, either singularly or in combination, the material is ferroic.

The domains that then develop in the crystals and crystallites form complex configurations, with domain walls that separate the domains. The domain state is a consequence of energy minimization, in which the energy cost of the domain walls is balanced by the energy gain associated with the spontaneous strain elastic energy and/or the electrostatic energy that corresponds to the polarization divergence has to be minimized. There are different types of domain walls that can be found in AFE and related materials.^{196,197,198}

7.1 Ferroelastic domain walls

Ferroelastic domain pairs meet at domain walls which exhibit mechanical compatibility – this limits the orientation of the habit planes to ensure that domain walls are stress-free; these are sometimes called permissible walls. The mathematical description for these types of ferroelastic walls can be found in classic papers by Fousek and Janovec,¹⁹⁹ and Sapriel.²⁰⁰ Those papers classify the strain and symmetry restrictions for the twinning of the domains. In orthorhombic crystals, the permissible walls are {001} for 90° domain walls; {110} for 60° domain walls; {112} for 120° domain walls. The presence of multiple walls in one grain can result in rather complex domain morphologies. In incommensurate AFE, the overall domain morphology always looks like a “checkerboard”.²⁰¹ It should be noted that the aforementioned are the walls conforming to the symmetry restrictions. In real AFE, Zig-Zag walls are allowed,²⁰² and indeed are sometimes necessary, due to two reasons. First, the minimum elastic/electrostatic energy can be satisfied not only by the “permissible walls” in AFE where an individual domain has essentially no net polarization. For instance, {110} wall that separates two 90° domains is quite common in pure PbZrO₃.²⁰³ Second, an antiphase boundary will break the “head-to-tail” configuration on the domain wall, locally. Under such circumstance, the Zig-Zag wall, namely the insertion of {110} sections to a {001} wall, is necessary to compensate for the dipolar mismatch.²⁰³

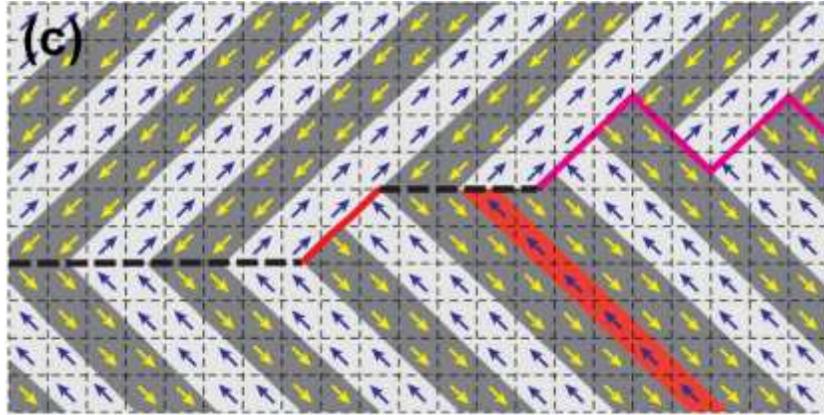


Figure 26. Schematic drawing of a real domain wall in PbZrO_3 adjacent to an APB (red stripe). The black dashed line is a normal $\{001\}$ wall, while the highlighted ones are the $\{110\}$ sections (Reproduced by permission from Ref. 203).

On cooling from the PE-AFE, the transformation for NaNbO_3 and PbZrO_3 would be from $m3m$ - mmm ; on application of an electric field large enough to induce switching, the AFE domains switch to FE ($mm2$). The basic switching was through two domain configurations in the FE states, with charged 60° and neutral walls. The Zig-Zag walls, under this circumstance, can also minimize the divergence in the polarization. Transmission electron microscopy is a very powerful tool to quantify the domain orientations, and diffraction contrast methods in bright field and dark can be used to determine the walls and the orientational relations between each domain as modelled by Amenlickx and co-workers.²⁰⁴⁻²⁰⁶ Also, electron holography and differential phase imaging allows for the atomic strain and polarizations to be determined.²⁰⁷⁻²¹²

7.2 Antiphase boundaries

Antiphase boundaries are linked to cases where the unit cell of the ferroic phase contains multiple unit cells of the prototype phase, as is the case with antidistortive phase transitions, such as antiparallel dipole alignment in an AFE, or octahedral tilt transitions. Antiphase boundaries appear when two domains come together and the boundary that separates them has an out of sequence ordering. These types of boundaries are also non-ferroelastic as there is no strain differences between adjacent regions. An example is an APB in PbHfO_3 is shown in Fig 27.²¹³ It can be clearly seen that the APB disrupts the local periodicity. Consequently, the APB region can display finite polarization. The order parameters in the two

domains separated by APB differs by a phase shift of π .²¹⁴ Thus, antiphase boundaries in AFE can also be called polar translational boundaries. Under diffraction contrast in TEM, they appear as straight lines. Combined with the ferroelastic walls, most AFE grains display a hierarchical domain structure. It should be noted that antiphase boundaries with different translational vectors exhibit different polar states,²¹⁵ Fig. 27(b) just illustrates one of the simplest cases. Also, compositional and mechanical tuning seem to favor the formation of certain types of antiphase boundaries.²¹⁶

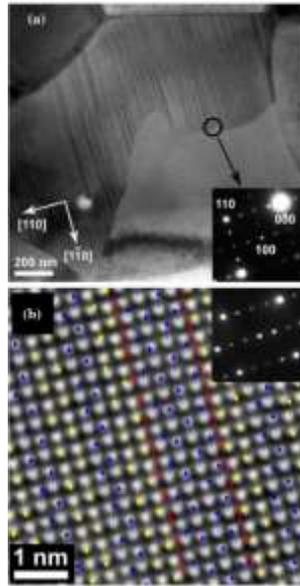


Figure 27. (a) Hierarchical domain structure in PbHfO₃; (b) HRSTEM mapping of an APB from the upper ferroelastic domain. The blue and yellow arrows correspond to the local polarization – an alternating pattern of two up/two down is observed on either side of the APB. The region between the dashed red lines is the APB in which the polarization periodicity is interrupted. (Reproduced by permission from Ref. 213).

7.3 Incommensurate Modulation

In order to increase the dielectric energy storage density, one current trend in AFE research is to increase the breakdown strength and E_F . This contrasts with actuator applications, in which E_F and hysteresis are both intentionally reduced. Reductions in E_F can be achieved, for example, in PbZrO₃ doped with Ti, as the Ti stabilizes FE over AFE ordering. Unfortunately, the doping range is rather narrow (AFE/FE MPB at PZT95/5). To broaden the range of achievable properties, co-doping is often utilized, with La on the A site

(PLZT) and Sn or Nb on the B-site (PNZST). It is speculated that the reduced E_F in these materials has its origin in incommensurate (INC) modulation. The room temperature ternary phase diagram and the composition-temperature phase diagram for PNZST are shown in Figure 28,^{217, 218} from which two important features of INC can be assessed. First, INC PbZrO_3 is pseudo-tetragonal, as opposed to orthorhombic. Second, the temperature at which the FE phase forms is below that for AFE if incommensurate, but above it for commensurate AFE (e.g. pure or Ba doped PbZrO_3). Such a change in the phase sequence has great impact on pyroelectric/electrocaloric effects. The multicell cubic phase was proposed because a strong deviation from Curie-Weiss behavior is observed above T_{max} , which resembles relaxor ferroelectrics.²¹⁹ SAED also proves that the $1/x\{110\}$ superlattice spots persist to the higher temperatures.

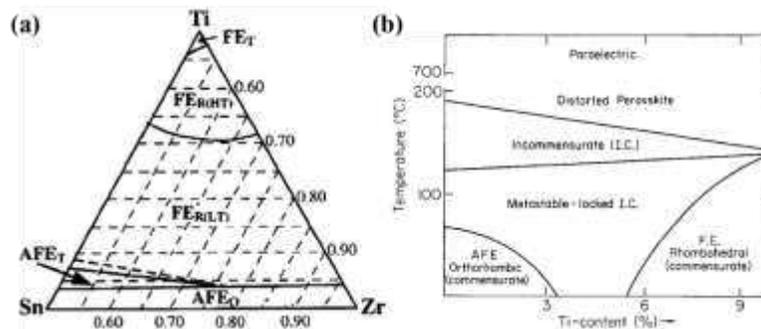


Figure 28. (a) Ternary phase diagram in PNZST (Reproduced by permission from Ref. 217); (b) Phase diagram of $\text{Pb}_{0.99}\text{Nb}_{0.02}[(\text{Zr}_{0.55}\text{Sn}_{0.45})_{1-y}\text{Ti}_y]_{0.98}\text{O}_3$ (Reproduced by permission from Ref. 218).

As described above, INC AFE deviates from the commensurate AFE in that the modulation wavelength (periodicity) is no longer $4d_{110}$ (in PbZrO_3 -based materials) but becomes irregular and can vary with temperature and composition. As can be seen from Figure 28b, in PNZST, the INC phase occurs at an intermediate Ti concentration, suggesting that it might be essentially a bridging state from AFE to FE, where the interactions favoring the two structures are competing. Indeed, the modulation wavelength increases with Ti addition, as manifested by the superlattice spot approaching the fundamental spots.²¹⁸ Similarly, upon cooling, the wavelength should keep decreasing until the incommensurate-commensurate

phase transition occurs at the lock-in temperature. But the INC wavelength is always temperature independent before being “locked-in”.²²⁰

For displacive-type incommensurate modulations, the perturbation can occur not only in the phase (periodicity), but also in the amplitude. So, do the dipoles in INC AFE still follow the stringently antiparallel arrangement? In PLZT, MacLaren discovered that the dipoles are not equal in magnitude but form a sinusoid (Fig. 29).²²¹ Chen confirmed the sinusoidal dipole wave in PNZST, but also observed that the atomic displacements have components along two orthogonal $\langle 110 \rangle$ directions.²²² More strikingly, they showed that polarization may not be fully compensated in INC AFE. This result is qualitatively consistent with Tan’s HRSTEM characterization in the same composition, which revealed the unbalanced cation displacements in the context of hierarchical domain structures.²²³ Very recently, Fu *et al.* also verified the “ferroelectric-like” dipole arrangement in PLZT using annular bright field STEM.²²⁴

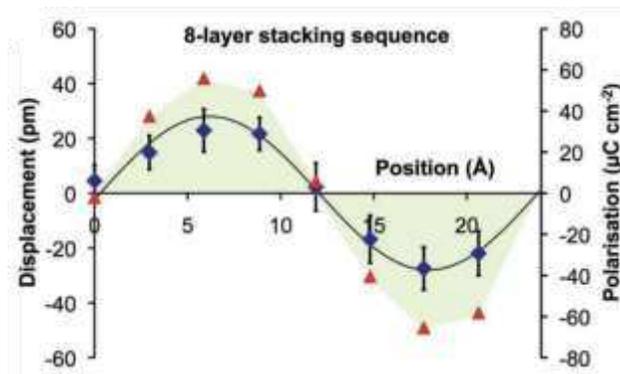


Figure 29: Atomic displacements and calculated polarization as a function of position in incommensurate PLZT (Reproduced by permission from Ref.221).

7.4 Domain Switching:

Domain switching and phase switching in AFE materials requires nucleation of the FE phase within the AFE, with subsequent domain wall movement. The nucleation process will be heterogeneous, and therefore defects and AFE boundaries aid the nucleation of the FE phase, and after nucleation the phase

will grow at the expense of the AFE ordering in the AFE domain. Defects such as dislocations have a strain gradient that can favor FE nucleation in an AFE; also, antiphase boundaries in a commensurate phase or the domain boundaries in an incommensurate phase can have sequences of dipoles that are locally parallel over a small distance that would also enhance the probability of a stable FE nuclei. There are a great number of details that have not been completely resolved with the switching in a double hysteresis loop. These processes may also involve INC intermediate phases, and large local strain gradients as the volume changes occur between the AFE and FE unit cells. The major hindrance to studying these issues is that the AFE to FE phase transition is very rapid at E_f , such that the nucleation process or any intermediate stage is difficult to catch. Generally, successful in-situ studies rely on non-uniform stimuli. For instance, in-situ biasing TEM using the E field applied through a sharp indenter has enabled studies of the nucleation and the domain wall motion in ferroelectric thin films.²²⁵ Recently, e-beam illumination, instead of electric field, has been utilized to trigger the AFE to FE transition in a PbZrO_3 crystal.²²⁶ An intermediate FE phase with cycloidal polarization order was demonstrated to exist transiently during the AFE—FE transformation. In addition, the FE/AFE phase boundary or the inter-phase interface are of particular interest for clear observations of the dynamics, on both global and local scale.^{227,228}

8.0 Antiferroelectric Applications

8.1 Pulse Power Capacitors

AFEs have, since the 1960s, been a part of the defense industry and are used for nuclear weapon triggers for fission, operating in a single-shot use. These must be processed with extremely high levels of accuracy and control in terms of the electrical and mechanical performance.²²⁹ The compositions of choice are based on the PZT 95/5 AFE. Pulse power is now becoming important in a number of other applications in defense, mining, renewable energy, and medical industries. Some include mine detection, testing platforms for lightning and electromagnetic pulse simulators, electromagnetic launchers, mineral and oil

exploration, blasting operations at mines and quarries, and neutron generator power systems. All these power supplies necessitate high energy density to permit miniaturization and are designed to undergo complete depolarization from a poled FE state to the AFE under an explosively triggered compressive shockwave. Specifically, the shock pressure compression can release the bound electric charges of poled ferroelectric (FE) ceramics within a short period of time (~microseconds), thereby generating a sharp current/voltage pulse with megawatts of electrical power.²³⁰ This charge then is supplied on the output terminals in the form of a high energy electrical pulse; the basic device structure is shown in Figure 30.²³¹ Traditionally, the focus on these AFE materials has been around PZT 95/5,⁴⁵ more recently lead-free alternatives have been reported based on $\text{AgNbO}_3\text{-KNbO}_3$ 94/6 solid solutions. Figure 31 shows the discharge characteristics for a lead free AFE material.²³² The energy densities in the lead -free systems are greater than the PZT ceramics. However, no efforts have been made to commercialize, such AFE, at this time. With such preliminary property observations as all these compositions are of interest to develop new classes of electromagnetic pulse weaponry that can disrupt or destroy communications, guidance systems, and weapons. These not only need to consider the high energy densities but also high yield performance that will depend on many processing details including high levels of chemical homogeneity, stoichiometric and microstructural control.

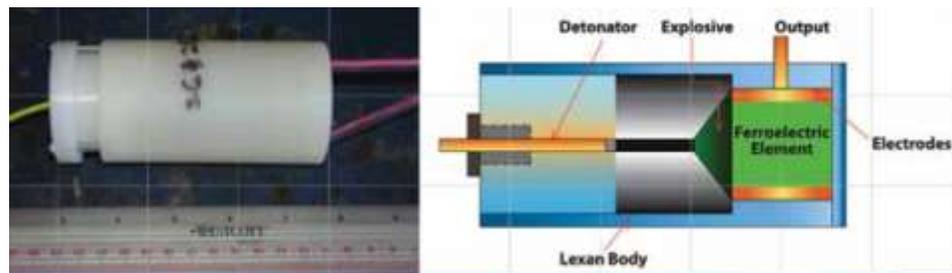


Figure 30. Example of an antiferroelectric capacitor for a detonator, along with a schematic.²³³

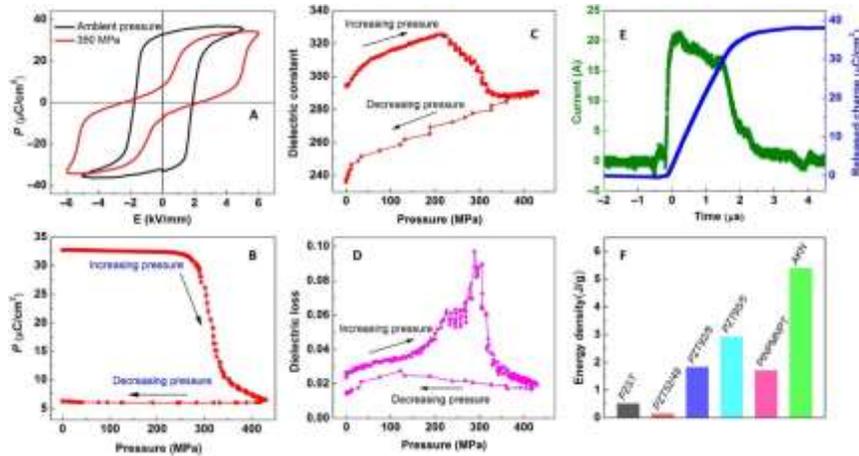


Figure 31. Explosive energy conversion performance in $(\text{Ag,Na})\text{NbO}_3$ (Reproduced by permission from Ref. 232).

8.2 AFE Multilayer Ceramic Capacitors

Multilayer ceramic capacitors (MLCC) are fabricated by tape-casting and screening printing metal electrodes; these dielectric layers and printed electrodes are laminated and stacked. The ability to form and control the dimensions of these layers requires the mixing of organic dispersants, binders, and solvents with the powders to form the slurries for the tape casting and pastes for the electrodes. After stacking, individual capacitors are cut out, and the organics are removed via a de-binding process. After this, the components are co-sintered into dense multilayers. Subsequently, a termination step interconnects the interdigitated electrodes on each side of the component to form parallel interconnections between the dielectric layers. A more detailed introduction to MLCCs can be found in several reviews.^{234,235} The basic structure of an MLCC device is shown schematically in Figure 32. The most widely used dielectrics are based on compositionally modified FE BaTiO_3 ; the second most important MLCC dielectric is a linear dielectric based on CaZrO_3 . However, there are a small number of AFE materials being considered owing to their high voltage high permittivity performance. The electrodes can be based on precious metal chemistries, such as Pt, Pd, Ag-Pd and Ag; these can all be sintered in air atmospheres, but with the exception of Ag, the electrodes in this family are expensive. Base metal or valve metal electrodes, such as Ni and Cu, mandate more complicated processing in order to avoid either oxidation of

the metals or reduction of the dielectric materials. Controlling the partial pressures of oxygen to balance the redox reactions is important, amongst many other detailed considerations. However, there is a substantial advantage in cost savings.

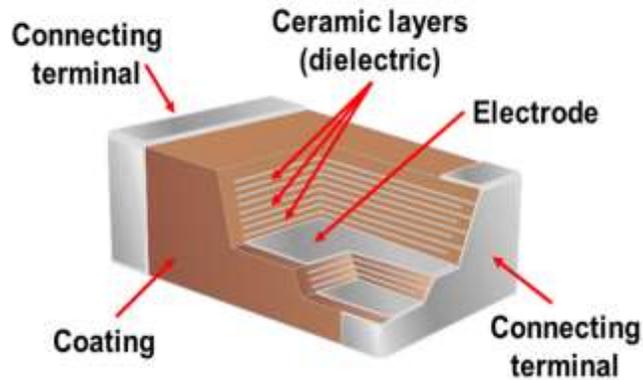


Figure 32: Cross-section of an MLCC

The capacitance of the devices is given by:

$$C = A n \epsilon_r \epsilon_0 / t,$$

where A is the effective overlap area, n is the number of interconnected layers, ϵ_r is the relative permittivity, ϵ_0 is the permittivity of free space, and t is the dielectric layer thickness.

Capacitor dielectrics are designed to co-optimize many physical properties, but the most important of these are the capacitance values, dielectric loss, resistance, operating voltage range, operational temperature range, and the physical dimensions (or case size) of the device. At high voltages, FE dielectrics have a decreasing permittivity, and linear dielectrics have a low permittivity, but AFEs have permittivity that increases with increasing voltage. Figure 33 shows the different field behavior of these different types of dielectric material: a) Linear, b) FE, and c) AFE with respect to polarization and electric field E , and the dielectric permittivity versus E .

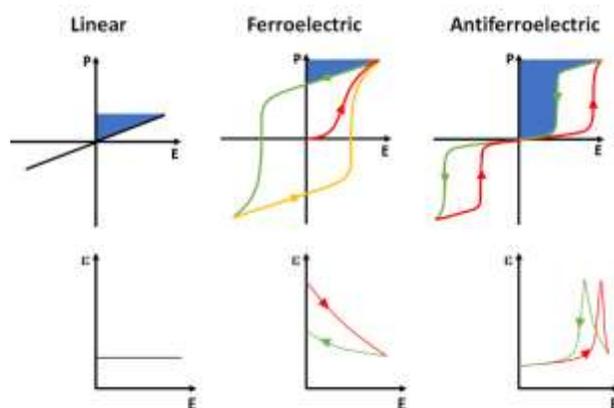


Figure 33: Schematics of polarization and permittivity as a function of DC bias field for linear dielectrics, ferroelectrics, and antiferroelectrics. The blue shaded areas correspond to the recoverable energy density.

The recoverable electrostatic energy density W_E is given by the shaded areas in Figures 33; it is apparent that AFE have relatively high energy density. To facilitate charging and discharging of the AFE, a base material, such as PZT 95/5, is modified with additives, such as La and Ca, to minimize the hysteresis and suppress large volume changes that would create high field losses and induce microcracking. So often, the structure is INC for the best performing AFE compositions.²³⁶⁻²⁴⁶ Chen *et al.* have shown that the dynamic switching of the AFE double hysteresis loops of a given AFE follows a scaling law with the energy density having dependence on variables such as the amplitude of applied field and its frequency.^{247,248}

Temperature stable AgNbO_3 based ceramics are usually fabricated by doping with Ta on the B-site, which decreases the temperature of the **M** phase transitions.¹⁶⁰ A heterogeneous distribution of Ta and Nb within the ceramic can then be utilized to suppress the temperature dependence of permittivity.²⁴⁹ $\text{Ag}(\text{Nb,Ta})\text{O}_3$ is, therefore, one of the highest permittivity, temperature stable ceramics and offers unique properties amongst dielectric ceramics between COG and X7R designations.²⁵⁰

Recently there has been a resurgence of interest in AgNbO_3 as a high energy density capacitor material.^{251,252} The recoverable energy density (W_{rec}) is optimized in AgNbO_3 through dopant strategies

that delay the onset of the field induced transition to higher values of E and which also facilitate a slimmer field induced region of the P - E hysteresis loop, as shown in Figure 34. Optimized compositions are typically RE doped on the A site, which gives rise to V'_{Ag} and are Ta doped on the B-site. $W_{rec} \sim 6.5 \text{ J/cm}^3$ has been achieved with conversion efficiencies around 70%.²⁵³ For AgNbO_3 , opening of the P - E hysteresis loop is not concomitant with a change in crystal class as observed in PbZrO_3 . Rather, the field induced phase retains the same crystal class and quadrupling as the AFE phase but exhibits inequivalent antiparallel displacements of the cations and thus conforms to a field induced ferroelectric phase.

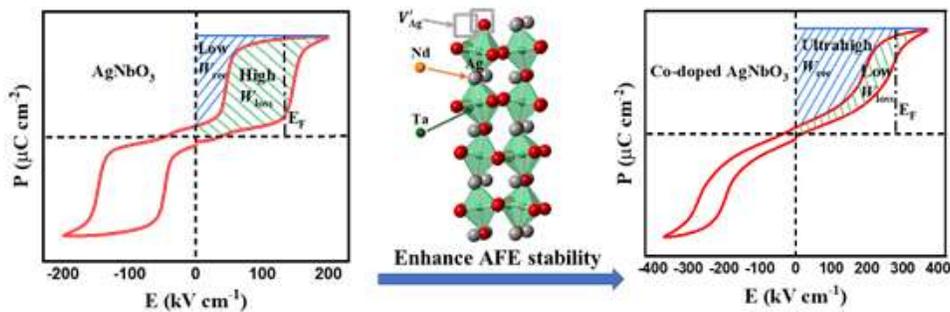


Figure 34. Schematic illustrating how the energy density is optimized in a RE, Ta doped AgNbO_3 (Reproduced by permission from Ref. 253).

In addition, lead-free AFE dielectrics have been made with the NaNbO_3 - NaTaO_3 systems. In this case, there is an interesting core shell microstructural development with the core being AFE, and the shell being INC; this limits the voltage saturation and provides high temperature dielectric materials. At this time, there has been no commercialization of the lead free AFE's.²⁵⁴

Some of the specific applications for AFE MLCC's include:

i) DC Link Capacitors for Power Electronics

Power electronic circuits require capacitors with high capacitance and high current density, low losses, high operating temperatures, and low equivalent series resistant and inductances to maximize operating frequencies. TDK Corporation has introduced a high-performance MLCC made of AFE PLZT with copper

electrodes called Ceralink™ that operates between -55°C to 150°C , at high voltages ~ 500 to 1000 volts, and $\sim 10 \mu\text{F}$, with high reliability.²⁵⁵ These capacitors have several property advantages over the film capacitors that are the traditional choices, including operating temperature range and suppression of overshoot associated with fast switching of power semiconductor devices. A comparison between various candidates is shown in Figure 35. As with all MLCC technologies, the reliability design is also a critical aspect of a successful product.

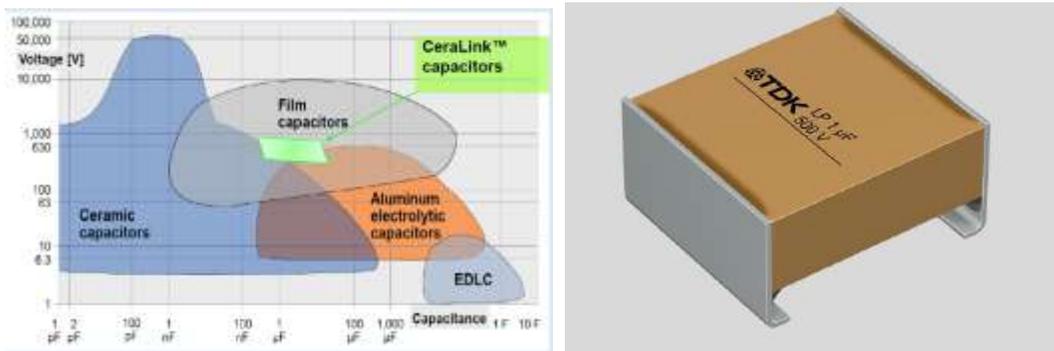


Figure 35. (Left) Comparison of antiferroelectric based capacitors with other technologies. (Right) picture of a commercial AFE capacitor from TDK (Reproduced by permission from Ref. 255).

ii) Defibrillator Capacitors

The defibrillator capacitors do not mandate the large high field repetition rates at high frequencies that DC-link capacitors are designed to withstand. These capacitors have far fewer cycles, and therefore the compositional design can be tailored to body temperature, and with the discharge pulse enabling the most effective stimulation of the cardiac muscle. The field-induced phase transition can, therefore, be less diffuse. As a result, the non-linearity can be used to control the discharge current time with some constant current plateaus. Figure 36 shows the discharge current and the corresponding hysteresis in PLZT 2/95/5 and 6/90/10.²⁵⁶⁻²⁶⁰

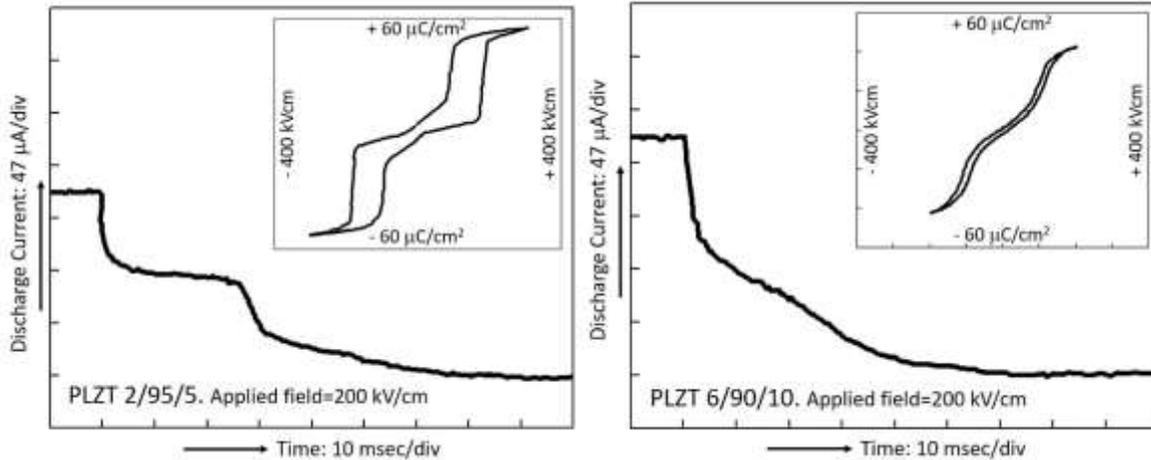


Fig. 36: Discharge current versus time in (a) PLZT 2/95/5, (b) PLZT 6/90/10. Insets show the corresponding PE loops (replotted from Ref. 259).

iii) Thin film AFE Embedded Power Capacitors

Although at this time of writing there is no commercialization of AFE thin films, there has been extensive research investigation of thin film AFE capacitors. The energy densities of AFE are extremely high, reported to be between 20 J/cm^3 to 80 J/cm^3 , as the breakdown strength is typically controlled by thermal breakdown. However, in the scientific literature, unfortunately the reviewing process does not always consider the charge-discharge cycling, and in some cases, the large instantaneous energy density storage values are not necessarily realistic for practical application. However, the most reasonable energy densities $\sim 30 \text{ J/cm}^3$ are still intriguing and high.²⁶¹⁻²⁶⁶ Such AFEs are of interest as power plane decoupling capacitors. This application was identified and considered for high frequency Multi-Chip-Module packages with embedded thin film capacitors having square hysteresis loops such as can be obtained with compositions like (Sn,Nb) doped PZT. Such AFEs can effectively supply an aerial capacitance $32 \mu\text{F/cm}^2$, as shown in Figure 37.²⁶²

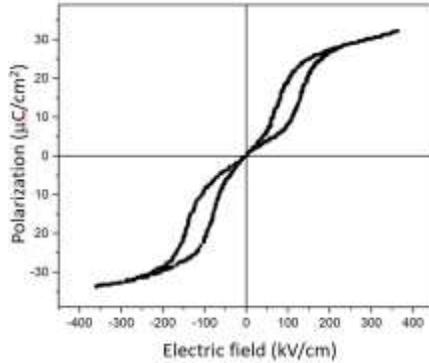


Figure 37: P-E hysteresis loop for $(\text{Pb}_{0.97}\text{La}_{0.02})(\text{Zr}_{0.6}\text{Ti}_{0.10}\text{Sn}_{0.30})\text{O}_3$ (replotted from Ref. 262).

8.3 Antiferroelectric Capacitor Memory Cell:

Recently, Intel was granted a patent (2018) that considers the advantage of using an AFE as a capacitor cell for embedded memory.²⁶⁷ An advantage of such a memory cell is the increased charge density, that may potentially scale better than in the FE equivalents. This may be of interest in neuromorphic computing platforms as the higher charge densities also allows for better distinguishing between the different logic states.²⁶⁸

8.4 AFE actuator applications:

The large volume change associated with AFE/FE phase switching prompts interest in the use of such materials for high strain actuators. For example, PLZT has a tetragonal symmetry that switches to the rhombohedral FE, of which the strain-electric field hysteresis is shown for the volume, longitudinal, and transverse switching in Figure 38. The series of phase transition and domain reorientation steps accounts for both the decoupling of the strain and polarization in the longitudinal case, and the coupling in the transverse case.^{7,269-272} As stated in the previous section, the E field endows texturing of the AFE domains.⁴⁸ Lu *et al.* provided further insights into these processes with a detailed in-situ neutron diffraction study. They determined that the field switching of the AFE-FE phase transition is not fully reversible, and the induced strain fields are elliptical and drive preferred orientations of the domain states.²⁷³

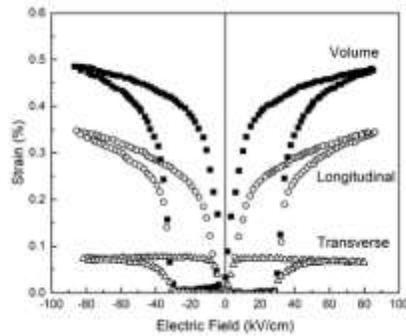


Figure 38. Longitudinal/transverse/volume strain as a function of E field (replotted from Ref. 7).

8.5 Microwave Dielectric Materials

AFE materials have been considered for high permittivity microwave frequency dielectrics. Lanagan and Wersing *et al.* looked at undoped and doped PZ, respectively.^{274,275} The rationale for these was that the $\tan\delta$ would be low, as there is no extrinsic domain contributions, and hence no relaxations in the GHz regime. Unfortunately, the persistence of FE phases and defects often contributed to unacceptable loss levels. Wersing utilized acceptor doping to reduce the extrinsic defect losses, but incomplete reproducibility owing to non-stoichiometric defects was problematic. However, AgNbO_3 in sintered composites with AgTaO_3 has produced temperature stable NPO (Negative-Zero-Positive) high frequency dielectrics.²⁷⁶ These have high permittivity relative to other microwave dielectrics with equivalent temperature stability.²⁷⁷ The properties of these AN–AT composite ceramics are compatible with several microwave electronic components, e.g. bandpass filters, high-capacity NPO multilayer capacitors, and would lead to the significant miniaturization of these devices. For the case of bandpass filters, an eight-times volume reduction could be expected, allowing ceramic filters with the size of surface acoustic wave (SAW) filters, but with superior improved power handling and low dielectric losses across a wider temperature range. Figure 39 is an image of a commercialized band pass filter with a major advantages in miniaturization relative to a $k=90$ high frequency dielectric.²⁴⁹

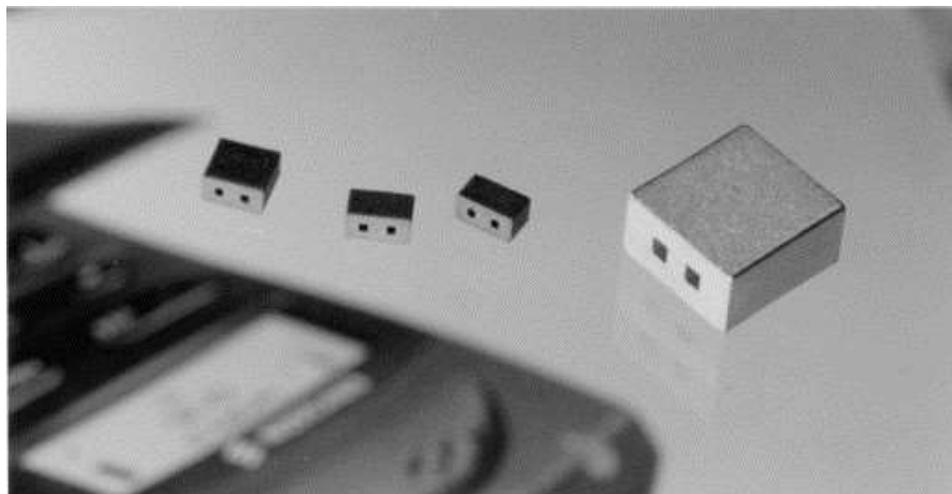


Fig. 39: Bandpass filters (1.8 and 0.9 GHz) produced from the ANT-ANT composite ceramics and a commercial 1.8 GHz bandpass filter based on $\text{Ba}_{6-x}\text{Nd}_{8+2/3x}\text{Ti}_{18}\text{O}_{54}$ with the permittivity ~ 90 (for the size comparison) (Reproduced by permission from Ref. 249).

9.0 New Opportunities for Future Directions for AFE

For a subgroup of dielectric materials that was discovered over 70 years ago, there is still much to be learned from AFE based materials. AFE are still under-researched relative to their FE counterparts. Also, in terms of compositions and crystal structures, there are few AFE materials relative to FE materials. It is hoped that this review aids the future exploration of new AFE materials. Thinking and predicting the future is always a risky endeavor, but here, some vision on trends that AFE research could provide over the next ten years or so is discussed. Three pathways are predicted to impact these research areas: materials discovery, scientific needs, and applied science with foreseeable application opportunities.

9.1 Materials Discovery:

A fertile new area to discover AFEs is in the families of molecular crystals, organic-inorganic hybrid perovskites, and 2-D materials. Computational discovery of such new materials must use well constrained physics-based algorithms, best practices from identification, and interfacing with high throughput synthesis methods. There have been recent reports of new FE materials in structures such as plastic/ionic crystals tetramethylammonium tetrachloroferrate(III) and tetramethylammonium

bromotrichloroferrate(III).²⁷⁸ These materials have cubic crystal structures in the PE, and therefore this permits many FE domains that can be poled for high performing piezoelectric and pyroelectric properties. At this time, there is no report of an AFE phase, but this family has only just been discovered. There are similar opportunities in the organic-inorganic hybrid perovskites. However, discovery of these materials for highly efficient solar cells pushed further exploration of this structure, and strong FE properties have also been reported. After those initial reports of FE, there are now emerging announcements of AFE properties.²⁷⁹⁻²⁸¹ For instance, in the (3-pyrrolinium) CdBr_3 hybrid perovskite, there is a PE-AFE-FE sequence of transitions, as can be observed in Figure 40.²⁸²

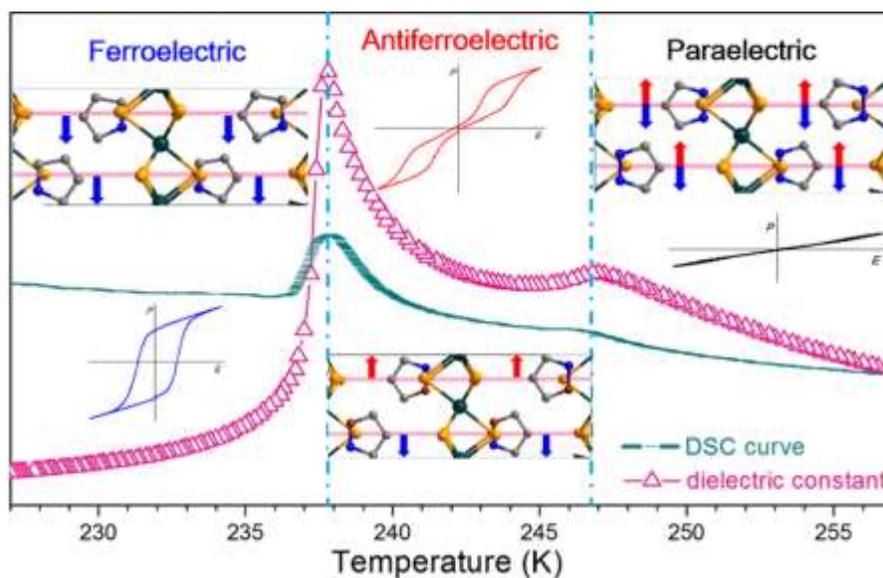


Fig. 40. PE-AFE-FE phase transitions in (3-pyrrolinium) CdBr_3 hybrid perovskite (Reproduced by permission from Ref. 282).

These organic and inorganic-organic hybrids have enormous potential, and the discovery process would benefit from data mining and machine learning algorithms, to narrow the focus of the synthetic chemists. In addition to the chemical selection for promising FE and AFEs, the hydroscopic nature of these materials also needs to be considered for long term success.

9.2 Future Scientific Directions:

There has been major progress in the scientific understanding of AFE through detailed crystallographic investigations, microscopy at the atomic level, understanding the relative energetics of the FE and AFE phases in compounds through detailed DFT calculations, and applying broad compositional studies to discover new AFEs. There are still many compositions and solid solutions that need thorough study to see if the understanding holds across more systems. There are also new crystal systems emerging with AFE that have been discussed in this review that need much broader investigation, particularly as some of them have extremely interesting coupled properties, such as the M-hexaferrites. There are still many questions regarding the details of the AFE-FE switching, regarding nucleation and growth of the FE phase in the forward switching and conversely the AFE nucleation at fields on back switching. In several systems, there is also an INC phase that develops with doping and/or as intermediate states in the AFE-FE switching process. The coupling of the electromechanical process at the local scale is also not understood. As pointed out in this review, the role of flexoelectricity may be fundamental to the properties and structures that underpin AFEs. The field requires higher levels of investigation, both experimentally and with theoretical approaches. The dynamics of the PE-AFE and AFE-FE phase transitions also need more detailed analysis in model single crystal systems, to understand the interplay of soft-mode coupling with various external boundary conditions: temperature, field, and mechanical stresses. The role of defect chemistry, its impact on high field behavior, and the impact of doping on the domain switching characteristics is also expected to be critical. The separation of dielectric loss mechanisms across broad frequency ranges, from infra-red, terahertz, and microwave is required. Likewise, determination of lattice modes, soft modes, domain dynamics, and conduction contributions to AFE behavior is necessary.

9.3 Future AFE Materials Engineering and Application Pulls

Relative to FE materials, applications have been limited for AFEs. However, the recent introduction of the mass-produced DC-link capacitor will reduce future uncertainties in business decisions around such materials. With many of the high performing AFEs being related to lead-based perovskites, there are still concerns over toxicity. So, the discovery of lead-free alternatives with high performance would be of great interest to industry to avoid future issues under the Restriction of Hazardous Substances (RoHS) legislation. Two important industrial application pulls are power electronics and 5G (and beyond), and in both these cases, electronic components that can withstand high temperatures and high charge-discharge rates, while maintaining low losses and stable temperature operations, need to be developed. AFE can provide opportunities in these domains. The AFE can also offer opportunities for MEMS structures, owing to the large electromechanical responses that can be achieved. The electrically induced strain effect of the antiferroelectric thin film produced under an electric field and its application in cantilever MEMS drive enables a large displacement, fast response, and low energy consumption, which can significantly improve performance of MEMS. AFE capacitive memories will also have opportunities in future computation and have already gained interest in neuromorphic computing owing to large polarizations and size effects that are less sensitive than in some FE cases. Molecular inorganic–organic AFE may offer large electrocaloric responses that could be integrated into flexible electronics to provide solid state actively cooled power electronic packages, and/or on larger scales for food–drug refrigeration and building air cooling. All these areas desperately need new technologies, and they are of such a scale that the solutions must be sustainable. Even with present FE based materials that are driven through a Carnot cycle, a coefficient of performance (COP) of six has been achieved in prototypes for electrocaloric refrigeration; this exceeds that of sublimation refrigeration technology, with $COP \sim 4$.²⁸³ So, from a global technology and environmental perspective, antiferroelectrics are an important dielectric material that deserve broader exploration and studies.

10.0 Acknowledgements

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