

## Chapter 1 : Structure and Properties of Ferroelectric Materials |

*All ferroelectric materials are pyroelectric, however, not all pyroelectric materials are ferroelectric. Below a transition temperature called the Curie temperature ferroelectric and pyroelectric materials are polar and possess a spontaneous polarization or electric dipole moment.*

Magnetoelastic Multiferroic Magnetoelastic multiferroics are both space-inversion and time-reversal anti-symmetric since they are both ferromagnetic and ferroelectric. Importantly, the combination of symmetry breakings in multiferroics can lead to coupling between the order parameters, so that one ferroic property can be manipulated with the conjugate field of the other. Ferroelastic ferroelectrics, for example are piezoelectric, meaning that an electric field can cause a shape change or a pressure can induce a voltage, and ferroelastic ferromagnets show the analogous piezomagnetic behavior. Particularly appealing for potential technologies is the control of the magnetism with an electric field in magnetoelastic multiferroics, since electric fields have lower energy requirements than their magnetic counterparts. Classification[ edit ] A helpful classification scheme for multiferroics into so-called type-I and type-II multiferroics was introduced in by D. Usually the structural distortion which gives rise to the ferroelectricity occurs at high temperature, and the magnetic ordering, which is usually antiferromagnetic, sets in at lower temperature. The independent emergence of magnetism and ferroelectricity means that the domains of the two properties are not necessarily robustly coupled to each other. In spite of this, most type-I multiferroics show a linear magnetoelastic response, as well as changes in dielectric susceptibility at the magnetic phase transition. The term type-II multiferroic is used for materials in which the magnetic ordering breaks the inversion symmetry and directly causes the ferroelectricity. In this case the ordering temperatures for the two phenomena are identical. The prototypical example is  $\text{TbMnO}_3$ , [16] in which a non-centrosymmetric magnetic spiral accompanied by a ferroelectric polarization sets in at 28 K. Since the same transition causes both effects they are by construction strongly coupled. Usually such an electric polarization arises via an inversion-symmetry-breaking structural distortion from a parent centrosymmetric phase. Such a displacement only tends to be favourable when the B-site cation has an electron configuration with an empty d shell a so-called  $d^0$  configuration, which favours energy-lowering covalent bond formation between the B-site cation and the neighbouring oxygen anions. As a result, in most multiferroics, the ferroelectricity has a different origin. The following describes the mechanisms that are known to circumvent this contraindication between ferromagnetism and ferroelectricity. Geometric ferroelectricity[ edit ] In geometric ferroelectrics, the driving force for the structural phase transition leading to the polar ferroelectric state is a rotational distortion of the polyhedra rather than an electron-sharing covalent bond formation. Such rotational distortions occur in many transition-metal oxides; in the perovskites for example they are common when the A-site cation is small, so that the oxygen octahedra collapse around it. In perovskites, the three-dimensional connectivity of the polyhedra means that no net polarization results; if one octahedron rotates to the right, its connected neighbor rotates to the left and so on. In layered materials, however, such rotations can lead to a net polarization. Since the ferroelectricity is not the primary order parameter it is described as improper. When the pattern of localized electrons is polar, the charge ordered state is ferroelectric. Usually the ions in such a case are magnetic and so the ferroelectric state is also multiferroic. Whether or not the charge ordering is polar has recently been questioned, however. Like the geometric ferroelectrics discussed above, the ferroelectricity is improper, because the polarization is not the primary order parameter for the transition to the ferroelectric state. The prototypical example is the formation of the non-centrosymmetric magnetic spiral state, accompanied by a small ferroelectric polarization, below 28K in  $\text{TbMnO}_3$ . Larger polarizations occur when the non-centrosymmetric magnetic ordering is caused by the stronger superexchange interaction, such as in orthorhombic  $\text{HoMnO}_3$  and related materials. The most obvious route is to use a rare-earth ion with a partially filled shell of f electrons on the A site. An example is  $\text{EuTiO}_3$  which, while not ferroelectric under ambient conditions, becomes so when strained a little bit, [31] or when its lattice constant is expanded for example by substituting some barium on the A site. Therefore composites combining magnetic and ferroelectric materials, either in layers or mixtures, with

coupling provided by the interfaces between them, are an attractive and established route to achieving multiferroicity. Here, strong ME coupling has been observed on a microscopic scale using PFM under magnetic field among other techniques. List of materials[ edit ] Most multiferroic materials identified to date are transition-metal oxides, which are compounds made of usually 3d transition metals with oxygen and often an additional main-group cation. Transition-metal oxides are a favorable class of materials for identifying multiferroics for a few reasons: The localised 3d electrons on the transition metal are usually magnetic if they are partially filled with electrons. Oxygen is at a "sweet spot" in the periodic table in that the bonds it makes with transition metals are neither too ionic like its neighbor fluorine, F or too covalent like its neighbor nitrogen, N. As a result its bonds with transition metals are rather polarizable, which is favorable for ferroelectricity. Transition metals and oxygen tend to be earth abundant, non-toxic, stable and environmentally benign. Many multiferroics have the perovskite structure. This is in part historicalâ€”most of the well-studied ferroelectrics are perovskitesâ€”and in part because of the high chemical versatility of the structure. Below is a list of some the most well-studied multiferroics with their ferroelectric and magnetic ordering temperatures. When a material shows more than one ferroelectric or magnetic phase transition, the most relevant for the multiferroic behavior is given.

## Chapter 2 : Ferroelectricity - Wikipedia

*The ferroelectric materials described in this book include a relatively complete list of practical and promising ferroelectric single crystals, bulk ceramics and thin films. Included are perovskite-type, lithium niobate, tungsten-bronze-type, water-soluble crystals and other inorganic materials, as well as organic ferroelectrics (polymers, liquid crystals, and composites).*

How things work Author: Nikhil Shelke Member Level: The various Ferroelectric materials, their theory, properties and applications are described in this article. Ferroelectricity is the phenomenon where spontaneous electric polarization of the material takes place. The reverse electric polarization is possible by applying an electric field. Ferroelectricity was discovered in Rochelle salt scientific name-Potassium Sodium Tartrate exhibited the properties of sudden electric polarization. Since its discovery, various uses have been devised and today, Ferroelectricity is used in various fields of electronics. The materials exhibiting the phenomenon of Ferroelectricity are called Ferroelectric Materials. Ironically, the Ferroelectricity or the Ferroelectric Materials do not have any connection to Iron ferrite. Crystal symmetry means the crystal can be grouped together into microscopic symmetry types. Microscopic symmetry types are introduced from microscopic symmetry elements. These elements combine together to form a point group. In a Ferroelectric Material, there are about 32 point groups. Out of the 32 point groups, 21 point groups do not have a center of symmetry. These non-symmetric point groups show piezoelectric effect along the directional axes. Polarization in the Ferroelectric Materials is directly related to the piezoelectric properties of the materials. Ferroelectric Materials  $\hat{=}$  Spontaneous Polarization Spontaneous polarization in Ferroelectric Material is defined as ability to polarize at a fast rate. It is the value of the charge per unit area on the perpendicular surface. Out of the 21 non-symmetrical point groups as explained above, only 10 point groups exhibit the spontaneous polarization property. The reason is that cancellation of the electric moments along different axes. The spontaneous polarization in Ferroelectric Material is directly proportional to the temperature. This phenomenon is called as Pyroelectric effect. Ferroelectric Materials  $\hat{=}$  Hysteresis Loop The plot of polarization in Ferroelectric Material to the applied electric field is called as the Hysteresis loop. As shown in the hysteresis loop, the direction of the polarization is reversed as the applied electric field is reversed. This is the basic difference between the pyroelectric materials and the Ferroelectric Materials. The pyroelectric materials do not possess polarization reversal and hence they are different from Ferroelectric Material. The theory behind polarization reversal is the domain reversal. The electric dipoles are formed within the Ferroelectric Material when an electric field is applied. But as the field is reversed, the direction of these electric dipoles reverses. This reversal in the direction results in polarization reversal. This is the basic fundamental principle behind the theory of Ferroelectric Material. Ferroelectric Materials  $\hat{=}$  Curie Point Curie point is the temperature below which the material shows Ferroelectric property. Thus, if the temperature of the material is below the Curie point, only then the material exhibits the Ferroelectric property. Depending upon the type of the crystal, there are various transitions for tetragonal, orthorhombic and rhombohedral crystals. Ferroelectric Materials  $\hat{=}$  Types.

## Chapter 3 : Ferroelectric Materials

*The research interest in FE-PV devices has been re-spurred by the recent discovery of above-bandgap photovoltage in materials with ferroelectric domain walls, electric switchable diodes and photovoltaic effects, tip-enhanced photovoltaic effects at the nanoscale, and new low-bandgap ferroelectric materials and device design.*

These materials can produce spontaneous polarization. By inverting the direction of applied electrical field, the direction of polarization of these materials can be inverted or changed figure 1. This is called switching. It can also maintain the polarisation even once the field is removed. These materials have some similarities over ferromagnetic materials which reveal permanent magnetic moment. The hysteresis loop is almost same for both materials. Since, there are similarities; the prefix is same for both the materials. But all the ferroelectric material must not have Ferro iron. All the ferroelectric materials exhibit piezoelectric effect. The opposed properties of these materials are seen in antiferromagnetic materials. Theory of Ferroelectric Materials The free energy of ferroelectric material based on Ginzburg-Landau theory without electric field and any applied stress can be written as Taylor expansion. Usually, it is used by adding some terms such as an elastic term, a gradient term and an electrostatic term to this free energy equation. Next; when we polarise a paraelectric material, we get a non linear polarization. However it is a function of field as shown in figure 3. Next, we take a ferroelectric material and electric field is given to it. We get a non linear polarization. It also exhibit nonzero spontaneous polarization without a peripheral field. We can also see that by inverting the direction of applied electrical field, the direction of polarization can be inverted or changed. Thus, we can say that, the polarization will depend on the present as well as the previous condition of electric field. The hysteresis loop is obtained as in figure 4. Curie Temperature The properties of these materials exist only below a definite phase conversion temperature. Above this temperature, the material will become paraelectric materials. That is, loss in spontaneous polarization. This definite temperature is called Curie temperature  $T_C$ . Most of these materials above  $T_C$  will loss the piezoelectric property as well. Examples of Ferroelectric Materials.

*Ferroelectric oxides, such as  $Pb(Zr, Ti)O_3$  (PZT) and lead-based compounds, constitute one of the best families of piezoelectric and ferroelectric materials suitable for the integration in devices, such as actuators, sensors and transducers.*

Structure and Properties of Ferroelectric Materials Author: These include ferroelectric hysteresis used in nonvolatile memories , high permittivity used in capacitors , high piezoelectric effects used in sensors, actuators and resonant wave devices such as radio-frequency filters , high pyroelectric coefficients used in infra-red detectors , strong electro-optic effects used in optical switches and anomalous temperature coefficients of resistivity used in electric-motor overload-protection circuits. In addition, ferroelectrics can be made in a wide variety of forms, including ceramics, single crystals, polymers and thin films – increasing their exploitability. This term paper helps to understand the basic theories behind the ferroelectric effect and the main ferroelectric material classes, discussing how their properties are related to their composition and the different ways they are made. Concept of ferroelectricity The concept of ferroelectricity refers to the spontaneous electric polarization of a certain material that can be readily reversed using an external electrical field. Ferroelectricity is due to parallel ordering of electric dipole moments in a substance in the absence of an applied electrical field. In ferroelectrics, domain structures are formed because adjacent dipoles tend to align themselves parallel to each other. Polarity results from the uneven partial charge distribution. The polarity of a electrically charged system is measured in terms of the electric dipole moment,  $p$  which is the product of charge,  $q$  and the displacement vector,  $r$ . When a material exhibits spontaneous electric dipole moment, it has ferroelectric property. The polarity can be reversed by applying an electric field in these materials. Phase transformation and hysteresis loop in ferroelectric materials Ferroelectric materials possess regions with uniform polarization called ferroelectric domains. Within a domain, all the electric dipoles are aligned in the same direction. There may be many domains in a material separated by interfaces called domain walls. For a ferroelectric single crystal, when grown has multiple ferroelectric domains. A single domain can be obtained by domain wall motion made possible by the application of an appropriate electric field. A very strong field could lead to the reversal of the polarization in the domain, known as domain switching. The main difference between pyroelectric and ferroelectric materials is that the direction of the spontaneous polarization in ferroelectrics can be switched by an applied electric field. The polarization reversal can be observed by measuring the ferroelectric hysteresis as shown in Figure below. As the electric field strength is increased, the domains start to align in the positive direction giving rise to a rapid increase in the polarization OB. At very high field levels, the polarization reaches a saturation value  $P_{sat}$ . The polarization does not fall to zero when the external field is removed. At zero external field, some of the domains remain aligned in the positive direction, hence the crystal will show a remnant polarization  $P_r$ . The crystal cannot be completely depolarized until a field of magnitude OF is applied in the negative direction. The external field needed to reduce the polarization to zero is called the coercive field strength  $E_c$ . If the field is increased to a more negative value, the direction of polarization flips and hence a hysteresis loop is obtained. The value of the spontaneous polarization  $P_s$  OE is obtained by extrapolating the curve onto the polarization axes CE. Electric Field P-E hysteresis loop for a typical ferroelectric crystal. Properties of ferroelectric materials All ferroelectric materials are pyroelectric, however, not all pyroelectric materials are ferroelectric. Below a transition temperature called the Curie temperature ferroelectric and pyroelectric materials are polar and possess a spontaneous polarization or electric dipole moment. The direction of the spontaneous polarization conforms to the crystal symmetry of the material. The reorientation of the spontaneous polarization is a result of atomic displacements. The magnitude of the spontaneous polarization is greatest at temperatures well below the Curie temperature and approaches zero as the Curie temperature is neared. All ferroelectric materials have a transition temperature which is Curie point  $T_c$ . The non-polar phase encountered above the Curie temperature is known as the paraelectric phase. On decreasing the temperature through the Curie point, a ferroelectric crystal undergoes a phase transition from a non-ferroelectric phase to a ferroelectric phase. If there are more than one ferroelectric

phases, the temperature at which the crystal transforms from one ferroelectric phase to another is called the transition temperature. Near the Curie point or transition temperatures, thermodynamic properties including dielectric, elastic, optical, and thermal constants show an anomalous behavior. This is due to a distortion in the crystal as the phase structure changes. Since all pyroelectric materials are piezoelectric, this means ferroelectric materials are inherently piezoelectric. This means that in response to an applied mechanical load, the material will produce an electric charge proportional to the load. Similarly, the material will produce a mechanical deformation in response to an applied voltage.

**Crystal Structures of ferroelectric materials**

The types of ferroelectric materials have been grouped according to their structure. There are four main types of structures include the corner sharing oxygen octahedra, compounds containing hydrogen bonded radicals, organic polymers and ceramic polymer composites. A large class of ferroelectric crystals is made up of mixed oxides containing corner sharing octahedra of  $O^{2-}$  ions. Perovskite is the corner sharing oxygen octahedral compound, a group of materials and the mineral name of calcium titanate  $CaTiO_3$  having a structure of the type  $ABO_3$ . Perovskite Crystal Structure of Barium Titanate  $BaTiO_3$  Barium Titanate will be used as example to illustrate the properties of the ferroelectric material is determined by their structures. The spontaneous polarization is along one of the  $[100]$  directions in the original cubic structure. As shown in Figure 3. Spontaneous polarization developed is the net dipole moment produced per unit volume for the dipoles pointing in a given direction in the Figure 4. Various A and B site substitutions in different concentrations have been tried to see their effect on the dielectric and ferroelectric properties of  $BaTiO_3$ . The simultaneous substitution into both A and B sites with different ions can be used to tailor the properties of  $BaTiO_3$ . The dielectric properties of  $BaTiO_3$  are found to be dependent on the grain size. This is because of the formation of multiple domains in a single grain, the motion of whose walls increases the dielectric constant at the Curie point. The movements of the domain walls are restricted by the grain boundaries, thus leading to a low dielectric constant at the Curie point as compared to coarse grained  $BaTiO_3$ .

**Conclusion**

As discussed, the important properties of the ferroelectric materials are determined by their structure. A combined theoretical and experimental result establishes a relation between crystallographic symmetry and the capability of a ferroelectric polycrystalline ceramic to switch. In addition, the ability to change their dimensions in an applied electric field makes these ferroelectric materials important for piezoelectric applications. The crystal symmetry and related strains of these materials are a strong influence on their switching behavior.

**Chapter 5 : Multiferroics - Wikipedia**

*Ferroelectric materials have been and still are widely used in many applications, that have moved from sonar towards breakthrough technologies such as memories or optical devices. This book is a part of a four volume collection (covering material aspects, physical effects, characterization and modeling, and applications) and focuses on the application of ferroelectric devices to innovative systems.*

Paraelectric polarization Ferroelectric polarization When most materials are polarized, the polarization induced,  $P$ , is almost exactly proportional to the applied external electric field  $E$ ; so the polarization is a linear function. This is called dielectric polarization see figure. Some materials, known as paraelectric materials, [4] show a more enhanced nonlinear polarization see figure. The electric permittivity  $\epsilon$ , corresponding to the slope of the polarization curve, is not constant as in dielectrics but is a function of the external electric field. In addition to being nonlinear, ferroelectric materials demonstrate a spontaneous nonzero polarization after entrainment, see figure even when the applied field  $E$  is zero. The distinguishing feature of ferroelectrics is that the spontaneous polarization can be reversed by a suitably strong applied electric field in the opposite direction; the polarization is therefore dependent not only on the current electric field but also on its history, yielding a hysteresis loop. They are called ferroelectrics by analogy to ferromagnetic materials, which have spontaneous magnetization and exhibit similar hysteresis loops. Typically, materials demonstrate ferroelectricity only below a certain phase transition temperature, called the Curie temperature  $T_C$  and are paraelectric above this temperature: Many ferroelectrics lose their piezoelectric properties above  $T_C$  completely, because their paraelectric phase has a centrosymmetric crystal structure. Typically, a ferroelectric capacitor simply consists of a pair of electrodes sandwiching a layer of ferroelectric material. The permittivity of ferroelectrics is not only tunable but commonly also very high in absolute value, especially when close to the phase transition temperature. Because of this, ferroelectric capacitors are small in physical size compared to dielectric non-tunable capacitors of similar capacitance. The spontaneous polarization of ferroelectric materials implies a hysteresis effect which can be used as a memory function, and ferroelectric capacitors are indeed used to make ferroelectric RAM [6] for computers and RFID cards. In these applications thin films of ferroelectric materials are typically used, as this allows the field required to switch the polarization to be achieved with a moderate voltage. However, when using thin films a great deal of attention needs to be paid to the interfaces, electrodes and sample quality for devices to work reliably. The combined properties of memory, piezoelectricity  $\epsilon$ , and pyroelectricity make ferroelectric capacitors very useful, e. Ferroelectric capacitors are used in medical ultrasound machines the capacitors generate and then listen for the ultrasound ping used to image the internal organs of a body , high quality infrared cameras the infrared image is projected onto a two dimensional array of ferroelectric capacitors capable of detecting temperature differences as small as millionths of a degree Celsius , fire sensors, sonar, vibration sensors, and even fuel injectors on diesel engines. Another idea of recent interest is the ferroelectric tunnel junction FTJ in which a contact is made up by nanometer-thick ferroelectric film placed between metal electrodes. The piezoelectric and interface effects as well as the depolarization field may lead to a giant electroresistance GER switching effect. Yet another hot topic is multiferroics , where researchers are looking for ways to couple magnetic and ferroelectric ordering within a material or heterostructure; there are several recent reviews on this topic. The change in the spontaneous polarization results in a change in the surface charge. This can cause current flow in the case of a ferroelectric capacitor even without the presence of an external voltage across the capacitor. Two stimuli that will change the lattice dimensions of a material are force and temperature. The generation of a surface charge in response to the application of an external stress to a material is called piezoelectricity. A change in the spontaneous polarization of a material in response to a change in temperature is called pyroelectricity. Generally, there are space groups among which 32 crystalline classes can be found in crystals. There are 21 non-centrosymmetric classes, within which 20 are piezoelectric. Among the piezoelectric classes, 10 have a spontaneous electric polarization, that varies with the temperature, therefore they are pyroelectric. Among pyroelectric materials, some of them are ferroelectric.

Chapter 6 : Ferroelectric Materials – Theory, Properties and applications

*Comparision of Paraelectric and Ferroelectric Materials for Applications as Dielectrics in Thin Film Integrated Capacitors  
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