

1.1. Introduction of Perovskite

The mineral Perovskite was discovered and named after the Russian mineralogist, L.A. Perovski, and initially found in the Ural Mountains of Russia in 1839 by Gustav Rose [Clarke (1987)]. The general formula of perovskite is ABO_3 . Where A is larger cations than B cations and O is the anion. The B ions can be taken an octahedral coordination, it may be from 3d, 4d or 5d transition metal ions. The Structure of perovskite materials is a large family of compounds having crystal related to the mineral perovskite $CaTiO_3$. Octahedral BX_6 derives the Structure of cubic ABX_3 perovskite with the A cation occupying the 12-fold coordination site formed in the middle of the cube of eight such octahedral. The ABO_3 types Perovskite are considered an FCC-derivative structure in which the larger A cation and oxygen together form an FCC lattice, and the smaller B cation occupies the octahedral interstitial sites. B cation nearest neighbor is oxygen only, and the Perovskite structure is displayed by many oxides, several of which have technological applications. The Perovskite family of oxides is probably the best-studied family of oxides, and also the mineral Perovskite itself is slightly distorted. Distorted Perovskites have great industrial importance for their magnetic and electric properties especially the ferroelectric tetragonal form of $BaTiO_3$.

In ideal Perovskite structures have the formula ABO_3 where A is larger cations occupy 8 corner positions, and B ions (smaller size) the body center position and oxygen ions occupy the centers of six faces. The A-O distance is $(a/\sqrt{2})$ while The B-O distance is equal to $(a/2)$ where a is the cubic unit cell parameter. The following relationship between the ionic radii holds: $(r_a + r_o) = \sqrt{2}(r_b + r_o)$, for an ideal structure, where the atoms are touching one another. Even though this equation is not exactly obeyed for the deviation from the ideal situation, Goldschmidt derived an equation for tolerance factor (t) which is applicable at room temperature to the empirical ionic radii.

$$t = \frac{(r_a + r_b)}{\sqrt{2}(r_b + r_o)} \quad (1.1)$$

The tolerance factor (t) describes the range of relative sizes for which the perovskite structure is stable. This structure is also found for lower t -values ($0.75 < t < 1.0$) while an ideal Perovskite t is unity. If tolerance factor (t) is close to being one, it will be cubic structure. Distorted perovskite structures have tolerance factor in the range of $0.75 \leq t \leq 0.95$ which are non-ferroelectric while those with ≥ 1.0 are ferroelectric [Wood (1951), Keith (1954), Roth (1957)]. If tolerance factor is less than 0.75, the compound does not crystallize in perovskite structure. The compound CaTiO_3 was considered to be cubic, but its true symmetry was later shown to be orthorhombic [Megaw (1946)].

ABO_3 types Perovskite can be classified in five classes on the basis of valencies of Cations A and cations B and in which valences of cations A is n and m for B cations and formula as $\text{A}^{+n}\text{B}^{+m}\text{O}_3$ [Yakel (1955), Galasso (1969)]. The valencies of anions must be equal to the sum of the valences' ($m+n$) of the cations to maintain charge neutrality. If the perovskite structures have the even valences of A and B, then all the ions in the structure should have 8 electrons in their shells. If it has an odd valence of A or B ions, then the ions in the structure may have more than 8 electrons in their outer shells. So, perovskite oxides exist following categories.

- (1) When cation A and B belong to first group elements and the fifth group elements of the periodic table respectively. Most of the compounds are either ferroelectrics or antiferroelectrics such as LiNbO_3 , KNbO_3 , AgNbO_3 , and AgTaO_3 and KTaO_3 [Matthias (1949)].
- (2) If cation A belongs to second group elements and cation B belongs to fourth group elements of the periodic table. Some important perovskite oxides of the type $\text{A}^{2+}\text{B}^{4+}\text{O}_3$

are CaTiO_3 , SrTiO_3 , and BaTiO_3 . These types of Perovskite may be used as dielectric and piezoelectric materials.

- (3) If cation A and B both belong to the third group of elements of the periodic table. In this category of the compound have Alkaline earth and trivalent ions (Y^{3+} , lanthanoids, Bi^{3+} , Tl^{3+}) at A site and tripositive transition metal ion on B site, i.e., $\text{A}^{+3}\text{B}^{+3}\text{O}_3$ type oxides such as BiFeO_3 . These perovskites are used for functional materials because of it has interesting properties of mixed conductivity by both ions and electrons or holes migration [Goodenough *et al.* (1974)]. A few systems display apparent oxygen defect, including $\text{LaMnO}_{3+\lambda}$, $\text{Ba}_{1-\lambda}\text{La}_\lambda\text{TiO}_{3+\lambda/2}$, $\text{EuTiO}_{3+\lambda}$ and $\text{LaCuO}_{3-\delta}$.

1.2. Perovskite substitution

The ideal perovskite structure may be modified by doping two types of B ions with suitable different size and charge. The general formula of ideal perovskite is ABO_3 , while after the incorporating on B site for which the general formula of the perovskite is $\text{A}_2\text{BB}'\text{O}_6$ (or $\text{AB}_{0.5}\text{B}'_{0.5}\text{O}_3$). But the totals charged on cations are equalled to charge on oxygen ions. If the charge of B and B' is different, in respective with the ideal structure of ABO_3 Perovskite, then the oxygen are slightly shifted toward the more charged cations and symmetry of B and B' cations is preserved.

Substituted Perovskite materials have a large number of technological applications, and they are well stabilized by their high dielectric constants (ϵ') and low loss of tangent [Fouskova, and Cross *et al.* (1970)]. Both of them are technologically important materials even in un-doped form, and also it's doping with different cations and modifies their properties [Shao *et al.* (2007), Rai *et al.* (2009), Prakash and Varma *et al.* (2006), Patterson *et al.* (2005)]

In general, there are two types of doping interstitial and substitution. Perovskite does not make an interstitial replacement, because of the close-packed structure of Perovskite. Perovskite has a lot of flexibility of substitution on A or B site. Therefore, it is made use by modifying their properties after substitution on cation site. The following factors affect the substitution modifications:

The Perovskite oxides can be substituted for the following types:

1.2.1. Isovalent substitution

1.2.2. Heterovalent substitution

1.2.3. Valence compensated substitution

1.2.1. Isovalent substitution

In isovalent substitutions, the substituent ion and the ion which it substitutes, have the same valence. The ion which replaces the same valence on either A site or B site or simultaneously on A and B site. For example of isovalent substitution, the substitution of Ca, Sr or Pb at Ba on A site of CaTiO_3 Perovskite and replacement of Ti ion by Zr, Sn or Hf ions on B site for isovalent substitution.

1.2.2. Heterovalent substitution

In this substitution process, it may be different valences on substitution. The substituent ion and the ion which is being substituted also may be on either A site or B site. The resulting substituted Perovskite will be produced to compensate the extra charge. There are two types of following heterovalent substitution.

(a) Acceptors substitution

When higher valencies substituted to lower valencies on A site or B site of solid compound. It creates holes due to generate the oxygen vacancies and less contribution of electrons from the substituent ion, e.g., substitution of Na^+ on Ba^{2+} and Co^{3+} on Ti^{4+} site in BaTiO_3 .

(b) Donors substitution

A lower positive ion substituted to higher valence on A or B site is known as donor substitution. The defect of solid compound requires a species having an effective negative charge for charge compensation in the crystal lattice of the host oxide, e.g., La^{3+} or Y^{3+} on Ba^{2+} and Nb^{5+} on Ti^{4+} site in BaTiO_3 separately [Zhi *et al.* (1999)].

1.2.3. Valence compensated substitution

There are two types of compensated substitution due to hetero valence and isovalent on A (e.g. $\text{Pb}_{1-x}\text{Ba}_x\text{Ti}_{1-x}\text{Sn}_x\text{O}_3$) and B sub lattice site $\text{M}_{1-x}\text{La}_x\text{Ti}_{1-x}\text{M}'_x\text{O}_3$ ($\text{M}_{1/4}$ $\text{Ca}^{2+}, \text{Sr}^{2+}, \text{Ba}^{2+}$ or Pb^{2+} and $\text{M}'_{3/4}$ $\text{Co}^{3+}, \text{Ni}^{3+}, \text{Fe}^{3+}$ etc). The crystal is maintained total electrical charge neutrality when substitution of a combination of ions at A and B sub-lattice sites [Prasad *et al.* (1988), Prakash *et al.* (1990), Christopher (1998)]. In this case there is a little chance of defect creation on valence compensated solid solutions (VCSS) e.g. La^{3+} ion on Ba^{2+} site and Co^{3+} on Ti^{4+} site simultaneously in $\text{BaTiO}_3:\text{Ba}_{1-x}\text{La}_x\text{Ti}_{1-x}\text{Co}_x\text{O}_3$.

1.3. ABO₃ type high dielectric constant Perovskites

A large number of ABO₃ type perovskite such as CaTiO₃, SrTiO₃, BaTiO₃, etc. possess high dielectric constant.

1.3.1. Calcium Titanate (CaTiO₃)

The mineral Perovskite (CaTiO₃) is one of the few minerals having the distorted Perovskite structure, although it has been suggested that the Earth's lower mantle may be composed mainly of MgSiO₃ Perovskite (for example, [Yagi, Mao & Bell, (1978)]. Because structural parameters of CaTiO₃ derived from the X-ray film study of [Kay & Bailey (1957)] deviate markedly from the systematic plots of other GdFeO₃ type Perovskites (Sasaki, Prewitt & Liebermann, 1983), we refined its crystal structure. A powder neutron study has been reported for this crystal [Koopmans, van de Velde & Gellings, (1983)]. CaTiO₃ is recently getting attention for its biocompatibility and implant-bone applications [Pecharromon *et al.* (1541), Ohtsu *et al.* (2007)] besides its use in electronics [Lemanov *et al.* (1999)]. The actual mineral Perovskite, CaTiO₃, represents a good starting point in this respect because it is stable at room pressure and thus amenable to various high-temperature measurements. The Perovskites of the CaTiO₃ class are generally characterized by a simple cubic lattice structure drop calorimetric measurements performed on CaTiO₃ Perovskite between 400 and 1800 K have shown the occurrence of two overlapping phase transitions at 1384, and 1520 K. Calcium titanate has relatively little value except as one of the ores of titanium, together with several others. It is reduced to give titanium metal or ferrotitanium alloys. [Heinz *et al.* 2005]

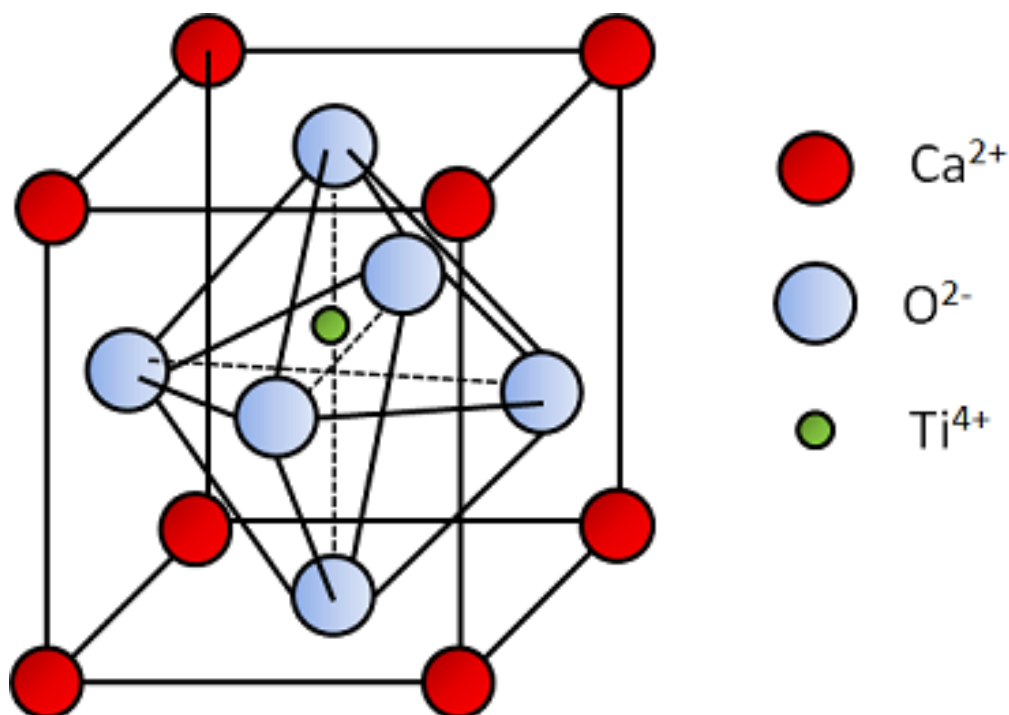


Figure 1.1. A Perovskite unit cell showing the off-centered titanium ion. [Park & Shrouf *et al.* (1997)]

Perovskite materials exhibit intriguing and unusual physical properties that have been extensively studied for both practical applications and theoretical modeling and the materials science and applications of perovskites have been a broad research area open to many revolutionary discoveries for new device concepts. Perovskite's potential applications are varied and include uses in sensors and catalyst electrodes, certain types of fuel cells, solar cells, lasers, memory devices and spintronics applications.

1.3.2. Strontium Titanate (SrTiO₃)

The study and applications of these devices depend crucially on the knowledge of the properties of the SrTiO₃ thin films. The dielectric constant of the SrTiO₃ layer determines the actual charge transferred to the superconductor by applying a certain gate voltage. The charge that can be transferred to a device using SrTiO₃, as a dielectric layer is limited by the product $\epsilon_{BD} E_{BD}$, where ϵ_{BD} is the dielectric constant ϵ evaluated at the breakdown field, E_{BD} . Neither ϵ nor E_{BD} has been reported for thin films so far, and the results for the dielectric behavior of bulk or single crystal SrTiO₃ [Neville (1972) *et al*, Mueller, Burkhard *et al* (1979), Sawaguchi *et al* (1962), Weaver (1959)] turn out to be inappropriate. In this letter, we present our results on the dielectric properties of thin SrTiO₃ films in the actual structure of a high T_c FET device. The Properties of strontium titanate are provided in table 1.1.

Table 1.1: Summary of the physical properties of SrTiO₃ [Marques (2009)].

Properties	Value
Lattice parameter at RT (nm)	0.3905
Atomic density (g/cm ³)	5.12
Melting Point (°C)	2080
Mohs hardness	6
Dielectric Constant (ϵ_r)	300
Thermal Conductivity (w/m.K)	12
Coefficient of thermal expansion ($\text{\AA}/^\circ\text{C}$)	9.4×10^{-6}
Refractive Index	2.31- 2.38

At room temperature, SrTiO₃ crystallizes in the ABO₃ cubic perovskite structure (space group *Pm3m*) with a lattice parameter of 0.3905 nm and a density of $\rho = 5.12 \text{ g / cm}^3$. The crystal structure is sketched in figure 2.1. The Ti⁴⁺ ions are six-fold coordinated by O²⁻ ions, whereas four TiO₆ octahedra surround each of the Sr²⁺ ions. Therefore, each Sr²⁺ ion is coordinated by 12 O²⁻ ions. Within the TiO₆ octahedra, while a hybridization of the O²⁻ *p* states with the Ti³⁺ *d* states leads to a pronounced covalent bonding [Leapman et al. (1982)], Sr²⁺ and O²⁻ ions exhibit ionic bonding character. Hence, SrTiO₃ has mixed ionic-covalent bonding properties. This nature of chemical bonding leads to a unique structure, which makes it a model electronic material.

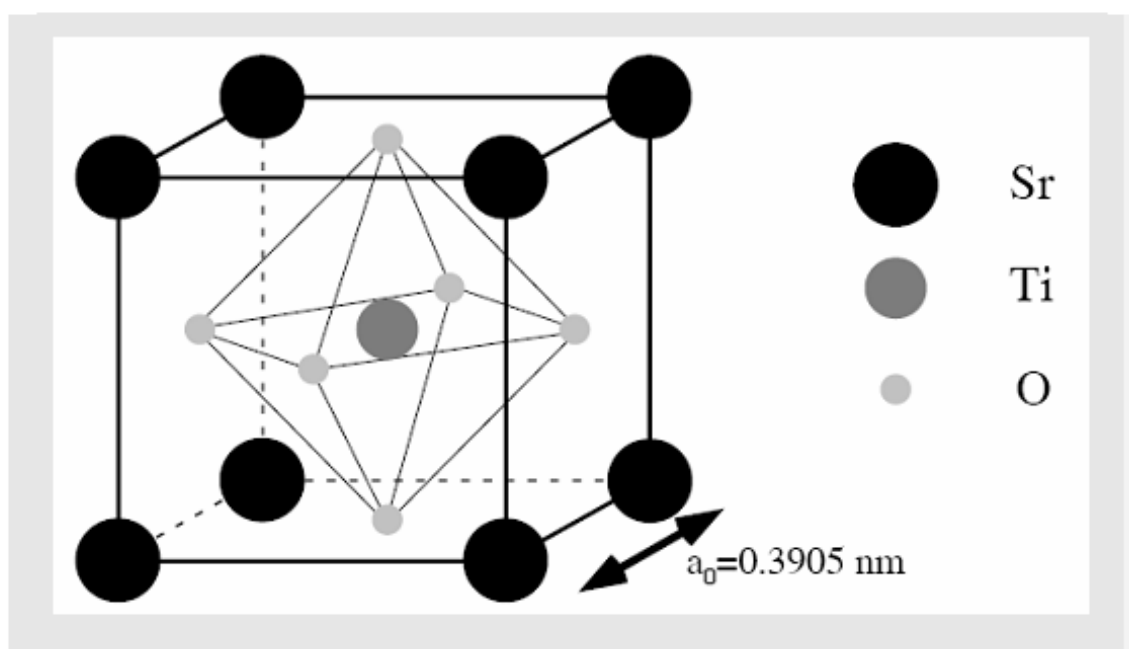


Figure 1.2. Atomic structure of SrTiO₃ at RT. [Marques (2009)].

Figure 1.2. shows the atomic arrangements for some of the major (high-symmetry) axial direction in SrTiO_3 . For any given planar direction (h, k, l) of a perovskite structure, there are always two distinct types of alternating equally spaced atomic planes having different areal densities of the three constituent elements; in this case, Sr, Ti, and O. For instance, the (100) SrTiO_3 surface can exhibit two different types of atomic alternating planes. One is formed by a TiO_2 plane and the other by a SrO plane [Groot et al. (1989)]

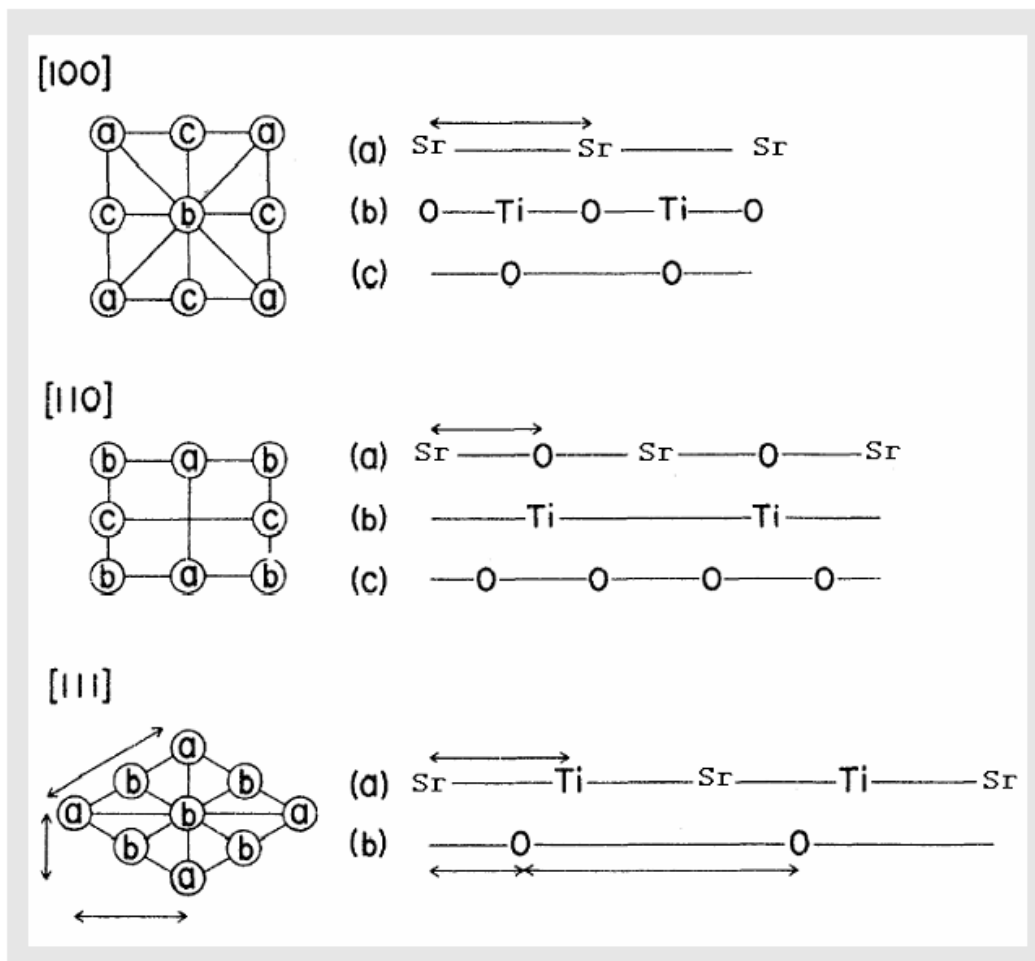


Figure 1.3. Atomic arrangements for the $\langle 100 \rangle$, $\langle 110 \rangle$ and $\langle 111 \rangle$ axial direction in SrTiO_3 [Groot et al. (1989)].

A distortion from cubic to lower symmetries occurs if the temperature is lowered or if a foreigner cation/dopant is introduced in the lattice (e.g., ion implantation). Distortions are assigned to three main effects: size effects, deviations from the ideal composition and the JahnTeller effect. It is rare to identify a single effect as responsible for the distortion of a certain perovskite. As an example of the complexity, cubic SrTiO₃ at RT has three more phase transitions upon cooling. SrTiO₃ bulk crystals are considered to be; tetragonal ($a = b \neq c$ and $C_{max} = 0.39 \text{ nm}$; space group $I4/mcm$) between 110 K – 65 K, due the opposite rotation of neighbouring oxygen octahedra, orthorhombic in the range 55 K – 35 K and possibly rhombohedral below 10 K as X -ray diffraction studies suggest [Rahmati (2004), Lytle (1964)]. In fact, there is no experimental evidence confirming for sure which structure SrTiO₃ exhibits below 10 K. Recently, PAC studies on the subject have confirmed that at 10 K a single low-symmetry phase is formed, which is not characterized by axial symmetry [Cao *et al.*(2000)].

1.3.3. Barium Titanate (BaTiO₃)

Barium titanate (BaTiO₃ or BTO) was synthesized to become the first and the most widely studied ceramic material, due to its excellent dielectric, ferroelectric and piezoelectric properties [N. Nikulin, (1988)]. The high dielectric constant of BaTiO₃ ceramics results from its crystal structure. BaTiO₃ has the Perovskite structure as shown in Figure (1.4).

In Figure (1.4), each barium ion is surrounded by 12 oxygen ions. The oxygen ions plus the barium ions form a face-centered cubic lattice. The titanium atoms reside in octahedral interstitial positions surrounded by six oxygen ions. Because of the large size of the Ba ions, the octahedral interstitial position in BaTiO₃ is quite large compared to the size of the Ti ions. The Ti ions are too small to be stable in this octahedral position. There

is minimum-energy positions off-center in the direction of each of the six oxygen ions surrounding the Ti ion. Since each Ti ion has a +4 charge, the degree of polarization is very high. When an electric field is applied, the Ti ions can shift from random to aligned positions and result in high bulk polarization and high dielectric constant [Richerson, (1992)]. Barium titanate has three crystalline forms: cubic, tetragonal, and hexagonal. The tetragonal polymorph is the most widely used because of its excellent ferroelectric, piezoelectric, and thermoelectric properties [Luo *et al.*, (2003)]. Temperature has a strong effect on the crystal structure and polarization characteristics of BaTiO₃. Above 120 °C (and up to 1400 °C), BaTiO₃ is cubic and the BaTiO₃ have a spontaneous random polarization as described above. In this temperature range, the Ti⁴⁺ ion lies in the center of an octahedron of oxygen ions (as shown in Figure 1.4.(a)).

The thermal vibration is high enough to result in the random orientation of the titanium ions in its octahedral interstitial position in BaTiO₃. The Ti⁴⁺ ion does shift position, resulting in polarization when an electric field is applied, but it returns to its stable central position as soon as the field is removed. Thus, there is no retained polarization, no hysteresis loop, and no ferroelectric behavior. As the temperature of BaTiO₃ is lowered slightly below 120 °C (Curie temperature), a displacive transformation occurs in which the structure of the BaTiO₃ changes from cubic to tetragonal (Figure 1.4. (b)). One crystallographic axis increases in length (unit cell goes from 4.010 to 4.022 Å) and the other two decrease in length (from 4.010 to 4.004 Å). The Ti⁴⁺ ion moves off-center toward one of the two oxygen ions of the long axis, resulting in a spontaneous increase in positive charge in this direction. This is illustrated in Figure (1.5. (a)).

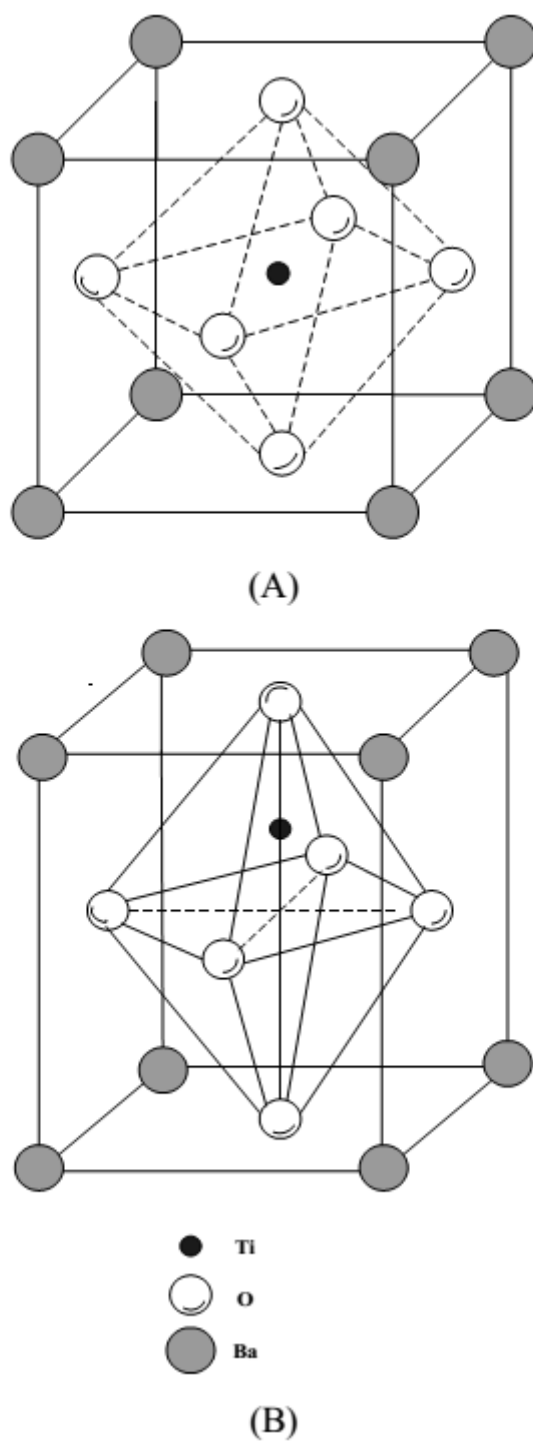


Figure 1.4. Schematic of the Perovskite structure of BaTiO₃ (A) Cubic lattice (above Curie temperature, 120°C) (B) Tetragonal lattice (below Curie temperature, 120°C) [Richerson, (1992)]

Application of an electric field opposite to the polarity of this original dipole will cause the Ti^{4+} ion to move through the center of the octahedral site and to an equivalent off-center position. This is shown in Figure 1.5. (b) This results in a reversal polarization, hysteresis in the E versus P curve, and ferroelectricity [Richerson (1992)].

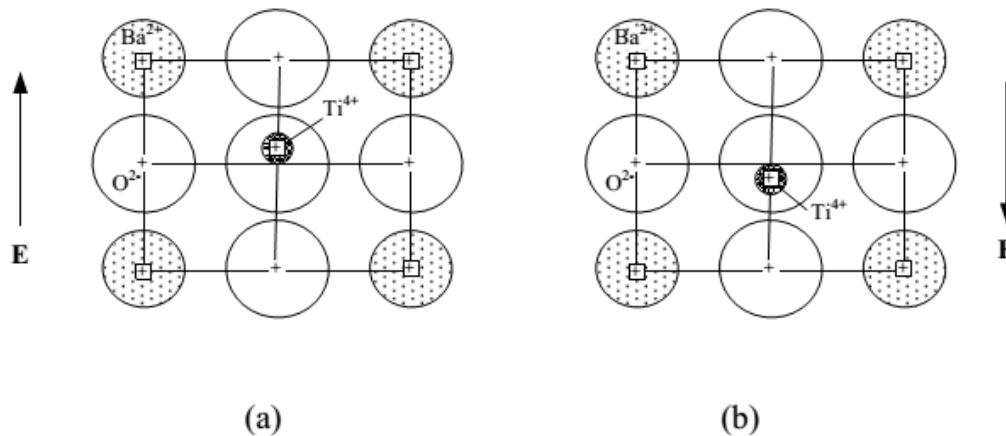


Figure 1.5. Reversal in the direction of spontaneous polarization in BaTiO_3 by reversal of the direction of the applied field [Richerson (1992)].

The dielectric properties of BaTiO_3 were found to be dependent on the grain size and temperature. At the Curie point, large-grained BaTiO_3 ($\geq 10 \mu\text{m}$) has a high dielectric constant because of the formation of multiple domains in a single grain, the motion of whose walls increases the dielectric constant at Curie point. For a BaTiO_3 with fine-grains ($\sim 1 \mu\text{m}$), a single domain form inside each grain. The movement of domain walls is restricted by the grain boundaries, thus leading to a low dielectric constant at the Curie point compared to coarse-grained BaTiO_3 . At room temperature, the dielectric constant of coarse-grained BaTiO_3 ceramics was found to be in the range of 1500-2000.

On the other hand, fine-grained BaTiO₃ exhibits a room temperature dielectric constant between 3500-6000. This is because the internal stresses in fine-grained BaTiO₃ are greater than in the coarse-grained material, which leads to a higher permittivity at room temperature [Ahmed *et al.*, (2006)].

1.4. Complex Perovskite

1.4.1. CaCu₃Ti₄O₁₂ (CCTO)

Calcium copper titanate (CCTO) has the chemical formula of CaCu₃Ti₄O₁₂, a novel electroceramic material with high dielectric permittivity (ϵ_r), of approximately 100,000 for single crystal and 10,000 for bulk material at room temperature which is also independent of temperature (100 – 600 K) and frequency (10^2 - 10^6 Hz). In (2000), Subramanian *et al.*, discovered that CCTO belongs to the family of ACu₃Ti₄O₁₂ (A = Ca, Sr, Ba, Bi_{2/3}, Y_{2/3}, La_{2/3}) type oxide of pseudo-cubic perovskite-related structure (space group: Im3) with a lattice parameter of 7.391 Å. The considerable value of ϵ_r remaining constant over a wide range of temperatures from 100 to 400 K for CCTO allows for its use in wide potential applications [Lohnert *et al.* (2014), Kretly *et al.* (2003), Ponce *et al.* (2015)]. The advancement of technology requires a material with giant ϵ value to reduce the size of electronic components, whereas the effective performance of these electronic components requires substantially low $\tan \delta$. For this reason, a significant number of theoretical and experimental researchers have been carried out to reveal the nature and the origin of the giant ϵ_r value of CCTO ceramics. Various processing routes (chemical and physical methods) of CCTO were adopted such as solid-state reaction, wet chemistry route, sol–gel, solution combustion synthesis, sonochemical-assisted route, and co-precipitation [Sulaiman *et al.* (2010), Yuan *et al.* (2010), Hua *et al.* (2012), Banerjee & Krupanidhi *et al.* (2010), Kim *et al.* (2007), Barbier *et al.* (2009)].

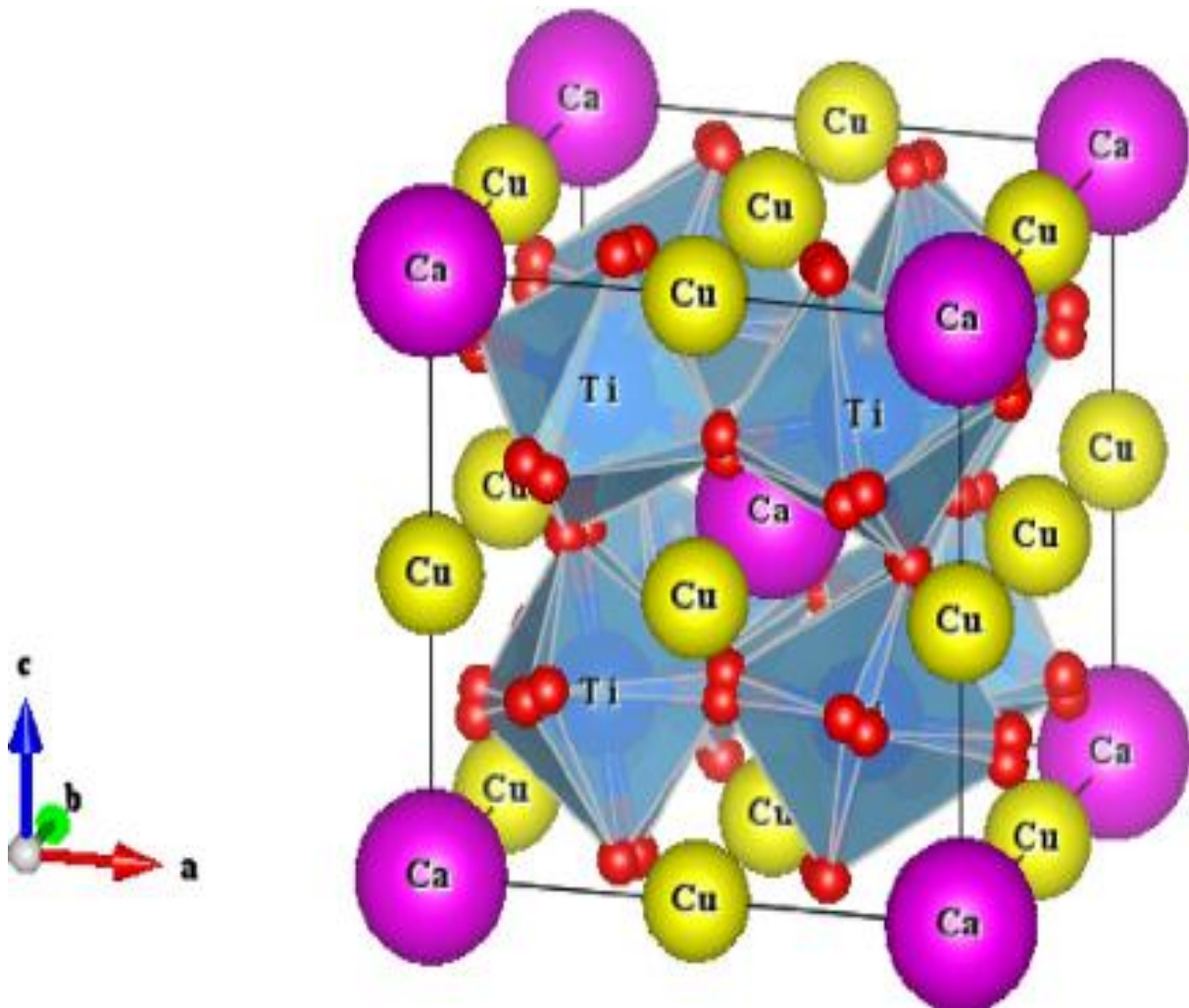


Figure 1.6. Crystal structure of CaCu₃Ti₄O₁₂ [Subramanian *et al.* (2000)].

CaCu₃Ti₄O₁₂ (CCTO) ceramics are potential candidates for capacitor applications due to their large dielectric permittivity (ϵ_r) values of up to 300,000. The underlying mechanism for the high ϵ_r is an internal barrier layer capacitor (IBLC) structure of insulating grain boundaries (G_b) and conducting grain interiors (bulk). This behavior is reviewed and discussed in detail. The origin of the IBLC structure is attributed to a small Cu non-stoichiometry in nominally insulating CaCu₃Ti₄O₁₂, which varies between the GBs and bulk. Such non-stoichiometry effects are studied in detail by analyzing bulk

ceramics of different composition within the ternary CaO-CuO-TiO₂ phase diagram using X-ray diffraction (XRD), scanning electron microscopy (SEM) and impedance spectroscopy (IS). At least two defect mechanisms are suggested to exist. It is further shown that the development of the defect mechanisms in CCTO and the concomitant formation of the IBLC structure strongly depend on the processing conditions of CCTO ceramic pellets such as the sintering temperature. Nominally stoichiometric CCTO bulk ceramics sintered at different temperatures are analyzed using XRD, SEM, and Impedance Spectroscopy (IS). The performance of CCTO ceramics for IBLC applications is controlled by subtle modifications in the compound stoichiometry that is strongly dependent on the ceramic sintering temperature.

1.4.2. Bi_{2/3}Cu₃Ti₄O₁₂ (BCTO)

Bi_{2/3}Cu₃Ti₄O₁₂ (BCTO) is one of the few members that have been presently confirmed isostructurally CCTO-like oxides. However, limited literature reported the BCTO ceramics prepared by the solid-state reaction [Szwagierczak (2008), Liu (2004)], and the dielectric constant of the ceramics is relatively low for practical applications. BCTO crystallizes as cubic Perovskite-related structure as shown in Fig. 1 with space group Im $\bar{3}$ and lattice constant $a = 7.413 \text{ \AA}$ [Subramanian *et al.* (2000), Subramanian and Sleight *et al.* (2002)]. In this structure, the Bi sites are 1/3 vacant to achieve charge neutrality. This might affect the dielectric behavior, rendering the study of this sample more interesting. The dielectric constant of BCTO was reported to be 1871 at 25 °C and 10⁵ Hz. Although it is not as high as that of CCTO, it is still much more extensive than ordinary dielectrics.

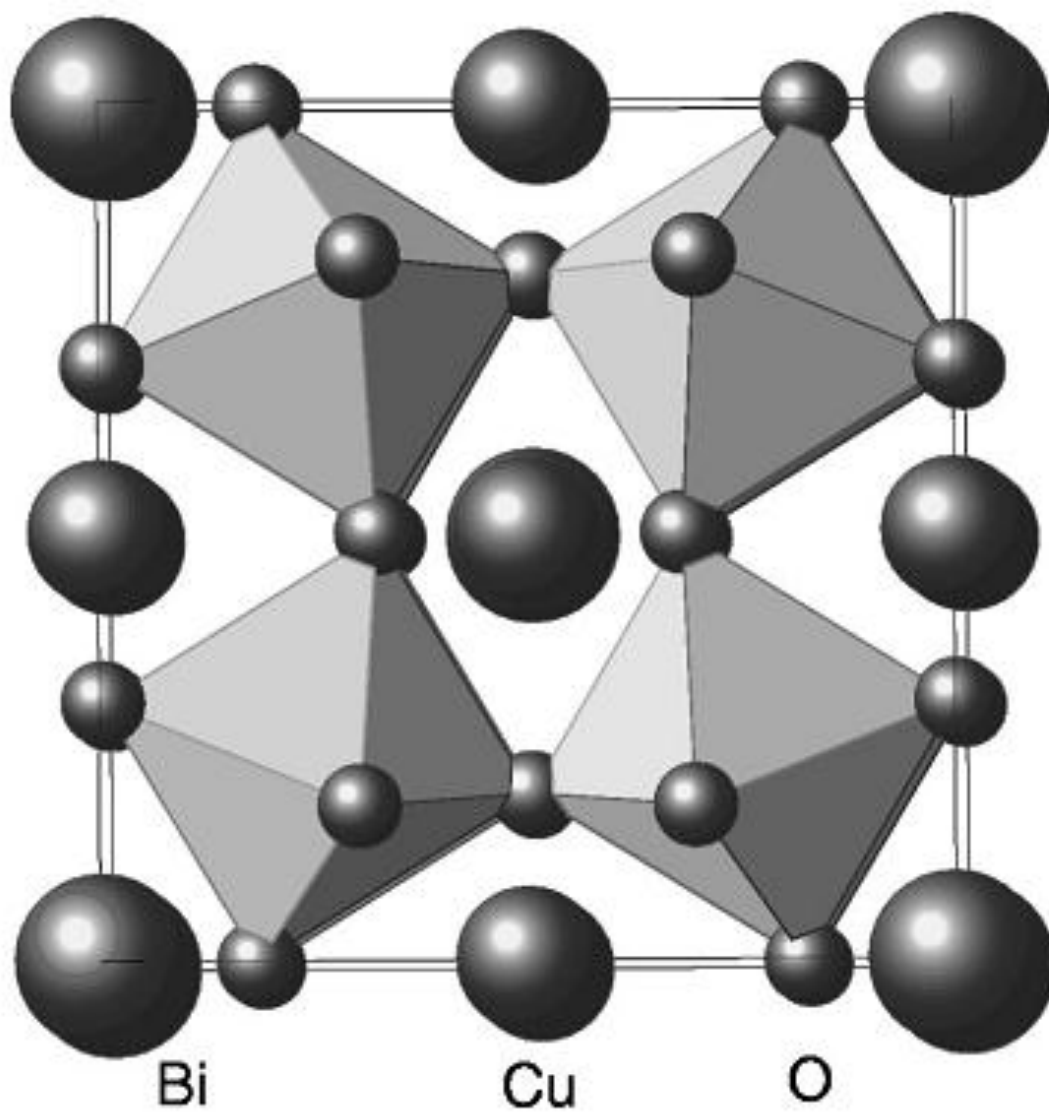


Figure 1.7. Crystal structure of BCTO [Deng *et al.* (2017)].

1.4.3. $\text{Y}_{2/3}\text{Cu}_3\text{Ti}_4\text{O}_{12}$ (YCTO)

$\text{Y}_{2/3}\text{Cu}_3\text{Ti}_4\text{O}_{12}$ (YCTO) is also an important class of material of ACTO series. It is believed to be isostructural to CCTO as reported in the literature [Jianjun *et al.* (2005), Liang *et al.* (2012), Junwei *et al.* (2015)]. It exhibits a high dielectric constant with excellent thermal stability. It has the comfort of being lead-free and eco-friendly, too. In our previous communications, we have reported the synthesis of YCTO ceramic by the semi-wet route at a relatively lower sintering temperature with significant dielectric constant [Sharma *et al.* (2014), Sharma *et al.* (2015), Sharma *et al.* (2017)]. Its dielectric properties, as well as microstructural details, were obtained by XRD, SEM, EDX and TEM analysis. The preparation of YCTO by the solid-state reaction method [Liang *et al.* (2012),] and Sol-Gel process [Junwei *et al.*(2015)] are also reported in the literature.

1.5. Applications of Perovskites

	APPLICATION
BaTiO_3	Multilayer Capacitor [Park (2005)]
$\text{Pb}(\text{Zr}_x\text{Ti}_{1-x})\text{O}_3$	Piezoelectric Transducer [Lendermann <i>et al.</i> (2004)]
BaTiO_3	P. T. C. Thermistor [Affleck and Leach (2005)]
$(\text{Pb}, \text{La})(\text{Zr}, \text{Ti})\text{O}_3$	Electrooptical Modulator [Nakada <i>et al.</i> (2003)]
BaZrO_3	Dielectric Resonator [Shi (2008)]
BaRuO_3	Thick Film Resistor
$\text{Pb}(\text{Mg}_{1/3}\text{Nb}_{2/3})\text{O}_3$	Electrostrictive Actuator [Takagi <i>et al.</i> (1993)]
$\text{Ba}(\text{Pb}, \text{Bi})\text{O}_3$ layered cuprates	Superconductor [Grumann <i>et al.</i> (1994)]
GdFeO_3	Magnetic Bubble Memory [Kanta and Kumar (2014)]

YAlO_3	Laser Host [Belt <i>et al.</i> (2003)]
$(\text{Ca}, \text{La})\text{MnO}_3$	Ferromagnet [Heffner <i>et al.</i> (2000)]
LaCoO_3	Refractory Electrode
KNbO_3	Second Harmonic Generator
SrCeO_3	Hydrogen sensor[Iwaraha <i>et al.</i> (1981)]
BaZrO_3	H_2 production/ extraction[Iwaraha <i>et al.</i> (1988)]
$(\text{La}, \text{Sr})(\text{Ga}, \text{Mg})\text{O}_{3-\delta}$	Solid electrolyte[Yamanaka <i>et al.</i> (2003)]

1.6. Composite Materials

The Composite material is a material made from two or more constituent materials with significantly different physical or chemical properties that, when combined, produce a material with characteristics different from the individual components. The individual components remain separate and distinct within the finished structure. The new material may be preferred for many reasons: common examples include materials which are stronger, lighter, or less expensive when compared to traditional materials. More recently, researchers have also begun to actively include sensing, actuation, computation and communication into composites,[McEvoy & Correll *et al.* (2015)].

1.6.1. Natural composites

Natural composites exist in both animals and plants. Wood is a made from long cellulose fibers (a polymer) held together by a much weaker substance called lignin. Cellulose is also found in cotton, but without the lignin to bind it together, it is much

weaker. The two weak substances lignin and cellulose collectively form a much stronger one. The bone in your body is also a composite. It is made from a hard but brittle material called hydroxyapatite (which is mainly calcium phosphate), and a soft and flexible material called collagen (which is a protein). Collagen is also found in hair and fingernails. On its own, it would not be much use in the skeleton, but it can combine with hydroxyapatite to give bone the properties that are needed to support the body.

1.6.2. Premature composites

People have been making composites for many thousands of years. One early example is mud bricks. Mud can be dried out into a brick shape to give a building material. It is sturdy if you try to squash it (it has good compressive strength) but it breaks quite easily if you try to bend it (it has reduced tensile strength). Straw seems very strong if you decide to stretch it, but you can crumple it up easily. By mixing mud and straw, it is possible to make bricks that are resistant to both squeezing and tearing and make excellent building blocks. Another ancient composite is concrete. Concrete is a mix of aggregate (small stones or gravel), cement and sand. It has a good compressive strength (it resists squashing). In more recent times it has been found that adding metal rods or wires to the concrete can increase its tensile (bending) strength. Concrete containing such rods or wires is called reinforced concrete.

1.6.3. Constructing composites

Most composites are made of just two materials. One is the matrix or binder. It surrounds and binds together fibers or fragments of the other material, which is called the reinforcement. A modern example, the first modern composite material was fiberglass. It is still widely used today for boat hulls, sports equipment, building panels and many car

bodies. The matrix is a plastic, and the reinforcement is glass that has been made into fine threads and often woven into a sort of cloth. On its own, the glass is very strong but brittle, and it will break if bent sharply.

The plastic matrix holds the glass fibers together and also protects them from damage by sharing out the forces acting on them. Some advanced composites are now made using carbon fibers instead of glass. These materials are lighter and stronger than fiberglass but more expensive to produce. They are used in aircraft structures and costly sports equipment such as golf clubs. Carbon nanotubes have also been used successfully to make new composites. These are even lighter and stronger than composites made with conventional carbon fibers, but they are still costly. They do, however, offer possibilities for making lighter cars and aircraft (which will use less fuel than the more massive vehicles we have now). The new Airbus A380, the world's largest passenger airliner, makes use of modern composites in its design. More than 20 % of the A380 is made of composite materials, mainly plastic reinforced with carbon fibers. The plan is the first large-scale use of glass-fiber-reinforced aluminium, a new composite that is 25 % stronger than conventional airframe aluminum but 20 % lighter.

1.6.4. Nanocomposite

It is a multiphase solid material where one of the phases has one, two or three dimensions of less than 100 nanometers (nm), or structures having nano-scale repeat distances between the different phases that make up the material. The idea behind Nanocomposite is to use building blocks with dimensions in nanometre range to design and create new materials with unprecedented flexibility and improvement in their physical properties. In the broadest sense, this definition can include porous media, colloids, gels, and copolymers, but is more usually taken to mean the solid

combination of a bulk matrix and nano-dimensional phase(s) differing in properties due to dissimilarities in structure and chemistry. The mechanical, electrical, thermal, optical, electrochemical, catalytic properties of the nanocomposite will differ markedly from that of the component materials. Size limits for these effects have been proposed, [Kamigaito (1991)] < 5 nm for catalytic activity, < 20 nm for making a hard magnetic material soft, < 50 nm for refractive index changes, and < 100 nm for achieving superparamagnetism, mechanical strengthening or restricting matrix dislocation movement.

Nanocomposites are found in nature, for example in the structure of the abalone shell and bone. The use of nanoparticle-rich materials long predates the understanding of the physical and chemical nature of these materials. [Yacaman *et al.* (1996)] investigated the origin of the depth of color and the resistance to acids and bio-corrosion of Maya blue paint, attributing it to a nanoparticle mechanism. From the mid-1950s nanoscale organo-clays have been used to control the flow of polymer solutions (e.g. as paint viscosifiers) or the constitution of gels (e.g. as a thickening substance in cosmetics, keeping the preparations in homogeneous form). By the 1970s polymer/clay composites were the topics of textbooks, [Theng *et al.* (1979)] although the term "nanocomposites" was not in common use.

In mechanical terms, nanocomposites differ from conventional composite materials due to the exceptionally high surface to volume ratio of the reinforcing phase or its abnormally high aspect ratio. The reinforcing material can be made up of particles (e.g. minerals), sheets (e.g., exfoliated clay stacks) or fibers (e.g., carbon nanotubes or electrospun fibers). The area of the interface between the matrix and reinforcement phase(s) is typically an order of magnitude greater than for conventional composite materials. The matrix material properties are significantly affected in the vicinity of the reinforcement. Note that with polymer nanocomposites, features related to local

chemistry, the degree of thermoset cure, polymer chain mobility, polymer chain conformation, degree of polymer chain ordering or crystallinity can all vary significantly and continuously from the interface with the reinforcement into the bulk of the matrix.

This large amount of reinforcement surface area means that a relatively small amount of nanoscale reinforcement can have an observable effect on the macroscale properties of the composite. For example, adding carbon nanotubes improves the electrical and thermal conductivity. Other kinds of nanoparticles may result in enhanced optical properties, dielectric properties, heat resistance or mechanical properties such as stiffness, strength, and resistance to wear and damage. In general, the nano reinforcement is dispersed into the matrix during processing. The percentage by weight (called mass fraction) of the nanoparticulates introduced can remain very low (on the order of 0.5% to 5%) due to the low filler percolation threshold, especially for the most commonly used non-spherical, high aspect ratio fillers (e.g. nanometer-thin platelets, such as clays, or nanometer-diameter cylinders, such as carbon nanotubes). The orientation and arrangement of asymmetric nanoparticles, thermal property mismatch at the interface, interface density per unit volume of the nanocomposite, and polydispersity of nanoparticles significantly affect the effective thermal conductivity of nanocomposites.

1.6.5. Ceramic matrices nanocomposite

In this group of composites, the main part of the volume is occupied by a ceramic, i.e., a chemical compound from the group of oxides, nitrides, borides, silicides, etc. In most cases, ceramic-matrix nanocomposites encompass a metal as the second component. Ideally, components, the metallic one, and the ceramic one are finely dispersed in each other to elicit the particular nanoscopic properties. Nanocomposite from these combinations was demonstrated in improving their optical, electrical and magnetic

properties [Kruis *et al.* (1998)] as well as tribological, corrosion-resistance and other protective properties [Zhang *et al.* (2003)]. The binary phase diagram of the mixture should be considered in designing ceramic-metal nanocomposites and measures have to be taken to avoid a chemical reaction between both components. The last point mainly is of importance for the metallic component that may easily react with the ceramic and thereby lose its metallic character. This is not an easily obeyed constraint because the preparation of the ceramic component requires high process temperatures. The safest measure thus is to choose immiscible metal and ceramic phases carefully. A good example for such a combination is represented by the ceramic-metal composite of TiO₂ and Cu, the mixtures of which were found immiscible over large areas in the Gibbs triangle of Cu-O-Ti [Effenberg *et al.* (2001)].

The concept of ceramic-matrix nanocomposites was also applied to thin films that are solid layers of a few nm to some tens of μm thickness deposited upon an underlying substrate and that play an important role in the functionalization of technical surfaces. Gas flow sputtering through the hollow cathode technique turned out as a slightly useful technique for the preparation of nanocomposite layers. The process operates as a vacuum-based deposition technique and is associated with high deposition rates up to some $\mu\text{m/s}$ and the growth of nanoparticles in the gas phase. Nanocomposite layers in the ceramics range of composition were prepared from TiO₂ and Cu by the hollow cathode technique [Birkholz *et al.* (2004)] that showed a high mechanical hardness, small coefficients of friction and a high resistance to corrosion.

1.6.6. Application of Composite

The most prominent advantage of modern composite materials is that they are light as well as durable. By choosing an appropriate combination of matrix and

reinforcement material, a new material can be made that exactly meets the requirements of a particular application. Composites also provide design flexibility because many of them can be moulded into complex shapes. The downside is often the cost. Although the resulting product is more efficient, the raw materials are often expensive.

1.7. Ceramic Dielectrics

Dielectrics are those insulators which do not flow charge but shift from their average equilibrium positions causing polarization. When a dielectric material is placed in an electric field, the amount of polarization caused is described by a dimensionless quantity called the dielectric constant. The electrically insulating material between the metallic plates of a capacitor is a common example of a dielectric. The polarization of the dielectric by the applied electric field increases the capacitor's surface charge for the given electric field strength. Dielectric constant, dielectric resistivity, dielectric loss, and dielectric strength will be interpreted in the following sections:

1.7.1. Dielectric Behaviour

(a) Basic concept of dielectric capacitor

A capacitor consists of two conductor plates filled with certain dielectric materials. It is common in the parallel-plate form, as shown in Figure 1.8. The function of Dielectric materials is bases of capacitors in the electronics devices. Capacitors have an energy-stored ability which is determined by the permittivity of the dielectrics and the geometry of the conductors. This phenomenon is known as capacitance which is denoted by C . it is independent of the potential difference between the conductors and the total charge on them. The dielectrics are kept on between two parallel plates and capacitance is approximately equal to the following:

$$C = \epsilon' \epsilon_0 \frac{A}{d} \quad (1.2)$$

Where C is the capacitance, ϵ' is the relative permittivity, ϵ_0 is the electric constant ($\approx 8.85 \times 10^{-12} \text{ Fm}^{-1}$), A is the area of overlap of the two plates, and d is the distance between the plates.

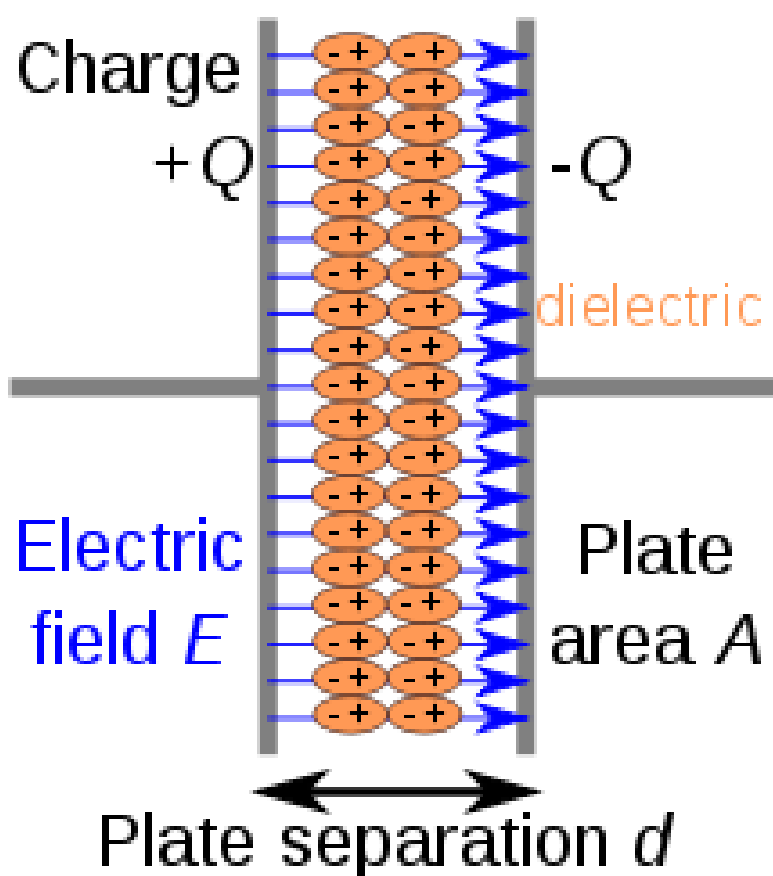


Figure 1.8. Polarized dielectric material [Seo *et al.* (2013)].

Obviously, the capacitance is inversely proportional to the separation distance between the plates, while directly proportional to the overlap area of the conductor plates and the relative permittivity of the dielectrics. The electric polarization is occurred when

an external voltage V is applied on the conductor plates. The positives and negative charges will accumulate on the two plates with equal content. It is called charge process of the capacitor. The electrical potential (caused by the accumulated charge $\pm Q$ on both plates) is equal to the external applied voltage V then charge process will be finished. Q/V is equal to the capacitance C of the capacitor. Sometimes, the relative permittivity of the dielectrics is changed by the external bias, causing the capacitance to vary. In this case, capacitance is defined concerning incremental change:

$$C = \frac{dq}{dv} \quad (1.3)$$

During the charging process, the charges are moved between the conductor plates by the function of external bias, indicating that work must be done and that the electric energy is stored in the dielectrics at the same time. Hence, the amount of the stored energy W could be obtained from the following formula:

$$W = \int_0^Q V dq = \int_0^Q \frac{q}{C} dq = \frac{1}{2} \frac{Q^2}{C} = \frac{1}{2} CV^2 = \frac{1}{2} VQ. \quad (1.4)$$

After the discovery of ABO_3 perovskites such as $BaTiO_3$ and $PbTiO_3$ [Shirane *et al.* (1950)], the detailed dielectric properties have been studied in perovskite. The high dielectric constant is desired for capacitive components in microelectronics. The high dielectric constant of perovskite is based on the polarization of the metal ions concerning the oxygen lattice. The relaxor ferroelectrics have high dielectric constant which are examples of disordered solid solutions, such as $(1-x)PbZn_{1/3}Nb_{2/3}O_3 \cdot xPbTiO_3$ (PZN-PT) [Pilgrim *et al.* (1990)] and $(1-x)PbMg_{1/3}Nb_{2/3}O_3 \cdot xPbTiO_3$ (PMN-PT). It is also pronounced a variation of the dielectric constant as a function of temperature and

frequency dispersion with large dielectric constants. Giant dielectric constant materials have found extreme importance for applications of capacitor, microelectronics and microwave devices and device implementation, e.g., as metal-oxide semiconducting field effect transistors (MOSFET's). The $\text{CaCu}_3\text{Ti}_4\text{O}_{12}$ ceramics shows a giant dielectric constant about 10^4 that is nearly constant from room temperature to 573 K [Subramanian *et al.* (2000), Ramirez *et al.* (2000), Almeida *et al.* (2002), Moriya *et al.* (2003)]. The barrier layer capacitor model is one of the main reasons for the origin of high dielectric constant; it has been claimed in the literature. The Li-ion conductor compound $\text{La}_{0.67}\text{Li}_{0.25}\text{Ti}_{0.75}\text{Al}_{0.25}\text{O}_3$ is defined as a dielectric material with a high electrical resistivity [Huang *et al.* (2011)] but an efficient supporter of electrostatic field.

The energy can be stored by an electrostatic field when the electrostatic flux lines are not interrupted and minimum current between opposite electric poles. This phenomenon can find applications in virtually any electricity-driven devices and useful in capacitors [Lines *et al.* (1977)]. Different types of capacitor are based on BaTiO_3 , $\text{PbMg}_{1/3}\text{Nb}_{2/3}\text{O}_3$ [PMN], $\text{PbZn}_{1/3}\text{Nb}_{2/3}\text{O}_3$ [PZN], and $\text{Pb}_{1-x}\text{La}_x(\text{Zr}_{1-y}\text{Ti}_y)\text{O}_3$ [PLZT] dielectric materials having the perovskite structure. BaTiO_3 , CaTiO_3 and SrTiO_3 Ceramics are used as energy storage materials [Waku *et al.* (1969)]. Recently, the fabrications of superior dielectrics are used in Wireless telecommunication [Reaney and Uvic *et al.* (2000)]. Dielectrics are mainly insulators that can be polarized by the application of electric field. When a dielectric material is placed in an electric field, electrical charges do not flow through it (like in conductors) but shift from their average equilibrium positions causing polarization. The amount of polarization caused is described by a dimensionless quantity called the dielectric constant.

1.8. Polarization

On placing in an electric field, the positive and negative charges of a dielectric are displaced from their equilibrium positions by very small distances throughout the volume of the dielectric. This results in the formation of a large number of dipoles each having some dipole moment in the direction of the field. The material is said to be polarized with a polarization P . The polarization is defined as dipole moment per unit volume.

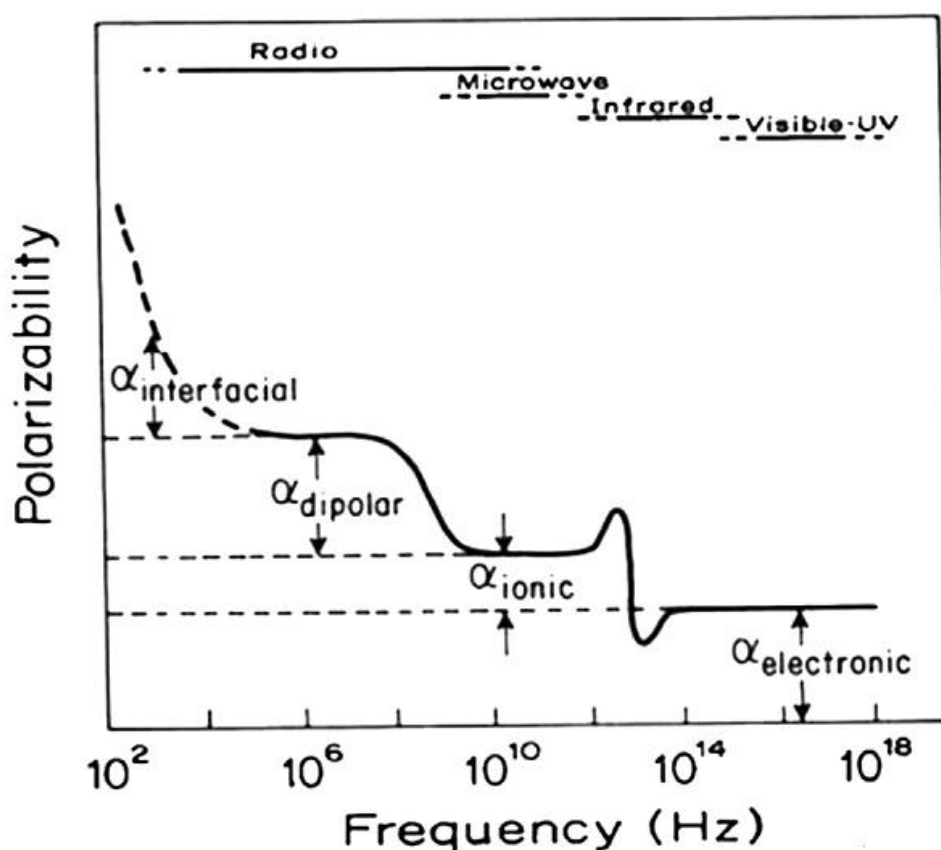


Figure 1.9. Typical response of the total polarizability of a crystal as a function of electric field Frequency [Singh *et al.* (2014)].

1.8.1. Types of Polarization

(a) Electronic Polarization

This kind of polarization arises due to the displacement of the electron cloud of an atom relative to its nucleus in the presence of an applied electric field. The polarization, as well as the dielectric constant of material at optical frequencies, results mainly from electronic polarization. This mechanism would result in low dielectric constant, up to 2–4, and can respond to very high frequencies around 10^{15} Hz.

(b) Ionic Polarization:

Ionic polarization arises due to a displacement of a charged ion relative to other ions in a solid. The ionic contribution is important at low frequencies.

(c) Dipolar Polarization:

The Molecular (dipolar) polarization arises due to polar substances that can orient themselves in the presence of an external electric field. The thermal agitation of the molecules tends to counteract the ordering effect of the electric field, and an equilibrium state is reached where in the different dipoles make all possible angles varying from zero to π radians with the field direction. It occurs at around 10^{11} to 10^{12} Hz.

(d) Space Charge Polarization:

Space charge (inter-facial) polarization arises due to the accumulation of charges at the interface or the grain boundary of a polycrystalline material. The ions diffuse over appreciable distances in response to the applied field-giving rise to re-distribution of charges in the dielectric medium [Valenzuta *et al.* (1994)]. The typical frequency range for this polarization is around 10^{-3} to 10^3 Hz.

$$P = P_{\text{electronic}} + P_{\text{ionic}} + P_{\text{molecular}} + P_{\text{interfacial}} \quad (1.5)$$

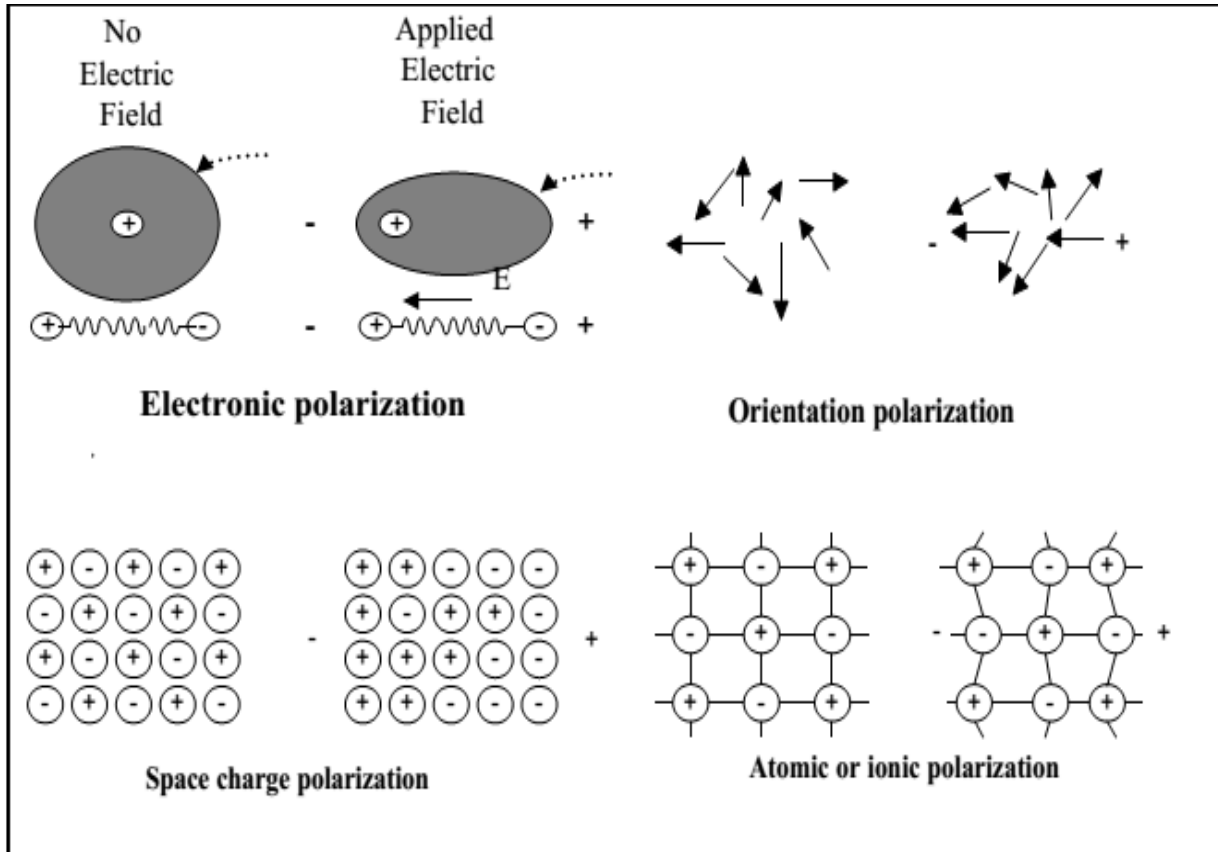


Figure 1.10. Types of polarization mechanisms [Richerson, (1992), Rose *et al.*, (1971)].

1.9. Dielectric constant

The dielectric constant is the ratio of the permittivity of a substance to the permittivity of free space. It is an expression of the extent to which a material concentrates electric flux, and is the electrical equivalent of relative magnetic permeability. Dielectric constant is the factor by which the capacitance of a parallel-plate capacitor is increased by inserting a dielectric in place of a vacuum. The insulator materials which have a low conductivity of roughly 20 orders of magnitude is the result of energy band gaps greater than 2 eV (compared to zero for metals). These dielectric materials are an essential part of the electronics industry. The dielectric constant is a physical quantity that has the ability of material to polarize in response to the field. It reduces the total electric field inside the material [Chen *et al.* (2009), Asami (2002)].

1.10. Dielectric loss

Dielectric loss quantifies a dielectric material's inherent dissipation of electromagnetic energy (e.g., heat). It can be parameterized regarding either the loss angle (δ) or the corresponding loss tangent $\tan(\delta)$. Both refer to the phase or in the complex plane whose real and imaginary parts are the resistive (lossy) component of an electromagnetic field and its reactive (lossless) counterpart. Dielectric loss, loss of energy that goes into heating a dielectric material in a varying electric field. For example, a capacitor incorporated in an alternating-current circuit is alternately charged and discharged each half cycle. During the alternation of polarity of the plates, the charges must be displaced through the dielectric first in one direction and then in the other, and overcoming the opposition that they encounter leads to a production of heat through dielectric loss, a characteristic that must be considered when applying capacitors to electric circuits, such as those in radio and television receivers. Dielectric losses

depend on frequency and the dielectric material. Heating through dielectric loss is widely employed industrially for heating thermosetting glues, for drying lumber and other fibrous materials, for preheating plastics before molding, and for fast jelling and drying of foam rubber.

The dielectric loss ($\tan \delta$) is a material property and a measure of energy loss in the dielectric during a cooperation. It does not depend on the geometry of capacitor. The dielectric loss is expressed as the loss tangent ($\tan \delta$) or dissipation factor can be defined as equation (1.6)

$$\tan \delta = \frac{\epsilon''}{\epsilon'} + \frac{\sigma}{2\pi f \epsilon'} \quad (1.6)$$

Where ϵ' is the real part, and ϵ'' is the imaginary part of the dielectric permittivity, and σ is the electrical conductivity of the materials And f is the frequency. The dielectric loss ($\tan \delta$) results from distortion, dipolar, interfacial, and conduction loss. The distortion loss is related to electronic and ionic polarization mechanisms and at high-frequency region. The interfacial loss creates from the extremely polarized interface induced by the fillers. The rotation of atoms or molecules in an alternating electric field is the main cause of dielectric loss of dielectric materials. The conduction loss represented the flow of actual charge through the dielectric materials and attributed to the dc electrical conductivity of the materials. The dielectric constant is usefulness of dielectric as an insulator material which is given by equation (1.7)

$$\epsilon'' = \frac{\tan \delta}{\epsilon'} \quad (1.7)$$

Where ϵ' is dielectric constant and $\tan \delta$ is the dielectric loss of dielectric materials. For this purpose, it is desirable to have a low dielectric constant and particularly a minimal loss angle. The energy loss in dielectric materials results from three processes as follows:

- i) Ionic migration losses (i.e., DC conductivity)
- ii) Relaxation losses for dipole reorientation due to ionic jump and
- iii) Ion vibration and deformation losses.

The energy loss (W) is proportional to the dielectric loss tangent ($\tan \delta$) and refers to the energy dissipated in a dielectric material. This can be determined by the following equation:

$$W = \pi \epsilon' \xi^2 f \tan \delta \quad (1.8)$$

Where ξ is the electric field strength, and f is the frequency. Therefore, a low dielectric loss is preferred to reduce the energy dissipation and particularly for high-frequency applications. In general, a dielectric loss under 5% is considered to be high, and 0.1% is quite to be low. The radio frequency (RF) applications also depend on low loss tangent due to avoid signal losses but much higher values can be tolerated for energy storage applications such as decoupling. In the high-temperature region, the presence of oxygen vacancies are an essential and rapid increase of dissipation factor is caused by free carrier conductivity. The concentration of free carriers depends on doping and temperature. The dissipation factor ($\tan \delta$) is inversely proportional to frequency in high-temperature range. Polycrystalline titanates, on cooling, rapid re-oxidation occurs above 1100 °C but effectively stops at some temperature between 600 °C and 900 °C. Therefore, the outside of each grain is well oxidized, but the interior of the grains remains oxygen deficient. The oxygen vacancies neutralized by 3d electrons on the titanium atoms

and formed two Ti^{3+} ions for every oxygen vacancy. Ti^{3+} ions and oxygen vacancies are bound by a small energy of 0.10–0.20 eV. Ti^{3+} attached with electrons for conduction making use of the narrow 3d conduction band. As a consequence, the conduction process can be described as electron hopping as following equation (1.9).



And unattached oxygen vacancies also contribute to the conductivity, but their mobility is much smaller than that of electrons [Newnham (1983)]. The experience of a torque tending to align the dipole moment with the applied field and neutralized bound defects do not participate directly in the conduction process. In this process creates dielectric polarization and dielectric loss.

1.11. Basic Principles of Impedance Spectroscopy

Temperature-dependent impedance spectroscopy (IS) enables different contributions to the dielectric and resistive properties of condensed matter to be deconvoluted and characterized separately [Barsukov and Macdonald *et al.* (2005), Schmidt (2007)]. IS is therefore, the method of choice to separately determine and investigate the dielectric properties of grain boundaries (Gb) and grain interior (bulk) regions in electrically inhomogeneous electroceramics such as CCTO [Adams *et al.* (2002)]. It is well established that different dielectric relaxation processes detected by IS such as those found in the GB and bulk regions. In the simplest case, be understood regarding the brickwork layer model where each GB or bulk type contribution is described by one RC circuit element consisting of a resistor and capacitor in parallel [Irvine *et al.* (1990)]. Several dielectric relaxations in series can be characterized by

several RC elements connected in series, where the macroscopic impedance is just the sum of all series RC impedances. The RC model works particularly well for insulators such as dielectrics, where the capacitor describes the ability of the material to store charge, and the parallel resistor illustrates the leakage current due to some un-trapped charge carriers bypassing the ideal charge storage element.

Impedance Spectroscopy data can also be represented in alternative formats using the standard conversions shown in Figure 1.11 for the real part of the dielectric permittivity (ϵ') or capacitance (C'). Such plots often contain important information on the resistance or permittivity of a specific relaxation. In a scenario of a ceramic sample such as CCTO with one grain boundaries (Gb) and one bulk (b) relaxation as represented by two RC elements connected in series, the following spectral features are expected as shown from the simulations presented in Figure 1.11.

- (a) In plots of real impedance versus imaginary impedance (Z' vs. Z'') two semicircles appear with each semicircle diameter corresponding to the respective resistance R ,
- (b) Z'' vs. frequency (f) plots show two relaxation peaks with peak heights of $R/2$ for each relaxation,
- (c) C' vs. f or ϵ' vs. f display two approximately f independent C' (ϵ') plateaus C_{GB}^* and C_b^* , that corresponds approximately to the GB (C_{GB}) and bulk capacitance (C_b) and show an average sharp drop at a distinct f .

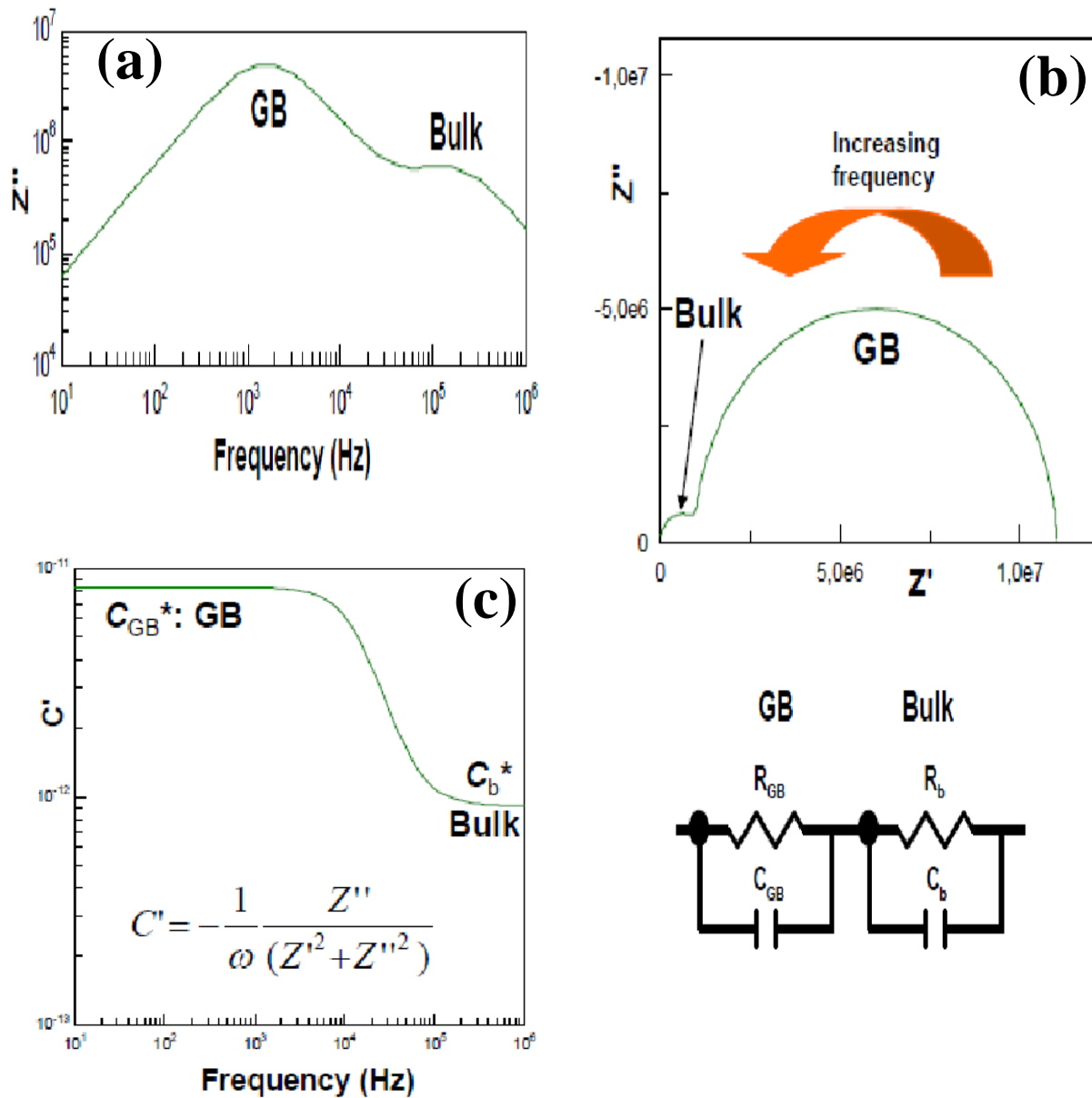


Figure 1.11. Simulated impedance spectroscopy (IS) data for two RC elements connected in series, presented in different formats: (a) Z'' [Ω] vs frequency (f), (b) Z'' [Ω] vs Z' [Ω] and (c) C' [Farad] vs frequency (f) Simulations were carried out with $R_{Gb} = 10 \text{ M}\Omega$, $R_b = 1 \text{ M}\Omega$, $C_{Gb} = 10 \text{ pF}$ and $C_b = 1 \text{ pF}$.

The resistance and capacitance values were chosen to represent a realistic scenario of one extrinsic GB- and one intrinsic bulk-type relaxation. In the framework of the brickwork layer model of two RC elements connected in series, the GB and bulk capacitance plateau C_{GB}^* and C_b^* depicted in the C' vs f plot in Figure 1.11 are both only an approximation for the G_b and bulk capacitance C_{GB} and C_b respectively. where C_{GB}^* contains all resistor and capacitor terms and C_b^* contains a contribution from the GB capacitance. The C_{GB}^* and C_b^* do not coincide exactly with the values of the capacitors C_{GB} (10 pF) and C_b (1 pF). The exact expressions for C_{GB}^* and C_b^* are given by equations (1.10) and (1.11) respectively.

$$C_{GB}^* = \frac{R_{GB}^2 C_{GB} + R_b^2 C_b}{(R_{GB} + R_b)^2} \quad (1.10)$$

$$C_b^* = \frac{C_{GB} \times C_b}{C_{GB} + C_b} \quad (1.11)$$

The GB and bulk resistance R_{GB} and R_b are sufficiently different, i.e. $R_{GB} \gg R_b$, then C_{GB}^* constitutes an excellent estimate for C_{GB} . This is usually the case for CCTO where R_{GB} and R_b commonly vary by more than 3 orders of magnitude. C_b^* is a good estimate for C_b for the case where the two capacitors C_{GB} and C_b are sufficiently different, i.e., $C_{GB} \gg C_b$. Z'' vs. f plots highlight the relaxation peak with the highest resistance R (e.g. the GB peak in CCTO). The approximate peak frequencies for GB or bulk relaxation peaks as depicted in Figure 1.11 are given in equation 4 for the respective plots of $-Z''$ vs. f (GB) using two ideal RC elements connected in series. Equation (4) implies an extrinsic GB-type relaxation with large resistance and capacitance to appear at lower f than the

bulk, which is a common feature in experimental impedance spectra from electroceramics.

1.12. Conductivity

The degree to which a specified material conducts electricity, calculated as the ratio of the current density in the material to the electric field which causes the flow of current. the rate at which heat passes through a specified material, expressed as the amount of heat that flows per unit time through a unit area with a temperature gradient of one degree per unit distance.

1.13. Magnetic Properties

Magnetic properties of ceramic are the significant class of materials which have a variety of application such as data storage, tunnel junction, and spin valves. The magnetic ceramic materials have some unique properties like magnetic coupling, low loss and high electrical resistivity which were altered by structure and composition of materials [Ahmed et al. (2004)]. The magnetic moment of a system measures the strength and the direction of its magnetism. The term itself usually refers to the magnetic dipole moment. Anything that is magnetic, like a bar magnet or a loop of electric current, has a magnetic moment. A magnetic moment is a vector quantity, with a magnitude and a direction. An electron has an electron magnetic dipole moment, generated by the electron's intrinsic spin property, making it an electric charge in motion. There are many different magnetic behaviors including paramagnetism, diamagnetism, ferromagnetism, antiferromagnetic and ferrimagnetic.

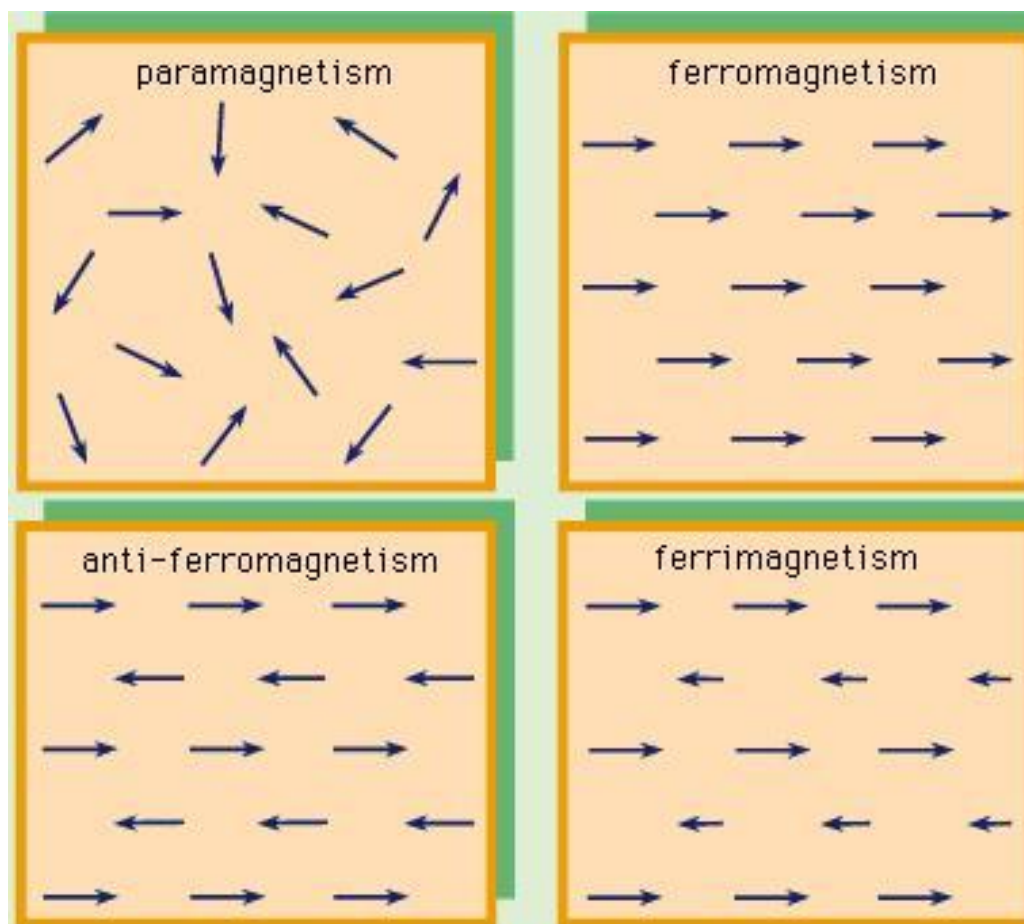


Figure 1.12. Types of Magnetism.

An interesting characteristic of transition metals is their ability to form magnets. Metal complexes that have unpaired electrons are magnetic. Since the last electrons reside in the d orbitals, this magnetism must be due to having unpaired d electrons. The spin of a single electron is denoted by the quantum number m_s as $+(1/2)$ or $-(1/2)$. This spin is negated when the electron is paired with another but creates a weak magnetic field when the electron is unpaired. More unpaired electrons increase the paramagnetic effects. The electron configuration of a transition metal (d-block) changes in a coordination compound; this is due to the repulsive forces between electrons in the ligands and electrons in the compound. Depending on the strength of the ligand, the compound may be paramagnetic or diamagnetic.

1.13.1. Magnetism, at its root, arises from two sources**(a) Electron magnetic moment**

The electron magnetic moment is the magnetic moment of an electron caused by its intrinsic properties of spin and electric charge. The value of the electron magnetic moment is approximately $-9284.764 \times 10^{-27}$ J/T. The electron magnetic moment has recently been measured to an accuracy of 7.6 parts in 10^{13} [Odom *et al.* (2006)]. The electron is a charged particle of charge $-1e$, where e is the unit of elementary charge. Its angular momentum comes from two types of rotation: spin and orbital motion. From classical electrodynamics, a rotating electrically charged body creates a magnetic dipole with magnetic poles of equal magnitude but opposite polarity. This analogy holds as an electron indeed behaves like a tiny bar magnet. One consequence is that an external magnetic field exerts a torque on the electron magnetic moment depending on its orientation concerning the field.

(b) Spin magnetic moment

The magnetic moments of the nuclei of atoms are typically thousands of times smaller than the electrons' magnetic moments, so they are negligible in the context of the magnetization of materials. Nuclear magnetic moments are nevertheless very important in other contexts, particularly in nuclear magnetic resonance (NMR) and magnetic resonance imaging (MRI). Ordinarily, the enormous numbers of electrons in a material are arranged such that their magnetic moments (both orbital and intrinsic) cancel out. This is due, to some extent, to electrons combining into pairs with opposite intrinsic magnetic moments as a result of the Pauli Exclusion Principle, or combining into filled subshells with zero net orbital motion. In both cases, the electron arrangement is to cancel the magnetic moments from each electron exactly. Moreover, even when

the electron configuration *is* such that there are unpaired electrons or non-filled subshells, it is often the case that the various electrons in the solid will contribute magnetic moments that point in different, random directions so that the material will not be magnetic. Sometimes, either spontaneously, or owing to an applied external magnetic field each of the electron magnetic moments will be, on average, lined up. A suitable material can then produce a strong net magnetic field.

The magnetic behavior of a material depends on its structure, particularly its electron configuration, for the reasons mentioned above, and also on the temperature. At high temperatures, random thermal motion makes it more difficult for the electrons to maintain alignment.

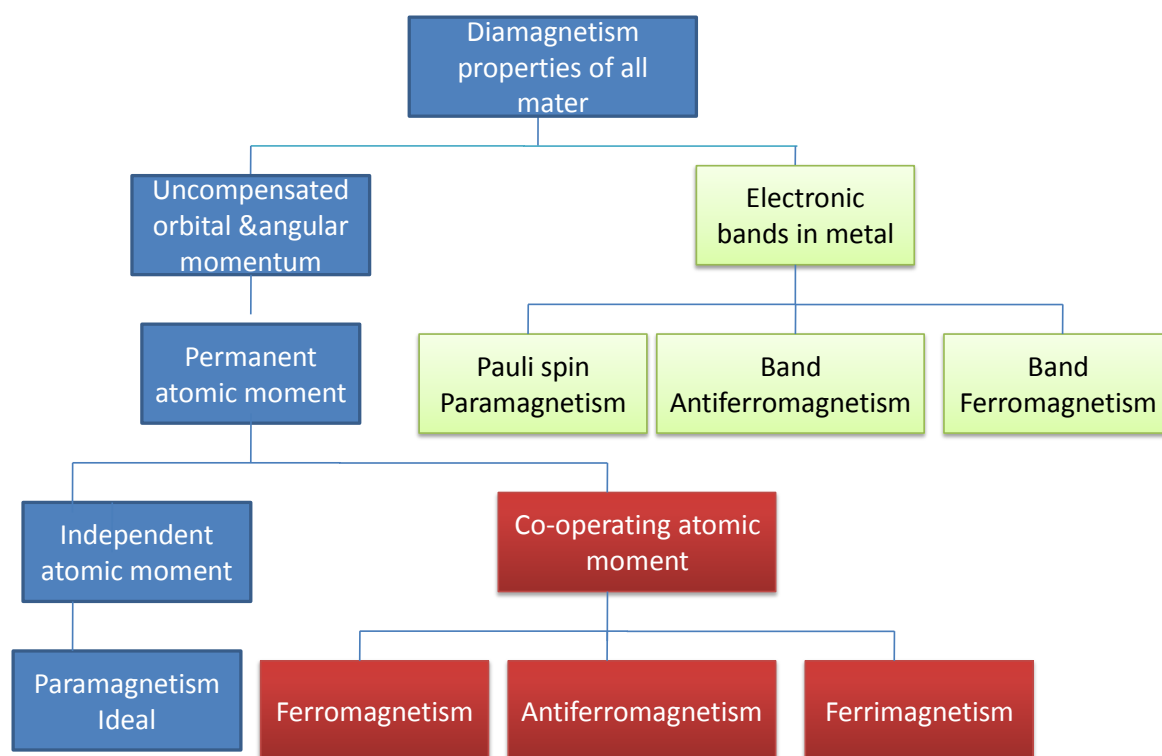


Figure 1.13. Flow chart of Magnetism.

1.13.2. Diamagnetism

Diamagnetism appears in all materials and is the tendency of the material to oppose an applied magnetic field, and therefore, to be repelled by a magnetic field. However, in an article with paramagnetic properties (that is, with a tendency to enhance an external magnetic field), the paramagnetic behavior dominates. Thus, despite its universal occurrence, the diamagnetic response is observed only in a purely diamagnetic material. In a diamagnetic material, there are no unpaired electrons, so the intrinsic electron magnetic moments cannot produce any bulk effect. In these cases, the magnetization arises from the electronic orbital motions, which can be understood classically as follows:

When a material is put in a magnetic field, the electrons circling the nucleus will experience, in addition to their Coulomb attraction to the nucleus, a Lorentz force from the magnetic field. Depending on which direction the electron is orbiting, this force may increase the centripetal force on the electrons, pulling them in towards the nucleus, or it may decrease the force, pulling them away from the nucleus. This effect systematically increases the orbital magnetic moments that were aligned opposite the field and decreased the ones aligned parallel to the field (by Lenz's law). This results in a small bulk magnetic moment, with an opposite direction to the applied field. Note that this description is meant only as a heuristic; a proper understanding requires a quantum-mechanical description. Note that all materials undergo this orbital response. However, in paramagnetic and ferromagnetic substances, the diamagnetic effect is overwhelmed by the much stronger effects caused by the unpaired electrons.

1.13.3. Paramagnetism

In a paramagnetic material, there are unpaired electrons, i.e., atomic or molecular orbitals with exactly one electron in them. While paired electrons are required by the Pauli Exclusion Principle to have their intrinsic spin magnetic moments pointing in opposite directions, causing their magnetic fields to cancel out, an unpaired electron is free to align its magnetic moment in any direction. When an external magnetic field is applied, these magnetic moments will tend to align themselves in the same direction as the applied field, thus reinforcing it.

1.13.4. Ferromagnetism

A ferromagnetic, like a paramagnetic substance, has unpaired electrons. However, in addition to the electrons' intrinsic magnetic moment's tendency to be parallel to an applied field, there is also in these materials a tendency for these magnetic moments to orient parallel to each other to maintain a lowered-energy state. Thus, even in the absence of an applied field, the magnetic moments of the electrons in the material spontaneously line up parallel to one another. Every ferromagnetic substance has its temperature, called the Curie temperature, or Curie point, above which it loses its ferromagnetic properties. This is because the thermal tendency to disorder overwhelms the energy-lowering due to ferromagnetic order. Ferromagnetism only occurs in a few substances; the common ones are iron, nickel, cobalt, their alloys, and some alloys of rare earth metals.

1.13.5. Magnetic Domain

The magnetic moments of atoms in a ferromagnetic material cause them to behave something like tiny permanent magnets. They stick together and align themselves with small regions of more or less uniform alignment called magnetic domains or Weiss

domains. Magnetic domains can be observed with a magnetic force microscope to reveal magnetic domain boundaries that resemble white lines in the sketch. Many scientific experiments can physically show magnetic fields. When a domain contains too many molecules, it becomes unstable and divides into two domains aligned in opposite directions so that they stick together more stable as shown at the right. When exposed to a magnetic field, the domain boundaries move so that the domains aligned with the magnetic field grow and dominate the structure (dotted yellow area) as shown at the left. When the magnetizing field is removed, the domains may not return to an demagnetized state. This result in the ferromagnetic material's being magnetized, forming a permanent magnet.

When magnetized strongly enough that the standard domain overruns all others to result in only one single domain, the material is magnetically saturated. When a magnetized ferromagnetic material is heated to the Curie point temperature, the molecules are agitated to the point that the magnetic domains lose the organization and the magnetic properties they cause to cease. When the material is cooled, this domain alignment structure spontaneously returns, in a manner roughly analogous to how a liquid can freeze into a crystalline solid.

1.13.6. Antiferromagnetism

An antiferromagnet, unlike a ferromagnet, there is a tendency for the intrinsic magnetic moments of neighboring valence electrons to point in opposite directions. When all atoms are arranged in a substance so that each neighbor is 'anti-aligned,' the material is antiferromagnetic. Antiferromagnets have a zero net magnetic moment, meaning they produce no field. Antiferromagnets are less standard compared to the other types of behaviors and are mostly observed at low temperatures. In varying temperatures,

antiferromagnets can be seen to exhibit diamagnetic and ferromagnetic properties. In some materials, neighboring electrons want to point in opposite directions, but there is no geometrical arrangement in which each pair of neighbors is anti-aligned. This is called a spin glass and is an example of geometrical frustration.

1.13.7. Ferrimagnetism

Like ferromagnetism, ferrimagnets retain their magnetization in the absence of a field. However, like antiferromagnets, neighboring pairs of electron spins tend to point in opposite directions. These two properties are not contradictory because, in the optimal geometrical arrangement, there is a more magnetic moment from the sublattice of electrons that point in one direction, than from the sublattice that point in the opposite direction. Most ferrites are ferrimagnetic. The first discovered magnetic substance, magnetite, is a ferrite and was initially believed to be a ferromagnet; Louis Néel disproved this, however, after seeing ferrimagnetism.

1.13.8. Superparamagnetism

The material is superparamagnetic if it is made of tiny single-domain non-interacting magnetic grains dispersed in some non-magnetic medium. How low is very small depends on properties of magnetic grains. A Typical value of their diameter is on the order of 10 nm. Since features of superparamagnetic materials rely crucially on the spontaneous magnetic moment of magnetic grains, it is implicitly understood that temperature is below the Curie or Neel temperature T_C of magnetic grains. It doesn't make sense to talk about superparamagnetism above T_C . When a ferromagnet or ferrimagnet is sufficiently small, it acts like a single magnetic spin that is subject

to Brownian motion. Its response to a magnetic field is qualitatively similar to the reaction of a paramagnet but much more significant.

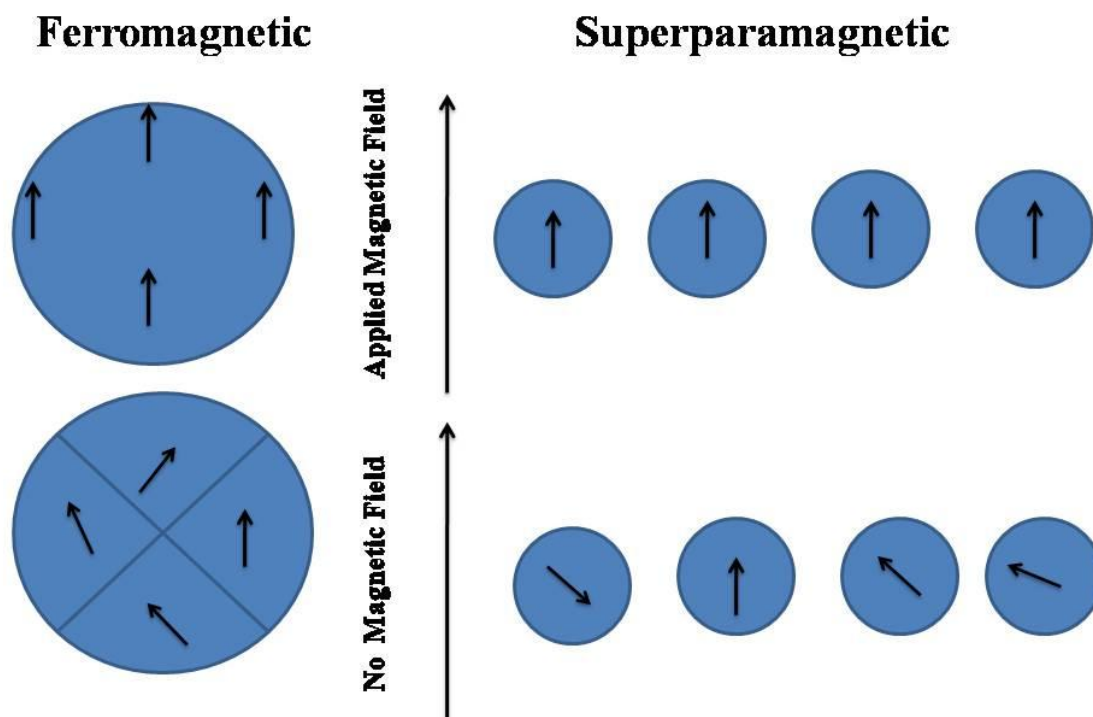


Figure 1.14. Ferromagnetic and Super paramagnetic.

In hard disk drives, information is stored by magnetizing small pieces of magnetic material on the platter. The former is composed of magnetic nanograins. Ferrofluids, which are a colloidal liquid of nanoscale magnetic grains suspended in a carrier liquid, is used for liquid seals (e.g., in HDDs), efficient heat transfer (e.g., in loudspeakers), in suspension systems and various medical applications. They also look nice when put into the vicinity of a permanent magnet.

1.14. Aim of study

The use of electronic devices (mobiles, camera, computers, Television, etc.) now a day is more demanding the continuous improvement in miniaturization of these devices. The memory and energy storage devices are demanding high dielectric constant and low loss materials scientist taking interest regarding better to serve these microelectronic devices.

(i) The work focuses synthesis characterization and application of dielectric, ferroelectric, and magnetic properties of materials and its dependence on temperature as well as frequency. Effect of sintering duration on composite and its effect on dielectric, and electrical properties.

(ii) Separate contribution of grain and grain boundary, microstructure, particle shape, temperature and frequency on the dielectric, and electric properties are widely studied.

(iii) To get good quality of ceramic materials solid state method and semi-wet route are used to monitor homogeneous mixing of metal ions and material synthesized at low sintering temperature as well as less duration. To get high dielectric constant and low dielectric loss the synthesized materials BT-BCT 5 and BTC are use as capacitor and memory storage devices.

The objective of present work is to synthesize following ceramic Composite using BaTiO_3 , $\text{CaCu}_3\text{Ti}_4\text{O}_{12}$ and $\text{Bi}_{2/3}\text{Cu}_3\text{Ti}_4\text{O}_{12}$ as end components at few concentrations. BaTiO_3 is ferroelectric whereas $\text{CaCu}_3\text{Ti}_4\text{O}_{12}$ and $\text{Bi}_{2/3}\text{Cu}_3\text{Ti}_4\text{O}_{12}$ have high dielectric constant and high dielectric loss.

1. $0.9\text{BaTiO}_3-0.1\text{CaCu}_3\text{Ti}_4\text{O}_{12}$ (BTC) by Solid State route
2. $0.9\text{CaCu}_3\text{Ti}_4\text{O}_{12} - 0.1\text{BaTiO}_3$ (CC-BT) by Solid State route
3. $0.5\text{BaTiO}_3-0.5\text{Bi}_{2/3}\text{Cu}_3\text{Ti}_4\text{O}_{12}$ (BT-BCT 5) by Solid State route
4. $0.6\text{Bi}_{2/3}\text{Cu}_3\text{Ti}_4\text{O}_{12}-0.4\text{BaTiO}_3$ (BC-BT) by Solid State route

Characterizations of the sample were carried out by different physiochemical methods by the following sequential steps:

- i. Study the crystal structure and single phase formation of the ceramic compositions using X-ray powder diffraction
- ii. Study of the surface morphology using Scanning Electron Microscopy (SEM)
- iii. Determination of particle size by Transmission Electron Microscopy (TEM).
- iv. Investigation of dielectric properties as a function of temperature as well as frequency.
- v. Besides, a correlation between dielectric behavior and those of microstructure and defect structure will also be established.
- vi. Rationalization of dielectric properties by impedance and modulus spectroscopic studies
- vii. Study of AC conductivity as a function of temperature and frequency to investigate the mechanism of conduction.
- viii. Different physiochemical techniques will characterize these ceramic. The powder X-ray diffraction will be recorded to study the crystal structure and single phase formation of the ceramic. Scanning electron micrographs of the ceramics will be recorded to study the surface morphology, and transmission electron micrographs will be obtained to determine their particle size. The purity and stoichiometry of each of grain and their grain boundary region will be assessed by the energy dispersive X-ray studies. To obtain high dielectric constant and low dielectric loss ceramic, the dielectric and electrical properties will be studied as a function of temperature as well as frequency. In addition, a correlation between dielectric behavior and those of microstructure and defect structure will also be established.