Chapter 1

Background & Introduction

1.1.Perovskite

The mineral Calcium titanium oxide ($CaTiO_3$) is known as perovskite oxide which was discovered in the Uralmountains of Russia by Gustav Rose in 1839 and is named after Russian mineralogist L. A. Perovski (1792–1856) [Cheng and Lin (2010)]. Mostly perovskite having the general formula of the form ABX_3 in which A and B are the cations that differs in their sizes and X is the anion forming the bonds A of both A and B [Warner (2012)]. Generally X is oxygen but sometimes it also may be halides, nitride and sulphides are possible. The general chemical formula of the perovskite compound is ABO_3 per unit cell with the orthorhombic structure of the space group Pnma [100, 101]. In ABO_3 structure, A and B cations have different sizes (where A > B) and occupy the cube corner positions (0, 0, 0) and at the body center positions (1/2, ½, ½) of the cube, respectively with oxygen in the face centered positions (1/2, ½, 0) that is face centered position of the cube [Giaquinta and Loye (1994), Pena and Fierro (2001)]. The corner of the lattice ie Cations A is generally an alkaline or rare-earth element in 12- fold cubo-octahedral coordination in manner and center cations B usually transition metal elements in 6-fold coordination surrounded octahedrally by anions 'O'[Vasala and Karpinen (2015)]. Distorted versions of Perovskites have great industrial importance for their magnetic and electric properties especially the ferroelectric tetragonal form of $BaTiO_3$ [Johnsson and Lemmens (2008)]. For the $A^{3+}B^{3+}O_3$ Perovskites the most symmetric structure observed is rhombohedral R3c (e.g. $LaAlO_3$) which involves a rotation of the BO_6 octahedral with respect to the cubic structure. However, this distortion from the perfect cubic symmetry is slight [100].

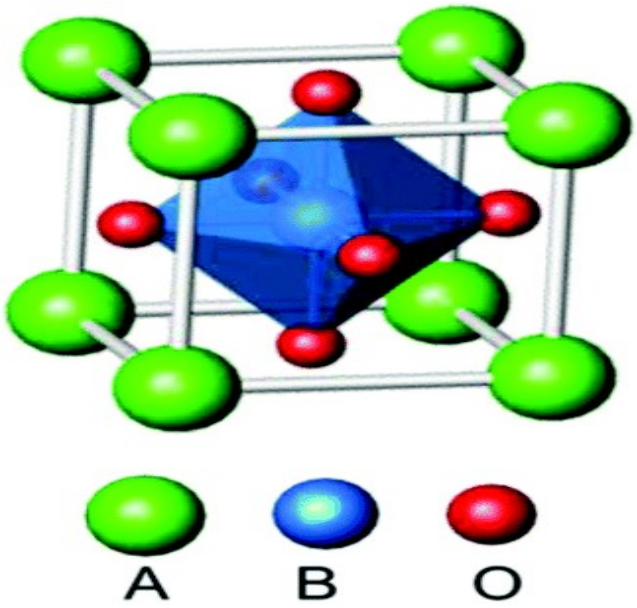


Figure 1.1 An ideal cubic perovskite structure ABO_3 with the space group $Pm\bar{3}m$ [Rabuffetti and Brutchey (2014)].

Table 1.1 Atomic positions of coordinates of the cubic perovskite structure

Site	Location	Co-ordinates
A cation	(2a)	(0, 0, 0)
B cation	(2a)	(1 /2, 1 /2, 1 /2)
O anion	(6b)	(1 /2, 1 /2, 0) (1 /2, 0, 1 /2) (0, 1 /2, 1/ 2)

The structure of an ideal cubic perovskite have the formula ABO_3, where the A cations at the corners of the cube, and the B cations in the centre with oxygen ions in the face-centered positions with the space group $Pm\bar{3}m$. 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. For an ideal structure of perovskite, where atoms touches with each other, the following relation holds for determination of ionic radii

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

Although, this equation is not valid for non-ideal condition, Goldsmith derived empirical rules in 1926, for the stability of ABO_3 types Perovskites with the help of tolerance factor (t) [Bhalla *et al.* (2000)].

According to him, Perovskites having the ionic radii r_A, r_B, r_O, respectively for the cations A, B and anions O. The following equation applied for determination of tolerance factor (t) of the ABO_3 type Perovskites:

$$t = \frac{(r_A + r_B)}{\sqrt{2(r_B + r_O)}} \quad (1.2)$$

where, t indicates the tolerance factors explained the range of relative sizes for the stability of Perovskites structure.

1.2 Conditions for the Perovskites structure on the basis of tolerance factor:

(i) If the value of tolerance factor lies in between 0.75 to 1.0, i.e. $0.75<t<1.0$, then compound having cubic structure.

(ii) If the value of tolerance factor lie in the range of $0.75 \leq t \leq 0.95$, then compound will be distorted Perovskites type structure and non-ferroelectric in nature while having ≥1.0, it becomes in ferroelectric in nature [Wood (1951), Roth (1957)].

(iii) If the value of t is less than 0.75, i.e. $t<0.75$, then the compound does not crystallize in perovskite structure [Keith and Roy (1954)].

There are some following data were observed from literature point of view regarding electronic configuration and geometry of the compound.

(i) According to Pauling corrected radii, the tolerance factor (t) of the perovskite structure should be 1.05.

(ii) The radius ratio between atom A and B (r_A: r_O) should be 1 or slightly higher.

(iii)Electro negativity of O^{2-} ions should be greater or equal to 2.5.

(iv)The I.E (Ionisation energy) value of B should be greater or equal to 40 kJ/mol.

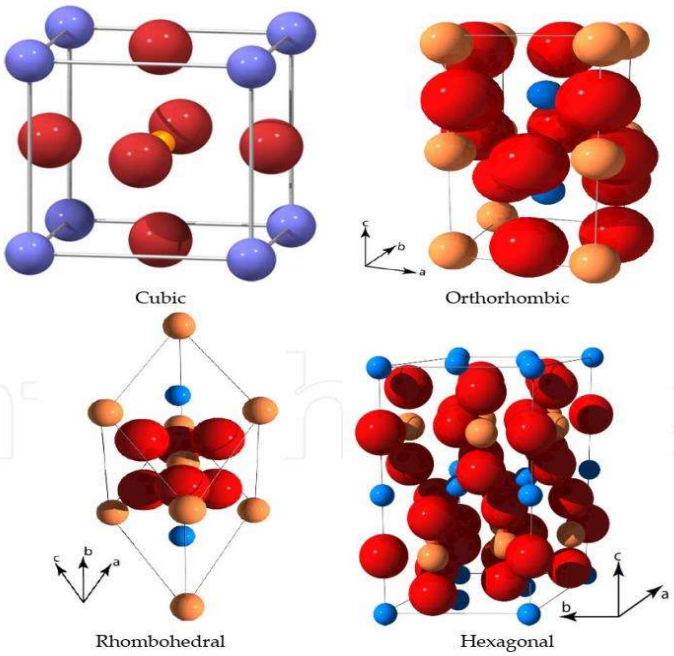
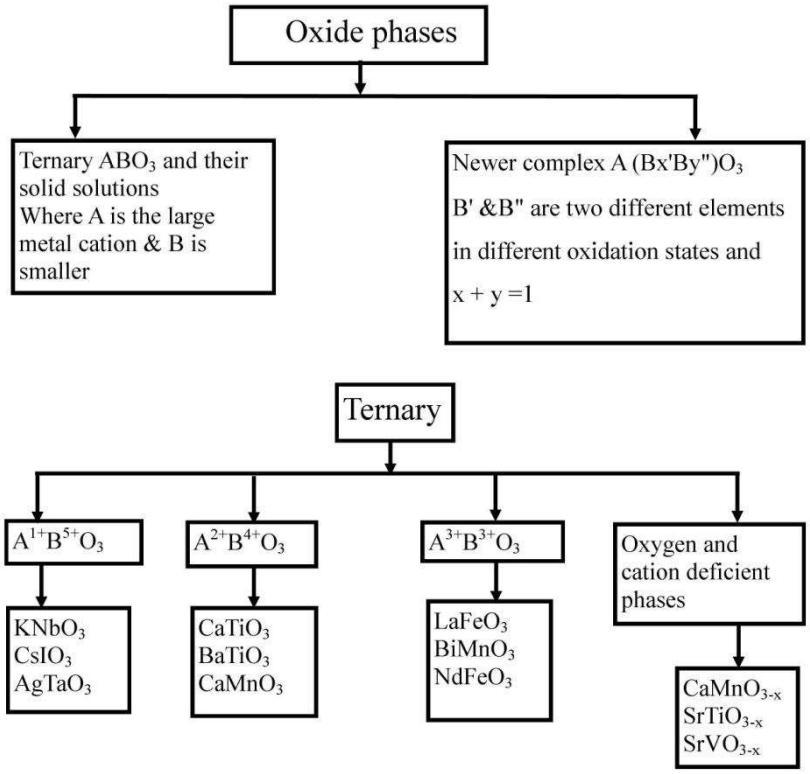


Figure 1.2 crystal structure of different perovskite unit cells in which Blue colors indicates cations A, yellow colors representing for B cations and red for oxygen anions forms octahedral complex with B atoms.

A versatility of the ABO_3 perovskite crystal structure and its ability to accommodate a wide range of ions with completely different chemical reaction states similarly as cation or ion vacancies area unit at the origin of enormous type of perovskite-based compounds with a large range of physical properties. The compound phases are chiefly divided into two types, the ternary ABO_3 kind and the newer complicated type of compounds $(AB'_xB''_y)O_3$, where B' and B'' are completely different components having several oxidation state and x + y = 1. On the basis of chemical reaction states, the ternary oxides are classified in to

$A^{1+}B^{5+}O_3$, $A^{2+}B^{4+}O_3$, $A^{3+}B^{3+}O_3$ [Galasso (2013)]. The detailed classification of Perovskites is shown in table **1.2**



(1) When the cations A and B belonging to Ist and Vth group elements in the periodic table, respectively, are exhibits ferroelectrics or anti-ferroelectrics. Some common example of $A^{1+}B^{5+}O_3$ type Perovskites is $KNbO_3$, $AgTaO_3$, $AgNbO_3$, $KTaO_3$ and $LiNbO_3$ [Matthias (1949)].

(2) $A^{2+}B^{4+}O_3$ ($CaTiO_3$, $SrTiO_3$, and $BaTiO_3$) types of Perovskites oxide are used as dielectric and piezoelectric materials. These are formed only when cations A belong to IInd group and B belongs to Vth goup element in the periodic table.

(3) In the crystal sytem of $A^{3+}B^{3+}O_3$ type of perovskite oxide such as $LaFeO_3$, $BiMnO_3$, $NdFeO_3$ and $PrCoO_3$ in which A sites prefer the occupied alkaline earth metal and trivalent metal cations and B sites may be regarded as trivalent transition metal cations.

These types of materials depict conductivity due to electrons or holes migration which made it more interesting functional materials. Others perovskite oxides like $CaMnO_{3-z}$, $SrVO_{3-z}$, $SrTiO_{3-z}$ etc. show oxygen and cations deficient phase.

Table 1.3 List of some Perovskites compounds with Application and their specific used.

Compounds	**Typical property**	**Application**	**Used**
$BaTiO_3$, $PdTiO_3$	Ferromagnetic property Piezoelectricity and high dielectric constant.	Multilayer ceramic capacitors (MLCCs), PTCR resistors and embedded capacitance.	Most widely used dielectric ceramic T_C = 125°C
(Ba Sr)TiO_3, (Bi, Na)TiO_3	Non-Linear dielectric properties.	Tunable microwave devices.	Used in the para-electric state.
Pb(Zr, Ti)O_3	Ferromagnetic property Piezoelectricity.	Piezoelectric transducers actuators and ferroelectric memories.	PZT most successful piezoelectric material.
$Bi_4Ti_3O_{12}$	Ferroelectric with high Curie temperature.	High-temperature actuators and Ferroelectric Properties.	Aurivillius compound T_C = 675°C
$(K_{0.5}Na_{0.5})NbO_3$,$Na_{0.5}Bi_{0.5}TiO_3$	Ferromagnetic property Piezoelectricity.	Lead-free piezo ceramics.	Performances not yet comparable to PZT but rapid progress.
$SrFeO_3$, $LaCoO_3$	Electrical conductivity.	Alternative dielectric materials and Internal barrier layer capacitors.	Multifunctional material.
$BiFeO_3$, $LaMnO_3$	Magnetic property.	Magnetic field detectors, Memories.	Most investigated multiferroic compound. T_C = 850°C
$LaCoO_3$, $BaCuO_3$	Catalytic property.	Cathode material in SOFCs and oxygen separation membrane	Used for Solid Oxide Fuel Cells cathodes.
$LaAlO_3$, $YAlO_3$	Host materials for rare-earth luminescent ions.	Lasers Substrates for epitaxial film deposition.	

1.3. Perovskite substitution

The ideal perovskite structure having the general formula ABO_3 and its dielectric properties can be enhanced by substitution of other metal cations at A site or B site or simultaneous of both of A and B sites. The substitution of metal ions from A or B site with other metal cations may be change the crystal structure due to change in M-O bond length and shifting in the position of metal ions from their original positions which increases the dielectric properties of the materials. Substituted perovskite structures have large dielectric constant and low dielectric value which is useful in various technological applications [Fouskova, and Cross (1970)]. The substitution in perovskite oxide material is favorable only If the size difference is less than 15% in between metal ions and other substituted ion otherwise deformation of crystal structure and phases may be changes on account of steric hindrance. However, intertial replacement of the metal cations is difficult in the perovskite type structure due to its close- packed structure. Therefore, for modification of its properties on the basis of valence state of metal ions, different type of substitutions in the perovskite is possible in the following manner.

1.3.1. Isovalent substitution

1.3.2. Heterovalent substitution

1.3.1. Isovalent substitution:

This type of substitution in ABO_3 perovskite structure on A or B site os simultaneously on both of A and B site is occurs if both of substituted ions and metal ion which is completely or partial replaced by it exist in the same valency state. The substitution of Ba^{+2}, Sr^{+2} and Pb^{+2} in the place of Ca^{+2} and Sn^{+4}, Zr^{+4} or Hf^{+4} in the place of Ti^{+4} ions for $CaTiO_3$ perovskite is an example of isovalent substitutions

1.3.2. Heterovalent substitution:

This type of substitution in the perovskite structure is due to different valency state of substituent ion and the ions which is completely/ partially replaced by these substituted ions. Due to which defects in theses materials is occurs on account of compensate extra charges. The heterovalent substitution in the ABO_3 perovskite is favorable at both A and B sites. Depending on the basis of valencies of the substituent ions on A and B site of ABO_3 pervoskite, this are categorized in two types.

(a)Acceptors substitutions:

In these substitutions, the oxidation state of substituent ion is smaller in comparison to that of oxidation state on A and B site of the perovskite materials. This type of substitution in the perovskite create a holes due to oxygen vacancies and the substituent ion gives more contribution to that of electrons, e.g., substitution of Na^{+} on $Ba^{2+}$and Co^{3+} on Ti^{4+} site in $BaTiO_3$.

(b) Donors substitutions:

These types of substitution take place in the ABO_3 perovskite materials when the oxidation state of A or B site ions have lower in comparison to that of substituent ions. That is why increases the effective nuclear charge of the dopant ions which were frustrated by cation vacancy or electron in the crystal lattice of the host materials. La^{3+} or Y^{3+} on $Ba^{2+}$and Nb^{5+}on Ti^{4+} site in $BaTiO_3$ separately is an example of donor substitution [Zhi *et al*. (1999)]

1.4. High dielectric constant ABO_3 perovskite

1.4.1. $CaTiO_3$

Calcium titanate is an inorganic compound with the chemical formula $CaTiO_3$ and it is stable at room pressure and thus responsible for various high-temperature measurements. It has low dielectric constant and exhibits paraelectric behavior at room temperature. Substitution of donor

dopants in $CaTiO_3$ materials enhances the internal boundary effect which makes better dielectric constant. The dielectric permittivity of the materials is also depends on the dopants concentrations as well as sintering atmosphere. Substitutions of Yttrium (≤0.75 mol %) and sintering of these materials in nitrogen atmosphere yields very high dielectric constant with ferroelectric relaxation type behavior. These mineral perovskite ($CaTiO_3$) shows phase transitions at 600 °C and 1000 °C because $CaTiO_3$ having orthorhombic structure at room temperature which converted in to tetragonal geometry at transition temperature 600 °C and finally becomes to be cubic symmetry at 1000 °C [Chourasia and Srivastava (2011)]. These types of materials is useful in various types of applications such as transducers gas lighter elements, electronic ceramic materials, piezoelectric as well as in immobilizing high-level radioactive waste, in sensors and solar cells, certain types of fuel cells, spintronics applications catalyst electrodes, lasers, and memory devices.

1.4.2. $BaTiO_3$

Barium titanate is a member of perovskite family having the general formula $BaTiO_3$ and appears as a powder in white color and is transparent when prepared as large crystals. It is ferroelectric ceramic materials which exhibits photorefractive effects and piezoelectric properties. Due to existence of these properties, these materials show very high dielectric constant. In the crystal structure of $BaTiO_3$, both of barium and oxygen having almost similar ionic radii (1.4 Å) which form face centered cubic type of lattice. Titanium (Ti^{+4}) ions situated at the B-site of the Perovskites form octahedral complexes with oxygen ions (TiO_6). Lower symmetry phases are stabilized at lower temperatures and involve movement of the Ti^{4+} to off-center positions. The remarkable properties of this material arise from the cooperative behavior of the Ti^{4+} distortions because Ti^{4+} ion move to new positions along the direction of applied

electric field. The ferroelectricity arises in the $BaTiO_3$ due to distortion of Ti^{+4} which improve dielectric constant of the materials. The high value of dielectric constant of barium titanate makes suitability for capacitor, nonlinear optics and electromechanical transducers [Aimi *et al.* (2014)].

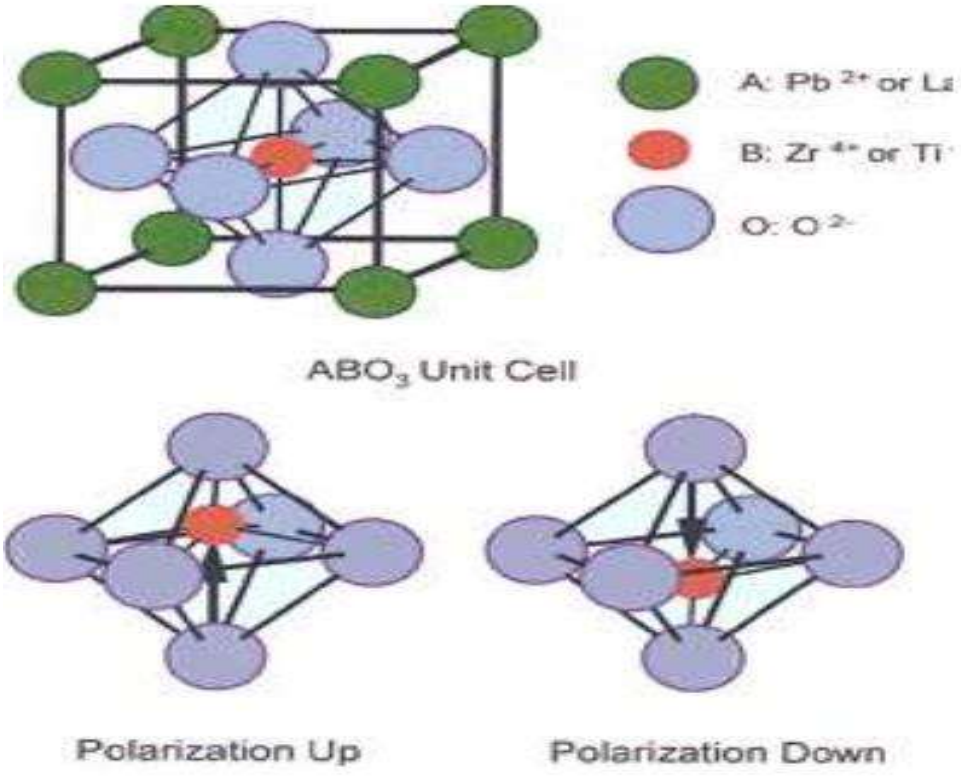


Figure 1.3 Distortion in polarization of Perovskite ABO_3 unit cell for $BaTiO_3$ due to displacement of the central metal cation in the tetragonal plane. The polarization up and polarization down indicates reversal of 180° for two of the six possible permanent polarization positions.

$BaTiO_3$ form five type of crystal structure such as cubic, tetragonal, hexagonal, orthorhombic and rhombohedral in which cubic and hexagonal structure exists in paraelectric whereas other structures exist in ferroelectric in nature. The existence of stability of hexagonal

barium titanate is observed above 1460 ºC and phase conversion of hexagonal to cubic occurs on cooling of barium titanate below of 1460 ºC. The ferroelectric-paraelectric transition of $BaTiO_3$ occurs at the Curie temperature (around 130 ºC) which is important factor in dielectric application. At this particular temperature, phase transition occurs from cubic to ferroelectric tetragonal structure in elongation along an edge and stable until 0 ºC. After that conversion of tetragonal phase in to orthorhombic occurs along diagonally and finally, orthorhombic phase transformed into rhombohedral at lower transition temperature – 90 ºC [Zhang *et al.* (2006)].

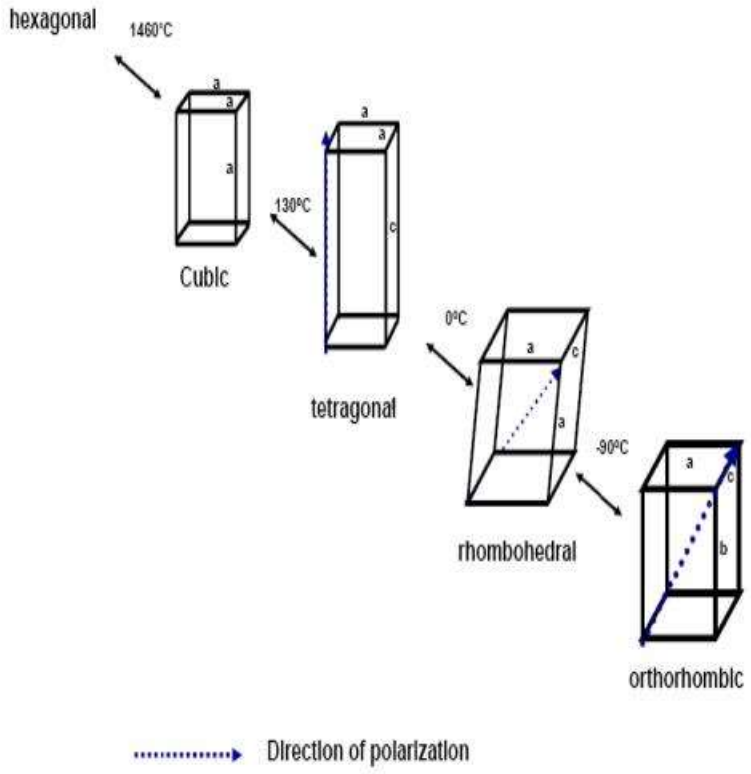


Figure 1.4 Phase diagram for conversion of $BaTiO_3$ Perovskite structure

1.4.3. (a) Strontium Titanate ($SrTiO_3$)

Strontium titanate with the general chemical formula $SrTiO_3$ is widely considered material due to possession of cubical structure at room temperature with indirect band gap of 3.2 eV and direct band gap of 3.75 eV [mathesis (1972), Pertosa et al (1978)]. The pure phase of $SrTiO_3$ has

dielectric constant around 300 at the room temperature, further its dielectric constant value enhanced up to 1.8×10^4 by substitution of yttrium. It approaches to ferroelectric phase transitions at lower temperature with a very large extent of dielectric constant $\sim 10^4$ but remains paraelectric behavior due to quantum fluctuation at the lowest temperature [Mitsui and Westphal (1961)]. It is mainly used as high temperature superconductor thin films [Chen et al (1988], oxygen sensor, in photolysis of water [Chang et al. (1983)].

Table 1.4 Physical properties of strontium titanate.

Properties	Value
Atomic density	5.12
Melting Point (°C)	2080
Thermal Conductivity (W/mK)	12
Coefficient of thermal expansion(Å/°C)	9.4×10^{-6}
Lattice parameter at RT (nm)	0.3905
Refractive index	2.31-2.38

(b) Crystal structure of strontium titanate

$SrTiO_3$ is a cntrosymmetric paraelectric material with a cubic perovskite (ABO_3) structure at room temperature. The space group is observed for this materials be *Pm3m* and the observed density as well as the lattice parameter $\rho = 5.12\ g\ /\ cm^3$ and 0.3905 nm, respectively. In the crystal structure (Fig. 2.1), the titanium (Ti^{+4}) are octahedrally co-ordinate with oxygen (O^{2-}) ions which form TiO_6 octahedral complex, however Sr^{+2} ions coordinately linked with four TiO_6 octahedra. Therefore, each Sr^{2+} ion is coordinated by 12 O^{2-} ions. Within the TiO_6 octahedra, while a hybridization of the $O^{-2}p$ states with the $Ti^{-3}d$ states leads to a pronounced covalent bonding [Leapman *et al.* (1982)], Sr^{2+} and O^{2-} ions exhibit ionic bonding character. Hence,

$SrTiO_3$ has mixed ionic-covalent bonding properties. This nature of chemical bonding leads to a unique structure, which makes it a model electronic material.

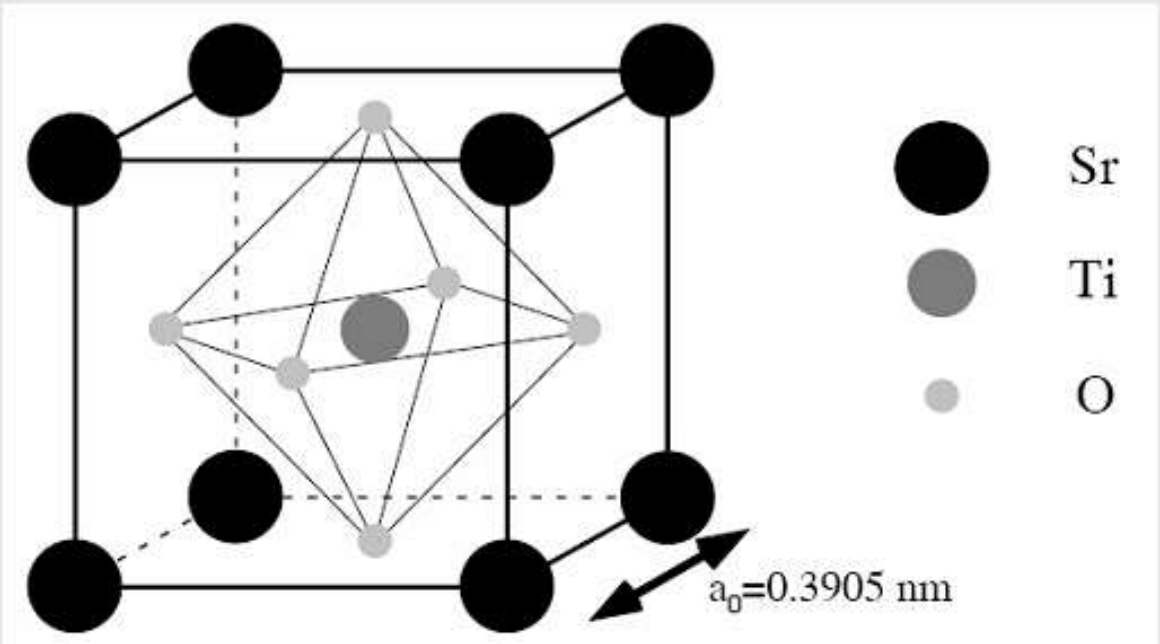


Figure 1.5 Atomic structure of $SrTiO_3$ a RT. The sizes of the spheres representing the atoms are arbitrary and are not related to atomic radii.

Distortion in $SrTiO_3$ from cubic to lower symmetry are arises due to substitution of foreigner cations in the lattice or lowering of temperature of which size effects, John Teller effect and deviations from ideal compositions is responsible for distortion of the crystal structure. It is rare to identify a single effect as responsible for the distortion of a certain perovskite. On account of which, $SrTiO_3$ perovskite that exhibits in cubic phase at room temperature transformed into tetragonal in between 110 K – 65 K temperature due to opposite rotation of neighboring oxygen and transition in the range of 55 K – 35 K temperature occurs from tetragonal into orthorhombic that finely change into lower symmetry rhombohedral below 10K as X -ray diffraction studies suggest [Rahmatikalkhoran (2004), Lytle (1964)]. In fact, there is no experimental evidence confirming for sure which structure $SrTiO_3$ exhibits below 10K.

The value of dielectric constant of various perovskite oxides along with their application are enlisted in Table 1.5

Table 1.5 Dielectric constant of different types of ceramic materials.

S. No	Composition	Dielectric constant	References
1	$CaCu_{2.70}Mg_{0.30}Ti_4O_{12}$	3.42×10^5	[Singh *et al.* (2013)]
2	$NiFe_2O_4$/MWCNT	1.06×10^5	[Soomro *et al.* (2017)]
3	$Na_{0.5}K_{0.5}NbO_{3+x}CuF_2$	250,000	[Weng *et al.* (2017)]
4	$0.5Bi_{2/3}Cu_3Ti_4O_{12}$-$0.5Bi_3LaTi_3O_{12}$	13.94×10^3	[Gautam *et al.* (2017)]
5	$Ba_6Y_2Ti_4O_{17}$ (BYTO)	1.5×10^3	[Yadava *et al.* (2016)]
6	Eu_2CuO_4	5×10^3	[Salame *et al.* (2014)]
7	T-type La_2CuO_4	10^3	[Salame *et al.* (2016)]
8	$0.5BaTiO_3$-$0.5\ Bi_{2/3}Cu_3Ti_4O_{12}$	43459	[Khare *et al.* (2016)]
9	$Ca[(Li_{1/3}Nb_{2/3})1exTix]O_3$	40,000	[George and Sebastian (2008)]
10	$Ba(Fe_{0.5}Nb_{0.5})O_3$-$Bi_{0.2}Y_{2.8}Fe_5O_{12}$	30,000	[Yang *et al.* (2017)]
11	$Ba_{0.75}Sr_{0.25}TiO_3$	24,000	[Huang *et al.* (2008)]
12	$CaCu_3Ti_4O_{12}$	20,000	[Tuichai *et al.* (2013)]
13	$K_{0.5}Na_{0.5}NbO_3$	20,000	[Bobnar *et al.* (2009)]
14	$Ba_4Sm_{9.33}Ti_{18}O_{54}$	10,000	[George *et al.* (2009)]
15	$Bi_{1.5}ZnNb_{1.5}O_7$	10,000	[George *et al.* (2007)]
16	Lead-lanthanum-zirconate-titanate	7819	[Limpichaipanit and Ngamjarurojana (2017)]
17	$Y_{2/3}Cu_3Ti_{3.95}In_{0.05}O_{12}$	5068	[Singh *et al.* (2016)]
18	$(Ba_{0.95}Ca_{0.05})(Ti_{0.95}Zr_{0.04})O_3$	3910	[Yang *et al.* (2011)]
19	$(Ba_{0.5}Na_{0.5})_{1-x}Yb_xTiO_3$	1357	[Han *et al.* (2017)]

Table. 1.6 Applications of various Perovskite oxides.

S.No	Ceramics	Application	References
1	$BaTiO_3$	Multilayer Capacitor	[Park (2005)]
2	Pb $(Zr_xTi_{1-x})O_3$	Piezoelectric Transducer	[Lendermann *et al.* (2004)]
3	$BaTiO_3$	P.T.C. Thermistor	[Affleck and Leach (2005)]
4	$(Pb,La)(Zr,Ti)O_3$	Electrooptical Modulator	[Nakada *et al.* (2003)]
5	$BaZrO_3$	Dielectric Resonator	[Wakino *et al.* (1986)]
6	$Pb(Mg_{1/3}Nb_{2/3})O_3$	Electrostrictive Acuator	[Takagi *et al.* (1993)]
7	$Ba(Pb,Bi)O_3$ layered Cuprates	Superconductor	[Grumann *et al.* (1994)]
8	$GdFeO_3$	Magnetic Bubble Memory	[Söderlind *et al.* (2009)]
9	$YAlO_3$	Laser Host	[Stefaniuk *et al.* (2006)]
10	$(Ca,La)MnO_3$	Ferromagnet	[Heffner *et al.* (2000)]
11	$SrCeO_3$	Hydrogen Sensor	[Iwaraha *et al.* (1981)]
12	$BaCeO_3$	Hydrogen Sensor	[Iwaraha *et al.* (1988)]
13	$BaZrO_3$	H_2 production/extraction	[Yamanaka *et al.* (2003)]

1.5. Capacitors

The capacitor is an electrical circuit which has tendency to store energy in the form of an electrical charge on application of voltage across it. It gives up the stored energy to the circuit whenever required. It is consist of two parallel metallic plates which are separated by dielectric material. This dielectric material can be made from a number of insulating materials or combinations of these materials with the most common types used being: air, paper, polyester, polypropylene, Mylar, ceramic, glass, oil, or a variety of other materials. The factor by which the dielectric material, or insulator, increases the capacitance of the capacitor compared to air is known as the Dielectric Constant, k and a dielectric material with a high dielectric constant is a better insulator than a dielectric material with a lower dielectric constant.

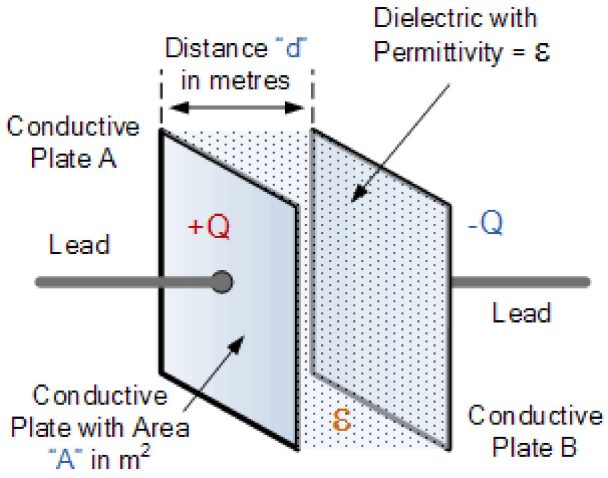


Figure 1.6 Parallel plate capacitor with the plates separated by distance'd' and area of each plate "A".

It is the dimensionless quantity and the actual permittivity of dielectric materials is the product of relative permittivity and permittivity in the free space between the plates. The actual permittivity (ε) is given for the dielectric materials as follows:

$$\varepsilon = \varepsilon_0 \times \varepsilon_r \tag{1.3}$$

Where, ε_0 and ε_r are the permittivity of free space and relativity permittivity ($\varepsilon_r > 1$) of the dielectric materials, respectively. The permittivity of a vacuum, ε_o also known as the "permittivity of free space" has the value of the constant 8.84×10^{-12} Farads per meter. As the value of relative permittivity is greater than 1 which implies that charge storage capacity of the materials is greater than free space in presence of electric fields. These properties are useful in capacitor applications. On the other hand, when the vacuum of free space is substituted by some other insulating material, then the complex permittivity (ε) becomes equal to relative permittivity (ε_r). In such conditions, capacitance (C) in farads of capacitor is written by the equation

$$C = \frac{\varepsilon_0 \varepsilon_r A}{d} \tag{1.4}$$

If n represents number of palates which are connected together within a single capacitor body separated from each other by distance (d) having surface area (A), then equation of capacitance in farads for single parallel plate capacitor should be

$$C = \frac{\varepsilon_0 \varepsilon_r (n-1)A}{d} \quad (1.5)$$

As the dielectric materials having the non-conductive properties, therefore it does not allow the flow of electric current throughout the materials. However, the atoms of the dielectric materials are get polarized under the application of electric fields of the applied voltage source that is why dipoles (positive and negative) are formed due to polarization. Due to which charge accumulation occurs on the plates and current flows throughout the capacitor until the potential difference are same the source potential. The dielectric constant is higher capacitance is also higher which can be realized in a given space. Therefore, materials of the high dielectric constant are favored in the practical design of embedded capacitors for miniaturization.

1.6. Dielectric materials

Dielectric materials are basically an insulator or very poor conductor of electricity that means practically, no current is flow throughout these materials on application of electric field because they have no loosely bounded free electron. But electric polarization developed in these materials and molecules of the materials get polarized that means alignment of the dipole moment occurs in the direction of electric field. The positive charges are slightly shifted towards electric field and negative charge opposite to that of electric field. It transfers electrical energy through the shifting of current and not through the process of conduction. The presence of dielectric material affects other electrical phenomena. The force between two electric charges in a dielectric medium is less than it would be in a vacuum, while the quantity of energy stored in an electric field per unit volume of a dielectric medium is greater. The capacitance of a capacitor filled with

a dielectric is greater than it would be in a vacuum. The effects of the dielectric on electrical phenomena are described on a large or macroscopic scale by employing such concepts as dielectric constant, permittivity, and polarization (electric polarization).

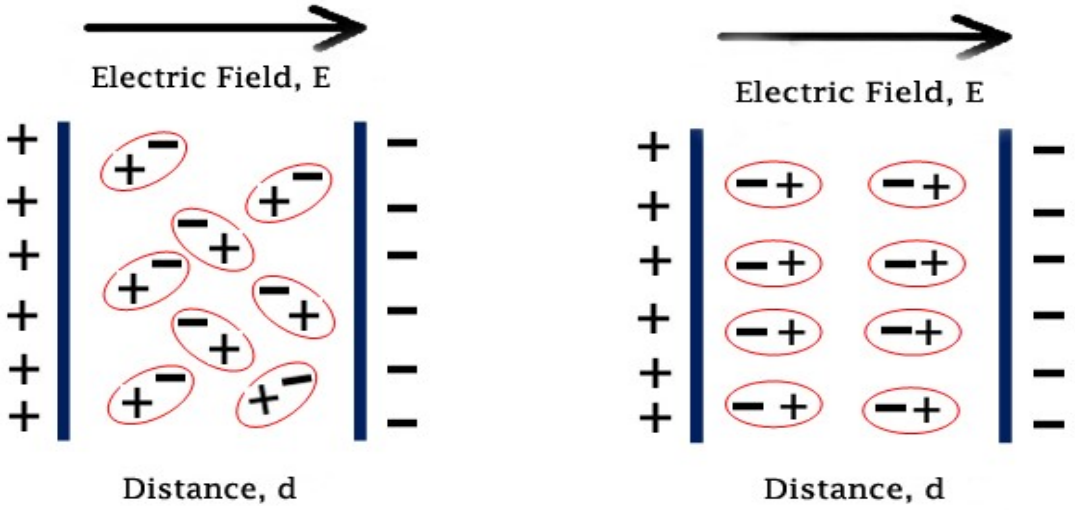


Figure 1.7 polarized and non polarized plates of an applied electric field.

1.7 Types of Polarization

Basically, there are four mechanisms of polarization:

1.7.1. Electronic or Atomic Polarization: This type of polarization occurs in all types of dielectric materials under the application of electric field. Separation of charges in an individual atoms rises in the materials when electric field is applied that means centre of electron cloud slightly shifted with respect to its nucleus and the atoms gets polarized having dipole moment (P)

$$P = \alpha \varepsilon E \qquad (1.6)$$

When the electric field is removed, both of electrons and nuclei return to their original position that is why molecules become depolarized. The total amount of polarization is small as compared to other polarization mechanism due to small displacement of charges [D.W. Richerson, (1992), Boukenter (1988)].

1.7.2. Ionic Polarization: This type of polarization occurs in the ionic solids that contribute to relative permittivity. No net polarization developed inside the materials occurs in the absence of electric field because dipole moment of the positive ion cancelled by the negative ions due to symmetry of the crystals. Induced polarization occurs in the materials due to small displacement of ions from their equilibrium positions. Therefore, inducing a net dipole moment in the materials.

1.7.3. Dipolar or Orientation Polarization: The materials which have permanent dipole moment in the direction of applied electric field, gives rise to Orientation Polarization. Materials such as HCl and H_2O etc included in this polarization and permanent dipole moment in these molecules arises due to charge distributions of ions [H. M. Rosenberg (1988)]. Consider the water molecules in which hydrogen containing positive charge and oxygen contains negative charge. This causes water molecules becomes dipolar. Net dipole moment per molecule will be zero in absence of an electric field because of cancellation of dipole moment occurs due to thermal agitation in the molecules. When an electric field is applied the molecule begins to rotate and aligns with the field, causing a net average dipole moment per molecule.

1.7.4. Interface or Space Charge Polarization: This type of polarization occurs in the materials due to movements of charges under the influence of applied electric field. This usually happens due to charge accumulation at an interface between two materials or at the grain boundaries and usually observed in amorphous or polycrystalline solids. This makes it different from orientation and ionic polarization. The space charges are random charges caused by cosmic radiation, thermal deterioration, or are trapped in the material during the creation process [D.W. Richerson, (1992)].

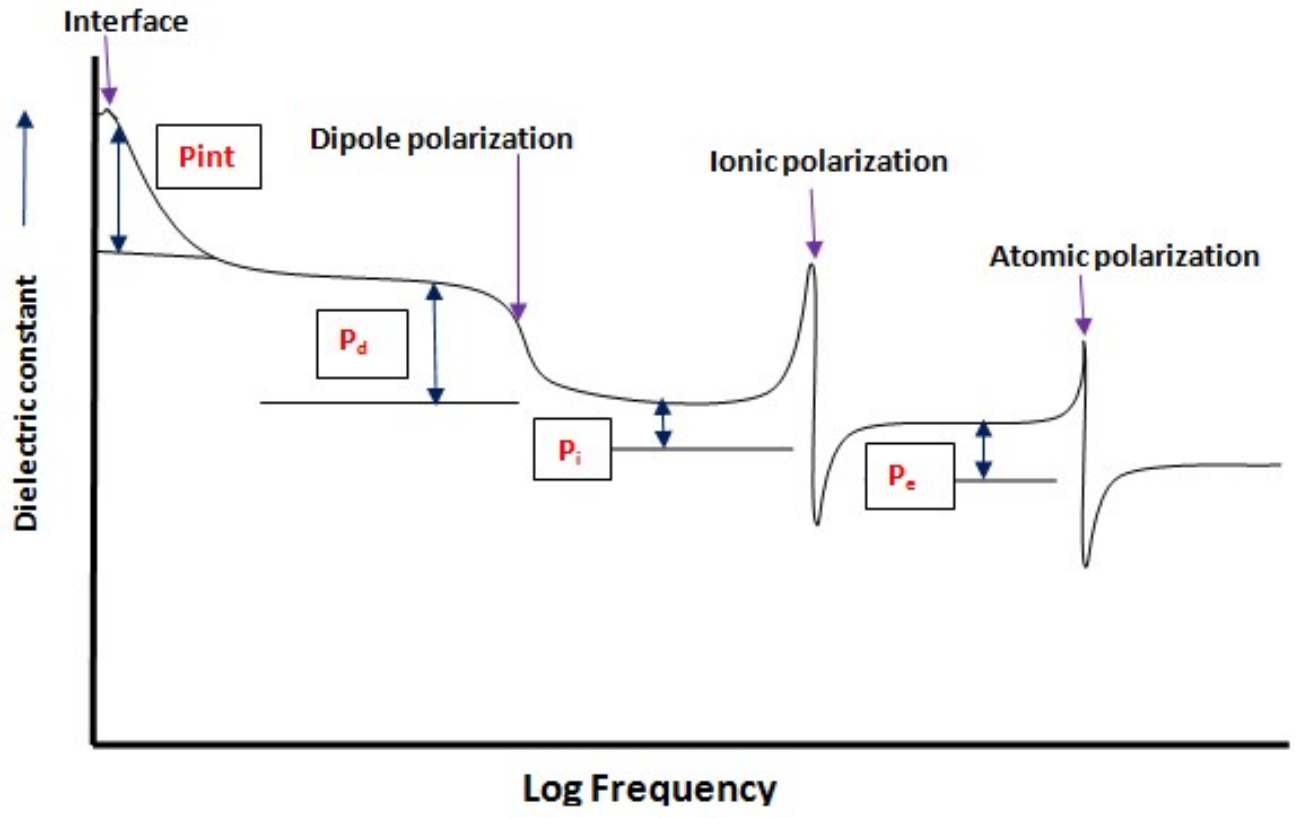
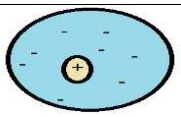
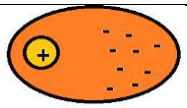
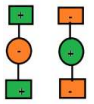
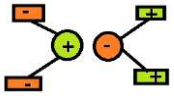
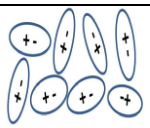
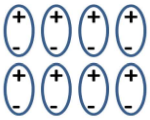
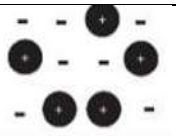
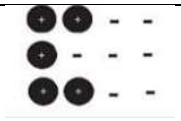


Figure 1.8 Schematic figures between dielectric constant vs frequency showing various mechanisms

Table. 1.7. Polarization mechanism of dielectric materials

Polarization Mechanism					
Type of polarization	**No E field (E=0)**	**Local E Field (E≠0)**	**Case where it is Observed**	**Frequency range where it is predominant**	**Strength of Polarization**
Electronic Polarization			Neutral atoms	~ 10^{15} Hz	Very weak
Atomic or Ionic polarization			Ionic species	10^{12} to 10^{13} Hz	Strong
Molecular or Orientation or Dipolar Polarization			Molecules with permanent dipole moment	10^{11} to 10^{12} Hz	Weak
Interfacial Polarization			Heterogeneous Systems	10^{-3} to 10^{3} Hz	Very strong

1.8 Dielectric constant

Dielectric material is the property of insulating materials, also known as dielectric which can polarized under the influence of electric field. When the dielectric are placed in between parallel plates, the positive and negative charge developed on application of external electric field which shifted in opposite direction from their equilibrium positions, induced polarization in the material. On increasing the electric flux density, the electrical polarization increases in the materials increases that is why its dielectric constant increases and have tendency to store the

electrical charges for long time. It is the ratio of capacitance (C) of materials to that of capacitance in vacuum ie C0 [D. W. Richerson, (1992)].

$$K = C/C0 \quad (1.7)$$

Where K(kappa) is the dielectric constant of the materials which is dimensionless quantity.

1.9 Dielectric loss

Dielectric loss is property of the dielectric materials and the loss of energy in the form of heat under the influence of an alternating electric field is termed as dielectric loss. It does not depend on the geometry of capacitor, It can be expressed as loss angle (δ) or loss tangent or Dissipation factor (D_f). Both refer to the phase in the complex plane whose real and imaginary parts are the resistive (lossy) component of an electromagnetic field and its reactive (lossless) counterpart and is defined as by the equation

$$tan\,\delta = \varepsilon''\varepsilon' + \sigma 2\pi f \varepsilon \quad (1.8)$$

where, ε' and ε'' are the real and imaginary part of dielectric permittivity, respectively and f is the frequency, and σ is the electrical conductivity of the materials. The loss of energy ie tangent loss (tan δ) in the dielectric materials is caused by dipolar interfacial, distortion and conduction loss of which distortion loss occurs at higher frequency region and governed by electronic and ionic polarization mechanism and conduction loss is related to the flow of actual charge through the dielectric materials which are attributed to dc electrical conductivity of the materials. The main source of dielectric loss in the materials is due to rotation of molecules or atoms in the presence of alternating electric field. The energy loss (W) related to the dielectric loss (tan δ) in the dielectric materials arises due to three process such as DC conductivity, Ion vibration and deformation loss, relaxation losses for dipole reorientation due to ionic jump [Shujahadeen (2018)]. Loss of energy (W) in dielectric materials can be determined by the equation

$$W \approx \pi\varepsilon' \xi 2f \tan \delta \quad (1.9)$$

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 [Ulrich and Schaper (2003)].

1.10 Impedance

Frequency dependence of dielectric spectroscopy is also regarded as impedance spectroscopy (IS) which can be expressed graphically in the form of Nyquist plot or cole- cole plot. This technique can be helpful for the accurate measurement of electrical properties of any type of materials such as solid or liquid over a wide range of frequencies. It is based on the interaction of electric dipole moment of the materials (often expressed by permittivity) with external electric field. Since the ac properties of materials can be highly affected by interfaces (grain boundaries, pores and interfaces between different phases), impedance spectroscopy is an appropriate method for studying composite materials [Gerhardt (1994)]. Alternating- current impedance spectroscopy allows measurement of the capacitance and loss tangent or real and imaginary impedance over a frequency range. The information about the presence of grain, grain boundary's and surface effect that influence on electron transfer reaction can obtained by utilizing impedance spectroscopy technique. The high value of dielectric constant of the materials is explained on the basis of internal barrier layer capacitance (IBLC) mechanism [Leret et al. (2007)]. According to IBLC mechanism, materials posses grains separated through grain boundaries in which grain having semiconducting in nature whereas grain boundaries are insulating properties. The higher value of grain boundaries resistance in comparison to that of grain resistance in the materials are responsible for high dielectric constant because of larger

difference in electrical conductivity of $CaCu_3Ti_4O_{12}$ [Chiodelli et al. (2004)]. Larger difference in conductivity developed space charge polarization that dominant in the lower frequencies (hertz to kilohertz) at the barrier layer between grain and grain boundary is important factor for giant dielectric constant of a wide variety of materials [(Gerhardt and Nowick (1986), Ramanujachary *et al.* 1988, Cao *et.al.* (1990)(a),(1990)(b) and Kim. *et al.* (1997)]. In some cases, semicircle of grains (bulk) or electrode appears at very high frequency is not appearing due to instrument limitation. After the measurement of Capacitance and tan δ with the help of LCR meter and measuring the current flow through the material in which L represents inductance, C represents capacitance and R represents resistance. All the parameters such as impedance *(Z*),* dielectric constant (ε*), electric modulus (*M**), and admittance (Y*) can be measured. These functions are in turn related to one another as follows [Gerhardt (1994)].

$$\varepsilon^* = \varepsilon' - j\,\varepsilon'' \tag{1.10}$$

$$Z^* = \frac{1}{R_g^{-1} + i\omega C_g} + \frac{1}{R_{gb}^{-1} + i\omega C_{gb}} = Z' - iZ'' \tag{1.11}$$

Where

$$Z' = \frac{R_g}{1+(\omega R_g C_g)^2} + \frac{R_{gb}}{1+(\omega R_{gb} C_{gb})^2}$$

And

$$Z'' = R_g\left[\frac{\omega R_g C_g}{1+(\omega R_g C_g)^2}\right] + R_{gb}\left[\frac{\omega R_{gb} C_{gb}}{1+(\omega R_{gb} C_{gb})^2}\right]$$

Z^*, Z' *and* Z'' represents complex, real and imaginary impedance, whereas R_g and C_g are resistance and capacitance of grains, R_{gb} and C_{gb} are the resistance and capacitance of grain boundary. $\omega = 2\Pi f$, f indicate frequency

$$M^* = M' + j\,M'' = 1/\varepsilon* \tag{1.12}$$

$$Y^* = Y' + jY'' = j_0 \varepsilon * \quad (1.13)$$

and $$\tan \delta = \frac{\varepsilon''}{\varepsilon'} = \frac{Z'}{Z''} = \frac{M''}{M'} = \frac{Y''}{Y'} \quad (1.14)$$

Since these functions are interrelated only one set of measurements is needed to calculate all of them (Macdonald 1987 and Gerhardt 1994). Studying dielectric data in the different functions allows different features to be recognized.

Three basically different regions for the exchange interactions between current and sample

(a) Inside the grains (bulk)

(b) At grain boundaries

(c) Surface of the electrodes

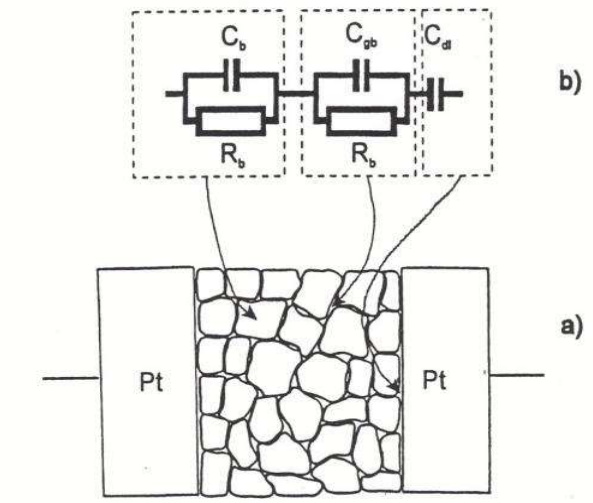


Figure 1.9 Complex impedance plane plot and equivalent circuit

1.11 Ferroelectricity

Ferroelectricity is the property of the materials which exist in single or polycrystalline form or dielectrics and having reversible spontaneous polarization over certain range of temperature that can be reversed in direction by the application of an appropriate electric field. This type of

materials was discovered in 1920 in Rochelle salt by Valasek. The phenomenon of the ferroelectric in the materials can be explained on the basis of hysteresis loop, shown in Fig.1.11.

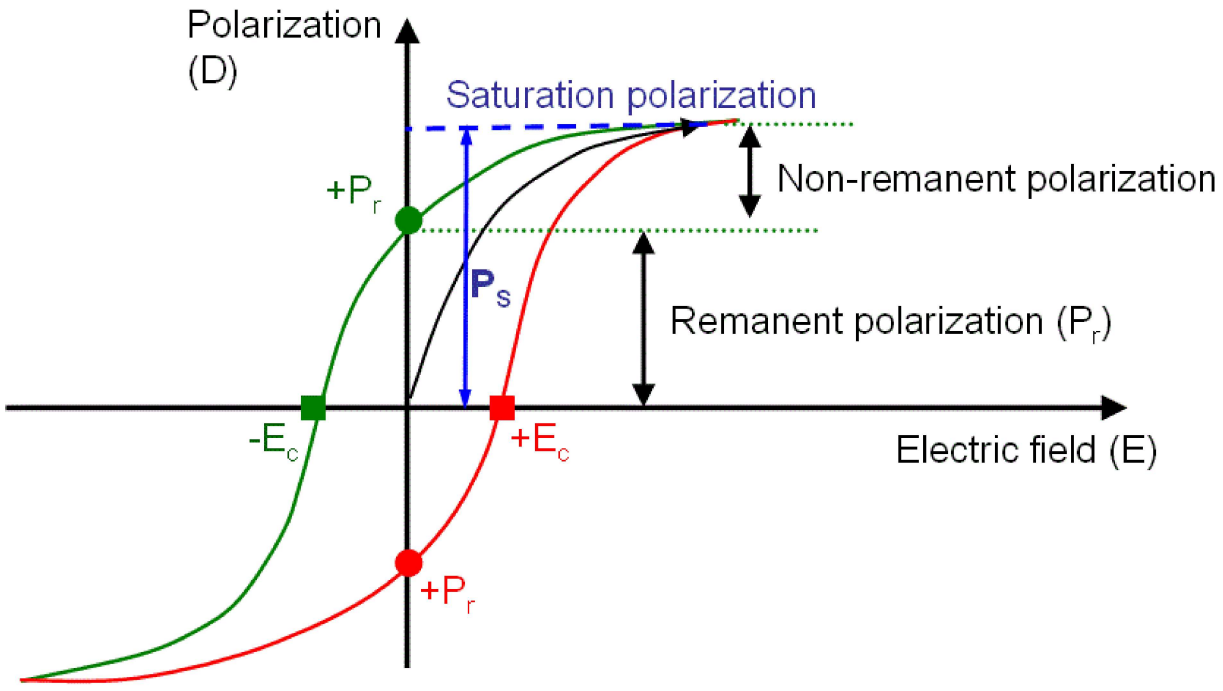


Figure 1.10 PE hysteresis loop

The remanent polarization and coercive field were measured with the help of polarization versus electric field variation for which saturation polarization must be present in the P-E hysteresis loop. The presence of polarization in the materials in absence of external electric field (E=0) is called remanent polarization whereas the value of field at zero polarization is called as coercivity field [Ghosh et al. (2016)]. A number of materials with perovskite (ABO_3) type structure that exhibits ferroelectricity such as KH_2PO_4 (KDP), $LiTaO_3$ (LT), $PbTiO_3$ (PT), $Pb(Zr,Ti)O_3$ (PZT), $NH_4H_2PO_4$ (ADP), $LiNbO_3$ (LN), $BaTiO_3$ (BT), $(Pb,La)(Zr,Ti)O_3$ (PLZT), and $(Pb,La)TiO_3$ (PLT) were discovered. The unusual dielectric constant observed in the $BaTiO_3$ (BT) is due to displacement of atoms from their original lattice point in the particular orientation

and attained nonceyrosymmetric structure resulting spontaneous polarization. Below the certain temperature called as Curie temperature (Tc), ferroelectricity observed in the materials however their ferroelectricity disappears above this temperature and transition of the ferroelectric phase in to paraelectric phase or transition order- disorder phase having higher symmetry than earlier.

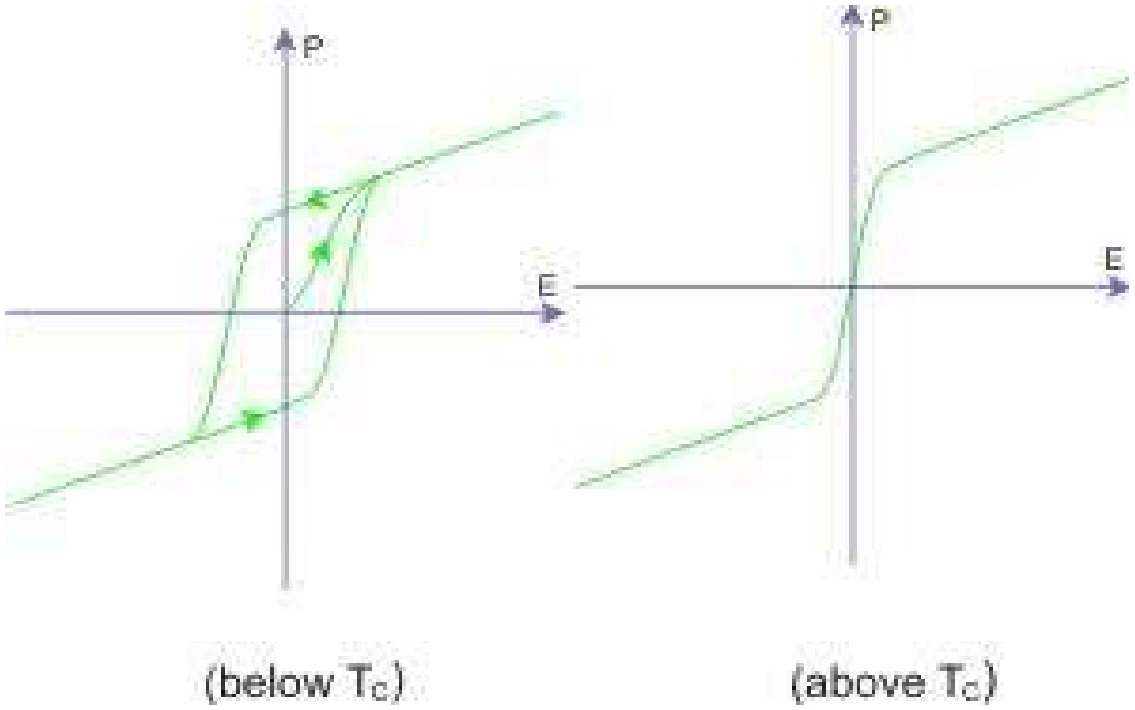


Figure 1.11 P-E hysteresis loops for $BaTiO_3$ above and below the Curie temperature (Tc)

For example, transformation of low symmetry tetragonal $BaTiO_3$ to higher symmetry cubic $BaTiO_3$ at about 120 ^oC while heating. The term paraelectric involves in cetrosymmetric suggests an analogy with paramagnetism where the dipoles are randomly oriented in the crystal that is why polarization becomes zero. Therefore, materials must be non-cetrosymmetric for existing ferroelectricity phenomenon which indicates that mechanical strain caused by phase transition will change not only the shape and volume of the materials but also change their refractive index. Hence, ferroelectric materials exhibit not only ferroelectric phenomena, but also pyroelectric,

electro-optic effects, and piezoelectric, which can be used for many technological applications such as light deflectors, displays and other electro-optic devices [(Qi *et al*., 2002)]

1.12 Magnetic properties

Magnetism is a property of matter which arises due to alignment of magnetic moment. The net flow of the electric charge and the magnetic moments of elementary particles produce a magnetic field which acts on other magnetic moments and the currents. On application of magnetic field, spin of electron in the materials tends to align themselves which increases the magnetic field strength. This increase is given by the parameter called magnetization (M).

Magnetic flux density of the materials is given by the equation

$$B= \mu_0 H+ \mu_0 M \qquad (1.15)$$

where, μ_0 is universal constant called as permeability of free space ($4\pi \times 10^{-7}$ H/m), H and M are the magnetic field strength and magnetization, respectively. Magnetization i.e. the net magnetic moment per unit volume of substance is defined as $M= \chi_m H$ and $\chi_m= \mu_r-1$ in which χ_m and μ_r represent magnetic susceptibility and relative permeability, respectively. Relative permeability μ_r is the ratio of permeability, is the measure of the degree to which a material can be magnetized and permeability of the vacuum ie $\mu_r = \mu/\mu_0$. The materials which have magnetic properties are used in the various types of applications such as tunnel junction, data storage, and magnetic recording media as well as in the video recorder, microwave devices. This type of materials having some special properties like low loss, high electrical resistivity and magnetic coupling which can be change by composition and structure of materials [Ahmed et al. (2005)]. As the magnetic properties of the nanoparticles depends on particle size, synthesis process, chemical

compositions and their morphological behavior because if the particle size is less than 100 nm, then its magnetic structure altered in Nanoscale in comparison to bulk materials [Willard et al. (2012)].

1.12.1 Origin of magnetism

The magnetism in the materials arises due to spin and orbital motion around the nucleous of an electron; they exhibit magnetic or non magnetic behavour. The material like transition metals have tendency to form magnet due to presence of unpaired electron in the d orbitals. The spin of a single electron is represented by the quantum number Ms +1/2 or -1/2. If the spinning of electron are paired with another in the orbital ,their magnetic moment cancelled out each other and shows weak magnetic field when electron are unpaired, result net magnetic moments [Jiles (1990), McCurrie (1999)].

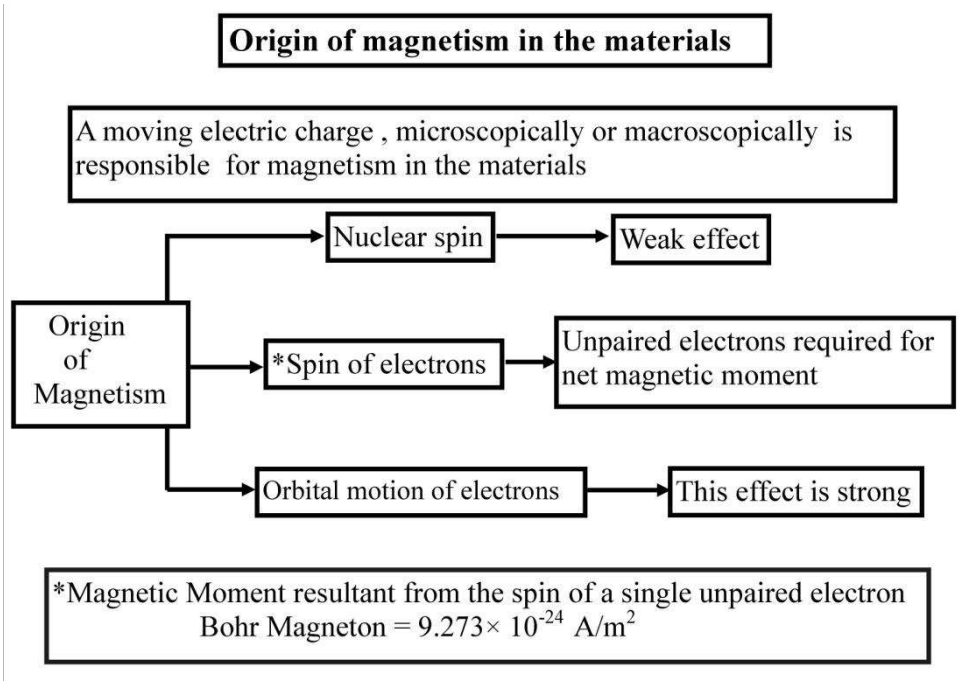


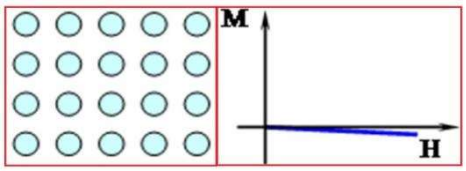
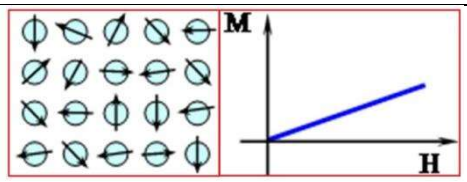
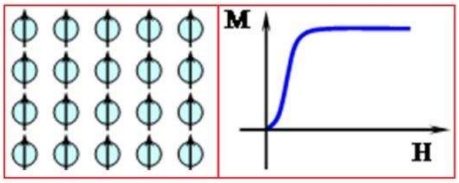
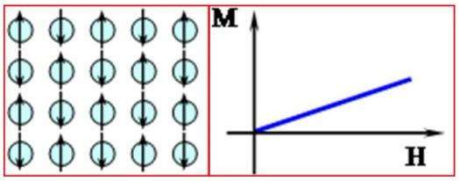
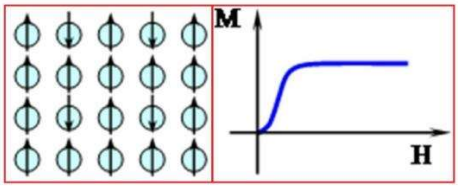
Figure 1.12 Flow chart for origin of magnetism in the materials.

1.12.2. Magnetic Domain

An area under which magnetization occurs in uniform direction within the materials is known as magnetic domains. That means the magnetic moment (or spines of electrons) of the individual atoms are randomly oriented within the certain regions of the magnetic materials. This certain region or area are approximately in millimetre in size contains billions of atoms. In the case of ferromagnetic materials the spinning of electrons are randomly oriented in absence of magnetic field which becomes soft in nature. These materials can be easily magnetized but their magnetization is not retaining in very long period, while the magnetic domains are aligned parallel in the same direction in presence of magnetic field. So that net magnetic moment of the materials is non-zero and exhibits strong magnetization. These materials are hard and having permanent magnetic moment and their magnetization does no ceases after removal of magnetic field.

In the nineteenth century, Michael Faraday was the first to start classifying substances according to their magnetic properties. Faraday classified them as either diamagnetic or paramagnetic and he based his classification on the force exerted on the materials when placed in an inhomogeneous magnetic field is mentioned in Table.1.8.

Table 1.8 A summary of the different types of magnetic behavior.

Types of magnetism	Susceptibility	Atomic/Magnetic behaviors		Example
Diamagnetism	Small & negative, -10^{-6} to 10^{-5}	Atoms have no magnetic moments		Au, Cu, Hg etc.
Paramagnetism	Small & positive, $+10^{-5}$ to $+10^{-3}$	Atoms have randomly oriented magnetic moments		O_2, NO etc.
Ferromagnetism	Large & positive (below Tc), Function of applied field, Microstructure dependent	Atoms have parallel aligned magnetic moments		Fe, H, Co, Ni etc.
Anti-ferromagnetism	Small & Positive $+10^{-5}$ to $+10^{-3}$	Atoms have mixed parallel and anti parallel aligned magnetic moments		Mn, Cr, MnO, NiO etc.
Ferrimagnetism	Large & positive (~3) Function of applied field, Microstructure dependent	Atoms have anti parallel aligned magnetic moments		Ba ferrite

1.12.3. Types of magnetic materials

(i) Diamagnetic

The materials which are weakly repelled by applied external magnetic field are called as diamagnetic. An applied magnetic field creates an induced magnetic field in them in the opposite

direction, causing a repulsive force. All the spins are cancelled with each other and hence, no magnetic moment is observed in these materials. This type of materials having negative magnetic susceptibility and less than one, are independent of temperature [Schenck (2005)]. The universal occurrence, diamagnetic behavior is observed only in a purely diamagnetic material. In these cases, the magnetization arises from the electrons' orbital motions.

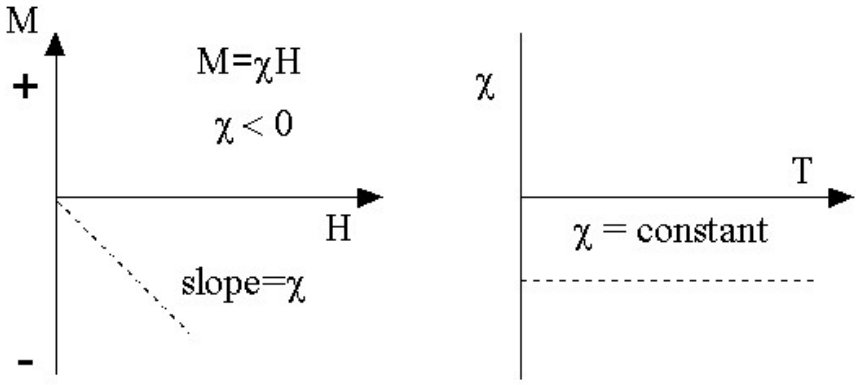


Figure 1.13 Diamagnetic structure

(ii) Paramagnetic

Paramagnetic substances which are weakly attracted in the applied external magnetic field. In these type materials, some of the atoms or ions have non zero magnetic moment due to presence of unpaired electron in the partially filled orbital's. However, the net magnetic moment (magnetization) is zero like diamagnetic substance when applied magnetic field is removed. Partial alignments of the magnetic moment take place in the magnetic field direction, resulting positive susceptibility with positive magnetization. The magnetism exhibits by these substance is called as paramagnetism. However, the direction of magnetic moment is randomly oriented due to thermal vibration with increasing of the temperature and thus magnetic susceptibility

decreases [Cullity (2011)]. The temperature dependent magnetic susceptibility is described by Curie's law,

$$\chi = {}^{C}/_{T} \qquad (1.16)$$

where χ is a susceptibility, C is a Curie constant and T is a temperature. In paramagnetic materials susceptibility is inversely proportional to their temperature. At the lower temperature materials are more magnetic. Curie's law is only suitable to system that contains non- interacting magnetic moments and assumed that individual magnetic moment does not interact with each other. Weiss modified Cuire's law using the idea of a molecular field.

$$\chi = C/T - \theta \qquad (1.17)$$

This equation is known as the Cuire-Weiss law. where θ is a measure of the strength of the magnetic interaction. The magnetic susceptibility of paramagnetic substances is small but larger than diamagnetic materials at normal temperatures and in moderate magnetic field. If the temperature is small or magnetic fields are high then magnetic susceptibility will be independent of the applied magnetic field.

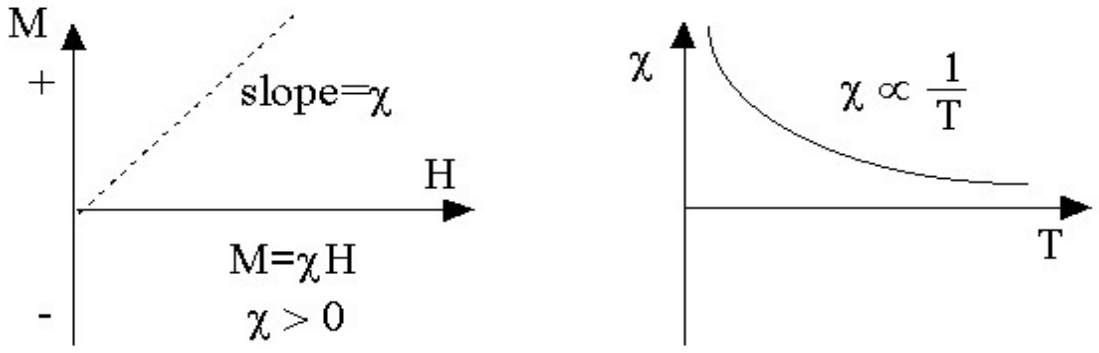


Figure 1.14 Paramagnetic structure

(iii) Ferromagnetism

Those substances which are strongly attracted by external magnetic field and are able to retain their magnetic properties after removal of external magnetic field are called as ferromagnetic substances. They have some unpaired electron due to which net magnetic moment of these materials are non zero. They have positive magnetic susceptibility along the magnetic field direction and retains have strong magnetic properties due to the presence of magnetic domains. Magnetic domains contain large number of atoms that are aligned parallel in the magnetic field direction. These domains are randomly oriented when it is in unmagnetized state and the net magnetic moments of these materials are zero. But in presence of external magnetic field, these domains are aligned parallel to each other in the direction of magnetic field. Examples of ferromagnetic materials: Iron, nickel, and cobalt etc. The properties of these materials changes at the Curie temperature (Tc) in which below Tc, it behaves as ferromagnetic and above it nature becomes paramagnetic.

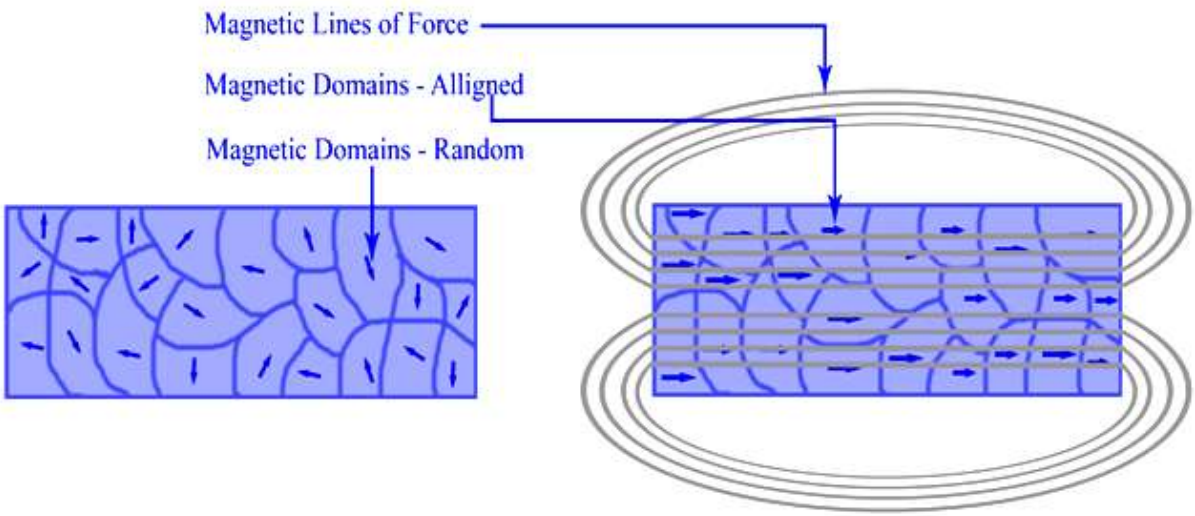


Figure 1.15 Ferromagnetism (a) nonmagnatized material and (b) Magnetized material with corresponding magnetic field

(iv) Anti-ferromagnetic

Antiferromagnetic materials are just like as ferromagnetic substances but alignment of their spins are anti parallel to each other when a magnetic field is applied and at temperatures below the critical temperature which is shown in Figure 1.16. Below this particular temperature known as Neel temperature, its magnetic ordering exists and vanishes above this temperature and became paramagnetic in nature. The magnetization of an antiferromagnet remains constant below Neel temperature and alignment of this antiparallel spin is retains whenever the external field is removed.

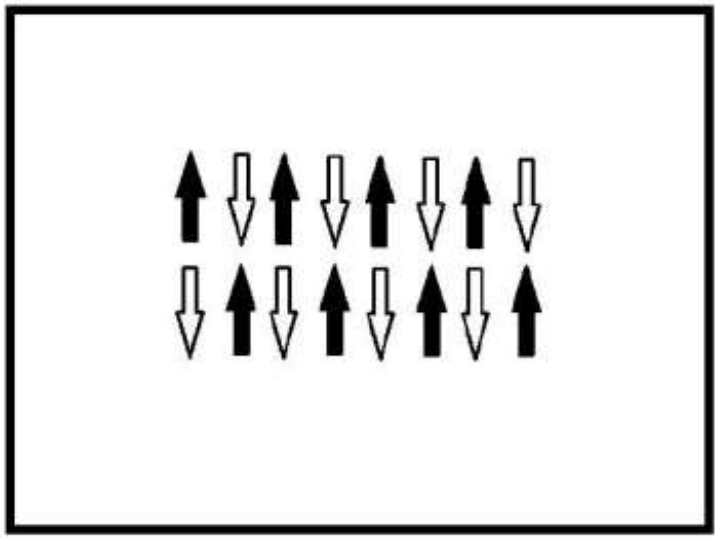


Figure 1.16 Anti-ferromagnetic structure

In a crystalline structure, the ions present in one plane having parallel spin alignment while other planes or adjacent plane having antiparallel spin an alignment that is why two opposite magnetic moment cancel to each others and hence net magnetic moment of materials becomes zero.

Superexchange interaction is also occurs in the antiferromagnetic materials due to antiparallel coupling between two magnetic cations with half- occupied orbitals through a non-

magnetic magnetic anion. This interaction occurs within the material only when electron coming from the same donor atoms and coupled with the receiving ion spins. For example, Manganese oxide crystal exhibits ionic nature due to antiferromagnetic phenomenon. In the superexchange interaction of MnO, O^{-2} anion having full field valency electron in the p-orbital donates the electron to the neighbouring open orbitals of of the Mn^{2+} ions. As the Mn^{2+} orbitals posses up-spin electrons therefore this orbital receives one down spin electrons from O^{2-} p orbital so that the remaing up-spin of O^{2-} electron of oxygen ions have tendency to donate to the next Mn^{2+} ion in the chain completing the bonds. However, this donation occurs in MnO crystal only when next next Mn^{2+} ion has it's d elections in the down-spin orientation.

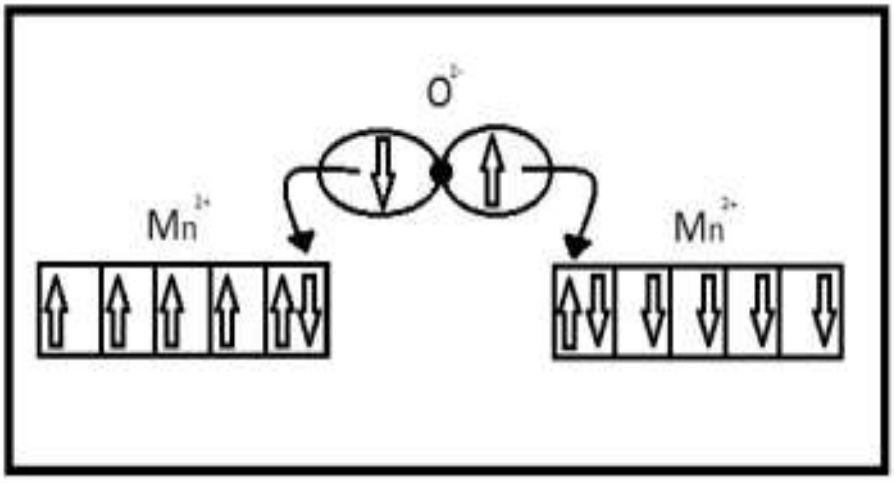


Figure 1.17 Superexchange interaction of MnO

(v) Ferrimagnetism

The word ferrimagnetism was inscribed by Nell in 1948 to describe the spontaneous magnetization in the materials from a non-parallel alignment of atomic magnetic moments [W P Wolf (1961)]. These ferrimagnetic materials exhibits anomalous behaviors to that of antiferromagnetic materials but have spontaneous magnetization due to unequal opposing

magnetic moments. This phenomenon occurred in the materials on account of the presence of populations of the different materials or ions such as Fe^{+2} and Fe^{+3}. Ferrimagnetism is exhibited by ferrites and magnetic garnet. For examples; Cubic ferrites (iron oxides with the other elements such as nickel, zinc, cobalt and aluminum), Yttrium iron garnet, and hexagonal ferrites such as $Fe_{1-x}S$, pyrrhotite, $PbFe_{12}O_{19}$ and $BaFe_{12}O_{19}$ etc., [Klein and Dutrow (2008)]. It has anisotropic properties as well as higher resistivity which are mainly useful in microwave devices such as circulators, isolators, and gyrators and permanent magnets.

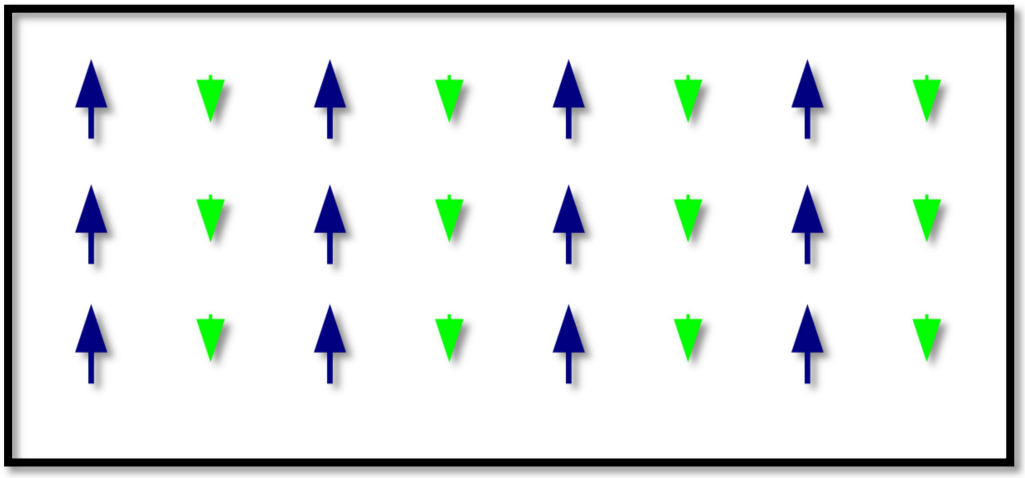


Figure 1.18 Ferrimagnetism structure

1.13 Superparamagnetism

Superparamagnetism appears in small ferromagnetic or ferrimagnetic nanoparticles (NPs). If the size of these NPs is small enough, their magnetization can randomly flip direction under the influence of temperature [Liu *et al* (2000), Song and Zhang (2004)]**.** It observed in those materials that having smaller in size and number of domains which is generally in between 10 nm and 150 nm in diameters of the particles and behaves as single magnetic domain [Goya *et al.* (2003)].. Single domain anisotropy energy equation for individual particles can be written as

$$E_{anisotropy}(\alpha) = -KV\cos^2\alpha \quad (1.18)$$

Where k is the uniaxial magnetic anisotropy constant, V is the volume of the particle, and α is the angle between the directions of magnetization. V is the volume of the particle and K is the uniaxial magnetic anisotropy constant. Superparamagnetic materials may be assumed as highly magnetized materials at any instant times. But the particles of these materials have zero remanent magnetization that observed at sufficiently long time period ie greater than 10^{-9} second and also having zero coercivity. Furthermore, a spontaneous demagnetization is observed in the Superparamagnetic materials due to thermal fluctuation as a result of which a saturated assembly results in the no hysteresis and zero coercivity. On account of this, these materials have been widely used in drug delivery, magnetic hyperthermia and magnetic resonance imaging [Batlle *et al.* (1988)]. This type of materials played major role in hard disk drives technology, in loudspeakers, in suspension systems as well as various medical applications and also observed in various rocks and living organisms. Blocking temperature indicated by T_B at which maximum magnetic moment is observed that depends on the size of the particles and decreases with increase in particle size, determine either material are ferromagnetic or Superparamagnetic [Koseoglu *et al*. (2011), Kodama *et al.*(1997)]. Below TB, material behaves like ferromagnetic and above this temperature, materials becomes Superparamagnetic. The M-H hysteresis curve for paramagnetism, Superparamagnetism and ferromagnetism are shown in the Fig.

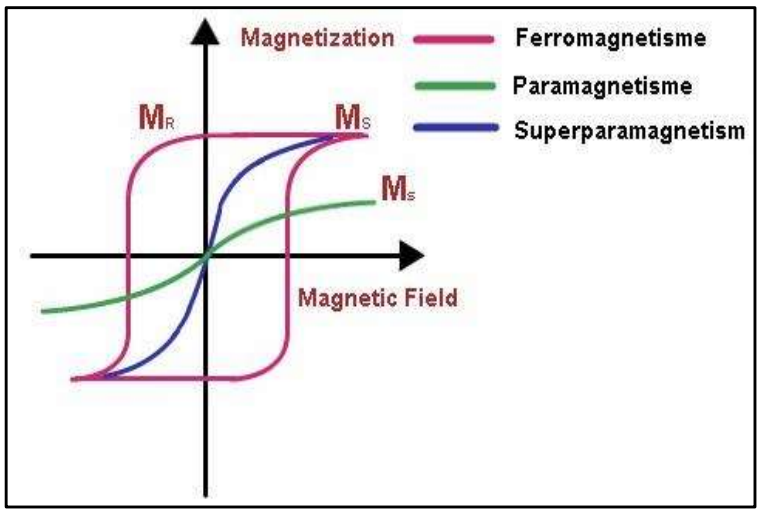


Figure 1.19 M-H hysteresis loop

1.14 Hysteresis loop

The magnetic properties of the materials can be learned with the help of hysteresis loop which exhibits the relation between the magnetizing force (H) and the induced magnetic flux density (B).It is indicated as B-H curve, is shown in Figure 1.10. The ferromagnetic substances like as iron get magnetized due to alignment of atomic domains themselves on application of external magnetic field and their magnetic properties conserved in the materials after removal of magnetic field because part of the alignment is retained. Once magnetized, the magnet will stay magnetized indefinitely. It requires a magnetic field in the opposite direction for demagnetized to this materials. This is the effect that provides the element of memory in a hard disk drive. Therefore, the relation in between *H* and *M* is not observed linear in such kinds of the materials. If a magnet is demagnetized (*H=M=0*) and the relationship between magnetic field strength (H) and magnetization (*M*) is plotted for increasing levels of field strength, *M* follows the initial magnetization curve. This curve increases rapidly at first and then reached the point of magnetic saturation indicated by the point "a" where almost all the magnetic domains are aligned and

small increases the magnetic flux density due to increase in magnetizing force. If the magnetic field is now reduced monotonically, *M* follows a different curve. When the field strength is reduced to zero then some of the magnetic domains aligned themselves but some of domains loss their alignment (from point a to point b) due to which magnetization get back from origin by an amount that is known as level of residual magnetism (remanance) in the material. The magnetic flux decreases to zero and moves to the point "c" due to reversing of magnetizing force because reverse magnetizing force invert ample of the domains. The point where the magnetic flux within the material is zero referred as coercivity (denoted by symbol 'c').

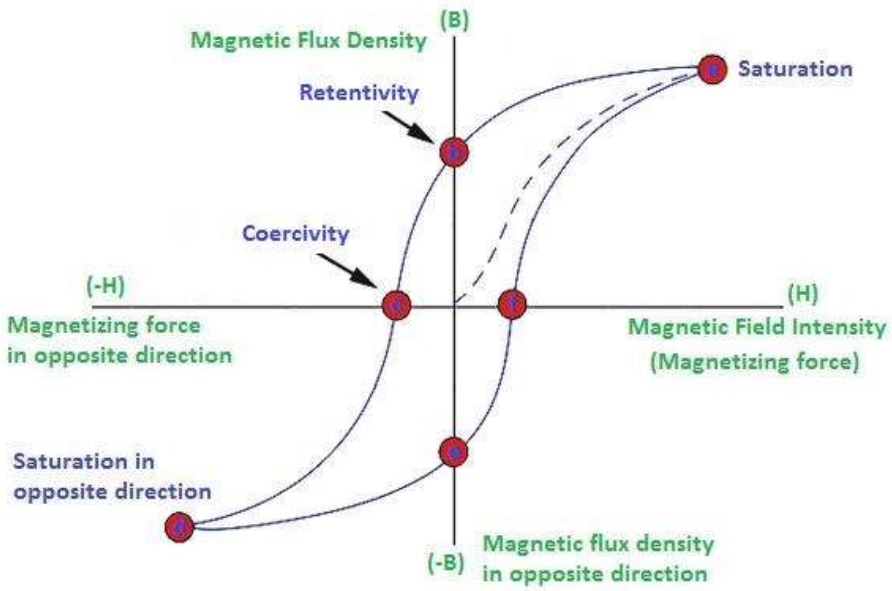


Figure 1.20 Hysteresis loop or B-H curve

Furthermore, the materials will again to attain the magnetic saturation but in opposite direction when magnetizing force is increased in the negative direction and reaches to the point "d". Reducing **H** to zero brings the curve to point "e." It will have a level of residual magnetism equal to that achieved in the other direction. Increasing **H** back in the positive direction will return **B** to

zero. Notice that the curve did not return to the origin of the graph because some force is required to remove the residual magnetism. The curve will take a different path from point "f" back to the saturation point where it with complete the loop.

The various parameters of the magnetic materials can be determined from the hysteresis loop as given below

(i) Retentivity – It measures the certain amount of residual magnetic field after getting saturation point at magnetizing force (H) is zero. (The value of **B** at point b on the hysteresis curve.)

(ii) Residual Magnetism or **Residual Flux -** the magnetic flux density that remains in a material when the magnetizing force is zero. It is remark that both of retentivity and residual flux density has the same value when the material has been magnetized to the saturation point. It is observed that when the magnetizing force did not attain to the saturation level. In this case, level of retentivity may be greater than the value of residual magnetism.

(iii) Coercive Force - The amount of reverse magnetic field which must be applied to a magnetic material to make the magnetic flux return to zero. (The value of **H** at point c on the hysteresis curve.)

(iv) Permeability, m - A property of a material that describes the ease with which a magnetic flux is established in the component.

(v) Reluctance - Is the opposition that a ferromagnetic material shows to the establishment of a magnetic field. Reluctance is analogous to the resistance in an electrical circuit.

The shape of the hysteresis loop gives the information for the magnetization of the materials. On the basis of hysteresis loops, two different materials are shown in the Figure 1.20. If the materials having wider hysteresis loop relative to other materials, then it containing high value of coercivity, reluctance, retentivity and higher residual magnetism but having lower permeability. Hence, these materials are known as hard magnet and their magnetic behaviour retained in the materials after removal of the magnetic field. On the other hand, if the materials posses' narrower hysteresis loops with reference to the other materials then the value of permeability is higher. However, it contains lower value of coercivity, reluctance, retentivity as well as lower residual Magnetism. Therefore, this type of materials is called soft magnetic materials and it can be easily magnetized and demagnetized.

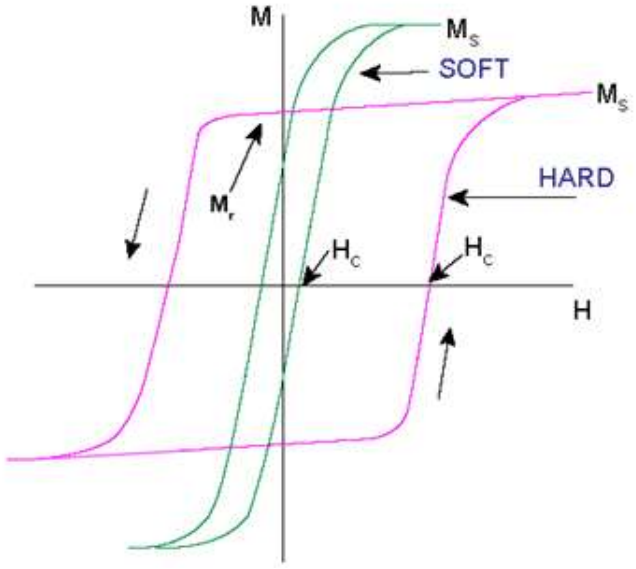


Figure 1.21 Hysteresis loop for Hard and soft magnetic materials

1.14.1 Types of ferrite materials:

On the basis of low or high coercivity in reference to magnetism of the materials, Ferrites are classified in to two types namely.

(i) Soft ferrites

(ii) Hard ferrites

(i) Soft ferrites: The materials especially ferromagnetic materials of cubical structure that posses' lower coercivity value is called as soft ferrites. The chemical formulas of soft ferrites are MO. Fe_2O_3, where M indicates transition metal cations (Fe, Ni, Mn or Zn etc.) [Collin (2007), Pozar (2011)]. These materials are easily magnetized in presence of magnetic field and easily demagnetized on removal of magnetic field. These materials having high dielectric constant and low dielectric loss and does not affected by impurities due to absence of any voids in the crystal structure. So, it can store energy or transfer magnetic energy in the form of alternating or other changing wave form. These materials cannot be simply used at high frequency because of eddy current losses. Soft magnetic materials have low hysteresis loss due to small hysteresis area. Susceptibility and permeability of these materials were high while coercivity and retentivity values are less.

(ii) Hard ferrite: Hard magnetic materials posses' high coercivity, high remanance and its high magnetocrystalline anisotropy. It does not demagnetize after removal of the magnetic field. Mostly Iron oxide and barium or strontium carbonates are used for manufacturing of hard magnetic materials. The most common hard ferrite materials are strontium ferrite, $SrFe_{12}O_{19}$ ($SrO{\cdot}6Fe_2O_3$), and Barium ferrite, $BaFe_{12}O_{19}$ ($BaO{\cdot}6Fe_2O_3$). The essential characteristic feature of hard ferrite to became permanent magnet is due to retention of high coercivity which persists to becoming demagnetized the materials. These materials also have

high magnetic permeability, so it is called as ceramic magnets. Due to possessing of these unusual properties, it is widely used in the various applications such as magnetic cheap, magnetic recorder, loud speakers, sensors, NMR/MRI body scanner, Disc Drives and Actuators, Microphones, printers and in house hold product such as refrigerator magnets etc [Sivakumar *et al.* (2004), Fu *et al.* (2003), Iqbal *et al.* (2008), Ketov *et al.* (2006)]. Depending on the crystal structure, Ferrites are categorized in to four groups such as spinal, garnet, orthogonal and hexagonal having Fe_2O_3 subunit. These are distinguished on the basis of Fe_2O_3 with respect to other oxide component in the ceramic which are summarized in the Table 1.9

Table 1.9 Classification of ferrites.

Sr. No.	Types	Molar ratio	Indication
1	Spinel	Fe_2O_3 – 1RO	RO is a transition metal oxide
2	Garnet	5 Fe_2O_3 – 3 R_2O_3	R_2O_3 is a rare earth metal oxide
3	Ortho	$MFeO_3$	M is rare earth elements like Ho, Dy, Er, Y, Yb, etc.
4	Hexagonal ferrite	6 Fe_2O_3 – 1RO	RO is a divalent metal oxide from group IIA e.g. BaO, CaO, SrO

1.14.2 Spinel ferrite: Ferrites having the general chemical formula,

$Me_{\delta}^{2+}Fe_{1-\delta}^{3+}\left[Me_{1-\delta}^{2+}Fe_{1+\delta}^{3+}\right]O_4^{2-}$

where, octahedral sites and tetrahedral sited are indicated inside the square of brackets and outside of the brackets, respectively. They have been widely used as ceramic materials because it is magnetically soft materials due to high magnetic permeability, high electrical resistivity and

low magnetic losses which are strongly depending on the cation distribution, preparation methods and their chemical compositions [Melagiriyappa and Jayanna (2009)]. The degree of inversion (δ) determines the crystal structure of different types of ferrites. Depending on the degree of inversion, these ferrites can be categorized in to three types:

(i) Normal Spinel ferrite: If degree of inversion (δ) is 1, Normal structure is obtained. In this ferrite structure, All the bivalent metal cations (Me^{2+}) occupied tetrahedral sites and trivalent (Fe^{3+}) cations adopted in octahedral sites. For example: zinc ferrite, $ZnFe_2O_4$ [$Zn^{2+}(Fe^{3+}Fe^{3+})\ O_4^{2-}$].

$$(M^{2+})_A\,[Me^{3+})_B\,]O_4$$

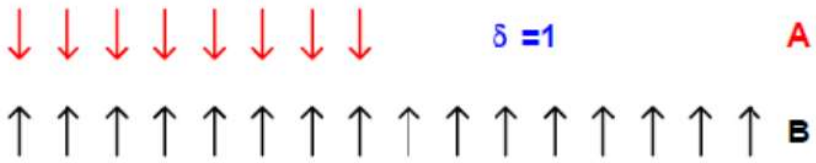


Figure 1.22 Normal Spinal

(ii) Inverse Spinel ferrites: The values of δ for these type ferrites are equal to zero. In these structures, all the bivalent metal cations are in the octahedral sites while half of Fe^{3+} metal cations and other half of Fe^{3+} cations are distributed in the octahedral and tetrahedral positions, respectively. The metal oxides such as Fe_3O_4, $CoFe_2O_4$, $NiFe_2O_4$ etc. are an examples of inverse Spinel ferrites having the general formula [$(Fe^{3+})_A\,(Me^{2+}Fe^{3+})_B\ O_4^{2-}$] in which Fe^{2+} ions occupy octahedral [B] sites [Li *et al.* (2004)].

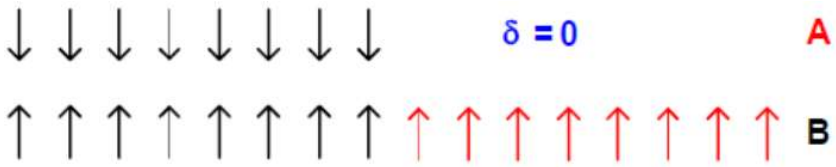


Figure 1.23 Inverse spinal

(iii) Mixed Spinel Ferrites: If the ferrite materials having the inversion degree (δ) in between 0 and 1, is associated with the mixed Spinel type structure of ferrite. This is also referred as random Spinel ferrite. In this crystal structure, the divalent cations (M^{+2}) are occupied on both of tetrahedral and octahedral sites. The general formula of the mixed Spinel ferrite is $Me_{1-\delta}^{+2}Fe_{\delta}^{+3}\left[Me_{\delta}^{+2}Fe_{2-\delta}^{+3}\right]O_4^{2-}$ .The value of δ depends on the nature of constituents as well as preparation technique. One of the most important mixed Spinel type ferrite is $MnFe_2O_4$ with inversion degree δ = 0.2.and other namely $MgFe_2O_4$.

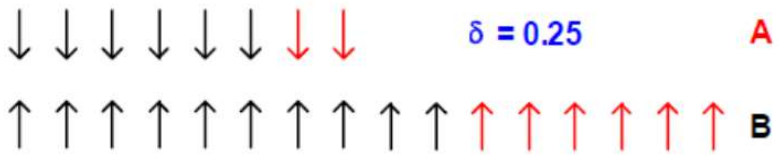


Figure 1.24 Mixed spinal

1.14.3 Garnet: The other groups of ferrites are garnet of the chemical formula $Me_3Fe_5O_{12}$ in which, Me represents trivalent metal cations such as yttrium or rare earth etc. The unit cell of ferromagnetic garnet is cubic that contains 160 atoms or eight molecules of $Me_3Fe_5O_{12}$ of which the metal cations (Me) surrounded by eight oxygen ions and occupy dodecahedral sites. Furthermore, Iron (Fe^{+3}) ions are distributed over octahedral and tetrahedral sites in the ratio of 2:3. Therefore, the cationic distributions of garnet structure is written in the form of $Me_3^cFe_2^aFe_3^dO_{12}$. These types of ferrite are usually magnetic materials having optical transparency and therefore, commonly used in data storage devices, telecommunications and in microwave high frequency applications [Akhtar *et al*. (2018)].

1.14.4 Ortho ferrites: The third groups of the ferrites are ortho-ferrite; having the chemical formula of $MeFeO_3$ of which Me represents large (M^{+3}) metal cations often as rare-earth metal cations, an alkaline or alkaline earth metals. The Fe metal ions present in this structure are

coordinately attached with the six oxygen atoms forms octahedral complex that is located on its centered position. For examples; $LaFeO_3$, $YFeO_3$ .The unit cell of these type ferrites contains orthorhombic with distorted perovskite structure with a space group *Pnma* (group 62, D_{2h}^{16}). These types of materials posses weak magnetic moment perpendicular to the antiferromagnetic axis and exhibits weak ferromagnetism due to small spin canting of the order 10^{-2} radian in the alignment of antiferromagnetic coupling [Coutinho *et al.* (2017)]. These materials are commonly useful in optical internet, electrical currents, in sensors of magnetic fields and in communication techniques etc.

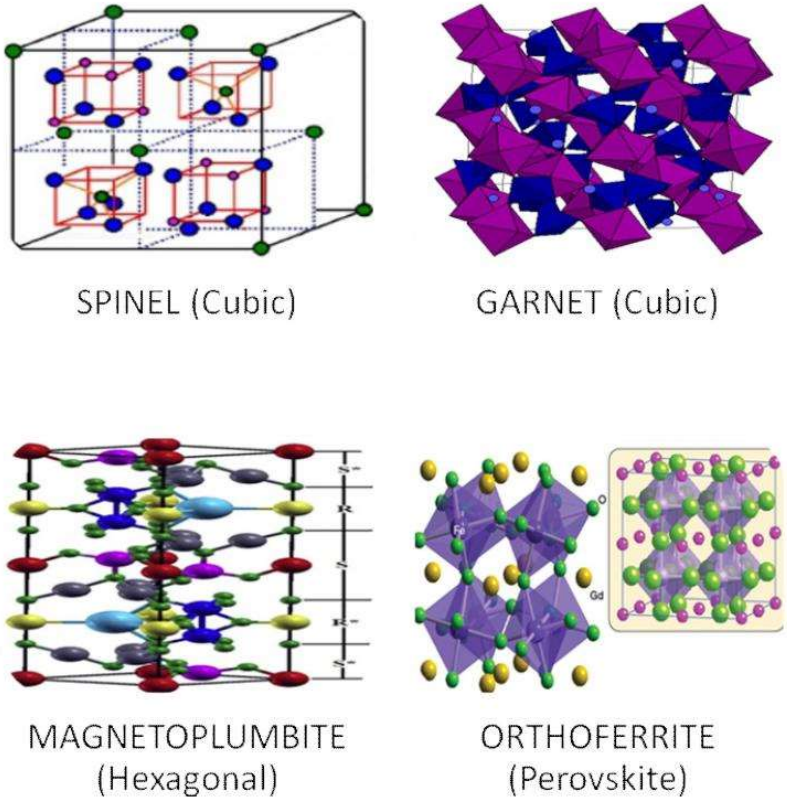


Figure 1.25 Crystal structures of different types of ferrites

1.14.5 Hexagonal ferrites: A new class ferromagnetic oxide material having permanent magnetic properties was introduced in 1952 .The possibility of hexagonal ferrite having the

general formula $AFe_{12}O_{19}$,where A= Ba, Sr, Ca or Pb) were made by workers at Philips laboratory at Eindhoven in the Netherlands. The continuous demands of these materials have been developed in the field of permanent magnet due to their high uniaxial magnetocrystalline anisotropy along c axis due to which they have much interest in the recent years because of various applications such as data storage, magnetic recording media, in electrical devices and microwave device [Sharma *et al.* (2003), Kools *et al.* (2002)]. Depending upon their arrangements of S, R, T blocks and their crystal structures, Hexagonal ferrites are categorized in six form such as M-type ($AFe_{12}O_{19}$), U-type ($A_4Me_2Fe_{36}O_{60}$) , W-type ($AMe_2Fe_{16}O_{27}$), X-type ($A_2Me_2Fe_{28}O_{46}$), Y-type ($A_2Me_2Fe_{12}O_{22}$), and Z-type ($A_3Me_2Fe_{24}O_{41}$), where A = Ba^{+2}, Pb^{+2},or Sr^{+2} etc. and Me is divalent transitions metal ion [Hibst (1988), Valenzuela (2005), Nedkov and Tailhades (2004)].

Magnetic behaviour in M-type barium hexaferrite ($BaFe_{12}O_{19}$) is only cause of Iron which forms five distinct layers such as three octahedral, one trigonal bipyramidal which is the unique feature of M-phase with d^3sp type bonding and one tetrahedral site. These are represented by the blocks namely S, R and T which is the rotational symmetry of S^*, R^* and T^* along the hexagonal c-axis. However, the crystal structure of these hexagonal ferrite materials are complex in which the metal cations in +2 and +3 oxidation state, are occupied inertial position of the crystal structures and heavy metal cations such Ba^{+2} or Sr^{+2} are insert in the oxygen layer. These ferrites having the space group: $P6_3/mmc$ and the lattice parameter a= b= 5.89 A˚ and c= 23.19 A˚. Among four blocks in the crystal structure of barium hexaferrite, The repeating unit of S- blocks having the compositions Fe_6O_8 or $[Fe_6^{3+}O_8]^{2+}$ (S^{2+}) formed two oxygen layer (O_4-O_4) with the Spinel structure and R blocks containing the compositions $[Me^{2+}Fe_6^{3+}O_{11}]^{2-}$ or $BaFe_6O_{11}$ with formation of three oxygen layer (O_4-BaO_3-O_4), whereas T block contain

composition $Ba_2Fe_8O_{14}$ or $[Ba_2^{2+}Fe_8^{3+}O_{14}]^0$ that formed four blocks of oxygen layer namely O_4-BaO_3-BaO_3-O_4. The sub-unit 'R' combines with 'S^{2+}' to give the neutral block (RS), with the total composition $MeFe_{12}O_{19}$ (M-phase) [Gunanto *et al.* (2018)].

1.15 Applications of hexaferrite

M-type barium hexaferrite ($BaFe_{12}O_{19}$), equivalent to $BaO{\cdot}6(Fe_2O_3)$, also called as BAM is came out in 1951 and useful in the most difficult areas for theoretical description. These are the world's first permanent materials and are a special type of ferrites which have hexagonal crystallographic structure. The importance of this materials in the world in recently years are due to possession of high Curie temperature, high saturation magnetization, high magneto-crystalline anisotropy along c-axis, high coercivity as well as high natural frequency with the excellent capability. It has been widely used in numerous applications like as video recorder; magneto-optic recording media, microwave devices and injection-molded pieces, random excess memory (RAM) and stealth technology [Harris *et al.* (2009), Cai (2010) *et al*]. There has been an explosion of interest in the last decades for solving various problems related to radar engineering, electromagnetic compatibility (EMC), signal integrity (SI), microwave engineering, and electromagnetic immunity (EMI). The hexagonal ferrites can be also used for pacification and ascertain of undesirable radiation within a few hundred GHz frequency bands for imparting proper nonreciprocal isolation in transmission, reception and in channels of generation. There are continuous demands in the field of science and nanotechnology, composites with carbon nanotubes, fiber orientation and in the development of nanofibres. Other applications of hexagonal ferrite materials including Spike Suppression, Handheld Devices, EMI filters, shield beads, consumer goods, Common Mode Chokes, Current Sensors, snap-on cores, flat cable beads etc.

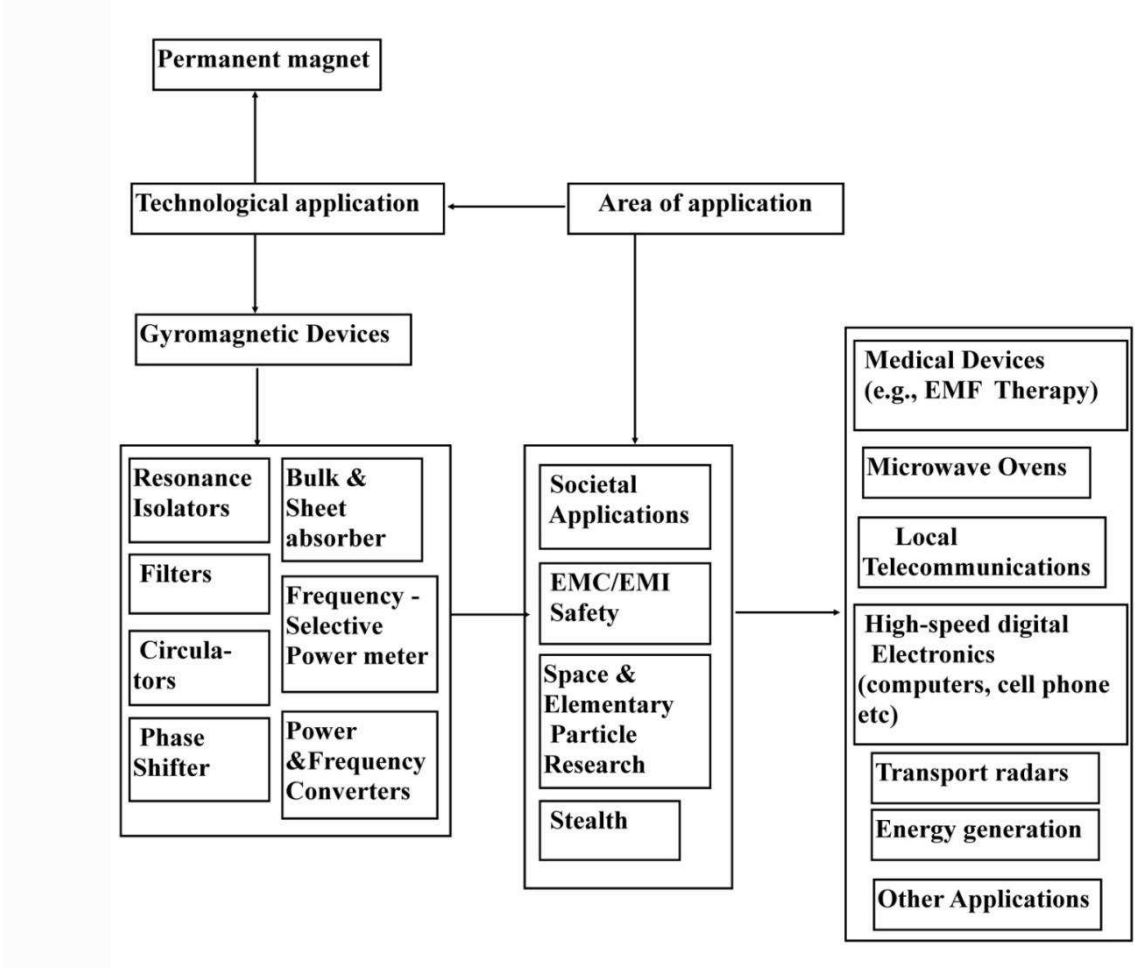


Figure 1.26 Applications of hexagonal ferrites

1.16 Aim of the present work

Hexagonal ferrites and their composite have been extensively used for understanding the theories of magnetism which are widely used in the wide range of technological applications. They exhibit some characteristics properties such as electrical, magnetic and microstructural which are mainly dependent on preparation methods, substitutions of various cations like divalent or trivalent, calcinations temperature sintering temperature, preparation time and amount of surfactant etc. Chemical methods are used for preparation of barium hexaferrite materials in the recent time because this method is most suitable low-cost technique than other synthesis methods to obtain good quality of the ceramic materials. Furthermore, benefits of this route is (a) increase

of the surface area of a solid (b) Manufacturing of a solid with a desired grain size, and (c) Easily mix together to form an homogeneous solutions.

Therefore, we can obtain homogeneous ultrafine hexagonal particles at lower sintering temperature and less time duration by the help of this technique for geometrical requirements of electronic devices such as mobiles, camera, computers, Television etc. Scientist taking interest to serve better electronic devices and memory that having high dielectric constant along with low value of dielectric loss.

(i) The work of thesis is focused on the synthesis and characterization of ceramic materials and various types of applications such as dielectric, magnetic as well as ferroelectric properties of the materials were reported.

(ii) The contribution due to grain and grain boundaries, morphological analysis, particle shape, dependence of temperature as well as frequency on the dielectric and electrical properties has been widely studied.

(iii) In order to get good quality of the ceramic materials, chemical route is used to observe to monitor homogeneous mixing of metal ions and material synthesized at low sintering temperature as well as less duration for improvement of dielectric constant and magnetic properties of the materials which are useful in the field of microelectronic devices and permanent magnate. The objective of present work is to synthesize following ceramic material and the effect of Co and Ni substitution in the Barium hexaferrite ceramic (BHF) by the Chemical route.

(i) $BaFe_{12}O_{19}$ (BHF) synthesized by the chemical route.

(ii) $BaFe_{12-x}Co_xO_{19}$ (x = 0.0, 0.05, 0.1, 0.2) synthesized by the chemical route.

(iii) $BaFe_{12-x}Ni_xO_{19}$ (x = 0.0, 0.05, 0.1, 0.2) synthesized by the chemical route and its composite with $Bi_{2/3}Cu_3Ti_4O_{12}$ (BCTO) was also included in the thesis.

Different types of physiochemical characterization of the following above materials in the sequential steps:

I. X-ray powder diffraction (XRD) study was used for the identification of phase formation and their crystal structure of the materials.

II. Scanning electron microscope (SEM) analysis has been performed for the detail morphological study of the fractured surface of the materials.

III. Transmission Electron Microscopy (TEM) is useful for the particle size determination.

IV. The dielectric properties, dependent on the both temperature as well as very thus been investigated.

V. The temperature and the frequency dependence of AC conductivity were explained on the basis of conduction mechanism.