

1.1 History of Perovskite

Calcium titanium oxide (CaTiO_3) type mineral is known as perovskite oxide. The mineral was discovered in the Ural Mountains of Russia by Gustav Rose in 1839 and is named after Russian Mineralogist G. V. Perovskiy (1792-1856). The simple perovskite has a cubic structure and the chemical formula ABO_3 per unit cell. In this case, the 'A' ions are at the corners of the unit cell with the 'B' ions at the center and the negative ions 'O' occupying the face-centered positions. The corner of the lattice is usually an alkaline earth or rare earth element. The center ions 'B' of the lattice, could be 3d, 4d, and 5d transition metal elements. The space groups were found to be P_{nma} .

Since 1940, these oxides are a class of materials that have been extensively investigated, due to their significance to fundamental research and their high potential for technological applications [M. E. Lines and A. M. Glass (1977)] including superconductivity, insulator-metal transition, ionic conduction characteristics, dielectric properties and ferroelectricity [Terki *et al.* (2005), Goudochnikov *et al.* (2007), Cabuk *et al.* (2007)]. Perovskite play a very important role for chemical tuning of composition and structure and thus display of an over abundance of physical and chemical behaviors with technological interest that depend on the processing conditions, oxygen content and ordering [M.E. Lines and A. M. Glass (1977), Yang *et al.* (2006), M. Bibes and A. Barthelemy (2007), Davies *et al.* (2008)] and they are noticeable for their multitude of structure-dependent electronic, magnetic, optical and catalytic properties [Banerjee *et al.* (2006), Mao *et al.* (2005), Mao *et al.* (2007), F S Galasso (2013)]. Their electrical properties range from insulators, semiconductors and some even exhibit metallic to superconductors characteristic [Seron *et al.* (2006), Huijben *et al.* (2006), Mateu *et al.* (2007), Chandler *et al.* (1993), Bhalla *et al.* (2000)].

The universal nature of the perovskite structure is the testament to its enormous structural and compositional suppleness. This suppleness allows perovskite oxides to be tuned to near an appropriate instability, be it structural, electronic, or magnetic in origin, which is essential for the oxide to be functionally useful [Dawber *et al.* (2005), Setter *et al.* (2006), Koinuma *et al.* (2005)]. Titanate perovskite is a strong interest because of their thermoelectric and ferroelectric properties, their unusual electrochemical characteristics, and their industrial applications such as memories, transistors and electrodes. Alkaline earth metal titanate included BaTiO_3 , SrTiO_3 , CaTiO_3 and their associated non-stoichiometric complexes. $(\text{Ca}, \text{Sr}, \text{Ba}) \text{TiO}_3$, are important ferroelectric materials, which are the most extensively studied and widely utilized perovskite-type materials. BaTiO_3 is ferroelectric and SrTiO_3 and CaTiO_3 are quantum paraelectric. The structural suppleness of perovskite has been exhibited to produce or enhance desirable solid-state properties such as ionic or electronic conductivity [Khenata *et al.* (2005)]. The well known perovskite family is also the titanium-based oxides which are gaining more and more attention due to its promising applications in gas detection, nonlinear optics and so forth.

CaTiO_3 is widely used as a wireless device in electronic ceramic manufacturers and BaTiO_3 was a ferroelectric, piezoelectric, and an insulating material is widely used as high permittivity, low dielectric loss, and dielectric behaviors [Inaguma *et al.* (1992)]. Whereas, SrTiO_3 was received much attention both theoretically and experimentally with respect to its defect chemistry and radiation resistance [Stirling *et al.* (1976), Denisov *et al.* (1983), Vogt, *et al.* (1984), Hamid *et al.* (2006)]. Nowadays, the structural properties of perovskite including order-disorder effects and formation of defects and impurities that can tailor the electronic and physico-chemical properties [Carrasco *et al.* (2006), Maksimov *et al.* (2007),

Volanti *et al.* (2007)]. The properties of these perovskite oxides may be modified to a novel system with completely unique characteristics. Over the last decade, extensive experimental and theoretical work on perovskite-based materials have demonstrated a strong interrelationship between distortions of the crystal structure and many processes and phenomena such as photoluminescence, ferroelectric, piezoelectric and pyroelectric properties [Paris *et al.* (2007), Moreira *et al.* (2008), Simões *et al.* (2008), Kato *et al.* (2004)].

1.2. Classification of Perovskite

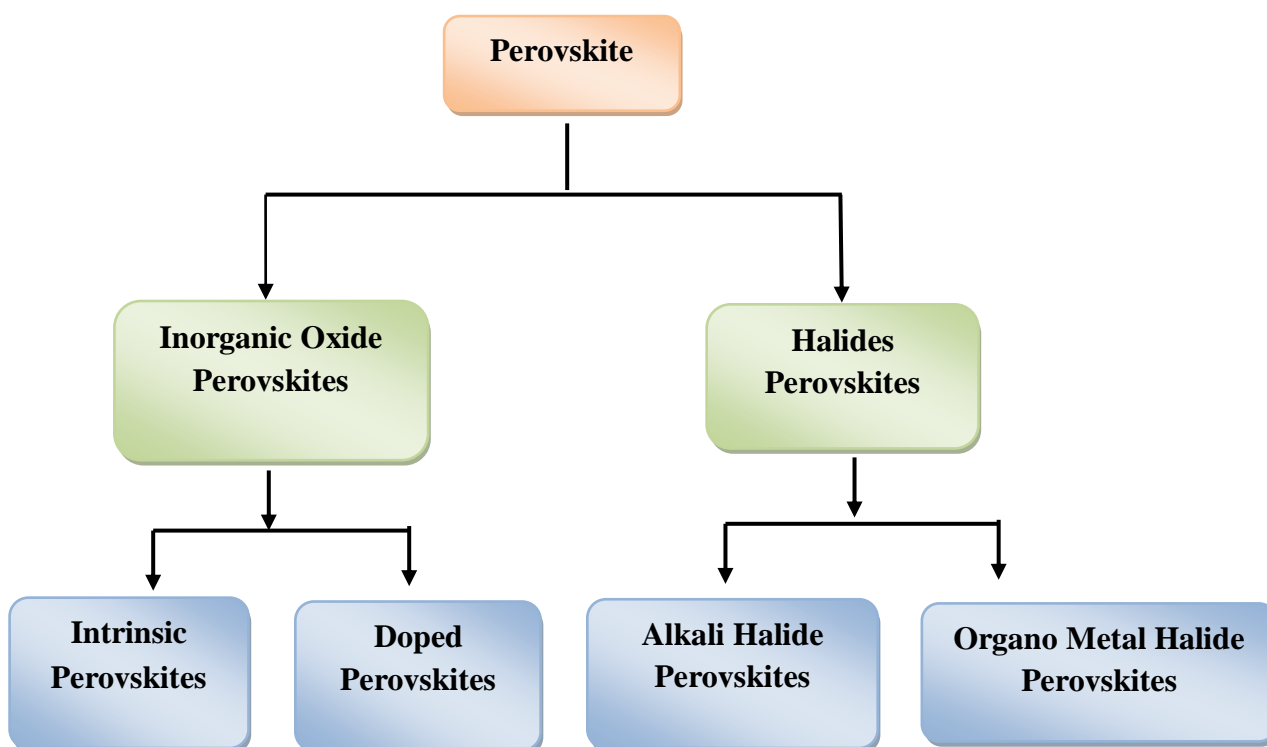


Fig.1.1. Classification of perovskite.

1.2.1 Type and Structures of Perovskite

I. ABO₃ Perovskite: The chemical formula of the perovskite structure is ABO₃ (Fig.1.2), where A and B denote two different cations. It consists of BO₆ octahedral connected to each other by corner oxygen, and A cations occupy the 12-fold coordination sites surrounding eight BO₆ octahedral [Kato *et al.* (2004)]. Therefore, the ionic radius of the A ion is larger than that of the B ion and the presence of two different size cation sites enables a wide variety of perovskite-type oxides. Perovskite oxides always receives the much attention for their electrical and photo-catalysis properties [Takata *et al.* (1997), Domen *et al.* (1990), Yoshimura *et al.* (1993)] and some example of perovskite used for ionic conductivity, ferromagnetic and piezoelectric i.e. BaTiO₃, PdTiO₃, SrTiO₃ and CaTiO₃ etc [Jonker *et al.* (1954), Rooksby *et al.* (1965)]. Perovskite also has structural suppleness regarding cation and anion vacancies. On the basis of this relationship, Goldschmidt proposed a tolerance factor (t) [Goldschmidt *et al.* (1926)], which represents a divergence from the ideal ratio of the ionic radii (equation 1.0).

$$t = \frac{r_A + r_O}{\sqrt{2}r_B + r_O} \quad (1.0)$$

where r_A , r_B and r_O presenting ionic radii of A, B and O ions respectively. The value of tolerance factor (t) is 1, its shows cubic structure but in case $t < 1$, A cation is too small to form a cubic structure, resulting in bends of the BO₆ octahedral network that reduces the space of the A cation site. Generally the range of perovskite compounds found to be $0.75 < t < 1$ and cubic-type forms when $t > 0.9$.

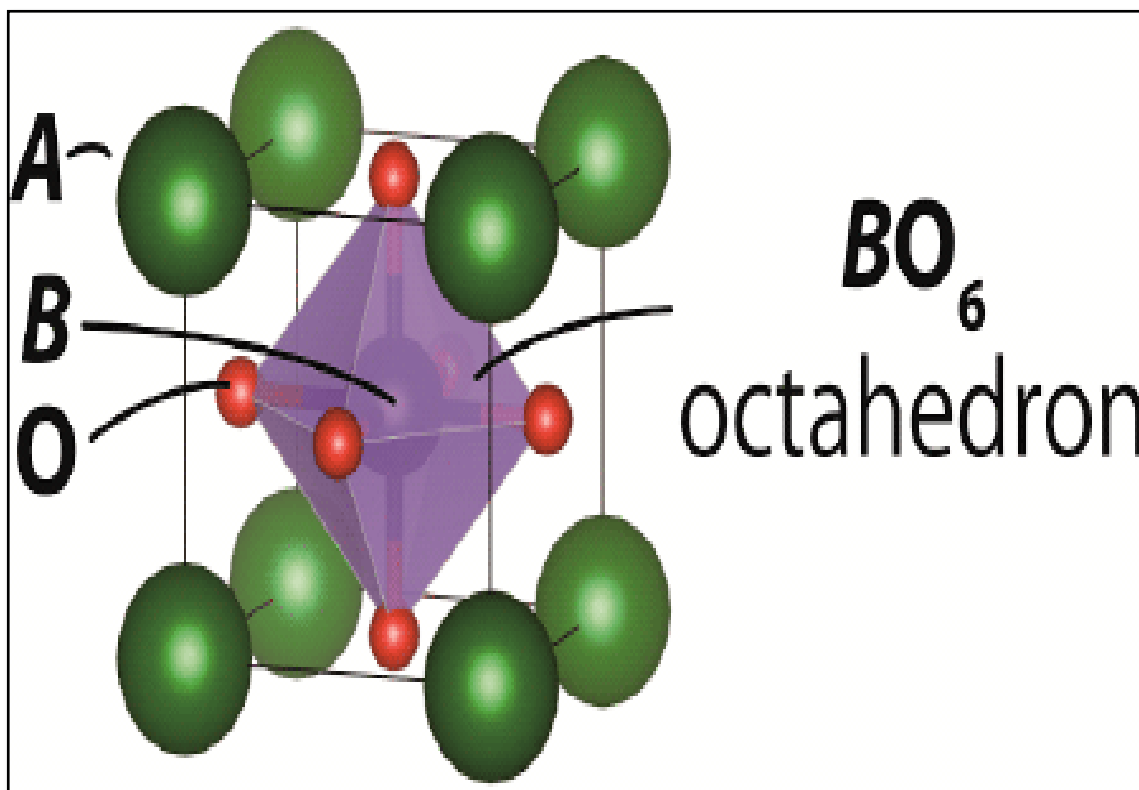


Fig.1.2. The structure of ABO₃ perovskite.

II. A⁺¹B⁺⁵O₃ Perovskite: KNbO₃, AgNbO₃, NaNbO₃ and LiNbO₃ are few examples of A⁺¹B⁺⁵O₃ perovskite. Cation A belong to first group elements and cation B belong to the fifth group elements of the periodic table. Among these, KNbO₃ and AgNbO₃ are ferroelectric, NaNbO₃ is anti-ferroelectric and LiNbO₃ is piezoelectric [Burisch *et al.* (1984)]. NaNbO₃ is an anti-ferroelectric with orthorhombic unit cell at room temperature but it's structure change with variation of temperature i.e; pseudo-tetragonal at 693 K, tetragonal at 833 K and cubic structure at 913 K. Mostly these perovskite compounds are widely used in electro-optics devices.

III. $A^{+2}B^{+4}O_3$ Perovskite: $A^{+2}B^{+4}O_3$ type perovskite most widely used in dielectric and piezoelectric materials, A cation belongs to second groups and B cation belongs to the fourth group of the periodic table. Mostly A and B present to divalent (Ca, Sr and Ba) and tetravalent ion (Ti, Zr and Sn). Among these perovskite widely studied materials are $ATiO_3$, where A= Ba, Bi, Ca, La and Pb. It also used to dielectric and piezoelectric materials. Perovskite compound $BaTiO_3$ and $CaTiO_3$ materials useful for a large number of an application such as piezoelectric, transducers gas lighter elements, electronic ceramic materials and in immobilizing high-level radioactive waste [Ball *et al.* (1998), Wang *et al.* (2001)].

IV. $A^{+3}B^{+3}O_3$ Perovskite: This type of compounds belonging to rare earth or yttrium ion on A site and a trivalent transition metal ion on B site. The particular interest of these compounds found to be technical application of functional materials and most interest properties such as mixed conductivity by both ions and electron or hole migrations [Googenough *et al.* (1974)]. Such materials can be employed in a solid electrolyte fuel cell (SOFC) as electrode materials for oxygen sensors and humidity sensors.

V. $(ABO_3)_n$ AO Perovskite: Ruddlesden and Popper have Mentioned a family of perovskite oxide with the general formula $A_{n+1}B_nO_{3n+1}$ ($(ABO_3)_nAO$), where, n is the number of ABO_3 perovskite layers separated by sole of AO rock salt layer [Boulahya *et al.* (2017)]. A and B show the rare or alkaline earth elements. It belonging to R-P homologous series, and most of used for the high oxide-ionic conductivity, R–P homologous materials with mixed ionic electronic conductors for electrodes in intermediate temperature solid oxide fuel cells [Amow *et al.* (2006), Lee *et al.* (2006), Aguadero *et al.* (2008), Song *et al.* (2011), Mazo *et al.* (2015), Huang *et al.* (2015), Boulahya *et al.* (2015)].

The interest of the R–P oxides as electrodes in intermediate temperature solid oxide fuel cells has been mainly focused on materials with a K_2NiF_4 like structure. K_2NiF_4 type materials present higher ionic conductivity than anion deficient ones due to the oxygen interstitial migration in the rock-salt type layers of the structure [Bassat *et al.* (2013), Kharton *et al.*(2001)]. Besides, octahedral rotation distortions play an important role in the oxide–ion migration of these materials [Li *et al.* (2015)].

VI. $A_2B_2O_5$ Perovskite: $A_2B_2O_5$ is a general formula for a large number of materials which exhibit an anion deficient perovskite (oxygen deficient perovskite) $ABO_{3-\delta}$ system. The brownmillerite considered the parent structure of $A_2B_2O_5$ ($A_2BB'O_5$) and giving rise to different derivatives, layered double perovskites, A site anion and anion vacancy ordered perovskites and perovskite oxide like compounds with crystallographic shear planes. Among anion deficient perovskites, $ABO_{2.5}$ (or $A_2B_2O_5$, $A_2BB'O_5$, and $AA'B_2O_5$, where A, A', B, and B' are cations of different kinds) are probably, the most popular and rich in a structural diversity. These type perovskites are used in high Curie temperature (T_c), superconductivity in Cu-based oxides, high electron and oxygen ion conductivity, and rich magnetic behavior, which makes them promising materials for different applications. $Ca_2Mn_2O_5$ and $Ba_2In_2O_5$ are the best examples of the oxygen deficient perovskite. The orthorhombic structure of $Ca_2Mn_2O_5$ has five coordinated square pyramid subunits between manganese and oxygen, in which all five oxygen atoms are linked with adjacent subunits through corner oxygen atoms, as shown in figure 1.3.

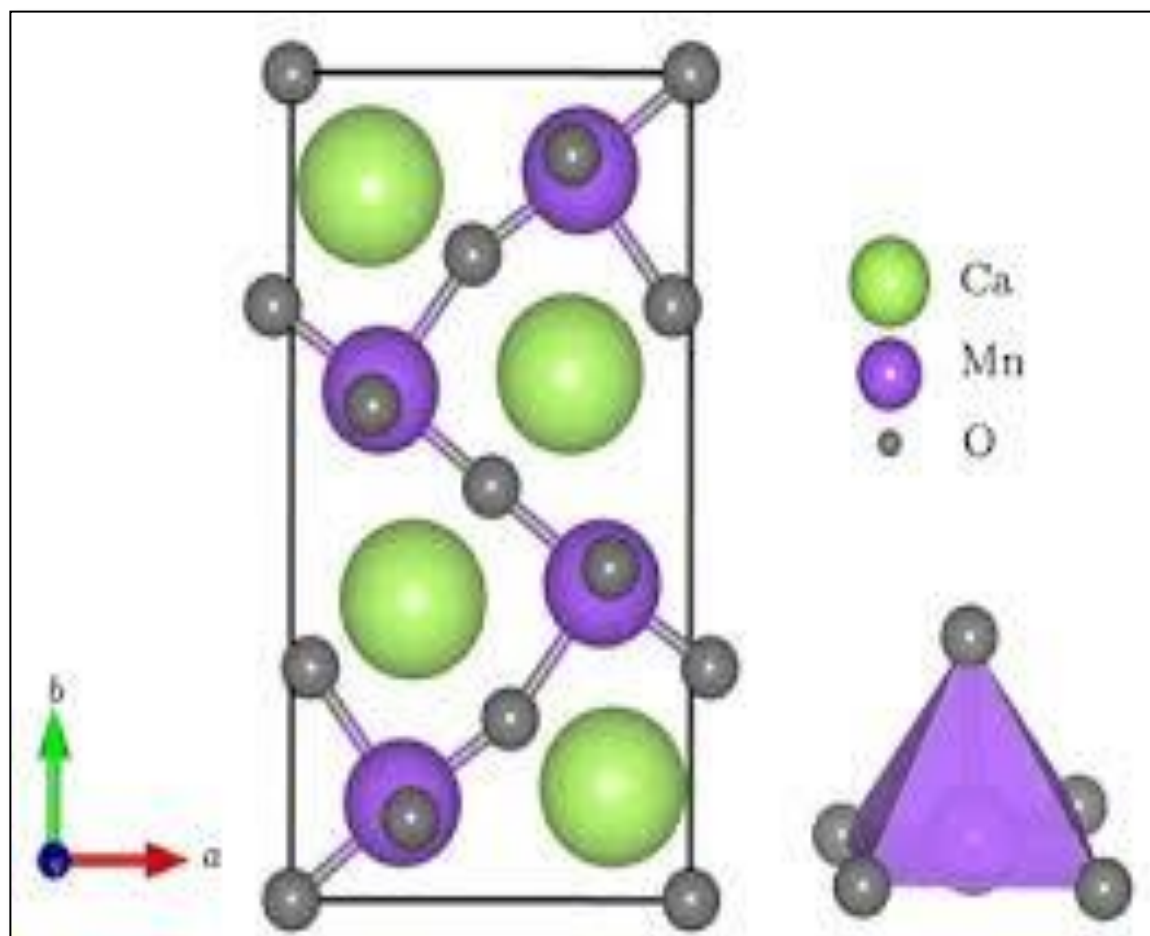


Fig.1.3. Structure of $\text{Ca}_2\text{Mn}_2\text{O}_5$ unit cell showing oxygen vacancy along the direction of normal A B plane.

The orthorhombic CaMnO_3 has six-coordinated octahedral subunits linked through the six oxygen atoms at the corner sites. Thus, oxygen deficient perovskite $\text{Ca}_2\text{Mn}_2\text{O}_5$ has intrinsic molecular level porosity on the oxygen deficient sites, which are beyond structural porosity, such as mesoporosity or macro-porosity [Kim *et al.* (2014)].

Table.1.1. Example of some perovskite explains property application and their use.

Compounds	Typical property	Application	Used
BaTiO ₃ , PdTiO ₃	Ferroelectric, Piezoelectric and Dielectric	Multilayer ceramic capacitors, Positive temperature coefficient resistor and embedded capacitance	Most widely used dielectric ceramic T _C = 125°C
(Ba Sr)TiO ₃ , (Bi, Na)TiO ₃	Ferroelectric, Dielectric	Tunable microwave devices	Used in the paraelectric state
Pb(Zr, Ti)O ₃	Ferroelectric, Piezoelectric	Aerospace vibration control and automobile industry	Piezoelectric transducers actuators
Bi ₄ Ti ₃ O ₁₂	Ferroelectric, Dielectric	High-temperature actuators	Aurivillius compound T _C = 675°C
(K _{0.5} Na _{0.5})NbO ₃ , Na _{0.5} Bi _{0.5} TiO ₃	Ferroelectric, Piezoelectric	Lead-free piezo-ceramics	Sensors, Actuators, Filters, Resonators, Multilayer Capacitor, Transducers
SrFeO ₃ , LaCoO ₃	Electrical conductivity	Alternative dielectric materials and Internal barrier layer capacitors.	Multifunctional material
BiFeO ₃ , LaMnO ₃	Magnetic	Magnetic field detectors and Memories	Most investigated multi ferroic compound. T _C = 850°C
LaCoO ₃ , BaCuO ₃	Catalytic	Cathode material in SOFCs and oxygen separation membranes	Used for Solid Oxide Fuel Cells cathodes.
LaAlO ₃ , YAlO ₃	Host materials for rare-earth luminescent ions	Laser Substrates for epitaxial film deposition	

1.2.2. Complex Perovskite

The complex perovskite $(A'A'')(B'B'')O_3$ type structure are well founded many technological applications due to configurational and compositional ductility of the perovskite octahedral texture. In these structure, cation A shows divalent species, although some compositions also consolidated trivalent rare earth, cation A with charge Indemnity conferred by the simultaneous consolidated of trivalent species like Al^{+3} , Ti^{+3} , and Fe^{+3} on the B site, for example $(Ca_{1-x}Nd_x)(Ti_{1-x}Al_x)O_3$ and $(Pb_{1-x}Ba_x)(Fe_{1-x}Ti_x)O_3$. A and B cations both are large difference in between size and charge, can also resulting in detractive of symmetry and changes the properties like that magnetic and dielectric behavior. The perovskite structure explains excellent latitude in chemical substitutions on both cations and therefore, a great deal over the control properties. The additional composition of perovskite A_3BX and BAX_3 inverse perovskite structure are belong to homologous series, such as $A_{n+1}B_nO_{3n+1}$ (Ruddlesden-Popper) [Ruddlesden *et al.* (1957), Ruddlesden *et al.* (1958)], $A_nB_nO_{3n+1}$ (Dion-Jacobson) [Dion *et al.* (1981), Jacobson *et al.* (1985)], $Bi_2A_{n-1}B_nO_{3n+3}$ (Aurivillius series) [B. Aurivillius (1949), B. Aurivillius (1950), B. Aurivillius (1951)]. The structures of some homologues series perovskite oxide explained anion deficient perovskite with many-sided properties like that $A_nB_nO_{3n-2}$ and its related to ABO_3 perovskite. Ruddlesden-Popper and Dion-Jacobson explained many application and properties of perovskite i.e; ferroelectrics, ionic conductors, superconductors, multiferroic and magneto resistant materials result from a complex and interaction between the crystal structure, electronic state of the transition metal, amount of defects and their mutual interaction. $CaCu_3Ti_4O_{12}$ (CCTO), $Bi_{2/3}Cu_3Ti_4O_{12}$ (BCTO), $Y_{2/3}Cu_3Ti_4O_{12}$ (YCTO) and $La_{2/3}Cu_3Ti_4O_{12}$ (LCTO), are few example of complex perovskite oxide.

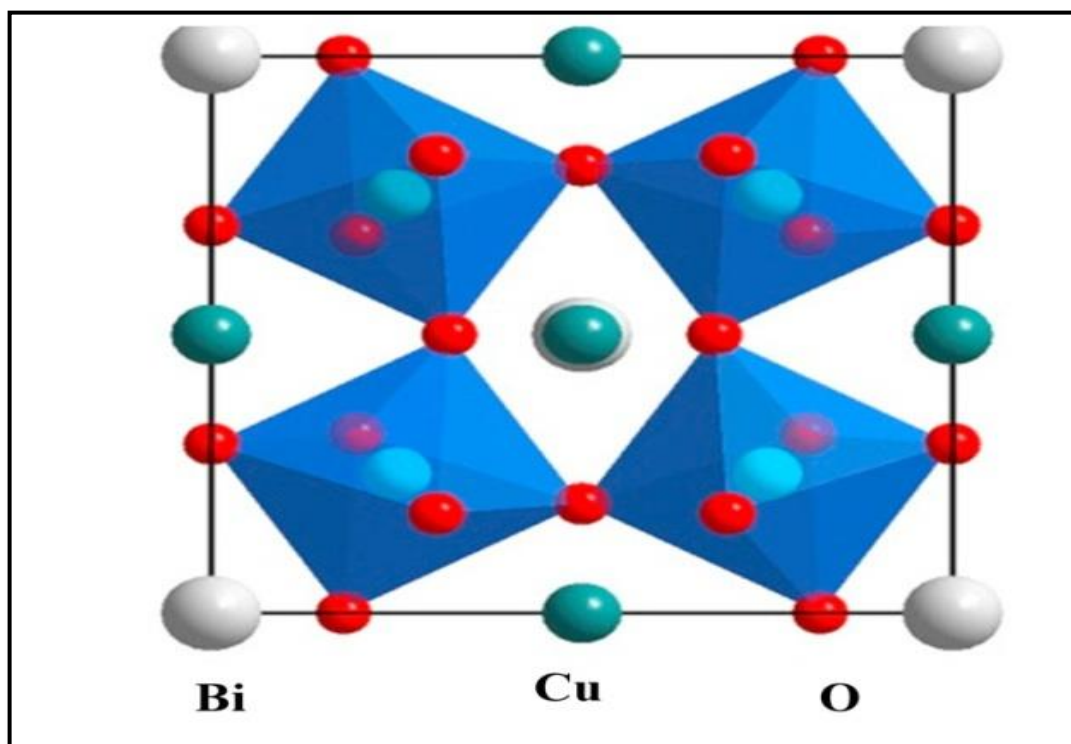


Fig.1.4. Crystal structure of Bi_{2/3}Cu₃Ti₄O₁₂ (BCTO).

Fig.1.4. shows the cubic structure of Bi_{2/3}Cu₃Ti₄O₁₂ complex perovskite and their space group is Im3 and lattice constant $a = 7.413 \text{ \AA}$. In this structure, the Bi sites are 1/3 vacant in order to achieve charge neutralism. This might affect the dielectric behavior, rendition the study of this compound more interesting. The Structure of BCTO similar to CCTO structure of complex perovskite.

1.3. Ceramic Materials

Ceramics are classified into two types, inorganic and non-metallic materials. They are used in our everyday life. These materials are found many properties; weak and strong, opaque and transparent, insulator, friable and tough, conductor and semiconductor, high melting and low melting, polycrystalline, single crystal, and composites etc. [Y.M. Chiang,

P.D. Birnie, W.D. Kingery, (1997)]. In general, there are many different methods used for synthesized materials, like semi-wet route, sol-gel method, solid state route and hydrothermal method.

Ceramic materials show excellent electrical properties and these materials do not allow path of an electric current even in a very strong electric field and thus are good insulators. If electric current allows to another path it shows electrical conductors. However, another route allows electric current flow a certain conditions or when energy thresholds has been reached and thus are useful semiconductors. Some ceramics do not conduct electricity but apply internal charge polarization and store an electrical charge in capacitors [D. W. Richerson, (1992)]. Examples of electro-ceramics like that lead zirconium titanate (PZT) for piezo-electrics, Zinc oxide for varistors, tin oxide as gas sensors, barium titanate for capacitors and lead lanthanum zirconium titanate (PLZT) used for electro-optic devices [D. Segal, (1989)].

Table.1.2. Physical properties and applications of some ceramic materials.

Material	Properties	Application
BaTiO ₃	high permittivity, high breakdown voltage Change of resistance with temperature	Capacitors Thermistors
PLZT	Change of birefringence with field	Electro-optics
PZT	Change of polarization with temperature	Pyroelectrics
LiNbO ₃	High piezoelectric coefficients	Piezoelectric, Transducers
ZrO ₂	Ionic conductivity	Gas sensors
Ferrites	Permeability, coercive field	Magnets
Al ₂ O ₃ , AlN, BeO ₃	Low permittivity, high thermal Conductivity	Packaging, Substrates

1.4. Composite Material

The composite material defined as a mixture of two or more than two materials (fillers, binder and reinforcement) different in composition. Most of the composite material is called the composition of materials or shortened to composites. A composite always shows different physical and chemical properties. Composites include strong ply carrying material is known as reinforcement and weaker materials are called matrix. Composite materials are used for an industrial application for their outstanding resistance to chemicals and most forms of corrosion. The composite materials are many useful and important properties i.e; low weight, low mass, matchless manufacturing and technological possibilities [Satyanarayana *et al.* (1990), Pathania *et al.* (2009)]. The dielectric constant and dielectric loss depend on temperature and frequency it's conclude reinforced composites for various electrical applications such as connectors, terminals, circuit boards, switches etc. Composite materials have excellent mechanical, electrical, chemical properties, which is used for various industries and part of automobile and aerospace.

1.5. Capacitors

The capacitor is a component which has the capability (*capacity*) of stored energy in the form of an electrical charge generates a potential difference across its plates, much like a small rechargeable battery. They are designed to release their energy very quickly. In its basic form, a capacitor consists of two or more parallel conductive plates does not touch each other, but is electrically far either by air or by a good insulating material such as mica, ceramic, plastic waxed paper, and liquid gel as used in electrolytic capacitors. The insulating layer between capacitors plates is known as *Dielectric*. The potential difference between the conductors, a static electric field develops across the dielectric, due to an alignment of

charges in the dielectric. This reason the positive charge to collect on one plate and negative charge on the other plate. The energy of the capacitor is stored in the electrostatic field. The mechanism of working of a parallel plate capacitor in a circuit, including the alignment of charges in the dielectric material is shown in Fig.1.5.

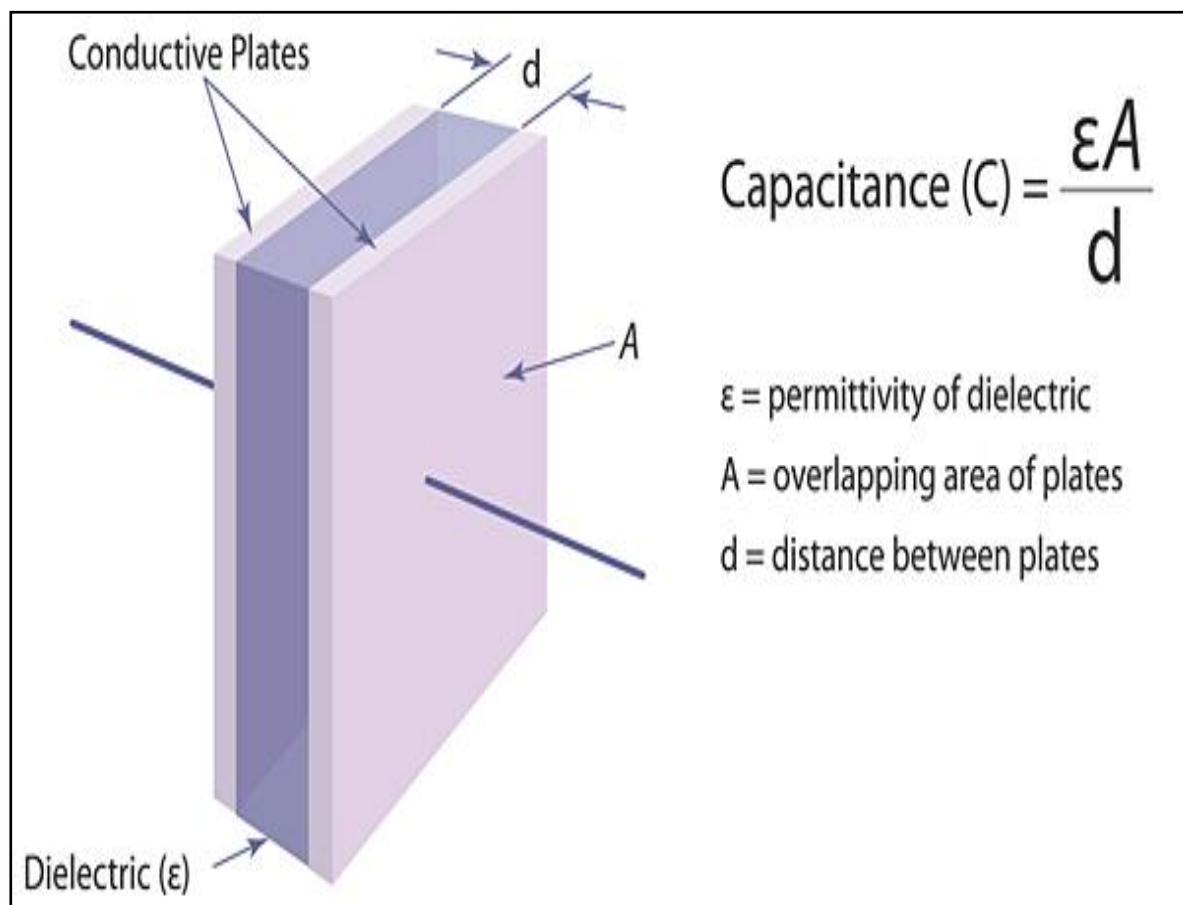


Fig. 1.5. Shows parallel plate capacitors in circuit, including the alignment of charges in the dielectric material [Mark Howard (2015)].

The capacitance of the parallel plate capacitor is shown in the equation:

$$C = \epsilon_0 A/d \tag{1.1}$$

where, ϵ_0 (8.854×10^{-12} F/m) is the permittivity of free space. 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

Ceramic materials described good electrical insulators to as dielectric materials and composite also explain the dielectric and electrical properties. When a dielectric is placed in an electric field, electric charges do not flow through the material, but only slightly shift from their average equilibrium position causing dielectric polarization as shown in Fig 1.6.

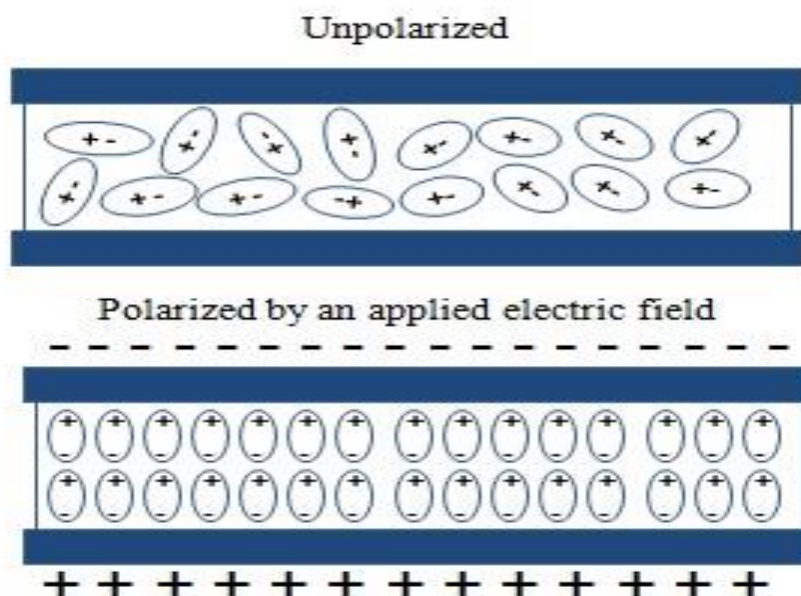


Fig.1.6. The polarized and non polarized plates of an applied electric field [Saint Jude (2012)].

So the system occupies an electrical dipole moment (μ) [D. W. Richerson. (1992)]. These dipole moment found per unit volume is called polarization ($P=\mu/V$). The moment is proportional to the electric field (E) and the polarization is proportional to the applied field [H. M. Rosenberg, (1988)] show in equation

$$P = n\chi_e E \quad (1.2)$$

Where, χ_e is the dielectric susceptibility; n is a constant that describes the dielectric ability to form dipoles [M. Allison, (2007)]. Since the dielectric susceptibility χ_e is equal to (ϵ_r-1) , where ϵ_r is the relative permittivity, the polarization will be [R.M. Rose, L.A. Shepard and J. Wulff, (1971)].

$$P = \epsilon_0 E (\epsilon_r-1) \quad (1.3)$$

The field that a molecule in the inward of a dielectric established between the plates of a charged condenser virtually experiences is known to be larger than the applied field. This is related to the polarization which exhibits on the surfaces of the dielectric. The actual field of a molecule is called the local field (E_{loc}). The dipole moment for a molecule by the local field is given by [R.M. Rose, L.A. Shepard and J. Wulff (1971)].

$$P_{mol} = \alpha' E_{loc} \quad (1.4)$$

where, P_{mol} is a moment and α' shows the polarizability of the molecule. For dielectrics containing N molecules per unit volume, the total dipole moment or polarization is:

$$P = N \alpha' E_{loc} \quad (1.5)$$

Substituting Equation (1.4) in Equation (1.5) gives

$$\chi_e = (\epsilon_r-1) = P / \epsilon_0 E_{loc} = N \alpha' E_{loc} / \epsilon_0 E \quad (1.6)$$

The presence of the dielectric material reduces the effective and various polarization mechanisms: Electronic polarization, orientation (dipolar) polarization, space charge

polarization, and atomic or ionic polarization. The net polarization P of the dielectric material, and is given as:

$$P = P_{\text{electronic}} + P_{\text{ionic}} + P_{\text{molecular}} + P_{\text{interfacial}}$$

1.6.1. Electronic Polarization

Electronic polarization occurs in all dielectric materials. When an electric field (E) acts on an individual atom, the electrons surrounding each nucleus are shifted very slightly in the direction of the positive electrode and the nucleus is very slightly shifted in the direction of the negative electrode and the atom acquires a dipole moment (P), so that:

$$P = \alpha' E \quad (1.7)$$

As soon as the electric field is removed, the electrons and the nuclei return to their original distributions and polarization disappears. The displacement of charge is very small for electronic polarization, so the total amount of polarization is small compared to the other mechanisms of polarization [D.W. Richerson, (1992) H. M. Rosenberg, (1988)].

1.6.2. Orientation Polarization

If the system is composed of heteronuclear (non-symmetrical) molecules then the disposition of the individual atoms within the molecule may be such that the molecule itself has a permanent dipole moment. Examples are H_2O , HCl , CH_3Br , Hf , and $\text{C}_2\text{H}_5(\text{NO}_2)$ [H. M. Rosenberg, (1988)]. For the H_2O , the covalent bonds between hydrogen and oxygen atoms are directional such that the two hydrogen atoms that have a net positive charge are on one side of the oxygen that has a net negative charge. Under an electric field, the molecule will align with the positive side facing the negative electrode and the negative side facing the positive electrode [D. W. Richerson, (1992)]. A molecule which is composed of different atoms is not necessarily polar. e.g. CO_2 is non-polar because the carbon and

oxygen atoms are arranged in a straight line with the carbon in the middle as shown in table 1.3. H₂O is polar because the ions are arranged in a triangle (table 1.3) [H. M. Rosenberg, (1988)]. Orientation polarization is better than electronic polarization, because larger charge displacement is possible in the comparatively a large molecules compared to the difference between electrons and nucleus in particular atoms [D.W. Richerson, (1992)]. In solids, however, the molecules are usually too tightly bound for the orientation polarization to occur. It is much more important in liquids and gases. Due to the randomizing effect of the thermal vibrations this type of polarization is more effective as the temperature is decreased and it gives rise to a dielectric constant, which is temperature dependent [H. M. Rosenberg, (1988)].

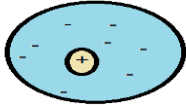
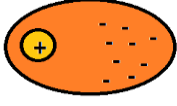
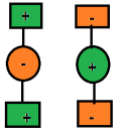
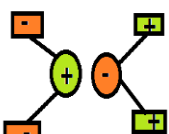
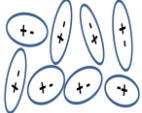

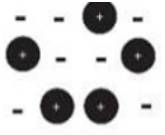

1.6.3. Space Charge Polarization

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)].

1.6.4. Atomic or Ionic Polarization

Atomic polarization involves displacement of atoms (ions) within a crystal structure when an electric field is applied, the field will tend to stretch bonds between the ions and this will change the moment of the molecule. The polarization effects is possible through this mechanism depending on the crystal structure, the presence of solid solution, and other coefficient [D. W. Richerson, (1992), H. M. Rosenberg, (1988)].

Table 1.3. Shows polarization mechanism of dielectric materials

Polarization Mechanism					
Type of polarization	No E field ($E=0$)	Local Field E ($E \neq 0$)	Case where it is Observed	Frequency range where it is predominant	Strength of Polarization
Electronic Polarization			Neutral atoms	$\sim 10^{15}$ 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

1.7. Dielectric Constant

The charge storage capability and extent of polarization of a material is always defined in terms of dielectric constant or relative permittivity. The electric field is applied to two flat plates of a metal, one plate becomes positive and the other negative. The electric field causes polarization in the material in the space between the conductive plates. The relative dielectric constant (k) compares the polarizability of the material with that of the vacuum between the plates [D. W. Richerson, (1992)].

$$k' = k_{\text{Material}} / k_{\text{vacuum}} \quad (1.8)$$

In other references; the relative permittivity is quoted as (ϵ_r), while, ϵ_0 is defined as the permittivity of the free space and ϵ is the permittivity of the dielectric material. The permittivity terms (ϵ_r , ϵ_0 , ϵ) will be used according to Equation (1.9).

$$\epsilon_r = \epsilon / \epsilon_0 \quad (1.9)$$

Materials with low dielectric constant are used for electrical insulator applications. Materials with high dielectric constant are used in capacitors for charge storage and other functions. High dielectric constant materials are favored in the design of embedded capacitors to achieve high energy density in a given space and further miniaturization. In an alternating field, dielectric constant (k) can be expressed as

$$k = \epsilon' - j\epsilon'' = \epsilon_0\epsilon_r - j\epsilon'' \quad (1.10)$$

where, ϵ' is real dielectric constant, and ϵ'' is imaginary dielectric constant. Real dielectric constant (ϵ') is directly related to the material. Ideally, the dielectric constant should be constant with respect to frequency, temperature, voltage, and time. However, each polarization mechanism has a characteristic relaxation frequency. The values of dielectric

materials can also vary with temperature, bias, impurity, and crystal structure by various extents depending on material types [R. K. Ulrich, L. W. Schaper, (2003)].

1.8. Dielectric Loss

Dielectric loss is a material property of the dielectric and is a measure of energy loss of the dielectric during ac operation. Dielectric loss is a result of distortion, dipolar, interfacial and conduction losses. Dielectric loss is expressed as the loss tangent ($\tan \delta$) or Dissipation factor (D_f), and is defined as:

$$\tan \delta = \frac{\sigma}{\omega \epsilon'} \quad (1.11)$$

where, ϵ' , ϵ'' are real and imaginary parts of dielectric permittivity, σ is electrical conductivity of the material and f is frequency. Energy loss (W) which is defined as the energy dissipated in a dielectric material is proportional to the loss tangent, and is expressed as:

$$W \approx \pi \epsilon' E^2 f \tan \delta \quad (1.12)$$

where E is electric field strength and f is frequency. Therefore, a low dielectric loss is preferred in order to reduce the energy dissipation and signal losses, particularly for high frequency applications. Generally, a dissipation factor under 0.1% is considered to be quite low and 5% is high [R. K. Ulrich, L. W. Schaper, (2003)].

1.9. Impedance

Impedance spectroscopy is a comparatively good and powerful method for characterizing many of the electrical properties of materials and their interfaces with electronically conducting electrodes. It may investigate the dynamics of bound or mobile charge in the bulk or interfacial regions of any kind of solid or liquid material and always used to ionic, semiconducting, mixed electronic–ionic, dielectrics (even insulators),

migration of charge carriers across grain and grain boundaries and other phenomena. Impedance spectroscopy applied a single-frequency voltage or current to the interface and measuring the phase shift and amplitude, or real and imaginary parts, of the resulting current at that frequency using either analog the circuit. The most important technique is based on analyzing the ac response of a system to a sinusoidal perturbation and consequent calculation of the impedance as a function of the frequency of the perturbation.

Impedance spectroscopy spectrum generally define two categories: (a) the material used itself, such as conductivity, dielectric constant, mobilities of charges, equilibrium concentrations of the charged species, and bulk generation–recombination rates; and (b) an electrode–material interface, such as adsorption–reaction rate constants, capacitance of the interface region and diffusion coefficient of neutral species in the electrode used itself.

It is important and not pried that modern advances in electronic automation have included impedance spectroscopy. Sophisticated automatic experimental equipment has been developed to measure and analyze the frequency response to a small-amplitude ac signal between about 10^{-4} and $>10^{-6}$ Hz, interfacing its results to computers chips, industrial quality control of paints, emulsions, electroplating, thin-film technology, materials fabrication, mechanical performance of engines, corrosion, and so on. The impedance can be represented as a real (Z') and imaginary (Z'') component. Depending on the material and hypothesized process, an electrical equivalent circuit can be constructed made of capacitors, inductors, resistors and other elements. Transforms can be used in order to obtain related values from the impedance. A few transformations are listed below [Reddy *et al.* (2006), Choudhary *et al.* (2009)].

Table 1.4. High dielectric constant of few oxide compounds

S.No.	Compound	Dielectric constant	Reference
1.	$\text{CaCu}_{2.70}\text{Mg}_{0.30}\text{Ti}_4\text{O}_{12}$	3.4×10^5	[Singh <i>et al.</i> (2013)]
2.	$\text{Bi}_{2/3}\text{Cu}_3\text{Ti}_4\text{O}_{12}$	2.9×10^4	[Gautam <i>et al.</i> (2017)]
3.	$\text{Ba}(\text{Fe}_{0.5}\text{Nb}_{0.5})\text{O}_3\text{-Bi}_{0.2}\text{Y}_{2.8}\text{Fe}_5\text{O}_{12}$	30000	[Yang <i>et al.</i> (2017)]
4.	$\text{Ba}_{0.75}\text{Sr}_{0.25}\text{TiO}_3$	24000	[Huang <i>et al.</i> (2008)]
5.	$\text{CaCu}_3\text{Ti}_4\text{O}_{12}$	20000	[Tuichai <i>et al.</i> (2013)]
6.	$\text{K}_{0.5}\text{Na}_{0.5}\text{NbO}_3$	20000	[Bobnar <i>et al.</i> (2009)]
7.	$\text{Bi}_{1.5}\text{ZnNb}_{1.5}\text{O}_7$	10,000	[George <i>et al.</i> (2007)]
8.	$0.5\text{BaTiO}_3\text{-}0.5\text{Bi}_{2/3}\text{Cu}_3\text{Ti}_4\text{O}_{12}$	43459	[Khare <i>et al.</i> (2016)]
9.	$\text{Ba}_6\text{Y}_2\text{Ti}_4\text{O}_{17}$	1.5×10^3	[Yadava <i>et al.</i> (2016)]
10.	Eu_2CuO_4	5×10^3	[Salame <i>et al.</i> (2014)]
11.	$0.5\text{Bi}_{2/3}\text{Cu}_3\text{Ti}_4\text{O}_{12}\text{-}0.5\text{Bi}_3\text{LaTi}_3\text{O}_{12}$	13.9×10^3	[Gautam <i>et al.</i> (2017)]
12.	$\text{CaCu}_{2.9}\text{Zn}_{0.1}\text{Ti}_4\text{O}_{12}$	5971	[Singh <i>et al.</i> (2013)]
13.	$\text{Y}_{2/3}\text{Cu}_3\text{Ti}_{3.95}\text{In}_{0.05}\text{O}_{12}$	5068	[Singh <i>et al.</i> (2016)]
14.	$\text{Bi}_{0.5}\text{Na}_{0.5}\text{TiO}_3$	5000	[Lin <i>et al.</i> (2004)]
15.	$(\text{Ba}_{0.95}\text{Ca}_{0.05})(\text{Ti}_{0.96}\text{Zr}_{0.04})\text{O}_3$	3910	[Yang <i>et al.</i> (2011)]
16.	SrTiO_3	2150	[Penn <i>et al.</i> (1997)]
17.	$\text{Bi}_4\text{Ti}_3\text{O}_{12}$	1400	[Xiang <i>et al.</i> (2006)]

The real and imaginary parts of the complex dielectric constant are represented as:

$$\epsilon' = \frac{Z''}{\omega C (Z'^2 + Z''^2)} \quad (1.13)$$

$$\epsilon'' = \frac{Z'}{\omega C (Z'^2 + Z''^2)} \quad (1.14)$$

The real and imaginary parts of complex electric modulus are represented as:

$$M' = \omega C Z'' \quad (1.15)$$

$$M'' = \omega C Z' \quad (1.16)$$

The loss tangent is given as

$$\tan \delta = \epsilon'' / \epsilon' = M'' / M' \quad (1.17)$$

the radial frequency, ω , is given as

$$\omega = 2 \pi f \quad (1.18)$$

with f being the frequency and the vacuum capacitance C is given in above (equation 1.1)

$$C = \epsilon A / d$$

with A is the area of the electrode and d is the thickness of the dielectric layer.

1.10. Magnetic Properties

Magnetism has its origin in the motion of charged particles, and the intrinsic magnetic moments (spins), of particles. The definition of the magnetic moment (m) due to movement of charge is

$$m = I \vec{S} \quad (1.19)$$

where \vec{S} is a vector area enclosed by the current loop. Three most important facts apply to magnetic materials are:

- a) Mostly magnetic materials are magnetic even in absence of any magnetic field and become magnetic when a weak magnetic field is applied.

- b) Some magnetic material heated at a certain critical temperature its shows very weak magnetization.
- c) Most of the magnetic materials show the magnetic response in the opposite direction of applied field.

The magnetic properties of gas, liquid and solid exhibited weak magnetic effect but greater periodicity of atoms in solids leads to stronger co-operative effects. Whereas the interplay of magnetic field is such that the magnetic moments of the atom is aligned, this leads to a very strong magnetic field called as ferromagnetism below a certain temperature known as Curie temperature (T_c).

“Which critical temperature materials lose their permanent magnetic properties, to be replaced by induced magnetism it’s known as the Curie temperature”.

In other words, we can say paramagnetic properties change to ferromagnetic behavior. The magnetic effects are found in the magnetic materials due to the atomic magnetic dipoles. These dipoles results are always presenting effective current loops of electrons in atomic orbits, due to these effects of electron spin and from the magnetic moments of atomic nuclei. However, the motions of the charged particle, form closed electric current loops; both are equivalent to magnetic dipoles. When such dipoles are subduced to the external electric field and them deportment a torque, which tends to align their magnetic moments in the direction of applied field. The degree of alignment is characterized by the total magnetic moment per unit volume is known as magnetization. The magnetic moment per unit volume is related to the applied magnetic field by the relation

$$m = \chi H \quad (1.20)$$

where χ is called the magnetic susceptibility of the material.

“Magnetic susceptibility is factually a measure of a material’s magnetization when subject to an applied macroscopic magnetic field”. Hence, substances with a relatively small negative magnetic susceptibility are classed as diamagnetic and positive magnetic susceptibility exhibited paramagnetic.

1.10.1. Types of Magnetic Materials

a) Diamagnets

Diamagnetic materials were exhibited negative magnetism and magnetic susceptibility to diatomic materials and susceptibility is independent of temperature. Diamagnetic materials opposed to an applied magnetic field, and therefore, to be repelled by a magnetic field which has no net magnetic moment [Akshay Kutumbale (2017)].

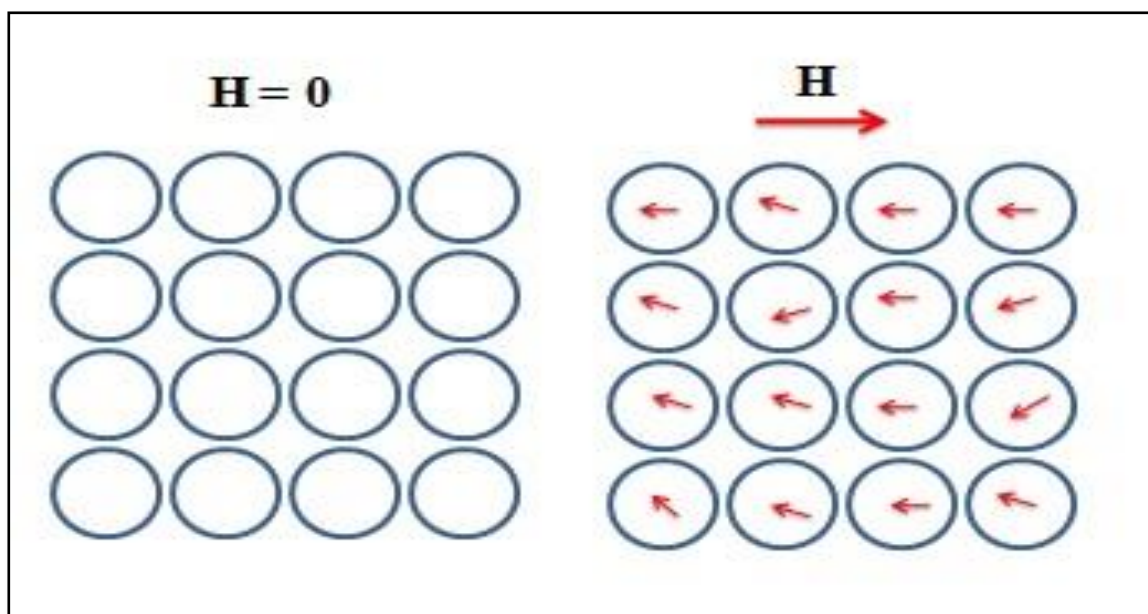


Fig.1.7. Diamagnetic structure of the materials.

The universal occurrence, diamagnetic behavior 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 electrons' orbital motions.

b) Paramagnets

Some materials exhibited permanent magnetic moments of atoms or ions which are act individually with mutual interaction and randomly distributed, this effect is called paramagnetism. However, in presence of the magnetic field, the magnetic moments align themselves in the direction of field. If there are no opposing forces acting, complete alignment of the magnetic moments can be produced and the specimen as a whole acquires a large magnetization in the direction of the applied field. However, the thermal agitation of atoms opposes the tendency and stab to keep the atomic dipoles in random directions. This results in only the partial alignment towards the field direction. Therefore, a very weak magnetization and small susceptibility are observed in the paramagnets.

Effectively materials with atoms of unpaired spins are paramagnetic. The variation of paramagnetic susceptibility with temperature is described by Curie's law.

$$\chi = C/T \quad (1.21)$$

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 Curie's law using the idea of a molecular field.

$$\chi = C/(T - \theta) \quad (1.22)$$

This equation is known as the Curie-Weiss law. where θ is a measure of the strength of the magnetic interaction [Cullity (2011)].

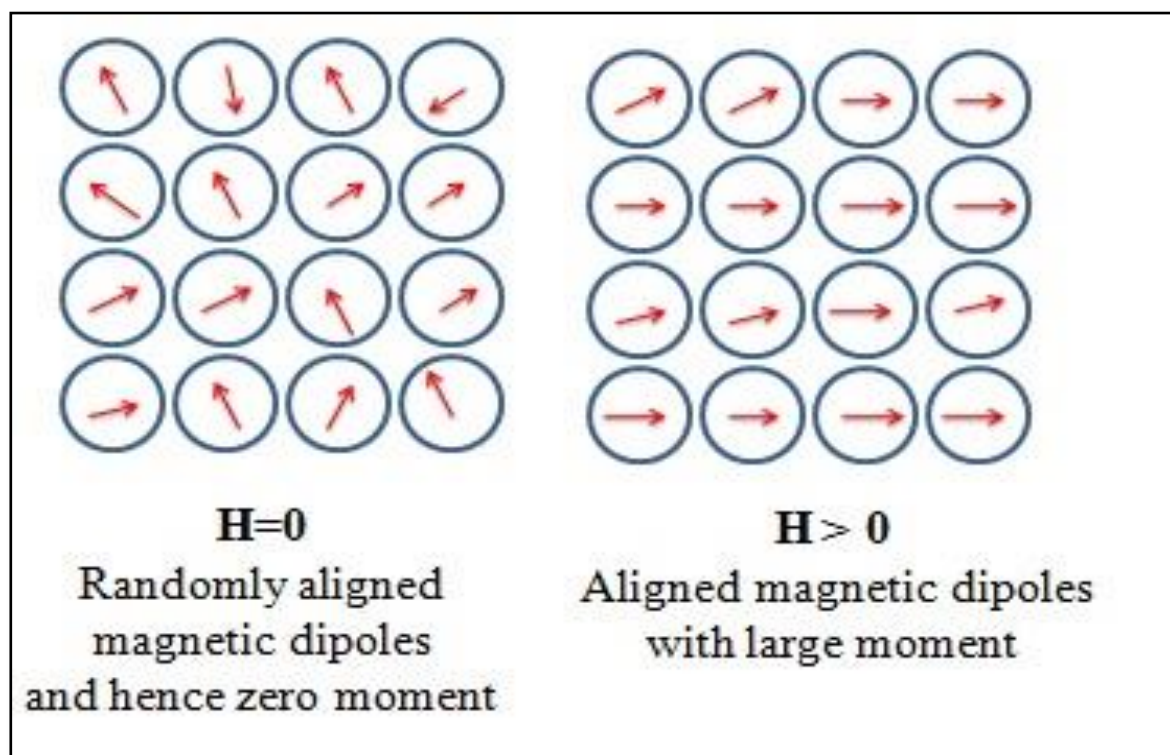


Fig.1.8. Paramagnetic structure of the materials.

c) Ferromagnets

Ferromagnetic materials like a paramagnetic substance have unpaired electrons and show permanent magnet. Since it exhibits magnetic property even in the absence of an applied field, however, it is found experimentally that the magnetization is increased when an external magnetic field is applied to the specimen. The magnetic moments of the electrons in the material spontaneously line up parallel to one another. All ferromagnetic materials have maximum temperature where the ferromagnetic property disappears as an

effect of thermal agitation. Ferromagnetic materials are paramagnets above the Curie temperature. Mostly ferromagnetic materials exhibit hysteresis. Hysteresis gives the response of materials to change in the applied field [Bakonyi *et al.* (2005)].

Below T_c Above T_c
Ferromagnetic \longleftrightarrow Paramagnetic

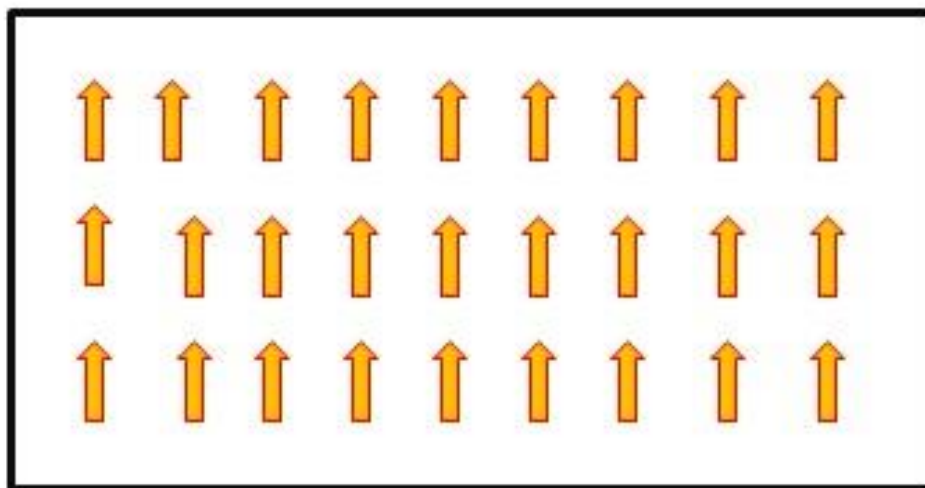


Fig.1.9. Ferromagnetic structure of the materials.

d) Hysteresis Loop

A hysteresis loop was found in between the induced magnetic flux density (B) and the magnetizing force (H). It is indicated to as the B-H loop. Figure 1.10 of hysteresis loop is shown below.

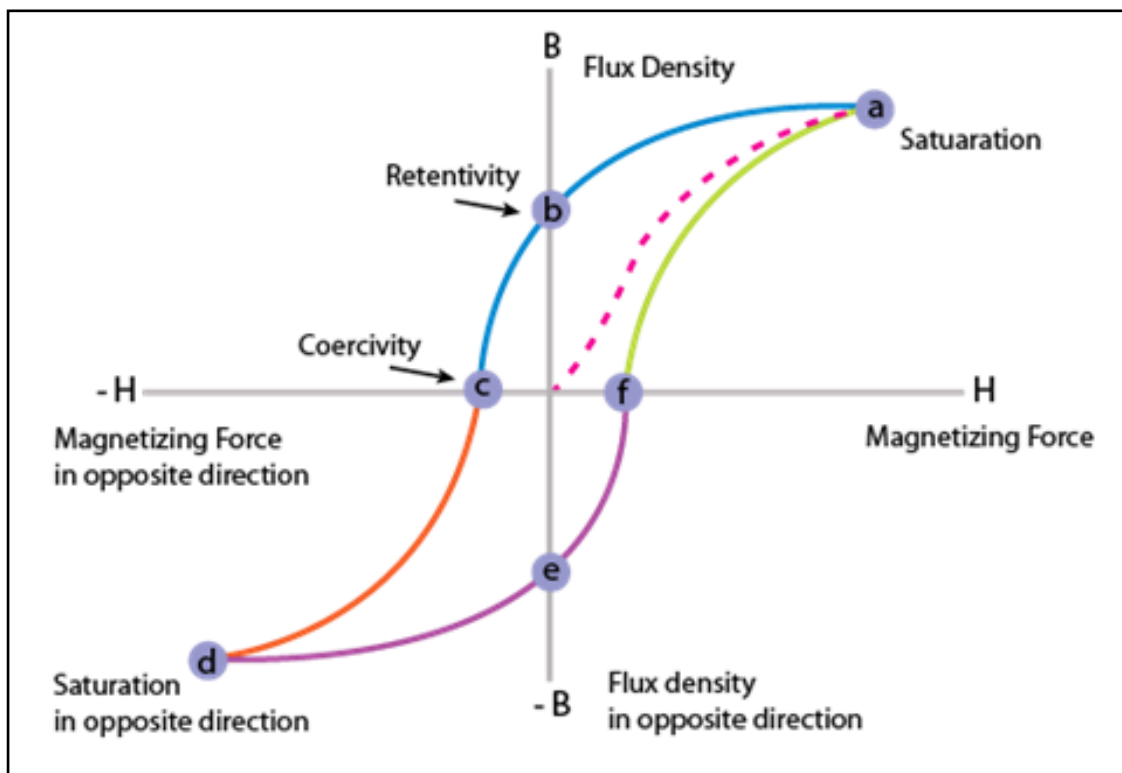


Fig.1.10. Hysteresis loop of the ferromagnetic materials.

The applied field is increased to a large positive value which is largely saturated the polarization of the material, B is then reduced to a negative value which is large enough to produce a saturation in reverse direction and then increased to zero once more. A symmetrical closed loop is obtained known as hysteresis loop. The magnetic induction remaining when the applied field is reduced from saturation to zero is called remanance, H_r . The size of the negative field required to reduce the induction to zero is called the coercivity H_c . In ferromagnetic materials, the spontaneous magnetization occurs below a certain temperature called as Curie temperature (T_c) and susceptibility given by Curie-weiss law.

e) **Anti-ferromagnets**

Anti-ferromagnetism materials exhibited complete magnetic moment cancellation, which has no net magnetic moment. The anti-ferromagnetic substance, the magnetic interactions occurs anti parallel coupling of adjacent atoms or ions, there is no spontaneous magnetization below the critical temperature. “Which above critical temperature, an anti-ferromagnetic substance loses its antiferromagnetism and becomes paramagnetic” this temperature is known as Neel’s temperature.

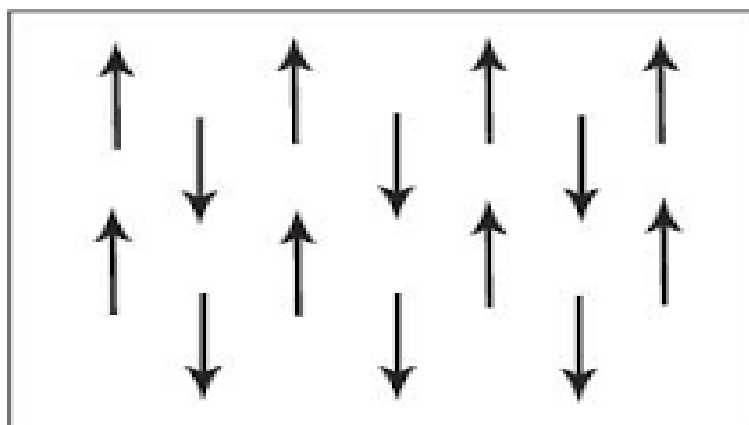


Fig.1.11. Anti-ferromagnetic structure of the materials

f) **Super-paramagnets**

A super-paramagnetic material shows small magnetism in ferromagnetic or ferromagnetic nano particles. It will exhibit a remnant magnetization and coercivity both of zero. Super-paramagnetic materials play a major role in the hard disk drive technology. Super-paramagnetic materials are also found in nature in various rocks and living organisms. Super-paramagnetic materials made of very small single-domain non-interacting

magnetic. The super-paramagnetic behavior is characterized by a typical relaxation time τ ; the time which the systems need to achieve zero magnetization after an external magnetic field is switched off:

$$\tau = \tau_0 \cdot \exp(KV/K_B T) \quad (1.23)$$

where τ_0 is the characteristic time (10^{-9} S), K is the anisotropy energy and V the volume of the particle: K_B is the Boltzmann constant, T is the temperature.

1.10.2. Hard and Soft Magnetic Materials

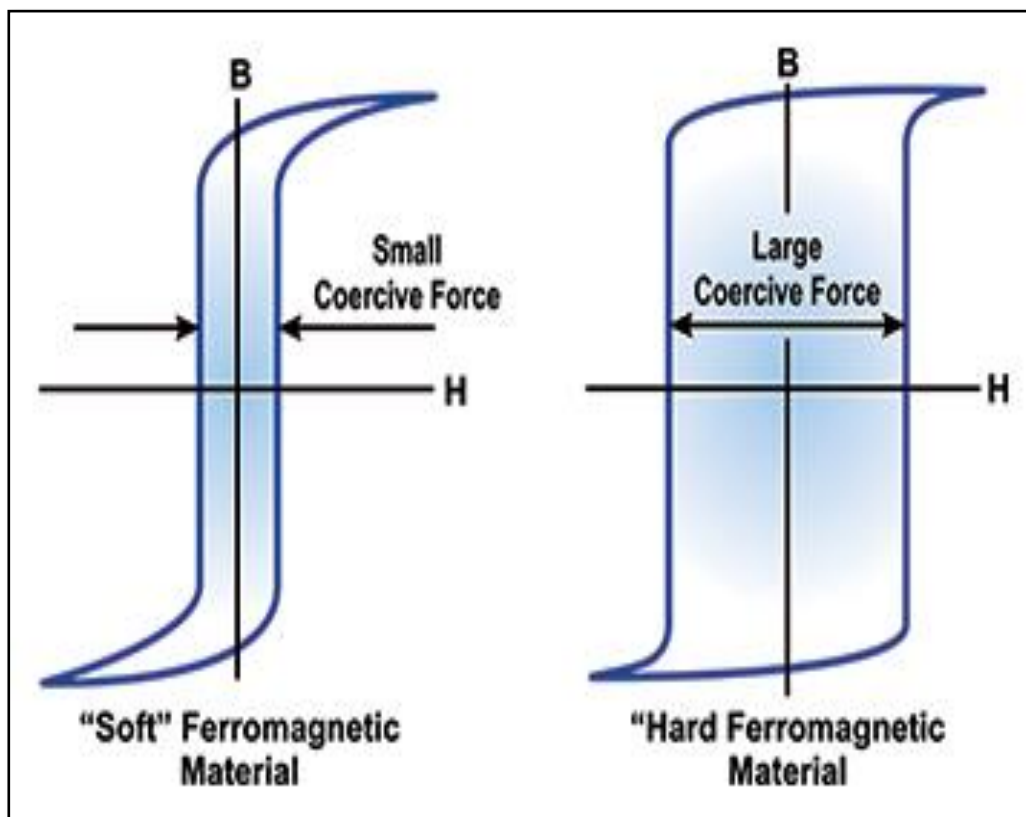


Fig.1.12. The hysteresis loops of soft and hard magnetic materials [Georges *et al.* (2014)].

a) Soft Magnetic Materials: Soft magnetic materials are used for making temporary magnets and easily magnetize and demagnetize. These materials should not possess any void and its exhibited mostly homogeneous structure, so that the materials are not affected by impurities. 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.

b) Hard Magnetic Materials: Hard magnetic materials generally show low initial permeability and high coercive force. These materials are generally used for disk media or for a permanent magnet application. Hard magnetic materials have large hysteresis loss due to large hysteresis area. Susceptibility and permeability of these materials low whereas coercivity and retentivity values are high.

1.11. Literature Survey

1) Calcium Copper titanate ($\text{CaCu}_3\text{Ti}_4\text{O}_{12}$)

A family of $\text{ACu}_3\text{Ti}_4\text{O}_{12}$ ($A = \text{Ca}, \text{Ba}, \text{Sr}$) compounds was discovered in 1967 [Deschanvres *et al.* (1967)] and their accurate structures were determined in 1979 [Bochu *et al.* (1979), L. Singh *et al.* 2014]. $\text{ACu}_3\text{Ti}_4\text{O}_{12}$ type oxides have a complex perovskite structure and are well known for their ability to produce high dielectric constants which have led to many important applications [Subramanian *et al.* (2000)] and first time suggested high dielectric constant of $\text{CaCu}_3\text{Ti}_4\text{O}_{12}$ [Subramanian *et al.* (2000), Ramirez *et al.* (2000)]. CCTO has a pseudo-cubic perovskite structure with the space group of $\text{Im}\bar{3}$ and the lattice parameter of 7.391\AA [Bochu *et al.* (1979)]. The very high dielectric constant ($\sim 10^4$) value exhibited by (CCTO), which is nearly constant in the temperature range of 100–600 K, makes it a promising material for many important industrial applications in microelectronics and memory devices as static dielectric constant of a material ultimately decides the degree of miniaturization. It may widely be used in the electronic industries to manufacture electronic components such as multilayer capacitor (MLCC), dynamic random access memory (DRAMs), microwave devices, electronic devices in automobiles and aircrafts [Yu *et al.* (2008), Ezhilvalavan *et al.* (2000), Kretly *et al.* (2003), Kretly *et al.* (2004)]. After several investigations, researchers have been reported on the dielectric properties of polycrystalline and single crystal CCTO ceramics, their high loss tangent ($\tan \delta > 0.05$ at 1 kHz) is still the most serious problem for applications based on capacitive components. Therefore, creation of a lead free high dielectric material with high dielectric constant and low loss tangent ($\tan \delta$), and good stability in wide temperature and frequency ranges are highly desired.

Subramanian *et al.* (2002), had interpreted the high dielectric constant in terms of its intrinsic crystal structure, i.e; arising from the local dipole moments which are associated with off center displacement of Ti ions, but the transition to a ferroelectric state is frustrated by the TiO₆ octahedral tilt being required to accommodate the Cu⁺² square planar coordination. However, noticing the existence of high degree of twinning with small domains in the single crystal, they also suggested that these twin boundaries might act as the barrier layer capacitance, thus offering a possible extrinsic explanation for the observed giant dielectric property.

In a study by Ramirez *et al.* (2000), it was speculated that the collective ordering of local dipole moments may be one of the possible reasons for its high dielectric constant value. In a single crystal, spatial in homogeneity of local dielectric response can give rise to giant dielectric constant [Cohen *et al.* (2003)]. Lunkenheimer *et al.* (2004) shown that the high dielectric constant in CaCu₃Ti₄O₁₂ is due to contact-electrode depletion effect. To date, the internal barrier layer capacitor (IBLC) formation explanation of giant permittivity value is comparatively widely accepted. Although, CCTO possesses giant dielectric constant, the dielectric losses are too high to commercialize it.

Dubey *et al.* (2011), suggested that Giant, static dielectric constant ($\sim 10^4$) exhibited by pseudo perovskite CaCu₃Ti₄O₁₂ (CCTO) can make it important for many applications in microelectronics and memory devices. Its dielectric constant remains almost unchanged between 100 and 500 K in the frequency range 10^2 – 10^6 Hz [Subramanian *et al.* (2002), Sinclair *et al.* (2002), Cohen *et al.* (2003)]. At temperature below 100 K, the dielectric constant drop rapidly to around 100 without any structural phase transition. In order to

explain the giant dielectric constant, several models have been proposed [Sinclair *et al.* (2002), Cohen *et al.* (2003)].

Sinclair *et al.* (2002), demonstrated that $\text{CaCu}_3\text{Ti}_4\text{O}_{12}$ is electrically heterogeneous with semiconducting grains and insulating grain boundaries, which forms internal barrier layer capacitor (IBLC).

Ahmadipour *et al.* (2016), study on Calcium copper titanate (CCTO) and suggested that CCTO has a novel electro-ceramic material with high dielectric constant of approximately 100,000 for single crystal and 10,000 for bulk material at room temperature. In addition, CCTO shows moderate dielectric loss ($\tan \delta \sim 0.15$) at a broad frequency region (up to 10^6 Hz), high positive temperature coefficient of resonant frequency ($\tau_f \sim +9.13$ ppm K^{-1}), and phase transition stability against temperatures of a wide range (100–400 K). The study of CCTO has been attracting interest due to its molecular structure and wide applications. For instance, it has been applied in capacitors, antennas, microwave devices, and sensors. CCTO for sensor applications shows benefit from the point of view of its polycrystalline porous nanostructures. One of the most significant properties of CCTO sensor is to detect and monitor gases and toxic species without decomposition or change in their structural arrangements. Researches have been carried out on CCTO to enhance its sensitivity and selectivity on gas sensing, chemical and bio-sensors. However, little work has been published on some aspects of CCTO sensing applications, and this still remains as a potential research area. The CCTO gas sensor is considered non-ohmic device because electric properties are greatly dominated by grain–boundary interface states [Bueno *et al.* (2008)]. These non-ohmic ceramic devices are also known as “metal-oxide” varistors

(variable resistors) applications of which are technologically important because of their electric characteristics that enable them to be used as solid-state switches with large-energy-handling capabilities. The varistors are also known as voltage-dependent resistors because they show a highly nonlinear current–voltage (I–V) characteristic. The first voltage-dependent resistors polycrystalline ceramics were developed around early the 1930s by the Bell System and consisted of partially sintered compacts of SiC. A voltage-dependent resistor-based system with very superior performance based on CCTO composition was announced in 2005 by Il-Doo Kim [Kim *et al.* (2006)], although parallel developments were reported in Brazil in the early part of 2008 [Joanni *et al.* (2008)]. This research revealed a mechanism responsible for remarkable electron transportation (n-type or p-type conductivity) which depends on the synthesis methods and experimental conditions Heiland *et al.* (1954), Bielański *et al.* (1957)].

2) Structure of $\text{CaCu}_3\text{Ti}_4\text{O}_{12}$

The crystal structure of CCTO [Whangbo *et al.* (2006)], shown in Fig.1.13 can be obtained from the ideal cubic perovskite structure by superimposing a body-centered ordering of Ca^{+2} and Cu^{+2} ions share in A-site [Adams *et al.* (2006)]. The size difference between Ca^{+2} and Cu^{+2} causes the TiO_6 octahedra to undergo remarkable tilting, leading to a body-centered cubic super cell of space group $\text{Im}\bar{3}$. Consequently, the Ti^{+4} ions engrossed centro-symmetric position in the octahedral sites. The tilted angle is so appropriate that the Cu^{+2} ions occupy mostly a square-planer environment [Ahmadipour *et al.* (2016)]. Tilting also significantly changes the coordination environments of the A-site cations which lead to a 4-coordinate square-planar environment for Cu and a 12-coordinate icosahedral environment for Ca.

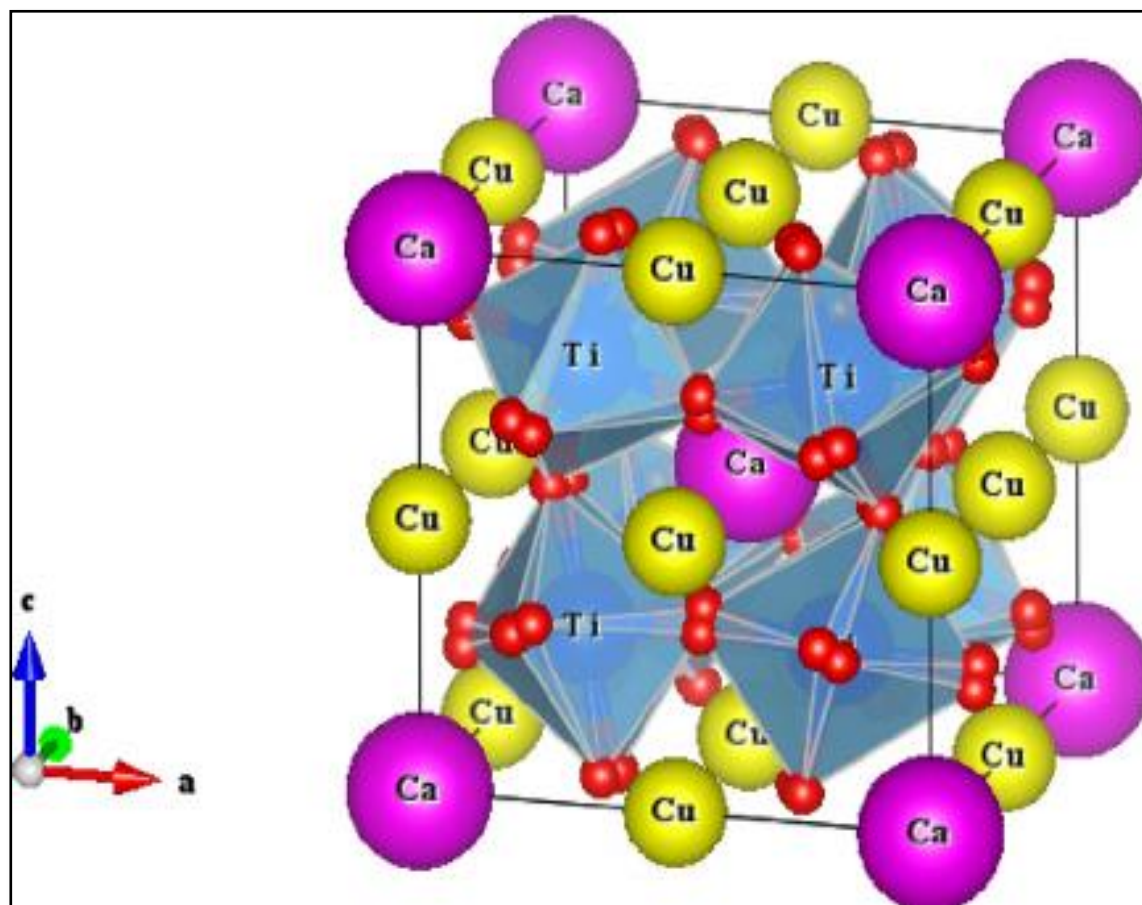


Fig.1.13. Crystal structure of CaCu₃Ti₄O₁₂ (CCTO) ceramic.

It is the mismatch in size and the bonding preferences of these two ions and the titanium that drive the large octahedral tilting distortion. The Ti⁺⁴ cations could be displaced off center along their one–threefold axis. However, this cannot be a pure ferroelectric transition, because the displacements occur along four different directions. Thus, CCTO has a perovskite-type structure where dielectric constant is increased by tension on the Ti-O bonds. Here in this study, an attempt has been made to minimize the loss.

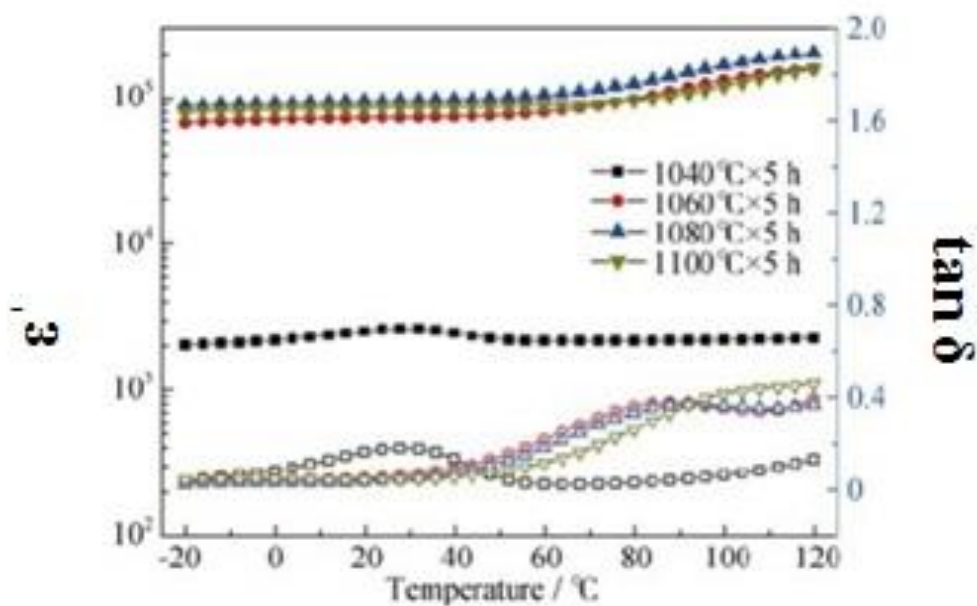


Fig.1.14. Plot of dielectric constant and $\tan \delta$ as a function of temperature for $\text{CaCu}_3\text{Ti}_4\text{O}_{12}$ at few selected temperature at 5 h.

The high dielectric constant of CCTO was found to be 10^5 at 1 kHz that is nearly constant in the temperature range of 100-600K. The value of dielectric constant is however dependent on sintering time and temperature. CCTO samples sintered at 1040, 1060, 1080, 1100 C for 5 h gives dielectric constant 10000 and dielectric loss 0.5 at 100 K show in figure 1.14. The best sample sintered at 1080 °C for 5 h exhibited a high dielectric constant of 98605 with a very low dielectric loss, $\tan \delta = 0.028$ at 1 kHz, which provides a possibility for the application of CCTO in modern microelectronics [Wei *et al.* (2014)]. The dielectric constant of CCTO is relatively high at lower frequencies than that at higher frequencies. The dielectric constant (ϵ') of materials depends on decreasing temperature or increasing

frequency and shows the Debye-type relaxation behavior [Liu *et al.* (2006)]. The characteristic relaxation frequency follows approximately the Arrhenius law [Homes *et al.* (2001), Ramirez *et al.* (2000)]. The high value of dielectric constant at lower frequencies in CCTO has been explained on the basis of barrier layers formation at grain and grain boundaries interface due to slight loss of oxygen occurring sintering of materials.

3) Bismuth Titanium Oxide ($\text{Bi}_4\text{Ti}_3\text{O}_{12}$, BTO)

Vehkamäki *et al.* (2006), Bismuth titanate ($\text{Bi}_4\text{Ti}_3\text{O}_{12}$, BTO) which belongs to a family of layered perovskite compounds first observed by Aurivillius, [Aurivillius *et al.* (1949)] has been widely studied for use as a ferroelectric material in electronics and optics, which can be written as a general formula of $(\text{Bi}_2\text{O}_2)^{+2} (\text{Bi}_2\text{Ti}_3\text{O}_{10})^{-2}$. The layered structure is constructed by alternative stacking of a triple layer of TiO_6 octahedral and a monolayer of $(\text{Bi}_2\text{O}_2)^{+2}$ along the c-axis. Single crystal, BTO have strongly anisotropic ferroelectric properties due to their layered perovskite structure. Although precise study of the structure indicates a monoclinic space group with $a = 5.450 \text{ \AA}$, $b = 5.4059 \text{ \AA}$, $c = 32.832 \text{ \AA}$, and $\beta = 90.01^\circ$, [Rae *et al.* (1990)] in practice the structure is often regarded as orthorhombic as β angle is very close to 90° . The spontaneous polarization of $\text{Bi}_4\text{Ti}_3\text{O}_{12}$ single crystals is angled ca. 4.5° from the a-b plane, resulting in spontaneous polarizations P_s of $50 \mu\text{C}/\text{cm}^2$ and $4 \mu\text{C}/\text{cm}^2$, in the a-b plane and c-axis directions, respectively [Cummins *et al.* (1968)]. BTO shows very high Curie temperature ($T_c = 675 \text{ }^\circ\text{C}$), which makes it useful for various applications such as memory elements, optical displays, and piezoelectric converters of pyroelectric devices in a wide temperature range from 20 to $600 \text{ }^\circ\text{C}$. BTO ceramics have been used in capacitors, transducers, sensors, etc. [Siriprapa *et al.* (2009), Trubnikov *et al.* (2009)]. The tuning of electric properties by compositional modification as well as the size

effect can meet commercial specifications for Curie temperature, conductivity, coercivity, compliance, etc. [Moure *et al.* (2009), Villegas *et al.* (2009)].

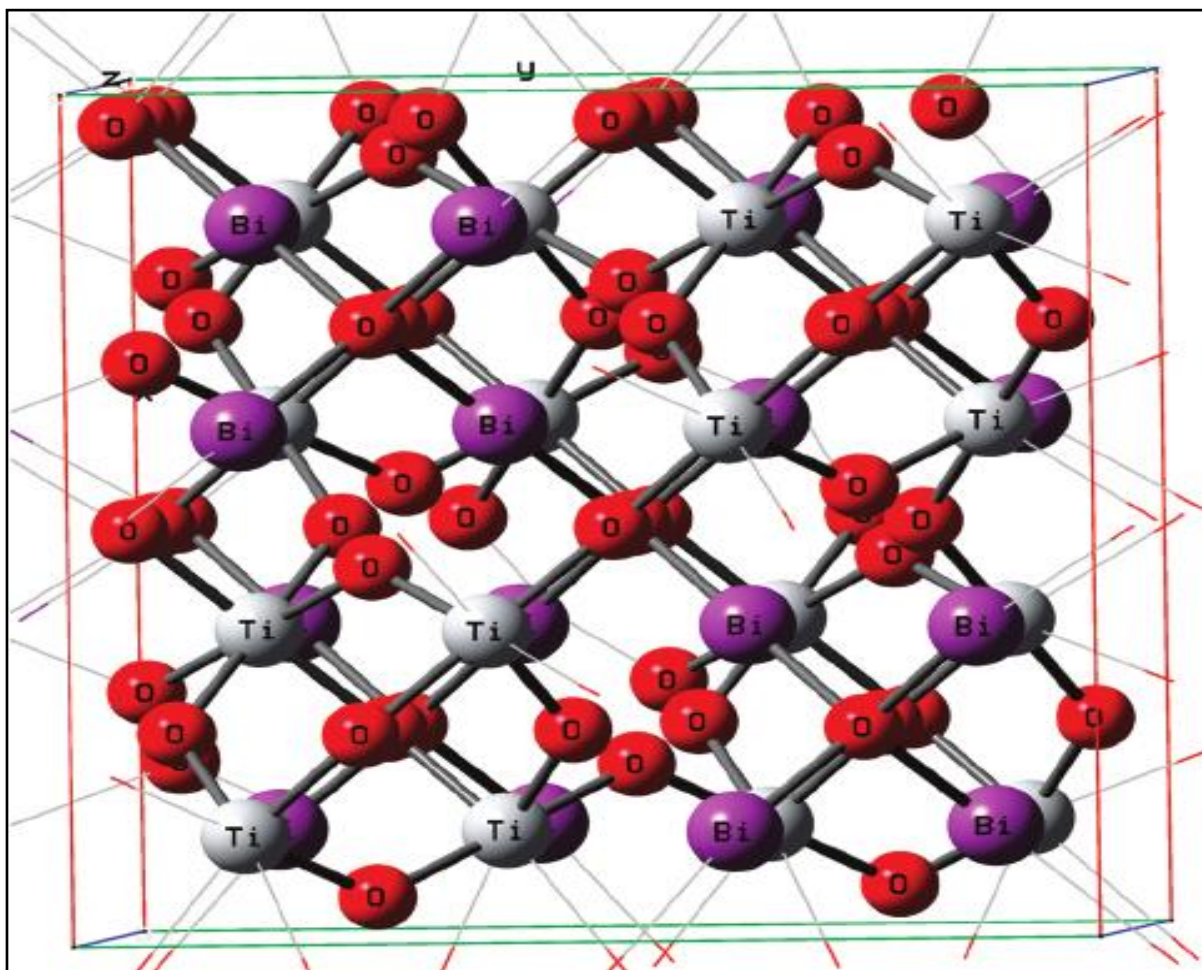


Fig.1.15. Crystal structure of $\text{Bi}_4\text{Ti}_3\text{O}_{12}$.

Macedo *et al.* (2004), explained the high dielectric constant of BTO synthesized by self-propagating high-temperature synthesis technique and suggested that at low temperature the dielectric constant is low and at high temperature dielectric constant is high. Above figure shows the dielectric constant BTO as a function of the temperature, at several frequencies. It

can be seen that the dielectric constant undergoes all frequency dispersion for all temperatures measured, due to the presence of conduction mechanisms in the material.

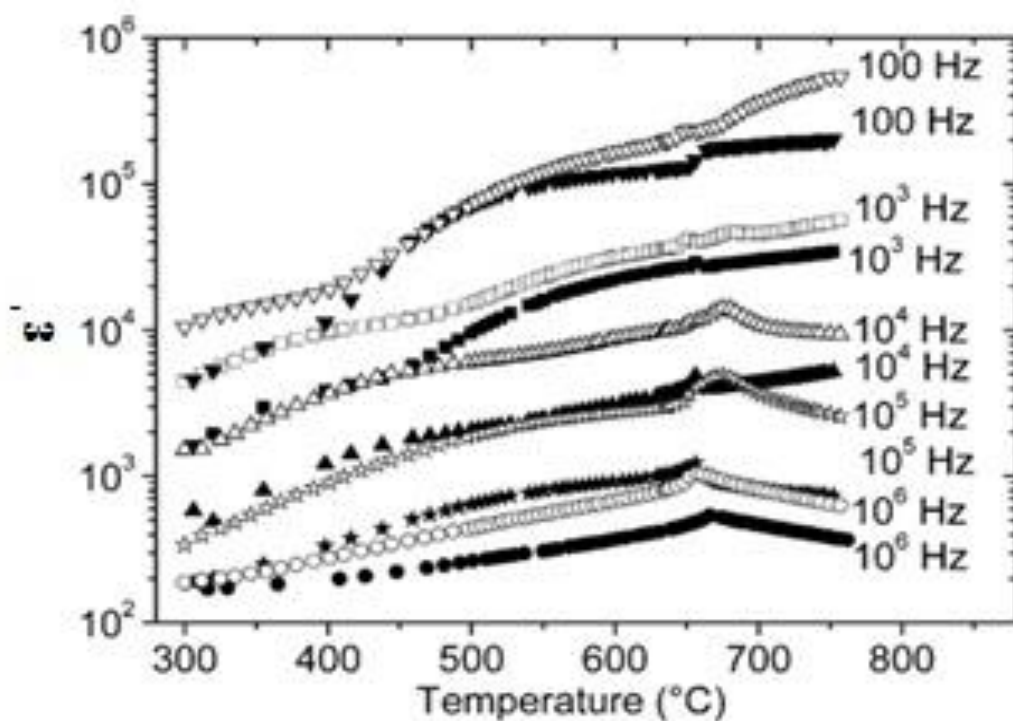


Fig.1.16. Plot of dielectric constant and as a function of temperature for $\text{Bi}_3\text{Ti}_4\text{O}_{12}$ at few selected frequencies.

1.12. Summary

In summary, the giant dielectric constants have been variously replanted to:

- 1) The barrier layer capacitance arising at twin boundaries [Subramanian *et al.* (2000)].
- 2) Disparity in electrical properties between grain and grain boundaries [Sinclair *et al.* (2002), Liu *et al.* (2004), Liu *et al.* (2005)].

- 3) Space charge at the interfaces between the sample and the electrode contacts [Lunkenheimer *et al.* (2002) and Lunkenheimer *et al.* (2004)].
- 4) Polarizability contributions from lattice distortions [S. Y. Chung (2005)].

Differences in electrical properties due to internal domains [Fang *et al.* (2005)],

- i. Dipolar contributions from oxygen vacancies [Li *et al.* (2004) and Fang *et al.* (2004)].
- ii. The role of Cu off-stoichiometric in modifying the polarization mechanisms [Fang *et al.* (2006)].
- iii. Cation disorder induced planar defects and associated in homogeneity [Zhu *et al.* (2007)].
- iv. Nanoscale disorder of Ca/Cu substitution giving rise to electronic contribution from the degenerate states of Cu occupying the Ca site contributing to the high dielectric constant [Wu *et al.* (2005)].
- v. To date, the IBLC explanation of extrinsic mechanism is comparatively widely accepted.

1.13. Aim of the present study

In perspective of above discussed study on unique properties of nanostructure perovskite materials mostly, metal oxide, ceramic and composite materials and their application in different field of science and technology. The continuous demand for miniaturization of electronic device such as cell phones, digital cameras, computers, microchips etc has created a keen interest to explore new capacitor materials exhibiting high

dielectric constant with low loss for application to microelectronics, microwave memory and capacitance based energy storage devices.

CCTO can meet both these requirements due to high thermal stability and colossal dielectric constant, stable between 100-600 K in the low frequency region 10^2 - 10^5 Hz. In fact, the complex perovskite $ACu_3Ti_4O_{12}$ (A= Ca, $Bi_{2/3}$, La) possess high dielectric constant. All of them could be promising candidate to replace relaxors as dielectric in multilayer capacitor (MLCC), dynamic random access memory (DRAMs), super capacitor and other memory device their smaller capacitive component lead to miniaturization of electronic devices with efficient performance. Such materials could be technically significant for introducing the state of arts in semiconductor integrated circuits, owing to their high reliability, high integration potentials good dielectric properties and excellent thermal conductivity as their thermal expansion coefficient close to silicon. It was desirable to investigate systematically new CCTO like materials processing temperature independent high dielectric constant and low dielectric loss with good thermal stability. $Bi_{2/3}Cu_3Ti_4O_{12}$ (BCTO) is very much similar to CCTO and has the same crystal structure.

In the present exploratory work, an attempt has been made to synthesized BCTO and $Bi_3LaTi_3O_{12}$ (BLTO) materials by semi wet route then characterization. In the semi wet route the solution of nitrate of all ions except titanium is used in solid form as TiO_2 . By using this method, these materials can be synthesized at a relatively lower temperature and short duration. The mixing process is performed in a sol state each constituent ion is uniformly dispersed in the resulting mixer after removing organic matter by heating in air. As per present literature, a few works have been reported on BCTO and BLTO ceramic.

Yang *et al.* (2006), have reported the dielectric constant value of BCTO ceramic in kHz range only which was prepared via solid state reaction method and [Tan *et al.* (2010)] also discussed dielectric behavior of BLTO ceramic derived from chemical solution deposition technique. Detail studies on BCTO and BLTO system regarding methods of processing, sintering time and temperature and their stoichiometric variations and its impact on various material properties has yet to be disclosed.

1. The work focused on synthesized BCTO and BLTO ceramic, their composite materials and study on their characterization.
2. The microstructure of the different ceramic will also be studied along with separation of grains and grain boundaries contributions to the electrical and dielectric properties at different temperature and frequencies.
3. The effect of sintering temperature and sintering duration and processing semi wet route or ball milling route etc will be studied so that one can obtain a good quality of BCTO and BLTO ceramic.
4. In the addition an effort will be make to get high dielectric constant and low dielectric loss BCTO and BLTO ceramic suitable for use as capacitor materials showing phase transition paramagnetic to ferromagnetic and also independent on frequency.

With these objectives mentioned the present exploratory research work is to synthesize the following BCTO and BLTO ceramic and its composite would be carried out in the following steps.

1. Synthesis of following ceramic and composite materials:

- $\text{Bi}_{2/3}\text{Cu}_3\text{Ti}_4\text{O}_{12}$ (BCTO)
- $\text{Bi}_3\text{LaTi}_3\text{O}_{12}$ (BLTO)
- $0.5 \text{Bi}_{2/3}\text{Cu}_3\text{Ti}_4\text{O}_{12} + 0.5 \text{Bi}_3\text{LaTi}_3\text{O}_{12}$ (BCLT-55)
- $0.9 \text{Bi}_{2/3}\text{Cu}_3\text{Ti}_4\text{O}_{12} + 0.1 \text{Bi}_3\text{LaTi}_3\text{O}_{12}$ (BCLT-91)
- $0.1 \text{Bi}_{2/3}\text{Cu}_3\text{Ti}_4\text{O}_{12} + 0.9 \text{Bi}_3\text{LaTi}_3\text{O}_{12}$ (BCLT-19)

2. Characterizations of ceramic and composite material

- i. The study of crystal structure and single phase formation of the ceramic composition using X-Ray powder diffraction.
- ii. Study of surface morphology using scanning electron microscopy (SEM)
- iii. Purity and their elemental composition of the materials will be studied by energy dispersive spectroscopy (EDX).
- iv. Study of magnetic behavior for the phase formation of ceramic and composite materials.
- v. Study of dielectric constant and impedance behavior using LCR meter.