CHAPTER 1
GENERAL INTRODUCTION
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1.1. Introduction

Natural resources including water, energy and fertile land are the basis of our life on earth and these resources are back bone of every economy. Current usage rate of these available resources in both developed and developing countries poses a concern for future generations due to their limited availability and non-renewable nature. Global consumption of these natural resources will be almost triple of the current consumption in future. In order to set a limit on the use of natural and non-renewable resources, alternate renewable energy sources have been of huge demand. The usage of alternate energy sources has two aspects, first being production of energy from non fossil sources and second being storage of the produced energy in some viable mean. Thus, the alternate energies sources like solar energy, wind power, fuel cells, geothermal and hydro-electric etc. will be the future energy sources, while energy storage can be in the form of chemical, biological, electrochemical, electrical, mechanical, thermal and electrical etc. In case of electrical energy, the batteries, capacitor, super capacitor, superconductor etc. are the optimum and viable storage media. The usage and performance of such devices rely on the involved active materials like ionic conductors, dielectric or magnetic materials, having appropriate properties. Thus, research on suitable ionic conductors or dielectric or magnetic materials is desired for development of useful devices or media for future generations. In view of this, the current material research has been focused on good ionic conductors or dielectric materials. For practical applications, an ionic conductor should have high ionic conductivity at moderate temperature or room temperature,
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high chemical stability and high compatibility with other components of the devices, while the good dielectric materials should exhibit high dielectric constant, high charge density, low leakage and high breakdown strength. In the present thesis, efforts were made to develop new oxide ion conductors and to study fundamental properties of some dielectric materials, and magneto-dielectric materials.

In this chapter, a brief introduction to the ionic conductor, in particular solid oxide ion conductor and dielectric materials including single phase or composites have been discussed. Also, the present status of the research on oxide ion conductors and dielectric materials is also mentioned. The properties and mechanism of these materials are explained on the basis of their structural features.

1.2. Solid state ionic conductors

Solid state ionic conductors are class of materials which exhibit higher ionic conductivity like liquid electrolyte and form an important part of fuel cell. After the discovery of large electrical conductivities in PbF$_2$ and AgF$_2$ by Faraday in 1938, the study on ionic conduction in solids became a blooming research area in materials science. Generally solid electrolytes are characterized by high ionic conductivity with negligible electronic conductivity. Ionic conduction in solid electrolytes originates from the motion of cations or anions in the bulk solid and they are referred as cationic conductors or anionic conductors, respectively. Such solid electrolytes have many advantages than analogous liquid electrolytes in devices, viz. as electrode materials in electrochemical devices like mobile telephones, laptops and pace makers etc. Ionic conductivity strongly depends on the temperature. At high temperature, conductivity of about 0.1 S/cm (1273 K) can be approached in certain solid electrolytes like yttria
stabilized zirconia (YSZ) and scandia-stabilized-zirconia (ScSZr) etc. [1]. However, certainly there is a need to develop improved electrolyte in terms of high conductivity and chemical stability for versatile application. In order to achieve these properties in a solid ionic conductor, two general research approaches have been followed and they are as follow.

1. Search for new compounds and structures for high levels of ionic conductivity.

2. Modification of existing materials by homogenous or heterogeneous substitution of isovalent or aliovalent ions.

A number of research efforts on ionic conductor show that ionic conduction in solid materials depends on their structural and micro-structural features. Most of the materials studied for oxide ion conduction contain oxygen vacancies and in all of them hopping of \( \text{O}^{2-} \) ions mediated by oxygen vacancies is the major conduction mechanism. Systematic investigations on conduction mechanism of crystalline materials suggest that the structures with following features show high ion conduction.

- Structures having larger unoccupied (vacant) sites equivalent to those occupied sites.
- The energy involved for migration of ions from one occupied site to the unoccupied sites must be small, i.e. site energy of the ions in occupied and unoccupied sites should be close.

Oxide ion conductivity has been observed predominantly in different class of structural materials with either intrinsic oxygen ion vacancies or amenable for the
formation of oxygen ion vacancies. Typical structures with potential to exhibits oxygen ion conductors are explained below.

1.3. Materials exhibiting oxide ion conductivity

As mentioned above, the structural features of crystalline materials have prime importance for exhibiting oxide ion conductivity. There are a number of structure types which has intrinsic structural arrangements or flexibility of the structure for sustaining anion defects and exhibit ion conduction.

1.3.1. Fluorite-type materials

Most extensively studied oxide ion conductors belong to the class of materials having fluorite-type structure. The term “fluorite” originates from the name of the mineral fluorite, CaF$_2$. Oxide ion conductors with the fluorite structure type are an exciting class of materials and are involved in many technological applications. The general formula of fluorite structure is AO$_2$ (where A is tetravalent cation and occupies face centered position of a cubic unit cell with anions (oxygens) in the eight tetrahedral sites) as shown in the Fig.1.1. One important feature of fluorite structure is its ability to sustain a high degree of substitution and large anion non-stoichiometry. Thus, the structure can form a highly disordered anion sublattice leading to fast oxide ion conduction [1b,2].

Thorium dioxide (ThO$_2$), uranium dioxide (UO$_2$) and ceria (CeO$_2$) etc. readily form fluorite-type crystal structure. Since the ionic radius of Zr$^{4+}$ is small to form eight coordinated polyhedra with O$^{2-}$, the zirconia (ZrO$_2$) form fluorite-type structure only at high temperature or by partial substitution with another (usually larger) cations or by creation of anion disorder. Cubic zirconia, a widely studied oxide ion conductor
is an example of fluorite-type oxide ion conductor. A common procedure to get oxide ion conductivity in fluorite structure of ZrO$_2$ is substitution of cation sites with aliovalent rare-earth ion, Y$^{3+}$, Sc$^{3+}$ etc. In order to maintain the electrical neutrality, such doping leads to anion vacancies and oxide ion conduction then proceeds through oxide ion jump via anion vacancies [1b,2]. Y$^{3+}$ is the most common dopant used for stabilizing the cubic fluorite-type phase of zirconia.

![Fluorite structure](image)

**Fig.1.1: Fluorite structure (cubic, Fm3m).**

The ionic conduction in fluorite-type structure is related to the intrinsic or extrinsic vacant sites for anions. Under the influence of an external electric field, the motion of oxygen ions through the oxygen vacancies creates a net current in oxide ion conductors. The easiest jump is along the edge of the cube formed by eight oxygen ions or vacancies. Hence, ionic conductivity of fluorite structure also depends on the size of the dopant ion and it tends to be highest for the cation with ionic radius close to host cation radius, e.g. Zr$_{1-x}$Sc$_x$O$_{2-x/2}$ and Ce$_{1-x}$Gd$_x$O$_{2-x/2}$ (CGO), etc. In such cases the dopants introduce vacancies in the lattice without significant alteration in structure and thus, the clustering or association of defects remains to minimum [2]. Similar to stabilized ZrO$_2$, fluorite-type Bi$_2$O$_3$ (i.e. δ-Bi$_2$O$_3$) is also a known oxide ion conductor. The highest oxide ionic conductivity among the known oxide conductors is observed
in δ-Bi$_2$O$_3$. However, the δ-Bi$_2$O$_3$ phase is stable only at high temperature, i.e. above 1002 K [3]. In order to stabilize the δ-Bi$_2$O$_3$ at room temperature, a number of substituents have been reported in literature [4]. At higher dopant concentrations, such solid solutions based ionic conductors often show a decreasing trend in conductivity. The interaction between the substituted ions and anions or vacancies resulting into defect cluster is the dominating reason for the decreasing trend in conductivity.

1.3.2. Pyrochlore-type materials

The second largest class of material exhibiting oxide ion conduction has pyrochlore-type structure. Pyrochlore oxides are named after the mineral pyrochlore, (NaCa)(NbTa)O$_6$F/(OH). The general formula of the pyrochlore structure is A$_2$B$_2$O$_6$O$'$, where A can be cations with 3+ or 2+ oxidation states and B can be cations with 4+ or 5+ oxidation states. The pyrochlore structure can be considered as an ordered variant of defective fluorite solid solution. In the defect fluorite structure, A and B cations are randomly distributed at face centered positions, whereas oxygen ions are occupied at the tetrahedral sites. The ordered pyrochlore has five different crystallographic sites for ions. The larger (A) cations are located at (16c) with coordinates (0 0 0) and have 8 fold coordination while the smaller (B) cations are occupied at 16d site with ($\frac{1}{2}$ $\frac{1}{2}$ $\frac{1}{2}$) coordinate and have six fold coordination. Two distinct types of anions (O and O$'$) occupy 48f (x 1/8 1/8) and 8a (1/8 1/8 1/8) sites, respectively. An additional position, 8b (3/8 3/8 3/8) is also available for anions in pyrochlore structure. Normally, this site is vacant in A$_2$B$_2$O$_7$ type pyrochlore. The 8a sites are surrounded by four A cations and 8b vacancy sites are surrounded by four B cations as shown in Fig.1.2. [5]. The nature of the polyhedra changes with the oxygen parameter x. The value of x ranges
between the theoretical values of 0.3125 and 0.375. At x = 0.375, the A cations are located in a perfect cube and there is no displacement of oxygen ions from a perfect cubic array whereas, B cations are in the center of highly distorted octahedral. At x = 0.3125, the B cations are in perfect octahedral coordination. Both polyhedra are distorted when the value of x lies between these two values.

Existence and stability of the pyrochlore is governed by the relative cationic radius and oxygen parameter “x”. The $A_2B_2O_6O'$ pyrochlore structure is found to be stable within radius ratio limit $1.40 \leq r_A/r_B \leq 1.71$, whereas the $A^{2+}B^{5+}O_6O_1$ pyrochlore structure, this limit is extended to wider range, viz. $1.4 < r_A/r_B < 2.2$. The cation pairs with $r_A/r_B$ smaller than 1.40 prefer to form defect fluorite structure due to the easy swapping of two cations [5a,6]. Apart from these structural aspects, the stability of pyrochlore also depends upon the temperature, pressure and procedures adopted for preparation. At higher temperature often materials can transform from perfect pyrochlore to defect fluorite structures.

**Fig.1.2: Pyrochlore structure (cubic, Fd3m).**
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As mentioned, the presence of intrinsic vacant oxygen sites makes them potential oxide ion conductor, due to easy migration of anion (oxygen ion) from occupied sites to vacant sites. Such anion migration can result in high oxygen ionic conductivity at higher temperature, viz. $\sim 10^{-2} \text{ S/cm at 1273 K}$ and thus, makes them promising candidates for SOFC (Solid Oxide Fuel Cell) application. Also, the wide tolerance range of composition and nonstoichiometry of pyrochlore compounds makes them favorable for varieties of applications like sensors, catalysts, dielectrics and in nuclear waste management.

In this thesis, two compositions as $\text{A}_2\text{B}_2\text{O}_7$, with $\text{A} = \text{Pr}^{3+}$ and $\text{B} = \text{Zr}^{4+}$ and $\text{Ti}^{4+}$ have been prepared and characterized in details. Among these, the composition $\text{Pr}_2\text{Zr}_2\text{O}_7$ has pyrochlore-type structure due to the satisfying ionic radius criteria. Also, the details of structures and electrical properties of $\text{Ca}^{2+}$ substituted pyrochlore-type $\text{Pr}_2\text{Zr}_2\text{O}_7$ have been explained. The $\text{A}_2\text{B}_2\text{O}_7$ type rare-earth (RE) titanates with $\text{Ti}^{4+}$ as B-site cation form monoclinic perovskite-type structure for $\text{RE} = \text{La}, \text{Nd}$ and $\text{Pr}$. The detailed structural and electrical properties of perovskite-type $\text{Pr}_2\text{Ti}_2\text{O}_7$ are studied in this work.

1.3.3. Perovskite-type materials

Similar to fluorite and pyrochlore, materials with perovskite-type structure have also been reported to exhibit higher ionic conductivity with suitable composition. The perovskite-type $\text{ABO}_3$ materials can give rise to anion vacancy upon substitution of suitable cations either at A or B sites. Several anion deficient perovskite-type materials are considered as promising materials for IT-SOFC (intermediate-temperature solid oxide fuel cell). In such structural materials oxygen ion conduction
occurs when oxygen ion jumps from one vacant site to adjacent vacant sites. Fig.1.3 depicts the structure of an ideal cubic ABO$_3$ perovskite lattice, where A cation are occupied at the corner of the cube and B cations occupy the center of the cube while the oxygen ions are at the face centered positions. In such arrangement, the smaller B cations are octahedrally coordinated by oxygen ions while the larger A cations are coordinated to twelve oxygen ions.

In the ideal cubic perovskite structure each cations (A and B) in the perfect size to be in contact with an oxygen anion, where the B-O distance is equal to a/2 and the A-O distance is a$/\sqrt{2}$, where a is the cubic unit cell parameter. The ratio of these expressions for the cell length is known as Goldschmidt Tolerance Factor and is denoted as $t$, which is applicable at room temperature. Thus, the ions can be assumed as rigid sphere following the relation given below is considered as formation criteria of perovskite structure.

$$r_A + r_o = t\sqrt{2}(r_B + r_o)$$

[1.1]
Where, $r_A$, $r_B$ and $r_O$ are ionic radii of the A and B site cation and oxygen ion, respectively.

The ideal cubic perovskite is formed when $t$ is close to 1 e.g. SrTiO$_3$ and it remains in cubic structure within the limit $0.89 \leq t \leq 1$ [7]. If the A ion is smaller than the ideal case, the $t$ value becomes less than one and it results in lower symmetric structure e.g. orthorhombic GdFeO$_3$ ($t = 0.81$) [8]. If $t$ is in the range of 1.00 to 1.13, the hexagonal symmetry of the perovskite structure is stable e.g. LaAlO$_3$, BaNiO$_3$ etc. Thus, the deviation from the limit of tolerance factor can be used to measure the degree of distortion in a perovskite structure.

The compositional and structural diversity of perovskites arise from the high flexibility of the structure with respect to cationic and anionic substitution, tolerance to distortion and cation order. Cation ordering either at A site or B site gives ordered superlattices for perovskites. The composition A$_2$BB'O$_6$ show the commonest type of cation ordered structure where the B-sites are ordered and the unit cell shows lower symmetry and larger unit cell parameters. The structural diversity in perovskites also arises from another aspect, which is the stacking of alternate AO and BO$_2$ layers. Ruddlesden-Popper (RP), Jacobson-Dion, Aurivillius-types layered perovskite structures are formed due to such stacking variations and differences in the layer structures. The third aspect of the structural diversity of perovskite is nonstoichiometry. The nonstoichiometry in perovskite structure is usually considered with respect to A site or anion deficiencies. In the anion deficiency, the compounds with the general formula A$_2$B$_2$O$_5$ exhibit ordered or disordered anion deficiency. The
Brownmillerite structure and \( \text{Ca}_2\text{Mn}_2\text{O}_5 \) structure are two examples of these ordered structures which are also of importance for solid state ionic conduction.

1.4. **Effect of temperature on ionic conduction**

With increasing temperature, the oxide ions become more labile due to their increasing vibrational amplitude and thus, they easily hop from occupied sites to vacancies. Additionally, the more defects are formed and defect clusters are collapsed with the increase in temperature. Hence, ionic conductivity always shows an increasing trend with increasing temperature. The variation of ionic conductivity, \( \sigma \), with temperature is generally described by Arrhenius equation

\[
\sigma = \frac{A}{kT} \exp \left( -\frac{E_a}{kT} \right)
\]

Where \( E_a \) = activation energy for ion migration, \( k \) = Boltzmann constant, and \( T \) = temperature.

The activation energy, \( E_a \), can be calculated easily from the slope of the \( \ln (\sigma T) \) versus \( T^{-1} \) plot. The pre-exponential factor, \( A \), is given by Eq (1.3)

\[
A = \frac{1}{3} (Ze)^2 n d^2 \nu_0
\]

Where, \( Ze \) is the charge of the carrier ion, \( n \) is the vacancy concentration, \( d \) is the unit jump distance of the ion (usually the closest pair distance), and \( \nu_0 \) is the attempt frequency.

From the above equations, it is clear that the conductivity increases with the dopant concentration. But this is valid only at lower concentration of dopant. At higher level
of dopant concentration the defect association arises, which adversely affects the ionic conductivity.

The ionic conductivity is related to the diffusion coefficient, $D$, through the Nernst-Einstein equation

$$\sigma = nq^2D/k_BT$$  \[1.4\]

Where, $q =$ ionic charge, $n =$ number of ions per unit volume, and $D =$ self-diffusion coefficient of ions.

The diffusion coefficient, $D$ is given as

$$D = zNc(1 - c)a_l^2v/k_BT,$$  \[1.5\]

Where, $Nc =$ concentration of ions, $a_l =$ distance between the sites, $z =$ number of nearest neighbour sites and $v =$ jump frequency.

The jump frequency is related to temperature as below

$$v = v_0 \exp (-E_a/k_BT)$$  \[1.6\]

Where $E_a =$ free energy barrier between two sites, $v_0 =$ site frequency of the ion.

1.5. **Practical importance of ionic conductors**

Solid state ionic conductors have wide range of practical applications some of them are explained below.

1.5.1. **Solid Oxide Fuel Cell (SOFC)**

Fuel cell is an electrochemical device which converts the energy of chemical reaction into electrical energy without involving combustion (heat) as an intermediate step. In a solid oxide fuel cell (SOFC) layout, as shown in the Fig.1.4, the anode and cathode are separated by an electrolyte that is an oxygen ion conducting material. Oxidant gas (usually the air) is supplied to the cathode, and the fuel is supplied to the
anode. Oxidant is reduced at the cathode side and fuel is oxidized at the anode. In general, on the cathode side, oxygen catalytically reacts with a supply of electrons to become oxygen ions, which diffuse through the electrolyte to the anode side. On the anode side, the oxygen ions react with hydrogen to form water and free electrons.

The basic components of a ceramic fuel cell stack are the electrolyte, the anode, the cathode and inter-connect. A load connected externally between the anode and cathode completes the electrical circuit. In this configuration, the difference of the chemical potential between oxidant gas and fuel is converted to the electrostatic potential difference of the anode and the cathode. Thus, the electromotive force can be obtained.

![Solid Oxide Fuel Cell (SOFC) layout](image)

**Fig.1.4: Solid Oxide Fuel Cell (SOFC) layout** [9].

The electrolyte is the prime component in SOFC and it should have several important properties, like (i) high ionic conductivity with negligible or no electronic conductivity (ii) enough mechanical strength (iii) chemical compatibility between...
electrode materials (iv) matching of the thermal expansion coefficient (TEC) with electrode material. Yttria-stabilized zirconia [(Y$_2$O$_3$)$_{0.08}$-(ZrO$_2$)$_{0.92}$] or (8-YSZ) is the most common electrolyte in SOFCs. Concerning to the electrodes, they must have a high electronic conductivity, sufficient porosity to allow transport of products of fuel oxidation from electrolyte/fuel electrode interface, should have high catalytic activity to quickly exchange charges, chemical and dimensional stability, matched thermal expansion coefficient with the electrolyte and interconnect materials. Currently, porous Ni is the most common anode material for SOFC application. Lanthanum manganite, suitably doped with alkaline earth elements La$_{0.8}$Sr$_{0.2}$MnO$_3$ (LSM) and La$_{0.6}$Sr$_{0.2}$Co$_{0.2}$Fe$_{0.8}$O$_3$ (LSCF) are also used as cathode material in standard SOFC.

1.5.2. Oxygen sensors

Oxygen sensors play an important role in pollution control from cement industries, automobile engine management, biological and food processing plants etc. [6]. Oxygen ion conductors can be used in these solid state potentiometric oxygen sensors. When sensor is exposed to gas environment, oxygen molecules gets adsorbed on the porous Pt electrode and dissociates into atomic oxygen, then these oxygen atoms diffuse in to the boundary of electrolyte and to other electrode as O$^{2-}$ ions. The overall reaction can be represented as

$$\frac{1}{2} O_2(g) + 2e^-_{Pt} + V_{O(YSZ)} \rightarrow O_{YSZ}^{X}$$ \hspace{1cm} [1.7]

The concentration of the oxygen in the environment is measured by equilibrium potential measurement on solid electrode–electrolyte cell using Nernst equation. The electrode used in oxygen sensor should possess the good catalytic activity for oxidation, reduction of oxygen and it should have porous microstructure to manifest
enough triple phase boundaries. Concerning to the electrolytes, they need to be a good oxygen ion conductor. YSZ is the most commonly used electrolyte in sensors with air as the reference electrode [10].

1.5.3. Oxygen pump

One of the important applications of oxygen ion conductor is in electrochemical pump to control the oxygen content in a flowing inert gas. It requires the application of external voltage across the wall of the solid electrolyte tube, through which the gases or liquids flow [11]. This technique has been followed for the removal of oxygen from liquid metals [12].

1.6. Literature survey on ionic conductors

Since the discovery of ionic conduction in solid state, research efforts have been made to find new materials and evaluation of the ionic conduction mechanism. Also, in last few decades the research got an impetus for the development of oxide ion conductors for practical application, like fuel cell. For better ionic conduction at lower temperature, electrical properties of wide varieties of materials have been investigated. In the aim of the present thesis work on oxide ion conductors, literatures on various types of potential electrolytes have been surveyed and they are summarized below.

1.6.1. Stabilized zirconia electrolytes

In the aim of solid electrolytes for SOFC, stabilized zirconia is the most widely explored electrolyte. The stabilized zirconia has fluorite type structure which is high temperature polymorph of pure monoclinic zirconia (ZrO$_2$). The cubic form of ZrO$_2$ has the good ionic conductivity but this polymorph cannot be retained below 2573 K [11b,13]. A common procedure to get oxide ion conductivity in zirconia is to stabilize
the high temperature polymorph at ambient temperature by doping of cation with lower valence [Y$^{3+}$, Sc$^{3+}$, Ca$^{2+}$ etc.]. YSZ is one of the best electrolytes considered for SOFC, but shows desired conductivity only at high temperature and thus, not suitable for low temperature applications [14]. Scandium stabilized zirconia (Zr$_{1-x}$Sc$_x$O$_{2-x/2}$, ScSZ) at the 8% doping level of Sc$^{3+}$ can be a potential replacement for YSZ. But high cost of Sc limits its application [1a,15]. Another drawback with ScSZ is that at higher scandia contents (e.g. 10–12 mole %), the cubic phase transforms to a rhombohedral phase. Cubic phase of zirconia can also be stabilized by other dopants Ca$^{2+}$, Yb$^{3+}$, In$^{3+}$, Sm$^{3+}$, Mg$^{2+}$ etc. [16]. The Yb$^{3+}$ substituted zirconia shows comparable conductivity with the YSZ and ScSZ, while Mg$^{2+}$ is the least efficient to improve ionic conduction. In both (YSZ, ScSZ) samples, the conductivity decreases with increasing the dopant concentration due to the association of point defects. The tendency of defect association increases with the increase in mismatch of the ionic radii of dopant and host ions. The effect of ionic radii of dopant ions on ionic conductivity, defect association and oxygen migration enthalpy has been investigated in large number of reports [17]. An alternate strategy to improve ionic conduction and to minimize the defect association in stabilized ZrO$_2$ is by codoping with alkaline earth-cations and other ions [18]. However, no significant improvement has been observed. Another research area of zirconia is focused on improving the density by appropriate sintering procedures, like using sintering aids [19] or using nano sized YSZ prepared by different methods [20].

### 1.6.2. Ceria based systems

Ceria (CeO$_2$) has the fluorite structure at ambient condition and has also been explored extensively for electrolyte application. Doping of CeO$_2$ with other oxides
such as rare-earth or alkaline-earth cations increases the oxygen ion vacancy and these materials exhibit high conductivity at lower temperatures. This makes them superior alternative electrolyte for decreasing operating temperature of SOFC. Like the case of zirconia, the highest conductivity is obtained for the lower size mismatch of the dopant and host radii. Codoping of Gd$^{3+}$ and Sm$^{3+}$ (in concentration of 10 to 20%) in CeO$_2$ shows higher conductivity than the YSZ at low temperature (773 -973 K) [1b]. However, the problems associated with ceria electrolytes is the ease of reduction at low oxygen partial pressure. Partial reduction of the Ce$^{4+}$ to the Ce$^{3+}$ leads to electronic conduction, nonstoichiometric and lattice expansion, which causes internal short-circuiting in the cell and associated mechanical stresses [21]. A number of attempts by the codoping with rare-earth ions have been made to increase the redox stability of these electrolytes [22]. However, this procedure had shown limited success. Ce$_{0.9}$Gd$_{0.1}$O$_{1.95}$ (CGO) codoped with Sm$^{3+}$ and Nd$^{3+}$ does not show improved results [23]. The sintering temperature of doped ceria can be decreased by addition of small amount of divalent transition metal ion (e.g Co$^{2+}$) [24]. CGO has the good chemical stability with the commonly used cathode material including LSM, LSC (La$_{1-x}$Mn$_x$O$_3$, La$_{1-x}$Co$_x$O$_3$) etc. which lead to its use it in composite cathode with LSM [25]. The interface interaction between the YSZ and cathode material can be minimized by using CGO as interlayer in between them [26].

1.6.3. δ-Bi$_2$O$_3$

In the aspect of solid electrolytes, δ-Bi$_2$O$_3$ has drawn considerable interest due to its higher ionic conductivity ($\sigma_0 = 2.3$ S/cm at 1073 K) compared to other solid electrolytes. On the other hand, δ-phase is stable only in the narrow temperature interval i.e. from 1003 K to its melting point 1073 K. The high ionic conductivity of δ-
Bi$_2$O$_3$ is due to its fluorite structure with intrinsic defects in oxygen sublattice. Stabilization of this high-temperature $\delta$-Bi$_2$O$_3$ phase at lower temperature has been achieved by doping with rare-earth ions such as $\text{Y}^{3+}$, $\text{Dy}^{3+}$, $\text{Er}^{3+}$ etc. [27] or combination of such ions with higher valent cations such as $\text{W}^{6+}$ or $\text{Nb}^{5+}$ [28]. However, substitution of Bi with other cations decreases the ionic conductivity. Minimum concentration of dopant is essential to stabilize the high temperature fluorite phase. Further increasing dopant concentration, the oxygen ion mobility again decreases due to decrease in the unit cell volume and increase in the average strength of the cation-anion bond. Thus, optimization of dopant concentration is desired for high ionic conductivity. First ionic conductivity increases with the ionic radius and another one is $X_{\text{min}}$ ($X_{\text{min}} = \text{minimum concentration of dopant required for stabilization of the fluorite structure}$) increase with the ionic radius. However, the influence of ionic radius on conductivity is smaller than the concentration of rare-earth dopant. Maximum ionic conductivity is observed for the Er and Y containing phases namely Bi$_{0.80}$Er$_{0.2}$O$_{1.5}$ and Bi$_{1-x}$Y$_x$O$_{1.5}$ ($x=0.23-0.25$) [27b]. These binary and ternary phases have higher ionic conductivity but with time they slowly transforms to vacancy ordered rhombohedral phase, which has the lower ionic conductivity. This phase transformation can be minimized by the incorporation of higher valent cations such as $\text{Zr}^{4+}$, $\text{Ce}^{4+}$, $\text{Nb}^{5+}$ and $\text{W}^{6+}$ [28-29]. Alternate problems associated with Bi$_2$O$_3$ electrolytes are due to the reduction in reducing atmosphere at the anode of SOFC. Such problems can be avoided by using thin layer of Sm$^{3+}$ incorporated ceria electrolyte on the anode side [30].
The high conductivity of doped lanthanum gallate (LaGaO$_3$) with Mg and Sr of general formula La$_{1-x}$Sr$_x$Ga$_{1-y}$Mg$_y$O$_{3.5}$ was reported by Ishihara et al. in 1994 [31]. At same temperature, the conductivity of the composition La$_{0.9}$Sr$_{0.1}$Ga$_{0.8}$Mg$_{0.2}$O$_{3.5}$ (LSGM) is higher (0.12 S/Cm at 1273 K) than the YSZ (0.034 S/Cm at 1273 K) and ScSZ [32]. LSGM not only have the comparable ionic conductivity with ceria at low temperature but also is superior to CGO in terms of higher chemical stability in low oxygen partial pressure. Simultaneous doping of Mg$^{2+}$ and Sr$^{2+}$ leads to the reduction in the GaO$_6$ octahedra tilt and hence increasing the symmetry, which is the responsible for the high oxide ion conductivity. Also, the negligible binding energy for Sr$^{2+}$ dopant cluster favors the high conductivity. In contrast, the Mg$^{2+}$ doping has significant vacancy trapping which increase activation energy for migration. Thus, the conductivity shows two distinct behavior with variation of temperature [33]. The ionic conductivity of LSGM can be improved by doping with the transition metals such as Co and Fe. In low concentration of Co (<0.1%) improved electrical conductivity is observed. Among all the transition metal dopants (Co, Ni, Fe etc.), the one with similar size to that of Mg$^{2+}$ is can be effective for stabilizing high-temperature cubic form [29,34]. Even though this material has high conductivity at low temperature, the formation of phase pure gallate is difficult due to segregation of secondary phases such as LaSrGa$_3$O$_7$ and LaSrGaO$_4$ during synthesis [46]. Also the high reactivity of LSGM with Ni, commonly used anode in SOFC, is also a limiting factor. In addition, it forms the ionically insulating phase between the LSGM and Ni containing anode due to chemical reaction at higher temperature [35]. Volatilization of Ga observed in reducing atmosphere, is another limitation of LSGM materials.
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1.6.5. \textbf{Ba}_2\text{In}_2\text{O}_5

Electrical conductivity of \text{Ba}_2\text{In}_2\text{O}_5 is purely oxygen ionic in dry atmosphere whereas it shows mixed ionic and p-type electronic conducting under oxidizing condition, and protonic in H\text{2}O containing medium. At the order-disorder temperature (1198 K) the crystal of \text{Ba}_2\text{In}_2\text{O}_5 changes from orthorhombic to tetragonal lattice and the later shows the fast ionic conduction. On further increase in the temperature to 1313 K, oxygen vacancies becomes fully disordered and exhibits pure ionic conduction with ionic transport number unity [36]. The high temperature cubic perovskite can be stabilized at lower temperature by cation substitution on either Ba or In site. Substitution of \text{In}^{3+} with dopants such as \text{Zr}^{4+}, \text{Ce}^{4+}, \text{Sn}^{4+} or \text{Hf}^{4+}, \text{Ga}^{3+}, \text{Al}^{3+}, \text{Sc}^{3+}, \text{Y}^{3+}, \text{Yb}^{3+}, \text{W}^{6+}, \text{Cu}^{2+}, \text{Ti}^{4+}, \text{Ta}^{5+}, \text{Nb}^{5+}) or \text{Ba} by \text{La}^{3+}, \text{Sr}^{2+} and \text{Pb}^{2+} have been used to stabilize the disordered cubic perovskite phase [37]. The ideal cathode material for this material is (\text{La}_{0.6}\text{Sr}_{0.4})(\text{Mn}_{1-x}\text{Fe}_x)\text{O}_3-\delta. However, the high reactivity of \text{Ba}_2\text{In}_2\text{O}_5 with CO\text{2}, and instability in reducing atmosphere etc. limit its usage in practical fuel cells [38].

1.7. \textbf{Dielectric materials}

Dielectric materials have the large technological applications and have increasing demand in the world of electronic devices. The degree of miniaturization in memory devices based on capacitive components, such a static and dynamic random access memories, depends on the dielectric constant of the material. Hence, a lot of research work is going on the dielectric materials. Dielectric materials are poor conductor of electricity and their main function are (1) to keep away the conducting plates from coming in contact, allowing for smaller plate separations and therefore higher capacitances, (2) to increase the effective capacitance by reducing the electric
field strength, (3) to reduce the possibility of shorting out by sparking (more formally
known as dielectric breakdown) during operation at high voltage [39]. The
capacitance is related to other factors as follows:

$$C = \varepsilon_0 \varepsilon_r \frac{A}{d}$$  \hspace{1cm} [1.8]

Where, $\varepsilon_0$ is the dielectric constant of the free space ($8.854 \times 10^{-12}$ F/m), $d$ is distance
between the plate, $A$ is area of the dielectric materials and $\varepsilon_r$ is the dielectric constant
of the dielectric layer.

The energy stored in the capacitor may be considered to be the same as the work done
in moving a charge from low to high potential and it can be written as

$$W = U = \frac{Q^2}{2C} \ (Q = CV)$$

$$= \frac{C^2 V^2}{2C}$$

$$U = \frac{1}{2} CV^2$$  \hspace{1cm} [1.9]

Where, $Q$ is charge on the metallic foils and $V$ is the potential difference between the
plates.

The dielectric constant is one of the fundamental electrical properties of solids [40].
Dielectric measurements give the ability of polarizability of ions in a solid. Variation
of the dielectric properties with frequency and temperature have the advantages in
understanding the polarization mechanism [55-58], the process of electrical
conduction [41], defect concentration [42] and nature of bonding [43].
1.7.1. Dielectric polarization

When a dielectric sample is placed in an electric field $E$, the opposite electric charges are displaced and acquire a permanent dipole moment. Thus, the dielectric material is polarized under the electric field. The polarization $P$ or dipole density can be represented by:

$$P = \frac{p}{v} \tag{1.10}$$

Where, $p =$ permanent dipole momentum $v =$ volume of the sample

Different types of polarizations, viz. electronic, ionic, dipolar, and spontaneous polarization as shown in the Fig.1.5 occur in dielectric materials when placed inside an electric field. Electronic polarization ($P_e$) occurs due to displacement of the center of negatively charged electron cloud relative to positive nucleus of atom by the applied electric field. Ionic polarization ($P_i$) occurs in ionic materials. In an ionic lattice, the positive ions are displaced in the direction of applied field whereas negative ions get displaced opposite direction to the applied electric field, giving rise to net dipole moment. If the molecules possess permanent dipole moment, such as $H_2O$ molecules, the rotation of these dipoles under an electric field will produce the dipolar polarization ($P_d$). Therefore, the dipolar polarization is strongly dependent on the frequency of the applied electric field and on the temperature. Space charge or interfacial polarization occurs in heterogeneous systems such as multi-component materials or incompatible chemical substance containing materials. The charge carriers are accelerated by an applied field until they are opposed by and/or trapped at the physical barriers in such these heterogeneous systems. This buildup of charges
causes the polarization of the material. Space charge polarization (Ps) is governing factor of dielectric properties. Electronic, ionic and orientation polarization arises when charges are locally bound in atoms, molecules, or structures of solids or liquids. By the application of low frequency field some of these bound charge carriers migrate over a distance. In case of space charge polarization, the motion of these charge carriers is reduced due to trapping of charges within the materials. Accumulation of these charges increases the overall capacitance of a material.

The total contribution of polarization to the dielectric constant is therefore a summation of the above mentioned individual polarization.

\[
Pt = Pe + Pi + Pd + Ps
\]

Fig.1.5: Schematics major polarization mechanisms Electronic polarization (b) ionic polarization (c) orientation polarization (d) space charge polarization [44].
1.7.2. Frequency response of dielectric mechanisms

Different types of polarizations respond in different way to the frequency. When the frequency of the applied field is sufficiently low, all types of polarization can be observed. Electronic displacement responds rapidly to the field reversals, and therefore no lag of the polarization contribution occurs up to $10^{17}$ Hz. Since ions are larger in size and are bound in the crystal structure, have less mobility. The polarization effect of ionic displacement decreases at $10^{13}$ Hz. At this frequency, the ionic displacement begins to lag the field reversals. Orientation polarization takes a time of the order of $10^{-12}$ to $10^{-10}$ sec to reach equilibrium value in liquid and solids. When the applied field has a frequency of $10^{10}$ to $10^{12}$ Hz, orientation polarization fails to reach its equilibrium value and contribute less to the total polarization as frequency increases. The space charge polarization in general is observed at lower frequency region where the ionic mobility does not follow the ac frequency. This is usually observed in Hz- to kHz range. Each dielectric mechanism has a characteristic “cutoff frequency.” As frequency increases, the slow mechanisms drop out in turn, leaving the faster one contributing to $\varepsilon_r$, as expected, capacitance value, i.e. dielectric constant, always decreases with increasing frequency.

1.7.3. Dielectric loss

Dielectric loss occurs when dielectric material interacts with alternating electric field. Due to different types of polarization there is a phase lag between the phase of the input field and output field which causes the energy loss. It can be represented as

$$\tan\delta = \varepsilon''/\varepsilon$$  \[1.12\]
Where $\varepsilon'$ is the relative permittivity or dielectric constant $\varepsilon''$ is the energy loss in the dielectric medium.

For good dielectrics $\tan\delta$ is insensitive to the frequency of the applied field. Depending on the response of the dielectric materials to the electric field or stress or temperature and then nature of dielectric constants, the dielectric materials can be grouped into different classes, namely ferroelectric/antiferroelectric, piezoelectric or pyroelectric. Subsequently, the brief introduction of such special dielectric materials is provided.

1.8. **Group of dielectric materials**

1.8.1. **Ferroelectrics**

Ferroelectric materials are special type of polar materials where the spontaneous polarizations possess at least two equilibrium states. The direction of the spontaneous polarization vector may be switched between those orientations by an electric field which appear as hysteresis loop as shown in Fig.1.6. All ferroelectric materials are piezo and pyroelectric materials. Analogous to ferromagnetic materials, ferroelectric materials have no net polarization due to formation of domains under normal conditions. When positive electric field is applied to ferroelectric material, polarization increases to saturation value known as saturation polarization ($P_s$), where all the dipoles are aligned parallel to one another. When the field is removed the polarization decreases to a remnant value, ($P_r$) and a coercive field, ($E_c$) is required to return the polarization to zero.
Depending on the structure of materials, the most of the polar dielectrics can be grouped to four classes as 1) Perovskite group, 2) Pyrochlore group, 3) tungsten-bronze group, 4) layered structure complex oxides group and 5) Hybrid composites group.

1.8.2. Perovskites

The most studied class of ferroelectric materials is perovskite group, which can also be divided into lead containing and lead free ferroelectrics. The dielectric properties of the ABO$_3$ perovskite materials have been investigated since long, due their ease of tunability by modifying the structure via A or B site substitutions as mentioned earlier. The average displacement of the Ti ions in BaTiO$_3$ along the c-axis from the centrosymmetric position gives the ferroelectricity. At the transition temperature ($T_c$~393 K), the tetragonal ferroelectric phase converts into paraelectric cubic phase. This transition temperature is also known as Curie temperature. Even though BaTiO$_3$ (BTO) has the easier synthesis methods, the narrow Curie transition

**Fig.1.6: Hysteresis loop of ferroelectric material [45].**
temperature ($T_c$) limits it to actual piezoelectric applications. The Curie temperature ($T_c$) of the BaTiO$_3$ can be increased by suitable substitution either at A or B site or at both sites. Unfortunately, although these type of materials have highest $T_c$, the relative permittivity at room temp is lower than the pure BTO [46]. Similar studies on isovalent ions with different radii such as Ca$^{2+}$, Ba$^{2+}$, Pb$^{2+}$, Cd$^{2+}$, Pr$^{3+}$ and Mn$^{3+}$ on the incipient ferroelectric, SrTiO$_3$ ($T_c = 40K$) indicates an increase in transition temperature [47]. In case of Pr doped SrTiO$_3$ ferroelectric behavior is observed [48]. Mn doped SrTiO$_3$ shows a broad dielectric maximum with relaxor like behavior [49] whereas Ba doped SrTiO$_3$ (BST) show adjustable Curie temperature. The $T_c$ in BST varies almost linearly depending on Ba/Sr ratio [50]. The effect of B site substitution and simultaneous A and B site substitutions with the ions of different size and polarizability show similar onset of the ferroelectric phase transition have attracted much less importance. However, they are promising as superior lead-free or low lead content piezoelectric materials [51]. Another important series of ferroelectric material with perovskite structure are the niobates. KNbO$_3$ has an orthorhombic symmetry at room temperature. It is known that KNbO$_3$ and related compounds show a high curie temperature ($T_c = 703$ K). (K,Na)NbO$_3$ (KNN) is one of the best ferroelectric materials in the niobate series. Although, these materials have high curie temperature, the major problems associated with alkaline niobates are synthesis and sintering [52], due to sublimation of alkaline earth metal at high temperature leading to deviated initial stoichiometry. In order to minimize the above stated problems, several additives like CuO, MnO$_2$, and CeO$_2$ have been used [53]. These additives follow liquid phase sintering at lower temperature and facilitate densification. Alternate procedure involves the substitution at A and B site. For A site, several cations such as Li$^+$, Ba$^{2+}$,
La$^{3+}$, Bi$^{3+}$, whereas for the B site Ti$^{4+}$, Sb$^{5+}$ or Ta$^{5+}$ are reported. Besides, use of powder sample of reduced particle size lead to sintered material at lower temperature [51,53].

1.8.3. Double perovskite

The simple perovskite structure (ABO$_3$) can be extended by substitutions, particularly of the A and B site cations. The substituent dopants may be located in the crystal lattice either randomly in the original perovskite structure, or the structure may become an ordered type in which the cations alternate regularly. Mostly only one cation is chosen for the A site substitution usually large species such as Sr$^{2+}$, Ba$^{2+}$, La$^{3+}$. Variation in the properties of double perovskite can also be studied by B site substitution. The most common substituents are the equiatom proportion of two ions with sufficiently different charge and size at B site, where charge or cation ordering is easily expected. The formula can be written as A$_2$BB’O$_6$ and can be described as the double perovskite. Structure of double perovskite is shown in the Fig.1.7

![Schematic diagram of double perovskite structure. The octahedral units are shown for BO$_6$ and B’O$_6$ polyhedra. Isolated spheres are for A cation.](image)

Fig.1.7: Schematic diagram of double perovskite structure. The octahedral units are shown for BO$_6$ and B’O$_6$ polyhedra. Isolated spheres are for A cation.
It has been observed that the charge difference between the B site cations is the most important factor for exhibiting cation order in perovskite structure. If the difference in the oxidation state is greater than two, highly ordered compounds are observed such as $A_2^{2+}B_1^{2+}B_1^{6+}O_6$ (e.g.; $\text{Sr}_2\text{FeWO}_6$) and $A_2^{2+}B_1^{1+}B_1^{7+}O_6$ (e.g.; $\text{Sr}_2\text{NaReO}_6$) compounds. If the charge difference is less than two, completely disordered or partially ordered structure is obtained. If the charge difference is equal to 2 then some of the compounds arrange in a partially, ordered structure (e.g. $\text{Sr}_2\text{FeSbO}_6$) and disordered structure can be achieved (e.g. $\text{Sr}_2\text{FeRuO}_6$). In the case of $(\text{La}_2\text{NiMnO}_6)$ LNMO, it is expected that the Ni and Mn ions are respectively in the 2+ and 4+ oxidation states in the ordered phase, while both are in the 3+ oxidation state in the disordered phase. Ordering in perovskite also depends upon the some of the following factors as follows:

i. **Size difference of the Cation**

Cation ordering also depends on the size difference between the B site cations, if the size difference is higher, high degree of cation ordering can be expected. In case of $\text{Sr}_2\text{MTaO}_6$ ($M^{3+}=$Sc, Cr and Fe) even though charge difference of 2 for all, $\text{Sr}_2\text{ScTaO}_6$ exhibits more ordered structure followed by $\text{Sr}_2\text{CrTaO}_6$ and $\text{Sr}_2\text{FeTaO}_6$.

ii. **Nature of the B site cation**

Nature of the B site cation also has significant influence on cation ordering. $\text{Sr}_2\text{FeSb}^{5+}\text{O}_6$ has more cation order than $\text{Sr}_2\text{FeTa}^{5+}\text{O}_6$. This is due to preferential formation of $\text{Sb}^{5+}\text{-O-}\text{Sb}^{5+}$ bonding. Since $\text{Sb}^{5+}$ has only s and p orbitals, available for bonding, they preferentially form $\text{Sb}^{5+}\text{-O-}\text{Sb}^{5+}$ bond whereas in case of $\text{Ta}^{5+}$ d orbital are available for the bonding and hence it does not show preference for $\text{Ta}^{5+}\text{-O-Ta}^{5+}$.
bond. Hence, a perfect intermixing of Fe\(^{3+}\) and Ta\(^{5+}\) is expected rather than Fe\(^{3+}\) and Sb\(^{5+}\) mixing. Hence, Ta\(^{5+}\) compounds are less ordered than the Sb\(^{5+}\) compounds. Along with the above stated points, the cation ordering also depends on the synthesis methods, annealing temperatures.

### 1.8.4. Tungsten-bronze structure

Tungsten-bronze structured materials have commercial importance as dielectric and ferroelectric materials. PbNb\(_2\)O\(_6\) and PbTa\(_2\)O\(_6\) [54] are among the first reported ferroelectric materials. Sr\(_x\)Ba\(_{1-x}\)Nb\(_2\)O\(_6\) (0.25\(\leq x \leq 0.75\)) (SBN) [55] ceramics are ferroelectric with tetragonal tungsten bronze structure (TTB). The TTB structure consists of complex array of corner shared BO\(_6\) octahedra as shown in the Fig.1.8. Such unique arrangements of BO\(_6\) octahedra, leads to interstitials available for different types of cations, thus the structure has the general formula (A\(_1\))\(_2\)(A\(_2\))\(_4\)(C)\(_4\)(B\(_1\))\(_{12}\)(B\(_2\))\(_{28}\)O\(_{30}\). Filled bronzes have no vacant sites whereas unfilled bronzes have vacant C site and partially occupied A sites. In general, monovalent ions are filled in A\(_1\) site and B sites by tetra, hexavalent (i.e., Ti\(^{4+}\), Nb\(^{5+}\), Ta\(^{5+}\), V\(^{5+}\) and W\(^{6+}\)). Often the C sites (being smaller), remain empty. Hence wide spectrum of Curie temperature and dielectric properties can be expected for the compounds of these families [56]. In case of Sr\(_x\)Ba\(_{1-x}\)Nb\(_2\)O\(_6\), the A\(_1\) site is occupied by both Ba and Sr ions whereas the A\(_2\) site is occupied by Ba ions and C sites are empty. Out of six A\(_1\) and A\(_2\) sites only five positions are occupied by the Ba and Sr and one remains empty. Most of the physical properties including ferroelectric, pyroelectric and electrooptic can be altered by changing its composition. As the value of x increases in the composition, the transition temperature decreases linearly from 523K to 330 K. At
x~0.6, a crossover from normal ferroelectric to relaxor is observed in Sr$_x$Ba$_{1-x}$Nb$_2$O$_6$ series [57].

Doping of Sr$_{2-x}$Ca$_x$NaNb$_5$O$_{15}$ with La$_2$O$_3$ increases the dielectric constant to 1662 with transition temperature 471 K. BaNb$_2$O$_6$ has two polymorphic phases, tetragonal phase which transform to orthorhombic above 1473 K. The dielectric properties of each phase are significantly different; viz. tetragonal phase has high dielectric constant whereas low dielectric loss for orthorhombic phase is observed. Coates et al. showed that BaNb$_2$O$_6$ is ferroelectric with a transition temperature about 343 K [58].

**1.8.5. Layered structure (Aurivillius Structure)**

Aurivillius type crystal structure was discovered by Aurivillius in 1949. The general formula of these structure is Bi$_2$A$_{n-1}$B$_n$O$_{3n+3}$ where n is the number of octahedral layers in the structure, A = Sr$^{2+}$, Ba$^{2+}$, Ca$^{2+}$, La$^{3+}$, Bi$^{3+}$, Pb$^{2+}$, K$^+$, B = cation suitable for octahedral configuration. Thus, B site cation is more size restrictive and is
typically occupied by Ti$^{4+}$, Nb$^{5+}$, Ta$^{5+}$, W$^{6+}$, Ga$^{3+}$, Al$^{3+}$ and Mn$^{3+}$ [59]. The structure consists of perovskite-like blocks of the form $(A_{n-1}B_{n}O_{3n+1})^{2-}$ sandwiched between two bismuth oxide $(Bi_{2}O_{2})^{2+}$ sheets. The number of perovskite layers can be 1, 2, 3 or more. Each can result in separate structure but perovskite layer and bismuth oxide layers are always in alternative position. Thus, it is possible to modify dielectric and ferroelectric properties by changing the chemical compositions. The effect of A site substitution is more useful than the B site substitution. Since cations at the B site have similar size, they do not play a major structural role in the polarization process. Most of the Aurivillius structures are orthorhombic at room temperature. After studying several isomorphic substitution Aurivillius developed the more general expression i.e., $(Me_{2}O_{2})(Me^{1}_{m-1}B_{n}O_{3m-1})$. However in $Bi_{4}Ti_{13}O_{12}$, Me and Me’ sites are occupied by the same ion. A large number of compounds with similar structure are known, some examples are PbBi$_{2}$Nb$_{2}$O$_{9}$ ($m = 2$), BaBi$_{4}$Ti$_{4}$O$_{15}$ and CaBi$_{2}$Nb$_{2}$O$_{9}$. BaBi$_{4}$Ti$_{4}$O$_{15}$ (BBT) has advantages over lead based materials as they have high fatigue resistance up to $10^{12}$ cycles. The majority of bismuth layer ferroelectrics have high Curie temperature (>673 K), low aging rate and low operational voltage [60].

1.9. Polymer nano-composites

The need for pulse power energy storage systems with high energy density has led to the development of polymer composite systems. The electrical density of the dielectric material can be written as

$$E = \frac{1}{2} \varepsilon_{0} \varepsilon_{eff} E_{b}^{2}$$

[1.13]

Where, $\varepsilon_{eff}$ is the effective dielectric constant and $E_{b}$ is dielectric breakdown strength. Therefore, it is essential to develop dielectric materials which can meet the demands
Chapter 1

of higher dielectric constant to increase the device capacitance and higher dielectric breakdown strength which will allow higher device operating voltage. Along with these two demands, development of low cost dielectric materials is also essentials. Generally organic polymers are low in cost but dielectric constant of these materials is also very low. The dielectric constant of the polymers can be increased by 1) introducing ceramic filler with high dielectric constant such as BaTiO$_3$ [61], CaCu$_3$Ti$_4$O$_{12}$ (CCTO) [62], Pb(Mg$_{1/3}$Nb$_{2/3}$)O$_3$-PbTiO$_3$ (PMNPT) [63], Pb(Zr$_x$Ti$_{1-x}$)O$_3$ [64], Al@Al$_2$O$_3$ [65], Al@C [66] into the polymer matrix. In order to obtain very high dielectric constant, large amount of ceramic fillers are required. In this process, at very high concentration of the ceramics, pores, voids, and imperfections are developed in the matrix which results in lowering the breakdown voltage. In addition, the ceramic particle loaded polymer loses its mechanical flexibility and poor quality composite films are obtained. 2) Another way is to prepare percolating systems by incorporating conductive fillers such as carbon black, carbon nanotubes, conductive fibres, or metal particles into the polymer matrix [67]. The effective permittivity is proportional to the filler (nano particle) loading. At higher filler loading, leakage current increases due to formation of conductive paths by conductive filler at percolation threshold. These problems can be avoided by the good dispersion of the nanoparticles of conductive filler in the polymer matrix. It can suppress the polarization losses generated from the interfacial moieties and also decreases the leakage current of device. This can be achieved by the effective filler shape and surface modification of the nanoparticles.
These polymer nano-composites have many practical applications such as ferroelectric media for flexible FeRAM devices, integral thin film capacitors, electrostriction systems for artificial muscles and electric stress control devices. Some of the dielectric polymers for capacitor applications are shown in the Table 1.1.

### 1.10. Relaxor ferroelectrics

Relaxor ferroelectrics differ from the normal ferroelectrics in their ferroelectric transition temperature. The typical characteristics of relaxor are [69]:

- No distinct domain structure within the phase-transition temperature range.
- Dielectric response with respect to temperature does not follow the classical Curie-Weiss law. \( \varepsilon_\infty = C/(T - T_c) \)
Where, $\varepsilon_r$ is the relative permittivity. The relaxor ferroelectrics are characterized by broad maximum and frequency dispersion of the dielectric permittivity at temperature around and below the $T_m$ and its magnitude ($\varepsilon_{\text{max}}$) decreases with increasing frequency.

- There is no clearly defined hysteresis loop observed in the phase-transition range.
- Presence of a diffuse phase transition temperature.

Various models have been proposed for the possible mechanism of the dielectric relaxation. From the studies of Smolensk et al., it was thought to consist of chemical inhomogeneity with different concentration of dopants in micro regions gives rise to different curie temperatures [70]. A super-paraelectric model for the relaxor ferroelectrics was proposed by Cross which suggest that in the high temperature region, the micro polar regions are being dynamically disordered by thermal motion. The height of the barrier between domain states is directly proportional to the volume of the polar micro region. The polarizations with low thermal energies will be trapped into a preferential orientation and form a polar micro domain or cluster [71]. This model is extended by Veihland et al. where the dispersion of the maximum dielectric constant temperature $T_{\text{max}}$, in terms of the AC frequency is described by the Vogel-Fulcher (V-F) relationship [72].

$$f = f_0 \exp \left[ -\frac{E_a}{(T_{\text{max}} - T_f)} \right]$$  \[1.14\]

Where, $f_0$, $E_a$, and $T_f$ are the fitting parameters.

The $T_f$ is described as a static freezing temperature.
Relaxation behavior is mostly found in the lead based perovskite oxides. In case of PbMg$_{1/3}$Nb$_{2/3}$O$_3$ (PMN) disorder in the lattice brought by differences in ionic radii (0.64 Å vs. 0.72 Å), valence (5+ vs. 2+), and electronegativity (1.6 vs. 1.2 on the Pauling scale) between Mg$^{2+}$ and Nb$^{5+}$ ions on the B site, introduce local ordering charge fluctuations, which produce dipolar defects and results into relaxor behavior. In lanthanum modified lead zirconium titanate (PLZT), the substitution of lanthanum for Pb$^{2+}$ produces randomly distributed Pb$^{2+}$ vacancies and at high concentration of vacancies, relaxation behavior is observed. In case of KTaO$_3$ substitution of Nb$^{3+}$ for Ta$^{3+}$ and Li$^+$ for K$^+$, produces off-site dipolar defects which lead to a relaxor state at low concentrations. Other lead perovskite oxides such as lead magnesium niobate (PMN), lead tin niobates (PSN), lead scandium tantalite (PST), lead indium niobates (PIN) also have the relaxor behavior.

1.11. **Scope of the present thesis**

In the aim of the present thesis, two different types of materials, either with fluorite or perovskite related structures, have been investigated for oxide ion conduction or dielectrics properties and they are explained sequentially. In the aspect of oxide ion conductor, several compositions such as Ln$_{1-x}$Bi$_x$O$_{1.5}$ (0.00 ≤ x ≤ 0.50) where Ln = Dy and Yb and pyrochlore-type Pr$_{2-x}$Ca$_x$Zr$_2$O$_7$ (0.00 ≤ x ≤ 0.20) have been investigated and the results are explained in Chapters 3 and 4. In the interest of dielectric materials, perovskite related Pr$_2$Ti$_2$O$_7$ and Ln$_2$CoMnO$_6$ (Ln = Eu and Y) have been investigated and they are explained in Chapters 4 and 5. In addition, several organic and inorganic hybrid materials, like PVDF-M (M = Co, Ni) have been prepared and their electrical properties are explained in Chapter 6. Besides, electrical properties of some complex oxides like InVO$_4$, CoFe$_2$O$_4$ are also investigated and are
explained in Chapter 7. Each chapter is organized with the introduction relevant to the particular subject of the study and the scope for further study, followed by the details of preparation, characterization, and property evaluation of individual system. Finally all the results of the studies are summarized in Chapter 8.