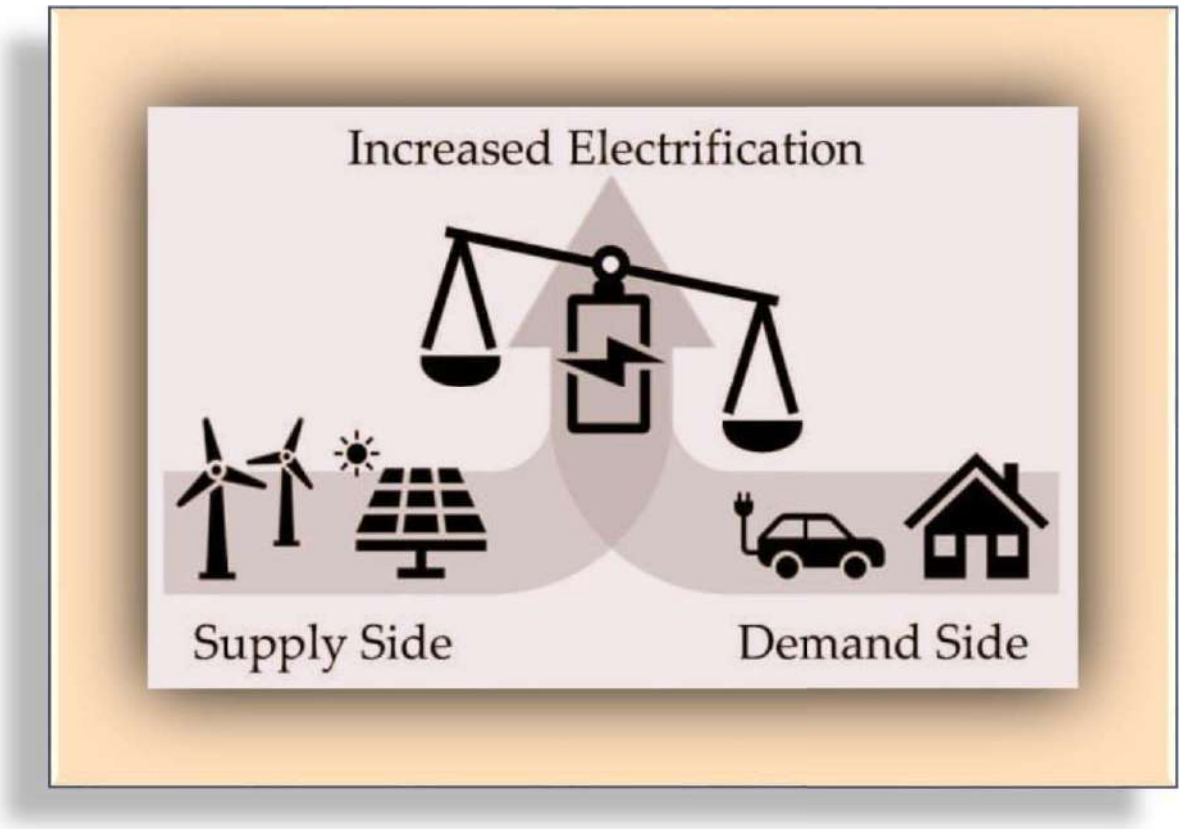
Chapter 1

Introduction and Literature review



Chapter 1: Introduction and Literature review

1.1 Energy requirement

Energy is the ability to do any work. It makes the things happen and helps us live. There are different forms of energy, like light, heat, electricity, etc., and all have different sources for their generation. A terminology known as Energy storage is the storage of energy for use later on. The storage of energy can be of any form of the energy that can be of Mechanical energy storage, Thermal energy storage, Hydrogen energy storage, Electrochemical energy storage of Electrical energy storage. The storage of energy helps in various ways, so it has been a very important part of human civilization for many thousands of years; in the initial phase of human civilization, thermal energy storage was used, but as the civilization developed and science and technology developed, different types of energy storage used in human civilization [1,2]. Different types of energy storage are categorized in the following **Figure 1.1.**

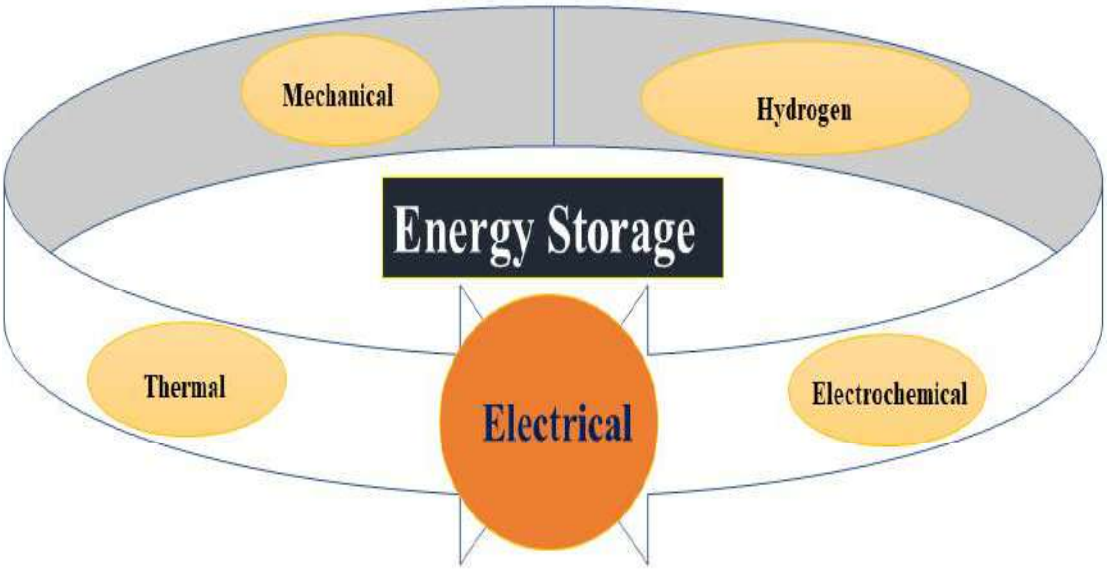


Figure 1.1: Various types of Energy and energy storage

1.2 Benefits of stored energy

The storage of energy is beneficial in many ways as follows:

(i). Power backup support: It provides energy during power outages.

(ii). Stability: It ensure energy available when energy demand is high.

(iii). Renewable Use: The store any type of energy can be use when it not produces from the sources.

(iv). Efficiency: Energy storage reduces the wastage of energy by storing the excessive produce energy.

(v). Convenience: The storage of energy ensures energy is ready for the use whenever needed.

(vi). Mobility: Storage energy provide Powers to portable devices like phones and laptops for the use during movement.

(vii). Cost effective: The storage of energy reduces the burden from the main source so that it is cost cutting.

(viii). Emergency support: The storage of energy provides energy in emergencies, like any natural disasters happens.

(ix). Grid Support: The storage of energy helps to balance the energy supply in the grid.

(x). Environmental Impact: The storage of energy reduces dependency on fossil fuels by storing green energy so that environment can be free from the pollutions.

1.3 Motivation (Electrical energy storage and consumptions):

Electrical energy is a form of energy that comes from the movement of charge particle electrons. Electrical energy storage is the process of storing electrical energy for futuristic use. This can be performed in various ways; electrical energy is stored in electrical devices like capacitors in the form of charge, while another electrical energy storage device is known as a battery, where electrical energy is stored in chemical form and released when demand is required. For the portable electronics devices and various kind of sensors there, are a need of compact electrical energy storage to operate them in various conditions, these requirements fulfilled by the use of capacitor as electrical energy storage device. In varying conditions, high-temperature and low-temperature environments also exist, where chemically and thermally highly stable dielectric materials are needed for capacitor manufacturing. Some other harsh condition also arises during the operation in a different place like mining, aerospace, transport, chemical treatment, food processing, defense, medical etc, and the central area of consumption of electrical energy in the form of storage is as shown in the following **Figure 1.2** where different regions are shown in symbolic form.

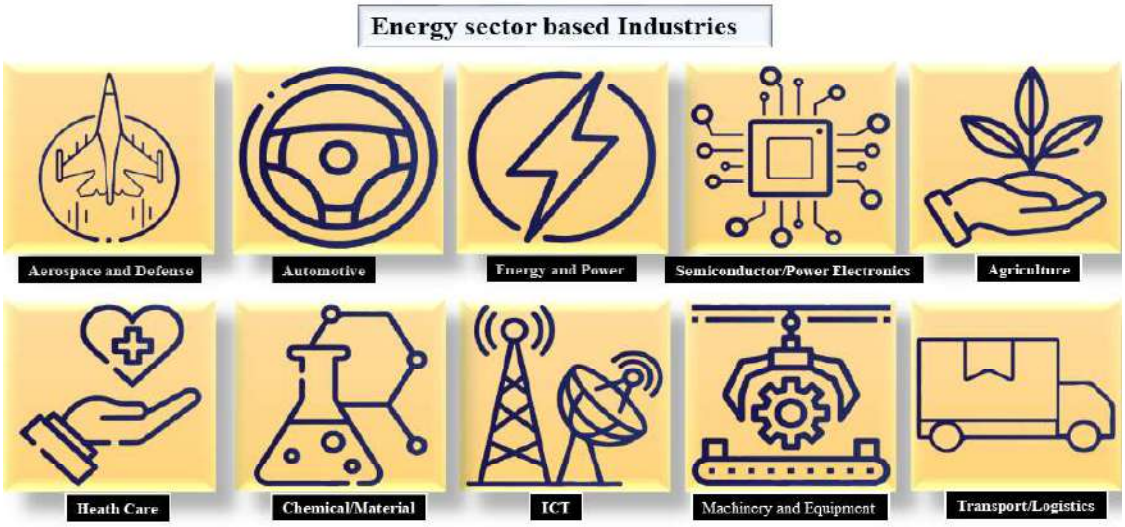


Figure 1.2: Various electrical energy sector based industries

According to many studies and scientific estimates, the Asia-Pacific region will have the most significant electrical energy-based devices and applications market in terms of value and consumption in the next few years, followed by North America and Europe. Countries like South Korea, Japan, China, India, Pakistan, South Korea, and Russia are advancing technologically in the Asia-Pacific region. These nations use electrical energy materials and devices in a variety of applications. One of the key factors influencing this market's growth in Asia Pacific is the use of Portable electronics technology and expansion in digitalization, communication, and information sectors, and the primary reason behind this change is rapid growth in urbanization in this part of the globe [3,4]. As shown in the following bar diagram **Figure1.3,** it is estimated that there will be a very huge market in the upcoming few years, about 276.13 billion $ worldwide, which is in currently time about 48.93 billion $ and rapidly increasing due to the rapid increase of urbanization and digitalization, In the F**igure1.4** the percentage of consumption of the electrical energy based devices and application in the different continent of the globe shown.

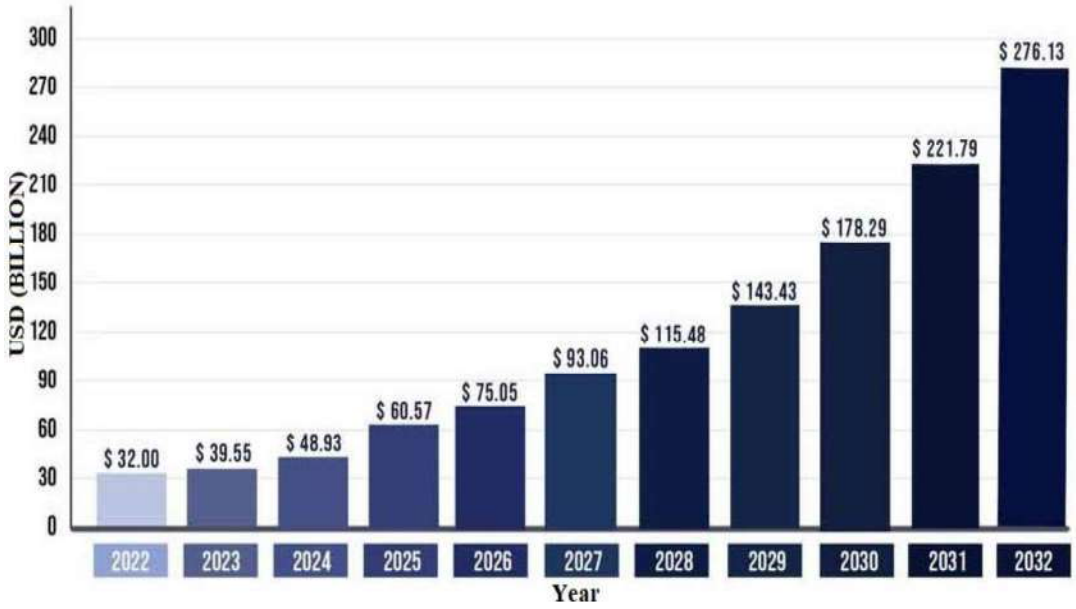


Figure 1.3: Generation of estimated revenue in different years

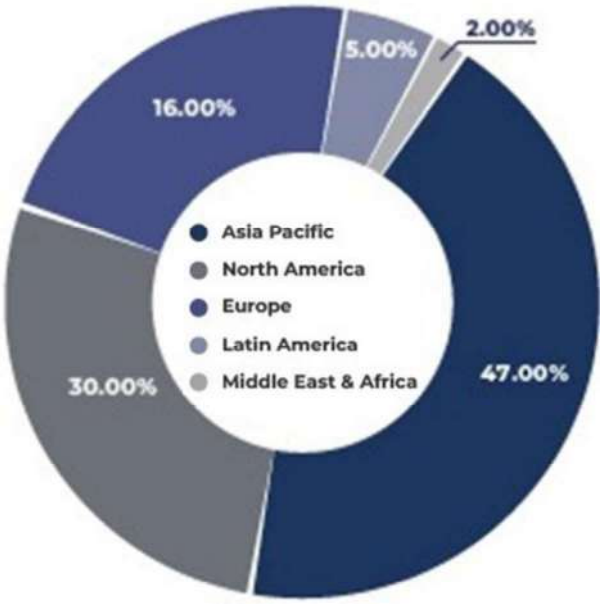


Figure 1.4: Consumption percentage of electrical energy storage devices and applications in different part of globe

As the globe faces severe environmental and economic concerns, the demand for renewable energy has grown more critical in recent years. Reducing carbon emissions, fighting the effects of climate change, and developing renewable energy sources, such as solar, wind, hydro, geothermal, and biomass, is essential to achieving energy independence [5]. Renewable energy is essential if we are to reduce our dependency on foreign oil and maintain energy security. In many countries, importing fossil fuels is a current activity despite the fact that it can be costly and politically problematic [6]. Renewable energy can solve the problem of shortage of fossil fuels around the world. Electrical energy materials have the potential to solve the energy problem.

A lot of electro-ceramic materials are used as sources of renewable energy, where ferroelectric, ferroelectric, Pyroelectric and dielectric materials can convert mechanical, thermal, or electromagnetic energy into electricity. For example, piezoelectric materials can be built into floors, roads, and other surfaces that get a lot of mechanical stress from foot traffic or vehicles. The generated electrical energy can be used to power nearby devices or

stored in batteries for later usage [7]. Ferroelectric materials always have an electric polarization that can be changed by applying an external electric field, because they can keep their polarity for long periods, they can be used to store energy in places like capacitors. Ferroelectric materials can also be used in energy harvesting devices because of pyroelectric properties, where they can turn heat energy into electricity [8]**.** Due to their high electrical resistance, dielectric materials can hold electrical charges when it placed in an external electric field. Thus, they can be utilized to manufacture capacitors, which are devices that store energy or used to filter electrical signals. Electromagnetic induction is the process by which dielectric materials can turn electromagnetic radiation into electrical energy. This means that dielectric materials can also be used in energy-harvesting devices [9]. Overall, using these materials to make renewable energy is still in the research and development stage, but they have a lot of potential for the future of sustainable energy. As technology improves, these materials may be used more often in a variety of ways, from powering small electronic devices to providing electricity to whole buildings. Photo luminescent materials absorb light energy and release it into the environment as light. It is possible to develop energy sources that produce electricity using this property through photovoltaics. In the photovoltaics process, light-emitting materials form in the layers, and those layers absorb solar radiation (sunlight) and convert it into electrical power. This technology is especially helpful for making solar panels that can be used in places that don't have access to other types of energy. Some photoluminescent materials can also store light energy for a long time and release it when it's needed. This makes them useful for lighting or other applications. Overall, photoluminescent materials also have great potential to change the energy industry and create more sustainable energy sources for the future [10].

1.4 Foundation

Dielectrics are the insulators that exist with permanent dipoles, and ferroelectrics are the materials having spontaneous polarization, while piezo electrics are the materials that generate an electric charge when a mechanical force is applied to materials and vice versa, which is proportionate to the mechanical force or displacement. The direct and reverse (Indirect) Piezoelectric effects are the two types of this characteristic. Pressure, force acceleration, and vibration sensors all use the direct effect concept, and the indirect piezoelectric effect applies to displacement actuators, surface acoustic waves (SAW), and ultrasonic wave sensors [11–13]. For example, Piezo generators convert mechanical energy into electrical energy (Direct piezoelectric effect), while piezo motors reverse the process (converse piezoelectric effect). By using direct or reverse piezoelectric effect, the same transducers can do both types of work [14]. Piezoelectric materials have been used as transducers, actuators, and sensors (Ultrasonic transducers) in aerospace systems (as vibration cancellation and optical positioning), industrial process management (as displacement actuators), and biomedical applications [15,16].

The most extensively utilized materials are single crystals lithium niobate ($LiNbO_3$), Lead magnesium niobate titanate (PMN-PT), and polycrystalline ceramic Lead Zirconate Titanate (PZT). Valasek et al investigated the phenomenon of ferroelectricity on Rochell salt in 1920. Bush and Scherrer developed a series of ferroelectric crystals in Zurich between 1935 and 1938 [17]. At the time Potassium dihydrogen phosphate (KH_2PO_4 KDP) and ammonium salts ($NH_4H_2PO_4$, ADP) were discovered during World War II, APD replaced underwater sound transducers and submarine detectors due to its high electromechanical coupling ratio. There was no advancement in the ferroelectrics field for a short time after the invention of the KDP Series. Barium Titanate ceramic with dielectrics constant up to 3000 at the ambient temperature was developed in 1945. It was the first ferroelectric with a non-piezoelectric design and no hydrogen bond [18–20].

1.5 What is Perovskite?

Perovskite is a compound with a crystal structure like a mineral known as Calcium Titanium oxide, with the formula $CaTiO_3$. Since 1940, these oxides have been a special class of materials that have been extensively investigated for research due to their significance and their very high potential for advanced technological applications. Perovskite oxide plays a crucial role in the chemical tuning of composition and structure in materials and thus shows a multiplicity of physical and chemical characteristics with advanced technological possibilities that depend upon whole processing conditions. In perovskite oxide, the electrical properties vary from insulators to semiconductors, and metallic and superconductor attributes are also possible. However, perovskite materials are still being studied and developed, and there is ongoing research to improve their stability and performance in various applications [21].

1.5.1 The historical background of Perovskite

Perovskite with the formula ABO_3 is called "simple Perovskite oxide". A researcher, Gustav Rose, found Perovskite oxide for the first time in Russia's Urai Mountain in 1839[22]. “Perovskite” is a word taken from the L.A. Perovskite (1792-1856), a Russian mineralogist. Perovskite with the chemical formula ABO_3, where A is in the corner of the cubic lattice, B is in the center, and O is on the face of the cubic lattice. The size of A is always bigger than the size of B in the perovskite system [23]. The perovskite crystal structure is shown in **Figure 1.5.**

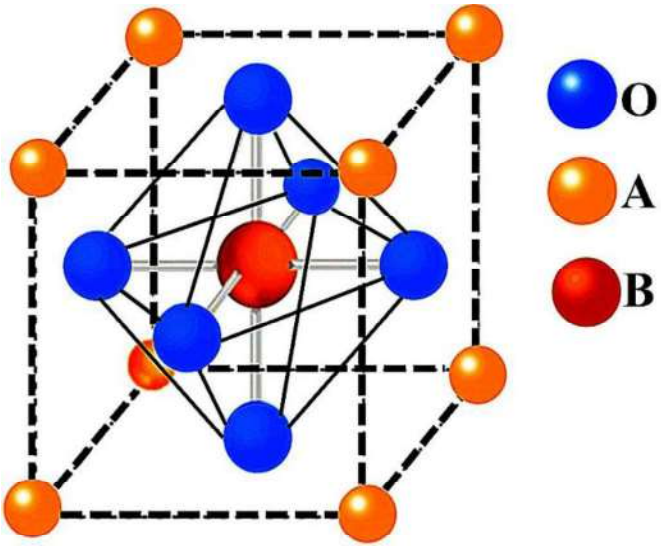


Figure 1.5: Simple Perovskite Structure

It has been noted that B mostly represents transition metals of the 3d, 4d, and 5d dimensions. Oxide ions are everywhere around the metal, and an octahedral position called BO6 occupies it. The letter A denotes alkaline earth metals in the Perovskite system [24]. Physicist Goldschmidt has developed the theory that describes the structure of perovskite oxide. According to this theory, the creation of the perovskite structure is determined by the oxide's tolerance factor (t) [25]. The tolerance factor is represented in the following equation.

$$t = \frac{(rA+rO)}{\sqrt{2}\,(rB+rO)} \qquad \text{.....,..(1.1)}$$

Where rA, rB, and rO refer to the ionic radii of the A, B (cation), and O, respectively (anion). In the equation that has been provided, the tolerance factor describes the range of relative size throughout which the structure of perovskite can remain stable. When the tolerance factor is between 0.95 and 1.0, the structure of perovskite will be cubic. The geometry of perovskite oxide is mainly dependent upon the tolerance factor. It was also found the compound with a tolerance factor in the range of 0.95 to 1.0 existed with a structure that

was non-ferroelectric and distorted, whereas the compound with a tolerance factor of 1 had a structure that was ferroelectric and hexagonal. If the tolerance factor value is less than 0.75, the chemical does not crystallize in the perovskite structure [26,27]

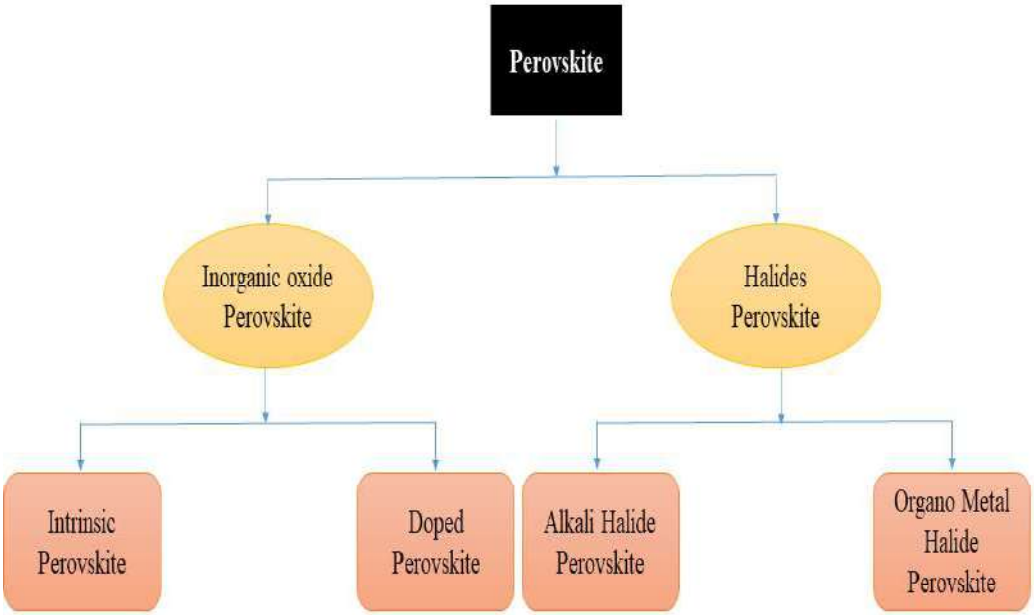


Figure 1.6: Classification of all type of Perovskite materials

1.5.2 Distorted Perovskite Structure:

A distorted perovskite structure is a variation of the ideal perovskite structure in which the octahedra are not perfectly as in ideal perovskite. The distortion can be caused by a number of variables, such as a difference in size between the A and B ions, a change in temperature, or pressure from the outside. The tilting of the octahedra is one way in which the structure of a perovskite can disarrange. In this case, the octahedra are not completely regular; rather, they tilt in distinct directions. The tilting can happen in different ways, like along the x-axis, the y-axis, or the z-axis. This can change the way the material works electronically and magnetically. The Breathing mode is a another type of distorted perovskite structure, in which the size of the octahedra changes over time. The changes in size can be in-phase or out-of-

phase, and they can change the way the material works electronically and magnetically[21]. Other distorted perovskite structures include the Polar mode, in which the center ion is moved away from the center of the octahedron, and one another type is Rotational mode, in which the octahedra rotate with respect to each other. Researchers gave a lot of attention to distorted perovskite structures because they have unique properties that can be tuned by changing the distortion parameters. They are good candidates for many applications, such as converting energy, catalyzing reactions, and making spintronic. The study of distorted perovskite structures is an active area of research, and it is expected to lead to the discovery of new materials with new properties[28].

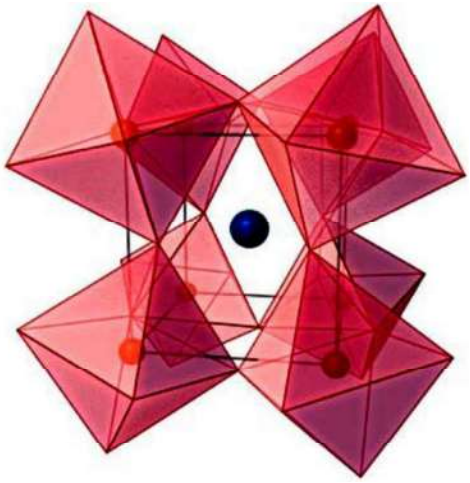


Figure 1.7: Distorted Perovskite Structure (Orthorhombic)

1.5.3 Applications of Perovskite Oxides:

The ability of the perovskite structure to accept a wide range of cations and anions that change its structure and properties has drawn high interest in this family of materials. These compounds exhibit ferroelectric, anti-ferroelectric, and Para electric properties at ambient temperature, making up a large category of dielectric materials. Due to their high electro-optic coefficients at room temperature, members of the perovskite family of type I (A_1+B_5+O_3) are

used in electro-optic devices. $KNbO_3$ and $KTaO_3$ of the aforementioned groups are employed in acousto-optic devices due to their high acoustic coefficients at ambient temperature [29,30]. Electro-optic materials, microwave surface acoustic devices, and holography memory devices are all made of $LiNbO_3$, $LiTaO_3$, and $KTaO_3$. At room temperature, compounds of the A_2+B_4+O_3 family have piezoelectric and ferroelectric characteristics. They are employed as piezoelectric transducers, phonograph pick-ups, air transducers, instrument transducers, underwater sound, and ultrasonic power wave filters, delay line transducers, gas lighter elements, dynamic and blast gauge accelerometers, and high voltage sources. They are also utilized in audio transmission and receiving, as well as ultrasonic cleaning machines, dielectric amplifiers, and information storage on electronic computers. $SrTiO_3$ is also another significant perovskite oxide in this family, which may be utilized to create positive temperature coefficient (PTC) thermistors and grain boundary barrier layer capacitors.

Additionally, it has also been used as a gas sensor in a Magneto hydrodynamic (MHD) application and for the photolysis of water. Thin $BaSnO_3$ films coated on an Al_2O_3 substrate are utilized to detect CO_2 and nitrogen dioxide gases at constant partial pressure. $SrSnO_3$ is a humidity sensor material. Ceramic boundary layer capacitors have also been made using $BaSnO_3$ and its solid solutions with titanates. In cellophane, B-site substituted compounds based on barium are employed as microwave resonators. Pb-based B-site substituted compounds are employed in the electronics sector and as multilayer capacitors for miniaturization [31–33].

1.6 Electro Ceramic Materials:

Ceramic materials are a class of inorganic, nonmetallic materials that have a crystalline structure and are made up of a mixture of metallic and nonmetallic elements, typically oxygen. Ceramic materials have diverse physical, mechanical, and thermal qualities that make them valuable for a wide range of applications, including electronics devices, energy storage devices, buildings, defense, space programs, and healthcare sectors [34]. Electro-ceramic

materials are an important subclass of ceramic materials because they have special electrical characteristics that make them particularly favorable in the electronic applications area. Ferroelectric materials, piezoelectric materials, and dielectric materials are examples of electro-ceramics, each with its own set of unique characteristics and uses [35]. Ferroelectric materials have spontaneous electric polarization that may be switched by applying an external electric field. Because of this, they may be used in a variety of applications, including memory devices, sensors, actuators, and electro-optic devices. Ferroelectric ceramic materials are primarily composed of perovskite structures, which have a cubic crystal lattice with a three-atom repeating unit [36,37]**.** Ceramics with dielectric properties are insulators that can hold electrical energy inside an electric field. When dielectrics are subjected to an electric field, they get polarized and store energy in the form of an electric field. Dielectric materials are helpful in a range of applications, including capacitors, energy storage devices, and microwave components, due to this characteristics, Ceramics such as alumina (Al_2O_3), Barium Titanate ($BaTiO_3$), and Lead Zirconate Titanate are examples of dielectric materials [38]. Ceramic materials are also frequently employed in various applications, such as construction materials, because of their great strength, durability, and resistance to environmental conditions such as temperature and moisture. Ceramic materials are also employed in healthcare for implants and prostheses because of their biocompatibility and ability to imitate the qualities of natural bone and tissue [39]. Ceramics are used in a lot of different ways in electronics, such as in capacitors, resistors, and printed circuit boards. They are valued for their high dielectric strength, thermal stability, and ability to withstand harsh environmental conditions like high temperatures, low temperatures, and humidity. Overall, ceramic materials and electro-ceramic materials are useful and versatile materials that are used in many

industries for a wide range of purposes. Because of their special qualities and wide range of uses, they are likely to continue to be important to technological progress in the coming years.

1.7 Composite ceramic material:

Composite ceramic materials are materials that are made by combining two or more different types of ceramics. These materials have unique mechanical, thermal, and electrical properties that make them useful in a variety of industrial and engineering applications. The following brief discussion is related to detail of composite ceramic materials along with their properties, types, and uses.

1.7.1 Characteristics of Ceramic Composites

The properties of composite ceramic materials are different from those of traditional ceramic materials. Among these properties are:

1. **High Strength:** Composite ceramic materials are known for their high strength and longevity. They are resistant to wear, corrosion, and chemical breakdown, which makes them good for use in harsh environments.

2. **High thermal conductivity:** Composite ceramic materials have excellent thermal conductivity, which makes them good for use in high-temperature applications. They can withstand in extreme temperatures without breaking down or losing their mechanical properties.

3. **Low Thermal Expansion:** Composite ceramic materials have a low coefficient of thermal expansion, which means that they don't grow or shrink much when the temperature changes. Because of this, they can be used in applications that require high dimensional stability.

4. **Electrical Insulation:** Composite ceramic materials are great electrical insulators, so they can be used in electrical and electronic applications.

1.7.2 Types of composite ceramic materials

Composite ceramic materials can be divided into two main types: ceramic matrix composites and polymer matrix composites.

1. **Ceramic Matrix Composites (CMCs):** Ceramic matrix composites are made by putting carbon fibers, silicon carbide fibers or ceramic fibers in a ceramic matrix. The reinforcing material makes the composite stronger and tougher and the ceramic matrix makes it stable at high temperatures and resistant to chemicals. CMCs are used in things like aerospace parts, gas turbines, and heat exchangers that need to withstand high temperatures and have good mechanical properties.

2. **Polymer Matrix Composites (PMCs):** A ceramic filler material and a polymer matrix, like epoxy or polyester, are used to make a polymer matrix composite. The ceramic filler improves the composite's mechanical properties, and the polymer matrix gives it flexibility and strength. PMCs are used for many different things, such as medical implants, car parts, and sports equipment.

1.7.3 Applications of composite ceramics:

Aerospace, automotive, medicinal, and electronics are just a few of the areas where composite ceramic materials are used. The following are some of the most typical uses for composite ceramic materials:

1. **Aerospace Components:** Composite ceramic materials are utilized in the aerospace sector to make parts for engines, rocket nozzles, and heat shields that can withstand at high temperatures.

2. **Automobile Components:** Composite ceramic materials are utilized in the automotive sector to produce parts like brake pads, clutches, and engine components that needed to be highly durable and strong.

3. **Biomedical Implants:** Composite ceramic materials are utilized in the biomedical sector to produce implants, such as dental implants, hip replacements, and spinal implants, that need a high degree of biocompatibility and mechanical strength.

4. **Electronics:** Components requiring superior electrical insulation, such as capacitors, resistors, and insulators, are made using composite ceramic materials in the electronics sector. Composite ceramic materials have special qualities that make them appropriate for usage in a variety of technical and industrial applications. Their strong strength, thermal stability, and electrical insulating qualities are well recognized. Ceramic matrix composites and polymer matrix composites are the two primary categories of composite ceramic materials. Numerous sectors, including aerospace, automotive, biomedicine, and electronics, utilize these materials. Further research and development into composite ceramic materials will lead to new products and technologies as well as new applications for them in a large range of industries.

1.8 Capacitor

A capacitor is a component that functions very similarly to a miniature rechargeable battery in that it can store energy in the form of an electrical charge and release it in the form of a potential difference between its two metallic plates, which are known as electrodes. This ability, known as its capacity, is built to discharge its stored energy in a very short amount of time. A capacitor is made up of two or more parallel conductive plates that do not touch each other but are kept electrically far apart either by air or by a good insulating material such as mica, ceramic, plastic waxed paper, and liquid gel as is used in electrolytic capacitors, This is the most fundamental form of a capacitor [40]. The term "dielectric" refers to the insulating layer that may be found between the plates of a capacitor. The potential difference between the conductors causes the development of a static electric field across the dielectric, which is caused by the alignment of charges inside the dielectric. Because of this, the positive charge

will gather on one plate, while the negative charge will accumulate on the other. The capacitor's energy is kept in the electric field by which it is surrounded [41]. **Figure 1.8** illustrates a parallel plate capacitor's working mechanism when connected to a circuit. This mechanism includes the alignment of charges inside the dielectric material.

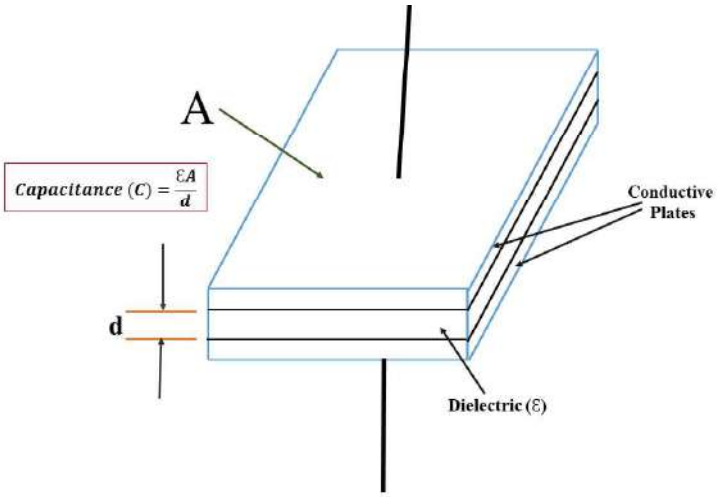


Figure 1.8: A prototype of Parallel plate capacitor

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

$$C = \varepsilon_0 A/d \qquad \text{..... (1.2)}$$

where ε_0 is the permittivity of free space with numerical value (8.854×10^{-12} F/m), When the dielectric constant is high, the capacitance that can be formed in a given space is also high. Therefore, when developing small integrated capacitors, those materials with a high dielectric constant are preferred.

1.9 Dielectric Materials

Dielectrics, or dielectric material, is an electrical insulator that can be polarized by an externally applied electric field. When a dielectric material is placed in an electric field, electric current does not flow through the material. When electricity doesn't flow through a material, the atoms only move a little bit from their average positions. This is called dielectric

polarization [42]. By making dielectric polarization happen, the positive charges moved in the direction of the field, and the negative charges moved in the opposite direction of the field. (For example, if dielectric polarization caused positive charges to move along the x-axis, then negative charges would move along the y-axis. When this happens, an electric field is formed in the material that does not favor the conduction of electricity. Notably, if the molecule bonded with the weakly bonded molecule, the dielectric material would not only become polarized, but it would also change its orientation. In this case, they will be lined up with the field's axes of symmetry [42].

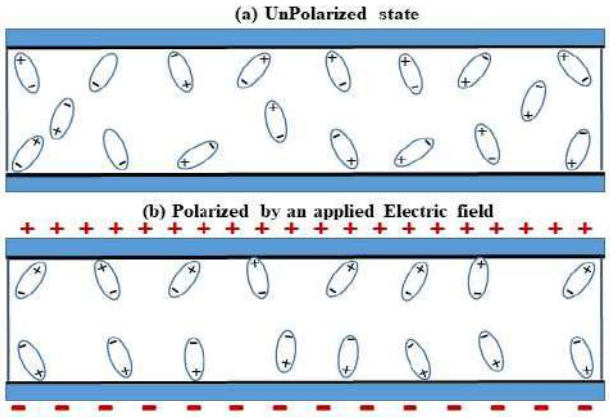


Figure 1.9: Dielectric material in two different states (a) UnPolarized state of dielectric material (b) Polarized by an applied electric field.

1.10 Polarization

When an electric field is applied to a dielectric material, dielectric polarization can occur within it. This effect causes the materials' electric dipoles to align in the same direction as the applied field. This process results in the creation of an electric polarization inside the material, which may be described by referring to the net dipole moment of the material expressed as a function of its unit volume. Dielectrics are non-conductive materials that make it difficult for electric charges to pass them [43]. Dielectrics are also known as insulators. Plastics, rubber, glass, and ceramics are a few examples of the types of materials that fall

within the dielectric category. When an electric field is applied to a dielectric substance, the electrons inside the material are moved from their positions of equilibrium, which results in the separation of positive and negative charges that are contained within the material. An electric dipole may be characterized as a positive charge and a negative charge that is separated by a short distance, and both contribute to the creation of an electric dipole inside the material. An electric dipole is created when the charges in the material are separated from one another. The size of the electric dipole moment is proportional to the intensity of the electric field as well as the polarizability of the materials [42]. Polarizability can be considered as a measure of a material's ability to become polarized in the presence of an electric field. When it comes to how easily a substance can be polarized, the most crucial factor to consider is the substance's polarizability. This is due to the fact that the electrons in the substance are more easily displaced from their positions of equilibrium, which results in a higher dipole moment. Dielectric polarization is a phenomenon that is essential to the operation of a wide variety of technological applications [44].

Capacitors are an example of one of the most common applications of dielectric polarization. Capacitors are devices that can store electricity by incorporating an electric field into their design. Two conducting plates are sandwiched a layers of dielectric substance to form a capacitor, when a voltage is applied to the plates, the dielectric material becomes polarized, which results in the storage of electric charge in the capacitor. Dielectric polarization is also an essential factor to consider in the design of electronic circuits. When designing circuits that work at high frequencies, the capacitance of the circuit is really important. It can have a big effect on how well the circuit performs, in these circuits, dielectric polarization can create an energy loss because it converts electrical energy into heat [45]. In

addition to this, the study of the characteristics of materials necessitates the consideration of dielectric polarization. It is possible to determine the dielectric constant of a material by observing how the polarization of the material changes when exposed to an electric field. The dielectric constant is a measurement of the material's capacity to store electrical energy[46]. Dielectric polarization is another method that may be utilized in the study of atomic structure and the characteristics of molecules. In particular, it may be used in the process of determining a molecule's dipole moment, which is an essential property of a molecule that is associated with the chemical characteristics of the molecule [47].

1.10.1 Electronics Polarization:

Electronic polarization occurs in materials, such as metals, with a substantial amount of free electrons. When such materials are subjected to an external electric field, the electrons are displaced from their equilibrium locations and form a dipole. The following expression describes the polarization of such materials.

$$P_e = N_e * e * \delta \qquad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots (1.3)$$

Where P_e is the electronic polarization, N_e is the number of free electrons per unit volume, e is the charge of an electron, and δ is the displacement of the electrons from their equilibrium positions.

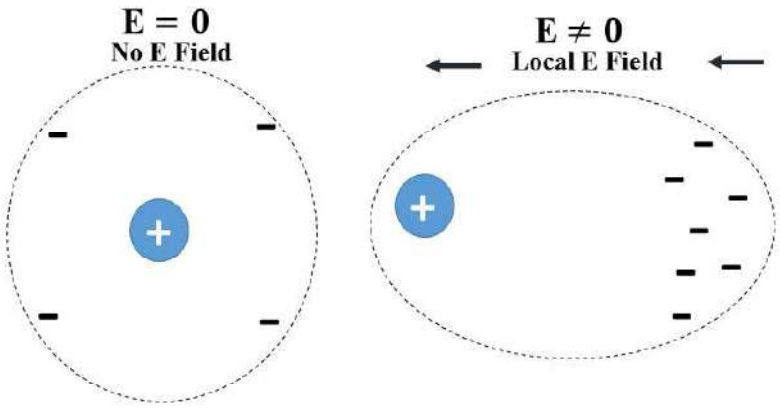


Figure 1.10: Phenomenon of Electronic polarization for E = 0 and E ≠ 0 for a dielectric material.

1.10.2 Ionic polarization:

Ionic polarization happens when there are ions in a material that have different charges. When an electric field from the outside is put on these materials, the ions move out of their normal positions and form a dipole[48]. The following formula describes how polarized these materials are:

$$P_i = N_i * e * \delta \qquad \text{……..……(1.4)}$$

Where Pi is the ionic polarization, Ni is the number of ions per unit volume, e is the charge of an electron, and δ is the displacement of the ions from their equilibrium positions.

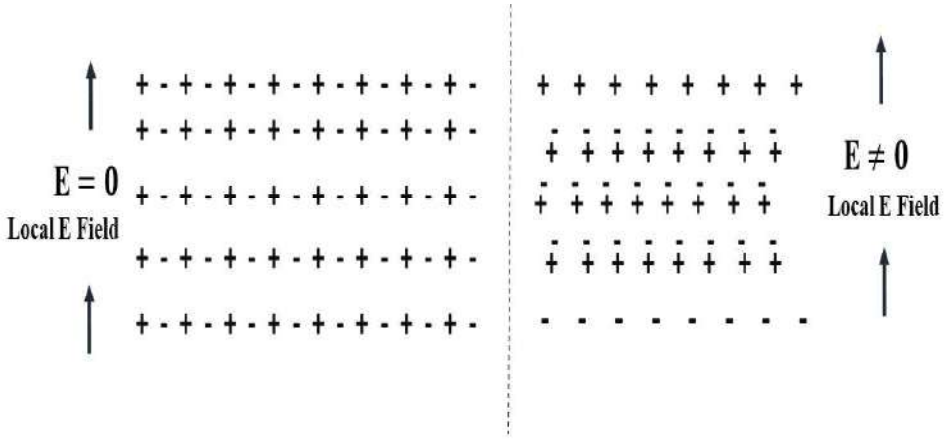


Figure. 1.11: Phenomenon of Ionic polarization for E = 0 and E ≠ 0 for a dielectric material.

1.10.3 Orientation polarization:

Materials having persistent dipoles, such as molecules with polar bonds, experience orientation polarization. Such materials exhibit overall polarization when an external electric field is introduced because the dipoles align themselves with the field[49]. The following formula describes the polarization of such materials:

$$P_o = N_o * \mu * E \qquad \text{……..……..(1.5)}$$

Where P_o is the orientation polarization, N_o is the number of permanent dipoles per unit volume, μ is the dipole moment of the dipoles, and E is the applied electric field.

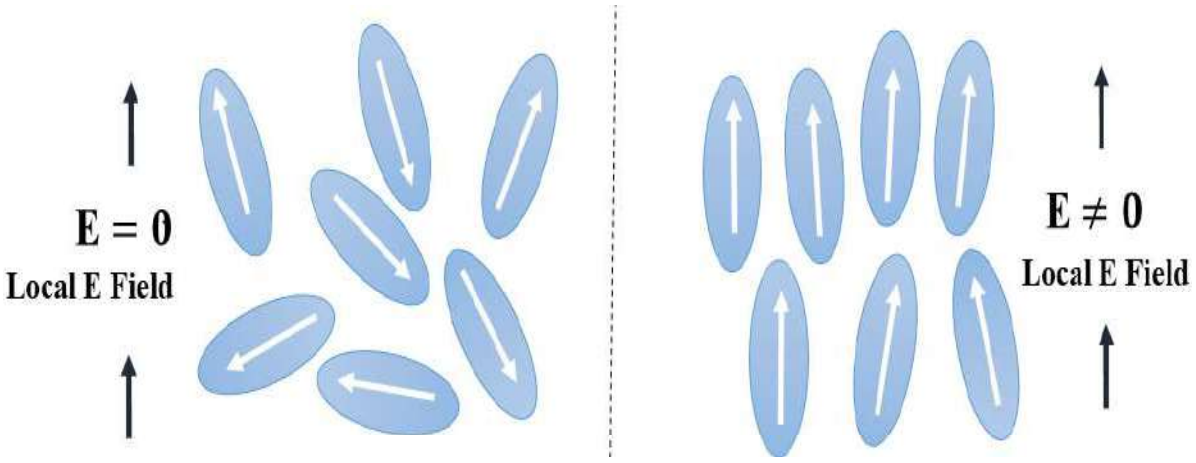


Figure. 1.12: Phenomenon of Orientation polarization for E = 0 and E ≠ 0 for a dielectric material.

1.10.4 Space Charge (Interfacial) Polarization:

Space charge polarization can occur in semiconductors and other materials with mobile charges due to their mobile charges. These materials accumulate charges at their interfaces when an external electric field is applied, forms an electric field which opposite the applied field[50]. The following formula may be used to describe the polarization of certain kinds of materials:

$$P_{sc} = \varepsilon_0 * \varepsilon_r * E \quad \text{…..…… (1.6)}$$

Where P_{sc} is the space charge polarization, ε_0 is the permittivity of free space, ε_r is the relative permittivity of the material, and E is the applied electric field.

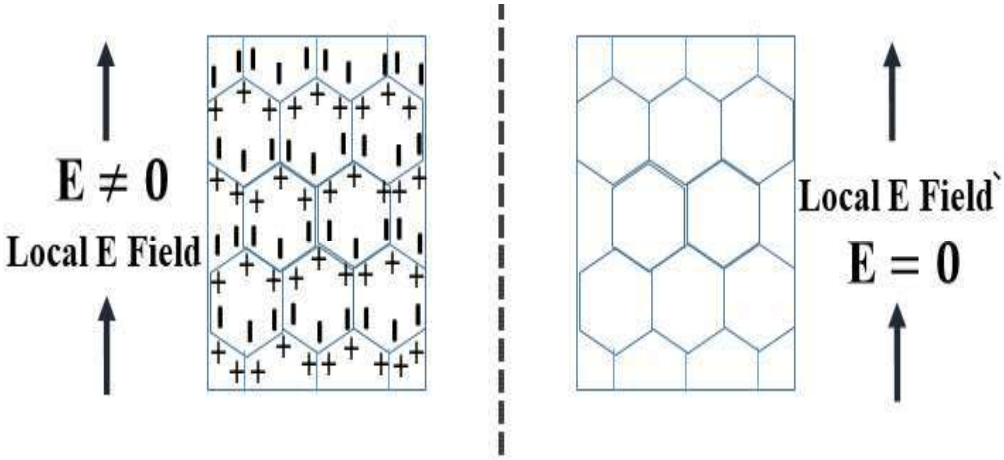


Figure. 1.13: Phenomenon of Space Charge polarization for E = 0 and E ≠ 0 for a dielectric material.

1.11 Ferroelectric Materials

Ferroelectricity is a unique phenomenon that may occur in certain dielectric materials. Ferroelectrics show spontaneous polarizations, which means a certain value of polarization remains in the materials after the removal of the external electric field. This phenomenon is analogous to ferromagnetism, which is the spontaneous magnetization seen in some types of materials [52]. In 1920, Valasek and Curie first time discovered the ferroelectric effect in Rochelle salt. Since that time, the phenomenon has been the topic of a significant amount of research and has been utilized in a wide variety of applications [53]. Materials are considered dielectric if they do not conduct electricity; however, they can store electric charges. When a dielectric material is placed in an external electric field, the charges inside the material move slightly from a center, forming an induced electric polarization. When the electric field is

removed from the majority of dielectric materials, the induced polarization that was present disappears.

Conversely, ferroelectric materials continue to remain polarized even after an electric field is no longer applied [50]. Ferroelectricity emerges from the asymmetry of the crystal structure of ferroelectric materials. Unlike most non-ferroelectric dielectrics, ferroelectric materials do not have symmetry in their crystal structure. It causes an imbalance between the positive and negative charges present in the substance. In ferroelectric materials, the spontaneous polarization is a result of the dipole moment introduced into the crystal structure by the unequal distribution of charges [1]. Ferroelectricity has been studied and used in many different fields, such as electronics, sensors, and data storage. In memory devices, where the polarization of the material can be used to store information, ferroelectric materials have been used. Ferroelectric materials have also been used in sensors, where the piezoelectric property of the material can be used to turn mechanical signals into electric signals [50].

There are different kinds of ferroelectric materials, such as perovskite oxides, Lithium Niobate, and Polyvinylidene fluoride (PVDF). Perovskite oxides are a group of materials with the general formula ABX_3, where A and B are cations, and X is an anion. Lead Zirconate Titanate (PZT) and Barium Titanate are both types of perovskite oxides ($BaTiO_3$). Another important ferroelectric material that is used a lot in electronics and communications is Lithium Niobate. PVDF is a polymer-based ferroelectric material that has received a lot of attention due to its flexibility and ease of usage [54].

1.11.1 Origin of Ferroelectricity:

Ferroelectricity can be described by looking at the material's crystal structure and how its atoms or molecules move. Most ferroelectric materials are crystalline solids with a non-centrosymmetric crystal structure. This means that the crystal doesn't have an inversion center. An inversion center is a point around which the crystal can be turned upside down without changing its properties. Because of this, the material has a net electric dipole moment, or polarization, This results from the arrangement of positive and negative charges in the crystal. The polarization of ferroelectric materials can be made stronger by aligning the individual electric dipoles within the crystal. This can happen through a process called "spontaneous polarization," caused by the movement of the material's atoms or molecules. The cause of spontaneous polarization is still being investigated, although it is assumed to be related to the unequal distribution of charge in the material, which causes electric fields inside the material [55]. These electric forces within the crystal can induce the atoms or molecules to move in a specific direction, which lines up the electric dipoles and makes the net polarization stronger. In short, ferroelectricity is caused by the alignment of electric dipoles within a material that has a non-centrosymmetric crystal structure [56].

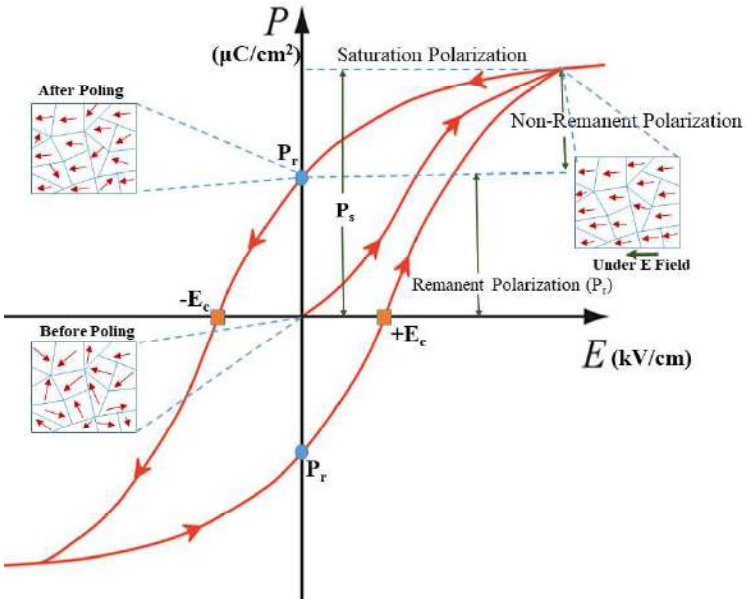


Figure. 1.14: Phenomenon of Ferroelectricity and Polarization-Electric Field loop in a dielectric material

1.11.2 Saturation Polarization:

Ferroelectric materials have a characteristic known as saturation polarization, which describes the highest degree of polarization that a material is capable of under an applied electric field. A ferroelectric material becomes net polarized when exposed to an external electric field because the internal dipoles of the material align in the direction of the field [57]. At the beginning, the polarization grows linearly with the intensity of the electric field, but after reaching a maximum value, additional strengthening of the electric field does not affect the polarization. The saturation polarization refers to this highest polarization value [58]. The size of the saturation polarization depends on many things, such as the structure of the crystals, the temperature, and what the material is made of. It is an important parameter that affects the electrical properties and performance of ferroelectric materials used in devices like capacitors, sensors, and memories. Understanding saturation polarization is important for making and improving various devices [57].

1.11.3 Remnant Polarization:

The term "remnant polarization" refers to the electric polarization of a material that persists even after the electric field that caused it has been removed. Ferroelectric materials, or those that spontaneously polarize in the absence of an external electric field, are the materials in which this behavior is frequently seen [59]. The remnant polarization of ferroelectric materials results from the alignment of the material's dipoles in its crystal structure. An electric field causes the dipoles to align in its direction, and when the field is removed, the dipoles continue to be aligned, producing a remnant polarization. Remnant polarization is a crucial characteristic of ferroelectric materials and is frequently used in various applications, including actuators, sensors, and non-volatile memory systems. For the development of this and other ferroelectric-based technologies, it is essential to understand and manage the remnant polarization [60].

1.12 Electrical Energy storage

The energy storage process of any dielectrics is the process of dielectric polarization and depolarization, which take place when an external electric field is applied and removed. The energy storage of process for any dielectric. The energy storage process of dielectric capacitors is completed mainly in three different stages, as shown in **Figure 1.16.**

Stage 1, When E = 0 mean there is no any external electric field applied, the net polarization inside the dielectric material is zero because random orientation of dipole moment. **Stage 2**, When E ≠0 means there is an external electric field applied, the net polarization inside the dielectric material is non-zero because the unidirectional arrangement of dipole gradually

reaches the maximum polarization value, then to the completion of energy storage process induction of macroscopic polarization charge occurs on the electrode surface. **Stage 3**, When E = 0 external electric field is removed, the oriented dipole moment will return to its initial random state, and the macroscopic polarization charge on the electrode will also be minimized because of the combined effect of the depolarization field and the thermal motion generated by the internal dipole moment. During this time, the external release of electrical energy is completed in the charging stage (stage 1-stage 2) and the external circuit, which stores the energy in the capacitor. The dielectric materials' overall stored energy density (Recoverable energy density) can be given as follows.

$$\mathbf{Wrec} = \int_{\mathbf{Pr}}^{\mathbf{Pmax}} \mathbf{EdP} \qquad \text{.....1.8}$$

The energy efficiency of the dielectric determine by the Capacitor charge-discharge efficiency (η) which is as follows.

$$\boldsymbol{\eta}\,(\%) = \frac{\boldsymbol{Wrec}}{\boldsymbol{Wrec+Wloss}} \qquad \text{.....1.9}$$

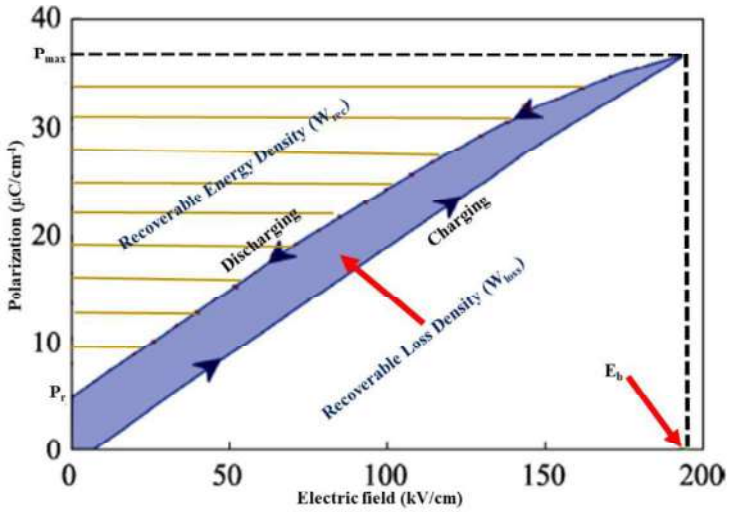


Figure 1.15: Electric Displacement-Electric Field (D-E) loop

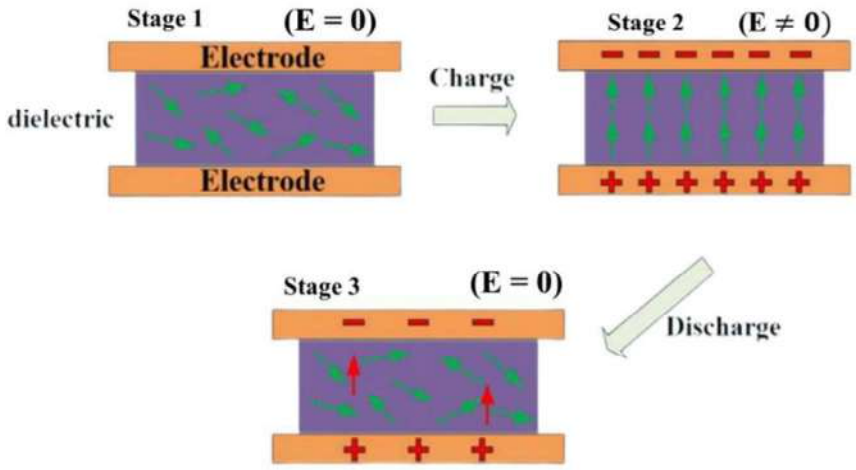


Figure1.16: Stages of Charging and Discharging of capacitors

1.13 Photoluminescence materials

Photoluminescence is a process in which a material emits light after photons make it excited. This effect happens in many materials, like semiconductors, organic molecules, and nanoparticle-based materials. It has many uses in areas like lighting, displays, sensing, and imaging. To understand the origin of photoluminescence, the energy levels of the material's constituent atoms or molecules are considered in the scenario. Electrons in an atom occupy certain energy levels, and transitions between these levels can result in photon absorption or emission. As a material absorbs a photon, an electron is excited to a higher energy level and then returns to its ground state by producing a lower-energy photon. This emitted photon correlates to the photoluminescence of the material [61].

The photoluminescence process may be divided into two distinct types as follows.

(a) Fluorescence, (b) Phosphorescence

Fluorescence occurs when an excited electron quickly relaxes, usually within nanoseconds, producing a photon with a lower energy and longer wavelength than the photon that was absorbed. The emitted light is often a different colour than the light that was absorbed. **Phosphorescence**, happens when an excited electron relaxes more slowly, on the scale of microseconds to seconds, producing a photon with a longer wavelength than the absorbed photon. This leads in a longer-lasting emission that may continue to exist after the excitation source is remove [62,63].

Photo luminescent materials can be put into two groups as follows.

1.13.1 Intrinsic and Extrinsic luminescent materials

Intrinsic Photo luminescent materials can glow without dopants or impurities. These include semiconductors like silicon, germanium, and gallium arsenide. These materials have a bandgap, allowing them to absorb photons and subsequently emit light. **Extrinsic Photo luminescent materials**, on the other hand, need dopants or impurities to glow in the light. These materials include phosphors, which are used in lighting and display, and biological probes, which are used for imaging and sensing applications [64,65].

Phosphors are an extrinsic photo luminescent materials that contains activators and dopants, which produce defects in the crystal structure. These defects act as traps for excited electrons, causing them to relax slowly and emit photons with longer wavelengths. Phosphors are frequently used in fluorescent lamps, LED lighting, and display screens and may be manufactured from a wide range of materials such as oxides, sulphides, and halides [66]. Biological probes are a form of extrinsic photo luminescent material that is utilized for imaging and sensing in biological systems. These materials generally comprise of a fluorescent dye attached to a biomolecule, such as an antibody or nucleic acid. When the probe

is excited by light, it generates a signal that may be recognized and utilized to see or measure the biomolecule which is targeted. Fluorescent proteins, such as green fluorescent protein (GFP), are another type of photo luminescent biological probe that is frequently employed in molecular biology and cell biology research. To summarize, photoluminescence is a fascinating phenomenon with multiple applications in a variety of disciplines. By studying the energy levels of the material's component atoms or molecules, the origination of photoluminescence can be understood, and the photoluminescence process may be split into fluorescence and phosphorescence. Photo luminescent materials are classified as intrinsic or extrinsic, including semiconductors, phosphors, and biological probes as examples. Researchers may continue to create novel materials and applications that take use of this unique phenomena by understanding the underlying principles of photoluminescence.

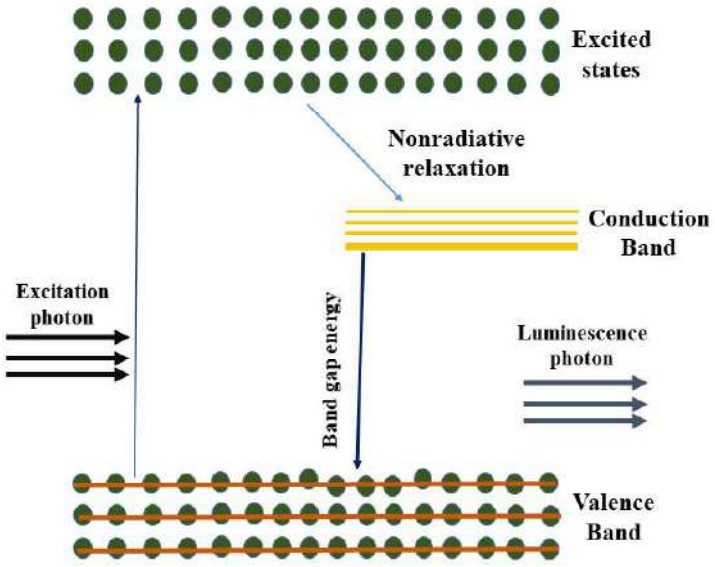


Figure. 1.17: Phenomenon of photoluminescence in a photo-luminescent material.

1.14 Properties of Lithium Niobate

$LiNbO_3$ is an important component in integrated and guided wave optics. It's a dielectric material created by researchers that doesn't exist in nature. It was revealed to be ferroelectric for the first time in 1949[67]. Lithium Niobate was made in single crystal form at Bell Laborites and thoroughly examined. According to their results, they have reported 5 research papers about materials structure and characteristics [68,69]. Its presently one of the most preferred electro-optic materials of the market. It is characterized by wide pyroelectric, electro-optic, piezoelectric, and photoelastic coefficient, which has a trigonal crystal structure. Lithium Niobate is birefringent by nature, it has practical acoustic characteristics and a high acousto-optic figure of merit [70].

Furthermore, it has a very significant high-volume photovoltaic effect. This phenomenon causes efficient charge movement inside the material, which, when combined with the linear lector-optic effect of the materials, can produce a large photorefractive effect (optically induced refractive-index alterations). Although Lithium Niobate is valuable in a wide range of technological applications, every textbook does not cover its physical as well as crystal structure of material. As a result, a large number of research papers must be extensively studied to gain a comprehensive understanding of their different types of characteristics as well as their structural information.

1.14.1 General Structure of Lithium Niobate

At temperature below the ferroelectric Curie temperature (approximate 1210°C), the Lithium niobate has a structure that consists of planar sheets of oxygen atoms in deformed hexagonal close packed arrangement. One third of the octahedral interstices in this structure are filled with Lithium atoms and one third with niobium atoms and left one third part is

unoccupied. In the +C plane, the atoms appear in the interstices in the correct sequences. Nb, vacancy, Li, Nb, Vacancy, Li, Nb, Vacancy, Li, Nb, Vacancy, Li…. [71]. The Li atoms in an oxygen layer c/4 apart from the Nb atom in the para-electric phase above the Curie temperature and the Nb atoms are Positioned between oxygen layers. Because of these certain placements the para-electric phase is nonpolar. While the temperature drops below the curie point, the crystals Elastic forces take over the and push the Li and Nb ions in to a new place. At temperature below 1210°C the charge separation caused by the shift of ions relative to the oxygen octahedral causes $LiNbO_3$ to spontaneously polarize[72,73]. As a result, $LiNbO_3$ is classified as displacement ferroelectrics. Other displacement ferroelectrics including barium titanate ($BaTiO_3$) and Lithium Tantalite ($LiTaO_3$)[74]. A $LiNbO_3$ crystal in the ferroelectric phase which has three-fold Rotation symmetry around its c-axis. As a result, it belongs to the Trigonal crystal system. It also has mirror symmetry around three planes that are 60 apart and intersect to produce a three-fold rotating axis[75].

1.14.2 Literature Survey related to $LiNbO_3$ materials

Several reviews have been published on their research works on the lithium niobate for the ceramic material form, as well as for the single crystal material form. Many characteristics of $LiNbO_3$ were covered in one of the well-known books on the theory and applications of ferroelectrics published in 1977 [76]; more than ten years later, a thorough summary was published in 1991 (Xu 1991). An outstanding book on the characteristics and development characteristics of $LiNbO_3$ was published by Kuzminov in 1999[77]. The book "Chemistry and Physics of Lithium Niobate" by Räuber was published (1978) and received positive reviews [78], and Weis and Gaylord (1985) compiled a list of the physical characteristics of the crystal structure of $LiNbO_3$[79]. "Properties of lithium niobate" (Wong

2002) was published and included updated data on $LiNbO_3$ in detail form [19]. The Photo refraction characteristics of LiNbO3, as well as the defects, ferroelectric switching, and applications, have also been investigated and reported [80]. There are a lots of researchers who reported their research on Lithium Niobate based ceramic as well as single crystal materials for the technological applications, in this part of my thesis we are discussing various reported research works as follow.

A.El Bachiri et al. synthesized $Li_{1-x}Nb_{1+x/5}O_3$ (where x = 0, 0.025, 0.045, 0.075) ceramic using solid-state reaction method for the study of dielectric and electrical properties. For the Dielectric characteristics at various temperatures between 300°C and 1000°C, they employed impedance spectroscopy. It was discovered through impedance analysis that there were two different types of conduction processes and that the conductivity data matched with the power equation, $\sigma_{ac}(\omega) = A\cdot\omega^{n1} + B\cdot\omega^{n2}$. In the conclusion part, they reported that the long-range ordering (almost frequency-independent) is responsible for the low-frequency conductivity, whereas the localized orientation hopping mechanism is responsible for the high-frequency conductivity [81]**.** S. Shimada et al. reported the effect of additives, such as CdO, on the sintering of $LiNbO_3$ because the sintering of $LiNbO_3$ is a significant concern in the 805°C -1100 °C temperature range based on Kingery's model of initial sintering and kinetics grain development. They demonstrated that the earliest phases of sintering of pure and CdO-added LN can be fitted to Kingery's equation, and they discovered that volume diffusion is operational in both circumstances. In this case, oxygen ions act as rate-controlling species, and the CdO additive increased the apparent diffusion coefficient of the rate-regulating species by 500 times. According to their findings, grain development follows cubic kinetics. There are some indications that secondary/impure phase formation

between LN and CdO, which inhibits discontinuous grain growth. They further summarize that additives such as CdO, Y_2O_3, ZnO, Fe_2O_3, and CaO enhance sintering, whereas Ta_2O_3, Sb_2O_3, Cr_2O_3, and ZrO_2 prohibit it [82]. C.R. Cena et al. synthesized the ceramic fibers of LiNbO3 from a simple precursor solution using the "blow-spinning" technique and reported the structural, dielectric, and electrical properties of the synthesized ceramic fibers. The Impedance Spectroscopy technique was utilized to determine the material's electrical characteristics, and with the help of Modulus analysis, they verified that the material has a hopping mechanism. The contribution of bulk and grain boundary effects plays a main role in the electrical conduction in prepared samples. The bulk resistance dropped as the temperature increased, which shows that the material is behaving naturally under Negative Temperature Coefficient Resistance (NTCR) conditions. While dc conductivity exhibited a normal Arrhenius type of electrical conductivity, the measured properties are shown in the **Figure 1.18,** it was revealed that the ac conductivity spectrum followed Jonscher's universal power law and synthesized material exhibits with an activation energy of 1.5 eV [83].

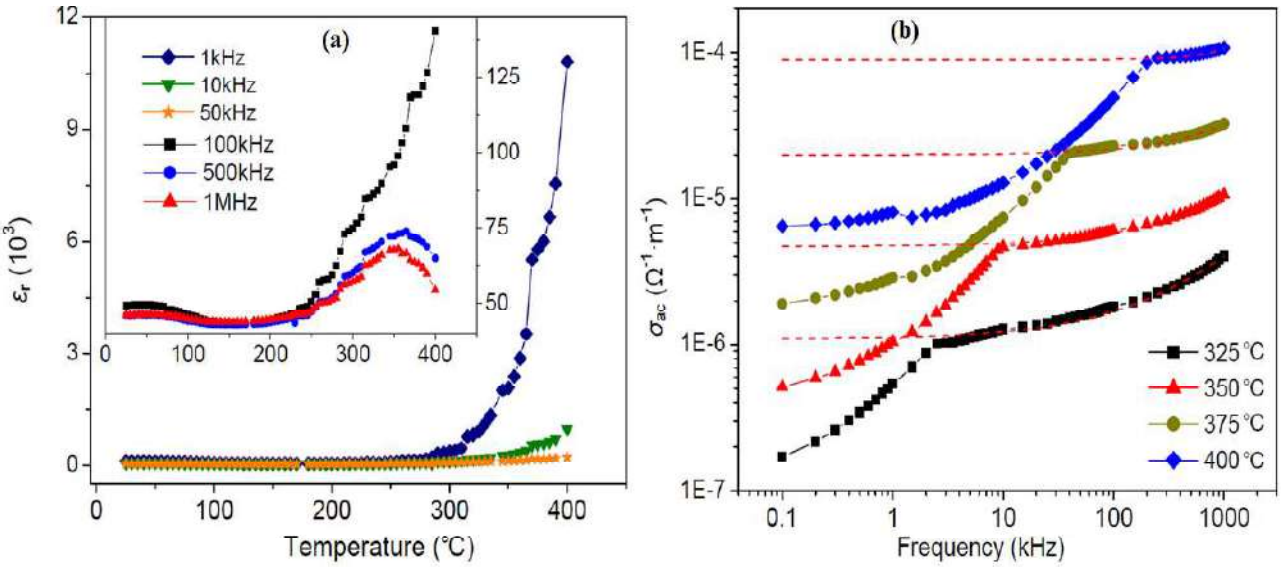


Figure 1.18 (a-b) Dielectric constant: (a) as a function of temperature at different frequencies (b) Variation of ac conductivity with frequency.

The band gap investigation for the LN for ferroelectric and paraelectric phases has been published by C. Thierfelder et al. The structurally relaxed ground state of both the ferroelectric and paraelectric of LN phases are obtained using density functional theory in generalized gradient approximation (DFT-GGA). Some previous reports of theoretical studies of the optical properties of LN based on a model screening function, and it was revealed that the estimated fundamental gap was at least 1 eV greater than the observed value. C. Thierfelder et al. used the full-potential linearized augmented plane-wave (FLAPW) approach for lithium niobate to perform first-principles GW calculations. According to their analysis, ferroelectric LN has a predicted band gap of 4.71 eV, whereas para-electric LN has a band gap of 4.21 eV. According to their findings, the band gap is noticeably reduced when compared to an earlier GW estimate that utilized a model named dielectric model function[84]. In a research article titled "Multifunctional behavior of mesoporous $LiNbO_3$," by S. Banerjee et al. in which they used a soft-template approach and developed mesoporous lithium niobate, as a soft template or surfactant, they used Pluronic P123. Three different characteristics of the prepared sample were examined, such as photoluminescence, ferroelectricity, and ferromagnetism, and the properties that were analyzed are shown in **Figure 1.19.** Their investigation indicated that oxygen vacancy was caused at wavelength 390 nm for photoluminescence at ambient temperature. The saturation magnetization of mesoporous $LiNbO_3$ at ambient temperature was also reported to be 0.019 emu/gm in the ferromagnetic study. This indicates an oxygen vacancy concentration of $4.9*10^{18}$/cc, which produced a magnetic moment in the samples. Additionally, they noted that the prepared samples exhibited a magneto-dielectric effect, with the dielectric constant rising by ~4.5% for a magnetic field of 10 kOe applied. This happened because the magnetostriction of the

material changed the lattice parameter, which led to an increase in the unit cell's dipole moment. The sample's ferroelectric characteristics were further validated by the PE hysteresis loop test.

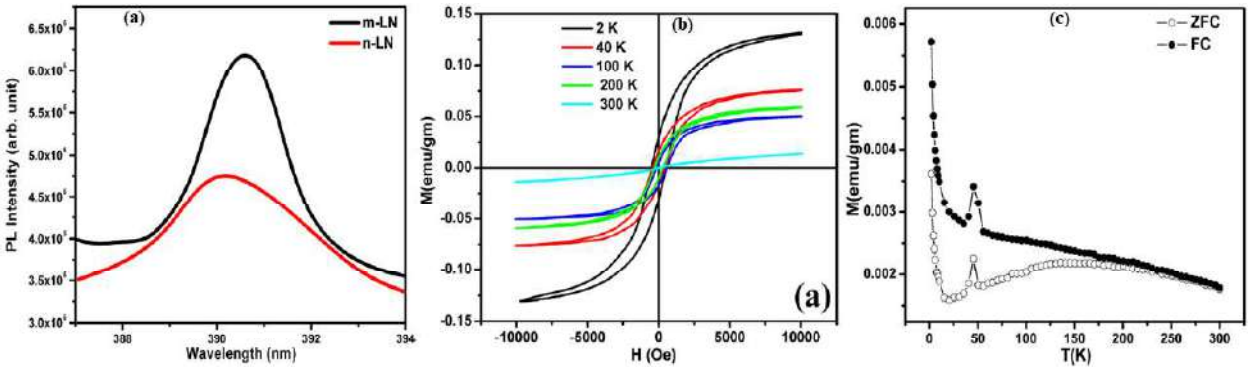


Figure. 1.19 (a-c): (a) Photoluminence spectra at room temperature of mesoporous and nonporous lithum niobate. (b) Magnetization as a function of magnetic field curve at different temperatures for mesoporous lithum niobate. (c) Variation of magnetization as a function of temperature under ZFC and FC conditions.

M. Tasson et al. published an article, "Piezoelectric study of poling mechanism in lithium niobate crystals at a temperature close to the curie point," and discussed the poling mechanism in lithium niobate crystals. In this article, the authors demonstrate three different mechanisms that may cause the orientation of a lithium niobate crystal's spontaneous polarization when cooling it through its curie point. There are three different approaches and two of which have never been reported previously. The first of the three approaches is the well-known impact of an applied electric field. The second is due to the presence of a temperature gradient, and the third is due to the presence of a composition gradient. They also revealed that all three mechanisms work in a very restricted temperature range of about curie point, which is roughly 3°C. They demonstrated that, at the curie temperature, spontaneous polarization of LN may be oriented by a thermal or compositional gradient in addition to the well-known impact of an electric field. They also presented a quantitative explanation based on strain gradient [85]. M. Manikandan et al. developed LiNbO3 ceramic through ball milling

solid state route and published an article titled "Multiferroicity in polar phase LiNbO3 at room temperature" based on multiferrocity in polar phase LN. They revealed a rhombohedral phase of $LiNbO_3$ with hexagonal unit cell symmetry for LN Ceramic. The weak ferromagnetic behavior of the LN produced by the Vibrating sample magnetometer (VSM) in LN Ceramic was explained by utilizing the Dzyaloshinskii - Moriya interaction generated by ferroelectric distortion in LN magnetic order. They also reported the electrical and dielectric characteristics, demonstrating two thermally triggered conduction processes obtained from the Arrhenius plot. The contribution of lithium-ion hopping and polarization components contributes significantly to the slow increase in dielectric constant below 493° K and the rapid increase in dielectric constant. All analyzed results are shown in the **Figure. 1.20,** and during the PE analysis, they obtained a lossy PE loop [72].

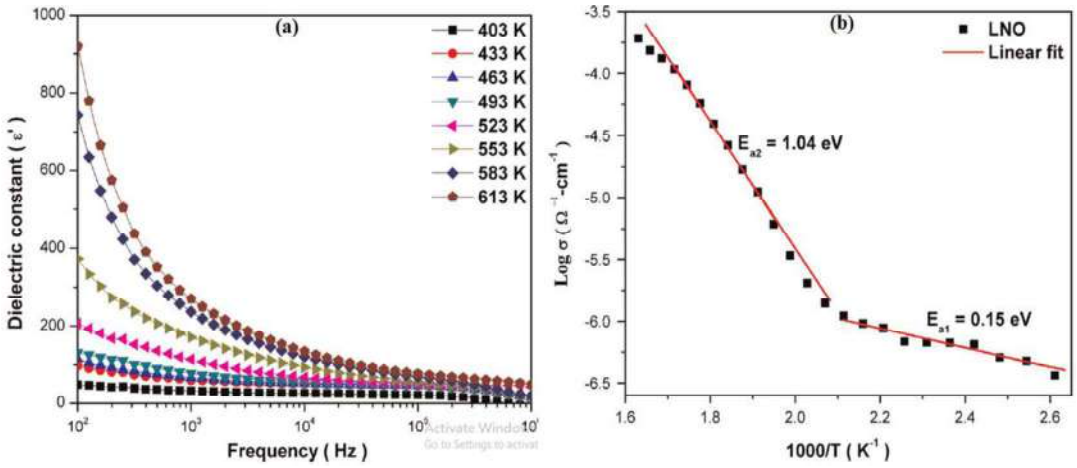


Figure. 1.20 (a-b): (a) Frequency dependent dielectric constant plots of $LiNbO_3$ in the temperature (b) Range 403°–613°K. Arrhenius plot of $LiNbO_3$ showing two thermally activated conduction processes.

A research article titled "The origin of hyper ferroelectricity in $LiBO_3$ (B = V, Nb, Ta, Os)," reported by Pengfei Li et al., shows how hyper ferroelectricity in $LiNbO_3$ originated. By using first-principles techniques and density functional theory, they have examined the

electrical and structural characteristics of $LiBO_3$ (B = V, Nb, Ta, and Os). Due to their shared instability in longitudinal optic phonon modes, they demonstrate that $LiBO_3$ is a member of the recently proposed class of hyper ferroelectrics (hyper FEs). They also proved that the structural instability resulting from short-range contacts causes hyperFE instability, which is different from conventional proper ferroelectricity, where the ferroelectric instability is generally generated by long-range coulomb interactions. This is present in the system due to the huge ion size mismatches [86]. K. Wang et al. developed a $LiNbO_3$ doped (Na,K) NbO_3-based lead-free piezo ceramic and sintered it at a lower temperature than usual by utilizing an additive Na_2O. Their published article demonstrated that when the phase transition temperature TOT migrated downward, the crystal structure changed from orthorhombic to tetragonal. They also revealed an improved piezoelectric constant (d_{33} = 280pC/N) and electromechanical coupling factor kp (48%) with high curie temperature (475°C) in the two-phase co-existence zone for the composition $0.92(Na_{0.535}K_{0.48})NbO_3$-$0.08LiNbO_3$. They also stated that their findings open new paths for low-temperature sintering of lead-free piezo ceramics based on $(Na,K)NbO_3$. The reported results of this research article is presented in **Figure 1.21** [87].

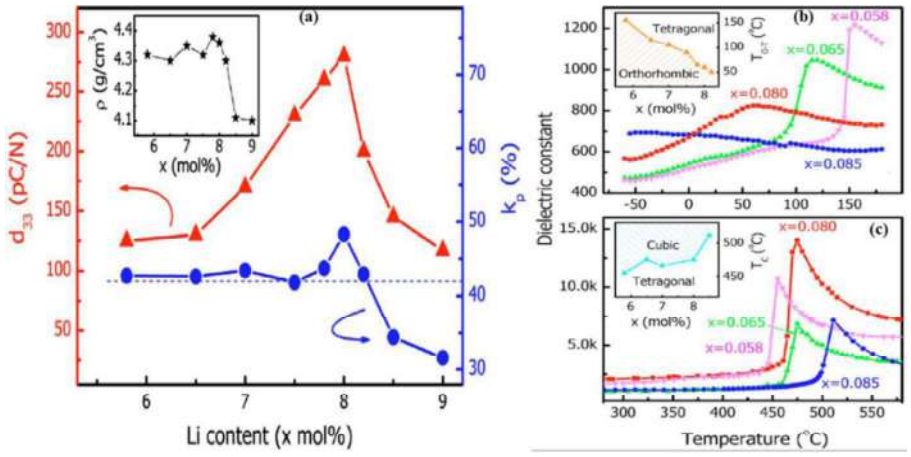


Figure 1.21(a-b): (a) Various properties of ceramics, dielectric constant of at 10 kHz in the range of (b) −60–180 °C and (c) 280–580 °C.

L. Arizmendi et al. have published a research article on the photonic use of $LiNbO_3$. According to their research, Laser emission can be generated at any wavelength in the transparent spectral spectrum of lithium niobate. It is possible to fabricate devices that control light using electrically and optically driven switches and modulators, narrow bandwidth filters, and couplers. Lithium niobate plays a significant role in the field of optical memories due to its greater stability and material inertness than polymer and organic materials, which are also used for holographic recording. It is an excellent material for permanent holographic components. Therefore, lithium niobate can also be used in applications such as phase-encoding key storage materials and encoded data memory. For example, an Interdigital electrode transducer is shown in the **Figure. 1.22** [88].

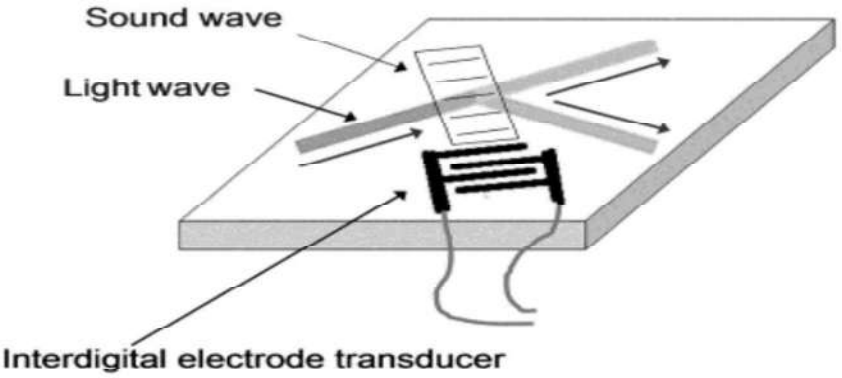


Figure 1.22: Interdigital electrode transducer for surface acoustic wave (SAW) generation in lithium niobate.

Roman N. Zhukov et al worked on thin film of Lithium Niobate to enhance the piezoelectric properties and published an article "Enhancement of piezoelectric properties of lithium niobate thin films by different annealing parameters". In their research work they grown thin film on a "cold" Si (111) substrate by RF magnetron sputtering. They tried to improve the piezoelectric properties by changing annealing parameters (heating and holding times), and the variation in the properties is shown by curve in the **Figure.1.23,** The key

challenge during their work was Lithium nonstoichiometric which causes impure phases, which disturbed the physical and structural characteristics of the synthesized film. According to piezo response signal distribution, samples heated to 700 °C for 12 minutes and 5 minutes have a limited volume of differentially orientated domains. They found a very low roughness that ranges from 1.4 to 2.4 nm[89].

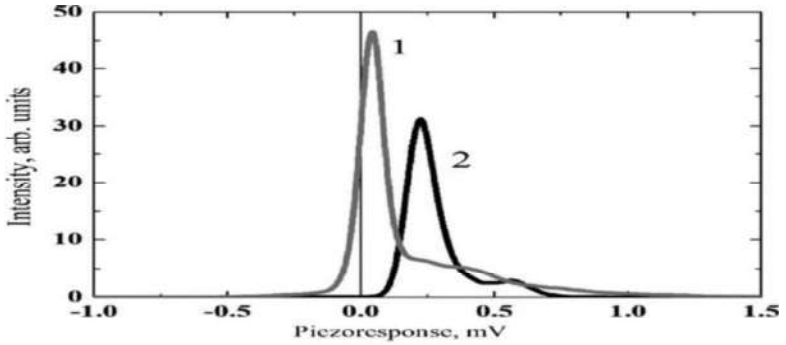


Figure 1.23: Histograms of distribution of piezo response signals for $LiNbO_3/SiO_x/Si$ (line 1) and $LiNbO_3/Pt/Si$ (line 2) heterostructures.

The effect of magnesium on the structure and properties of $LiNbO_3$ prepared from polymeric constituents has been investigated by A.Z. Simoes et al., They revealed that the unit cell volume of the rhombohedral phase in the system increases with an increase in magnesium doping concentration. Mg+2 ion was substituted for niobium ion in the rhombohedral phase, and Mg+2 promoted the densification of LN Ceramic, which resulted in secondary phase formation. Due to the formation of $LiNb_3O_8$ and $MgNb_2O_6$ phases at the grain boundaries as a result of an increase in additive concentration, the electrical properties Kp and d_{33} are reduced. **Figure 1.24** represents the XRD patterns of doped and pure $LiNbO_3$ powders [90].

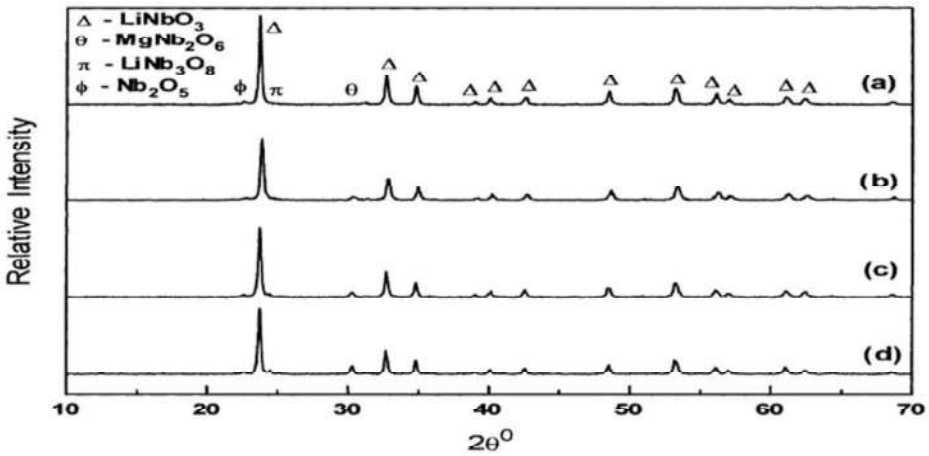


Figure 1.24: XRD patterns of doped and pure $LiNbO_3$ powders doped with different concentration of magnesium and calcined at 600 C for 3 h.

The function of cerium in lithium niobate for the application of holographic recording has been investigated by Xuefeng Yue et al. They demonstrated a photochromic phenomenon in an LN crystal doped with cerium and manganese. Cerium is a red-sensitive photorefractive center active in $LiNbO_3$ and plays an important role in charge transfer during holographic recording. The two-center recording in the sample is not as effective as in iron and manganese doubly doped crystals because the photovoltaic constant in the Ce doped crystal is only one-third that of the Fe doped sample, according to a comparison of the properties of prepared crystals that is doped with other elements. Ce-doped LN significantly affects the reflection geometry, where diffusion is common and less sensitive recording is obtained in the Ce-doped crystal [91]. Another research study by D.K. Mcmillon et al. examined the holographic recording in LN with 12 dopants, including Fe:Ce, Fe:Cr, and Fe: Mn. Each crystal shows measured transmission spectra, and holograms were also written in each crystal at wavelengths ranging from 457 to 671 nm. They revealed that the most significant reaction is in Fe single- and group-formed double-doped crystals. The optimal wavelengths for single-doped Mn and Ni crystals are 514 nm and 671 nm, respectively, where they exhibit the most incredible responses. The most promising choice was discovered to be a Ni-doped crystal for

dynamic holography. Although Fe: Cr double-doped crystal had extremely high absorption and scattering issues, it recorded powerful holograms at every wavelength, while Tb and Rh-doped crystal had a weak response. This article informed that due to differences in the experimental arrangements of each wavelength, it is not possible to compare wavelengths quantitatively [92]. Anil Tumuluri et al. examined the luminescence characteristics of $LiNbO_3$ polycrystalline ceramics with the effects of Sc_2O_3 and Lu_2O_3 doping, and they employed the solid state reaction technique to synthesize the ceramics. For all of the samples with illumination in the UV range (370 nm), they saw strong violet fluorescence at 414 and 435 nm. Apart from this, pure $LiNbO_3$ blue emission was seen at 473 nm with excitation at 289 nm. The measured peak is redshifted to 505 nm and exhibits green emission at 525 nm with changes in the dopant concentration of Sc_2O_3. The morphology and XRD analyses further revealed that some unreacted Lu_2O_3 aggregates as tiny crystals at the grain boundaries. All the analyzed properties are shown in the **Figure 1.25** [93]**.**

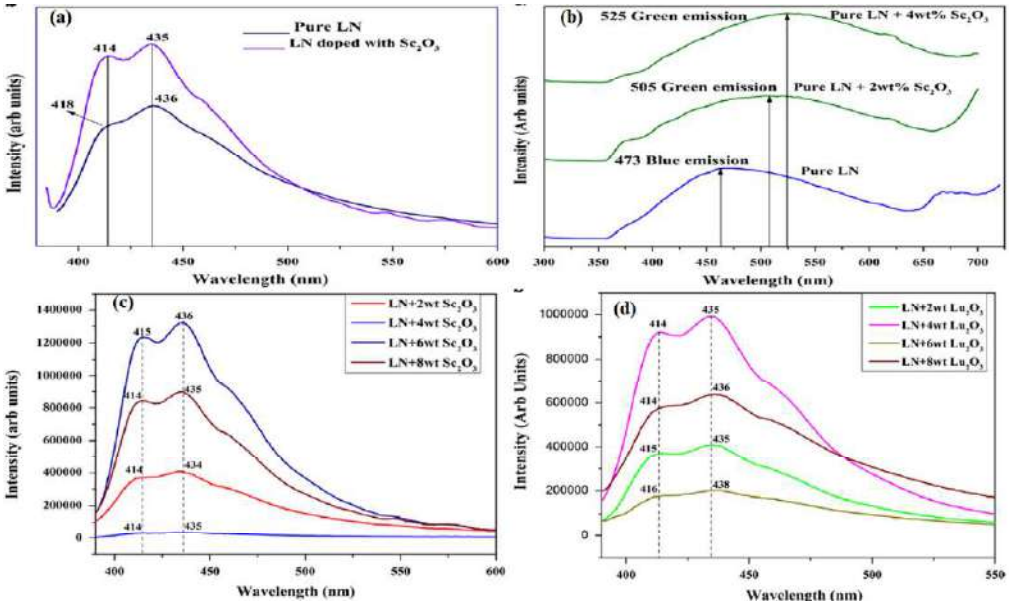


Figure 1.25 (a-d): (a) Emission spectra of LN doped with Sc_2O_3 at an excitation wave length of 370 nm. (b) Emission spectra of LN doped with Sc_2O_3 at an excitation wavelength of 289 nm. (c) Variation of intensities in emission spectra of LN with Sc_2O_3. (d) Variation of intensities in emission spectra of LN with Lu_2O_3 doping.

Rajeev Bhatt et al examined the optical and photoluminescence characteristics of $LiNbO_3$ crystals doped with Cr_2O_3 at 0.1, 0.25, and 0.5 mol%. For the growth of a single crystal, the Czochralski method was utilized. In their Optical Transmission study, researchers discovered strong absorption bands in the visible area with photon energies ranging between 1.9 eV to 2.57 eV. A strong red shift of 60 nm was detected in the UV absorption edges of the doped crystals, and analyzed results are shown in the **Figure 1.26,** It was also confirmed that Cr^{3+} produced impurities, which causing an overall drop in the Li/Nb ratio. With Cr doping, the absorption coefficient rises while the band gap reduces. Photoluminescence (PL) recorded at 900 nm confirmed that it is a promising material for laser amplification [94].

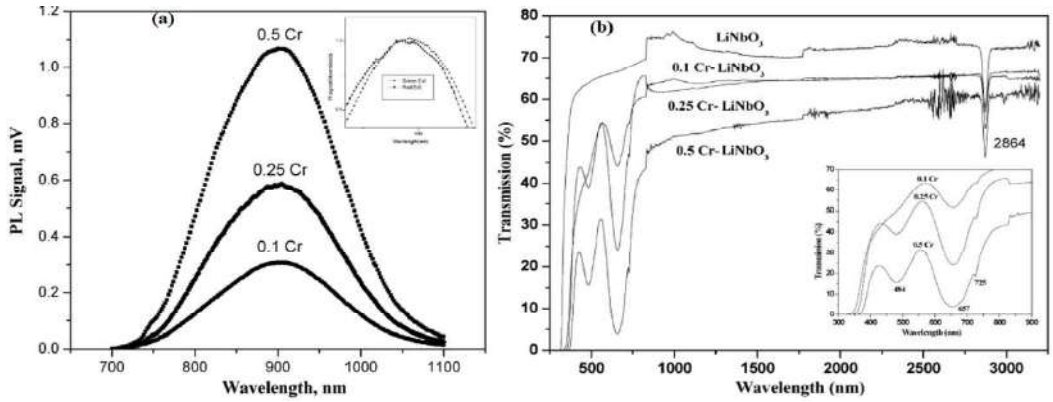


Figure. 1.26: (a) Photoluminescence spectra for Cr-doped $LiNbO_3$ crystals (b) Transmission spectra for undoped and Cr-doped $LiNbO_3$ crystals.

V. Doni Pon et al. examined Fe/Cu/Ni-doped $LiNbO_3$ for optoelectronic applications, and the samples were synthesized through a hydrothermal synthesis process. It was revealed that absorbance intensity reduces in doped materials as the Nb site is replaced by Ni, Fe, and Cu ions. The band gap investigation demonstrated that the absorption edge of Cu ions shifted towards red due to the significant polarizability effect, which may reduce the band gap of crystals [95]**.** Atsushi Baba et al. published an article titled "High-temperature ultrasonic

transducer up to 1000 °C using lithium niobate single crystal", in their report they stated that they invented a high-temperature transducer using a single crystal of lithium niobate for structural health monitoring (SHM) in a power plant which is shown in the **Figure 1.27,** They heated an LN crystal transducer in an electrical furnace and demonstrated that several echoes were recorded consistently until the temperature reached roughly 1000 °C [96].

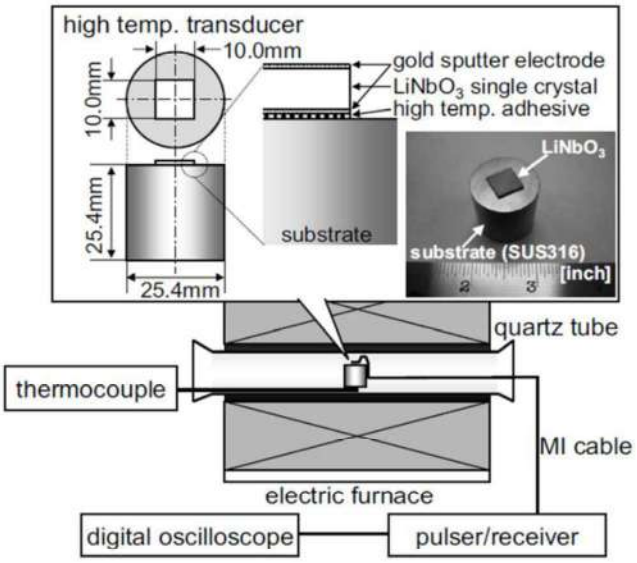


Figure 1.27: Schematic configuration of a high temperature transducer and experimental setup.

Irzaman et al. synthesized a material that was lanthanum-doped lithium niobate thin films and deposited them on p-type Si (100) wafer using a chemical solution deposition method to examine the optical and structural characteristics. They demonstrated that the band gaps for undoped 5% and 10% lanthanum-doped thin films were 2.75, 2.80, and 2.43 eV, respectively [97]**.** Ryotaro Inoue et al. published a research article titled "Enhanced photovoltaic currents in strained Fe-doped $LiNbO_3$ films," in which they discussed their thin-film experiments to determine the effects of strain on the characteristics of the photovoltaic current (J_z) for Fe doped LN. Compared to bulk Fe-LN crystals, the J_z values for the film surprisingly increased by approximately 500 times with a tensile strain in the

P_s direction. During DFT calculations, it was discovered that tensile strain causes an increase in off-center displacement of Fe^{2+}, which is in the opposite direction of Ps. They also demonstrated that adjusting lattice strain may improve the photovoltaic effect in the Fe-LN system [98]**.** Kiyoshi Nakamura et al. used rotating Y-cuts of a single $LiNbO_3$ crystal to step up a Small-size transformer with no output voltage saturation, which is shown in the **Figure 1.28 (b).** It was revealed that a maximum value of $k_{23}.k_{33}$ for a 130° rotated Y-cut LN plate stretched in the Z' direction is best suited for piezoelectric transformers and the electrode configuration is essential for the output characteristics [99].

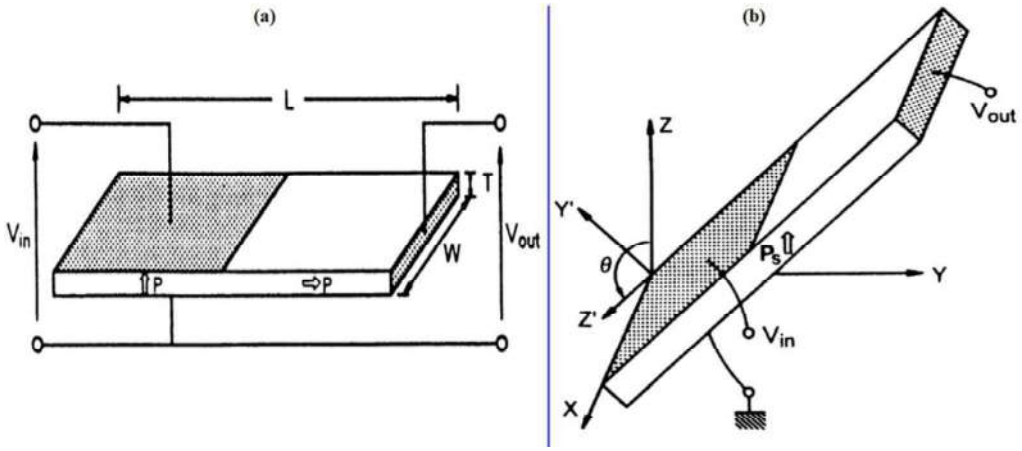


Figure 1.28: (a) Piezoelectric ceramic transformer proposed by Rosen (b) Piezoelectric transformer using a rotated Y-cut $LiNbO_3$ single crystal.

An another research article by Paula Maria Vilarinho et al. reported about whether $LiNbO_3$ and $LiTaO_3$ are bioactive or not. They examined these two ceramics after immersing them in simulated bodily fluid (SBF) for varying period of time, and the development of structures resembling cauliflower apatite suggested that $LiNbO_3$ and $LiTaO_3$ were bioactive with live tissues[100].

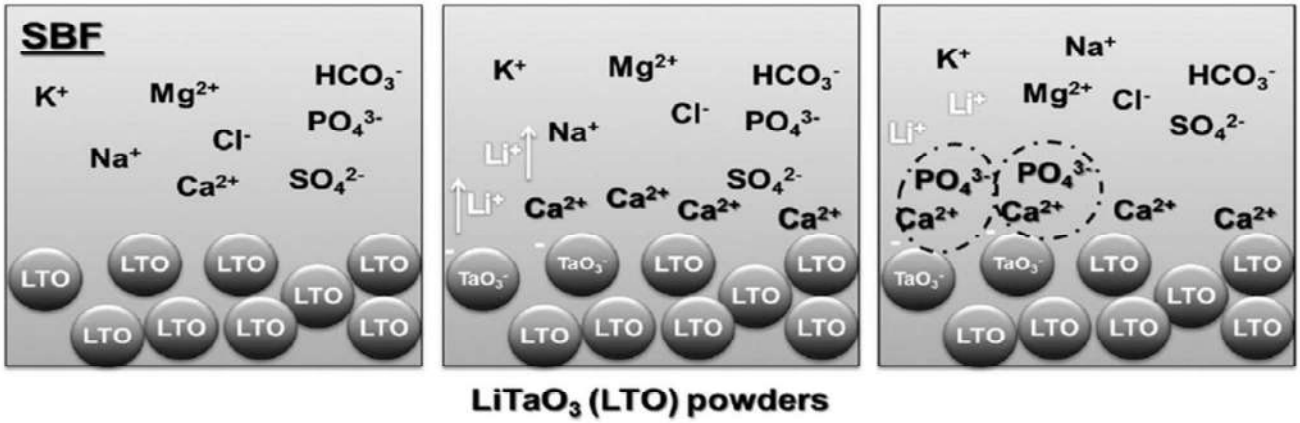


Figure 1.29: Proposed model for apatite formation on $LiTaO_3$ powders in SBF.

Manojit De et al. developed lithium niobate-bismuth ferrite solid solutions and published a report on the structural, electrical, and ferroelectric characteristics of the samples. They revealed that the grain and grain boundary effects from the Nyquist plot contributed to the composition of $Bi_{0.60}Li_{0.40}Fe_{0.60}Nb_{0.40}O_3$. AC conductivity that varies with temperature illustrates the activation energy for conduction. Frequency dependent electrical modulus and impedance investigation also indicated the non-Debye type relaxation behavior, and all reported results are shown in the **Figure 1.30** [101].

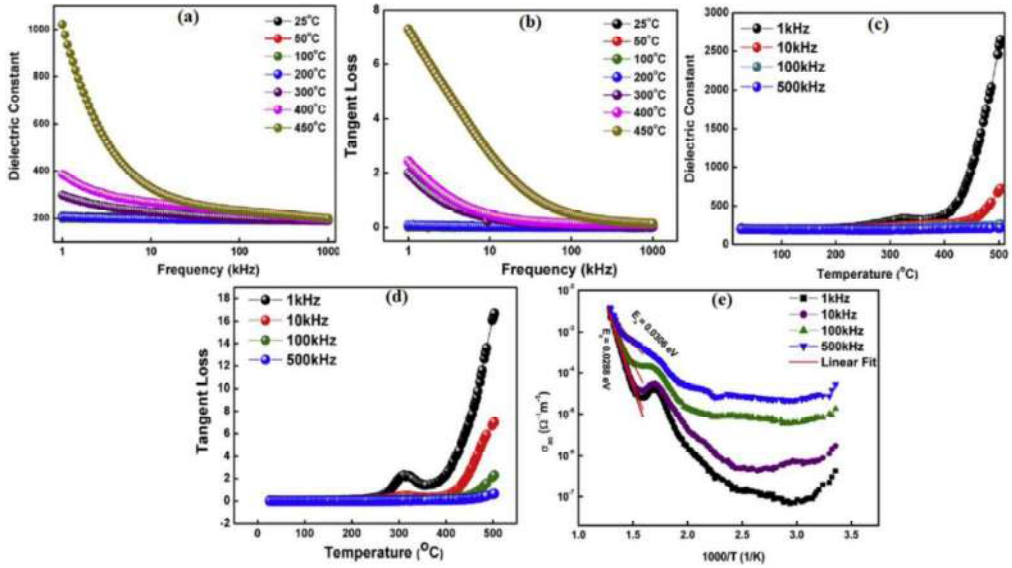


Figure 1.30: (a) Frequency dependent Dielectric constant (b) Frequency dependent tangent loss (c) Temperature dependent Dielectric constant (d) Temperature dependent tangent loss (e) Temperature dependent AC conductivity.

Carlos A. Diaz-Moreno et al. developed $LiNbO_3$ nanoparticles using a solid-state reaction method, and they have examined the structural and ferroelectric properties of these nanoparticles. The ferromagnetic effect was also observed when a sample was heated to a reduction in an environment with 5% hydrogen/argon. When a sample is heated, single atoms like Li and Nb are observed to have poor stability and diffusion, which is related to vacancies and defects that change with structural properties [102]. D. Xue et al examined the dielectric characteristics of $LiNb_{1-y}Ta_yO_3$-type mixed single crystals for the compositions y = 0:00; 0.81, 0.92, 0.97, and 1.00. The results of this research showed that the dielectric responses of the synthesized system linearly decrease with rising Ta concentration. It also demonstrated that the addition of dopants to Li sites could change the dielectric properties more drastically because of the increased sensitivity of that lattice site [103]**.**

A high-speed LN electro-optic modulators (EOM), which is based on photonic crystal nano-beams, were developed and published in an article on by Mingxiao Li et al, in which they utilized thin-film lithium niobate and that is shown in the **Figure 1.31,** They proved the effectiveness of an EOMs device with a wide modulation bandwidth of 17.5 GHz, a substantial tuning efficiency up to 1.98 GHz V−1, and a tiny electro-optic modal volume of 0.58 μm^3. The fabricated device was capable of electrically controlling the High-Q cavity mode in both the adiabatic and non-adiabatic regimes and observing transitions between them, and with just 22 fJ of low switching energy per bit, they were able to accomplish high-speed electro-optic switching at 11 Gb s^{-1} [104].

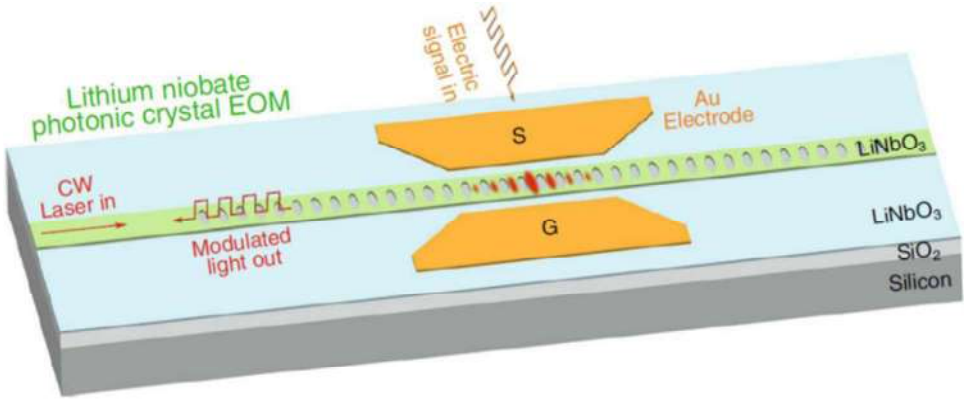


Figure 1.31: Schematic of the LN photonic-crystal EOM.

1.15 Objectives of the Present work

We have focused on the Dielectric, Ferroelectric, and Photo luminescent property-based ceramic materials that have generated a great understanding of attention because of their special characteristics for current and upcoming applications in a wide range of industries like sensor development industry, optoelectronics devices industry, photonics devices industry, and energy storage based industry. To progress in these sectors, it is important to develop new materials having a combination of dielectric, ferroelectric, and luminous properties. The purpose of the present research work in this field is to design and synthesize environmentally friendly, nontoxic/lead and Bismuth free novel materials with high curie temperatures for different kinds of high-temperature applications. Therefore, lithium niobate ceramic material, with improved dielectric, ferroelectric, and luminous characteristics, was considered for this research work. The proposed ceramic materials are useful in a variety of applications, including sensors, light-emitting diodes (LEDs), and other optical properties-based applications. Therefore, different characteristic investigations of these materials can provide important information on their fundamental and chemical as well as physical properties. To obtained the desired properties of proposed materials, it can be either directly added with other materials or doped with other materials, these type addition or substituting can bring a change in crystal structure as well as their defects and impurities can be controlled and application based properties can be easily obtained. Such materials must be developed using a multidisciplinary technique that includes conceptualization, synthesis of materials, and characterizations. In summary, the research being done in this area that has might be the potential to transform optoelectronics and photonics completely.

The research of Lithium Niobate based ceramic materials in the thesis is concentrated on their synthesis, characterization, results and discussion for the diverse high temperature applications including properties like dielectric, ferroelectric, and optoelectronic.

1. This study also investigates the role of various dopant/addition of materials in the sintering of properties of lithium niobate, as lithium evaporation occurs at lower temperatures than sintering temperatures, makes it very challenging to sinter lithium niobate ceramics.
2. In this thesis, the effects of factors such as sintering temperature, sintering environment, density, porosity, morphological structure, grains, grain boundaries, and secondary phases on the dielectric, ferroelectric, and optoelectronic properties of the synthesized material are investigated in depth.
3. Lithium niobate-based ceramic materials' improved dielectric, ferroelectric, and optoelectronic characteristics are particularly useful in a variety of applications and those are synthesized using simple synthesis techniques which is solid state reaction method by using high energy ball mill. The following ceramic materials based on lithium niobate are discussed as follows.

   (i) $LiNbO_3$ + x(wt%) K_2O where (x = 0,,1.36,,2.72,4.08,5.44)

   (ii) $Li_{(1-x)}Sm_{x/3}NbO_3$ where (x=0, 0.01,0.02,0.03,0.04,0.05)

   (iii) $(1-x)LiNbO_3$-$x(Li_{0.5}Dy_{0.5})TiO_3$, where (x= 0.0, 0.00625, 0.0125, 0.025, 0.05, 0.1, 0.2)

   The following physiochemical characterizations were successively carried out in this research project in order to investigate the above-discussed characteristics of synthesized Lithium Niobate based ceramic materials.

(i) The phase formation and crystal structure of the materials were identified using an X-ray powder diffraction (XRD) analysis at room temperature.

(ii) Scanning electron Microscopy (SEM) analysis was used to conduct comprehensive morphological investigation of sintered pellets and powder at room temperature.

(iii) The chemical state/elemental oxidation state of the synthesized materials was investigated at room temperature using X-ray Photoelectron Spectroscopy (XPS).

(iv) Thermogravimetric analysis (TGA) was used to investigate the thermal behavior of the ceramic up to 1000 °C.

(v) Fourier-transform infrared spectroscopy (FTIR) is used to investigate various chemical bonds and analyses the purity of system's chemical composition evaluation.

(vi) Photoluminescence characteristic of synthesized materials were performed at room temperature through fluorescence spectrometer for the emission spectra.

(vii) Optical properties like absorbance characteristics of the synthesized samples were investigated through UV-visible Spectrophotometer at room temperature.

(viii) The frequency and high temperature dependent various Dielectric characteristics have been examined through Impedance analyzer.

(ix) At room temperature, the PE-analyzer was used to examine the ferroelectric behavior of synthesized materials.

(x) Energy storage density and energy efficiency also calculated for the synthesized materials.

1.16 Scope of this Thesis

The primary goals of the thesis are the synthesis and development of a bulk form of distinct types of Lithium niobate-based environmentally friendly ceramic materials for high-temperature applications by using their dielectric, ferroelectric, and optoelectronic characteristics by employing solid-state reaction techniques at low-cost.

- In the thesis's first chapter, which is devoted to the introduction, discussion of fundamental science, which is basic of the characteristic of synthesized materials, as well as a literature survey of some earlier and current research publications and books on $LiNbO_3$ ceramic and single crystals materials, that are based on synthesis processes, their properties, characterizations, and applications.
- The experimental portion of the current research is covered in Chapter 2, where the synthesis of all different materials using the solid state reaction technique is addressed along with the necessary precursors for the synthesis of the materials. The basic operating principles of each instrument and the relevant characterizations of the materials are also covered in this chapter.
- The synthesis of K_2O added (by weight percentage wt%) $LiNbO_3$ for high-temperature dielectric and ferroelectric applications, as well as their optoelectronic characteristic, are the basic discussion of Chapter 3. In-depth discussions of the improved dielectric, ferroelectric, and tuned optoelectronic characteristics are provided in this chapter.
- The 4^{th} chapter contained a detailed investigation of Rare Earth Samarium ion (Sm^{3+}) incorporated Lithium niobate which is ($Li_{(1-x)}Sm_{x/3}NbO_3$), that is synthesized for different compositions using a solid state reaction technique for a number of

applications such as energy storage based devices and optoelectronics characteristic based. The increased various properties were also thoroughly detailed in this chapter.

- The 5th chapter is dedicated to the development of a Lithium Niobate-Dysprosium Titanate (1-x)$LiNbO_3$-x($Li_{0.5}Dy_{0.5}$)TiO_3 solid solution-based ceramic using a solid-state reaction process for diverse compositions, which has never been reported before. This chapter also revealed a detailed discussion about the synthesized materials' improved and tuned properties and their futuristic applications.
- The 6th chapter presents a summary of the entire present research work of his thesis, which is based on current research findings and recommendations is also discussed for future research related to this work.

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