Chapter

Perovskite Ferroelectric

Paramjit Kour and Sudipta Kishore Pradhan

Abstract

The spectrums of properties exhibited by ferroelectric materials are dielectric, ferroelectric, piezoelectric and pyroelectric effect. This is the makes these materials to have a wide range of useful application. Infrared detectors are used pyroelectric effect of ferroelectric materials. It is used in nonvolatile memories due to have ferroelectric hysteresis. Its piezoelectric properties make them useful for actuator, radio frequency filter, sensor, and transducer. Ferroelectric capacitors are used, their good dielectric behavior. According to the necessity of the system they are available in different form such as single crystals, ceramics, thin film, and polymer, composite. The diversity of properties ferroelectric materials always attracted the attention of engineers and researchers. Size reduction of this material from micro to nanoscale established an enormous consideration to develop nanotechnology. Its vast use of different filed imposed the in detail research in adding to the development of processing and characterization method. This chapter will put some light on some fundamental principle of ferroelectricity, the list of perovskite materials and their application.

Keywords: PZT, $BaTiO_3$, $CaTiO_3$, PT, PLZT, Kb

1. Introduction

Like ferromagnetic materials, the functional properties of ferroelectric materials find wide range of applications, ranging from actuators and sensors to memory or optical devices. A ferroelctric class of materials cannot define in a single sentence. So before we define the ferroelectric materials, we should classify dielectric materials. Dielectric is belonging to a class of insulating materials that on the application of an electric field shows dielectric polarization [1]. Here the center of symmetry plays a significant role for their properties. Crystal structure with a center of symmetry have such an arrangement of atoms around a point or center that by the inversion, we can get the same arrangement of atoms in the crystal. Dielectric materials belong to a group of non Centro symmetric crystal structure. In 432 point group the entire non Centro symmetric point group shows piezoelectric properties [2]. The properties due to which voltage obtains form charge a separation in the face due to the mechanical stress and vice versa. Both direct and inverse piezoelectric effects have a wide range of application in electronic devices [3]. Barium titanate is an example of non-centrosymmetric piezoelectric material used in microphone and transducer [2–4]. In non centrosymmetric crystals there is an axis of symmetry, called polarity. These piezoelectric polar crystals are shown pyroelectricity. With changes in temperature there is a charge separation. The cells of polar structure have efficient dielectric polarization, so often called a spontaneous polarization. Either by stress or by a change in temperature the dipole moment of these polar structures is change. The is a charge separation in the surface, results in the spontaneous polarization. So the polar dielectric spontaneous polarization direction and magnitude can be modified with the applied stress. Zinc oxide, which belongs to family of polar dielectric shows wurtzitecrystal structure [5]. In this structure, between hexagonally packed oxygen ions layer, Zn2+ions are at the tetrahedral site.

Between these layers dielectric, whose spontaneous polarization depends on the direction and magnitude of the applied stress. Adequate amount of stress can change the direction of spontaneous polarization. But the exclusion of the stress does not bring back the original magnitude and direction of the spontaneous polarization. These families of polar dielectric are called ferroelectric. **Figure 1** shows the way the Centro symmetric, acentric, polar and ferroelectric, dielectrics are related to each other. Many review articles shown the history of ferroelectric [6–12]. Many great scientist open the path of discovery of the ferroelectric.

Pyroelctricity was studied by Brewster. Piezoelectricity was discovered by J. P. Curie. Debye, Boltzmann, Pockelsetc helps in conceptualizing the polarization in the dielectric. It was E. Schoridgener, who coined the term ferroelectricity, but JoesphValasek known for the discovery of ferroelectric. In 1920 the Rochelle salt (sodium potassium tartrate) shows spontaneous polarization which can be switch with the magnitude and direction of the applied field. This is the first manifestation of the ferroelectricity in a crystal. That is the trademark of ferroelectricity. Logically effectively the term ferroelectricity is defined as the switchable polarization between two or more stable state by the application of electric field. There exist some exceptions. Some semiconductor materials show ferroelectric properties. They do not posses electric polarization. In some ferroelectrics materials the spontaneous polarization cannot be switched with the electric field. This is either due to they are too conducting or reach the electrical break down first. This ferroelectric property first observed in Rochelle salt. But later it is observed in oxides, polymer, ceramics, and liquid crystal. When it is about ferroelectric property, the perovskite structure materials have a special importance. So in this chapter, we will discuss some perovskite ferroelectrics which are used in various electronics devices. According to the structure, there are five types of structure. (i) Organicpolymer (ii) Charge ordered ferroelectrics (iii) Magnetic order ferroelectric (iv) Corner-sharing oxygen octahedral (v) Hydrogen bonded radical compound (v) Ceramic polymer composites [11]. Among these ferroelectricgroup a mostly used ferroelectrics are the corner sharing oxygen octahedral oxides.

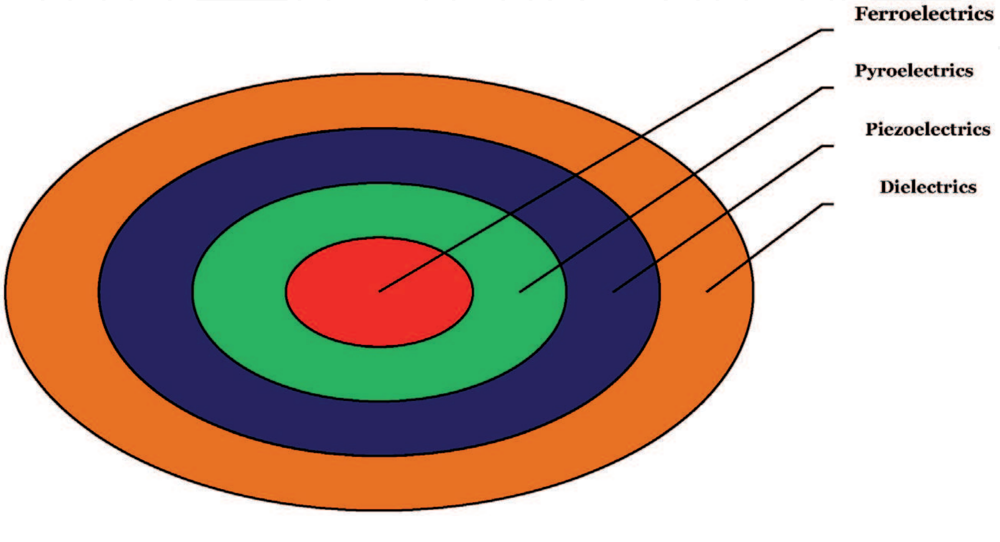

Figure 1.
Ven diagram of ferroelectric fit into different materials.

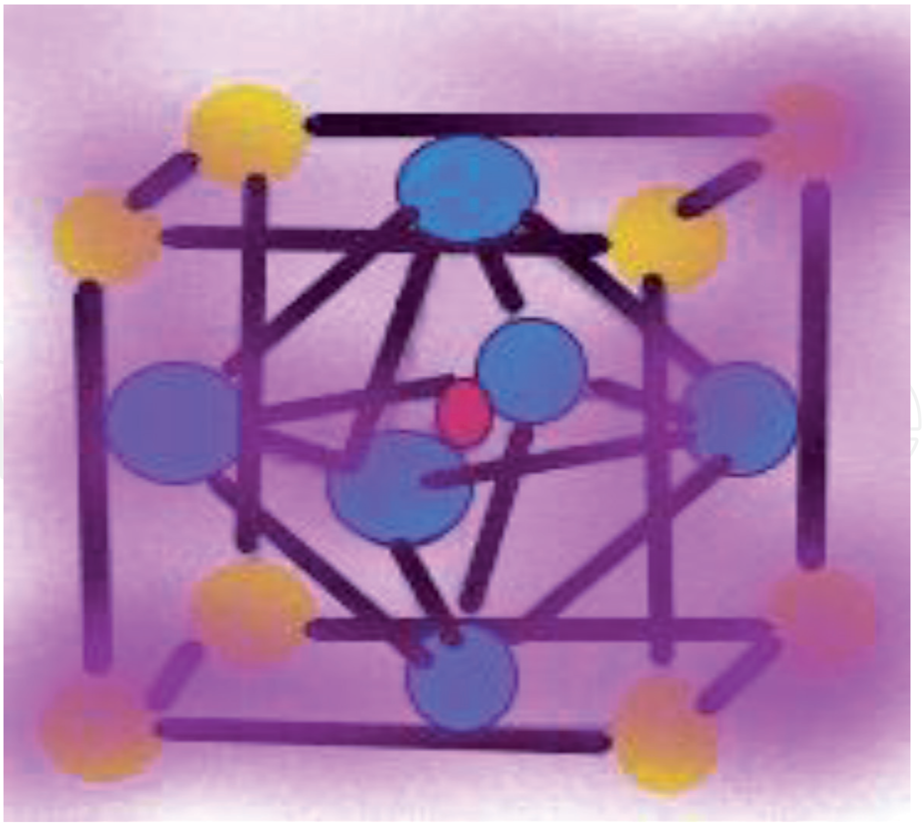

Figure 2.
Shows the schematic diagram of perovskite structure.

Basically, the corner sharing oxygen octahedral oxide structures is represented as $A^{a+}B^{b+}O_3$ [12]. **Figure 2** shows the schematic figure of O^{2-} ions corner sharing oxygen octahedral. The B^{b+} cation is seated within every octahedron. The b of the cation has the value lies in between 3 to 6. A^{a+} ions lie in the gap among the octahedral with its value of *a* is in between 1 to 3. A nonpolar lattice has been observed in prototype forms by the overlap of A^{a+}, B^{b+}, and O^{2-} ions geometric center. The total polarity of the lattice is obtained by displacement of A and B ions with respect to the O^{2-} ions. Due to change in temperature, phase transition takes place. This will result in displacement of ion results in a change in lattice structure. Spontaneous polarization will produce due to the displacement of ions in the arrangement of dipoles if there is no recompense pattern in the diploe.

2. Perovskite ferroelectrics

It is a family of a subgroup of corner sharing oxygen octahedral material's exhibiting ABO_3 structure. This family contains some mostly used piezoelectric and ferroelectric ceramics. Some member which is used in different field of Technology are strontium titanate (STO), barium titanate ($BaTiO_3$), ($SrTiO_3$), lead titanate ($PbTiO_3$), barium strontium titanate (BST), PZT, potassium niobate (KN) ($KNbO_3$) etc. Some of these perovskite are discussed in detail as follows.

2.1 Barium titanate ceramics

Barium titanate which a member of perovskite family exhibit good piezoelectric, ferroelectric and high dielectric constant. This FE ceramics are used in first piezoelectric transducer. But now it is mostly used in multilayer capacitors (MLCs) due to having a high dielectric constant. It is also used in positive temperature coefficient

Resistance (PTCR), sensor, PTC Thermistors, IR detectors, RAM, sonars and in electro optic devices. By doping Barium titanate which is insulator in pure form can be changed into a semiconductor. Barium titanate basically white powder of inorganic compound. With a decrease in temperature the octahedral TiO_6 undergoes distortion gives rise to five structural phase transition from hexagonal, cubic, tetragonal, orthorhombic, and rhombohedra. Very large spontaneous polarization and high dielectric constant are observed in this phase due to the distorted octahedral. At Curie point, i.e. above 120°C the distorted octahedral of TiO_6 comes to equilibrium result in an isotropic cubic structure [13, 14] so only this phase does not exhibit FE properties.

Capacitor, MLC etc. used first $BaTiO_3$ as the dielectric ceramic with large dielectric constant and dielectric loss for manufacturing. The factor that affects the dielectric properties of the materials is not only its structure but also its synthesis route which will reflect in its size of the grain, density, purity etc. [15]. The Applied frequency of the electric field, temperature and do pants also affects the dielectric properties of the materials [16–23].

The dielectric constant of Barium titanate prepared by any method increase depends on the grain size and distribution of grains [17, 24]. At room temperature the frequency dependent dielectric constant decreases at low frequency and then increases slightly and become constant at high frequency. Temperature dependent dielectric constant decreases at higher temperature [25]. Ions of different size can be can be added to the perovskite structure. So doping at both A and B site of this perovskite structure is used to tolerate its electrical properties [26]. At A site mono, die and trivalent acceptor do pants are substituted to produce P-type semiconductor, whereas N type semiconductor are obtained by donor dopant of tri, tetra and pentavalent ions at the B site of the perovskite. The concentration of the dopants also affects the electrical properties of Barium titanate. Increase in concentration of Donor dopant makes the semiconducting ceramics to an insulating one. Barium titanate ceramics have application in various engineering fields.

2.1.1 Multilayer capacitor (MLCs)

Mostly $BaTiO_3$ is used in capacitor due to having a high dielectric constant. In thin dielectric form packed in a minimum space not only with high capacitance but also mechanically tough [27]. It is used as passive component in the circuit for large scale integration (LSI). It is also cost effective one with the use of internal electrode made of, nickel (Ni) and copper (Cu) [28].

2.1.2 (s2) PTC thermistor

The high resistivity of $BaTiO_3$ makes it as good candidates for PTC thermistor. Doping at A and B site of $BaTiO_3$ convert them as a semiconducting material. Below the Curie temperature these semiconductor materials have low resistance. Above crystal particle boarder barrier layer persuades by the surface state. So FE characteristics with high dielectric constant exhibit by this crystal boundary of high resistance. So below Curie temperature the potential barrier is small. Low resistivity has been exhibited in these materials due to effortlessly penetration of electron. The height of potential barrier increases above the Curie temperature makes electron difficult to pass through it results in increasing the resistivity of the material.
In various electronics circuits this semiconducting $BaTiO_3$ materials are used as constant temperature heaters or switching devices. For temperature or parameter related to temperature can be detected, measured and control of temperature with

the use of this PTC thermistor. Among all the available sensor materials PTC has the highest temperature coefficient of resistance.

2.1.3 Nanogenerator (NG)

High piezoelectric effect with biocompatibility make them use as Nanogenerator. Piezoelectric potential is induced in between the two electrodes of NG, this is due to mechanical stress. Commercial devices can be work using this generated electrical energy without an external energy source.

2.2 Strontium titanate ($SrTiO_3$)

Another member of perovskite family is strontium ferrite STO ($SrTiO_3$) is a complex oxide. It exhibits cubic structure at room temperature. O^{2-} ions are bonded with six folded coordinate to Ti^{4+} ions and with twelve folded coordinate to Sr^{2+} ion. Each Sr^{2+} ion lies in between four TiO_6 octahedral. To decrease in temperature, it undergoes a phase transition. The first transition below room occur at −168°C. The opposite rotation of adjacent oxygen octahedral at this term turns the cubic structure to tetragonal structure. To further decrease in temperature at −236°C the changeable phonon modes turns the tetragonal structure to orthorhombic structure. The orthorhombic structure is change to rhombohedra structure at −263°C [29]. As Curie–Weiss law suggests the dielectric constant increases with the phase transition below room temperature. At this temperature due to quantum fluctuations leads to the quantum PE [30]. The charge storage capacity is high, chemical stability, optical transparency in the visible region with good insulating properties makes it use in modern electronics applications such as phase shifters, high-voltage capacitors, delay lines, filters, tunable oscillators etc. [31–33]. It is used in cancer treatment and in thermo – electric generators due to they have insolubility and high melting point properties [34, 35]. It shows photoconductivity when exposed to light due to having an direct gap and indirect band gap of 3.75 eV and 3.25 eV respectively [36]. Its conductivity increases with the contact of light to the crystal. Its conductivity persists for several days, with small decay [37, 38].

The first oxide, which is superconducting below 0.35 K is the strontium oxide (STO) [39]. It can be used as a tremendous substrate for superconductors with a high operating temperature and for oxide-based thin films. It is used as single-crystal substrate due to the enhanced electrical conductivity of niobium doped STO for the growth of perovskite oxides. It is also used for other ferroelectric and magnetic oxide substrate due to its large lattice parameter. Variation of temperature and pressure parameter can lead to increase oxygen vacancies in both crystal and thin films of $SrTiO_3$. So it becomes more conducting due to stimulate free electrons in the conduction band and also opaque. This used as gate-dielectric material due to the growth of high quality growth of epitaxial $SrTiO_3$ layers on silicon without forming silicon oxide Furthermore, it allow the incorporation of other perovskite oxides based thin-film on top of silicon [40]. It is also used for its piezoelectricity, ferroelectricity and Pyro electricity application in nanoscale [41–44]. It is used for various technological applications such as in super capacitor, nonvolatile memory, tunable microwave capacitors, ultralow-temperature scanning microscopies, high-density dynamic random access memories, soft phonon devices, oxygen sensors [45, 46].

2.3 Barium strontium titanate (BST)

The model of $BaTiO_3$ (BTO) has been used to develop Barium strontium titanate ($Ba_xSr_{1-}xTiO_3$ perovskite. This perovskite also undergoes phase change at it

Curie temperature depend upon the ratio of Ba:Sr. If the ratio decreases the curie temperature decreases. The dielectric constant at the Curie temperature of BST is more than BTO. BST is simply ferroelectric with spontaneous polarization below the Curie temperature. Nearly T_c the tenability of BST has extremely high in the FE phase. So in this phase find application for non volatile application. Above the Curie temperature the pyroelectric BST finds its applications in tunable microwave device associate with low dielectric loss and high dielectric constant. It also finds application in phase shifters, tunable filters and tunable antennas due to its composition dependent curie temperature with permittivity depends electric field.

Due to its high value of capacitance make it useful to construct high capacitance capacitor. It has uses in tunable microwave devices tunable capacitor, phase shifters, tunable transformers. BST varactors are a good replacement of the presently used semiconductor varactor and mechanical tuners. It is not only the drawback of large size with small tuning speed of mechanical tunners, but also small power handling capability of semiconductor varactor. BST also used in band pass and low pass tunable filter.

Semiconductor based phase shifter are used in fighter aircraft radar and cellular telephone base stations are associated with high loss at microwave frequencies with low power use ability. BST is the best replacement of these semiconductor based phase shifter associate with small loss, inexpensive and with better power handling properties. It is used in micro strip antenna. In tunable microwave application thin film of BST is used. The reduced size with small weight makes it compatible with microwave circuit. Dielectric constant not decreases sharply with the variation of the thickness of the film [47–49]. When it's used in metal–insulator–metal capacitor shows high dielectric constant, low dielectric loss, high leakage current density, high charge storage density makes it's used in dynamic random access memory (DRAM).

2.4 Lead titanate ($PbTiO_3$)

Another member of perovskite family is the inorganic lead salt of titanic acid compound, i.e. Lead titanate ($PbTiO_3$). Yellow powder of lead titanate is water insoluble. It shows a high Curie point of 490°C. It shows second order phase transition due to which it changes from cubic pyroelectric phase to ferroelectric tetragonal phase. At room temperature it shows the tetragonal structure belongs to *P*4 mm space group. It undergoes large volume change when cooled below the Curie temperature. It is not easy to formulate it in the bulk form. There is formation of crack during manufacture due to strain. To reduce this strain various dopants are used to modify the lead titanate. Ferroelctric lead titanate find its uses in, resonators, actuators, IR sensors, ultrasonic transducers and MLCs etc. [50–52]. Various process such as melting, Co precipitation, decomposition, hydrothermal, sol–gel, chemical vapor deposition, molecular beam epitaxy (MBE), molten salt methods, solid state method and sputtering is used to prepare thin films, single crystals and ceramic powders of $PbTiO_3$ [53–74]. For advance electromechanical devices, it is the capable building blocks. It can be prepared in micro tube, Nano sized powder and nanowire by the use of hydrothermal method [68, 75–79]. It is one of the most used materials for the fabrication of sensors, memory capacitors, optoelectronics devices etc. [76, 79].

2.5 Lead zirconate titanate (PZT)

Lead zirconate titanate with perovskite structures is an inorganic intermetallic compound. It is a solid solution of lead zirconate and lead titanate represented as [Pb (Zr_xTi_{1-x}) O_3, $0 \le x \le 1$]. PZT has Pb^{2+} ions at A site with random occupation of B site by Ti^{4+} and Zr^{4+} ions. It undergoes phase change with composition, but also with temperature. Above its Curie temperature it shows the pyroelectric effect with cubic structure. It undergoes a structural change from PE cubic phase either to FE rhombohedral phase or tetragonal phase. The spontaneous polarization in these structures is oriented in< 100⟩ and ⟨111⟩ set of directions for tetragonal and rhombohedral phase respectively. The morphotropic phase boundary is around at 52/48 of Zr/Ti ratio separating FE tetragonal and orthorhombic phases. At this boundary PZT has shown maximum dielectric and piezoelectric constants. Rhombohedral phase with 8 possible domains and tetragonal phase with 6 domains with total 14 domains are equally favorable at this composition. Piezoelectric PZT ceramics can be tailored according to application with ions having valence diverse from the host ions in the lattice. Especially PZT at MPB is modified to form soft and hard PZT. Acceptor ions are used either by the use of Al^{3+}, Fe^{3+} at B site and Na^{+} and K^{+} at A site of the perovskite to produce oxygen vacancies in the lattice [80, 81]. Donor ions PZT produced domains wall motion fromed by Nd^{3+}, La^{3+} at A site where as Nb^{5+}, Sb^{5+} at B site in the lattice [82–85]. Hard PZT formed by donor doping shows low dielectric constant, small electrical losses, small piezoelectric co-efficient with high coercive field. So it is difficult to pole and dipole the sample and make them useful for rough applications. Whereas soft PZT has shown larger losses, high dielectric constant and piezoelectric co-efficient. So they can easily dope and dipole. They are used in FeRAM, actuator of STM/AFM type, ultrasound transducer, capacitor with high dielectric constant, IR sensor, etc. High value of piezoelectric coefficient of FE PZT make them useful for micro sensor, micro actuator used micro electromechanical system (MEMS) devices [86–88]. Nano rods, wire and hollow tube of PZT are now used for different application [89–98]. PZT Nanogenerator are used for piezoelectric effect to produce piezoelectric energy in the microscale. The intrinsic polar crystal structure of PZT nanofibers shows high piezoelectric voltage constant. High aspect ratio of nanostructure PZT overcomes extremely brittle nature observed in bulk PZT and its thin films and used for generation of energy in alternating loads [89, 90].

2.6 Lead magnesium niobate (PMN)

Single crystal of Pb $(Mg_{1/3}Nb_{2/3})$ O_3 (PMN) materials belongs to the FE relaxor materials and are used in [99], and the work in the electrostrictive actuators with high-strain and capacitor with high dielectric constant [100–102]. The Perovskite type structure of Pb (B_1, B_2) O_3 formula with lower valence B_1 such as Zn^{2+}, Mg^{2+}, Fe^{3+} and Ni^{2+} and higher valency B_2 is such as Ta^{5+}, Nb^{5+} and W^{5+}. On cooling below the Curie temperature relaxor PMN ferroelectrics shows a wide dispersive and the diffused phase transition. Heterogeneity in composition on a microscopic scale leads to the diffuse phase transition in the relaxor ferroelectric.

In micoregion the stoichiometry is not obeyed by disorder B-site leads to change in FE transition temperatures leads to broadening dielectric peak. Strong frequency dependent dielectric constant has been observed in the relaxor ferroelectric. Curie temperature changes linearly with frequency with high dielectric loss below this temperature. Some relaxor shows second order phase transition. This relaxor remnant polarization is starting to decrease from Curie temperature and becomes zero with the increasing in temperature [103–106].

2.7 Potassium niobate ($KNbO_3$)

KN ($KNbO_3$) is also exhibited perovskite structure. It shows interesting ferroelectric properties at low temperature. It shows three phase transitions simple displacive type at low temperature with different symmetry and PE phase at high-temperature [107]. Oxygen behaves as rigid body in the octahedral and vibrates about Nb atoms [108]. Liberation of oxygen octahedral leads to the irregular anisotropy exhibited by oxygen atom due to mean square displacements. Its structure shows two subshell obtained from the splitting of oxygen octahedron. Six niobium atoms are from the third nearest sub shell. 24 oxygen atoms form a fourth adjacent octahedral shell consists of four sub shell of six atoms. Fifth shell is made of 12 niobium atoms. Neutron diffraction study predicts the structural change with temperature $KNbO_3$. It shows three phase transition from cubic to tetragonal, tetragonal–orthorhombic and orthorhombic–rhombohedral at $T \approx 418°C$, 225°C and 10°C respectively [109, 110], Transverse optic mode exhibited by $KNbO_3$ is softened with lessening temperature obtain from Raman, IR and inelastic neutron scattering [111–113]. Soften mode frequency obtain from dielectric measurement is good agreement with values calculated Cochran from $\omega^2 \propto (T{-}T_0$ with $T_0 \approx 370°C$ Curie–Weiss temperature [114]. $KNbO_3$ Curie–Weiss constant was found to be about $2.8{\times}10^5$ K. Displacive model is used to calculate this shows good agreement with the theoretical value. Large electromechanical coupling factor with zero temperature coefficients at room temperature exhibited by KN crystal is used for piezoelectric application [115, 116]. Surface acoustic wave (SAW) filter prepared using $KNbO_3$ find its application in mobile phones and television receivers [115, 116]. The crystal symmetry of KN crystal shows 49.5° rotation about the y axis by the x-cut [117, 118]. In high quality fiber shape these crystals show small lattice defects [119]. Different melting temperature hinders to grow high quality and large size KN crystal [115]. Both Bridgman (BM) technique and Top-seeded solution growth (TSSG) method is used, however the Bridgman (BM) technique is the easier one to grow bulk shape KN crystals [120–124]. Phase diagram suggests line compounds are formed when these crystals are developed from high-temperature solutions [125]. A peritectic transformation is shown when it grows from molten stoichiometric composition. KN in nanorod form are used capacitor and nano (NG) [126].

2.8 Sodium niobate ($NaNbO_3$)

This is also the member of perovskite family, but with anti ferroelctric properties. Six phase transition in between −200 to 650°C range affects its structural, dielectric, and optical properties. Phase transition at 200,360 and 480°C has been observed due to off center displacement of Nb ion with tilting of oxygen octahedral. Its stable cubic structure of the *Pm3m* space group has been observed at high temperature, i.e. >640°C [127, 128]. The orthorhombic structure of the phase *Pbcm* space group has been observed at room temperature is antiferroelctric one. At 360°C the antiferroelcetric orthombic structure with *Pbma* space group undergoes phase transition to antiferroelectric orthorhombic structure with a *Pnmm* space group associated with maximum dielectric constant [129–134]. $NaNbO_3$ single crystal exhibit low-frequency relaxation processes [135]. Distinct discontinuity is observed in mean relaxation time and relaxation parameter at Curie temperature Tc. At high temperature, low frequency relaxation increases due to crystalline structure disorder. This leads formation of local dipole in the polar region [136]. Stimulating electrical and mechanical properties of Sodium niobate-based ceramics make them a useful candidate for many technological applications [136–147]. At attainable electric fields this well-known antiferroelectric shows FE properties. Cost effective lead-free nanowire based $NaNbO_3$ piezoelectric has a high-output [148]. So it find application in hologram and optical data storage having high density [137–143]. It also used as nanocapacitors, NGs and in the memories of nanoscale [148–150]. For large-scale lead-free piezoelectric NG may be $NaNbO_3$ nanowires is one of useful candidate [151].

3. Conclusions

Several reports on ferroelectric materials and their use for different piezoelectric application has been studied in the last few years. As discussed in this chapter the effect of perovskite structure affect its ferroelectric properties. Doping in these perovskite structures also responsible for the enhanced of its properties by tailoring its crystal structure. These materials now investigated in the composite, nanowire and the nanorods form to make the device mechanically robust and more compact. This is a vital field for the research, as a key element in the digital world.

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