ABSTRACT

In recent years, there is a need for the development of lead-free alternative ferroelectrics to replace the utmost lead-based ferroelectrics (e.g., Lead zirconate titanate (PZT)) due to the toxicity of lead. With the advance of environmental consciousness, it is the current tendency to develop excellent lead-free materials. Ferroelectricity was first discovered in 1921 by J. Valasek. Valasek discovered that the polarization of sodium potassium tartrate tetra hydrate ($NaKC_4H_4O_6.4H_2O$), known as Rochelle salt, could be reversed by application of an electric field. So this Rochelle salt first had known ferroelectric material. Unfortunately, Rochelle salt loses its ferroelectric properties if the composition slightly changed, which made it rather unattractive for industrial applications. Rochelle salt was a popular material in initial trainings, since it was easily grown as large single crystals of excellent optical quality, then its water solubility finally led to its disuse in later years. After that barium titanate ($BaTiO_3$) was discovered to be ferroelectric behavior in 1945 by A Von Hippel and is perhaps the most common material when one thinks of ferroelectricity. Lead free Barium titanate ($BaTiO_3$) is the first ferroelectric ceramic belongs to perovskite structure exposed in 1945 and usage in capacitor application and piezoelectric transducer devices applications, pyroelectric sensor. After the discovery of $BaTiO_3$, a large number of ferroelectric oxides of different structural family have been discovered and studied to catch out their suitability for various device applications.

$BaTiO_3$ ceramics prepared by using solid state reaction method at different sintering temperature. The variation of dielectric constant with temperature shows a broadened maximum value at 130 ^{0}C, indicating the ferroelectric phase transition (T_c). It has been reported that the sintering temperature of $BaTiO_3$ ceramic increases the density and shifts the Curie temperature with increase in the dielectric properties. AC conductivity in the compound increases with increase in temperature which may be recognized due to oxygen vacancies and shows negative temperature coefficient of resistance (NTCR) effect.

Ceramics of La doped $(Ba_{1-x}La_x)(Ti_{0.815}Mn_{0.0025}Nb_{0.0025}Zr_{0.18})_{0.995}O_3)$ (BLTMNZ) for (x = 0.04, 0.10 and 0.20) and $(Ba_{0.9575}La_{0.04}Ca_{0.0025})(Ti_{0.815}Mn_{0.0025}Nb_{0.0025}Zr_{0.18})O_3$ were prepared by using high temperature solid-state reaction method. X-ray diffraction analysis of confirmed that the ceramics possess a perovskite structure with orthorhombic symmetry and small amount of second phase ($MnTiO_3$ 3%). Ca doping in $(Ba_{0.96}La_{0.04})(Ti_{0.815}Mn_{0.0025}Nb_{0.0025}Zr_{0.18})_{0.995}O_3)$ shows

the formation of single perovskite phase with monoclinic symmetry. According to XRD pattern of La doping, it confirms that the intensity increases with concentration which also indicates the existence of better crystalline phase. The diffraction peaks shifted slightly towards higher angle side. The dielectric studies confirmed that Curie temperature shifted to lower temperature and dielectric loss decreases with the increase La doping. In Ca doped sample, dielectric constant increases and dielectric loss decreases as compared $(Ba_{1-x}La_x)(Ti_{0.815}Mn_{0.0025}Nb_{0.0025}Zr_{0.18})_{0.995}O_3)$ ceramics. The low value of activation energy obtained for the ceramics could be attributed to the effect of electronic contribution to the conductivity.

$1-x(Na_{0.4725}K_{0.4725}Li_{0.055}NbO_3)-x(BiFe_{0.5}Ta_{0.5}O_3)$ for x = 0.005 and 0.007 has been synthesized using solid-state reaction technique. Effects of $BiFe_{0.5}Ta_{0.5}O_3$ (BFT) substitution on the structure, microstructural and electrical properties of $Na_{0.4725}K_{0.4725}Li_{0.055}NbO_3$ (NKLN) samples have been studied through performing X-ray diffraction, Scanning electron microscopy (SEM) and dielectric measurements. XRD shows that both samples have a mixed phase with a monoclinic structure at room temperature and peaks shift slightly to a greater angle as doping concentration of BFT increases in NKLN ceramics. The value of the dielectric constant increases and ferroelectric–paraelectric phase transition temperature shifts towards the higher temperature side as we increase BFT substitution from 0.005 to 0.007. Two peaks in the dielectric constant can be correlated to the two phase transitions from ferroelectric to ferroelectrics and ferroelectrics to paraelectric at temperatures 210 ^{0}C and 405 ^{0}C respectively. For BFT doped NKLN- 0.007), the peaks in the dielectric constant can be ferroelectric-paraelectric phase transition (T_c) at 405°C from monoclinic to cubic. Impedance analysis indicates the presence of mostly bulk (grain) resistive contributions in the materials at higher temperatures whereas complex modulus plots shows the presence of grains as well as grain boundary contributions in the materials. They also confirm the typical behavior of negative temperature coefficient of resistance (NTCR) and the presence of non-Debye type of relaxation phenomenon in the materials.

$0.9(BaZr_{0.15}Ti_{0.85}O_3)-0.1(NiFe_2O_4)$ composite hereby denoted as BZTNF-0.1 assisted with microwave power (at 0%MW, 15%MW, 30%MW and 50%MW) were synthesized by the conventional solid state reaction technique. XRD patterns showed that all the samples have both phases, perovskite (BZT) with tetragonal symmetry and spinel (NF) with cubic symmetry were present. This confirms the successful preparation of the di-phase composite. The value of the dielectric constant increases with increasing microwave power and phase transition temperature shifts towards the higher temperature side. The maximum value of dielectric constant (ε′) is 17307 for 50 % at 100 Hz. Further, the values of dielectric constant were high at low frequency (i.e. 100 Hz) and decreased for higher frequencies. The low value of activation energy obtained for the ceramic samples could be attributed to the influence of electronic contribution to the conductivity. Impedance analysis indicates the presence of mostly bulk (grain) as well as grain boundary contributions in the materials at higher temperatures whereas complex modulus plots shows the presence of only bulk (grain) resistive contributions in the materials at higher temperatures. BZTNF-0.1 at different sintering temperatures also confirm the typical behavior of negative temperature coefficient of resistance (NTCR) and the presence of non-Debye type of relaxation phenomenon in the materials.

The whole work has been described in 6 chapters. This work gave us an understanding to carry out a detail systematic study of $BaTiO_3$ and effect of the dopants at A or B-site of the BZT, KNN and ferroelectric –ferrite composites system and to optimize the structural and electrical properties of the material for a device application.

The research work present in the thesis began with chapter 1 on general introduction on lead free ferroelectrics, ferroelectricity of perovskites and crystal symmetry giving a general idea of these phenomenon's and its related mechanism. It includes the aim and objective of thesis.

Chapter 2 deals with detail literature review of ferroelectric, piezoelectric and ferromagnetic materials. It includes the description of dielectric, piezoelectric, ferroelectric, phase transition, polarization and properties of lead free ferroelectrics.

Chapter 3 deals with the detail description of research methodology used in carrying out the present work. Here we discuss the experimental processes of all the process by which we measure the different structural, dielectric and ferroelectric parameter. It also discusses the method of sample preparation. All the samples of lead free ceramic have been prepared by using solid state reaction technique in suitable stoichiometry.

Chapter 4 discusses the detail description of results and discussion. This chapter deals with the study of structural and electrical properties of $BaTiO_3$, BLTMNZ, Ca doped BLCTMNZ-0.04, BFT doped NKLN and NF doped BZT ceramics. All ceramic samples were prepared by high temperature solid state reaction method. X-ray diffraction analysis is used to calculate the different structural properties like crystal structure, lattice parameters, lattice strain, X-ray density, porosity, unit cell volume, volume mol fraction and crystalline size etc. Electrical analysis is used to calculate the different electrical parameters like dielectric constant, Curie temperature, activation energy and electrical behavior of samples.

The entire chapters are closed up with summary and conclusion of the whole work in chapter 5. From the studies proceed out it can be concluded that $BaTiO_3$, BLTMNZ, Ca doped BLCTMNZ-0.04, BFT doped NKLN and NF doped BZT ceramics prepared by high temperature solid state reaction method are a good candidates for electrical materials and it can be used for real device applications.

Chapter 6 is purposed to discuss the future direction of this research work.