SUMMARY

Lead oxide-based perovskites exhibit some of the highest piezoelectric coefficients of known compounds and are now widely used in transducers and other electromechanical devices. However, the toxicity of lead oxide and its high vapor pressure during processing have resulted in an increasing demand for environmentally benign alternative materials. Aurivillius has shown that a number of compounds of bismuth exist which are structurally composed of perovskite like layers separated by \((\text{Bi}_2\text{O}_2)^{2+}\) layers. The perovskite like layers can occur as single, double or triple layers between the \((\text{Bi}_2\text{O}_2)^{2+}\) layers. These Bismuth layered structure ferroelectrics are thought to be promising materials for lead-free ferroelectric oxides for their device applications to sensors, actuators, and nonvolatile random access memories (NvRAMs). This is because of their relatively high Curie temperature, low dielectric constant, low dielectric dissipation factor, low aging rate, high dielectric breakdown strength, and strong anisotropic electromechanical factor. The general formula for these bismuth materials is given as

\[
[\text{Bi}_2\text{O}_2]^{2+} [\text{A}_{m-1}\text{B}_m\text{O}_{3m+1}]^{2-}
\]

where \(A\) is a combination of ions with twelve fold coordination (e.g., Bi, Na, Sr) and \(B\) is a combination of ions suitable for six fold coordination (e.g., Ti, Nb) and \(m = 1, 2, 3, 4, 5\) which gives the number of pseudo-perovskite layers separated by bismuth oxide layers.

In these materials, it is expected that the fatigue free property of Bi-layered perovskites originates from the protective role of \((\text{Bi}_2\text{O}_2)^{2+}\) layers. That is, the role of \((\text{Bi}_2\text{O}_2)\) layers positioned between ferroelectric perovskite units is considered to be the compensation of space charges built up near the electrode and/or suppression of ionic diffusion. In
addition, these Bi-layered ferroelectrics have a relatively more robust structure, since they do not contain Pb ions with high volatility. The value of $m$ in BLSFs is closely related to the ferroelectric properties and structure instabilities. Higher order structures may have larger remanent polarization, with the increased number of perovskite units generating ferroelectric properties. An increase in $m$ in certain component systems led to an increase in the lattice parameters in the $a$-$b$ plane and an increase in strain energy originating from the size mismatch between the bismuth oxide layers and perovskite layers which will make the structure unstable. The reason may be the existence of a maximum number of $m$ in BLSFs. Therefore the studies about these compounds are concentrated on the members with $m$<5.

SrBi$_4$Ti$_4$O$_{15}$ is a four layered compound of BLSFs. The pseudo-perovskite block (SrBi$_2$Ti$_4$O$_{13}$)$_2^-$ is sandwiched between (Bi$_2$O$_2$)$_{2^+}$ layers. The BO$_6$ octahedra in SBT are all TiO$_6$. The chains of O-Ti-O in the TiO$_6$ octahedra are connected with each other in the plane perpendicular to the c-axis, but those along the c-axis are interrupted by the presence of (Bi$_2$O$_2$)$_{2^+}$ layers. The properties of these materials basically depend upon the TiO$_6$ octahedra in case of compounds Ti is at the center of these compounds. The polar axis in these materials is $a$-axis and the polar components are confined within pseudo perovskite blocks along the crystallographic ab-planes. Spontaneous polarization almost takes place in the direction parallel to the bismuth layer (the crystallographic $a$ ($b$) axis). There is no spontaneous polarization in the direction perpendicular to the bismuth layer (the c-axis).

It is commonly known that proper element doping in the perovskite-type unit of BLSF can effectively optimize the ferroelectric properties. Understanding of these materials in view of their A and B site substitutions on structural effects in turn to their microstructure & electrical properties is rapidly catching up. In our study, BLSF with $m$ = 4 is selected
because they have larger values of the relative dielectric constant and curie temperature than those with lower m numbers. Some researchers fabricated these materials (such as CaBi4Ti4O15, SrBi4Ti4O15, BaBi4Ti4O15 and PbBi4Ti4O15) for application to dielectric/ferroelectric capacitors and piezoelectric devices. Their research indicated that the dielectric properties of these materials could be changed depending on the species of the A-site cations. Thus in the present work, A-site substitution in SrBi4Ti4O15 is focused.

The present thesis entitled “Synthesis, Impedance spectroscopy and Electrical studies on some rare earth doped Bismuth layered structure ferroelectric materials” consists of five chapters. Each of these chapters contains studies and discussions on some A-site modified compounds. The contents of the thesis are given below:

Chapter I Introduction
Chapter II Synthesis and Experimental Techniques
Chapter III Characterization
Chapter IV Dielectric, Ferroelectric and Piezoelectric studies
Chapter V Impedance and Conductivity studies

The compounds selected under the framework of present thesis are SrBi4Ti4O15, Sr0.8Na0.1Nd0.1Bi4Ti4O15, Sr0.9Na0.2Nd0.2Bi4Ti4O15, Sr0.1Na0.4Nd0.4Bi4Ti4O15, and Na0.5Nd0.5Bi4Ti4O15. These compounds are prepared by making use of two different synthesis techniques: sol gel method and solid state method. Main aim of the present work is to understand the effect of double ion doping of Na and Nd for Sr position in A-site on its different physical properties. Dielectric, Ferroelectric, Electromechanical properties, Impedance, AC and DC conductivity studies are done on these compounds. Effect of A-site
modification on these properties is discussed and also the results obtained for compounds prepared by different synthesis routes are compared.

Chapter I is an introduction to this thesis. A brief review of Ceramics, Electroceramics, Dielectrics, Piezoelectrics, Ferroelectrics, their characteristics and classification based on their structure etc are given. Various equations involved in these properties are presented. Also a brief review of work done in the field of bismuth layered structure ferroelectrics along with the references to the literature are presented. Different studies done on different layered structure ferroelectrics are listed. The aim of the present work is presented at the end of this chapter.

Chapter II gives details of the procedure adopted in the synthesis viz. solid state sintering route and sol gel route. Sol gel method that is used in the present study is based on modified polymeric precursor method based on the Pechini process. Metal nitrates are used as the starting cations. Citric acid is used as chelating agent. The polymerization is promoted by the addition of ethylene glycol. The flowchart indicating the processes involved in solid state and sol gel method are given. Calcination and sintering temperature for all the compounds prepared are also listed in a table. The experimental techniques used for X-ray diffraction (XRD), Scanning Electron microscope (SEM), Density, Impedance, dielectric measurements, AC and DC conductivity measurement, electromechanical properties are also given in this chapter. At the end of this chapter, estimates of the errors in physical properties measured are given.

Chapter III presents the XRD, SEM and density studies done on all the prepared samples. The room temperature XRD patterns taken on calcined powders of all the samples confirmed the formation of the compound. There are no observable secondary phases present
in the XRD patterns indicating the formation of complete SBT phase. In the present investigation, X-ray data of compounds is indexed based on the ASTM data available for parent compound and the lattice parameters are evaluated using XLAT software. All the recorded peaks are indexed based on the orthorhombic structure of SBT. The maximum intensity is observed approximately at 30° of 2θ value, corresponding to (1 1 9) reflection, which is also observed in the parent compound. The main peak (1 1 9) in the XRD patterns is found to shift towards lower 2θ values with increase in the doping of Na and Nd. This shift of (1 1 9) peak explicitly shows that upon doping, the lattice space $d_{110}$ increases because of doping of smaller ions. Decrease in $a$, $b$, $c$, lattice parameters and volume $V$ with increase in composition is observed in both sol gel and solid state method. The instabilities of the layer structure is related to the distortion of the perovskite layers and the size mismatch between the $(\mathrm{Bi}_2\mathrm{O}_3)^{2+}$ and the perovskites layers. In general, the $a$ and $b$ lattice parameters show a continuous evolution as a function of the averaged ionic radii of A and B cations whereas $c$ parameter is affected more by the degree of the substitution, $x$. The incorporation of smaller radii ions may have attributed to the enhanced rotation of $\mathrm{TiO}_6$ octahedra in the a-b plane of crystal structure without the enhancement of the whole shift of perovskite blocks with respect to $(\mathrm{Bi}_2\mathrm{O}_3)^{2+}$ layers along the a axis. This has resulted in the decrease in lattice parameters. Also there is decrease in the orthorhombic distortion and increase in the orthorhombicity with doping.

Microstructural features are studied using the scanning electron micrographs. The average particle size as calculated from SEM graphs for the powders showed a smaller grain size in case of sol gel. The SEM images show grains in the form of platelets. Average grain
size is calculated for all the samples and it is found that the sol gel samples showed larger grain growth after sintering.

There is reduction in the sintering temperature by making use of sol gel method. Also lowered sintering temperature is observed with doping. Percentage density is calculated by making use of X-ray density and experimental density. High density is obtained in case of solid state samples. Also there is increase in density with increase in the doping concentration of Na and Nd.

Chapter IV presents the results and discussion on the dielectric, ferroelectric and electromechanical properties of Sr\(_{1-x}\)Na\(_x\)Nd\(_x\)Bi\(_2\)Ti\(_2\)O\(_{15}\) system (x = 0, 0.1, 0.2, 0.4 and 0.5) prepared by both solid state and sol gel method.

From dielectric measurements, it is found that the Curie temperature (T\(_c\)) increases with increase of x value. Dependence of Curie temperature on ionic displacements associated with the sample is discussed. These ionic displacements could be influenced by several factors including ionic size, tolerance factor and ionic polarizability. There is deduction in tolerance factor with the substitution of lower ionic radii cations in A-position. As the size of the A-site cation decreases, the lattice mismatch between TiO\(_6\) and AO planes in the perovskite-type unit of ATi\(_2\)O\(_3\) increases and the structural distortion becomes more pronounced. This distortion leads to the higher Curie temperature. It is also observed that the T\(_c\) value is high for a particular sample prepared by solid state when compared with sol gel.

There is a decrease in room temperature dielectric constant and dielectric constant at T\(_c\) with doping. The dielectric constant decreased from 2336 to 737 in case of sol gel samples whereas from 2041 to 221 in case of solid state samples. This reduction is attributed to the decrease in ionic polarization with the increase in Na and Nd doping. Also it is found
that the values of dielectric constant are high for sol gel samples when compared with solid state samples. This may arise due to the better homogeneity obtained in the sol gel process.

Low values of dielectric losses are found for all these samples. The room temperature dielectric loss for sol gel samples SS0p0, SS0p1, SS0p2, SS0p4 and SS0p5 are 0.051, 0.023, 0.022, 0.020 and 0.024 respectively. The room temperature dielectric loss for solid state samples CS0p0, CS0p1, CS0p2, CS0p4 and CS0p5 are 0.028, 0.023, 0.027, 0.022 and 0.048 respectively. It is observed that dielectric loss is high for pure SBT. This high dielectric loss value for pure SBT may be attributed to the low density/high porosity when compared to other samples. The values of dielectric loss are fairly low, and remain almost constant up to phase transition. The sharply increased dissipation above phase transition in all the samples is caused by an increase in electrical conductivity at high temperature, which may be due to the creation of oxygen vacancies.

Polarization vs. Electric field loops for all the samples confirm the ferroelectric nature of the sample. There is a decrease in the remanent polarization (2Pr) and coercive field (2Ec) with increase in the concentration of Na and Nd. It is observed that there is a decrease in 2Pr value from 19.6 μC/cm² to 2.8 μC/cm² and coercive field value from 85.3 kV/cm to 45.2 kV/cm for the maximum doping (x = 0.5) for sol gel samples. Also there is a decrease in 2Pr value from 17.1 μC/cm² to 1.4 μC/cm² and coercive field value from 81.7 kV/cm to 30.2 kV/cm for the maximum doping (x = 0.5) for solid state samples. This decrease in 2Pr value with doping is attributed to the increase in domain pinning. Domain pinning has occurred because of creation of oxygen vacancies and dipolar defects caused by the substitution of different valence cations (Na⁺ and Nd³⁺) for Sr²⁺ ion. These dipolar defects interact strongly with domain boundaries bringing about domain pinning.
Here also, the values of remanent polarization and coercive field are high for sol gel samples when compared to solid state samples. The reason is again the better homogeneity obtained fro sol gel process.

The resonance plots for sol gel and solid state samples indicates that the material is piezo-electrically active. The values of $k_t$ and $k_{\text{eff}}$ for pure SBT prepared by sol gel method are 0.47 and 0.44 respectively where its values in solid state method are 0.57 and 0.52 respectively. Theses values are higher than those reported in the literature. There is no systematic variation in the values of $k_t$ and $k_{\text{eff}}$ with increase in the concentration of Na and Nd doping. But larger values of $k_t$ and $k_{\text{eff}}$ are observed for composition $x = 0.1$ and 0.4 in both sol gel and solid state method with exception of $x = 0.5$ in sol gel method. The electromechanical coupling factor values are high for solid state samples than sol gel samples.

Chapter V deals with the detailed Impedance and conductivity studies. Effect of space charge polarization in the samples is found from $Z'$. $Z''$ vs frequency plots. The significant broadening of $Z''$ peaks on increasing temperature suggest the presence of a temperature-dependent relaxation process in the materials. The relaxation process may be due to the presence of electrons/immobile species at low temperature and defects at higher temperature. Heterogeneities may have arise in these samples because of disorder resulting from random occupation of Na and Nd with different ionic radii and valence sites in A site of the $\text{ABO}_3$ lattice of SBT.

Cole Cole or Nyquist plots showed the presence of grain and grain boundary effects with larger contribution coming from grain boundaries. Equivalent circuit built for these samples consist of a series array of two subcircuits (resistor and capacitor joined in parallel)
in series with a resistor. The values of these resistances and capacitances are calculated using simulation software provided with the AUTOLAB PGSTAT 30 Low Frequency Impedance Analyzer. It is observed that there is an increase in the values of grain and grain boundary resistances with increase in the doping concentration of Na and Nd in both sol gel and solid state samples except for x = 0.4 composition. This shows that the conduction in the grain and grain boundary is effected by the dopant concentration. It is also seen that the grain boundary resistance values are high for sol gel samples when compared with solid state samples. This increase can be considered taking into account grain size. Activation energy for conduction calculated for these samples showed that conduction mechanism is basically dominated by grain boundary conduction through hopping electrons created due to oxygen vacancies. A possible mechanism for the formation of vacancies is given.

Capacitance values calculated for grain and grain boundary increases with temperature and shows a peak around transition temperature. This behaviour shows that capacitance is associated with the net polarization of ferroelectric domains. These ferroelectric domains are formed when small, individual atomic displacements in the lattices are linked cooperatively.

The calculated values of activation energy for relaxation for grain and grain boundary suggested that the grain boundaries required higher activation energies for hopping across them than the grains. This indicated possible grain boundary barrier formation against electron conduction. The activation energy for conduction and activation energy for relaxation are approximately equal in grains as well as grain boundaries. This indicates that the charged species involved in conduction and relaxation mechanism are the same.
It is noted that the AC Conductivity at room temperature increased with increase in the doping of Na and Nd at Sr site. Also AC conductivity at room temperature is high for solid state samples than for sol gel samples. AC conductivity phenomenon in these samples corresponds to the short range hopping of charge carriers through the trap sites separated by energy barriers of varied heights. The two-term power relation is used to characterize the frequency dependence of AC conductivity. The parameters $s_f$, $s_2$ (low and high frequency slopes) and $\omega_p$ (hopping frequency) are calculated from the AC conductivity plots at different temperatures to get more information about the conduction mechanism. The exponents $s_f$ and $s_2$ exhibit a dependence with temperature. Variations in the exponent $s$ occur if the polarizability of the involved material depends on the energy barrier for a simple hopping process between two sites. Conduction in the low frequency region is attributed to short-range translational hopping mechanism ($\text{Ti}^{4+} \leftrightarrow \text{Ti}^{3+}$) for $0<s_f<1$. In the higher frequency region, the conduction is attributed to the reorientational hopping mechanism via dipole formation ($\text{Ti}^{3+} - V_o$) for $0<s_2<2$. Hopping conduction mechanism occurs via polarons.

DC conductivity value does not follow a systematic pattern with doping concentration. However, solid state sample showed lower conductivity value compared to sol gel sample. DC conduction is basically due to the migration of oxygen vacancies in layered compounds. It is observed that the DC activation energy values at higher temperature regions are high compared to activation energy at lower temperature regions. At higher temperatures, the increased activation energies increase vacancy concentration as well as the motion of oxygen vacancies. That is the reason the DC conductivity is high at higher temperatures.
Some of the important points (conclusions) that are drawn from the above studies are given below

(1) For A site substitution with smaller ionic radius ions, lattice parameters decreased.

(2) Curie temperature $T_c$ increased with the decrease of average ionic radius of A site cation where as the dielectric constant at room temperature and at $T_c$ increased.

(3) Substitution of smaller ionic radius ions at A site increased the room temperature dielectric constant values and $T_{\text{max}}$, and decreased slightly the room temperature dielectric loss values.

(4) From polarization vs electric field studies, highest remanent polarization is observed for pure SBT when compared to the doped samples.

(5) From electromechanical property studies, it is observed that the materials under study are piezo-electrically active. But larger values of $k_1$ and $k_{eff}$ are observed for composition $x = 0.1$ and $0.4$ in both sol gel and solid state method with exception of $x = 0.5$ in sol gel method.

(6) From the detailed AC and DC conductivity studies, it is observed that the hopping conduction mechanism dominates and the impedance relaxation is attributed to the oxygen vacancy related phenomenon and also due to the defects formed because of the random occupation of different valence ions at A-site.

On comparison of properties studied for samples prepared by both sol gel and solid state method, it is found that

(1) Lower sintering temperature is obtained by making use of sol gel method.

(2) Sol gel samples showed high $T_c$, high dielectric constant values.
(3) High remanent polarization and coercive field values are obtained in case of sol gel samples.

(4) The electromechanical coupling factor values are high for solid state samples.

(5) AC conductivity at room temperature is high for solid state samples.

(6) Solid state sample showed less DC conductivity value compared to sol gel sample.
SCOPE FOR FUTURE WORK

The discovery of Aurivillius Bismuth layer compounds has triggered a concerted effort to understand and optimize their remarkable properties. These compounds have been thoroughly investigated from the viewpoint of both structure and properties. The long-range goal is to reliably evaluate new materials in advance of synthesis, thereby streamlining and guiding the development of high performance materials. The major applications of these materials are Non-volatile random access memories, dynamic random access memories, Actuators, Sensors and optical modulators etc. In view of the above, there is enough scope for further work in these samples as stated below:

1. Different doping at A/B site to yield maximum dielectric constant and polarization required for ferroelectric applications.

2. Developing different synthesis techniques (precursor methods) to get homogeneous powder with small particle size.

3. Measurements of structures, detailed characterization of how they are mediated by the bulk chemistry and the thermal processing.

4. Physically, it is important to study the microstructure of doped compounds for better understanding the substitution effect. Therefore, Transmission Electron Microscopy studies can be done for microstructural studies.

5. Understanding the role of compositional order/disorder arising of doping at a variety of length scales and its impact on electromechanical properties and performance is important. The final goal is to develop some excellent piezoelectric ceramics for high temperature applications.
6. Measurements of piezoelectric properties under pressure. This will help separate chemical from structural defects.

7. Pyroelectric studies can be done to study the variation of polarization with temperature.

8. Ferroelectric bulk materials have major commercial importance, but thin films prepared from these materials have recently been the focus of significant research efforts. Development of ferroelectric thin films of bulk materials helps to perform fatigue studies.
LIST OF PUBLICATIONS

1. Electrical properties of cationic substituted SrBi$_2$Ta$_2$O$_9$
   
   **Rizwana**, G. S. Kumar and P. Sarah
   

2. Impedance Spectroscopy of Na and Nd doped strontium bismuth titanate
   
   **Rizwana**, T. Radha Krishna, A. R. James and P. Sarah
   

3. Dielectric, Ferroelectric and Piezoelectric properties of Sr$_{0.8}$Na$_{0.1}$Nd$_{0.1}$Bi$_4$Ti$_4$O$_{15}$
   prepared by sol gel and solid state technique
   
   **Rizwana**, A. R. James and P Sarah
   

4. AC conductivity and Dielectric studies on Sr$_{0.8}$Na$_{0.2}$Nd$_{0.2}$Bi$_4$Ti$_4$O$_{15}$ Ceramic
   
   **Rizwana**, T. Radha Krishna and P Sarah
   
   Communicated, Modern Phys. Letts., 2007

5. Ferroelectric properties of Sr$_{1.2x}$Na$_x$Nd$_x$Bi$_4$Ti$_4$O$_{15}$ (0≤x≤0.5) Ceramics
   
   **Rizwana**, T. Radha Krishna and P Sarah
   

6. Comparison of properties of Sr$_{1.2x}$Na$_x$Nd$_x$Bi$_4$Ti$_4$O$_{15}$ (x=0-0.5) Ceramics prepared by sol gel and solid state method
   
   **Rizwana**, A. R. James and P Sarah
   
   Communicated, Ceramics International, 2007

7. Impedance studies on Na$_{0.5}$Nd$_{0.5}$Bi$_4$Ti$_4$O$_{15}$ Ceramic
   
   **Rizwana**, T. Radha Krishna and P Sarah
   
   Communicated, Modern Phys. Letts., 2007

8. Study of effect of doping on grain and grain boundary parameters of Sr$_{1.2x}$Na$_x$Nd$_x$Bi$_4$Ti$_4$O$_{15}$ (x=0-0.5) Ceramics using Impedance Spectroscopy
   
   **Rizwana**, A. R. James and P Sarah
   
PAPERS PUBLISHED IN PROCEEDINGS OF CONFERENCES

1. Effect of lanthanum on Characteristics and Electrical properties of $\text{Ca}_{0.1}\text{Sr}_{0.9}\text{Bi}_2\text{Ta}_2\text{O}_9$
   National Conference on Ferroics, CVR College of Engineering (2006), pg. no. 91
2. Characterization and Electrical properties of polycrystalline $\text{Ca}_{0.1}\text{Sr}_{0.9}\text{La}_x\text{Bi}_{1-x}\text{Ta}_2\text{O}_9$
   National Seminar on Ferroelectrics and Dielectrics, Delhi University, New Delhi (2004), pg. no. 195
3. Dielectric characterization of $\text{Ca}_{0.1}\text{Sr}_{0.9}\text{R}_{0.1}\text{Bi}_{1.9}\text{Ta}_2\text{O}_9 \ (R=\text{La, Nd, Pr})$ ceramics
   International Symposium of research students on Materials science and Engineering, IITmadras, Chennai (2004), PO-AC-9