Appendix

Preparation, structural analysis and properties of La$_{(x)}$Bi$_{(1-x)}$Fe$_3$O$_3$ Perovskite

A 1.1 Introduction

A 1.2 Synthesis of Ferrites by conventional routes

A 1.2.1 An oxide method

A 1.2.2 Decomposition method

A 1.2.3 Precipitation technique

A 1.2.4 Solid state reaction and sintering

A 1.3 Synthesis of La$_{(x)}$Bi$_{(1-x)}$Fe$_3$O$_3$ system for varying x values

A 1.3.1 Characterization study of La$_{(x)}$Bi$_{(1-x)}$Fe$_3$O$_3$

A 1.4 Results and discussion

A 1.5 Measurement of Dielectric properties

A 1.6 Conclusion

1.7 References
Appendix

Preparation, structural analysis and properties of La$_{x}$Bi$_{(1-x)}$Fe$_{3}$ perovskite

A 1.1 Introduction

In order to appreciate the non conventional methods, outlined in the thesis brief experimental results consisting of conventional powder metallurgy is described in this appendix. The Bismuth ferrite was prepared by dry powder technology.

Recently, due to the increased technological importance the single phase magneto electric materials have gained attention from scientists, researchers and industrial community. Single phase magneto electric materials have been extensively synthesized by active working groups in USSR.

BiFeO$_3$ is of particular interest in view of its potential applications as a good magneto electric material. It shows ferroelectric behavior with high curie temperature of about 1043°k and antiferromagnetics ordering below Neel temperature of about 647 k [1,2]. It shows many anomalies in dielectric behavior with respect to temperature. We intended to synthesize similar products by making use of standard solid state (ceramic) and microwave sintering methods. The structural and few dielectric properties of La substituted BiFeO$_3$ have been studied in the present experiments

A 1.2 Synthesis of Ferrites by conventional routes

The Polycrystalline ferrites are formed using solid state reaction. In order to complete such reaction in reasonable time, an intimate mixture of the two oxides must be raised to a high temperature, probably of the order of 1400°C. Commercially the material will most likely to be required in a solid form, perhaps as a rod, and the substance produced by the reaction will then be powdered again, formed into desired shape and again heated to a high temperature to grow the solid by a sintering process. Here both initial and final
firing plays an important role. This sintered polycrystalline body is not truly solid but contains many pores. The quantity, size, shape and distribution of these pores through the body will vary with different forming techniques, firing temperatures and atmospheres and with firing time. Clearly, pore distribution and size will affect the physical properties.

Methodology: Various methods of synthesis [3] of mixed oxide systems are outlined in this section.

A 1.2.1 Oxide method

Here, high purity oxide materials in the proportionate amount required by the final product are mixed together. For this, wet milling procedure in a rubber lined pot using SS balls is carried out. After milling the mixture is dried and fired at a moderately low temperature (500-700°C). The resulting material is again broken up and milled. This may have to repeat out for several times to obtain the high degree of homogeneity.

A 1.2.2 Decomposition method

Here, instead of using oxides as starting materials, one may use salts such as carbonates, nitrates and oxalates, which may be milled (mixed) in the required proportions as the salts, and then pre-heated, usually in air, to produce the oxides by thermal decompositions.

A 1.2.3 Precipitation technique

In this procedure precipitation of hydroxide and oxalate is carried out. To avoid the lengthy milling process involved in dry mixing, attempts have been made to precipitate simultaneously the required hydroxide from a solution so that the precipitate contains the required metals in the correct proportion, already intimately mixed [4].

Above are the well-recognized methods of achieving the mixing of the metals in the right proportions and under conditions such that oxide formation is possible, if the oxides are not already present. There still remains reacting of the mixture and sintering to form the final body, two processes which may occur simultaneously.
A 1.2.4 Solid state reaction and sintering:

The solid state reaction is relatively slow one, a form of diffusion process which can often be usefully expedited by employing elevated temperatures. Here, frequently the furnace temperatures in the region of 1300°C to 1450°C have been used. These temperatures are maintained for several hours while reaction proceeds and the charge are then slowly cooled. In the un-reacted state the mixture is arranged to have the correct proportions of the metals; in order to obtain the right proportions of the correct valence metal ions in the final product, careful control of the furnace atmosphere is essential. This is specific in case of preparing magnetic oxides containing ions which have valence states such as Fe, Mn, Cu, CO. It is important that when sintering into final form and ‘controlled atmosphere’ reactions are carried out together metals shall be in their correct valence states in the mixtures initially prepared. Otherwise the resulting sintered solid will contain many cracks and imperfections which occur through the oxidation reactions taking place throughout the compressed powder. The reacted material is then ground to a fine powder form before being pressed or extruded into the required shape. The fine powder is mixed with some form of binder such as 1% polyvinyl alcohol or 1% ammonium alginate solution which later volatilizes. Applied pressure used for compaction is commonly several tons/square inches. The compacted material is then refired to sinter to a solid mass at temperature up to about 1450°C. The procedure is as shown in the adjoining flowchart.

For synthesis of single crystals there are number of methods such as Veraruil, flame-fusion, or tri-cone process, The Bridgman-Stock Barger method for synthetic magnetite crystals 1cm in diameter and about 4 inch in long [5]. The flux-melt technique was used for nickel and zinc manganese ferrite [6].

A 1.3 Synthesis of La$_x$Bi$_{(1-x)}$FeO$_3$ system for varying x values

Experimental

The polycrystalline samples of rare earth element substituted bismuth ferrite BiFeO$_3$ were synthesized. It is one of the important magneto electric materials [7]. In our
laboratory an attempt was made to substitute La in BiFeO$_3$ to form a ferroelectric material La$_x$ Bi$_{1-x}$ FeO$_3$. These are the polycrystalline samples synthesized using standard solid state reaction. A procedure for standard ceramic method was followed with $x = 0.0, 0.1, 0.2, 0.3, 0.4, 0.5, 0.6, 0.7, 0.8, 0.9$ to $x = 1.0$.

The basic oxides Bi$_2$O$_3$, La$_2$O$_3$ and Fe$_2$O$_3$ were mixed together in molar proportion. Each sample was ground for 3 hrs duration. These mixtures were pre-sintered at 750$^\circ$C for 12 hrs followed by grinding each for an hour duration. The fine homogeneous powders of these compounds were mixed with 2-3 drops of saturated solutions of polyvinyl alcohol (PVA) (Mol. Wt. 124000) acting as a temporary binder. This mixture was then pressed and compacted to form the pellets using applied pressure of 5 tons/ (inch)$^2$ using a hydraulic press for 15 minute in air. Each pellet having dimension of 10mm diameter with thickness of 3-4 mm. were kept in a desiccators. Later the pellets were finally sintered for 24 hrs at 950$^\circ$C. in air and then furnace cooled. A programmable furnace was used with proper parameter set facilities on the front panel control board.

A 1.3.1 Characterization study of La$_x$ Bi$_{1-x}$ FeO$_3$

The samples were then characterized using various characterization techniques such as XRD using Phillips X-ray diffractometer (Model PW1840) and Bruker D8 advance to get the structural information and phase formation. An electrical characterization was done. A capacitive structure was formed using silver paste and conducting electrodes. The dielectric measurements were carried out by using a programmable furnace, LCR bridge (Model 3532 Hioki) as a function of frequency in the range 50 Hz to 100 KHz in steps. The simultaneous measurements of resistance, conductance, impedance and loss coefficient were measured at room temperature by varying the frequency. The measurement of the impedance, conductance and loss coefficient was done as are shown in the respective graphs. The SEM study for morphological study can give the microstructural information over a wide range of magnification. The values of dielectric constants were calculated for the samples with variable x values. The table shows the corresponding values.
A 1.3.2 Measurement of dielectric properties

**Dielectric constant K**

The most common and significant non-linear property of ferroelectric materials is the dielectric constant $K$ (dimensionless parameter) or the dielectric permittivity $\varepsilon$. Since $\varepsilon$ expresses the behavior of polarization it is important and close to heart of Ferroelectricity. $K$ rarely remains constant. It changes with applied field, stress, temperature, frequency and other parameters. Fig A1 shows the variation of dielectric constant with frequency at room temperature. The values are high at low frequencies and decrease rapidly with increasing frequency. Similar behavior was observed in many other dielectric materials reported earlier for La$_{(1-x)}$Sr$_x$CoO$_3$ and Bi$_x$La$_{(1-x)}$FeO$_3$ [9, 12] prepared by different chemical routes. This is due to the fact that at low frequencies, dipoles are able to follow the variation in the applied voltage. With increasing frequency the dipoles are not able to follow the variations of applied field. The dielectric relaxation results in high value of dielectric constant at low frequencies and low value of dielectric constant at higher frequencies. The value typically decreases rapidly in the range from 70 Hz to 20 kHz and thereafter it remains almost constant. This compound shows relatively low value at $x= 0.1$ while for $x=0.3$ it shows higher value. This shows that with increasing the La concentration in BiFeO$_3$ compounds the value of dielectric constant enhances.

<table>
<thead>
<tr>
<th>Freq(Hz)</th>
<th>$x=0.1$</th>
<th>$x=0.3$</th>
<th>$x=0.5$</th>
<th>$x=0.7$</th>
<th>$x=0.9$</th>
</tr>
</thead>
<tbody>
<tr>
<td>50</td>
<td>3.64</td>
<td>22.06</td>
<td>5.73</td>
<td>3.50</td>
<td>28.21</td>
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<tr>
<td>100050</td>
<td>1.61</td>
<td>1.31</td>
<td>0.0561</td>
<td>0.088</td>
<td>123.57</td>
</tr>
<tr>
<td>20050</td>
<td>1.48</td>
<td>0.86</td>
<td>0.0564</td>
<td>0.085</td>
<td>98.39</td>
</tr>
<tr>
<td>30050</td>
<td>1.38</td>
<td>0.63</td>
<td>0.0586</td>
<td>0.081</td>
<td>91.55</td>
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<tr>
<td>40050</td>
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<td>0.0578</td>
<td>0.080</td>
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</tr>
<tr>
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<td>0.077</td>
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<tr>
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<td>0.34</td>
<td>0.0575</td>
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<td>0.075</td>
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</tr>
<tr>
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<td>0.0576</td>
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</tr>
<tr>
<td>90050</td>
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<td>0.23</td>
<td>0.0581</td>
<td>0.074</td>
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<tr>
<td>100050</td>
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<td>0.21</td>
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<td>0.073</td>
<td>72.33</td>
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</table>

**Table:** Data shows calculated values of Dielectric constant for $\text{La}_{(1-x)}\text{Bi}_{(1-x)}\text{FeO}_3$ system.
This enhancement of the value of dielectric constant in substituted samples is associated with the electronic structure of Bi$^{+3}$ and A-B bond in ABO$_3$ type structure. The electronic configuration of Bi$^{+3}$ tends to create the ‘cloud’ of electric dipole polarization (a local ferroelectric phase) around itself due to the local displacement of surrounding ions. Also La substitution causes the weakening of A-B sub-lattice interaction allowing less resistance to polarization and enhances dielectric constant values.

The impedance ($Z$), conductance ($G$) and loss coefficient ($D$) were also measured. The corresponding plots for impedance measurement are as shown in fig A2, A3 and A4.

**Impedance**

As seen from the graph fig A2 impedance decreases with increasing the applied frequency for the samples of La$_{x}$Bi$_{1-x}$FeO$_3$ system for $x= 0.1, 0.3, 0.5, 0.7, 0.9$. It has been observed that in general all the samples with varying $x$ values provide high impedance at low frequencies but drastic reduction is observed as the frequency is increased. The Change in the value of impedance with increasing frequency demonstrates
and purity of the material. The basic conduction mechanism in ferroelectrics can be ionic and/or electronic in nature and this helps in understanding of electrical transport properties in ferroelectric material.

**Conductance G**

The corresponding nature of conductance is shown in the plots in figure A3. The behavior shows the variation in conductance value. This is due to change in the inherent material's impedance which is due to small change in the capacitance with increasing frequency. Its reactance $X_c$ plays an important role. Density and mobility of charge carriers are the key qualities for inner details of the conductivity. The mechanism of charge transport can be sufficiently understood from the measurement of conductivity and Hall coefficient. Hopping model considers that the conductivity is because of changes in the mobility of charge carriers with temperature.

![Figure A 3: Variation of Conductance (G) with frequency (Hz) in La$_x$Bi$_{1-x}$FeO$_3$ system for $x= 0.1, 0.3, 0.5, 0.7, 0.9$.](image-url)
**Loss Coefficient D**

Figure A4 shows the variation of loss coefficient with frequency at room temperature for all the samples prepared so far by this method. As loss coefficient D behaves differently again for the sample with \( x = 0.9 \) and it definitely points out a different crystalline structure or morphology controlled by the defects in these samples which is responsible for the observed behavior. Most polar dielectrics are very good insulators and hence show low value of dissipation factor \( \tan \delta \) which shows anomalous behavior at \( T_c \).

![Figure A4: Variation of Loss coefficient (D) with frequency (Hz) in \( \text{La}_{(x)} \text{Bi}_{(1-x)} \text{FeO}_3 \) system for \( x = 0.1, 0.3, 0.5, 0.7, 0.9 \).](image)

The behavior in each of these cases indicate that the response is not linear nor a monotonous with respect to the value of \( x \). It is thus clear that the properties are optimized at a particular composition and such kind of result will prove useful for low frequency applications. Figure A5 Shows Variations of Conductance (G), Impedance (Z), Loss
Coefficient (D) and Dielectric constant (K) with respect to concentration (x) of La substituted in La<sub>x</sub>Bi<sub>(1-x)</sub>FeO<sub>3</sub> system for x = 0.1, 0.3, 0.5, 0.7, 0.9 measured at a constant frequency of 50 Hz.

**Figure A5** Variations of Conductance (G), Impedance (Z), Loss Coefficient (D) and Dielectric constant (K) with respect to concentration (x) of La substituted in La<sub>x</sub>Bi<sub>(1-x)</sub>FeO<sub>3</sub> system for x = 0.1, 0.3, 0.5, 0.7, 0.9 measured at a constant frequency of 50 Hz.

**A 1.4 Results and discussion**

*Structural analysis: XRD*

The XRD pattern for the samples prepared with varying x values are as shown in fig A6. The X-ray diffraction data were collected using a Bruker AXS D8 Advance diffractometer with CuKα radiation at a step of 0.02°/s in the range 2θ = 10° to 90°. The structural study was carried out using the XRD spectra. Figure A1 shows the XRD spectra for samples of La<sub>x</sub>Bi<sub>(1-x)</sub>FeO<sub>3</sub> system synthesized by varying the values of x. The patterns
were referred and compared with the standard JCPDS data [10]. The unit cell parameters are in good agreement with the literature [1, 11] and JCPDS data card no 37-1493, 74-2203. The single phase formation of these compounds was confirmed using XRD studies. The samples with $x = 0, 0.2, 0.4, 0.6$ are found to be orthorhombic while the samples with $x = 0.8$ is triclinic. The structure closely resembles with that of the standard perovskite $ABO_3$ type.

![XRD spectra for La$_{(x)}$Bi$_{(1-x)}$FeO$_3$ system by varying values of X.](image)

**Figure A 6:** XRD spectra for La$_{(x)}$Bi$_{(1-x)}$FeO$_3$ system by varying values of X.

**SEM**

The morphological study was done using the scanning electron micrographs. The micrographs are for varying x values in the La$_{(x)}$Bi$_{(1-x)}$FeO$_3$. The SEM images are as shown in figure A7. The Micrographs are clear and corresponds to typical grain size of few micrometers for the samples with varying x values. The SEM pictures of La$_{(x)}$Bi$_{(1-x)}$FeO$_3$ powders showed that all the samples prepared have primary fine particles with a small tendency of agglomerates formation and high porosity. All La$_{(x)}$Bi$_{(1-x)}$FeO$_3$ solid solutions have a large crystallite sizes in (\textasciitilde 1 \mu m). The specific surface area must be larger. This preparation method is rather simple and the powders thus synthesized are expected to be good candidate as catalysts and sensor element or device of various types. The shapes of these are
different such as for $x=0.3$ and $x=0.7$ it shows spherical particles whereas others have oval, disc and flat shapes. The grain boundaries are distinct and clear. A magnified view for samples of $x=0.7$ shows some elongated shaped grains as seen from figure A7.

![Figure A 7 SEM Micrographs: $\text{La}_{x}\text{Bi}_{(1-x)}\text{FeO}_3$ system for $X=0.1, 0.3, 0.5, 0.7, 0.9$](image)

A 1.5 Conclusion

The multiferroic samples synthesized by solid state reactions have been analyzed by different characteristics tools and it is confirmed that reasonably good perovskite type of samples were prepared which exhibit good dielectric constants at lower frequency. Similar synthesis was supposed to be carried out by MW sintering which is left for the future plan. Magnetic properties remain to be investigated.
APPENDIX

A 1.6 Reference

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