Chapter 2

Synthesis of phase pure BiFeO$_3$-NaNbO$_3$ nano composites and its Structural, Electric, magnetic and magnetoelectric studies

Abstract

Solid solutions of BiFeO$_3$ (BFO) and NaNbO$_3$ [i.e. ($\text{Bi}_{1-x} \text{Na}_x$) ($\text{Fe}_{1-x} \text{Nb}_x$)O$_3$] were prepared by different methods. Solid state reaction, Co precipitation method, Sol-gel method and modified sol-gel method (Pechini method) were used. In most of the cases occurrence of secondary phases was the drawback. As a conventional preparation technique, solid-state reactions based on oxides and carbonates of metal components have been used, with thermal treatments around 700-850 °C. Here the major drawback is the reproducibility of the process was quite poor. Newly developed sol-gel methods (Pechini type) provide facile ways to get high quality products. In this chapter the various synthesis routes employed for the preparation of the current composites have been detailed. The Pechini method has been employed for the further preparation because of the formation of phase pure samples and reproducibility. Compounds prepared by Pechini method have shown high electric and magnetic property compared to the compounds prepared by other techniques. Structural analysis using XRD and TEM has shown that phase pure samples were obtained with reduced particle size. The observations encountered reveal that particle size plays a crucial role in deciding the electric and magnetic properties. The multiferroic character of nanoparticles is confirmed through magneto electric (ME) coupling studies. The good coexistence of ferroelectric and ferromagnetic behaviors in the composite provides the possibility to achieve a measurable ME effect. The highest value of the magneto electric coefficient (α) is observed for $x=0.1$ ($\alpha=0.13$ Vcm$^{-1}$Oe$^{-1}$) and it reduces for higher $x$ values. The reduced size and absence of impurity could be the reason for the enhancement in electrical property. Low loss tangent value observed in the samples is a remarkable improvement.
Chapter 2

2.1 Introduction

Multiferroics exhibit the entwined nature between the two distinct phenomena of ferroelectricity and ferromagnetism, which allow them to utilize for novel device concepts that would not be attainable by either ferroelectric or ferromagnetic materials. BiFeO$_3$ (BFO) is one of the well known single phase multiferroic material with distorted perovskite (ABO$_3$) structure. The perovskite BiFeO$_3$ possesses a ferroelectric transition $T_c \sim 830{\degree}C$ and antiferromagnetic transition at $T_N \sim 370{\degree}C$. BFO is unique amongst many multiferroics, as its ferroelectric and magnetic transition temperatures are well above the room temperature raising the possibility of potential devices based on magneto electric (M-E) coupling operating at room temperature. However, BFO has few limitations such as high leakage current that allows current to pass through it when a high voltage is applied. It has high dielectric loss and low polarization. In order to solve these inherent problems, several attempts have been made in the recent past such as doping it with rare earth elements like samarium, lanthanum etc. at the appropriate atomic sites and/or fabricating its composites. Multiphase multiferroics are successful approach to overcome the limitations of single phase materials such as the small magneto electric coupling. Recently a lot of attempts have been concentrated on the research and development of high performance lead-free piezoelectric ceramics such as alkali niobates. NaNbO$_3$ has been found as an excellent candidate as it is a good piezoelectric and ferroelectric material. Hence BiFeO$_3$-NaNbO$_3$ composite material is expected to improve the multiferroic property. Solid solutions of BFO and NaNbO$_3$ have been prepared in different compositions with a general formula $(Bi_{1-x}Na_x)(Fe_{1-x}Nb_x)O_3$ where $x = 0$, 0.05, 0.1, 0.5 and 0.7 using solid state reaction, coprecipitation method, sol-gel method and modified sol-gel method (Pechini method). Structural characterization using XRD, SEM and FTIR of all samples were carried out. In this chapter, the magnetic, electric and magnetolectric coupling study of phase pure $(1-x)BiFeO_3$-$xNaNbO_3$ composites for $x=0$, 0.05, 0.1, 0.5 and 0.7 are detailed.
2.2 Experimental techniques

2.2.1 Solid State Reaction

Bi$_{1-x}$Na$_x$Fe$_{1-x}$Nb$_x$O$_3$ ceramics with x=0, 0.05, 0.1, 0.5 and 0.7 were prepared by solid state reaction process using starting materials of Bi$_2$O$_3$ (99% Sigma-Aldrich), Fe$_2$O$_3$ (99% Sigma-Aldrich), Na$_2$CO$_3$ (99% Sigma-Aldrich), and Nb$_2$O$_5$ (99% Sigma-Aldrich). The raw materials were carefully weighted in stoichiometric ratio and mixed by using an agate mortar with acetone as medium for 4-5 hours. The slurries were dried and heated at 500 °C for 1 hour. The calcined powder were ground again using agate mortar for 1-2 hours and pressed uniaxially into pellets of 12 mm diameter. The pellets were sintered at various temperatures from 700 °C to 850 °C for different time periods from 1-5 hours.

2.2.2 Co-precipitation method

Initially BiFeO$_3$ is prepared by solid state reaction. Co-precipitation method is used for the preparation of NaNbO$_3$. For the preparation of NaNbO$_3$, Niobium oxide, sodium hydroxide, ethyl alcohol, ammonium carbonate and standard ammonia solution were used and all the starting materials were of AR grade. A stoichiometric amount of NaOH was dissolved in distilled water (100 ml) and required quantity of Nb$_2$O$_5$ was dissolved in hydrogen fluoride (HF) after heating in a hot water bath for 10 hours. Then, an equal amount of ethyl alcohol was added to the above solution mixture containing both sodium hydroxide and niobium fluoride. The aqueous solution of ammonium carbonate and ammonium hydroxide were added with constant stirring to reach pH 9 to ensure complete precipitation of sodium carbonate and niobium hydroxide. The precipitate was filtered, washed several times with distilled water to remove anions and dried in an oven at 100 °C for 12 hours. The oven dried powders were calcined at various temperatures ranging from 200 °C-800 °C for 12 hours. The obtained powder samples were mixed with BiFeO$_3$ which was already prepared by solid state reaction.

2.2.3 Modified sol gel (Pechini) method

The solid solution ceramics of Bi$_{1-x}$Na$_x$Fe$_{1-x}$Nb$_x$O$_3$ with x=0, 0.05, 0.1, 0.5, and 0.7 were prepared by modified sol-gel method called pechini method. AR grade of Ammonium Niobate Oxalate (C$_4$H$_4$NNbO$_9$-xH$_2$O) (Sigma-aldrich > 99% pure), Bi(NO$_3$)$_3$ (Sigma-aldrich > 99% pure), Fe(NO$_3$)$_3$ (Sigma-aldrich >
99% pure), NaNO₃ (Sigma-aldrich > 99% pure) were used as raw materials. Firstly, the raw materials were carefully weighted in stoichiometric ratio and dissolved in Citric acid aqueous solution (in 1:1 molar ratio with respect to the total metal cation) and pH value was adjusted to 5 using ammonia solution (NH₃·OH). The clear solution thus obtained was dried at 100 °C to form gel and the gel was burnt at 500 °C to get the ceramic powders. After that the powder was ground and pressed into pellets. Finally the pellets were sintered at 850 °C for 1 hour to get the final sample. The crystal structures of the samples were examined using Phillips X’Pert Pro XRD with Cu-Kα radiation (1.54056 Å). Step scanned powder XRD data was collected in the 2θ range 10°-80° at room temperature on the finely ground sample. Detailed structural analysis was performed using Scanning Electron Microscope (JEOL JSM 6390) and Transmission Electron Microscope (JEOL JEM 2100). The absorption spectrum was taken using a UV-VIS spectrophotometer (SHIMADZU, UV-2450). The relative dielectric constant (ε) and dissipation factor (tan δ) at room temperature were measured using an LCR meter (Agilent E4980A). The magnetoelectric coupling was determined using a lock in amplifier technique and magnetization measurements were performed using SQUID magnetometer.

2.3 Results and discussions

2.3.1 X-Ray Diffraction Analysis

![XRD patterns](image)

Figure 2.1 XRD patterns of (1-x)BiFeO₃-xNaNbO₃ samples for x=0, 0.1 and 0.5 prepared by Co-precipitation method. Secondary phases are marked by *
Synthesis of phase pure BiFeO$_3$-NaNbO$_3$ nano composites...

Figure 2.2 XRD patterns of (1-x)BiFeO$_3$-xNaNbO$_3$ samples for x=0, 0.05, 0.1, 0.5 and 0.7 prepared by Solid state reaction (sintered for different time periods). Secondary phases are marked by *

Figure 2.3 XRD patterns of (1-x)BiFeO$_3$-xNaNbO$_3$ samples for x=0, 0.05, 0.1, 0.5 and 0.7 synthesized by Pechini method.
Figure 2.1 shows the XRD patterns of \((1-x)\text{BiFeO}_3-x\text{NaNbO}_3\) samples for \(x=0, 0.1\) and 0.5 prepared by co-precipitation method. Co-precipitation method is cheap and easy but the presence of large amount of secondary phases is the drawback of this method. Figure 2.2 shows the XRD patterns of \((1-x)\text{BiFeO}_3-x\text{NaNbO}_3\) composite system for \(x=0, 0.05, 0.1, 0.5\) and 0.7 prepared by solid state reaction. Eventhough peaks corresponding to secondary phases are present, the intensity of the peak decreases by increasing the sintering time. Most of the secondary peaks disappear for 5 hour heating. But we couldn’t adopt solid state reaction for large scale synthesis due to difficulty in reproducibility. Hence, we found Pechini method as the best synthesis route for further study. Figure 2.3 shows the XRD pattern of \((1-x)\text{BiFeO}_3-x\text{NaNbO}_3\) composite system for \(x=0, 0.05, 0.1, 0.5\) and 0.7 at room temperature prepared by Pechini method. The peaks that correspond to \text{BiFeO}_3\ and \text{NaNbO}_3\ are indicated by B and N respectively. XRD data reveals that both the phases of \text{BiFeO}_3\ and \text{NaNbO}_3\ are present in the composite system. Non-perovskite phases such as \text{Bi}_2\text{Fe}_4\text{O}_9\ and \text{Bi}_2\text{O}_3/\text{Fe}_2\text{O}_3\ were not detected in the XRD spectra which is a common occurrence when we adopt other techniques for the preparation. In the XRD spectra it could be observed that as \(x\) increases the peaks corresponding to orthorhombic \text{NaNbO}_3\ appear. Also, as the content of \text{NaNbO}_3\ is increased from \(x=0.1\) to \(x=0.7\), the diffraction peaks corresponding to \text{NaNbO}_3\ phase increases remarkably and the diffraction peaks corresponding to \text{BiFeO}_3\ phase decreases gradually. The obvious peak splitting in the XRD spectrum shows the rhombohedral structure of nanoparticles, consistent with the structure of BFO ceramics.\(^{23-28}\) The crystal structure changes from rhombohedral to orthorhombic by increasing the amount of \text{NaNbO}_3\ phase in the composite. The crystallite size was calculated from the full width at half maximum (FWHM) of the diffraction peaks using the Scherrer’s equation. The calculated values of particle size are 6.2 nm, 10.9 nm, 41.7 nm and 79.2 nm for \(x=0, x=0.1, x=0.5\) and \(x=0.7\) respectively.
2.3.2 Transmission Electron Microscopy

![ TEM images of (1-x)BiFeO₃-xNaNbO₃ samples for (a) x=0, (b) x=0.1, (c) x=0.5, (d) x=0.7. ]

A typical TEM image of the BiFeO₃-NaNbO₃ samples prepared by the present sol-gel method are shown in Figure 2.4. The average particle size estimated from TEM images came out to be 6 nm, 10 nm, 43 nm and 80 nm for x=0, 0.1, 0.5 and 0.7 samples respectively and is consistent with the XRD analysis. The HRTEM and SAED patterns of x=0.1, 0.5 and 0.7 are shown in Figure 2.5. Both HRTEM and SAED pattern confirm the polycrystalline nature of the samples. The lattice spacing (d) calculated from the HRTEM image (Figure 2.5) matches with JCPDS values corresponding to BiFeO₃ and NaNbO₃. The d value 0.23 and 0.34 corresponds to (221) and (121) planes of orthorhombic
NaNbO$_3$ (JCPDS 89-8957). Similarly $d=0.39$ corresponds to (100) plane of rhombohedral BiFeO$_3$ (JCPDS 74-2016). The SAED patterns show the presence of sharp diffraction spots, which is a clear indication of well developed, crystalline nanoparticles. The diffuse diffraction spots indicate the nanosize of the synthesized material.

![HRTEM images](image.png)

**Figure 2.5** HRTEM images of (1-x)BiFeO$_3$-xNaNbO$_3$ samples for (a) $x=0.1$, (b) $x=0.5$, (c) $x=0.7$. Inset shows corresponding SAED patterns.
2.3.3 Scanning Electron Microscopy

Figure 2.6 SEM images of (1-x)BiFeO$_3$-xNaNbO$_3$ samples for (a) x=0.1, (b) x=0.5

Figure 2.6 shows SEM images of x=0.1 and 0.5 compositions. The grain size from SEM images could not be predicted as it contains agglomerated nanoparticles. But one can see the small particles spread over the edges and middle portion of the SEM images which are in nanometer size.

2.3.5 FTIR Spectroscopy

Figure 2.7 shows the FTIR spectra of the samples. The band at 637 cm$^{-1}$ corresponds to the bending modes of vibration of bismuth oxide and the band at 810 cm$^{-1}$ is due to Fe-O bond which indicate high crystalline BiFeO$_3$ phase. The peak at 1091 cm$^{-1}$ may be due to the C-C bond. It is probable that some of the hydrated carbonates detected in the high temperature FTIR samples are a consequence of a reaction between the powders, after thermal decomposition with moisture and carbon dioxide in the air during sample storage prior to recording the FTIR spectra. The broad absorption bands from 3000 cm$^{-1}$ to 3600 cm$^{-1}$ arose from the antisymmetric and symmetric stretching of bond H$_2$O and OH-1 groups. As we have sintered the sample at high temperature (>800 °C), this band corresponds to the absorption of water from the environment. The bands at 1040 cm$^{-1}$, 1385 cm$^{-1}$ indicate existence of nitrate ions and band at 918 cm$^{-1}$, 1383 cm$^{-1}$ correspond to stretching vibrations of nitrate ions. A peak at 2335 cm$^{-1}$ is representative of nitrile and the band at 2928 cm$^{-1}$ is due to C-H stretching vibrations.
2.3.4 Linear optical study

The UV-Visible absorption spectra of composites are shown in Figure 2.8 (a). The absorption cut-off wavelength of the as prepared composite samples lies between 500-600 nm which is close to the reported value for pure BFO (ie 560 nm), suggesting that the present material can absorb visible light in the wavelength range of 400–565 nm. The UV-Visible absorption spectroscopy is frequently used to determine the energy bandgap of the powder samples from their absorption spectra. The optical band gap was determined from the Tauc plot (Figure 2.8 (b)). The tangent line, which is extrapolated to \((Ea)^2 = 0\), gives the band gap \((Eg)\). The band gap values for each composite is shown in
Table 2.1 which is in agreement with values from previous reports. Pure NaNbO$_3$ have reported Eg value of 3.3-3.4 eV. Incorporation of NaNbO$_3$ increases the band gap energy of the composite which is probably due to the interaction between BiFeO$_3$ and NaNbO$_3$.

Table 2.1: Bandgap energy of the samples

<table>
<thead>
<tr>
<th>Sl. No</th>
<th>Sample name</th>
<th>Bandgap energy (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>X=0</td>
<td>1.7</td>
</tr>
<tr>
<td>2</td>
<td>X=0.1</td>
<td>1.9</td>
</tr>
<tr>
<td>3</td>
<td>X=0.5</td>
<td>2.3</td>
</tr>
<tr>
<td>4</td>
<td>X=0.7</td>
<td>2.8</td>
</tr>
</tbody>
</table>

Figure 2.8 (a) UV-Vis diffuse absorption spectra of the BiFeO$_3$-NaNbO$_3$ nanoparticles, (b) Plot of $(E\alpha)^2$ versus photon energy (E).
2.3.6 Magnetic study

To understand the magnetic behavior, the Magnetization (M) versus applied field (H) is measured for BFO and BiFeO$_3$-NaNbO$_3$ composite samples which are shown in Figure 2.9. Here, one could observe good hysteresis behaviour indicating ferromagnetic (FM) behaviour of BFO (Figure 2.9 (a)) with a coercivity of about 2.7 kOe at room temperature. The magnetization curves are not saturated with in the field up to 30 kOe. It is obvious that BFO exhibits a nonlinear magnetization dependence on magnetic field, nonzero remnant magnetization (Mr) and coercive field (Hc) here. The highest magnetization observed at RT at a magnetic field of 30 kOe is 0.7 emu/g for BFO. Generally for bulk BFO, the hysteresis loop observed will be linear indicating antiferromagnetic ordering of spins at the ground state. Recent researches on BFO showed that nanoparticles of BFO have high saturation magnetization and found a ferromagnetic hysteresis loop even at room temperature.$^{19}$ It was

Figure 2.9  M-H loop of (1-x)BiFeO$_3$-xNaNbO$_3$ samples for (a) x=0, (b) x=0.05, (c) x=0.1, (d) x=0.5
suggested by Neel that this might be due to the finite number of magnetic moments in nanoparticles, which may lead to a difference in the number of spin in the two sub lattices because of random occupancy of lattice sites.\textsuperscript{44,45} This results in an uncompensated magnetic moment that leads to enhanced magnetic properties. The ceramic composition $x=0.05$, has shown good magnetic property considerably larger than BFO. The maximum magnetization observed for this composition is 1.8 emu/g. For $x=0.1$ composition, the hysteresis loop is similar to a typical weak ferromagnetic ‘S’ shaped curve. For $x=0.1$ composition, the hysteresis loop shows linear behavior which represents AFM ordering of spins characteristics of bulk BFO.\textsuperscript{50, 50} When $x$ increases to $x=0.5$, the magnetic phase decreases again and the hysteresis loop become linear. For our composite sample, the ferromagnetic behaviour can be due to reduced particle size and absence of impurity. Also, numerous magnetization studies of antiferromagnetic nanoparticles have shown that the magnetization in large applied fields is considerably larger than that in the corresponding bulk materials.\textsuperscript{45} Magnetic parameters associated with nanoparticles are summarized in Table 2.2.

Table 2.2: Magnetic parameters of samples

<table>
<thead>
<tr>
<th>Sample Name</th>
<th>Size nm</th>
<th>M at 30 kOe Emu/g</th>
<th>Hc kOe</th>
<th>Mr emu/g</th>
</tr>
</thead>
<tbody>
<tr>
<td>X=0</td>
<td>6</td>
<td>0.71</td>
<td>2.713</td>
<td>0.12</td>
</tr>
<tr>
<td>X=0.05</td>
<td>21</td>
<td>1.69</td>
<td>1.8</td>
<td>0.19</td>
</tr>
<tr>
<td>X=0.1</td>
<td>10</td>
<td>0.019</td>
<td>0.7</td>
<td>0.002</td>
</tr>
<tr>
<td>X=0.5</td>
<td>43</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
</tbody>
</table>
2.3.7 Magneto electric coupling Study

![Figure 2.10](image1.png)

**Figure 2.10** ME voltage as a function of AC magnetic field

<table>
<thead>
<tr>
<th>Sl. No.</th>
<th>Sample Name</th>
<th>ME coefficient ((\alpha)) (Vcm(^{-1})Oe(^{-1}))</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>X=0</td>
<td>0.062</td>
</tr>
<tr>
<td>2</td>
<td>X=0.05</td>
<td>0.046</td>
</tr>
<tr>
<td>3</td>
<td>X=0.1</td>
<td>0.130</td>
</tr>
<tr>
<td>4</td>
<td>X=0.5</td>
<td>0.0086</td>
</tr>
<tr>
<td>5</td>
<td>X=0.7</td>
<td>0.0038</td>
</tr>
</tbody>
</table>

![Table 2.3](image2.png)

**Table 2.3**: Magnetoelectric coupling coefficient

![Figure 2.11](image3.png)

**Figure 2.11** ME voltage as a function of DC magnetic field
The variations of ME voltage with AC magnetic field is plotted in Figure 2.10. The ME output voltage measured up to 100 Oe (for Hac) shows linear increase with increasing magnetic field. When a magnetic field is applied to a magnetoelectric material, the material is strained. This strain induces a stress on the piezoelectric, which generates the electric field. This field could orient the ferroelectric domains, leading to an increase in polarization value. The magnetoelectric effect in multiferroics is fully described by the magnetoelectric coupling coefficient. From the slope of the graph, coupling coefficient ($\alpha$) is determined and it is found to decrease with increase in NaNbO$_3$ content. The high value of ME coefficient, $\alpha = 0.13$ V/cm$^2$Oe$^{-1}$ is observed for x=0.1 which indicates the strong coupling of electric and magnetic phases in this composition. Tabulated values of magnetoelectric coupling coefficient are given in Table 2.3. Figure 2.11 shows variation of ME voltage with DC magnetic field for fixed AC field of 10 Oe.

2.3.8 Magnetic and Electric hysteresis of (0.9)BiFeO$_3$-(0.1)NaNbO$_3$ composite

![Figure 2.12](image)

Figure 2.12 (a) Magnetization (M) versus magnetic field (H) plot of x=0.1 composition at 6K and 300 K (inset shows a zoomed view of the central portion).
Eventhough high magnetization values for $x=0.05$ composition could be achieved, the magnetoelectric coupling in the particular composition is low. Higher magnetoelectric coupling is observed in $x=0.1$. To understand the magnetic and electric behavior in detail, the Magnetization ($M$) versus applied field ($H$) and electric polarization ($P$) versus applied electric field ($E$) were measured for $x=0.1$. Figure 2.12 shows Magnetization ($M$) versus applied field ($H$) for $x=0.1$ at two different temperatures. Room temperature electric polarization ($P$) as a function of applied electric field is plotted in Figure 2.13. For bulk BFO the magnetic hysteresis loop is generally observed to be linear, indicating antiferromagnetic ordering of spins at the ground state. But here the magnetic hysteresis loop is similar to a typical weak ferromagnetic ‘S’ shaped curve. The small hysteresis loop observed at 6 K represents a soft magnetic phase with a low coercive field. It is found that the saturation is attained within the field of 40 kOe. And the highest magnetization observed within the 60 kOe is 0.025 emu/g. At 300 K the hysteresis loop shows linear behavior which represents AFM ordering of spins characteristics of bulk BFO.\textsuperscript{10,41} From the magnetization measurement, one can realize that the good multiferroic property of the selected composition ($x=0.1$) is contributed by the electric phase rather than the magnetic phase. To measure the ferroelectric property, we observed the ferroelectric hysteresis loop of the selected composition at a

**Figure 2.13** Electric polarization ($P$) as a function applied electric field ($E$) for $x=0.1$ composition
frequency of 50 kHz as shown in Figure 2.14. The ferroelectric hysteresis loop is not saturated within the field of 6 kV/cm. A maximum polarization of 3.8 µC/cm$^2$ could be achieved which is higher than reported values of BFO at room temperature.$^{54}$ Ceramic BFO have reported polarization value of 2.5 µC/cm$^2$ but thin films of BFO$^{55,56}$ have polarization values approximately 80 µC/cm$^2$.

### 2.3.9 Dielectric study

The frequency dependence of dielectric constant ($\varepsilon$) for (1-x)BiFeO$_3$–x NaNbO$_3$ (x=0, 0.1, 0.5, 0.7) at room temperature in the frequency range 100 Hz to 2 MHz is shown in Figure 2.14. The inset shows the dielectric loss (tan $\delta$) with frequency. The variation of dielectric constant with frequency is very much consistent with that of other compounds/composites.$^{22,34}$ It is evident that the dielectric constant and loss tangent decrease with increase in frequency. In the starting low frequency range both $\varepsilon$ and tan $\delta$ have higher values. The $\sigma$ and tan $\delta$ values decrease gradually as frequency is increased from 100 Hz to 10 KHz and then decreases slowly and become almost constant up to 2 MHz for all compositions. The observations may be explained by the phenomenon of dipole relaxation.$^{34}$ The dielectric constant ($\varepsilon$) of all the samples was found to decrease with increase of frequency in the low frequency region. This phenomenon can be attributed to the space charge relaxation effect. At low frequencies, the space charges are able to follow the frequency of the applied field, whereas these space charges do not find time to undergo relaxation at high frequency region.$^{28}$ At high frequency, electric dipoles are unable to switch with frequency of the applied field. This is a general feature of dielectric materials.$^{22}$
It has been observed that at low frequency region, the dielectric constant is found to be dependent on different kinds of polarization (electronic, atomic, interfacial and ionic) whereas at high frequency region, only electronic polarization mainly contributes for the dielectric constant. So there is a sharp decrease in dielectric constant at high frequency. The values of the dielectric loss have been found to be very low at high frequencies and may find applications of these materials in high frequency microwave devices. The decrease of tan δ with increase in frequency can be explained on the basis of Koop’s phenomenological theory. The low losses may be attributed to the nanosized grains. The low frequency dielectric dispersion has increased with increase in NaNbO₃ concentration and it was maximum for x=0.7. It should be noted that the dielectric constant is found to increase with increase in NaNbO₃ content. Also the dielectric constant is found to increase with decrease in particle size because of the presence of nanosized grains which act as a large insulating barrier for mobile charge carriers. The dielectric constants of sol gel synthesized samples are very much higher as compared to samples prepared by solid state synthesis. It is clearly observed that sol-gel synthesized samples have very high value of dielectric constant in low frequency region in comparison with the previous reports on other rare earth doped BiFeO₃.
AC conductivity studies were carried out for a better understanding of the frequency dependence of electrical property of the materials. Figure 2.15 shows variation of AC conductivity as a function of frequency. The conductivity $\sigma_{ac}$ was calculated using the dielectric data and empirical relation.

$$\sigma_{ac} = \varepsilon_0 \varepsilon_r \tan\delta$$

where $\varepsilon_0$ is the permittivity of free space and $\omega$ is the angular frequency. The conductivity curve shows that $\sigma_{ac}$ increases with frequency which is a common feature of semiconductors.\textsuperscript{41} The increasing trend of $\sigma_{ac}$ with frequency in the low frequency region might be attributed to the disordering of cations between neighboring sites and presence of space charges.\textsuperscript{44}

2.4 Conclusion

Phase pure BiFeO$_3$-NaNbO$_3$ nanocomposite samples were successfully synthesized using Pechini method. XRD and TEM analysis show that all the particles are in the nanometer size and no secondary phases were formed during the synthesis. The average crystalline size estimated from TEM images varies from 6 nm to 80 nm and consistent with XRD studies. The HRTEM images confirm the presence of BiFeO$_3$ and NaNbO$_3$ phases. The reduced size and absence of impurity were attributed for the high dielectric constant and good ME coupling. For the selected composition $x=0.1$, improved
magnetoelectric coupling is observed which indicate the good multiferroic property in the selected composition. We report significant increase in the ferroelectric property for the selected composition x=0.1 with electric polarization value 2.5 $\mu$C/cm$^2$. We can conclude that the addition of NaNbO$_3$ enhance the electric property and hence magnetoelectric coupling property of the composite. By increasing x from 0.1 to 0.5, the electric property increases while the magnetoelectric coupling decreases. Hence, it may be concluded that good multiferroic behavior is achieved for x=0.1 composition. The purity and reduction of size may be the reason for enhanced electric and magnetic properties of the present set of samples compared to their bulk form. Also, the composite exhibits magnetic moment at room temperature. The room temperature dielectric study shows that the low frequency dielectric dispersion is increased with increase in NaNbO$_3$ concentration and it was maximum for x=0.7. It should be noted that the dielectric constant is found to increase with increase in NaNbO$_3$ content while there is no much increase in dielectric loss indicating their potential applications.
Synthesis of phase pure BiFeO$_3$-NaNbO$_3$ nano composites...

References

1. Ruimin Yao, Chuan Bao Cao, Chunrui Zheng, Qiang Lei, RSC Adv, 2013, 3, 24231-24236.


