Chapter 2

Effect of Reduced Particle Size on the Magnetic, Raman & Dielectric Spectroscopy of Chemically Synthesized BiFeO₃ Nanocrystals: Signatures of Spin-Phonon and Magnetoelectric Coupling

Outline

In this chapter, we report the effect of reduction in particle size on the temperature dependent magnetization, Raman and dielectric spectroscopy of chemically synthesized BiFeO₃ nanocrystals with average grain size of 55 nm. Due to the nanosize effect, the M-H loops show a significant coercivity starting from 390 K with an anomaly located in the vicinity of 150 K in our $H_c$ vs. $T$ as well as $M_r/M_s(50 \text{ kOe})$ vs $T$ curves. At this temperature, both $H_c$ and $M_r/M_s(50 \text{ kOe})$ undergo minima. Additionally, our results for the first time show the evidence of existence of a low temperature anomaly due to spin-glass transition in the range from 40-44K in the field cooled magnetization curves. In bulk single crystals,
this transition is reported to be situated at around 50 K, however, this transition remained so far undiscovered in the recent studies on BiFeO$_3$ nanoparticles due to the insufficient temperature resolution. The significant shift in this transition towards lower temperature can be attributed to size dependent effects. The Raman spectroscopy (90 – 700 K) shows two sets of transitions in the lowest Raman E mode, associated with Bi-O bond motion situated in the close proximity to the spin reorientation transitions reported in BiFeO$_3$, thereby proving the existence of possible coupling between magnons and phonons for the particle size below the helical order parameter (62 nm). These transitions are slightly shifted in temperature in comparison to the bulk single crystals. We also observe a step like behavior in Raman peak position around Néel temperature suggesting that the phonons are getting influenced by the magnetic ordering in nanosized BiFeO$_3$ The low temperature (20- 325 K), frequency dependent (1 – $10^6$ Hz) dielectric constant and loss tangent measurements show that the loss tangent (~$10^{-3}$) and ac conductivity values (~ $10^{-8}$ Ohm$^{-1}$-cm$^{-1}$) are orders of magnitude lower than the reported values BiFeO$_3$ ceramics indicating high levels of ionic purity of our samples. The real part of permittivity shows slight reduction in its value (~30) in comparison to the bulk single crystals. Similar to the Stokes Raman shift, its temperature dependent dielectric constant also shows four weak anomalies at~ 85, 168, 205 and 230 K situated in the close proximity with spin reorientation transitions indicating the magnetoelectric coupling.

The work described in this chapter is published as –

- **Effect of Reduced Particle Size on the Magnetic Properties of Chemically Synthesized BiFeO$_3$ Nanocrystals.**

- **Temperature-Dependent Raman and Dielectric Spectroscopy of BiFeO$_3$ Nanoparticles: Signatures of Spin-Phonon and Magnetoelectric Coupling.**
2.1 Introduction:

After the initial work by Curie and other researchers on the magnetoelectric effect, where ferroelectric and ferromagnetic/antiferromagnetic order parameters couple in the same phase, there is a recent surge in the development of new synthesis methods as well as to fully understand the physical properties of these multifunctional materials. Among these materials, BiFeO$_3$ (BFO) is one of the most widely studied materials in this class; mostly in bulk single crystal, polycrystalline and epitaxially grown thin film forms. BFO crystallizes in rhombohedrally distorted perovskite structure with space group $R3c$ below its $T_c$ (1100 K). Recently, people have also started investigating the effects on the magnetoelectric coupling after manganese, calcium, niobium substitution in the lattice to decrease the ac conductivity, increase dielectric constant and magnetization. The usefulness of doping related enhancement in ferroelectric polarization is under a question mark as it may not be truly ferroelectric in origin. Moreover, even in the pure undoped BFO, the bulk phase structural, optical, dielectric and magnetic properties are not completely understood. One of the major reason behind relatively larger attention given to this material is its antiferromagnetic (AFM) nature with reasonably high Neel temperature ($T_N = 380^\circ C$) and ferroelectric (FE) ordering below its Curie temperature $\sim 1100$ K above which it undergoes a transition from rhombohedral to orthorhombic symmetry and becomes cubic above $\sim 1200$ K. However, there is a lack of clear understanding as which of these two transitions is truly associated to the FE ordering. The coexistence of FE and AFM ordering at room temperature makes this material one of the most promising candidate for room temperature magnetoelectric (ME) applications. The fascination towards this material is never ending with newer information being added by several groups. Magnetic ordering in BFO is quite complicated because of Dzyaloshinsky-Moriya (DM) interaction which results in a canted AFM ordering of Fe$^{3+}$ spins in the system. These canted Fe$^{3+}$ moments induce a lattice strain which increases the free energy of the crystal. To minimize the free energy of the crystal, spiral spin structure is superimposed on the AFM ordering resulting into rotation of the spins. The order parameter of this helical ordering between two successive planes is found to be around $\sim 620\AA$ in the bulk BFO. For bulk BFO, the magnetic hysteresis loop shows a typical AFM behavior with zero coercivity.
Room temperature magnetoelectric (ME) coupling in BFO has also excited a lot of interest in recent years though the origin of this coupling is still debated. In BFO, electrical and magnetic dipole ordering originates in different sublattices; Bi-O orbital hybridization due to Bi $6s^2$ lone pair is the origin of ferroelectricity whereas Fe-O-Fe antisymmetric Dzyaloshinskii-Moriya (DM) exchange interaction gives rise to interesting magnetic ordering. In recent years, the phonon behavior in multiferroic materials has gained interest due to the study of HoMnO$_3$ by Raman and IR spectroscopy and LuMnO$_3$ by transmittance and reflectance measurements which showed the importance of studying phonons in multiferroic materials. Raman studies on epitaxial BFO films and single crystals showed the spin-phonon coupling. Singh et al. reported for the first time, room temperature Raman spectra with phonon mode assignments in epitaxially grown thin films. Haumont et al. showed an anomaly near Néel temperature in Raman phonon modes (315, 380, and 550 cm$^{-1}$) in BFO single crystals proving the possible multiferroic character playing the role in the strong phonon anomaly. Kothari et al. and Fukumura et al. showed presence of all the 13 Raman modes predicted by the group theory on single crystal and polycrystalline BFO. Recently, through low temperature Raman measurements, some studies have reported the existence of coupling between ferroelectric and magnetic order parameters in polycrystalline bulk materials.

The dielectric properties of BFO in various forms have also been widely studied in single crystalline, ceramic and thin film forms. However, most of these dielectric studies are reported in temperature range higher than room temperature ($> 300$ K) and do not investigate the relation between magnetic anomalies at low temperature with dielectric parameters which are reported below 300 K only. Recently, Scott et al. related low temperature dielectric anomaly and their magnetic coupling in ceramic and single crystalline BFO and reported the existence of coupling between FE & AFM order parameters in single crystal and ceramic BFO. The BFO polycrystalline samples showed a decrease in the real part of permittivity ($\varepsilon'$) values from 114.4 to 97.2 and loss tangent ($\tan \delta$) values from 9.22 to 0.26% when the frequency is increased from 0.01 to 1MHz. The FE behavior of BFO thin films showed high $\varepsilon'$ and $\tan \delta$ values in the low frequency range with continuously decreasing trend at the frequencies higher than 1kHz. The bulk BFO is reported to show relatively low resistivity and high loss tangent.
which prevents from studying the polarization loop behavior at and above the room temperature and hinders its potential applications in FE and ME devices. BFO single crystals showed FE hysteresis loop at low temperatures (< 100 K) only, with spontaneous polarization value of $P_S = 6.1 \, \mu C/cm^2$ which is much lower than expected from the materials with such a high FE transition temperature accompanied with large lattice distortion. On the other hand the observation of orders of magnitude higher $P_s$ in thin films (up to 50-60 $\mu C/cm^2$) accompanied with enhanced magnetization (up to 1 $\mu_B$/unit cell) was attributed to be originating from the higher conductivity and oxygen deficiency in these thin films due to the presence of significant amount of Fe$^{2+}$. It is therefore non-trivial and a challenging task to synthesize high resistive BFO as the ceramic synthesis and thin film methods usually result in secondary phases such as Fe$_2$O$_3$, Bi$_2$O$_3$ and Bi$_2$Fe$_4$O$_9$. Additionally, the presence of slight non-stoichiometric oxygen in BFO often leads to the presence of Fe$^{2+}$ and lattice defects thereby resulting into unwanted increase in the conductivity at room temperature due to hopping mechanism from Fe$^{2+}$ to Fe$^{3+}$, significant Maxwell-Wagner type of contributions in the dielectric constant and weak ferromagnetism etc. The high leakage current in bulk BFO synthesized by solid solution methods also leads to serious dielectric breakdown at fields < 100 KV/cm which makes them unsuitable for practical devices. To overcome this problem and to get higher resistive material, people have tried various approaches such as doping with various rare earth and transition metal ions and solid solution of BFO with other ABO$_3$ perovskite materials but these methods also often result into impure phases. Nanosize effects on the physical properties of both magnetic and ferroelectric counterparts of multiferroics are studied in depth in past several decades due to their potential applications in various nanoscale devices. The observation of Verwey metal to insulator transition and large spin dependent magnetoresistance in chemically synthesized and organically passivated Fe$_3$O$_4$ nanoparticles with size as small as 6-8 nm and the shift in the Verwey transition temperature from 120 K (in bulk) to around 90 K (in nanoparticles) is reported. Similarly, the observation of ferroelectric-paraelectric transition in biosynthesized BaTiO$_3$ nanoparticles with size 5-6 nm and the shift of this transition at lower temperature is also reported. Therefore, the interest in the investigation of size dependent properties of multiferroic materials is non-trivial leading...
to few recent reports on this topic in BFO. This is largely due the fact that below the particle size ~ 62 nm, there is an enhancement in both ferroelectric and magnetic polarization because of the combined action of exchange and spin-orbit interactions which produces spin canting (away from perfect AFM ordering). Recently, people have reported that below 100 K, nanosized BFO exhibits sizable hysteresis and finite coercivity. Such a deviation from bulk to nano is observed due to the breaking of the helical ordering or incomplete rotation of the spins along the AFM axis which gives rise to higher magnetization. The decrease in particle size below the periodicity of helical ordering gives rise to the suppression of modulated spin structure which improves the magnetization in nanoscale particles. However, in absence of quality magnetization data, some of these studies remain poorly concluded. Moreover, sometimes, the properties of BFO are reported to be masked with presence of the impurity phase of Fe$_3$O$_4$.

However, the effect on the reduced size (below the helical order parameter) on the phonons and the dielectric behavior at low temperature (in the vicinity to the spin reorientation transitions) is not studied so far. The temperature dependent Raman and impedance spectroscopy in BFO nanoparticles is required to answer some of the fundamental questions including: (1) what is the temperature dependent frequency behavior of $|\varepsilon|$ and tan $\delta$ at low temperature in the proximity of magnetic transition in nanosized BFO? (2) Do the relaxation behavior, dielectric constant and loss tangent remain same in nanosize as for bulk BFO? (3) Is there any direct/indirect coupling between the breaking of spiral ordering on the dielectric parameters and FE ordering? (4) What is the fate of FE and AFM ordering transitions and spin-phonon coupling in nanosized BFO?

In this chapter, we have tried to answer some of these questions by doing a careful temperature dependent Raman and dielectric spectroscopy and heat flow measurements on chemically synthesized BiFeO$_3$ nanoparticles with average size ~ 50-60 nm.
2.2 Hydrothermal synthesis of BiFeO$_3$ nanoparticles:

We have developed a modified hydrothermal route to synthesize the BFO nanoparticles based on complexing the metal ions with the citric acid followed by the hydrothermal process. Recently, we applied the similar approach to synthesize GdCrO$_3$ nanocrystals.\textsuperscript{39} In contrast to the usual ceramic methods which are used to make bulk BFO and often give impurity phases (most common impurities are Bi$_2$O$_3$ and Fe$_2$O$_3$) and, wet-chemical method adopted by us gave highly pure BFO nanoparticles without any impurity phase due to ionic level mixing. For this purpose, stoichiometric amounts of iron nitrate (Fe(NO$_3$)$_3$.9H$_2$O, Merck, 98%), bismuth nitrate (Bi(NO$_3$)$_3$.5H$_2$O Merck, 98%), and an equal amount of citric acid (metal/citric acid molar ratio = 1/1) (obtained from Merck, 99.5% ) were dissolved in the deionized water by stirring it for 6 h, to complex the metal ions with the citrate ions. This was followed by the dropwise addition of ammonia solution (28 wt. %) to neutralize the unreacted citric acid as well as to raise the pH value of the solution near 9.2 resulting into a sol formation. The sol was transferred to a 200 ml capacity autoclave with Teflon liner followed by the hydrothermal treatment at 150$^\circ$C for 20 h. The precipitate was in turn filtered, washed with deionized water, re-filtered and finally dried at 160$^\circ$C for 5 h. The dried powder was calcined at 350$^\circ$C for 6 h to get crystalline phase and used for further physical property measurements discussed below unless mentioned otherwise. In another case, we calcined the part of these particles at 750$^\circ$C for 6 hours to study the effect of particle size growth on the magnetic properties.
2.3 Characterization:

2.3.1 X-ray diffraction and Pawley refinements:

In figure 2.1, we have shown the powder x-ray diffraction pattern (XRD) of the as-synthesized BFO nanocrystals recorded by a PANalytical X’PERT PRO instrument using an iron- filtered Cu-Kα radiation (λ=1.5406 Å) in the 2θ range of 10°- 80° with a step size of 0.02°. We used the Materials Studio Software from Accelrys Inc. to perform the Pawley refinement to determine the lattice parameters of the BFO nanocrystals from the experimental data. The pseudo-Voigt peak shape was selected for these refinements. The refined lattice parameter were calculated as $a = b = 5.574±0.001$, $c= 13.850±0.002$Å.

![XRD pattern comparison](image)

**Figure 2.1:** Room temperature experimental powder XRD pattern compared with the simulated and difference NPD profiles (using Pawley refinement) for BiFeO$_3$ nanocrystals. The blue lines are the reference values for BiFeO$_3$ taken from the JCPDS Card No. 140181.
with an excellent Rwp value of 4.94%. The difference in the experimental and simulated data is also shown in figure 2.1. In the supporting information, we have shown the zoom view of different parts of complete XRD profile which clearly shows the absence of any impurity phase (See supporting information). The average crystallite size as calculated using Debye-Scherer formula was found to be around 36 nm.

2.3.2 Determination of shape and size of the BiFeO₃ nanoparticles:

To further investigate microstructure and topography, we used the FEI (model Tecnai F30) high resolution transmission electron microscope (HRTEM) equipped with field emission source operating at 300 KV to image BFO nanocrystals on carbon-coated copper TEM grid. The TEM images in figures 2.2 A & B show particles with a quasi

![TEM Images](image)

**Figure 2.2:** (A,B) Transmission electron micrograph (C) High resolution TEM images showing the lattice fringes (D) Selected Area Electron Diffraction (SAED) pattern of BiFeO₃ nanoparticles.
spherical morphology and size ranging from 50-60 nm. The average size calculated from TEM images was around 55 nm. In figure 2.2C, we have shown the high resolution TEM image where we could notice well pronounced lattice fringes indicating very good level of crystallinity. The selected area electron diffraction pattern (SAED) in figure 2.2D shows a nice dot pattern that again clearly exhibits highly crystalline nature of BFO nanocrystals. In figure 2.3, we have shown the TEM images of BFO particles recalcined at 750°C for 6 h. These images show that particles that were initially 55 nm in sized have fused together nicely to form larger particles with average size of 0.5 μm.

![Figure 2.3](image)

*Figure 2.3: (A, B) Transmission electron micrograph of BiFeO₃ particles calcined at 750°C. Growth of the particle size can be clearly seen in comparison to the TEM images in figure 2.2*

### 2.4 Optical properties:

#### 2.4.1 UV-vis absorption spectroscopy measurements:

In figure 2.4, we have shown the UV–vis -NIR spectra for the BFO nanocrystals in the diffused reflectance mode taken using a Jasco UV-vis-NIR spectrometer (model V570) operated at a resolution of 2 nm. In the UV–vis -NIR spectra, we observed a broad absorption band in the range of 450-600 nm. This absorption is due to two types of electronic transitions. The first excitation is due to the electronic transition from $^6A_1$ state
to $^{4}T_{1}$ ($^{4}G$) state and the second one is due to the excitation from $^{6}A_{1}\rightarrow^{4}E$, $^{4}A_{1}$($^{4}G$) ligand field transitions and the field transfer band tail.$^{40}$ These transitions overlap with each other and give a broad band as seen in figure 2.4. The absorption below 450 nm is associated with charge transfer transition ($d$-$d$) of Fe$^{3+}$ ions from $^{6}A_{1}$ to $^{4}E$ ($^{4}D$) and $^{4}T_{2}$($^{4}D$) level.$^{40}$

2.4.2 X-ray photoelectron spectroscopy measurements:

In figures 2.5 A & B, we have shown the room temperature x-ray photoelectron spectroscopy (XPS) data to confirm the oxidation state of the Bi and Fe to validate the formation of the pure phase. For this purpose the high resolution XPS data was collected by using a VG Microtch, model ESCA 3000 equipped with ion gun (EX-05) for cleaning the surface spectra. The binding energy resolution was 0.1 eV. We used Shirley algorithm for background correction and chemically distinct species were resolved using a nonlinear least square fitting procedure. The core level binding energies were aligned with the carbon binding energy of 285 eV. Figure 2.5A shows the XPS spectra of Fe$^{3+}$. The deconvoluted peaks are shown in the inset of figure 2.5A. Here, a small peak (referred as pre-peak) at a relatively lower binding energy (around 706 eV) arises probably due to the lattice defects. It is known that for the nanoparticles, it is energetically unfavorable to afford defects in the core of the particles, however, nanoparticle’s surfaces can have impurities leading to the generation of this pre-peak. We could also notice two most intense peaks at 711.7 and 723.8 eV which were assigned to the Fe$^{3+}$ $2p_{3/2}$ and $2p_{1/2}$ states.$^{41}$ The expanded view in inset of figure 2.5A shows deconvoluted peak pattern of Fe$^{3+}$ $2p_{3/2}$ multiplet which has a great importance due to its sensitivity towards the chemical changes in the neighborhood which reflects in the peak.

Figure 2.4: The UV–vis-NIR spectra for BiFeO$_3$ nanocrystals at room temperature in diffuse reflectance mode.
shape and broadening. We could see that the peak assigned to $2p_{3/2}$ core levels is unusually broad. Usually, the peak of high spin Fe$^{3+}$ ions is broadened significantly compared to Fe (0 state) and low spin Fe$^{2+}$ state. This broadening is explained by the electrostatic interaction and spin orbit coupling between the $2p$ core hole and unpaired 3d electrons of the iron ions and crystal field splitting of the 3d orbital into $t_{2g}$ and $e_g$ level.$^{42}$ Here, since each iron ion is surrounded by six oxygen ions in an octahedral environment so the oxygen ions create a weak field around the Fe$^{3+}$ ions that makes the system high spin with unpaired 3d electrons. Another reason behind the observation of relative broadness of almost all the peaks can be due to the reduced coordination number of surface atoms due to the reduced particle size in our BFO nanoparticles. Due to the reduced coordination number, the electron density around the Fe$^{3+}$ ions at the particle surface would be less so the shielding of the iron nucleus is decreased causing the electrons to be pulled closer to it. Such a decrease in the shielding value will require

\[ \text{Figure 2.5: (A) & (B) XPS spectra for Fe (2p) & Bi (4f) on BiFeO}_3 \text{ nanoparticles (scatter curves) respectively. The lines represent the deconvoluted peaks. Inset of (A) shows the deconvoluted peaks of Fe (2p).} \]
higher energy to withdraw an electron from the $2p$ shell which will result into the peak broadening. In our study, we also found a small peak at 715 eV which is again considered as a surface peak arising due to the decrease in coordination number of Fe$^{3+}$ cations located at the surface. In addition to the broadening of the peak, a small peak was also observed at higher binding energy near 717 eV which is the satellite peak due to shake up process. The observation of such a satellite peak is common in the high spin Fe$^{3+}$ states and arises due to the shake up process in which during the ejection of the $2p$ shell photoelectrons, small amount of kinetic energy of photoelectrons is lost thereby promoting the movement of the electrons from the $3d$ orbital to the empty $4s$ orbital. In figure 2.5 B, we have shown the high resolution core spectrum for Bi $4f$. The two strongest peaks at 158.0 and 164 eV correspond to Bi $4f_{7/2}$ and Bi $4f_{5/2}$ respectively. The shoulder that appeared at the higher binding energy side corresponds to partially oxidized bismuth ions on the surface. We believed that this is the first detailed x-ray photoelectron spectroscopy study reported so far on the BFO system. This high resolution XPS study rules out any impurity of Fe$^{2+}$ in our samples. Additionally, the ac conductivity values $\sigma_{ac}$ (at 300K) on our BFO samples were almost three orders of magnitude lower ($\sim 10^{-8} \Omega^{-1} \text{cm}^{-1}$) than observed for micron sized polycrystalline samples which is attributed to the very high ionic purity as well as grain effects in our samples as any presence of Fe$^{2+}$ will contribute to larger hopping conduction due electron exchange between Fe$^{2+}$ and Fe$^{3+}$ which is commonly seen in multivalent.

2.4.3 Raman spectroscopy measurements:

Raman spectroscopy is an important tool and has been used by few groups to investigate BFO in single crystals, polycrystalline and thin film forms. The Raman spectra were recorded on a HR 800 Raman spectrophotometer (Jobin Yvon-Horiba, France) using monochromatic radiation emitted by a He-Ne laser (632.8 nm), operating at 20 mW. We observed quite sharp well resolved Raman peaks at 300 K (shown in figure 2.6) with all the 13 Raman modes ($4A_1+9E$) for the rhombohedral R3c structured BiFeO$_3$ nanoparticles. Kothari et al. reported all the 13 Raman modes in polycrystalline BiFeO$_3$ with grain size in microns with three strong $A_1$ peaks at 135, 167,
218 and weak peak at 430 cm\(^{-1}\). \(^{21}\) In our case, we found strong peaks at 139, 169, 425 and a weak peak situated at 216 cm\(^{-1}\). We could observe all the 9 E Raman modes with strongest situated at 72 cm\(^{-1}\). The peak situated at around 139 cm\(^{-1}\) is assigned to the Bi-O vibration modes which is responsible for the coupling between magnetic and electric parameter.\(^{37}\)

**Tables 2.1: Comparison of the Raman mode positions (cm\(^{-1}\)) from our present study on BiFeO\(_3\) nanoparticles (figure 2.6), with reported data on bulk polycrystalline BiFeO\(_3\) by Kothari et al. and data on single crystalline BiFeO\(_3\) by Fukumura et al.**

<table>
<thead>
<tr>
<th>Raman modes</th>
<th>Our study</th>
<th>Kothari et al.(^{21})</th>
<th>Fukumura et al.(^{22})</th>
</tr>
</thead>
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<tr>
<td>A(_1)-1</td>
<td>139</td>
<td>135.15±1.38</td>
<td>147</td>
</tr>
<tr>
<td>A(_1)-2</td>
<td>169</td>
<td>167.08±0.38</td>
<td>176</td>
</tr>
<tr>
<td>A(_1)-3</td>
<td>216</td>
<td>218.11±1.38</td>
<td>227</td>
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<td>A(_1)-4</td>
<td>425</td>
<td>430.95±16.69</td>
<td>490</td>
</tr>
<tr>
<td>E</td>
<td>260</td>
<td>255.38±0</td>
<td>265</td>
</tr>
<tr>
<td>E</td>
<td>276</td>
<td>283.0±0</td>
<td>279</td>
</tr>
<tr>
<td>E</td>
<td>348</td>
<td>351.55±8.66</td>
<td>351</td>
</tr>
<tr>
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<td>321.47±3.76</td>
<td>375</td>
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<tr>
<td>E</td>
<td>467</td>
<td>467.6±2.46</td>
<td>437</td>
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<tr>
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<td>473</td>
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<tr>
<td>E</td>
<td>98</td>
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<td>136</td>
</tr>
</tbody>
</table>
The presence of all 13 modes is also clear from table 2.1 where we have compared the positions of the Raman modes seen by us with the earlier reported data on single crystal and polycrystalline samples. Recently, in a temperature dependent Raman studies on these BFO nanoparticles (80-670 K), we saw the effect of reduced size on Raman spectra of where at low temperature, we observed two sets transitions in the lowest Raman E mode, associated with Bi-O bond motion at temperatures situated in the close proximity to spin reorientation transitions proving a direct indication of coupling between magnons and phonons. These transitions are shifted in temperature in comparison to the bulk single crystals indicating the size effect in BFO. We also observed that there was no change in lowest E mode Raman peak position around bulk Néel temperature, suggesting the absence of antiferromagnetic ordering due to breaking of helical ordering of Fe$^{3+}$.46

2.5 Magnetic properties measurements:

We performed a detailed DC magnetic susceptibility vs. temperature measurements in field cooled (FC) and zero field cooled (ZFC) conditions as well as magnetic field vs. magnetization (M-H) hysteresis measurements on the BFO nanoparticles using a Physical Property Measurement System (PPMS) from Quantum Design Inc. San Diego, USA equipped with a 7 Tesla superconducting magnet. These measurements were done using a vibrating sample magnetometer attachment of PPMS.

Figure 2.6: Room temperature raman spectra of BiFeO$_3$ nanoparticles.
For this purpose, the BFO nanoparticles were packed nicely inside a plastic sample holder which fits into a brass sample holder provide by Quantum Design. The magnetic signal from the sample holder was negligible to affect our data accuracy. We collected M-H loops in a field sweep from -50 k Oe to 50 k Oe at a rate of 25 Oe/sec where data

Figure 2.7: (A, B) M-H loops taken at various temperatures (C,D) zoomed view of A, B respectively (E) variation of coercivity $H_C$ with the measurement temperature (F) temperature dependence of $M_{s(50 \text{ kOe})}$ and $M_r/M_{s(50 \text{ kOe})}$ for BiFeO$_3$ nanoparticles.

For this purpose, the BFO nanoparticles were packed nicely inside a plastic sample holder which fits into a brass sample holder provide by Quantum Design. The magnetic signal from the sample holder was negligible to affect our data accuracy. We collected M-H loops in a field sweep from -50 k Oe to 50 k Oe at a rate of 25 Oe/sec where data
was collected at every second at the vibrating frequency of 40 Hz. To map various transition regions, we collected the M-H loop of as-synthesized BFO nanoparticles at a range of temperatures. In figures 2.7 A & B, we have shown some representative M-H loops at various temperatures. Figures 2.7 C & D show corresponding zoom views to highlight the opening-up of the hysteresis loops. We can see a significant amount of nonlinearity in the M-H curves starting from 390 K which is accompanied with coercivity of 295 Oe. The coercivity value goes down to 225 Oe at 300 K. In contrast to earlier reports on the bulk polycrystalline and single crystal forms of BFO which showed linear M-H loop with absence of coercivity at room temperature, our results here indicated a clear nanosize effect. As we mention earlier that the size of our BFO nanoparticles was less than size of the spiral ordering which would result in the breaking of the spiral ordering inducing a small ferromagnetism in the antiferromagnetic lattice. In figure 2.7 E, we have plotted a curve showing the coercivity values with temperature. It should be noted that the M-H loop mapping in such a way is not reported in literature for BFO nanoparticles and to the best of our knowledge, for the first time, we could detect a signature of the magnetic transition at around 150 K in the coercivity values which might be associated with the frustrated spins created by the breaking of spiral ordering. It is seen that from 350 K to 150 K there is a decrease in the coercivity value followed by a sharp increase below 150 K. At 300 K, the value of magnetization at 50 k Oe was nearly 7.2 emu/g, which corresponds to the particle size of 50-60 nm as per the magnetization vs. particle size data calculated by Park et al. which is in a good agreement with the particle size calculated by us from TEM image. In figure 2.7 F, we have shown the magnetization at 50 k Oe and the Mr/Ms(50 kOe) vs temperature curve. Both the curves shows a series of inflection points indicating various transitions discussed here. To check the change in the magnetic properties for the larger particles, in figure 2.8, we have compared the M-H loops of BFO nanoparticles (~ 55 nm) and the 750°C calcined samples (~ 500 nm). As discussed above, the bulk polycrystalline (average size 500 nm) form of BFO showed linear M-H loop with absence of coercivity at room temperature and down till 10 K. This shows a remarkable change in the magnetic properties of BFO as a function of particle size.
In figure 2.9A, we have shown the DC magnetization vs. temperature curves for 200 Oe, 500 Oe and 1000 Oe external field in zero field cooled (ZFC) and field cooled (FC) modes. For all these measurements, the cooling and heating rate was kept at 1.5 K.

**Figure 2.8:** (A, C, E) Comparison of M-H loops taken at 10, 50 and 300 K respectively for BFO nanoparticles and 750°C calcined sample. (D, E, F) Zoomed view of panels A, C and E respectively.

In figure 2.9A, we have shown the DC magnetization vs. temperature curves for 200 Oe, 500 Oe and 1000 Oe external field in zero field cooled (ZFC) and field cooled (FC) modes (FC). For all these measurements, the cooling and heating rate was kept at 1.5 K.
per minute and the data was collected at every second after averaging over 40 Hz. A large difference between ZFC-FC curves is observed which is due to the spin-glass type behavior previously seen in bulk single crystals of BiFeO₃. However, in contrast to the earlier reports on bulk single crystals, the splitting of these two curves is more pronounced in our nanosized BFO particles and increases at higher field values. Such a deviation is obvious in nanoparticles of BFO because nanosize induces extra strain, coordination distortion and lattice disorder on the surface compared to bulk particles which result in a different frustrated spin structure and high magnitude of magnetic spins - strain interaction.

**Figure 2.9:** (A) Zero field cooled (ZFC) & field cooled (FC) curves at 200 Oe, 500 Oe and 1000 Oe external field values. (B) field dependence of spin glass transition (C) field dependence of spin glass transition shown in ZFC curve (line is shown just to indicate the transition point).
The ZFC curves for all the magnetic field values showed a prominent and broad peak at lower temperatures. The peak temperature decreases with an increase in the applied magnetic field values. Surprisingly, we observed that this behaviour is unique to the nanosize effect of BiFeO₃ and absent in bulk single crystal and polycrystalline samples with much larger grain size. It is shown in Figure 2.10A on 750°C calcined sample that such broad peak (spin reorientation transition) is absent in size greater than the critical spiral ordering (62 nm). The origin of this transition (known as spin reorientation transition) is due to the orientation of Fe⁺³ spins which are generated by the breaking of antiferromagnetic spiral ordering and as the orientation of Fe⁺³ spins

Figure 2.10: (A) Zero field cooled (ZFC) & field cooled (FC) curves at 500 Oe external field values for both BFO nanoparticles and 750°C calcined samples. (B) spin glass transition in FC curve for BFO nanoparticles and absence in 750°C calcined samples (C) spin glass transition shown in ZFC curve for BFO nanoparticles and absence in 750°C calcined samples.
are highly field dependent therefore we saw a field dependence in the peak temperature as the external magnetic field would change the orientation of Fe$^{3+}$ spins towards the field direction. Due to this orientation there was an overall decrease in the magnetic susceptibility with an increase in the field and the transition temperature shifted towards lower temperature from 145 K to 110 K. This transition was also reported by Park et al. for BFO nanoparticles, however, the dependence of this transition on the applied magnetic field was not reported earlier. In figures 2.9 B & C, we have shown the zoom view of the FC and ZFC curves for 200 Oe and 500 Oe field values respectively. Figure 2.9 B shows a broad and smooth hump in the FC curves for our BFO nanoparticles. For bulk BFO single crystals, this transition has been reported at 50 K as a very sharp cusp. The transformation of a sharp cusp in bulk BFO to a broad, smooth hump clearly reflects the nanosize effect which was not observed previously in BFO nanoparticles. In figure 2.10 B, we have compared FC data of BFO nanoparticles and 750°C calcined BFO which shows clearly that no cusp is present around 50 K in 750°C calcined BFO particles. We believe that the Park et al. might have easily missed this transition in their nanosized BFO samples due to the quality of their experimental data where they took the susceptibility measurements at every 10 K temperate steps unlike in our study where the data is collected at every 0.2 K. We also noticed that with the increase in the magnetic field from 200 Oe to 500 Oe, this transition is shifted from $\sim44$ K to $\sim40$ K (figure 2.9 B). We did not observe this transition at 1000 Oe field values which was large enough to smear-out this weak transition of spin-glass nature. Moreover, a significant shift in this transition from 50 K (seen in bulk single crystal) to the range of 40-44 K is due to the reduced size effect. Surprisingly, in bulk polycrystalline BFO, this transition is not reported. The reasons for which are unknown and point of future study. The zero field cooled curves (200 Oe & 500 Oe) showed this transition as change in the inflection point as shown in figure 2.9 C. In figure 2.10, we have compared the ZFC-FC data of 55 nm particles with the 500 nm particles obtained after recalcination at 750°C for 6 h. A closer look at the ZFC and FC behavior shown in figures 10 B & C reveals remarkable changes in the properties of nanosized BFO in comparison to the bulk samples (calcined at 750°C).
2.6 Magnetoelectric coupling probed by Raman spectroscopy:

The Raman spectra were recorded on a HR 800 Raman spectrophotometer (Jobin Yvon- Horiba, France) using monochromatic radiation emitted by a He-Ne laser (632.8 nm), operating at 20 mW. Temperature dependent Raman spectra have been recorded using LINKAM THMS 600 heating/freezing stage connected to a TP 94 temperature programmer in a temperature range from 90 – 700 K. The Raman spectra recorded at 300 K showed quite sharp and well resolved Raman peaks with all 13 Raman modes (4A1+9E) for the rhombohedral \( R3c \) structured BFO nanoparticles in figure 2.6. Kothari et al. reported all the 13 Raman modes in polycrystalline BFO with grain size in several microns with three strong \( A_1 \) peaks at 135±1.38, 167±0.34, 218±0.45 and a weak peak at 430±16.69 cm\(^{-1}\). We could observe all the 9 E Raman modes with strongest peak situated at 74 cm\(^{-1}\) at 300 K which confirms the FE phase in BFO as it is associated with the motion of Bi-O bonds which controls the dielectric constant. The modes at 74, 139, 430 cm\(^{-1}\) can be attributed to E modes and mode 175 cm\(^{-1}\) can be assigned to the \( A_1 \) mode. It is known both theoretically and experimentally that the FE ordering in BFO is governed by stereochemically active \( Bi^{3+} \) ions with \( 6s^2 \) lone pair which take part in relatively lower wavenumber Raman modes in BFO (< 167 cm\(^{-1}\)).

\[ \text{Figure 2.11: Representative temperature dependent Raman spectra of BiFeO}_3\text{ nanoparticles reflecting two sets of spin-glass transitions.} \]
peak position vs temperature curves. In figure 2.12A, the Raman E mode at 74 cm\(^{-1}\) showed sudden dips in the peak shift values at temperatures centered around ~113, 148, 203 and 253 K (within the error of ±5 K) respectively. Among them, the observed transitions at ~148 K and 203 K are in the close proximity to the broad magnetic transition of spin reorientation nature. In panels 2.12 B, C and D, we have also plotted

**Figure 2.12:** The temperature dependent variation in the Raman peaks of three E mode (74, 139, 430 cm\(^{-1}\)) is shown in panels A, B & D and \(A_1\) mode (175 cm\(^{-1}\)) is shown in panel C for BiFeO\(_3\) nanoparticles.

the temperature dependence of Raman peaks of 139, 175, 430 cm\(^{-1}\) where some of these transition which were clearly noticed in figure 2.12 A, are either weak or absent. As we
mentioned earlier that the Raman peak situated at 74 cm\(^{-1}\), is most intense and associated with motion of Bi-O bonds and therefore most sensitive to the magnetic transitions as well transitions of dielectric origin. The presence of these anomalies in the Raman shift for this peak (as well as in the magnetic measurements) indicates the coupling between the FE and the spin excitations associated with the magnetic cycloid at 148 K and 203 K in size \(\sim 55\) nm. A recent temperature dependent Raman study on micron sized polycrystalline BiFeO\(_3\) (grain size \(\sim 65.7\) μm) showed a sudden drop in intensity of A\(_1\) mode (177 cm\(^{-1}\)) at nearly 143 K and sudden increase at 193 K due to an additional magnetic transition representing a spin – reorientation.\(^{23}\) The other two transitions at 113 and 253 K seen in figure 2.12 A could be related to the other set of magnons which were described in incommensurate model of de Sousa.\(^{49}\) These transitions were reported by Scott et al. at 90 and 240 K on the Raman studies on BFO in bulk single crystal form.\(^2\) These transitions were seen in all other E and A\(_1\) modes Raman peaks with little shift in transition position (figure 2.12). We believe that this is the first ever reported indication of existence of the coupling between both the order parameters at nanosize by the coupling between the electric and spin reorientation transitions in nanosized BFO. The significant shift in the transition temperature from 90 K (single crystal) to 113 K (present data) can be attributed to the size dependent effect of BFO. However, till date, there is a lack of clear understanding in literature to explain the origin of these coupling even in the bulk phase. In figure 2.11, we have shown the representative complete Raman spectra in the range of spin reorientation transitions. It has been noted that there is a shift in the all four Raman modes around the spin reorientation temperature.

Next, we did temperature dependent Raman study on the same sample above room temperature (till \(\sim 670\) K). From figure 2.13A, it is clear that the 74 cm\(^{-1}\) peak (lowest E mode) show remarkable shift in its position in the vicinity of reported Néel temperature \(\sim 643\) K identified with the step like anomaly. This marked anomaly was observed by us in other Raman bands too (figure 2.13B, C & D) though weaker in nature in comparison to 74 cm\(^{-1}\) mode. It is known that this magnetic transition in bulk BFO is not accompanied by the structural transition.\(^{50}\) Earlier Raman studies on bulk BFO single crystals are also consistent with our observation on nanosized BFO where an strong phonon anomaly was observed for the first time around Néel temperature in form of...
similar step like feature.\textsuperscript{50} Haumont et al suggested that multiferroicity of BFO may be the reason for the observation of this strong phononic anomaly.\textsuperscript{50} High temperature dielectric studies on bulk polycrystalline BFO samples also report very weak anomaly near Néel transition.\textsuperscript{51} Our observation clearly shows the presence of AFM ordering transition in our BFO with grain size less than the critical size of 62 nm.

![Graph](image.png)

**Figure 2.13:** Step like anomalies around magnetic Néel transition is shown as the wavenumber variation for E modes (74, 139, 430 cm\(^{-1}\)) in panels A, C & D and for A mode (175 cm\(^{-1}\)) in panel C as a function of temperature for BiFeO\(_3\) nanoparticles.

### 2.7 Thermal measurements:

To study the existence of FE transition in our BFO nanoparticles, in figure 2.14, we have shown the differential thermal analysis (DTA) results exhibiting the heat flow data in a broad temperature range obtained using SDT model Q600 from TA Instruments,
USA. The data was taken at a heating rate of 10°C/m under a nitrogen flow at 100ml/m. The heat-flow curve on our 55 nm BFO, shows no signature of anomaly in the vicinity of the reported Néel temperature. However, we found two very sharp well defined peaks situated at 1094 and 1223 K respectively. It is reported that at 1100 K, BFO undergoes a structural transition from rhombohedral to orthorhombic or monoclinic phase and at around 1200 K; it transforms into the cubic phase. As we indicated earlier, it is not clear till date, out of these two transitions, which one is the ferroelectric-paraelectric transition. Heating beyond this temperature range leads to the decomposition of BFO. Unfortunately, we could not extend our Raman measurements on BFO nanoparticles around the FE Curie transition due to experimental limitation of our instrument where BFO is supposed to show a complete loss of Raman spectrum above Curie temperature.

2.8 Magnetoelectric coupling probed by dielectric spectroscopy:

To probe the dielectric response in the proximity of the magnetic transitions in BFO at low temperatures, we used a Novocontrol Beta NB Impedance Analyzer with a home-built sample holder to couple with a Janis Inc. helium closed cycle refrigerator. The dielectric response was mapped in a frequency range from 1 to $1 \times 10^6$ Hz at 1 volt (rms) and in a temperature range from 20-325 K at a close interval of 1 K ($\pm 0.2$ K). A compressed circular pellet, with 13 mm diameter, pelletized by applying 5-6 ton pressure was kept in the customized sample holder to form circular parallel plate capacitor.
geometry. In the figure 2.15, the frequency dependent $\varepsilon'$ and $\tan \delta$ are plotted at two different representative temperature values.

Overall, the values of $\varepsilon'$ at room temperature (~28) are not very much different from reported for ceramic samples with crystallite size in microns$^{13,29}$ but smaller compared to the reported values on bulk single crystals$^{13}$ and much smaller in comparison to the typical perovskite ferroelectrics such as BaTiO$_3$, and PZT etc.$^1$ Catalan et al argued that smaller values of dielectric constant in BFO in comparison to the conventional perovskite FE materials might be due to the fact that in BFO the polarization comes from the A site (Bi atoms). On the other hand, in BaTiO$_3$, the polarization is attributed to the B sites (Ti atoms).$^1$ For most FEs, the domain size varies following the relation: Domain Size $\propto$ (Particle size)$^m$. $^{52}$ It is considered that the decrease in polarization (or dielectric constant) with decreasing particle size is not an intrinsic size effect due to depolarization fields. This decrease might be due to surface effects such as surface tension, strain and increase in porosity. Intrinsic size effects occur below ~15 nm which is material specific and nothing to do with depolarizing field.$^{53}$ Recently, we reported a significant decrease in the dielectric constant of 6-8 nm tetragonal phase of BaTiO$_3$ and showed that FE phase does exist in this size range even though the dielectric constant values are quite low in comparison to bulk values.$^{36}$ The dielectric constant of nanosized materials might also be slightly underestimated in our studies due to experimental problems such compaction not

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Figure 2.15: Frequency dependence of real part of permittivity value ($\varepsilon'$) and loss tangent ($\tan \delta$) for BiFeO$_3$ nanoparticles for two representative temperature values.
being closed to 100% of theoretical density and the contact issues. It should be noted here that several studies on bulk polycrystalline BFO have reported unreasonably high $\varepsilon'$ values (as high as $10^4$ for 100 Hz and 300 K).\textsuperscript{25, 51} Clearly, these values are not intrinsic and probably the effect of presence of oxygen deficiency and Fe$^{2+}$ etc which is a common problem and can be easily noticed from unusually large loss tangent values (sometimes close to 1) due to ionic impurities.\textsuperscript{54} These samples with unusually high dielectric constant might also show high degree of polarizability but as a word of caution- high polarization does not always indicate high ferroelectricity or multiferroicity.\textsuperscript{55} Similarly, giant dielectric constant values were reported in CuO which might also have originated from the presence of high level of Cu$^{3+}$ impurities.\textsuperscript{56} The high level of ionic purity is reflected in the tan $\delta$ (between $0.5 \times 10^{-3}$ to $2 \times 10^{-3}$) values of our samples which are almost 3 orders of magnitude smaller than that for bulk BFO. Due to higher sensitivity of our instrument (tan $\delta < 10^{-4}$) coupled with unique design of our in-house developed sample holder for low temperature measurements, it was possible for us to measure these values accurately. Generally, BFO prepared by solid solution or ceramic methods show much higher dielectric loss due to higher conductivity which causes leakage current. As we discussed earlier, the higher dielectric loss is inherently due to ionic impurities (Fe$^{2+}$), oxygen nonstoichiometry and lattice defects which is unavoidable in bulk ceramic synthesis. Higher dielectric loss leads to lower ferroelectric polarization in pure material such as spontaneous polarization, remnant polarization and coercive field. Therefore, even though dielectric constant values of our nanocrystalline BFO are in the same range as that of bulk ceramic samples (as discussed earlier) but the surprisingly observation of nearly $10^{-2}$ to $10^{-3}$ times lower loss tangent values in our samples are remarkable improvement and shows much lower level of ionic impurity.\textsuperscript{13, 27, 29}

In figure 2.15, the $\varepsilon'$ value increases slightly as the frequency decreases. We observed that frequency dependence of $\varepsilon'$ and tan $\delta$ for our samples is quite weak without any resonance peak in the scanned frequency range. The slight increase in the value of $\varepsilon'$ at lower frequency is due to the presence of different type of polarization factors such as interfacial, dipolar, ionic, atomic and electronic which becomes significant at low frequencies.\textsuperscript{57} Here, the response of grains and their boundaries (interface) at different frequencies plays a crucial role where the contribution from core of nanoparticles will be.
significant at higher frequencies and the surface of the particles and their connectivity with neighboring particles will contribute at relatively lower frequency regions. However, in figure 2.15, the fact that the frequency response of $\varepsilon'$ and $\tan \delta$ at different temperature doesn’t show any sudden peak or any other feature (often seen in bulk relaxor FE samples) till 1 MHz makes the contributions of particle and its boundary indistinguishable in this range. Higher than 1 MHz dielectric spectroscopy results might show some resonance peaks which is beyond the limit of our instrument at present. It should be noted that several of the earlier dielectric studies done on ceramic samples or thin films showed a strong unusual frequency dependence and Maxwell-Wagner (MW) type of contributions to the dielectric constants due to reasonably high conductivities. In contrast, our results do not show any strong frequency dependence in dielectric constant and loss tangent. In the bulk BFO, the dispersion of dielectric constant and loss tangent with frequency is reported to be high because at lower frequency in the bulk ceramics, oxygen and bismuth vacancy in the lattice mainly contributes in the dielectric constant and loss tangent value. But as we pointed out earlier our wet chemically synthesized nanocrystalline BFO is likely to have quite less lattice impurities and dislocations, so such high dispersion were not observed in the dielectric constant and loss tangent with frequency.

In the figure 2.16 A, we have shown the variation of $\varepsilon'$ and $\tan \delta$ with temperature for few representative frequency values here we observed that at high temperatures (> 250 K) there is a significant increase in $\varepsilon'$ values. At higher temperatures, the charge carriers are free to move through the lattice causing enhanced polarization which results in high dielectric value. Similar to the anomalies seen in the Raman spectra discussed above, the zoom view of $\varepsilon'$-T curve (figure 2.16 B) shows four weak anomalies situated at around 85, 168, 205 and 230 K. In bulk single crystals and ceramic BFO, these anomalies were reported which were extremely weak in nature. Redfern et al argued that in BFO since these anomalies are far weaker than those associated with any FE transitions, therefore, they might arise due to the weak coupling with magnetic order parameter. In figure 2.16B, among the four transitions, the observed transitions at ~168 K and 205 K are in close proximity to the broad magnetic transition of spin reorientation nature reported by us on the same material. The observation of transitions shows that
the coupling between FE and cycloid spins exists for particles around 55 nm in size. The other two transitions observed by us (figure 2.16 B) at ~ 85 and 230 K could be related to the other set of spin reorientation transition which was reported by Scott et al. at 90 and 240 K using the Raman studies on bulk single crystal BFO. We believe that this is the first ever reported indication of existence of the coupling between both the order parameters at nano size by the coupling between the electric and spin reorientation.

Figure 2.16: (A & B) Temperature dependent variation of real part of permittivity ($\varepsilon'$) and (C&D) loss factor ($\tan \delta$) of BiFeO$_3$ nanoparticles.

transition in nanosize BFO. It is important to note that out of these four anomalies, two anomalies (90 K and 230 K) were also noticed by us in the $\tan \delta$ - T curves (figure 2.16C). Surprisingly, earlier studies on BFO ceramics failed to see any signature of these spin reorientation anomalies in dielectric loss tangent curves. We believe earlier studies
might have easily missed these transitions due to their subtleness. However, it is worth pointing out that in our dielectric measurements did not show anomaly associated with spin-glass transition in the range 40-45 K seen by us in magnetic measurements on 55 nm particles. This transition was reported by Scott’s group in ε-T measurements on single crystal (55 K) and in ceramic samples (50K).13 However, the observation of spin glass transition in BFO is full of mysteries and still not resolved as one recent dielectric measurements as well as ac and dc magnetization study done on BFO single crystal did not find anomaly from 2-120 K.58

2.9 Electrical conductivity measurements:

Ionic impurity of mixed valent nature leads to higher dielectric constant (sometime colossal in nature) which may not be always related to the desired ferroelectric polarization.55 Dielectric and polarization probing may be misleading when ac conductivity and polarizability do coexist in the same material.55 So it is always important to always check the conductivity values carefully before reaching to any conclusion about the ferroelectric polarization. The ac conductivity $\sigma_{\text{ac}}$ was calculated by the following relation: $\sigma_{\text{ac}} = 2\pi f_0|\varepsilon|\tan \delta$. The variation of $\sigma_{\text{ac}}$ with temperature is shown in the figure 2.17 for 948 kHz frequency. For all the frequency values, the $\sigma$ increases

![Figure 2.17: (A)Temperature dependent variation of real part of conductivity ($\sigma'$) of BiFeO$_3$ nanoparticles at frequency 370, 592, 948 kHz. The inset shows the zoom view of the $\sigma'$–T curve at 948 kHz frequency. (B) log $\sigma'$ vs. 1000/T plot at frequency 370, 592, 948 kHz.](image)
with temperature. The $\sigma$ (300K) for our BFO samples was almost three orders of magnitude lower ($3 - 6 \times 10^{-8} \ \Omega^{-1} \ \text{cm}^{-1}$) than observed for micron sized polycrystalline samples which is attributed to the very high ionic purity as well as grain effects in our samples.\textsuperscript{26} A slight non-stoichiometric composition of oxygen in BFO creates $\text{Fe}^{+2}$ within the iron sublattice. The coexistence of $\text{Fe}^{+2}$ and $\text{Fe}^{+3}$ in the octahedral sites in the BFO lattice favors the electron hopping conduction from $\text{Fe}^{+2}$ to $\text{Fe}^{+3}$ via oxygen ions.\textsuperscript{25} Much smaller ac conductivity is quite desirable in BFO and its presence in our samples indicates less probability of hopping conduction between $\text{Fe}^{2+}$ and $\text{Fe}^{3+}$. The concentration of $\text{Fe}^{+2}$ in the lattice is very sensitive to calcinations temperature and it increases with temperature due to increased loss of oxygen. But in our case, we could rule out this possibility due to relatively low annealing temperature. Our high resolution x-ray photoelectron spectroscopy study also did not show any traces of $\text{Fe}^{+2}$ impurities.\textsuperscript{47} We believe that in BFO nanoparticles, it may the breaking of the spiral ordering which results high value of conductivity for given frequency. When the crystal becomes smaller, the rapid increase of domain wall energy makes the domain configuration unfavorable, thereby promoting single-domain structure in smaller crystals which results more domains and also more domain walls, per unit volume than the bulk. These domain walls will become more technologically important as the particle goes to nanoscale. J. Seidel et al have proved that enhanced conductivity in BFO nanomaterials correlates with structurally driven change in electrostatic potential and local electronic structure which results in the decrease in the band gap at the domain wall.\textsuperscript{60} As the frequency increases conductivity value increases for a given temperature (not shown here). In the top panel of figure 2.17 we have observed two peaks around 90 and 230 K which correspond to the reorientation transition in BiFeO$_3$ nano materials. During the reorientation transition, iron spins moves from one crystallographic axis to another which is magnetic origin but again favor the electron-hopping conduction mechanism.

In the lower panel of figure 2.17, we have shown log $\sigma$ vs. 1000/T for various frequencies. The activation energy $E_a$ varies by orders of magnitude in different temperature regions. At room temperature $E_a$ is around $\sim .03$ eV. For micron sized BFO particles, the $E_a$ was found to be 0.126 eV at around 290$^\circ$C and increases 10 times to 1.26 eV as temperature goes high.\textsuperscript{24} There are no reports of $\sigma_{ac}$ below room temperature for
BFO in any form. In our case, the lower values of activation energy and its strong temperature dependence seems to be due to the reduced particle size. The grain boundary does not contribute towards the temperature dependence of activation energy and it is purely due to the conduction mechanism inside the particle.

2.10 Conclusion:

BiFeO₃ nanoparticles with average size 50-60 nm were synthesized using modified hydrothermal method. The phase was confirmed using x-ray diffraction study. Pawley refined lattice parameters were $a = 5.574\pm0.001$, $b=5.574\pm0.001$, $c=13.850\pm0.002\text{Å}$ with excellent $R_{wp}$ value of 4.94%. High resolution TEM showed that the particles were of excellent crystallinity. Collectively, our studies on the magnetization measurements indicated new information on this material in form of presence of spin glass transition at lower temperatures and its deviation from the bulk transition temperature. Strong bifurcation in the field cooled and zero field cooled curves was quite similar to bulk single crystals but different then micron sized polycrystalline materials. The origin of these transitions (both in bulk and nanophase) needs to be further studies especially the origin of transition situated between 40-50 K. Temperature dependent Raman study show the existence of two pairs of transitions as dips in the Raman shift vs temperature at three E mode (74, 139, 430 cm⁻¹) and one $A_1$ modes (175 cm⁻¹) in the close proximity of the spin reorientation transition. These transitions are more pronounced in the lowest E mode (74 cm⁻¹) which has a polar character and controls the dielectric constant. This indicates the coupling between the ferroelectric and spin excitations associated with the magnetic cycloid. These two sets of anomalies were also observed in $\varepsilon'$ -T curve with slight shifting in temperature. Out of these four anomalies two anomalies at 90 and 230 K were also observed in our loss tangent and real part of conductivity data. High temperature Raman spectra show remarkable shift in Raman mode for three E modes and $A_1$ mode around Néel temperature. Thermal studies did not show any endo/exothermic peak around Néel transition but showed both the ferroelectric-paraelectric transitions. The conductivity of BFO samples at 300K was almost three orders of magnitude lower ($3 - 6 \times 10^{-8} \ \Omega^{-1} \ \text{cm}^{-1}$) than observed for micron sized polycrystalline samples which is attributed to the very high ionic purity as well as grain
effects in our samples. It was further confirmed by the \( \tan \delta \) value which is \( 10^{-2} \) to \( 10^{-3} \) times lower than the polycrystalline samples. In contrast to bulk BFO which shows strong frequency dependence in \( \varepsilon' \) and \( \tan \delta \) value, nanocrystalline BFO don’t show the relaxation behavior in the frequency range (1-\( 10^6 \) Hz).
2.11 References:


