Chapter 3
Surface Effects on Morin Transition, Exchange Bias Enhanced Spin Reorientation and Dielectric Spectroscopy in Chemically Synthesized DyFeO₃ Nanoparticles

Outline

Giant linear magnetoelectric effect was observed by Y. Tokura’s group recently in multiferroic DyFeO₃ which demands a detailed investigation of its magnetic properties. Here, we report the synthesis of DyFeO₃ nanoparticles using a surfactant-less hydrothermal method with a detailed magnetic property measurement and temperature and frequency dependent dielectric spectroscopy and ac magnetic susceptibility. The as-synthesized DyFeO₃ nanoparticles showed excellent crystallinity with average particle size in the range 50-60 nm. Detailed DC magnetization measurements in the temperature range of 3- 350 K could isolate the presence of Dy⁺³-Fe⁺³ and Dy⁺³- Dy⁺³ superexchange interactions which showed-up as spin reorientation transitions in various temperature regions due to differing magnitude of their interactions resulting into continuous rotation of antiferromagnetic component of Fe⁺³ spins with cooling of sample. Nanosized DyFeO₃ showed spin-reorientation transitions near 315 and 70 K due to the Dy⁺³-Fe⁺³
interaction accompanied with an opening up of the hysteresis loop followed by antiferromagnetic ordering around 4 K due to a possible Dy$^{3+}$-Dy$^{3+}$ interaction. We also observed significant effect of the particle size reduction on the magnetic properties. The main effects seen by us were in terms of (1) pronounced spontaneous spin reorientation transitions (2) the absence of Morin transition and (3) presence of temperature dependent exchange bias in the DyFeO$_3$ nanoparticles. We present a detailed mechanism to explain these features based on the interplay of Dy$^{3+}$ and Fe$^{3+}$ spins as well surface disorder, anisotropy, canting etc. The measurement of the dielectric properties was carried out in a broad temperature (20-325 K) and frequency (1–10$^6$ Hz) range. The dipolar relaxation phenomenon of non-Debye type was observed in the DyFeO$_3$ (DFO) nanoparticles, as confirmed by the Cole–Cole plots. The higher values of $\varepsilon'$ at the lower frequencies are explained on the basis of the Maxwell–Wagner model. Cole–Cole analysis enabled us to separate the contribution of relaxation times, resistance and capacitance in grain and grain boundaries in DyFeO$_3$ nanocrystals. We found that with increasing temperature, the contribution of grain boundary resistance increases in comparison to the grain resistance. We also performed spin relaxation studies in broad temperature and frequency range. Both the in-phase or real ($\chi'$) and out-of-phase or imaginary ($\chi''$) components of the ac magnetic susceptibilities of the DyFeO$_3$ shows clear evidence at spin reorientation transition around 70 K and $T_N$ (Dy) around 4K as reported by us in ourlier study using the dc magnetic behaviour.

The work in this chapter is published as-

- **Surface Effects on Morin Transition, Exchange Bias and Enhanced Spin Reorientation in Chemically Synthesized DyFeO$_3$ nanoparticles.**  

- **Dielectric and spin relaxation behaviour in DyFeO$_3$ nanocrystals.**  
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3.1 Introduction:

The recent surge in the interest in the rare earth orthoferrites emanates from the possible spin-orbital coupling between adjacent antiferromagnetic ions. Among them, the DyFeO$_3$ has been recently reported to show giant linear magnetoelectric (ME) coupling. The orthoferrites with a chemical formula $Ln$FeO$_3$ ($Ln$ = Lanthanide) generally crystallizes in the orthorhombic perovskite structure in which the FeO$_6$ octahedra get distorted to the extent decided by the size of rare earth ions. An interesting aspect of these rare earth perovskites is that by varying the size of the rare earth ions we might expect not only the variations in A-O and B-O interactions (which results into some distortion of the oxygen polyhedral and finally affects the ferroelectric behaviour) but also the electrical conductivity which decreases with increase in atomic number has been observed.

For another well studied perovskite ferrite- BiFeO$_3$, it is the particular orientation of 6s lone pairs of Bi ions or dangling bonds which creates local electrical dipoles due to which Bi ions will move away from the center of symmetry of oxygen environment, resulting into the lowering of crystal symmetry and inducing ferroelectricity in BiFeO$_3$. If the smaller Dy$^{3+}$ ions replace the larger Bi$^{3+}$ ions in BiFeO$_3$, then to form the close pack structure, the oxygen ions get displaced from their original positions and this displacement deforms the lattice and causes the rotation of the FeO$_6$ octahedra and results the perovskite structure in DyFeO$_3$ (DFO) to deform. It is well known that the electrical and the magnetic properties of these rare earth ferrites are governed by the Fe$^{3+}$–Fe$^{3+}$ interaction (spin coupling of the 3d electrons). By introducing rare earth ions (Dy$^{3+}$) into the lattice, the Dy$^{3+}$–Fe$^{3+}$ interactions appear (3d–4f coupling), leading to changes in both the electrical and magnetic behavior of the ferrites.

Some of these rare earth orthoferrites, chromites and manganites show quite intriguing magnetic properties evidenced by a series of order-disorder transitions due to the competing magnetic interactions between various cations presenting a complicated picture as the interaction between dissimilar ions is highly dependent upon the size of these cations, temperature and the strength and direction of applied magnetic field. This reflects into a significant decrease in the Néel transition temperature from 740 K for...
LaFeO$_3$ to 623 K in LuFeO$_3$ as well as change in the temperatures at which various spin reorientation (SR) transitions are observed in these compounds. Similar features are also observed in chromites where the Néel transition temperature decreasing from 289 K in LaCrO$_3$ to 143 K in YCrO$_3$. This decrease is associated with decrease in the change in the enthalpy and entropy at magnetic transition. Even for the rare earth manganites, a gradual decrease in the antiferromagnetic (AFM) transition is associated with the increase in the size of rare earth ion (from 150 K for LaMnO$_3$ to $\sim$40 K for EuMnO$_3$). These changes in the magnetic transitions perhaps originate from the increased lattice distortion and decreased interionic distances with an increase in the ionic radii of rare earth ions.

Among these compounds, DFO is the only rare earth orthoferrites which shows Morin transition at 35 K followed by three anomalous transitions at temperatures 77, 130, 270 K originating probably due to the field induced spin reorientation (SR) effect originating from competing magnetic interaction between Dy$^{3+}$ and Fe$^{3+}$ ions. The transition observed at very low temperature $\sim$ 4.2 K was explained by the Dy$^{3+}$- Dy$^{3+}$ antiferromagnetic ordering, similar to the transition at 7 K in GdCrO$_3$ due to Gd$^{3+}$-Gd$^{3+}$ interaction reported by us and other groups. In DFO, the location of Fe$^{3+}$ ion in a particular plane decide the magnetic interaction with another ion. Despite of showing interesting properties such as giant magnetoelectric effect, DFO is not probed much so far for its magnetic properties (such as magnetic hysteresis loop vs. temperature) even in the bulk phase. The only available magnetic studies were focused on the Mossbauer spectrometry to probe field induced SR transitions in DFO.

The ME effect in these compounds is dictated by the ordering of spins and electrical dipoles where the length scales of these order parameters become important. There are very few materials reported in the literature which exhibit large ferroelectric polarisation and magnetoelectric (ME) coupling. To achieve large ME effect, it is essential that the origin of the ferroelectric polarisation should be magnetic. Recently, Tokura et al. reported that single crystal of DyFeO$_3$ (DFO) had gigantic magnetoelectric (ME) phenomena and spontaneous polarisation below $\sim$3.8 K. The origin of the ferroelectric polarization in the multiferroic DyFeO$_3$ phase is supposed to be the exchange striction working between adjacent Fe$^{3+}$ and Dy$^{3+}$ layers with the respective

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layered antiferromagnetic components. So the anomalous behaviour of ferroelectric polarisation suggests that in this system, ferroelectric polarisation depends not only on the magnetic structure of Dy$^{3+}$ but also on that of Fe$^{3+}$. The value of spontaneous polarisation is quite large as for the spin-driven ferroelectrics and also comparable to orthomanganites.

Due to the importance of the length scale, it was realized recently that it was important to understand the change in the physical properties of these materials as a function of particle size to have a tunability over the ferroelectric and magnetic properties in these ME materials for their potential use in nanoscale devices. Recently, we reported size dependent magnetic properties of BiFeO$_3$, where we found that below 100 K, BiFeO$_3$ exhibits sizable hysteresis and finite coercivity. The effect of reduced size on temperature-dependent Raman and dielectric spectroscopy of chemically synthesized BiFeO$_3$ nanoparticles (average size $\sim$50-60 nm) was further studied and observed that the loss tangent, ac conductivity and real part of permittivity values are lower than the reported values for BiFeO$_3$ ceramics, indicating high levels of ionic purity in BiFeO$_3$ nanoparticles. The dielectric and spin relaxation studies of DFO can further provide valuable information about conduction phenomena, frequency dependence of dielectric loss, phase transitions and domain dynamics in nanostructured multiferroic materials. No report, to our knowledge, has so far been made to study the dielectric and ac magnetic susceptibility measurement on nanocrystalline DFO. Keeping in view the importance of DFO as giant magnetoelectric material, in this report, we have investigated DFO nanoparticles using ac impedance spectroscopy and ac magnetic susceptibility techniques. As the electrical properties of such materials largely depend on the grain and grain boundaries so in order to understand them, all electrical parameters such as real and imaginary permittivity, relaxation dynamics, activation energy, its spreading factor and their individual contributions must be separately investigated.

However, the rare earth ferrites, manganites and chromites have not been explored for their size dependent properties as the synthesis of these rare earth complex oxides with a control over particle morphology while maintaining crystallinity is nontrivial. The conventional chemical techniques such as coprecipitation, reverse-
micelle, hot injection etc. are unable to produce the desired phase. Due to this reason, the physical properties of most of these materials are reported mostly in the bulk phases (such as single crystals and polycrystalline form).

### 3.2 Hydrothermal synthesis of DyFeO$_3$ nanoparticles:

Here, we have successfully developed a modified hydrothermal route$^{10}$ to synthesize the DFO nanoparticles based on complexing the metal ions with the citric acid followed by the hydrothermal process. The hydrothermal synthesis process is known to have an edge over other synthesis routes because of its simplicity, low-cost and better yield. Above all, the hydrothermal process is known to produce particles with very good crystallinity and has potential for scaling-up. The rationale behind using this technique in the DFO synthesis is that the high pressure in the reaction vessel helps in stabilizing the crystalline phase which is not possible at ambient pressure. This method was employed by us earlier to synthesize LuMnO$_3$, GdCrO$_3$ and BiFeO$_3$ nanoparticles—three difficult materials in the multiferroic family of compounds to crystallize in nanosize with a proper control over crystallinity.$^{10, 18, 20}$ In the present case, the stoichiometric amounts of iron nitrate (Fe(NO$_3$)$_3$, 9H$_2$O, Merck, 98%), dysprosium nitrate hydrate (Dy(NO$_3$)$_3$, H$_2$O, Aldrich, 99.9%), 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, so that the metal ions can be completely complexed to 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 the 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. Then the dried powder was calcined at 400 $^\circ$C for 6 h.
3.3 Characterisations:

3.3.1 X-ray diffraction measurements:

In figure 3.1, we have shown the powder x-ray diffraction pattern (XRD) of the as-synthesized DFO nanocrystals. The data is compared with the JCPDF data file #470069, which shows the formation of highly crystalline pure phase except one small peak around 29° which could be due to Dy$_2$O$_3$. We think that the imbalance of Fe$^{3+}$ ions due to unreacted Fe$^{3+}$ ions could have washed away in the washing process after the synthesis of material. Which is also consistent with the fact that we do not see the peaks for Fe$_2$O$_3$ phase.

The average crystallite size as calculated using Debye-Scherer formula was found to be around ~40 nm.

![Figure 3.1: A comparison between powder X-ray diffraction pattern of DyFeO$_3$ nanocrystals with the data from JCPDS Card No. 470069.](image)

3.3.2 Determination of shape and size of the nanoparticles:

To further investigate microstructure and topography, we used HRTEM measurements on as-synthesized DFO nanoparticles. In figure 3.2 (A) and 3.2 (B), we have shown two sets of representative TEM images taken on same sample from various part of the grid. In the inset of figure 3.2(B) we have shown the particle size distribution in our sample. Here, we clearly observe the formation of partly faceted, plate-like, with size ranging from 50-60 nm. The average size as seen in TEM image is slightly larger.
than the crystallite size obtained by the Scherrer equation. We also observe that the particles on the TEM grids overlap at few places (or try to stack-up sometime) after drying out of solvent which is due to the use of surfactant-less synthesis technique as well as the plate like morphology of the particles. In figure 3.2 (C), we have shown the high resolution image where we can notice well pronounced lattice fringes indicating very good level of crystallinity. The selected area electron diffraction pattern (SAED) in figure 3.2 (D) shows a nice dot pattern that clearly exhibit highly crystalline nature of

Figure 3.2: (A), (B) Transmission electron microscopy images of as-synthesized DyFeO$_3$ nanoparticles. The inset shows particle size distribution graph of DyFeO$_3$ nano particles. (C) High resolution TEM image showing the lattice fringes (D) Selected area electron diffraction pattern of DyFeO$_3$ nanoparticles.
DyFeO$_3$ nanocrystals. It is interesting to note the origin of plate like morphologies in as-synthesized particles in DFO. Even, in our previous studies on the synthesis of GdCrO$_3$ and BiFeO$_3$ nanoparticles, we had reported the formation of similar plate like morphologies. We believe that in the formation of plate like nanoparticles in the synthesis adopted by us, the role of nitrate and citrate ions is extremely important and requires a careful investigation which is the subject of our future study. It is known that apart from other factors such as twinning, stacking faults etc., the shape control in the wet-chemical synthesis can also be driven by the preferential binding of ionic ligands, surfactants to the particular lattice facets due to their variable degree of affinity from one facet to another which allows the growth of particular facets while restricting the growth of others. In the case of our hydrothermal synthesis, the strong affinity of both nitrate and citrate ions with metal ions at particular crystalline facets might have promoted the formation of negatively charged anisotropic structures much similar to the role of halide ions in the formation of anisotropic gold nanoparticles. However, experimentally, it is quite challenging to prove the role of preferential binding of ionic ligands on the overall morphologies. Careful surface studies using x-ray photoelectron and Raman spectroscopies might provide a clear understanding.

3.4 X-ray photoelectron spectroscopy measurements:

In figures 3.3 (A) & (B), we have shown the room temperature x-ray photoelectron spectroscopy (XPS) data to confirm the oxidation state of the Fe and Dy to validate the purity of the phase formation. Figure 3.3 (A) shows the XPS spectra of Fe$^{3+}$. There are two most intense peaks at ~711 and ~724 eV which were assigned to the Fe$^{3+}$ 2$p_{3/2}$ and 2$p_{1/2}$ states. In addition to the broadening of the peak, a small peak has also been observed at higher binding energy near 717 eV which is the satellite peak due to shake up process. In figure 3.3 (B), we have shown the high resolution core spectrum for Dy 3d$_{5/2}$ core level. The peak at 1296 eV corresponds to Dy 3d$_{5/2}$ states. This is the first detailed XPS study reported so far on the DFO.
3.5 Magnetic properties measurement:

As we mentioned earlier, even for the bulk DFO phase, the detailed magnetization studies such as behavior of coercivity, susceptibility as a function of temperature were never reported in literature. Therefore, we performed a detailed DC magnetization vs. temperature measurements as well as magnetic field vs. magnetization hysteresis measurements on the DFO nanoparticles. In figure 3.4 (A), we have shown some representative M-H loops at selected temperature values showing dramatic variation in the shape of the curves with temperature. In the figure 3.4 (B), we have shown the zoom view of the M-H loops at 3, 70, and 370 K. In the figure 3.4 (C) and 3.4 (D), we have plotted the temperature dependence of coercivity ($H_c$), magnetization at 50 k Oe ($M_s$) and ratio of remanent magnetization ($M_r$) and $M_s$. Our DFO nanoparticles show sizable coercivity of $\sim$ 240 Oe even at 370 K. The coercivity value increases sharply with decreasing temperature\textsuperscript{20} and reaches its maximum at 70 K ($\sim$ 580 Oe). Further, below 70 K, it shows a decreasing trend and hits minimum at around 4 K ($\sim$ 150 Oe). The coercivity again shoots-up below 4 K as shown in figure 3.4 (C). We will discuss the origin of these features in coming sections. In figure 3.4 (D), there is almost an exponential drop in the $M_s$ value with the increase in temperature. Similar feature around 4K has been

\textit{Figure 3.3:} (A) & (B) core level XPS spectra for Fe (2p) & Dy (3d) respectively taken on DyFeO$_3$ nanoparticles (scatter curves). The lines represent the deconvoluted peaks.
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Figure 3.4: (A) M-H loops taken at various temperatures (B) zoom view of the M-H loops at 3, 70, 370 K (C) variation of coercivity $H_C$ with the temperature. The error in the field measurement was less than $\pm 25$ Oe and the error in temperature measurement was $\pm 0.1$ K. (D) temperature dependence of $M_S(50 \text{ kOe})$ and $M_r/M_S(50 \text{ kOe})$ for DyFeO$_3$ nanoparticles. The $M$. Std. Err. for moment is in the range of $10^{-6}$ emu.

observed in the temperature dependent $M_r/M_S$ behavior. Further, above 4K, $M_r/M_S$ value follows an increasing trend and reaches maximum around 300K. In M-H hysteresis curves, we observed that the M-H hysteresis loops were shifted considerably towards the negative side of the field i.e. the samples showed exchange bias type of signatures. In figure 3.5 (a), we have shown the zoom view of M-H loops at 300 and 100 K where the curve at 300 K showed much larger shift in comparison to the curve at 100 K. In figure
Figure 3.5: (A) Exchange bias at room temperature (B) variation of exchange field $H_{ex}$ with the temperature for DyFeO$_3$.

3.5 (B), we have shown a temperature dependent exchange field which is larger at higher temperature values but goes down sharply at lower temperature.$^{27}$ In figure 3.6 (A), we have shown a representative set of FC & ZFC curves taken at 50, 200, 400 and 5000 Oe respectively. Various regions of interest are highlighted in figures 3.6 (B), (C) and (D). Following important features could be summarized: (1) a small hump near 315 K in FC curve which is a first reorientation transition coming out of Dy$^{+3}$ and Fe$^{+3}$ interaction (2) a second reorientation transition near 70 K because of a weak AFM coupling between Dy$^{+3}$ and Fe$^{+3}$ moment (3) a strong AFM coupling between Dy$^{+3}$ and Dy$^{+3}$ moment near 4 K. Most of these features were never seen directly by the DC magnetization measurements by previous researchers. Another important observation by us in the ZFC-FC curves was the absence of Morin transition in our samples which was earlier reported in single crystalline DFO sample by Holmes et al.$^{28}$

Now, let us discuss in detail the possible physical origin of these intriguing features as seen in the M-H and M-T data sets. It is reported that the bulk DFO undergoes an antiferromagnetic transition below its Néel temperature of 645 K.$^{3}$ On the basis of their magnetic properties, the rare earth orthoferrites can be divided into two categories.
In the first category falls those orthoferrites which have diamagnetic rare earth ions (like Y$^{+3}$) and the magnetic interaction is strongly dependent upon the Fe$^{+3}$-Fe$^{+3}$ SE(supper exchange) interaction and the magnetism is indirectly influenced by the size and lattice spacings of the rare earth ions.$^{29}$ The second category consists of those orthoferrites which have magnetic rare earth ions (like Gd$^{+3}$), the magnetic interactions are not only dependent upon Fe$^{+3}$-Fe$^{+3}$ exchange interaction but also Gd$^{+3}$-Fe$^{+3}$ and Gd$^{+3}$-Gd$^{+3}$ interactions.$^{30}$ Here, not only the size of the rare earth ions but their magnetic anisotropies play a crucial role which decide the fate of the spin reorientation transitions.

*Figure 3.6:* (A) Representative zero field cooled, field cooled curves at 50, 200, 400, 5000 Oe external field. (B), (C), (D) show the zoom views of three different parts of (A).
In comparison to Gd\(^{3+}\) ions (paramagnetic nature), Dy\(^{3+}\) ions have stronger anisotropy in the crystal which finally results more complex picture of reorientation transition as discussed below.\(^{31}\) As we mentioned earlier that DFO shows a series of magnetic transitions due to the competing interactions between Dy\(^{3+}\)-Dy\(^{3+}\), Dy\(^{3+}\)-Fe\(^{3+}\), Fe\(^{3+}\)-Fe\(^{3+}\) ions. Just below the Néel temperature (645K), the Fe\(^{3+}\)-Fe\(^{3+}\) interaction dominates and at lowest temperature of measurements, the Dy\(^{3+}\)-Dy\(^{3+}\) interactions are the dominant ones (figure 3.6 (B)). On the other hand, the Fe\(^{3+}\)-Dy\(^{3+}\) interactions are observed at the intermediate temperature ranges (figures 3.6 (C) and (D)). In our earlier paper, in the case of GdCrO\(_3\), we explained the mechanism behind the competing interactions appearing in different temperature zones.\(^{10}\) The similar mechanism is applicable in the case of DFO as well. Below the Néel temperature (645 K), the spins of different Fe\(^{3+}\) ions interact antiparallely through the SE (super exchange) mechanism and give the G-type of AFM ordering.\(^{8}\) Here, the Fe\(^{3+}\)-Fe\(^{3+}\) interactions are much stronger in comparison to Dy\(^{3+}\)-Dy\(^{3+}\) and Dy\(^{3+}\)-Fe\(^{3+}\) interactions by the orders of magnitude.\(^{10}\) In DFO, the Fe\(^{3+}\) ions sit in the octahedral geometry surrounded by six O\(^{2-}\) ions that leads to the splitting of 3\(d^5\) orbital into \(t_{2g}\) and \(e_g\). The \(t_{2g}\) and \(e_g\) orbitals are half filled and the half filled \(e_g\) orbitals hybridize with 2\(p\) orbital of O\(^{2-}\) where two Fe\(^{3+}\) ions interact via O\(^{2-}\) ions in 180\(^{\circ}\) position and each Fe\(^{3+}\) ion has six Fe\(^{3+}\) nearest neighbors and therefore, the total SE interaction is a sum of them. On the other hand, Dy\(^{3+}\) and Fe\(^{3+}\) ions interact with each other via O\(^{2-}\) at 90\(^{\circ}\) position and this interaction is weaker in nature and therefore dominates at lower temperatures only. As each Fe\(^{3+}\) ion has eight Dy\(^{3+}\) nearest neighbors, the total Dy\(^{3+}\)-Fe\(^{3+}\) SE interaction will be a sum of them. The Dy\(^{3+}\)-Dy\(^{3+}\) SE interaction is still one order of magnitude weaker than the SE interaction between Dy\(^{3+}\) and Fe\(^{3+}\) and shows up around 4 K. We now correlate the influence of these interactions on the features seen by us in the magnetic measurements. At higher temperatures, half filled Fe\(^{3+}\) \(d\)-orbital \((e_g)\) and O\(^{2-}\) \(p\)-orbital hybridization is more stable than the Dy\(^{3+}\) \(f\)-orbital and O\(^{2-}\) \(p\)-orbital hybridization. However, as the temperature decreases further well below the Néel temperature, \(f\)-orbitals in Dy\(^{3+}\) ions and \(p\) orbitals of oxygen also start interacting, resulting into the onset of Fe\(^{3+}\)-O\(^{2-}\) Dy\(^{3+}\) interaction. This interaction is weak AFM as here the half filled \(e_g\) orbital of Fe\(^{3+}\) overlaps with one end of oxygen \(p\)-
orbital and the other end of the same overlaps with a more than half filled \( f \)-orbital of \( \text{Dy}^{3+} \). This results into the reorientation of G-type component of \( \text{Fe}^{3+} \) moment to WFM component around 315 K (figure 3.6 (D)). This weak AFM SE coupling gives rise to opening up of hysteresis loop (shown in figure 3.4 (B)) and consequently the remnant magnetization increases. Here, it should be noticed that it is not just the SE interaction between \( \text{Fe}^{3+} \) and \( \text{Dy}^{3+} \) but the \( \text{Fe}^{3+} \) spins also get canted due to the Dzialoshinski-Moriya (DM) \(^{32}\) type antisymmetric exchange interaction between \( \text{Fe}^{3+} - \text{Fe}^{3+} \) ions which plays a very important role here.\(^{33}\) These canted moments of \( \text{Fe}^{3+} \) induce an opening of the hysteresis loop which continues till 70 K and below this \( \text{Dy}^{3+} \) moments strongly interact antiferromagnetically with another \( \text{Dy}^{3+} \) moments which results again in the closing of the hysteresis loop (fig. 3.4 (C)). Below the room temperature, around 70 K \( \text{Fe}^{3+} \) moments continuously get reoriented from one crystallographic axis to another due to the increased \( \text{Dy}^{3+} - \text{Fe}^{3+} \) interactions and a sharp peak is observed in the ZFC-FC curves at 70K (figure 3.6 (B & C)). Below 70 K, \( \text{Dy}^{3+} \) moments start ordering antiferromagnetically with other \( \text{Dy}^{3+} \) moments which results into the decrease in the coercivity which also reflects in the ZFC-FC curves. It is very interesting to note that at low temperature and high magnetic field, DFO shows relatively higher value of magnetization in comparison to the reported values for some other orthoferrites such as \( \text{GdFeO}_3 \), \( \text{LuFeO}_3 \) and \( \text{EuFeO}_3 \). It might be due to the contribution of orbital magnetic moment in the total magnetic moment where \( f \) orbital electrons play a crucial role for deciding the direction of spins and thereby overall magnetization.\(^{34}\)

In our nanosized samples, in addition to these intercationic competing SE interactions, the increased surface anisotropy and the amount of uncompensated/canted surface spins due to the increased surface to volume ratio also contributes in the opening up of the sizable hysteresis loop below the Néel temperature as seen in figure 3.4 (B & C). In case of bulk materials where the particle size is large and the particles are randomly oriented, the contribution of isotropic exchange energy is larger in comparison to the anisotropic energy contribution. Therefore, the weaker magnetic transitions like spin reorientation transitions which are highly dependent upon the direction of spins and
the applied magnetic field might get a bit suppressed by the isotropic term in bulk phase in comparison to the nanophase. However, as the particle size goes to smaller scale, the surface to volume ratio increases which finally results in to an increase in the surface anisotropy as well as dipolar interaction.\textsuperscript{35} To explain the magnetic signature of nanocrystalline DFO, all the energy terms like anisotropic energy, isotropic energy, DM exchange energy, dipolar energy, Zeeman energy and magneto electrostatic energy will contribute significantly.\textsuperscript{36} This is the reason why in contrast to the SR transitions seen by us in our nanocrystalline DFO, the Dy\textsuperscript{3+}-Fe\textsuperscript{3+}, Fe\textsuperscript{3+}-Fe\textsuperscript{3+} and Dy\textsuperscript{3+}- Dy\textsuperscript{3+} interactions resulting into various subtle reorientation transitions (as seen in various panels of figure 3.6) can be easily missed in the bulk DFO. The mechanism behind the unique exchange bias feature seen by us in DFO nanoparticles (not observed earlier in bulk BFO) can also be explained by the exchange coupling between the ferromagnetic surface spins and AFM core spins. The change in the AFM character of the core spins with the temperature results into the temperature dependent exchange field as seen in figure 3.5 (B) where all the magnetic transitions reported in ZFC-FC around 315, 70 and 4 K are also observed in the case of temperature dependent exchange field. The exchange field shows a maximum around 315 K and decreases continuously with a small hump near 70 K. Further, below 70 K it again decreases and reaches to zero around 4 K and further it shoots up at 3 K. This type of exchange coupling behavior is quite common in nanosized AFM systems and nicely reviewed by Nogues et al.\textsuperscript{27}

At the end, let us discuss the possible reason behind the absence of Morin transition in our nanosized DFO. As we discussed earlier, DFO is the only rare earth orthoferrite which is reported to show Morin transition at 35K in bulk single crystalline form where the AFM vector of coupled Fe\textsuperscript{3+} ions reorient from $a$- axis to $b$-axis in the lattice.\textsuperscript{28} The Morin transition, which is also a type of spin-reorientation transition, takes place as a first order transition and widely studied in bulk $\alpha$-Fe$_2$O$_3$ where it occurs at $T_M$=263 K.\textsuperscript{37, 38} The particle size dependence of Morin transition in $\alpha$-Fe$_2$O$_3$ is also reported which is believed to decrease with decreasing particle size and it has been reported that there is no Morin transition above liquid helium temperature in $\alpha$-Fe$_2$O$_3$. 

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particles with diameters smaller than \( \sim 20 \) nm.\(^{37}\) Below 20 nm, the surface spins deviate strongly from the AFM easy axis.\(^{37}\) The absence of an anomaly at 35K (Morin transition) in the M-T curve of our nanocrystalline DyFeO\(_3\) indicates that the change in the order at this transition is very small. The spin frustration near the nanoparticle surfaces, the finite distribution of particle sizes, and surface strain all might be playing important role to diminish Morin transition in our case.

### 3.6 Dielectric properties measurement:

To probe the dielectric response in the proximity of the magnetic transitions in DFO at low temperatures, we used Novocontrol Beta NB Impedance Analyzer with a home-built sample holder to couple with a helium closed cycle refrigerator (Janis Inc.). The dielectric response was mapped in a frequency range from 1 to \( 1 \times 10^6 \) Hz at 1 volt (rms) in the temperature range from 20-325 K at a close interval of 1 K. A compressed circular pellet, with 13 mm diameter was kept in a custom designed sample holder to form circular parallel plate capacitor geometry.

The frequency dependent plots of the real \( (\varepsilon') \) parts of complex dielectric permittivity \( (\varepsilon^*) \) of DFO at few temperature values in 50 to 300 K range are shown in various panels of figure 3.7. The nature of dielectric permittivity related to free dipoles oscillating in an electric field may be described in the following way. At very low frequencies \( (\omega \ll 1/\tau, \text{ where } \tau \text{ is the relaxation time}) \), dipoles follow the field and the real part of the dielectric constant \( \varepsilon' \approx \varepsilon_0 \) (value of the dielectric constant in a quasistatic field). As the frequency increases \( (\omega < 1/\tau, \text{ where } \tau \text{ is the relaxation time}) \), dipoles begin to lag behind the field and \( \varepsilon' \) slightly decreases. When frequency reaches the characteristic frequency \( (\omega = 1/\tau, \text{ where } \tau \text{ is the relaxation time}) \), the \( \varepsilon' \) value drops (relaxation processes). At very high frequencies \( (\omega > 1/\tau, \text{ where } \tau \text{ is the relaxation time}) \), dipoles can no longer follow the field and \( \varepsilon' \approx \varepsilon_\infty \) (high frequency value of \( \varepsilon' \)). Approximately, this is the behaviour which is observed in figure 3.7(a) where the \( \varepsilon' \) increases with decreasing frequency. In addition to the various types of polarization contribution (interfacial, dipolar, atomic, ionic, electronic) in the dielectric constant, the dielectric behaviour of nanostructured materials is also influenced by enormous number of interparticle
interfaces and defects present at these interfaces which can cause a change of space charge distribution. Under applied ac electric field, these space charges oscillate and can get trapped by these interfacial defects at nanoparticle surfaces, resulting into the formation of additional space charge polarization. Interfaces in nanostructured materials might also have oxygen ion vacancies, which are equivalent to positive charges; giving rise to additional dipole moments. At lower frequencies, the high value of dielectric constant seen by us is mainly due to the space charge polarization.

Figure 3.7: (a) Frequency dependence of real part of permittivity ($\varepsilon'$) value at different temperature (b) $\varepsilon'$ vs. $f$ curves in 125- 200 K temperature range (c) $\varepsilon'$ vs. $T$ curves at different frequencies (d) $d\varepsilon'/dT$ vs. $T$ curves at 5 Hz for DyFeO$_3$ nanoparticles.

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As the temperature increases, more and more dipoles are oriented in the field direction after overcoming the thermal activation energy barriers, resulting into an increase in the value of the dielectric constant, as observed in figures 3.7a. In figure 3.7 (b), it is noticed that there is a sudden drop in \( \varepsilon' \) in the temperature range 100 to 200 K where \( \omega = \frac{1}{\tau} \) and with increasing temperature this drop is shifted towards higher frequency side. In figure 3.7 (c), we have shown the temperature dependent dielectric constant for the frequency range 5 Hz to 506 kHz where below 100K, \( \varepsilon' \) values show a plateau region and above 100K, there is a sudden increase in the \( \varepsilon' \) value followed by a knee (shown by an arrow) above which \( \varepsilon' \) gradually increases further at higher temperature values. We also noticed strong frequency dependence in the onset of jump as well as the knee temperature in the \( \varepsilon' \) values above 100 K with a shift in these features in \( \varepsilon' \) values towards higher temperatures at high frequencies. It should be noticed that the value of \( \varepsilon' \) also goes down with increasing frequency. In figure 3.7 (d), we have shown the zoom view of the first derivative of \( \varepsilon' \) with temperature shows a peak at around 33 K. At present, the origin of this peak is not clear to us.

Next, we studied the dielectric loss in DFO nanoparticles. The variation of dielectric loss with frequency at different temperatures for DFO nanoparticles is shown in figure 3.8a which shows a strong resonance peak. This peak shifts towards higher frequencies with increasing temperature. We also observed a strong peak in the dielectric loss (\( \tan \delta \)) vs. T curves in the temperature range 100–200 K (figure 3.8 b) where the peak temperature shifts towards higher temperature with increasing frequency. In (\( \tan \delta \)) vs. T curves, this peak is followed by almost linear increase in \( \tan \delta \) at further higher temperatures. There are two opposite factors contributing simultaneously in the value of \( \varepsilon'' \) with the increase in temperature. The first factor which results in an increase in \( \tan \delta \) value with the increase in temperature is due to an increase in the number of charge carriers in DFO by thermal activation (showing the semiconducting behaviour of the sample) which facilitates the electron hopping from Fe\(^{2+}\) and Fe\(^{3+}\) at the nanoparticle surfaces. As we indicated earlier, very small amount of Fe\(^{2+}\) ions might exist at nanoparticles surface due to oxygen deficiency and reduced coordination number. \(^{19,40,41}\)
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The second factor which results in the decrease in $\tan \delta$ value is due to the fact that with increased temperature, electrical dipoles can easily align in the field direction and hence the energy spent during polarization decreases with temperature which finally reduces the value of imaginary dielectric constant with increase in temperature. The dielectric loss in low temperature range (30-50K) shows unusual behaviour (figure 3.8c). Firstly, there are apparent peaks at 40 K that do not change position much with change in the frequency. Secondly, as the frequency increases, there is a decrease in the strength of $\tan \delta$. For example, for the 1 Hz curve, the maximum value of $\tan \delta$ is almost 0.11 while it is only about 0.03 at 105.3 kHz.

Figure 3.8: (a) temperature dependent of dielectric loss value at different frequency (b) frequency dependent dielectric loss at different temperature (c) Zoom view of dielectric loss value between temperature range 20-60 K (d) plot of $\ln f$ vs. $1000/T$ for DyFeO$_3$ nanoparticles.

The second factor which results in the decrease in $\tan \delta$ value is due to the fact that with increased temperature, electrical dipoles can easily align in the field direction and hence the energy spent during polarization decreases with temperature which finally reduces the value of imaginary dielectric constant with increase in temperature. The dielectric loss in low temperature range (30-50K) shows unusual behaviour (figure 3.8c). Firstly, there are apparent peaks at 40 K that do not change position much with change in the frequency. Secondly, as the frequency increases, there is a decrease in the strength of $\tan \delta$. For example, for the 1 Hz curve, the maximum value of $\tan \delta$ is almost 0.11 while it is only about 0.03 at 105.3 kHz.
To further understand the relaxation behaviour, we calculated the activation energy of the relaxation process. The activation energy ($E_a$) in a thermally activated relaxation process is generally related to the relaxation time $\tau$ by the Arrhenius equation:

$$\tau = \tau_0 \exp\left(\frac{E_a}{k_B T}\right)$$  \hspace{1cm} (1)

where, $\tau$ is the relaxation time, $E_a$ is the mean activation energy for relaxation, and $k_B$ is the Boltzmann constant. This equation can also be written as (where $f=1/\tau$):

$$\ln f = \ln f_0 - \frac{E_a}{k_B T}$$  \hspace{1cm} (2)

Figure 3.8(d) represents the plot between $\ln f$ vs. $(1000/T)$ which shows a very nice linear fit with the values of $E_a$ and $f_0$ 0.20eV and $4.07 \times 10^{10}$ Hz respectively.

It appears clearly that the width of the peak in $\tan \delta$ curves also increases with frequency which shows that there is a possibility of distribution of relaxation process. The width of the relaxation peak in figure 3.8(a, b) cannot be accounted for monodispersive relaxation process and points towards the possibility of distribution of relaxation times. One of the most convenient ways for checking the polydispersive nature of dielectric relaxation is through the complex Argand plane plot of $\varepsilon''$ and $\varepsilon'$ usually called Cole - Cole plot. For the quantitative analysis of dielectric spectra and the relaxation time, the Cole-Cole equation has been described by the empirical relation $^{42,43}$

$$\varepsilon^* = \varepsilon' - i\varepsilon'' = \varepsilon_\infty + \frac{\varepsilon_s - \varepsilon_\infty}{1 + (i\omega\tau)^{1-\alpha}}$$  \hspace{1cm} (3)

here, $\varepsilon_\infty$ is the high frequency limit of $\varepsilon$, $\varepsilon_s$ is the low frequency limit of $\varepsilon$, $\varepsilon_s-\varepsilon_\infty$ is a dielectric strength, $\omega = 2\pi f$ is the angular frequency, $\tau$ is the mean relaxation time and $\alpha$ represents the distribution of the relaxation time which in geometric terms represents the displacement of the arc’s centre below the real axis. Figure 3.9 shows the plots between real $\varepsilon'$ and imaginary $\varepsilon''$ components of the complex impedance at 175 and 80 K.
in the 1 Hz to 1 MHz frequency range. Here, the parameter $\alpha$ characterizes the distribution of relaxation time or spreading factor. It increases with internal degrees of freedom of relaxors, indicating a departure of electrical response from an ideal condition. When $\alpha$ goes to zero, equation (3) reduces to classical Debye’s formalism. It is depicted from the Cole-Cole plot in figure 3.9 that the centre of the semicircles arc is below the x axis, therefore, it does not follow the Debye relaxation process (for which $\alpha = 0$). The spreading factor $\alpha$ can be deduced from the angle subtended by the radius of the circle with the $\varepsilon'$ axis passing through the origin of the $\varepsilon''$ axis. The spreading factor $\alpha$ is measured from the expression for the maximum value of imaginary part of permittivity, given by

$$
\varepsilon''_{\text{max}} = \frac{(\varepsilon_s - \varepsilon_\infty) \tan \left[ \frac{(1 - \alpha) \pi}{4} \right]}{2}
$$

where $\varepsilon''_{\text{max}}$ is the maximum value of imaginary part of permittivity from Cole–Cole plot. From this plot, since centre of the semicircle arc lies below the x-axis so the relaxation process of the DFO is quite different from that of monodispersive Debye-type (where $\alpha = 0$).

**Figure 3.9:** Cole-Cole plot of DyFeO$_3$ nanoparticles at 175K and 80K temperature.

In figure 3.9 (left panel), we have shown two impedance arcs in two separate frequency
ranges at temperature 175 K. This suggests that two different relaxation mechanisms are present in the measured frequency and temperature range. The semicircle in the high-frequency region is representative of the bulk properties of DyFeO$_3$ nanoparticles (contribution from core of the particles). Another semicircle arc in the low frequency region is related to the grain boundaries of these nanoparticles. In both the cases, the centre of semicircles lies below the real axis which shows that the relaxation behaviour is deviating from Debye type. The spreading factor $\alpha$ was calculated from the above equation for both the semi circle arcs and the values for grain and grain boundary were calculated as 0.453 and 0.68 respectively. Therefore, the non-zero value of $\alpha$ confirms the polydisperse nature of dielectric relaxation in the present DFO sample as discussed above. However, it is interesting to note that at lower temperature around 80 K (figure 3.9, right panel), there is only one arc present at higher frequency range which suggests that there is no contribution of grain boundary at this temperature. As temperature increases, a slight amount of oxygen loss can occur which facilitates the appearance of dipoles formed with an adjacent host ion and enlarge the rattling space available for dipole vibration, which as a consequence leads to the short-range hopping of the ions and gives rise to relaxation at lower frequency range and consequently grain boundary contribution increases. The spreading factor $\alpha$ is 0.39 for the semicircle at 80 K. It is clear that $\alpha$ decreases with decreasing temperature. From the Cole-Cole plot we could also calculate several other parameters. The ratio of the diameters of these two arcs indicated that the resistance associated with the bigger arc is much larger than that of the small arc. It suggests that the resistance in the equivalent circuit is dominated by grain boundary resistance.

In figure 3.10a, we have shown the temperature dependent variation of resistance of grain and grain boundary calculated from Cole-Cole plots. We could conclude from the this figure that as the temperature increases from 90 to 170 K, the grain resistance decreases from 2.78 to 2.65 $\Omega$ where as grain boundary resistance decreases from 5.41 to 4.85 $\Omega$ with increase in temperature from 175 to 260 K.
Similarly capacitance of grain and grain boundary is calculated using the relation: $\omega RC = 1$ \( (5) \) where $\omega$ is the angular frequency at the maxima of the semicircle for the component and $R$ and $C$ are the resistance and capacitance respectively. Figure 3.10(b) shows the temperature variation of $C_g$ and $C_{gb}$ obtained from Cole–Cole plots. It can be seen that the values of $C_g$ and $C_{gb}$ decrease with the increment in the temperature. Frequency of the top point of the Cole–Cole plot is relaxation frequency of the orientational polarization ($f_r = 1.29$ Hz for 80 K semicircular arc in Fig. 3.9) and at this frequency dielectric value is maximum. The frequency, where the semi-circle crosses with ordinate axis, corresponds to the minimum dielectric losses of applied field. From the peak of each semicircle of the Cole–Cole

*Figure 3.10: (a), (b), (c) Temperature dependent resistance, capacitance and relaxation time curves for grain and grain boundary contributions respectively.*
plots, the relaxation times due to various effects (grain and grain boundary) were estimated. Figure 3.10c shows the variation of relaxation times $\tau_g$ and $\tau_{gb}$ with inverse of temperature. These plots are almost linear and obey an Arrhenius relationship:

$$\tau = \tau_0 \exp \left( \frac{E_a}{k_B T} \right)$$  \hspace{1cm} (6)$$

where $E_a$ is the activation energy for conduction. The values of activation energy due to different contribution as obtained by least squares fitting are $E_g = 0.06$ eV, $E_{gb} = 0.14$ eV.

3.7 Electrical conductivity measurement:

If we assume that all the dielectric loss in the measuring temperature range is due to the conductivity of the sample, then we can calculate the frequency and temperature dependence of ac conductivity ($\sigma$) from $\varepsilon''$ using following equation$^{19}$:

$$\sigma = \omega \varepsilon_0 \varepsilon''$$ \hspace{1cm} (7)$$

where $\omega$ is the angular frequency, $\varepsilon_0$ is the permittivity of free space. Figure 3.11a shows the log–log plot of frequency dependence of ac conductivity for DFO at 100 and 150 K temperatures. Conductivity value start increasing around the dielectric loss peak frequency when $\omega \approx \omega_{\text{max}}$. As the frequency increases ($\omega >> \omega_{\text{max}}$), $\sigma (\omega)$ exhibits dispersion, increasing in a power-law fashion: $\sigma(\omega) \propto \omega^n$ and log–log plot becoming almost linear. Exponent $n$ represents the degree of interaction between the mobile ions and the lattice around them. However as the temperature increases, the interaction between the charge carriers and the lattice increases which leads to a decrease in $n$ value from 0.95 to 0.77 as the temperature increases from 250 to 350 K. Below 200K, conductivity show a small hump which shifts towards lower frequency with decreasing temperature. It is explained by the space charge polarisation occurring due to oxygen deficiency. It is to be mentioned that at high temperature, some amount of oxygen loss can occur which facilitates the formation of dipoles with an adjacent host ion and enlarge
the rattling space available for dipole vibration, which as a consequence leads to the short-range hopping of the ions and gives rise to relaxation. The oxygen ions jump between the vacancies, are considered to be responsible for the transition from short-range to long-range hopping and may explain the marked ionic conductivity which shift towards higher frequency side as the temperature increases.

It is seen that $\sigma$ value decreases with frequency and extrapolation towards lower frequency will give $\sigma_{dc}$ value which follow Arrhenius law.

$$\sigma_{dc} = \sigma_0 \exp\left(\frac{-E_\sigma}{k_B T}\right)$$

where $\sigma_0$ is the pre exponential factor and $E_\sigma$, $k_B$ and $T$ are the activation energy for the conduction, Boltzman’s constant, and absolute temperature, respectively. The activation energy for conduction ($E_a$) was calculated from the slope of the straight lines obtained when $\sigma_{dc}$ are plotted against $1000/T$ of samples in figure 3.11b. The activation energy calculated from $\log \sigma_{dc}$ vs $1000/T$ plot is 0.092eV. Similarly, lower value of activation energy around 0.03eV was also found in nanocrystalline BiFeO$_3$ by us and its strong

**Figure 3.11:** (a) Real part of ac conductivity vs. frequency curves at two temperature values (b) temperature dependent dc conductivity.
temperature dependence seems to be due the oxygen deficiency and reduced particle size. On basis of the summary of conduction mechanisms and associated activation energy values for various semiconductive ferroelectric materials reported by Raymond, the conduction mechanism is charge hopping when the activation energy is <0.4 eV. As the activation energy for our material is well below this value we expect this mechanism to apply here as well.

3.8 ac magnetic susceptibility measurement:

To probe the magnetic phase transition and domain dynamics, we performed ac magnetic susceptibility measurement using Physical Property Measurement System.

Figure 3.12: Real and imaginary parts of ac magnetization shown in various temperature range for DyFeO₃ nanoparticles.
(PPMS) from Quantum Design Inc., San Diego, CA. Recently we have shown the detail DC magnetization measurements for DyFeO$_3$ nano particle and able to isolate the presence of spin-reorientation transitions near 315 and 70 K due to the Dy$^{3+}$-Fe$^{3+}$ interaction accompanied with an opening up of the hysteresis loop followed by antiferromagnetic ordering around 4 K due to a possible Dy$^{3+}$- Dy$^{3+}$ interaction.\textsuperscript{46} For detail investigation these magnetic interaction AC magnetic susceptibility is an extremely sensitive technique to detect anomalous behaviour in rare earth ferrite systems such as that caused by spin-reorientation transitions (SRT) which are induced by temperature, magnetic field, domain wall motions, reversible rotation of the magnetic moments or small impurities. To detect these phase transitions at a low temperature, the ac magnetic susceptibility of the DyFeO$_3$ nanoparticles at a lower excitation field (H = 10 Oe) was measured in the temperature range 3-100K and frequency range 10 – 10000 Hz (figure 3.12). The real part of ac susceptibility shows a sudden change in slope at 70 K and imaginary part shows a dip near 70K in figures 3.12 (B, D). This transition temperature corresponds to the spontaneous spin reorientation transition of iron spins T$_{SR}$ due to the coupling between rare earth sublattice with the magnetic moment of Fe sub lattice (Dy - Fe) interaction which was reported by us on the same material using dc magnetization.\textsuperscript{46} At lower temperature, the susceptibility $\chi'$ increases with decreasing temperature until a sharp peak is observed (figure 3.12A). This sharp peak near 4 K corresponds to the transition from weak ferromagnetic coupling (Dy-Fe), to antiferromagnetic coupling (Dy-Dy) (Néel temperature). This is also consistent with the fact that we did not observe any frequency dependence in this transition temperature (figure 3.12A). Around this antiferromagnetic transition, the imaginary part $\chi''$ (figure 3.12C) starts decreasing where $\chi'$ shows a sharp increase before 4 K. At low frequency $\chi''$ shows a single peak at around 10 K at 10 Hz where $\chi'$ goes to minima and with increasing frequency this peak shift towards higher temperature side. In general, temperature induced frequency dependent peak in $\chi''$ is associated with dissipation from domain-wall movement, and the drop in $\chi''$ can be understood in terms of pinning of the domain-wall motion in DyFeO$_3$.
3.9 Conclusions:

we have shown that it is possible to synthesize DyFeO₃ nanoparticles in single phase using simple hydrothermal process with high crystallinity. Our studies on the magnetization measurements indicate new information on this material in nanosized. Overall, in this case the detailed magnetic properties emphasize the collective as well as individual roles played by the Dy³⁺ and Fe³⁺ ions at various temperatures. Our results for the nanoparticles shows that DyFeO₃ undergo reorientation transition at 70 and 315 K where the direction of the net magnetic moment rotates continuously from one crystallographic axis to another due to antisymmetric and anisotropic –symmetric exchange interaction between Fe³⁺ and Dy³⁺. On further cooling DyFeO₃ shows magnetic ordering of the rare earth ions at 4 K. The coexistence of FM and AFM phase at 300 K is supported by the by the shift in hysteresis loop at room temperature which is also explained by the presence of exchange coupling between FM surface and AFM cores at 300 K. we have also studied the dielectric and spin relaxation behavior of the DyFeO₃ nanoparticles synthesized by the wet chemical method. We have found from the imaginary part of the impedance spectra that grain and grain boundary both are contributing in relaxation mechanism as further confirmed by the Cole-Cole spectra. An analysis of cole- cole spectra confirm that resistance and capacitance of grain and grain boundary is temperature dependent and continuously decreasing with increase in temperature but relaxation time increases with temperature. All these measurement confirms that relaxation mechanism is governed by Maxwell – Wagner relaxation. Ac magnetic susceptibility measurement shows that spin reorientation transition takes place around 70 K. During this transition temperature there is remarkable change in slope in both the in-phase and the out-of-phase magnetic susceptibility components. Below this temperature around 4 K real component shows a sharp peak for Neel transition and imaginary component shows a dip in value which corresponds to pinning of the domain wall motion.
3.10 References:


4. Aono, H.; Traversa, E.; Sakamoto, M.; Sadaoka, Y., Crystallographic characterization and NO$_2$ gas sensing property of LnFeO$_3$ prepared by thermal decomposition of Ln-Fe hexacyanocomplexes, Ln[Fe(CN)$_6$]center dot nH$_2$O, Ln = La, Nd, Sm, Gd, and Dy. *Sensors and Actuators B-Chemical* 2003, 94, (2), 132-139.


