CHAPTER 7
SUMMARY AND FUTURE SCOPE

The present thesis is aspired to report the experimental studies on synthesis, structure, dielectric, magnetic and optical properties of modified bismuth ferrite (BiFeO$_3$) materials with rare earth (RE) ions on A-sites and transition metal (TM) ions on B-sites. This chapter summarizes the overall outcome of my research work whose system/section wise results are mentioned in the previous chapters.

The fundamental characteristics of multiferroics, literature survey and objectives are well described in chapter 1. The experimental procedures for synthesizing these specimen samples and measurement techniques used to characterize these materials are illustrated in and chapter 2.

The research outcome, included in the thesis, is mainly focused on preparation and characterization of various samples with different chemical compositions in following systems:

1. BiFeO$_3$
2. Bi$_{1-x}$Pr$_x$FeO$_3$ (x = 0.05, 0.10, 0.15 and 0.20)
3. Bi$_{1-x}$Y$_x$FeO$_3$ (x = 0.05, 0.10, 0.15 and 0.20)
4. Bi$_{1-x}$Pr$_x$Fe$_{1-x}$Ti$_x$O$_3$ (x = 0.05, 0.10, 0.15 and 0.20)
5. Bi$_{1-x}$Y$_x$Fe$_{1-x}$Ti$_x$O$_3$ (x = 0.08, 0.16 and 0.24)

The present research work comprises our studies on single phase formation, dielectric magnetic and optical properties of the samples with various compositions in above systems.

7.1 Bi$_{1-x}$Pr$_x$FeO$_3$ (x ≤ 0.20) SYSTEM

1. Series of compositions with x ≤ 0.20 in the system Bi$_{1-x}$Pr$_x$FeO$_3$ (BPFO) have been prepared by solid state ceramic method. All these compositions have shown single phase formation with a few impurity phases for compositions with lower concentration of Pr i.e. for x ≤ 0.05. All these compositions are found to exhibit rhombohedral structure symmetry with c/a ratio minimum for x = 0.10. The lattice parameters are found to decrease upto x = 0.10 and thereafter increases with x. The variation in the micro-strain is found to be in agreement with the structural changes i.e. change in lattice parameters with
x. Pr substitution in BFO has been found to eliminate the impurity phases for \( x \geq 0.10 \). SEM micrographs have shown a decrease in grain size with increasing \( x \).

2. Dielectric studies of these samples have shown two dielectric anomalies one at low temperature (\( \sim 150^\circ C \)) and another one at high temperature at \( \sim 370^\circ C \). The former one has been attributed to the defects or impurities which is found to be completely disappeared for \( x = 0.20 \), indicating a reduction in the defect concentration with increasing \( x \). This has also been evident from substantial reductions in dielectric loss and hence indirectly the current density with increasing \( x \). The reduction in the dielectric loss with increasing \( x \) has influenced the remanent polarization (\( P_r \)) which has shown a significant increase with increasing \( x \). Composition with \( x = 0.20 \) has shown substantial enhancement in the value of remanent polarization. M-H behavior at room temperature have revealed a linear increase in remanent magnetization (\( M_r \)) with \( x \). M-T plots for two samples with \( x = 0.0 \) and 0.20 have shown an anomaly close to the temperature \( T_N (\sim 370^\circ C) \), a characteristic temperature of BFO, below which it follows AFM type magnetic order. Dielectric plots (\( \varepsilon_r \) vs T) have also shown an abnormal behavior around this temperature. Further, magnetic behavior shows that there is a transition from modulated anti-ferromagnetic state (AFM type) for \( x = 0.0 \) to the weakly ferromagnetic state (canted spin AFM) for \( x = 0.20 \) at room temperature. These dielectric and magnetic studies have shown a co-relation in their dielectric and magnetic anomalies which suggests that there exist a multiferroic magneto-electric coupling between dielectric and magnetic polar order.

3. FTIR spectra shows two broad absorption peaks at 430 cm\(^{-1}\) and 560 cm\(^{-1}\) which is assigned to the bending and stretching of Fe-O and Bi-O bonds due to distortion in \( \text{BO}_6 \) Octahedra. Splitting of absorption peak again around 430 cm\(^{-1}\) for the compositions with \( x = 0.15 \) and 0.20 may be attributed to the distroition of \( \text{FeO}_6 \) Octahedra. This distroition in \( \text{FeO}_6 \) octahedra may cause the development of residual magnetic moment due to canted type spin order of Fe-O-Fe network (weak ferromagnetism) in these compounds. This is also in agreement with structural disorder caused by increase in lattice parameters for \( x \geq 0.10 \).

4. Photoluminescence spectra for all these samples show a band gap of 2.67 eV. Two weak yellow emissions at 545nm and 564nm may be attributed to the electronic transitions of Pr\(^{3+}\) states.
7.2 Bi$_{1-x}$Y$_x$FeO$_3$ (x ≤ 0.20) SYSTEM

1. Compositions with x ≤ 0.20 in the system Bi$_{1-x}$Y$_x$FeO$_3$ (BYFO) have shown solid solution formation. All the prepared compositions have shown single phase formation with minor impurities. All these samples are found to have rhombohedral structure. Due to distortion in the unit cell and defect formation, no uniform variation of lattice parameters have been obtained for these samples, however, the ratio c/a has been found to decrease with increasing x and volume of the unit cell has been found to decrease with increasing x. The variation of micro-strain and crystallite size is almost similar to the Pr doped BFO compositions. SEM micrographs of these samples have revealed the average grain size less than ~ 4µm and the grain size has been found to decrease with increasing x.

2. Two dielectric anomalies have been observed in the dielectric plots, one at low temperature (~ 200 °C) for x ≤ 0.10 which may be ascribed to the presence of defect concentration/impurities in BYFO samples and the other one at ~ 370 °C for x = 0.20 may be attributed to the characteristic temperature (T$_N$) of BFO. In addition to these, another peak is observed at even high temperatures say T = 450 °C for the samples with x = 0.15 and 0.20 which may be attributed to the Maxwell-Wagner type polarization caused microheterogeneities which supports our observations of an increase in dielectric constant with increasing x in these samples. So, Y substitution has been found to be more effective to improve dielectric constant than dielectric loss. The room temperature data in conductivity plots (ln$\sigma$ vs 1000/T plots) has revealed the decrease in conductivity with x which further supports our structural and electrical analysis. The decrease may be attributed to the suppression of defects with increasing concentration in these materials. Suppression of defects leads to reduced current density and eventually enhance remanent polarization. The value of remanent polarization (P$_r$), estimated from P-E loops of these samples, has been found to increases linearly with x upto x = 0.15, followed by a nonlinear increase in P$_r$ with x for x = 0.20. M-H loops have shown AFM type magnetic behaviour at room temperature. Hysteresis loop behaviour of the samples in BYFO samples are almost similar to BPFO samples. Improved polarization can be attributed to the reduction in defect formation i.e. Bismuth evaporation due to Y ions which are more tightly bound with oxygen ions in the lattice leading to the reduced oxygen vacancies also. Fe$^{3+}$ ions are the origin of the magnetic anisotropy, which leads to weak ferromagnetism in these samples.
3. The presence of two vibrational modes at 442 cm\(^{-1}\) and 545 cm\(^{-1}\) in the FTIR spectra may correspond to the bending and stretching of Bi-O and Fe-O bonds respectively. Shift of absorbance peak at 442 cm\(^{-1}\) with x may be attributed to the distortion in FeO\(_6\) octahedra. This distortion may be responsible of the occurrence of weak ferromagnetism in these samples similar to BPFO samples.

4. PL spectra of compositions with x \(\leq 0.20\) show blue emission at 458 nm, indicating the optical band gap of 2.67eV. The emissions at 561 and 584 nm in yellow region may be attributed to the electronic transitions of Y\(^{3+}\) states. The observation of the blue emission at 458 nm i.e. optical band gap in the blue region along with other (yellow) emissions in the visible region may find applications in optoelectronic devices.

7.3 Bi\(_{1-x}\)Pr\(_x\)Fe\(_{1-x}\)Ti\(_x\)O\(_3\) (x \(\leq 0.20\)) SYSTEM

1. In order to see the effect of co-substitution, we have synthesized Pr and Ti co-substituted BiFeO\(_3\) (BPFTO) ceramics with x \(\leq 0.20\) in the form of solid solutions. Rietveld refined XRD data has confirmed structural transition from rhombohedral (R3c) with x \(\leq 0.10\) to orthorhombic (Pnma) phase with 0.10 < x \(\leq 0.20\). Lattice parameters have been determined, though the lattice constant systematically decreases as long as structure is rhombohedral upto x = 0.10, thereafter, there is a slightly increase when the structure is orthorhombic, however, the volume of the unit cell has been found to decrease with increasing x. The variation in the lattice constant may be due to distortion in BO\(_6\) octahedra caused by offvalent ionic substitution and hence the structural changes. Decrease in the cell volume with x may be due to smaller ionic radii of substitutent ion (r\(_{Pr}\) = 1.126Å and r\(_{Ti}\) = 0.605Å) as compared to host ions (r\(_{Bi}\) = 1.17Å and r\(_{Fe}\) = 0.645Å).

2. Dielectric measurements from room temperature to 550\(^\circ\)C at few frequencies have revealed some anomalies that infer more than one dielectric processes. The two dielectric anomalies are clearly seen in \(\varepsilon_r\) vs T plots, the first one at around 200\(^\circ\)C and second one at \(~370^\circ\)C. The first anomaly has been found to shift to higher side of temperature and the second one occurs almost at the same temperature. The shift of the onset temperature of first anomaly with x may be due to change of Fe\(^{3+}\) to Fe\(^{2+}\) in the compound caused by Ti\(^{4+}\) substitution at Fe\(^{3+}\) in the lattice. As the concentration of Ti increases, the onset temperature shift to high temperature side. The frequency dependent response of this anomaly is clearly seen in tan\(\delta\) vs T plots which is temperature dependent, indicating relaxation of complex defect dipoles in this temperature regime. The other dielectric anomaly at \(~370^\circ\)C, which is temperature independent, may be due to magnetic
transition temperature of pure BFO. Conductivity behaviour reveals that in the low temperature range (region - I), conduction occurs via localized hopping of charge carriers among defects. With increasing temperature, the re-orientation of defect dipoles takes place in this temperature range which is frequency dependent (region - II). This is followed by two subsequent frequency independent region (region – III & IV) with increasing temperature. On estimating activation energy values in these linear regions, it is expected that in these temperature regimes, conduction occurs via doubly ionized oxygen vacancies over the short and long range respectively. It is more interesting to note that the frequency dependent hump is found to be disappeared for \( x = 0.15 \) and 0.20. This clearly suggests that with increasing \( x \), defects like oxygen vacancies are significantly reduced and hence the defect dipoles, hence no conductivity relaxation is seen, however, the frequency dependent persists which is due to localized hopping of charges among these defects.

3. The values of remanent polarization (\( P_r \)) has been found to increase with increasing \( x \). It is further to be noted values of \( P_r \) are relatively larger for the samples in BPFTO system as compared to the respective sample in BPFO system, indicating that Ti substitution is more effective in enhancing remanent polarization of the samples in BPFTO than BPFO. Ti substitution has shown reduced dielectric loss and hence current density, which is, further, expected to support enhanced \( P_r \) with \( x \) in these materials. M-H behaviour shows that appearance of open hysteresis for all the samples except \( x = 0.00 \) which may be attributed to the development of weak ferromagnetism. A significant change in remanent magnetization \( M_r \) magnetic behaviour with \( x \) in BPFTO samples with respect to the BPFO samples may be due to Ti ions at Fe-sites and hence, enhancement in \( M_r \) may be attributed to the partial destruction of a spiral spin structure due to insertion Ti leading to the breaking of Fe-O-Fe spiral network in BFO lattice.

4. FTIR spectra show the presence of the broad absorption band due to overlapping of Fe-O and Bi-O vibration groups.

5. UV-visible spectra reveal that band gap changes from 2.26 eV for \( x = 0.00 \) to 2.08 eV for \( x = 0.20 \), which explores the utilization of these materials for optoelectronic devices in the visible range.

7.4 \( \text{Bi}_{1-x}\text{Y}_x\text{Fe}_{1-x}\text{Ti}_x\text{O}_3 \ (x \leq 0.24) \) SYSTEM

1. Y and Ti co-substituted BiFeO\(_3\) (BYFTO) ceramics with compositions \( x \leq 0.24 \) have been synthesized by solid state ceramic route. XRD patterns of these samples have shown
single phase formation. Rietveld refinement of XRD data has confirmed structural phase transition from rhombohedral (R3c) with \( x \leq 0.16 \) to orthorhombic (Pnma) phase for \( x = 0.24 \). Volume of the unit cell has been found to decrease with increasing \( x \). The variation in the lattice constant with \( x \) is found to be non systematic this may be due to distortion in BO\(_6\) octahedra in random manner. This distortion is found to occur due to offivalent ionic substitution which has lead to the structural changes. Decrease in the cell volume with \( x \) may be due to smaller ionic radii of substitutent ion (\( r_Y = 0.90\) Å and \( r_{Ti} = 0.605\) Å) as compared to host ions (\( r_{Bi} = 1.17\) Å and \( r_{Fe} = 0.645\) Å).

2. Dielectric plots (\( \varepsilon_r \) and tan \( \delta \) vs T ) have shown two dielectric anomalies, one at low temperature ~200°C and the other one at high temperature ~300°C which infer two dielectric processes, the first one seems to be due to relaxation of complex defect dipoles in the intermediate temperature region and another one is at ~350°C due to characteristic magnetic transition temperature ‘\( T_N \)’ of pure BFO. Similar to BPFO samples, The first one is temperature and frequency dependent, clearly observable in tan \( \delta \) vs T plots for these samples. This may be attributed to the relaxation of defect dipoles. Similar to the BPFTO system, conductivity behaviour has been devided into four temperature regimes. Activation energy values, determined using linear region in the respective temperature regime except T2 regime (region - II), have indicated that in regime T1(region - I), localized conduction occurs via hopping of charge carriers among the defects in the materials. In region T2 (region - II), conduction relaxation occurs due to re-orientation of dipoles. Whereas, in the temperature regimes T3 and T4 (region – III & IV), conduction occurs via doubly ionized oxygen vacancies over the short and long range respectively.

3. M-H hysteresis loops at room temperature have illustrated that weak ferromagnetism arises with increasing Y and Ti concentration in BFO. Appearance of open M-H loop with increasing \( x \), except \( x = 0.00 \) reveals improved magnetization in BYFTO samples. Increase in magnetization with \( x \) is attributed to the partial destruction of spiral spin structure, which is caused by breaking of Fe-O-Fe chain in BFO due to insertion of Ti\(^{4+}\) ions. P-E hysteresis loops have revealed that remnant polarization increases with co-substitution of Y and Ti in BFO. This has been further supported by reduction in concentration of defect or current density with increasing \( x \).

4. FTIR spectra shows two broad absorption peaks at 430 cm\(^{-1}\) and 554 cm\(^{-1}\) which may be assigned to the stretching and bending of Fe-O and Bi-O bonds due to buckling in BO\(_6\) Octahedra.
5. UV-visible spectra reveals that band gap changes from 2.26 eV for \( x = 0.00 \) to 1.97 eV for \( x = 0.24 \), which explores the utilization of these materials for optoelectronic devices in the visible range. The decrease in band gap with \( x \) may be due to the origin of intermediate forbidden energy/defect levels between conduction and valence band.

7.5 SCOPE FOR FUTURE WORK

1. A lot of research on the study of doping of foreign elements on A and B-sites in ABO\(_3\) type structures like BiFeO\(_3\) has been investigated and enormous research articles are reported in the last few years. However, with in the limit of solid solutions of varieties of systems, impedance study in details could not be carried out in these compounds, only a limited study on Impedance Spectroscopy of a few selected compositions has been made. So, these type of materials can be exploited to understand inside story of the material i.e. grain and grain boundary phenomenon via impedance spectroscopy.

2. Dielectric behaviour is not well explored in the studies made so far. Polarization mechanisms, revealed from dielectric behaviour over the wide temperature range, can be better worked out with the help of impedance spectroscopy which also help to understand fundamentals of dielectric polarization in the dielectrics with defect complexities.

3. Since, study of the defect chemistry of these materials is very promising, it is, therefore, interesting to study the atmospheric effect on the electrical conduction behavior of these compounds.

4. Nano-structural studies on the structural properties and its effect on multifunctional properties open a new dimension for research worldwide. For example, preparation of thin films can be taken up to understand the influence of electrical and magnetic properties at such scales. This would help further, in undertaking the commercialization of the studied compositions.

5. Sol gel method can be used to synthesis these powders. This will not only produce single phase, but also very fine powders which may even give better properties.

6. Many researchers have used microwave synthesis and sintering method for the fabrication of many ferroic ceramics, especially PZT based compounds. It would be worthwhile to use microwave heating for the synthesis and sintering of BFO based compounds.