Chapter-6

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6.1: Conclusions

The objective of the present thesis work, which is broadly divided into two parts, is to study the following aspects of BaTiO$_3$ based ferroelectrics and magneto-electric composites:

1. The first part deals with the improvement of ferroelectric and dielectric properties of BaTiO$_3$
   a. With suitable chemical doping, tuning the transition temperature of BTO close to room temperature and therefore resulting in enhanced ferroelectric as well as electro-caloric effect near room temperature. Also, exploring the novel phenomena like re-entrant relaxor like phase transition, phase-coexistence etc., with chemical doping in doped BTO ceramics.
   b. Controlling the microstructure of BTO ceramics for better ferroelectric and dielectric properties. Microwave assisted radiant hybrid sintering is used for this purpose and finally the aging phenomena is studied in the un-doped polycrystalline BTO ceramics.

2. Second part deals with the study of magneto-electric composite materials. BTO is used as ferroelectric material and nickel zinc ferrite is used as magnetic component of the studied composites. Since the phenomena of ME coupling is a strain mediated one, detailed study is undertaken by varying / controlling the stress / strain in polycrystalline ceramics and thin film composites by
   a. Changing the relative concentration of cation among the tetrahedral and octahedral sites in nickel zinc ferrite. The cation distribution in ferrites is known to change the magnetostriction property of ferrites, but the consequence of this on ME coupling is not explored in literature.
   b. Controlling the growth morphology of the constituent phases, this is expected to introduce residual stress in the prepared films. And finally, a case study using in-situ MOKE is attempted to tailor magnetism of thin ferromagnetic layers using ME coupling.
For the preparation of polycrystalline ceramic samples solid-state reaction with conventional radiant heating and microwave assisted radiant heating are used in the present work. While for the preparation of thin films, pulsed laser deposition and electron beam evaporation are used. Various characterization methods viz., x-ray diffraction, atomic force microscopy, magneto-optic Kerr effect, $^{119}$Sn Mössbauer measurements, scanning electron microscopy, Raman spectroscopy, magnetization, ferroelectric (conventional P-E and PUND), specific heat and dielectric measurements are used for the study of prepared samples. The results of BTO ceramics emphasizing the ferroelectric and dielectric properties are discussed in chapter-3. Results of BTO based composite magneto-electric materials are presented in chapter-4 and chapter-5.

First part of chapter-3 reports structural, dielectric, ferroelectric (FE), $^{119}$Sn Mössbauer and specific heat measurements of polycrystalline BaTi$_{1-x}$Sn$_x$O$_3$ (x=0% to 15%) ceramics. Phase purity and homogeneous phase formation with Sn doping is confirmed from x-ray diffraction and $^{119}$Sn Mössbauer measurements. With Sn doping, the microstructure is found to change significantly. Better ferroelectric properties at room temperature, i.e., increased remnant polarization (38% more) and very low field switchability (225% less) are observed for x=5% sample as compared to other samples and the results are explained in terms of grain size effects. With Sn doping, merging of all the phase transitions into a single one is observed for x=10% and for x=5%, the tetragonal to orthorhombic transition temperature is found close to room temperature. As a consequence better electro-caloric effects are observed for x=5% sample. BaTiO$_3$ doped with 15% Sn shows the co-existence of ferroelectric and relaxor behavior in the broad temperature range and finally shows the re-entrant relaxor like behavior probed by temperature dependent XRD, dielectric and ferroelectric measurements.

The second part of chapter-3 discusses the structural, dielectric and ferroelectric properties of polycrystalline BTO ceramics prepared with hybrid sintering i.e., microwave assisted radiant heating (MARH). It is observed that the permittivity ($\varepsilon$) and true switched ferroelectric charge density ($Q_{sw}$) of BTO ceramics can be enhanced by employing MARH. An enhancement of 58% in $\varepsilon$ and 17% in $Q_{sw}$ is observed for the BTO sample prepared with 30% microwave power applied during MARH as compared to the conventional
radiant heating. The results are explained in terms of microstructure resulting from the microwave assisted sintering. And finally, third part of the chapter-3 reports the aging and de-aging behavior of un-doped polycrystalline BTO explored with the P-E measurements. The double hysteresis (P-E) loop is observed for the aged sample and it is observed that the relationship between the aging time and the developed internal bias field is similar to as that of reported for acceptor doped BTO and other ferroelectric materials in literature. However, the relaxation rates are quite different as compared to that of acceptor doped BTO. This is explained in terms of defect concentration. The de-aging behavior is studied with different methods viz., thermal relaxation, combined use of temperature and applied electric field. Heating the sample slightly above its \(T_c\) and cooling in the presence of external applied dc-field is observed to completely remove the pinching and bring the internal bias field to zero.

Chapter-4 discusses the preparation of polycrystalline magneto-electric BTO–NiZnFe\(_2\)O\(_4\) ceramics and their characterization using x-ray diffraction, scanning electron microscopy, magnetization and ferroelectric measurements. The present chapter is broadly divided into two parts. The first part of chapter-4 deals with the study of polycrystalline BTO-NiZnFe\(_2\)O\(_4\) composites prepared with conventional solid-state reaction method. Since the magnetic and magneto-striction properties of NiZnFe\(_2\)O\(_4\) can be tuned by changing the cation distribution, this aspect is exploited in the present work to tailor the magneto-electric (ME) properties of BTO–NiZnFe\(_2\)O\(_4\) composites. However, the electrical resistivity of the ferrites is usually more than an order of magnitude less as compared to typical ferroelectric materials, in such ME composites therefore what becomes an important issue is the leakage current contribution from ferrite phase to the observed polarization. Therefore, before probing the effect of NiZnFe\(_2\)O\(_4\) cation distribution on ME coupling of BTO-NZFO composites, the fraction of the NiZnFe\(_2\)O\(_4\) phase is optimized for better ferroelectric (FE) and ME properties. Maximum ME coupling is observed for 10% ferrite in the composite from Positive Up Negative Down (PUND) measurement, which is more advanced as compared to conventional ferroelectric (P-E) loop to capture the true polarization. Once the fraction of NiZnFe\(_2\)O\(_4\) phase is optimized, series of composite ceramic samples viz., 0.9BTO-0.1Ni\(_{1-y}\)Zn\(_y\)Fe\(_2\)O\(_4\)
(y=0 to 1.0 at an interval of 0.2) are prepared in order to look at the variation of ME coupling as a function of cation distribution. The prepared composites are studied by x-ray diffraction (XRD) for phase purity; room temperature magnetic (M-H) and ferroelectric (P-E) loops to check for the coexistence of magnetic and electric orderings at room temperature. Finally, P-E loop measurements at room temperature are carried out after subjecting the composites to magnetic field poling to check for the ME coupling. The maximum ME coupling has been found for the composite consisting Ni$_{0.8}$Zn$_{0.2}$Fe$_2$O$_4$ as a magnetic phase and explained in terms of magneto-striction behavior.

The second part of chapter-4 reports the preparation of 0.9BaTi$_{0.95}$Sn$_{0.05}$O$_3$ (BTSO)-0.1Ni$_{0.8}$Zn$_{0.2}$Fe$_2$O$_4$ composite multiferroics with MARH sintering. Simultaneous existence of ferroelectric and magnetic order has been studied by the room temperature P-E loop and M-H loop measurements. When prepared using MARH, it is observed that Ni$_{0.8}$Zn$_{0.2}$Fe$_2$O$_4$ grains are uniformly distributed in the BTSO matrix as compared to the composite sample prepared with only radiant heating. Enhanced dielectric as well as switched charge density and reduction of leakage current have been observed for the composite samples prepared with MARH. The results are explained in terms of microstructure of the prepared composites. The present results demonstrate that one can enhance/tune the functional properties of multiferroic BTSO-NZFO composites employing MARH preparation, which can be considered as a new approach for the preparation of composite multiferroics with enhanced dielectric and ferroelectric properties.

Finally, chapter-5 discusses the structural, magnetic, ferroelectric and magneto-electric (ME) studies of bilayer thin films of BaTiO$_3$ (BTO)-Ni$_{0.5}$Zn$_{0.5}$Fe$_2$O$_4$ (NZFO) prepared using pulsed laser deposition on platinized silicon substrate. Thickness of BTO layer (≈400 nm) is kept the same and the thickness of the NZFO layer is varied from 25–150 nm to study the effect of magnetic layer thickness. The prepared films are studied using grazing incidence x-ray diffraction (GIXRD), Raman spectroscopy, atomic force microscopy (AFM), magnetization and ferroelectric loop tracer measurements. From GIXRD, all the films are found to be polycrystalline in nature. Ferroelectric (tetragonal) and cubic phases of BTO and NZFO, respectively, is confirmed from the Raman
measurements. It is observed from the AFM data that the growth of NZFO layer is correlated with that of bottom BTO layer for thickness ≈ 75 nm resulting in stress on the BTO phase evidenced from shifting of Raman mode corresponding to BTO. Room temperature magnetic and ferroelectric properties are shown by recording the room temperature M-H and P-E loops. Further, PUND measurements are carried out to capture the true ferroelectric polarization of the films. ME properties of the films was probed by recording P-E measurements and PUND in the presence of external magnetic field and it is observed that the ME coupling is maximum for the film with NZFO layer thickness of 75 nm. The observed results are explained in terms of stress mediated ME coupling and indicate that inherent stress, if present, plays a role in ME composites apart from stress generated by the ferrite phase due to magneto-striction. Second part of chapter-5 deals with the case study on Co/BTO thin film. Co was deposited on BTO/Si in ultra high vacuum (2x10\(^{-8}\) mbar) with the help of e-beam evaporation and simultaneous in-situ magneto-optical Kerr effect (MOKE) data has been recorded in the longitudinal geometry. Temperature dependent MOKE data has been recorded from 450 K to 300 K. Broad anomaly in the coercive field has been observed around the 430-373 K, which correspond to the curie temperature of BTO depicts the possibility of controlling the magnetic properties of thin films using strain mediated ME coupling.

In a nutshell, following points are highlighted in the present thesis work.

- The functional properties of BTO viz. ferroelectricity and electro-caloric are enhanced with suitable doping (i.e., Sn at Ti site) which also resulted in novel phenomena such as re-entrant relaxor. Better ferroelectric properties at room temperature, i.e., increased remnant polarization (38% more) and very low field switchability (225% less) are observed for 5% Sn doping sample as compared to other samples and the results are explained in terms of grain size and FE domains configurations.
The observed considerable EC strength in Sn doped BTO makes it a promising candidate for non-toxic, low energy (field) and room temperature based applications.

Ageing and de-aging behavior in un-doped BTO has been studied by means of PE loops. Electric poling has been found suitable for de-aging.

Room temperature magneto-electric coupling has been tuned in BTO-NZFO composites by means of cation distribution in the magnetic phase and probed by PE and PUND data before and after the magnetic poling.

Microwave assisted radiant hybrid sintering has been used for the preparations of ferroelectric and multiferroic composites in the present work. As a consequence of the two directional heating better microstructure is observed resulting in improved functional properties.

Role of residual stress on the magneto-electro coupling in composite thin films is unambiguously presented.

6.2: Future scope

- Measuring the electro-caloric (EC) strength using direct methods i.e., measurement of temperature change directly with the application of external electric field. Even though, both the direct and the Maxwell relation approach (which is used in the present work and also mostly by other researches) are reported to yield the same EC values, the direct measurement of EC is an experimental challenge and is expected to be free from errors, if any.

- Establishing quantitative relation between defect concentrations and aging phenomena in BaTiO$_3$ based ferroelectric (FE) thin films. Ion beam irradiation would be used for this purpose. Various FE compounds are studied in this context either with different valence cations doping to create defects or with accidental defects which are formed during the synthesis. However, the quantitative relationship between the defect
concentration and the aging phenomena is yet to be reported. This could be mainly because of the fact that it is not possible to estimate the defect concentration quantitatively in the case of doped FE samples. Therefore, irradiating BTO thin films with different doses of swift heavy ions (which would make it possible to simulate / calculate the generated defect concentration) is expected to establish a relation between the defect concentration and the rate of aging.

• Exploring the role of residual stress/strains on magneto-electric (ME) coupling phenomena in epitaxial BaTiO$_3$ (BTO) based composite thin films. Since the ME phenomena is a strain mediated one, the presence of residual stresses which can be introduced because of lattice mismatch, thermal mismatch, compositional deficiencies etc., is worth of exploring. Epitaxial thin films of BTO with different thickness values, which is expected to introduce epitaxial strains, would be deposited for this purpose using pulsed laser deposition and integrated with a suitable ferromagnetic layer. Reciprocal space mapping measurements which gives the unambiguous information regarding the epitaxial strains, would be carried out to estimate the residual strain in the films and would be correlated with the ME coupling.