

**INVESTIGATIONS ON STRUCTURAL AND  
MULTIFERROIC PROPERTIES OF  $\text{BiFeO}_3$  -  $\text{ABO}_3$  TYPE  
SOLID SOLUTION CERAMICS PREPARED  
BY SOL - GEL ROUTE**

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## SYNOPSIS

The term ‘multiferroic’ was initially coined by Schmid [1] to define a material possessing two or more primary ferroic properties (ferroelectricity, ferromagnetism, ferroelectricity) which occur in the same phase. Such materials can exhibit a coupling between any of these two properties, making the field of multiferroics very attractive for research from the both fundamental and technological point of view as well [2–6]. In the past one decade or more, an extensive research has been carried out in the field of multiferroics to find the solutions of a few problems faced by researchers worldwide [3]. To restore these properties, the stoichiometry has been a great challenge in these materials [4]. Co-existence of more than two ferroic orders at room temperature, especially in bismuth ferrite, has been the subject of major concern for the scientists worldwide which involves fascinating physics to couple the two physical phenomenons. One of the most appealing aspects of multiferroics is the so-called magnetoelectric (ME) effect, which means ferroelectric polarization can be controlled by a magnetic field and conversely, magnetization can be controlled by an electric field. This effect could be exploited for the development of new applications such as novel spintronics and spin valves with electric field tuneable devices, or even non-volatile multi storage devices like FeRAMs (ferroelectric random access memories) and MRAMs (magnetic random access memories). Though, there are limited materials that exhibit a strong ME effect. Most of them almost are antiferromagnetic and possesses weak ferromagnetism [4-5], which is governed by two mechanisms, one originates from anisotropic super-exchange interactions, leading to weak ferromagnetism, normally have higher Néel temperatures. The other one is from single spin anisotropy energy and materials with this type of magnetism tend to have low Néel temperatures [Mariya 1960], which limits their applications.  $\text{BiFeO}_3$  (BFO) is a unique class of materials which possesses G-type antiferromagnetism and ferroelectricity simultaneously at room temperature.

In general, magnetoelectric phenomenon exhibits coupling between magnetization and electric field or polarization and magnetic field. Induction of polarization (P) by applied magnetic field (H) or vice-versa has been observed long back in 1888 in an experiment carried out by Rongten where dielectric material gets magnetized when placed in an electric field [6]. Later in 1894, Curie recommended the possibility of magnetoelectric effect in some crystals [7]. In 1961,  $\text{Cr}_2\text{O}_3$

was recognized as first magnetoelectric material, which has shown magnetoelectric coupling coefficient of the order of  $10^{-12}$  S/m [8]. The first multiferroic material discovered was nickel iodine boracites ( $\text{Ni}_3\text{B}_7\text{O}_{13}\text{I}$ ) with magnetic ordering below  $T_N$  ( $\sim 60$  K) and ferroelectric one below  $T_C$  ( $\sim 400$  K) [9-10]. The boracites are also unfeasible materials for device applications as they have large unit cell and grow in needle shapes, which exhibit magnetoelectricity only at extremely low temperatures [11].

For integration of ferroelectricity and magnetism, the conceptually simplest strategy is to synthesize materials with discrete functional units. An alternative way is attributed to  $\text{ABO}_3$  type perovskite oxides, wherein A-sites are usually occupied by cations with a  $ns^2$  electron configuration, such as  $\text{Bi}^{3+}$ ,  $\text{Pb}^{2+}$ , which favor the stability of ferroelectrically distorted structures. While, B-sites are occupied by transition metal ions contributing to magnetism. Normally, non-centro-symmetric distribution of charged ions along with magnetic ions in the same formula unit provides a strong ferroelectricity and magnetism. This strategy evades the mutually exclusive ferroelectricity and magnetism at the same site because; ferroelectricity originates from A-site ions and magnetism generated from B-site magnetic ions. It provides an effective combination of the electric and magnetic orders along with a mutual control between them.  $\text{BiFeO}_3$  and  $\text{BiMnO}_3$  are the well known examples for this class of materials, where A-site ions via the lone pair mechanism lead to the ferroelectricity and B-site ions produced magnetism. In  $\text{BiFeO}_3/\text{BiMnO}_3$ , the shifting of  $\text{Bi}^{3+}$  ions from centro-symmetric positions relative to surrounding oxygen ions induce ferroelectricity and unpaired magnetic spins of  $\text{Fe}^{3+}/\text{Mn}^{3+}$  ions provide magnetism. Amongst all single phase multiferroics,  $\text{BiFeO}_3$  (BFO) is the widely investigated material. Perovskite oxides in general do not have the same mechanism for the origin of spontaneous polarization. In  $\text{BaTiO}_3$ , shift of center Ti ion is responsible for ferroelectricity while in  $\text{PbTiO}_3$  (PT) the lone-pair electrons of Pb ion along with the shift of Ti-ion both are responsible for spontaneous polarization below  $T_C$  [12]. In case of magnetic perovskites, magnetization comes from unpaired d-electrons of the B - site cations like  $\text{Fe}^{3+}$ ,  $\text{Mn}^{3+}$ ,  $\text{Cr}^{3+}$  etc. Thus, existence of magnetism in these type of materials is caused by spin order [13-14], magnetic exchange interaction [15], and charge order [16]. Based on these ideas, new oxides have been theoretically predicted to be magneto - electric multiferroic, which further await direct experimental verification [17-18]. Meanwhile, the world wide attention has been

drawn to study BFO in the last few years. Smolenskii's group found it difficult to grow BiFeO<sub>3</sub> into single crystals [19]. Also as bulk materials, BFO samples are found to be highly conducting. High conductivity in this specimen has been explained in term of defects like oxygen vacancies and mixed variable valence states of Fe as well [19-20].

So far, BiFeO<sub>3</sub> (BFO) is the only single phase material that shows multiferroic orders at room temperature. It possesses rhombohedrally distorted perovskite crystal structure with R3c space group symmetry, ferroelectricity with high Curie temperature ( $T_C \sim 830^\circ\text{C}$ ) and G-type antiferromagnetism with Neel Temperature ( $T_N \sim 370^\circ\text{C}$ ) [21]. Though, these materials are reported to have low magnetization due to antiferromagnetic order of cycloid spin structure [18], while, from device point of view, a large magnetic moment is required in addition to the strong ferroelectricity. In view of this, BiFeO<sub>3</sub> is thought to be one of the few existing multiferroics, which can be expected as a useful material for device application at room temperature. In BFO, the presence of incommensurate cycloid spin structure, with a periodicity of 62 nm along [111] results in the cancellation of macroscopic magnetization and hence leading to very small magnetic moment [22-23]. Moreover, a large leakage current density caused by charge defects, nonstoichiometry and secondary phases make it difficult to observe a well-saturated ferroelectric hysteresis loop. These properties of BFO hinder its use in electronic devices. In order to improve electrical and magnetic properties, partial substitution of rare-earth ions at Bi<sup>3+</sup> - sites or/and transition metal ion at Fe<sup>3+</sup> - sites have been carried out [23-27]. Actually, these substitutions have already been found to be effective to modify ferroelectric or the magnetic properties to the some extent in recent years. However, still few issues like leakage current, defects formation etc. could not be resolved well and therefore, there is a huge scope to improve electrical and magnetic properties by compositional tuning i.e. by substitution of foreign element in BiFeO<sub>3</sub>. With this background in mind, the objective of the present work is to study BiFeO<sub>3</sub> – ABO<sub>3</sub> type solid solutions formation and to investigate its structural, electrical, magnetic and ferroelectric properties of solid solutions compounds. The literature survey, experimental procedure for synthesis and characterization of specimen samples, results and discussion of research work have been organised into eight chapters of this thesis. Chapter wise description of the research work is discussed in the following sections.

### **Aim of the present work:**

The objective of the present work was to enhance the multiferroic properties of BFO by substitutional method which can be done by synthesizing solid solutions of BFO – ABO<sub>3</sub> type compounds. For this, following steps have been taken into consideration.

1. To optimize the synthesis process for the preparation of pure phase of BiFeO<sub>3</sub> (BFO) and other end member ABO<sub>3</sub> compound (PZT) separately in order to have self reliability.

2. After optimizing synthesis process, the followings systems have been chosen to synthesize in the form of solid solutions.

(i) (1-x) BiFeO<sub>3</sub> – (x) PbZr<sub>0.52</sub>Ti<sub>0.48</sub>O<sub>3</sub> [abbreviated as (1-x) BFO – (x) PZT] for composition range  $0.0 \leq x \leq 1.0$

(ii) (1-x) BiFeO<sub>3</sub> – (x) Ba<sub>0.70</sub>Sr<sub>0.30</sub>TiO<sub>3</sub> [abbreviated as (1-x) BFO – (x) BST] with  $x \leq 0.20$ .

(iii) (0.70) BiFeO<sub>3</sub> – (0.30) PbTiO<sub>3</sub> [abbreviated as (1-x) BFO – (x) PT] with Co doping upto  $x \leq 0.12$ .

3. All these materials have been prepared after optimising synthesis process followed by structural and electrical characterizations.

**Chapter I:** This chapter describes a brief introduction about ferroelectricity, magnetism and multiferroicity along with different types of multiferroic materials, the origin of ferroism and history of these materials. In addition to this, it includes literature survey on recent developments and motivation to carry out research work in the field of multiferroics.

**Chapter II:** The details of experimental techniques for the synthesis and characterization of materials, used in due course of the present work, have been described in this chapter. Optimization of synthesis route and processing conditions has been carried out for a few samples i.e. end members in BFO – PZT system to ensure reliability and reproducibility. For this, BFO has been synthesized by solid state as well as sol-gel route and it has been found that BFO prepared by sol-gel route has shown relatively better properties than the sample prepared by solid state route. Thereafter, all the samples have been prepared by sol-gel route. All the samples have

been heat treated at appropriate temperature to form solid solutions. Structural characterization for all these samples has been carried out using X-ray diffractometer (XRD) and Raman spectroscopy. A few samples in each composition for every system have been sintered in the form of cylindrical pellets and coated with silver paste. These samples have been used for the purpose of electrical characterization like dielectric measurements from room temperature to 500°C using Impedance Analyser (NOVO Control,  $\alpha$  - AT, Germany). Hysteresis loop measurements have been carried out using P – E loop tracer and VSM (Lakeshore VSM 7410). Current density of all these samples has been measured at room temperature using Precession Analyzer.

**Chapter III:** This chapter describes the optimization of synthesis process for BFO and BFO modified PZT ( $\text{PbZr}_{0.52}\text{Ti}_{0.48}\text{O}_3$ ). Pure BFO has been synthesized by sol-gel and solid state route. Since, sol-gel route is known to produce pure phase formation at slightly lower temperature than solid state route. It has been observed that pure phase formation of BFO has been obtained only at  $\sim 750^\circ\text{C}$  whereas by solid state route, it shows some impurity phases which are found to be eliminated when heat treated at high temperature. Similarly, the processing conditions of the other end member (PZT) have also been optimized. For this, sintering temperature has been optimized for BFO modified PZT. Composition with  $x = 0.05$  in  $(1-x)$  PZT –  $(x)$  BFO system has been prepared by sol-gel route. Structural characterization has revealed pure phase formation of PZT as well as BFO modified PZT. Lattice parameters have been determined by Rietveld refinement of XRD data. Electrical and magnetic properties have been measured. On comparing the results, it has been found that Sol-Gel route would be more appropriate and convenient to synthesize the materials in the form of single phase solid solutions.

**Chapter IV:** This chapter describes the preparation of solid solution compounds in the  $(1-x)$  BFO –  $(x)$  PZT system within the composition range  $0.0 \leq x \leq 1.00$ . All these composition have been prepared by sol-gel method followed by structural characterization using x-ray diffraction (XRD) and Raman spectroscopy. The structural analysis of XRD data for all the samples has been carried out by Rietveld refinement using Full Prof software. This analysis has revealed the structural stability with rhombohedral (R3c) phase for  $x \leq 0.10$ , monoclinic (Cc) for  $0.20 \leq x \leq 0.40$ , monoclinic (Cm) for  $0.50 \leq x \leq 0.70$ , coexistence of monoclinic along with tetragonal

symmetry (Cm+P4mm) for  $x = 0.80$  and  $0.90$  and pure tetragonal (P4mm) for  $x = 1.00$ . These phase transitions have been well supported by Raman spectroscopy. The lattice parameters and % of phases in the two phase coexistence region have been determined.

**Chapter V:** In this chapter detailed study on the dielectric, ferroelectric, magnetic properties and leakage of all the compositions ( $x$ ) within the range  $0.0 \leq x \leq 1.00$  in  $(1-x)$  BFO –  $(x)$  PZT system have been carried out. Various aspects of dielectric, leakage current, ferroelectric magnetic and electrical conduction behaviour of these compositions are examined. It has been observed from  $\epsilon_r$  vs  $T$  plots in the temperature range  $40^\circ\text{C} - 500^\circ\text{C}$  at 1, 10, & 100 kHz that overall, three dielectric anomalies are seen. First one at  $\sim 250^\circ\text{C}$ , second one at  $\sim 350^\circ\text{C}$  and third one, although, does not appear for  $x \leq 0.20$ , however seen for higher  $x$ , say  $x \geq 0.30$ . The corresponding peaks for  $x = 0.40$  are found to occur at  $\sim 150^\circ\text{C}$ ,  $350^\circ\text{C}$  and  $\sim 450^\circ\text{C}$  respectively. First anomaly is attributed to defects states in BFO, second to magnetic transition temperature i.e. Neel temperature and third one to Maxwell Wagner type effect upto  $x < 0.50$ . Further, for higher  $x$ , PZT rich composition side i.e.  $0.50 \leq x \leq 0.70$ , three dielectric anomalies have been clearly observed which are found to shift towards low temperature side with increasing  $x$ . low temperature anomalies are found to disappear for  $x = 0.90$  and  $1.0$ . For  $x = 1.0$ , dielectric anomaly occurs at  $\sim 385^\circ\text{C}$  which agrees well with reported data. High temperature anomalies may be assigned to ferroelectric to paraelectric transition which takes place around Curie Temperature ( $T_c$ ).  $T_c$  has been found to decrease as PZT content increases i.e. for  $0.50 \leq x \leq 1.0$  which seems to be due to active role of Pb at Bi site and Zr/Ti at Fe sites. The possibility of defects are not be ruled out for BFO rich side compositions, which seems to be decreased with increasing  $x$  and therefore, low temperature anomalies are suppressed for higher concentration of dopant ( $x$ ). This can be understood by observing dielectric loss which decreases with increasing  $x$  upto  $x < 0.50$ . Further, this anomaly is seen to be frequency and temperature dependent which may be attributed to defects, and with increasing  $x$ , decrease in defect concentration eventually suppresses the dielectric anomalies in dielectric plots. These dielectric anomalies are frequency dependent for  $0.50 \leq x \leq 0.90$  and becomes independent for  $x = 1.00$ , indication transition from relaxor to non-relaxor behavior in these these materials. Temperature dependent conductivity has been classified in a few temperature regimes  $T_1$ ,  $T_2$ ,  $T_3$  and  $T_4$  starting from low temperature to high temperature respectively. The linear behaviour in the temperature regimes ( $T_1$ ) indicates an

Arrhenius type thermally activated hopping process. The hopping charge carrier dominates at low temperature, small polaron and oxygen vacancy dominates in intermediate and high temperature range respectively. Remanent magnetization has been found to increase with  $x$  upto  $x \leq 0.30$  and thereafter starts decreasing which may be attributed to the increasing concentration of non magnetic ions at B-site in BFO lattice. Remanent polarization has been found to increase with increasing  $x$ . The enhanced polarization may be understood in terms of increased stereochemical activity due to addition of Pb ions at A-sites and reduction in leakage current density, which is suggested due to restricted Bi evaporation due to  $Ti^{4+}/Zr^{4+}$  addition at  $Fe^{3+}$  sites.

**Chapter VI:** In this chapter, structural, dielectric, ferroelectric and magnetic properties of a few compositions with  $x \leq 0.20$  in  $(1-x)$  BFO –  $(x)$   $Ba_{0.70}Sr_{0.30}TiO_3$  (BST) have been discussed. It has been established that even a small fraction of Ba/Sr substitution at A-site and Ti at B –site can significantly enhance the magnetic and ferroelectric properties of BFO and hence magnetoelectric effect. All these BFO – BST ceramics, prepared by sol-gel technique, have shown single phase formation. Rietveld refinement of XRD data and Raman analysis confirmed the compositional driven phase transformation from rhombohedral upto  $x = 0.15$  to tetragonal for  $x = 0.20$ . Ionic radii of alkaline rare-earth elements  $Ba^{2+}$  (1.42 Å) and  $Sr^{2+}$  (1.26 Å) are quite larger than that of  $Bi^{3+}$  ion (1.17 Å) at A-sites and  $Ti^{4+}$  (0.604 Å) is less than  $Fe^{3+}$  (0.645 Å) at B-sites. Significant difference in the ionic radii of host and substituent cations has lead to the distortion in the lattice and hence structural phase transition which eventually leading to the modified properties of BFO – BST solid solution compositions. The improved dielectric properties obtained are due to change in volume of unit cell, caused by tetragonal distortion. Dielectric loss has been found to decrease with increasing  $x$  upto  $x \leq 0.20$  which reveals the reduction in defect concentration with increasing  $x$ . It has been further supported by measuring current density. Current density has been found to be decrease with increasing  $x$ , eventually modifying ferroelectric hysteresis loop which in turn has enhanced remanant polarisation. Magnetic measurements have shown a weak ferromagnetic behaviour for  $x = 0.00$  and enhance magnetization has been obtained for the samples with increasing dopant concentration ( $x$ ). The highest magnetization with characteristic M-H loop has been obtained for  $x = 0.20$  which may be due to suppression of spin cycloid structure of Fe-O-Fe network due to insertion of Ti at Fe sites.

**Chapter VII:** This chapter describes our studies on a typical solid solution composition of 0.70BFO – 0.30PT with doping of Co with  $x \leq 0.12$ . In this chapter, an effort has been made to enhance magnetization by modifying BFO – PT solid solution with the doping of Co transition metal ion. In addition to this, its effect on the structural, dielectric, ferroelectric properties and conduction have been studied. In view of the above, Co doped BFO – PT [i.e.  $(0.70)\text{Bi}(\text{Fe}_{1-x}\text{Co}_x)\text{O}_3 - (0.30)\text{PbTiO}_3$ , where  $x = 0.03, 0.06, 0.09$  and  $0.12$ ] ceramics were prepared by sol-gel technique. Rietveld refinement of XRD patterns demonstrated the co-existence of tetragonal (P4mm) and rhombohedral (R3c) symmetry phases for pure and all dopants up to  $x = 0.06$ . Thereafter, structural transformation has been observed from two phase (R+T) co-existence to tetragonal (T) phase upto  $x = 0.12$ . These structural transitions with increasing  $x$  may be attributed to the ionic radii mismatch between Co and host cations (Fe and Ti). Dielectric studies have revealed that dielectric constant ( $\epsilon_r$ ) increases and dielectric loss ( $\tan \delta$ ) decreases with  $x$  for all dopants. This improvement in dielectric constant may arise due to increased volume percentage of tetragonal phases with  $x$ . Reduction in the value of  $\tan \delta$  with  $x$  indicates that the formation of oxygen vacancies are suppressed. Suppression in defect concentration is also supported by measurement of Leakage current density which is found to decrease with increase  $x$ . M-H hysteresis data has revealed weak ferromagnetism for BFO – PT solid solution and enhanced magnetization for  $\text{Co}^{2+}$  modified BFO – PT ceramics. It has been observed that large value of remanant magnetization ( $M_r$ ) for  $\text{Co}^{2+}$  modified ceramics has been obtained which may be attributed to the contributions of magnetic moment due to high spin state electrons in d orbital (no of Bohr magneton). In general, the magnetization has been found to increase with increasing  $x$ .

**Chapter VIII:** The chapter describe the summary of the results and future scope. It has been clearly observed that the BFO – PZT system shows solid solution formation in the composition range  $0.0 \leq x \leq 1.00$  with various phase transformation from rhombohedral, monoclinic and two phase co-existence to tetragonal phase for the intermediate compositions. Similarly, BFO – BST system has shown phase transition from rhombohedral for  $x = 0.0$  to tetragonal symmetry for  $x = 0.20$ . Multiferroic properties (remanant polarisation and magnetization both) have been found to improve with increasing  $x$ . It has been observed from transition metal ion (Co) doped BFO – PT

system, multiferroic properties are found to be enhanced with increasing x. Decrease in current density with x (supported by decrease in  $\tan \delta$ ) in all the systems indicates reduction in defect concentration which finally improves ferroelectricity in these samples. Activation energy values have been estimated in different linear temperature regimes in all the systems. Based on these activation energy values, the appropriateness of conduction mechanism active in these materials, has been suggested. This chapter also discusses the future scope and related issues of the BFO – ABO<sub>3</sub> type solid solutions in the form of thin films for memory applications.

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## LIST OF PUBLICATIONS

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### **PAPER PRESENTED IN CONFERENCES**

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- [2] **Subhash Sharma**, Vikas Singh and r. K. Dwivedi, “*Synthesis and dielectric behavior of (1-x)Pb(Zr<sub>0.52</sub>Ti<sub>0.48</sub>)O<sub>3</sub> - xBiFeO<sub>3</sub> solid solutions by Sol-gel process*,” International conference and workshop on Nanostructured ceramics and other nonmaterials (ICWNC-2012), held at Delhi University, March 13-16, 2012.
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