

STUDY OF ISOVALENT AND ALIOVALENT IONS SUBSTITUTION IN BiFeO_3 MULTIFERROIC CERAMICS

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DOCTOR OF PHILOSOPHY

By

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SYNOPSIS

The term multiferroics has been coined to describe materials in which two or all three ferroic orders, i.e. ferromagnetism, ferroelectricity and ferroelasticity occur in the same phase [1]. Herein, the spontaneous magnetization (M_s) can be reoriented by external magnetic field (H); spontaneous polarization (P_s) can be reoriented by external electric field (E), and the spontaneous deformation (ϵ_s) can be reoriented by external stress (σ). Multiferroics are interesting not only because they show coexistence of ferroelectric and magnetic properties, but also due to the magnetoelectric effect, in which electrical polarization can be induced by applying magnetic field and magnetization can be induced by applying an electric field. This type of effect can be utilized for the designing of novel spintronic devices such as tunnelling magnetoresistance (TMR) sensors, spin valves with electric field tunable functions [2] and multi-state memory devices in which data are written electrically and read magnetically [3].

In 1888, Rontgen observed that a moving dielectric body placed in an magnetic field, became magnetized or vice-versa [4]. Moreover, these are not the intrinsic effects in materials. In 1894, Curie envisaged the probability of magnetoelectric effect in some crystals [5] using crystal symmetry considerations which were subsequently coined by Debye as “magnetoelectric effect” [6]. Cr_2O_3 was the first material in which magnetoelectric effect was successfully observed with magnetoelectric coupling coefficient ~ 4.13 ps/m [7]. In the past, more than 100 compounds have been discovered exhibiting the magnetoelectric effect and remains key materials for the highly fascinating multiferroic research [8]. Unfortunately, in single phase compounds the magnetoelectric effect is usually too weak to be practically applicable.

One way to substantially improve the coupling between electric and magnetic orders is to utilize strong internal electromagnetic fields in the materials with large magnetic and electric susceptibilities. It is well known that the largest magnetic/electric susceptibilities are found in ferromagnetic/ferroelectric materials respectively. Ferroelectrics with ferromagnetism, i.e. ferroelectromagnets could be utilized for an improved magneto-electric effect [9]. Consequently, the term multiferroics was coined by Schmid, for those compounds which possess two or more primary ferroic orders (ferroelectricity, ferromagnetism, and ferroelasticity) [10].

It has proved difficult to discover new intrinsic multiferroic materials because the

mechanisms driving ferroelectricity and ferromagnetism are generally incompatible. Ferroelectricity is usually generated by transition metal compounds with empty d-orbits (d^0). For example, in BaTiO_3 the ferroelectricity is caused by cooperative shifting of the Ti^{4+} cation along the [111] direction; this off-centering is stabilized by covalent bonding between the oxygen 2p orbitals and the empty d-orbitals of Ti^{4+} [11]. On the other hand, ferromagnetism usually requires a transition metal with partially filled d-orbitals. Consequently, a different approach is required to combine these two properties.

For integration of ferroelectricity and magnetism, the conceptually simplest strategy is to synthesize materials with discrete functional units. Normally, we add the non-centro-symmetric units, which provide a strong dielectric response and ferroelectricity, together with magnetic ion units. An alternative way is attributed to ABO_3 type perovskite oxides, wherein A-sites are usually occupied by cations of a $(ns)^2$ valence electron configuration, such as Bi^{3+} , Pb^{2+} , which favor the stability of ferroelectrically distorted structures. While, B-sites occupied by magnetic ions contributing to 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. However, in this type of multiferroics, the coupling between ferroelectric and magnetic ordering is very weak due to their different source of origin.

The A-site in ABO_3 perovskite structure is always occupied by the ions with $(ns)^2$ electrons such as Bi^{3+} and Pb^{2+} . It allows magnetic transition metal ions to occupy B-site in ABO_3 structure so that the mutually exclusive condition to induced both magnetism and ferroelectricity is partially relaxed. BiFeO_3 and 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 Bi^{3+} ions from centro-symmetric positions relative to surrounding oxygen ions induced ferroelectricity and unpaired magnetic spins of $\text{Fe}^{3+}/\text{Mn}^{3+}$ ions provide magnetism. Amongst all single phase multiferroics, BiFeO_3 (BFO) is the widely investigated material.

In bulk form, BFO has been known to be an antiferromagnetic-ferroelectric multiferroic [12, 13]. It has antiferromagnetic Neel temperature $T_N \sim 643$ K and ferroelectric Curie

temperature $T_C \sim 1103$ K. BFO possess distorted rhombohedral perovskite structure with space group $R3c$ [14, 15]. The Fe magnetic moments are arranged in ferromagnetic manner within the pseudo cubic (111) plane, while connected antiferromagnetically between adjacent planes. Such type of magnetic ordering of Fe moments is known as G-type antiferromagnetic ordering. The observation of a macroscopic magnetization (i.e. weak ferromagnetism) is allowed due to symmetry driven canting of the antiferromagnetic sublattices if Fe spins are aligned perpendicular to [111] axis [16, 17]. However, the observation of macroscopic magnetization and linear magnetoelectric effect is prohibited due to a superimposed spiral spin structure in which the antiferromagnetic axis rotates through the crystal with an incommensurate long wavelength period ~ 62 nm [18-19].

Moreover, the synthesis of the BFO single phase is complicated, on one hand, by the high probability of the formation of impurity phases and, on the other hand, by the strong dependence of the physical properties on the oxygen stoichiometry and crystal perfection. Low leakage current as well as presence of magnetic moments in the crystal is compulsory for the practical application of BFO; therefore, particular interest has been paid for improving the dielectric properties, suppression of antiferromagnetic cycloidal spiral spin order and to ensure the optical behavior in visible range of BFO. Substitution of foreign elements might be an effective way to enhance the macroscopic magnetic moment because chemical doping can change electrical conductivity along with improvement in magnetic behavior via changing the ligand field of Fe ions.

Thus, BFO has drawn tremendous interest from researchers in recent years, both for the multiferroic properties and their applications as well as for use as a basis for lead-free ferroelectric and piezoelectric ceramics. Polycrystalline ceramics study has provided a great opportunity for understanding the fundamental properties of BFO because they are easy to synthesize as well as they provide a larger diversity of easily attainable compositional modifications compared to single crystals. This is because a slight change in atomic composition can produce large distortion within perovskite unit cell that might have dramatic impacts on the properties of the material such as structural evolution, transport properties, magnetic properties and polarization. Within the last decade, enormous growth has been made in the understanding of bulk BFO.

Objectives of the present work:

The main objectives of the present work are

1. To study the effects of isovalent ions (Dy^{3+} , Eu^{3+} , Gd^{3+}) substitution at A site in BiFeO_3 and isovalent (Gd^{3+} and Pr^{3+}) and aliovalent (Zr^{4+} and Ti^{4+}) ions cosubstitution at A and B sites, respectively in BiFeO_3 ceramics.
2. To study phase formation, surface morphology by using XRD, Raman and SEM/FESEM techniques for better understanding of the properties of these materials.
3. To investigate the magnetic, dielectric and optical properties of synthesized materials and its correlation with their structure in order to understand the fundamental physics which would lead to open the door to design the practical devices utilizing multiferroic properties.

Materials synthesized:

1. **Single A site doped BiFeO_3 systems:** $\text{Bi}_{1-x}\text{Dy}_x\text{FeO}_3$ ($x = 0.0, 0.03, 0.05, 0.07, 0.10, 0.12$), $\text{Bi}_{1-x}\text{Eu}_x\text{FeO}_3$ ($x = 0.0, 0.03, 0.05, 0.07, 0.10, 0.12, 0.15$) and $\text{Bi}_{1-x}\text{Gd}_x\text{FeO}_3$ ($x = 0.0, 0.03, 0.06, 0.10, 0.12, 0.15$) ceramics synthesized by the solid state reaction method.
2. **A and B sites codoped BiFeO_3 systems:** $\text{Bi}_{1-x}\text{Gd}_x\text{Fe}_{1-y}\text{Ti}_y\text{O}_3$ ($x = 0.0$ and 0.10 ; $y = 0.03, 0.06, 0.10$), $\text{Bi}_{1-x}\text{Gd}_x\text{Fe}_{1-y}\text{Zr}_y\text{O}_3$ ($x = 0.0$ and 0.10 ; $y = 0.03, 0.06, 0.10$), $\text{Bi}_{1-x}\text{Pr}_x\text{Fe}_{1-x}\text{Zr}_x\text{O}_3$ ($x = 0.03, 0.06, 0.10$) and $\text{Bi}_{1-x}\text{Pr}_x\text{Fe}_{1-x}\text{Ti}_x\text{O}_3$ ($x = 0.03, 0.06, 0.10$) ceramics prepared by the solid state reaction method.

Chapter I deals with introduction to multiferroics and magneto-electric. This chapter features other key material aspects in the design of novel devices such as actuators, transducers and storage devices. The physical concepts of multiferroicity along with the current challenges for the integration of magnetism and ferroelectricity into a single-phase system are the highlight of this chapter. The idea and possible outcomes of combining the electric and magnetic orders are summarized in detail to understand the motivation of undertaking this research topic. Further, we have discussed about the problems associated with single phase BiFeO_3 multiferroic and strategies to overcome these problems by chemical substitution.

Chapter II describes the experimental part of the entire thesis work, wherein the detailed aspects of synthesis and characterization methods are included. Thus, for synthesis process, solid state reaction synthesis route and for characterization, the physical principle, design and construction part of X-ray diffraction (XRD), Raman spectroscopy, Scanning electron microscopy (SEM), Vibrating samples magnetometer (VSM), Superconducting quantum interference device (SQUID), Electron spin resonance (ESR), UV-Visible spectrometer, and Fourier transform infrared (FTIR) spectroscopy and dielectric measurement are discussed in detail.

In **Chapter III**, we discuss the detailed result obtained during the Dy doping in BFO ceramics. Various aspects of structural, magnetic, vibrational, optical and dielectric responses for different concentration of Dy doped BiFeO₃ were examined. The structural analysis results of XRD and Raman spectroscopy are presented along with the temperature dependent magnetization studies. The ESR studies to confirm the hence obtained magnetic properties due to changes in magnetic behavior of Fe³⁺ ions are discussed. Other optical studies along with the possible application of such a multiferroic material are also presented at the end of the chapter. Finally, complex impedance study enables us to separate the grain and grain boundary contributions in the materials and the grain and grain boundary contributions decrease with increase in temperature indicating a negative temperature coefficient of resistance for all samples.

(The results of this work are published in (i) Journal of Physics and Chemistry and Solids, vol. 75, pp. 105, 2014, (ii) Ceramic International, In Press, doi: 10.1016/j.ceramint.2014.11.012)

Chapter IV features the detailed result obtained during the Eu doping in BFO ceramics. Various aspects of structural, magnetic, vibrational, optical and dielectric responses for different concentration of Eu doped BiFeO₃ are examined. The structural analysis results of XRD and Raman spectroscopy and room temperature magnetization studies are presented in this chapter. The optical studies via UV-Vis and Raman spectroscopy for analyzing the band gap engineering and substitution induced structural transformation respectively are discussed in detail.

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Chapter V explains about the Bi substitution by transition element Gd as well as the Gd-Ti co-substitution for Bi and Fe respectively. The composition induced structural and phase analysis results for Gd substituted BFO ceramics are detailed with the help of XRD and corresponding Rietveld refinement. The enhancement in magnetic behavior and formation of magnetic clusters are summarized by analyzing magnetic and ESR measurements. The correspondence of reported results is supported by the particle size estimation from XRD and FESEM.

Similarly, the effects of substitution of Ti/Zr at Fe-site and Gd at Bi-site in BFO are summarized in this chapter. The composition induced structural and phase analysis results are detailed with the help of XRD and corresponding Rietveld refinement. The enhancement in magnetic behavior and formation of magnetic clusters are summarized by analyzing magnetic and ESR measurements. Some useful electrical measurements of dielectric properties are also included in this chapter.

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In **Chapter VI**, we discuss about the effect of Pr and Zr codoping at Bi and Fe site in BFO respectively. Rietveld analysis of XRD patterns and Raman spectra are presented to study the phase identification and structural analysis. Presence of weak ferromagnetism has been confirmed from magnetic measurement and ESR spectroscopic technique. Reduction in concentration of Fe^{2+} ions is also confirmed from XPS analysis and dielectric measurement. Band gap information and vibration study are also discussed for Pr and Zr codoped BFO ceramics. Finally, the effect of Pr and Zr codoping on the impedance and modulus behavior of BiFeO_3 lattice is also discussed.

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In **Chapter-VII**, effect of Pr and Ti co-substitution on structural, magnetic, optical and dielectric properties of BFO ceramics has been studied. Like previous cases structural phase analysis is determined with X-ray diffraction and Raman spectroscopy. Along with microstructural studies,

magnetic performance has been observed at room temperature and low temperature. XPS studies in full spectral range together with individual spectra of the related elements are studied in details. The optical band gap and vibrational bands are studied by UV-Vis and FTIR techniques. Further, the decrease in the conductivity on increasing Pr and Ti concentration in BiFeO₃ is attributed to an enhancement in the barrier properties leading to suppression of lattice conduction path arising due to lattice distortion as confirmed from impedance analysis.

The results of this work are published in (i) Ceramics International, vol. 40, pp. 7805, 2014, (ii) Journal of Material Science: Material in electronics, In Press, doi: 10.1007/s10854-014-2431-z)

In **Chapter VIII**, we summarized the key results and conclusions obtained from the thesis hence presented. This chapter also discusses the future scope and related issues of the A/B site or A and B site co-substitution in BFO and other ABO₃ type ceramics.

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LIST OF PUBLICATIONS

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