SYNTHESES AND CHARACTERIZATIONS OF MUTIFERROIC NANOPARTICLES

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By

A. Bismibanu, M.Sc.,M.Phil.,
[*Reg.No.* **P4041**]

Research Guide
Dr. M. Alagar, M.Sc., M.Phil., M.Ed., Ph.D
Head & Associate Professor of Physics (Rtd)
Ayya Nadar Janaki Ammal College (Autonomous)
Sivakasi - 626 124.

MADURAI KAMARAJ UNIVERSITY
(University with Potential for Excellence)
MADURAI - 625 021.
TAMIL NADU
INDIA

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1. INTRODUCTION

Multiferroic materials that are simultaneously ferromagnetic and ferroelectric in the same phase have attracted great attention of the researchers worldwide **[1-5].** Multiferroic materials exhibit magnetoelectric (ME) effect. The ME effect means magnetization controlled by electric field and the polarization controlled by magnetic field. The magnetic and ferroelectric coupling leads to potential applications in data storage, microwave devices, sensors and memory storage devices **[6-7].** Multiferroic materials have high electrical permittivity and high magnetic permeability. $BiFeO_3$ (BFO) is the most studied multiferroic material which exhibit ferroelectric and antiferromagnetic properties at room temperature in single phase.

1.1 IMPORTANCE OF $BiFeO_3$

$BiFeO_3$ is an inorganic chemical compound with a perovskite structure. It was first produced in the late 1950s. Bismuth ferrite has always been considered to be antiferromagnetic its bulk form. It is ferroelectric multiferroic having an antiferromagnetic Neel temperature of T_N=850 ºC and the ferroelectric Curie temperature of Tc=370 ºC **[8].** One interesting thing should be noted that $BiFeO_3$ possesses the perovskite and not the "ferrite" structure. $BiFeO_3$ in bulk form can be described as a rhombohedrally distorted ferroelectric perovskite having the space group R3c. It is observed that each Fe^{+3} spin is surrounded by six antiparallel spins on the nearest Fe neighbours, that is, a G-type antiferromagnet. This implies that magnetic moments of iron are ferromagnetically coupled within the pseudocubic (111) planes and are anti-ferromagnetically coupled between adjacent planes. The drawbacks of BFO are high leakage current density, chemical fluctuation, large coercive field and inhomogeneous magnetic spin structure. The leakage current arises due to the non – stoichiometry of the single phase $BiFeO_3$ candidate. In fact, synthesis of $BiFeO_3$

always produces oxide impurities with different bismuth to iron ratios. Such as $Bi_{25}FeO_{39}$ and $Bi_2Fe_4O_9$. The impurity phases will produce a charge imbalance that induces large current leakage, making it difficult to detect a well saturated ferroelectric hysteresis loop.

1.2 SIGNIFICANCE OF DOPING IN $BiFeO_3$

$BiFeO_3$ show poor ferroelectric performance due to enormous current both in bulk and thin films. It is proved that the electrical leakage is caused by oxygen vacancies and Fe ions with different valences via the formation of shallow energy centers inside the bandgap. Many attempts have been made to enhance the ferroelectric and ferromagnetic properties of $BiFeO_3$ via ion substitution to introduce a chemical pressure into the crystal to vary the electric and crystalline structure. Doping of rare earth metal (Gd, Sr, Pr, Tb etc) **[9-12]** ions at the Bi-site, doping of transition metal (Ni, Co, etc) **[13, 14]** ions for the Fe – site and co-substitution with (Y, Mn), (Sm, Co) and (Eu, Co) at both Bi and Fe site **[15-17]** is a powerful way to improve the multiferroic properties. Doping of BFO has been shown effective in suppressing the cycloid structure and enhancing the magnetic moment.

It is found that the dopant ion substitution has a strong influence on the magnetic character of $BiFeO_3$. Minor attention has been paid to influence the co-doped BFO on the magnetic and ferroelectric property. The low leakage current density and well saturated polarization hysteresis loops with a large remnant polarization were observed in Bi- site doped BFO. Therefore, the multiferroic properties are expected by doping and co-doping of $BiFeO_3$.

2. OBJECTIVES OF THE PRESENT WORK

In the present work, to improve the ferromagnetic and ferroelectric properties of BFO various substitution strategies were carried out. The main objectives of the present works are:

- To synthesize and to observe characterizations of the doped and co-doped $BiFeO_3$
    1. Using various methods (co-precipitation, sol-gel and sonochemical methods).
    2. Pr at various concentrations doped at Bi site.
    3. Dy at various concentrations doped at Bi site and Pr (5%) at Bi site.
- To compare and identify the multiferroic materials with enhanced properties.

2.1 MATERIALS SYNTHESIZED

In the multiferroic materials under study are given in the following.

1. Undoped BFO is prepared by various methods (co-precipitation, sol-gel and sonochemical).
2. A-site doped and co-doped BFO are prepared by sonochemical methods and it is listed below.
    - $Bi_{1-x}Pr_xFeO_3$ (x = 5%, 10% and 15%)
    - $Bi_{0.95-x}Pr_{0.05}Dy_xFeO_3$ (x = 1%, 3% and 5%)

2.3THESIS OUTLINE

The thesis is presented as eight chapters. The brief outline of the work presented in different chapters is given below.

Chapter I explains the introduction, background and motivation of the research work presented in the thesis along with aim and objectives.

Chapter II gives a detailed literature of the area under study. The works published earlier related to the structural, optical, morphology, ferroelectric and ferromagnetic properties and the scope of current studies are discussed.

Chapter III discusses the method of synthesis of all the doped and co-doped bismuth ferrite samples. This chapter illustrates all the characterization techniques carried out for analysis of their properties under investigation.

Chapter IV presents the results on the bismuth ferrite nanoparticles have been prepared by co-precipitation, sol-gel and sonochemical method. The phase identification of prepared sample is characterized by X – ray powder diffraction (XRD), which confirms the rhombohedral structure. The DRS spectra show bands in UV and visible region and the optical band gap is calculated using Kulbeka – Munk function. The P-E loop tracer shows the ferroelectric behavior and the low leakage current density is observed to be 1.1 x 10^{-6} Amp/cm^2at ±30 kV/cm for BFO sample using sonochemical method**.** The BFO synthesized by co-precipitation and sol-gel methods exhibits anti-ferromagnetic property and sonochemical method exhibit ferromagnetic property with finite coercivity. The surface morphology of the samples determined using SEM. It exhibited that the porosity is disappeared and impurities also suppressed in pure BFO using sonochemical method. The presence of Bi, Fe, O in BFO is confirmed by Energy Dispersive X-Ray Spectrometer (EDAX).

Chapter V deals with the synthesis and investigation of the multiferroic properties of Pr doped $BiFeO_3$ nanoparticles. A series of $Bi_{1-x}Pr_xFeO_3$ (x = 0.0, 0.05, 0.10 and 0.15) nanoparticles were prepared by sonochemical method. A systematic study of structural, optical, morphological, ferroelectric and ferromagnetic properties of Pr doped BFO has been carried out. The average crystallite size of $BiFeO_3$ and Pr doped $BiFeO_3$ nanoparticles are in the range of 32-38 nm. The optical energy bands corresponding to C-T and d-d transition are watched from Diffusion reflectance spectra. Room temperature P-E curves of the Pr doped $BiFeO_3$ samples showed improved ferroelectric characteristics and reduced the leakage current density compared to undoped $BiFeO_3$. The saturation Magnetization (Ms) has been improved with Pr doping BFO and greatest value is 1.273 emu/g for P15BFO. The surface morphology of the samples determined using SEM. It exhibited that the large rectangular grains is disappeared and form small sized rectangular grains combined with the star shaped particles. The presence of Pr doping element in BFO system is confirmed by Energy Dispersive X-Ray Spectrometer (EDAX).

Chapter VI presents the structural, optical, morphological and multiferroic properties of (Pr,Dy) co-doped $BiFeO_3$ synthesized by sonochemical method. All the samples are indexed to a rhombohedral structure with the space group (R3c) are confirmed by X-Ray diffraction and Rietveld refinement patterns. The optical energy bands corresponding to C-T and d-d transition were watched from Diffusion reflectance spectra. The greatest value of saturation polarization is 0.4247 $\mu C/cm^2$ for P5D1 sample. The leakage current density increment in Pr-Dy co-doped BFO samples is ascribed to the arrangement of oxygen vacancies. For the doped samples P5D1, room temperature (RT) magnetic parameters such as the saturation magnetization (Ms) and coercive field (Hc) were significantly higher than that of P5 nanoparticles. The morphology and the grain size of the samples are studied by Field Emission Scanning Electron Microscope. The Energy Dispersive X-Ray Spectrometer (EDAX) confirmed the presence of two doping elements (Pr and Dy) in BFO system.

Chapter VII summarises the results of all the works are compared, discussed and conclusions drawn from the present work. Table 1 shows the magnetic and ferroelectric parameters of the doped and co-doped $BiFeO_3$ nanoparticles. In case of undoped $BiFeO_3$ using sol-gel method presents the significant magnetic and ferroelectric properties. In case of Pr doped BFO samples, $Bi_{0.85}Pr_{0.15}FeO_3$ shows enhanced magnetic and ferroelectric properties. In case of (Pr,Dy) doped BFO samples, $Bi_{0.94}Pr_{0.05}Dy_{0.01}FeO_3$ exhibits incredible the magnetic and ferroelectric properties.

Chapter VIII presents the scope of future work. In future, thin film of multiferroic composites will be fabricated and magnetic and ferroelectric properties will be investigated

Table 1. Magnetic and ferroelectric parameters of doped and co-doped $BiFeO_3$ nanoparticles.

S. No	Sample	Method	Saturation Magnetization (Ms) emu/g	Retentivity (Mr) emu/g	Coercivity (Hc) Oe	Remnant Polarization (Pr) μC/cm^2	Coercive field (Es) kV/cm
1.	$BiFeO_3$	Co-precipitation	0.0015	3.68E-4	376	0.365	10.88
		Sol-gel	**0.988**	**0.68**	**509**	**0.054**	**5.46**
		sonochemical	0.063	0.022	1090	0.034	7.93
2.	$Bi_{0.95}Pr_{0.15}FeO_3$	Sonochemical	1.273	0.08	50	0.017	3.40
3.	$Bi_{0.94}Pr_{0.05}Dy_{0.01}FeO_3$	Sonochemical	1.582	0.003	649	0.144	0.288

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List of Publications based on the research work

1. **A. Bismibanu**, Pradeep Reddy Vanga, Thangaraj Selvalakshmi, M. Ashok, M. Alagar, "Investigations on Structural, Optical and Multiferroic Properties of Bismuth Ferrite Nanoparticles Synthesized by Sonochemical Method", *Journal of Electronic*

Materials, 47, 6373-6377 **(2018)**, Impact Factor: 1.676, DOI 10.1007/s11664-018-6581-2.

2. **A. Bismibanu**, M. Alagar, J. S. Mercy Jebaselvi, C. Gayathri, "Preparation and Characterization of Bismuth Ferrite Nanoparticle Using Sol-Gel Method", *International Journal for Research in Applied Science & Engineering Technology*, 6, 1-4, **(2018),** SJ Impact Factor: 6.887.
3. **A. Bismibanu,** Pradeep Reddy Vanga, M. Alagar, Thangaraj Selvalakshmi, I. B. Shameem Banu, M. Ashok. Effect of (Pr,Dy) co-doping on structural, optical and electrical properties of $BiFeO_3$ nanoparticles via sonochemical method, SN Applied Sciences (accepted for publication).

Proceedings of International / National Conferences / Seminars

1. A. Bismibanu, M.Alagar, Structural, morphological and ferroelectric properties of bismuth ferrite nanoparticles by sonochemical method, Proceedings of CSIR sponsored National Conference on New-Generation Materials for Energy Applications held at B. S. Abdur Rahman Crescent Institute of Science & Technology, Vandalur, Chennai during 21st & 22nd October 2019.

Papers Presented in National Conferences.

1. A. Bismibanu, M. Alagar, Structural, Chemical and morphological properties of $BiFeO_3$ nanoparticle in National Conference on Materials for Energy Devices (NCMED – 2K16), November 23 & 24, 2016, The standard Fireworks Rajarathnam College for Women, Sivakasi. (Oral Presentation).
2. A. Bismibanu, M.Alagar, Structural, morphological and ferroelectric properties of bismuth ferrite nanoparticles by sonochemical method in National Conference on New-Generation Materials for Energy Applications, 21st & 22nd October 2019, B. S. Abdur Rahman Crescent Institute of Science & Technology, Vandalur, Chennai. (Oral Presentation).

Attended in National / International level Conferences.

1. Attended 4 days International Conference on Functional Materials, September 07-10, 2016, PSN College of Engineering and Technology, Tirunelveli.
2. Attended 2 days UGC sponsored National Conference on Advanced Materials and Its Applications – NCAMA 2K17, July 6 & 7, 2017, The standard Fireworks Rajarathnam College for Women, Sivakasi.