INVESTIGATION OF MULTIFERROIC PROPERTIES OF SCANDIUM SUBSTITUTED BISMUTH FERRITE

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Indian Institute of Technology Hyderabad

Department of Physics

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Lastly, I offer my regards to all of those who supported me in any respect during the completion of the project.

ASMITA KUMARI

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Dedicated to

My beloved parents and my grand parents

Abstract

Polycrystalline $BiSc_xFe_{1-x}O_3$ (x = 0, 0.05, 0.1 and 0.15) compounds were synthesized by conventional solid state route. All the compounds crystallize in the class of rhombohedral structure with R3c space group. A systematic structural distortion has been observed in all the compounds. From the room temperature magnetization hysteresis loops, weak ferromagnetism is observed in Sc substituted BFO which could be due to suppression of spiral modulated spin structure. Basic antiferromagnetic nature has not been changed with Sc substitution. Antiferroelectric behavior has been observed in Sc substituted BFO compounds which will be due to the structural distortions. Antiferroelectric character dominates the ferroelectric character with the Sc substitution.

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Contents

Chapter1

INTRODUCTION

1.1Perovskite structure:

General formula of perovskite structure is ABO_3.Perovskite structure is a cubic structure which can be easily distorted by accommodation of many different element. It expand, contract, and rotate bond angles in order to accommodate a wide range of cation sizes.

For the cubic unit cell of perovskite A-site atom in the corner ,B-site at the center and oxygen atoms remains at the center of the face of the cube.
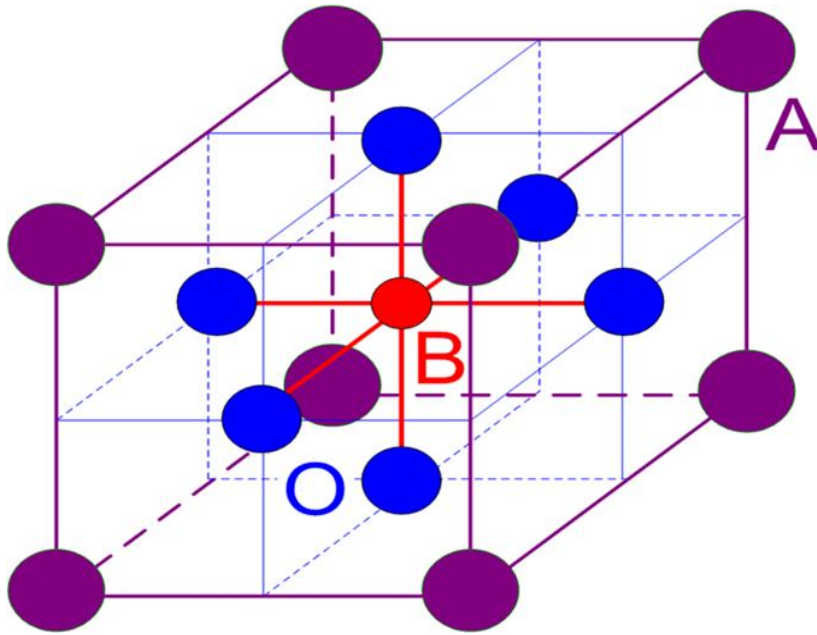

FIG 1   The schematic representation of the perovskite lattice structure[2].

The tolerance factor, t, quantifies the degree to which a particular ABO_3compound fits in this structure.

$$t = \frac{r_A + r_O}{\sqrt{2}(r_B + r_O)}$$

Here, r_A, r_B and r_O are the radii of A, B and O ions. $0.75 < t < 1.05$ for most of the material. If B radius are small, the oxygen octahedra are unstable due to oxygen-oxygen ionic repulsion and $r_A < \sqrt{2}(r_O + r_B)/r_O$ is adjusted by rotations of oxygen octahedral$BiFeO_3$ is rhombohedral and has distortions along the seudocubic [111] direction. Most of the mutiferroic material are of perovskitestructure[1].

1.2 Ferroelectricity:

The ferroelectric materials have permanent dipole moment in the absence of electric field. Example of ferroelectric material are $BaTiO_3$, $Pb(Zr,Ti)O_3$, and Rochelle salt, $NaKC_4H_4O_6$. In linear dielectric materials the polarization is proportional to the applied field. In ferroelectricity addition hystesis loop is formed. When an electric field is applied to the sample by applying a voltage across two electrodes, it gets polarized. Polarisation direction can be changed by changing the direction of electric field. [5].

The region in ferroelectric material in which there is uniform parallel dipole moment is called domain. Region between two domain is called domain wall. In the absence of electric field domains are randomly oriented so that resultant polarization is zero. When electric field is applied dipole moment of all domain align in field direction, resulting saturation polarization.

Ferroelectric materials are also piezoelectric, meaning voltage appears across the sample when it is mechanically stretched or compressed. In the converse piezoelectric effect, the lattice expands or contracts when an electric field is applied.
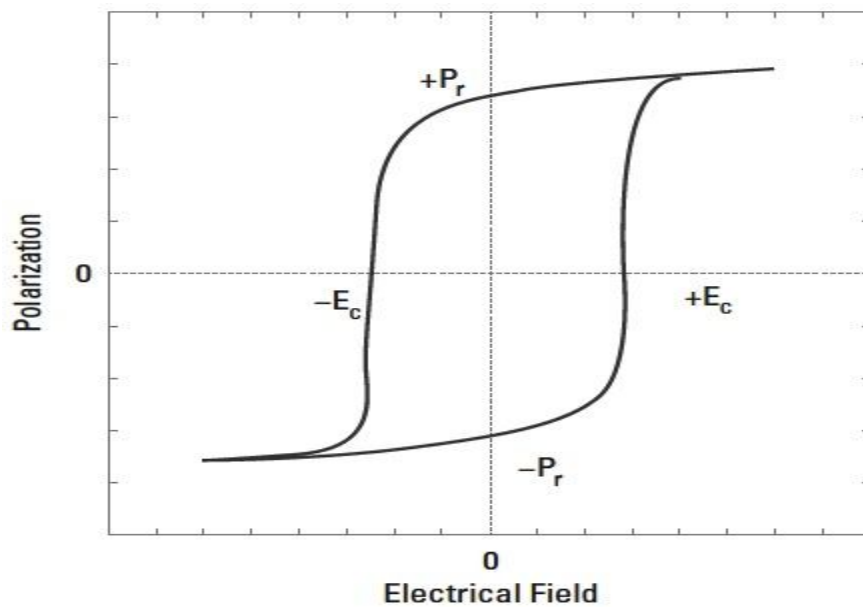
Figure 1.2 Ferroelectric hysteresis loop[3]

1.3 Ferromagnetic:

Solids have atoms with permanent magnetic moments which interact strongly. The effect of interaction is to produce magnetizations in ferromagnetic solids. Magnetic moment of ferromagnetic material is homogeneous in a particular region called domain.In a perticuar domain spins are oriented in the same direction.Region between two domain iscalled domain wall .When magnetic field is not applied all domains of the ferromagnetic material are randomly aligned,so that resultant magnetic moment of zero.If we increase the magnetic field in a particular direction magnetic moment of all domain will try to orient in field direction. The field at which all magnetic moment align in same direction is called saturation field and magnetization at that point is called saturation magnetization.

 The fraction of the saturation magnetization which is retained when the driving field is removed is called the remanence of the material. All ferromagnets have a maximum temperature where the ferromagnetic property disappears as a result of thermal agitation.This

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temperature is called the Curie temperature. The Curie temperature gives an idea of the amount of energy takes to break up the long-range ordering in the material. The Curie temperature of iron is about 1043 K.
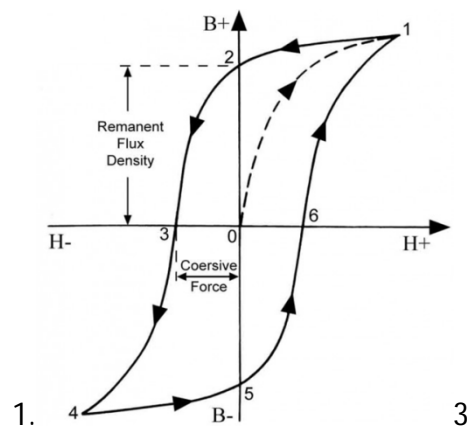

1.   3

Figure 1.3 Ferromagnetic hysteresis loop[4].

1.4 Antiferromagnetism:

Antiferromagnetism was discovered in 1938 by Bitter, Squire and Tsai,while working on magnese oxide.In antiferromagnetic material ,magnetic moment which is related to spin of electron are regularly arranged but points in opposite direction.Antiferromagnetism may exist at low temperature and vanishes at or above a temperature called" Neel" temperature[6].
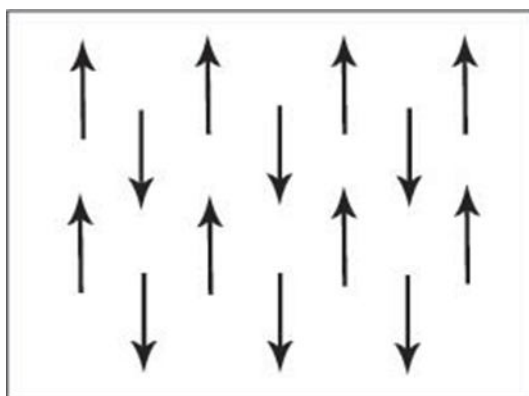

Figure 1.4 Antiferromagnetic spin alignment.

1.6 Multiferroics:

History: Multiferroic was first observed by Rontgen in 1888. He found that dielectric became magnetized when it is moved in electric field and conversely became polarized when it moves in magnetic field. In 1894 P. Curie discussed magnetic and electric property correlation in low symmetry crystal. Debay first used the term magneto electric in 1926. Magneto electric effect was first observed in Cr_2O_3 but magnitude of this effect was small. Later many research carried on different materials.The first material which was showing simultaneously ferromagnetic and ferroelectrics behavior nickel iodine boracite, $Ni_3B_7O_{13}I$. $Pb(Fe_{2/3}W_{1/3})O_3$ and $Pb(Mg_{1/2}W_{1/2})O_3$ was the first discovered compound in which Ferro electricity was caused due to Mg and W and magnetic order is due to Fe^{3+} ion. Multiferroic materials become the hot topic of research in recent year because it allows the creation of devices in which electric and magnetic ordering can be mutually controlled[6].

Multiferroic material is a material in which both ferroelectric and ferromagnetic order exist in same phase.Spontaneous polarization can be switch by magnetic field and spontaneous magnetization can be switch by electric field. Such materials have all the potential applications of both their parent ferroelectric and ferromagnetic materials.

As both ferroelectric and ferromagnetic property exist simultaneously in multiferroic its allowed physical, structural and electronic properties are restricted to those which occur both in the ferromagnetic and in ferroelectric materials.
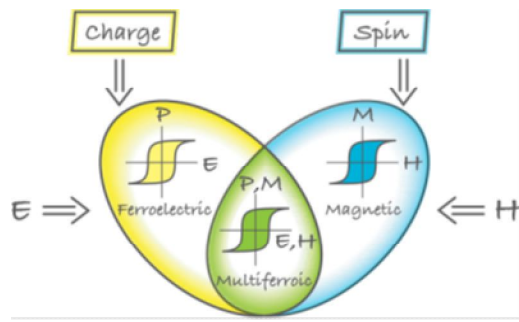
Figure 1.5 Multiferroics combine the properties of ferroelectrics and ferromagnetics[7].

Type-I and type-II multiferroics

In type I multiferroics origins of ferroelectricity and ferromagnetism is different and often due to different active 'subsystems' of a material. The origin of ferroelectricity can be (i) the presence of a transition metal (TM) with d^0 configuration, just as in $BaTiO_3$; (ii) the presence of bismuth or lead where the FE is predominantly due to lone pairs of Bi^{3+} and Pb^{2+}. In general FE ordering temperature is much higher than the magnetic one in type I multiferroics[8].

In type-II multiferroics ferroelectric and ferromagnetic orders are strongly coupled. Magnetic order cause ferroelectricity. In type-II materials the FE ordering temperature is same asthe magnetic one [8].

1.7 Bismuth ferrite crystal structure:

BiFeO3 is rhombohedral at room temperature with the space group R3c. Which is equivalent to six formula unit of BFO in hexagonal cell, lattice the lattice constant ahex =5.579 Å and chex = 13.869 Å. However, the most easy view of $BiFeO_3$ is pseudocubic perovskite[9].setting of BiFeO3 wit with apc = 3.96 $A^0$and αpc = 89.4^0. Octahedra are rotated in alternating directions about the [111] axis by 13^0.
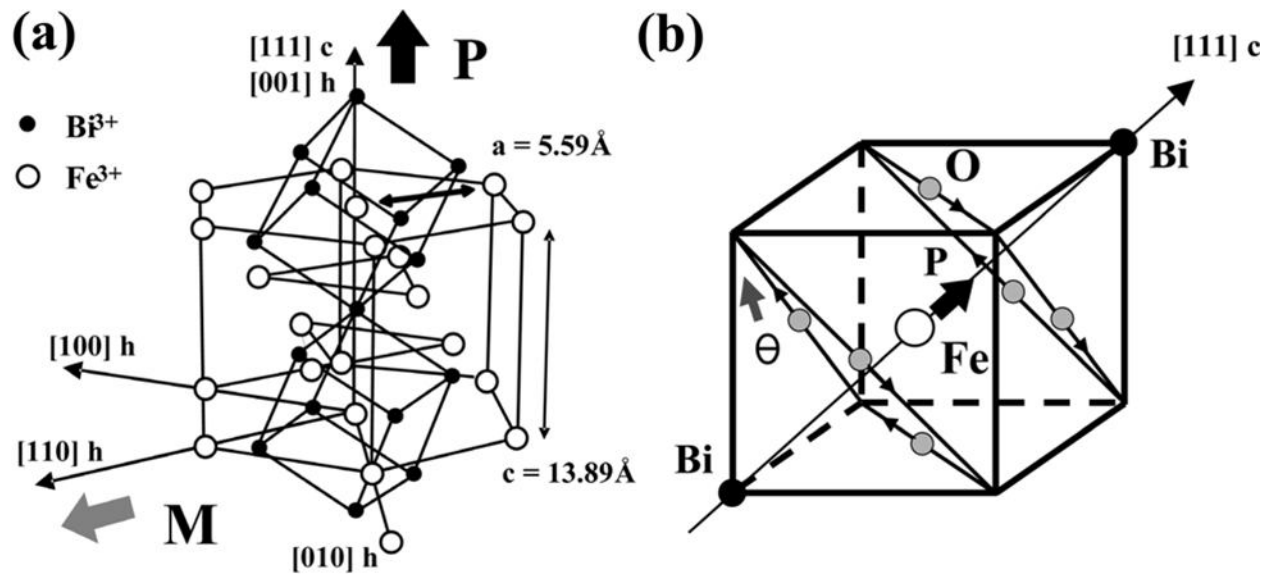
Figure 1.5(a)Hexagonal & (b) pseudo-cubic R3c BFO

Electrical and Magnetic property of bismuth ferrite:

$BiFeO_3$ is ferroelectric with relatively high Curie temperature T_C=1100 K and exhibits antiferro-Magnetic with high Neel temperature T_N = 643 K. Magnetic moments of are coupled ferromagnetically within the pseudocubic (111) planes and antiferromagnetically between adjacent planes. $BiFeO_3$has G type anti ferromagnetic ordering. It has weak ferromagnetism caused by residual moment from the canted Fe^{3+} spin structure of length 620 A^0[8].BFO show ferroelectricity because $6S^2$ lone-pair of hybri Bi^{+3}hybridize with O 2p orbital,which improve the ferroelectricity by shifting Bi^{+3} towards the oxygen ion.

1.8 Letrature review

Incorporation of BFO in to practical device application is limited due to its high leakage current and antiferromagnetic nature. In order to improve the multiferroic character of BFO,

substitution of elements at A or (and) B- site is the most effective technique. Generally, rare earth elements or divalent alkaline earth elements will be substituted at A- site and transition metal elements at B- site. Among all these elements, diamagnetic ions like La^{3+}, Ba^{2+}, Y^{3+}, etc., effectively tuned the multiferroic properties of BFO.

Shan T. Z et al reported that substitution of diamagnetic element La^{3+} at A-site effectively destruct the spin cycloid structure. Enhanced magnetic and electric properties are attributed to the magnetoelectricinteraction[11].

Khomchenko V. A et al substituted heterovalentCa, Sr, Pb, and Ba elements at A- site and observed that larger size ion can effectively suppress the magnetic spiral spin structure and improve the magnetization in BFO[12].

Mishra R. K et al observed improved dielectric and magnetic properties with Y substitution[13].

From the above discussion, it can be concluded that diamagnetic ion substitution at A- site will effectively tune the multiferroic properties. Multiferroic properties can also be tuned by substitution of elements at B- site.

In this work, diamagnetic ion Sc^{3+} has been chosen to substitute at B- site. Larger ionic size of Sc^{3+} than Fe^{3+} ion size creates internal chemical pressure in the lattice and consequently distorts the lattice. Moreover, d^0 electrons in Sc^{3+} may favours off centring in the octahedra which in turn improves ferroelectricity.
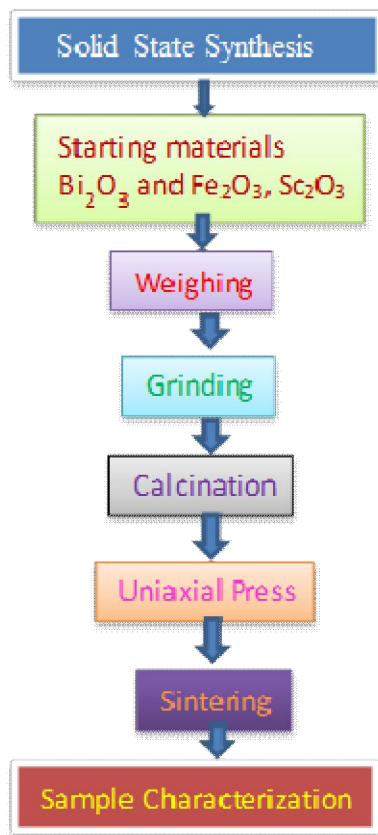
1.9 Objective

- To insvestigate multiferroic property of $BiFeO_3$ by dimagnetic element substitution at B-site.

- Compound of interest is Scandium (Sc^{3+}) substituted at B-site

2 EXPERIMENTAL METHOD

2.1 Sample Preparation: Sample was prepared using solid state method which includes following steps.

Calcination

Calcinations is the process of subjecting a substance to the action of heat, but without fusion, for the purpose of causing some change in its physical or chemical constitution. The objects of calcination are usually: (1) to drive off water, present as absorbed moisture, (2) to drive off carbon dioxide, sulpherdioxide,or other volatile constituent.

Sintering

The process consists of solid particle bonding followed by continuous closing of pores from a large open porosity sintering process converts the green microstructure to the microstructure of the dense ceramic component.The sintering to essentially pore free bodies.

Sample Preparation

Pure and B-site Sc doped BFO ceramics were prepared by solid state synthesis method.For $BiFe_{1-x}Sc_xO_3$ (x=0.0 0.05 ,0.10 ,0.150) pure powders of Bi_2O_3 , Fe_2O_3 and Sc_2O_3 were used. Stoichiometric weight of Bi_2O_3 , Fe_2O_3 and Sc_2O_3 should be weighted by sensitive
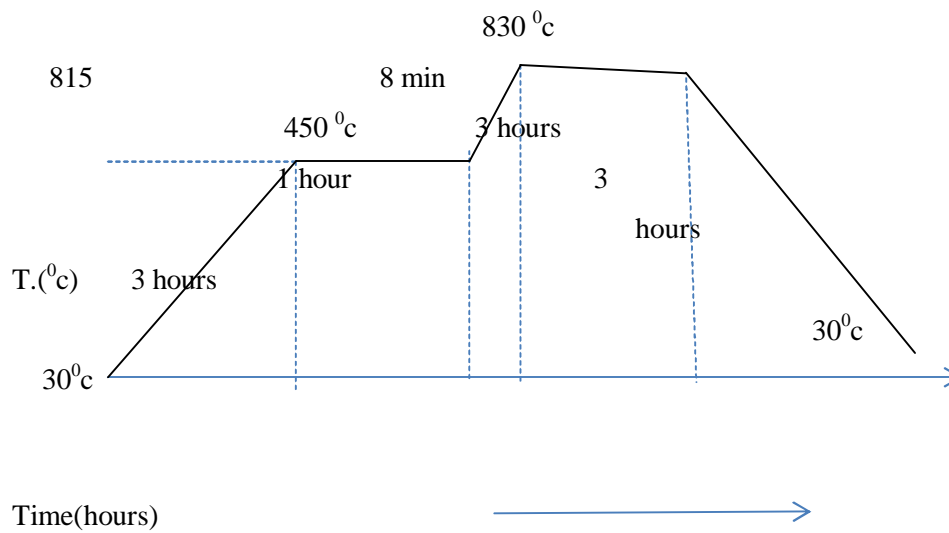
weighing balance for the preparation of pure BFO or doped one with 5% ,10% ,15% Scandium.

The stoichiometric weight of the particular sample is grinded for two hours continuously. Grinded powder is kept forthe calcination in the furnace .Programming for calcination in the furnace is given below.
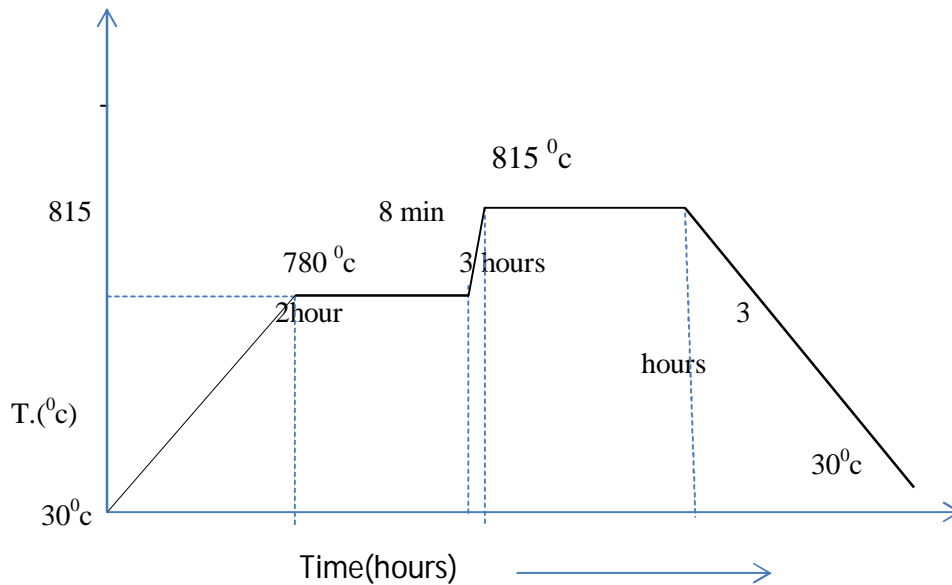
After calcination, PVA is aaded in the sample. PVA acts as bindinder . it increases the density of the sample.Bindersould be mixed properly in the sample.Now a proper shape is given to the sample by making it as pallet of circular geometry.Diameter of each pallet is approximately 8 mm and thickness 0.6 to 0 .7 mm. Pallet formed by giving 5 tones pressure to the powder sample.Now sample are ready for sintering.We kept these sample in the furnace .Setting of the furnace is given below.

830 ^{0}c

815   8 min

450 ^{0}c   3 hours

1 hour   3

                 hours

T.(^{0}c)   3 hours

                                      30^{0}c

30^{0}c

Time(hours)

After sintering our sample are ready for characterizations

2.2 X-RAY Diffraction

.Generation and properties of X-rays

X-rays are electromagnetic waves whose wavelengths range from about 0.1 to 100 X 10^{-10} m. They are produced when rapidly moving electrons strike a solid target and their kinetic energy is converted into radiation. The wavelength of the emitted radiation depends on the energy of the electrons. if target of a smaller atomic number such as copper or molybdenum, then we observe very sharp spikes appearing above this smooth background radiation. These very sharp spikes are called characteristic lines and the X-ray radiation is termed characteristic radiation. These sharp lines are caused by electrons being knocked out of the K shell of an atom and then the electrons from the L shell cascading down into the vacancies in this K shell. The energy emitted in this process corresponds to the so-called K alpha and K beta lines.

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Diffraction of X-rays

For x-ray diffraction a beam of x-ray ,of wavelength λ, are incident on the surface of the crystalline material at an incident angle θ. The x-ray are scattered by sample according to Bragg's law.

$n\lambda = 2d\sin\theta$

Where n is an integer and d is the distance between the crystal planes. When there is coherent scattering from the crystalline planes the Bragg condition is satisfied and a Bragg peak appears in the diffraction pattern.

2.3 Vibrating Sample Magnetometer

The Vibrating Sample Magnetometer (VSM) is a commonly used instrument for the study of magnetic moments in many materials as a function of applied magnetic field.If any material is placed in a uniform magnetic field, a dipole moment will be induced in the sample proportional to the product of the sample susceptibility and the applied field. If the sample is made to undergo sinusoidal motion, the resulting magnetic flux changes near the sample will induce an electrical signal in suitable placed stationary coils.This signal will be proportional to the moment, amplitude, and frequency of vibration.

The material under study in the VSM is inserted in the sample holder so that it rests centered in a pair of pickup coils between the poles of an electro magnet. The sample holder is mounted using a sample rod in a transducer assembly which passes through the center of a driving coil. The transducer is driven by a power amplifier which itself is driven by an oscillator. The magnetic sample under study is constraint to vibrate only along the vertical axis. As it does so, it

induces a signal in the sample pickup coils as described above. The magnitude of this signal is dependent on the magnetic properties of the sample itself.

Chapter 3
Results and Discussions

3.1 Structure characterization

Fig. 3.1(a) shows the XRD patterns of polycrystalline $BiFe_{1-x}Sc_xO_3$ (BFO-Sc)[x = 0 (BFO), 0.05 (BFO-Sc5), 0.1 (BFO-Sc10) and 0.15 (BFO-Sc15)] compounds. Fig. 3.2(b) shows the enlarged view of the XRD patterns from 21° - 23°. All the X-ray diffraction peaks are well matched with rhombohedral $BiFeO_3$ peaks with R3c space group (JCPDS file number 86-1518). A trace amount of secondary phases like $Bi_{25}FeO_{40}$ is observed and found to be suppressed completely at 15% Sc substituted BFO compound. Lattice parameters are calculated in a hexagonal frame of reference. Goldschmidt tolerance factor t, defined as $t = (\langle r_A \rangle + r_O) / \sqrt{2}(r_B + r_O)$ where <r$_A$> is the average radius of Bi^{3+} at A site and r$_B$ and r$_o$ are the radii of Fe^{3+} and O^{2-} respectively, can be used to study the variation in structural parameters. As the size of Sc^{3+} is larger than the ionic size of Fe^{3+}, substation of Sc at Fe site increases the average B-site size, which decreases the

tolerance factor. Change in tolerance factor indicates that lattice is distorted with the substitution. Change in lattice parameters and lattice volume are given in table.3. 1. With the increase of Sc content, the volume of the unit cell increases continuously due to the larger ionic radius of Sc^{3+} as compared to that of Fe^{3+} ionic size. From this, it is concluded that the substituted Sc^{3+} ion occupied the B-site (Fe site) and creates internal chemical pressure in the lattice which will be responsible for the enhanced magnetic and electric properties in BFO.
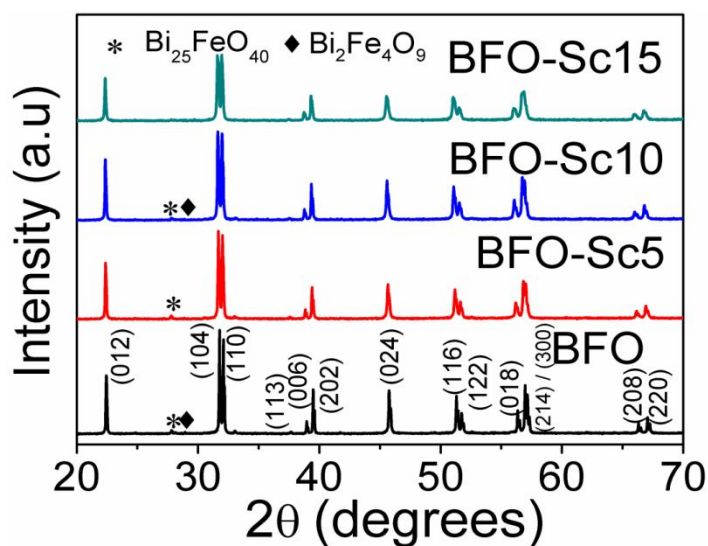

Figure 3.1(a) XRD patterns of $BiFe_{1-x}Sc_xO_3$ (x = 0, 0.05, 0.1 and 0.15) compounds.

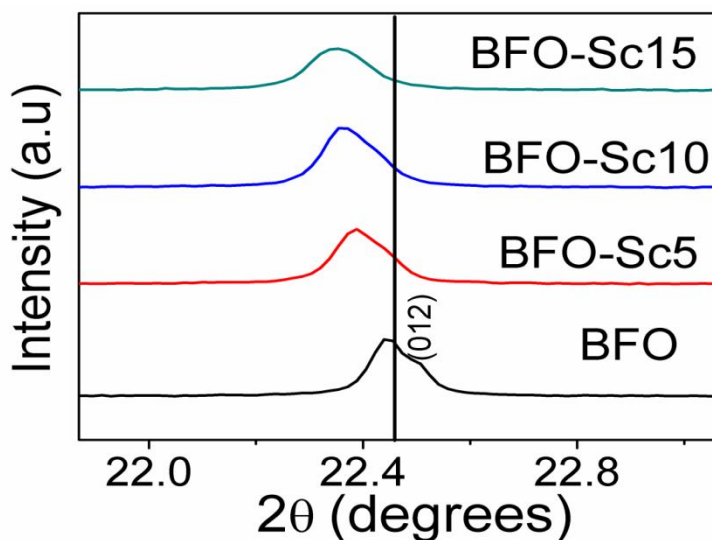Figure 3.2 (b) Enlarged view of XRD patterns of $BiFe_{1-x}Sc_xO_3$ (x = 0, 0.05, 0.1 and 0.15) compounds near 22°.

Compound	$BiFeO_3$	$BiSc_{0.05}Fe_{0.95}O_3$	$BiSc_{0.1}Fe_{0.9}O_3$	$BiSc_{0.15}Fe_{0.85}O_3$
Crystal structure	Rhombohedral			
Space Group	R3c			
Lattice Parameters				
a (A˚)	5.5827	5.5907	5.6041	5.6064
c (A˚)	13.8783	13.9083	13.9458	13.9528
Cell volume $(A˚)^3$	372.02	376.47	379.30	379.80

Table 3.1 Lattice volume is increasing.

3.2 Magnetic properties

Fig. 3.3 shows magnetization ($M – H$) curves of BFO and BFO-Sc compounds have been recorded up to a maximum magnetic field of 10 kÖe at room temperature. BFO consists of G-type antiferromagnetic ordering superimposed with spiral modulated spin structure (SMSS). In BFO, the Fe^{3+} magnetic moments are coupled ferromagnetically in the pseudo cubic (111) planes, but antiferromagnetically between the adjacent planes. The existence of a weak

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ferromagnetic moment is permitted by the crystal symmetry of BFO.As the Sc content increases, the average radius at B-site increases which in turn changes the interatomic distances and the Fe – O – Fe bond angle. BFO shows the linear variation of magnetization with the magnetic field. Suppression of SMSS is evidenced from the appearance of weak ferromagnetism in the magnetization curves. Suppression of SMSS should be the prime cause in the enhanced magnetic properties in Sc substituted BFO. However, much improved in magnetization has not been seen in Sc substituted BFO. It may be due to weakening of superexchange interaction with the substitution diamagnetic Sc^{3+} ion at Fe^{3+}. Insert in Fig. 2 shows the enlarged view of magnetization data near origin.The remanent magnetizations M_r of BFO, BFO-Sc5, BFO-Sc10 and BFO-Sc15 compounds, are respectively 0.00024, 0.00071 and 0.00033 and 0.0017emu/g.
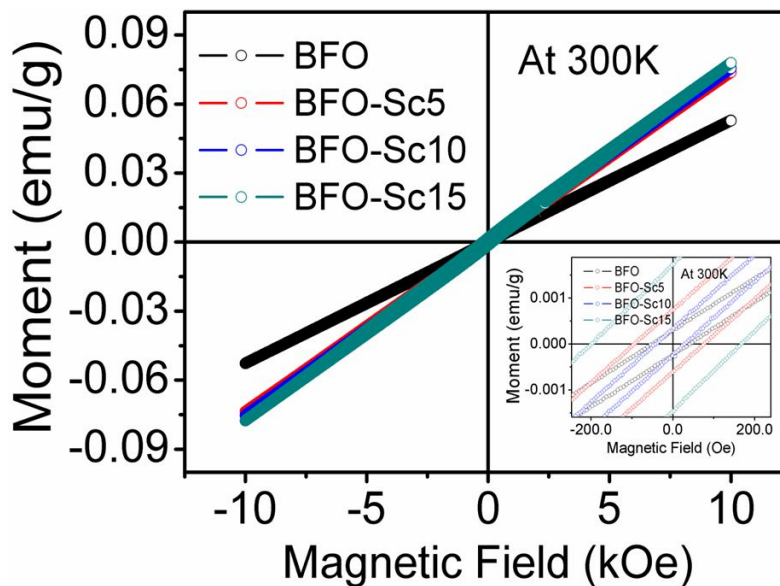

Figure 3.3. Magnetization hysteresis loops (*M-H*)of $BiFe_{1-x}Sc_xO_3$ (x = 0, 0.05, 0.1 and 0.15) compounds at room temperature.

3.3 Ferroelectricity

Fig. 3.4 shows the room temperature P-E hysteresis loops for BFO and BFO-Sc compounds at 100Hz. Although BFO shows a remnant electric polarization of 9µC/cm2, it did not show saturated hysteresis loop. Leakage contribution is expected in the observed behaviour in this compound. Antiferroelectric behaviour is observed in Sc substituted BFO. As Sc content increases, antiferroelectric character dominates over the ferroelectric character. This antiferroelectric behaviour was explained on the basis of aging effect in BFO [14] and also on the basis of structural changes in rare earth substituted BFO [15]. Substitution of larger ionic size Sc^{3+} in BFO decreases tolerance factor which in turn changes the crystal structure. It can be expected that the observed behaviour in the substituted compounds could be due to structural distortion. However, further structural studies are required to explain the antiferroelectric behaviour in the substituted compounds. Structural studies are our future studies to explain the mechanism.
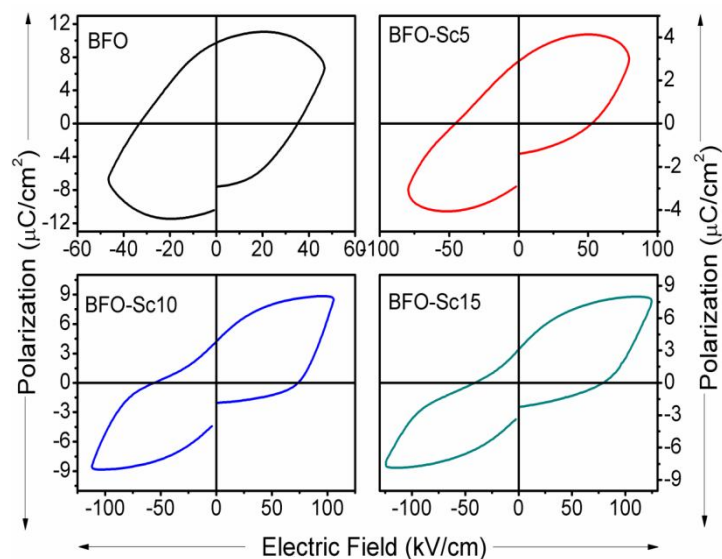

Figure 3.4 Polarization hysteresis loops (*P-E*)of $BiFe_{1-x}Sc_xO_3$ (x = 0, 0.05, 0.1 and 0.15) compounds at room temperature.

CONCLUSION :

Polycrystalline $BiSc_xFe_{1-x}O_3$ (x = 0, 0.05, 0.1 and 0.15) compounds were synthesized by conventional solid state route. All the compounds crystallize in the class of rhombohedral structure with R3c space group. A systematic structural distortion has been observed in all the compounds. Weak ferromagnetism is observed in Sc substituted BFO due to suppression of spiral modulated spin structure. Antiferroelectric behavior has been observed in Sc substituted BFO compounds which will be due to the structural distortions.

References

[1],H. D. Megaw and C. Darlington.Geometrical and Structural Relations in the RhombohedralPerovskites. . A 31, 161 (1975).

[2]Sheng-Yuan Chu1*, Cheng-Shong Hong2.Effects of the MnO additives on the properties of Pb(Fe2/3W1/3)-PbTiO3 relaxors: comparison of empirical law and experimental results. vol. 101, pp. 054117, 2007.

[3]V.C. Kumar.FRAM MCUs For Dummies, Part 1.2012

[4]Basic Electrical Engineering Part 5: Magnetic Materials

[5] J. F. Nye, Physical Properties of Crystals, (Oxford University Press, 1985).

[6]Annales de Physique (Paris) L. Néel, Propriétéesmagnétiques des ferrites; Férrimagnétismeetantiferromagnétisme, 137–198 (1948).

[7]Daniel Khomskii.Classifying multiferroics: Mechanisms and effects.20 (2009)

[8]Journal of the Korean Physical Society, Vol. 33, No. 2, August 1998

[9] B. Ruette, S. Zvyagin, A. P. Pyatakov, A. Bush, J. F. Li,V. I. Belotelov, A. K. Zvezdin and D. Viehland, Phys.Rev. B 69, 064114 (2004).

[10] Nogués J and SchullerI . Exchange bias J. Magn. Magn.Mater. 192 203,1999

[11] Shan-Tao Zhang, Ling-Hua Pang, Yi Zhang, Ming-Hui Lu, and Yan-Feng Chen, Preparation, structures, and multiferroic properties of single phase, Bi1xLaxFeO3 (x = 0–0.40) ceramicsJ. Appl. Phys. 100, 114108 (2006)

[12] V. A. Khomchenko, D. A. Kiselev, J. M. Vieira, Li Jian, A. L. Kholkin, Effect of diamagnetic Ca, Sr, Pb, and Ba substitution on the crystal structure and multiferroic properties of the BiFeO3 perovskite J. Appl. Phys. 103, 024105

[13] RK Mishra, Dillip K Pradhan R N P Choudhary and A Banerjee, Effect of yttrium on improvement of dielectric properties and magnetic switching behavior in BiFeO3, J. Phys.: Condens. Matter20(2008) 045218

[14]G. L. Yuan, Y. Yang, Siu Wing Or, Aging-induced double ferroelectric hysteresis loops in $BiFeO_3$multiferroic ceramic, Appl. Phys. Lett., 91, 122907 (2007)

[15]By Daisuke Kan, Lucia Pa´lova´, VaratharajanAnbusathaiah, Ching Jung Cheng, ShigehiroFujino, ValanoorNagarajan, Karin M. Rabe,andIchiro Takeuchi, Adv. Funct. Mater.20, 1108–1115,.2010.