Effect of rare earth element doping in bismuth ferrite

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Abstract

In the present work, neodymium and magnesium doped bismuth ferrite (BFO) has been prepared by sol-gel method. The structural properties have been investigated using XRD, FTIR, SEM . Average grain size is found below 22 nm. Magnetic properties of the samples have been investigated at the room temperature using M-H loops. Enhancement in magnetic properties have been observed.

Introduction

Multiferroics have become hot topic in the last decades because of simultaneous presence of ferroelectric and magnetic orders and their applications in sensors and storage devices .Ferroic materials are defined by ferroic order parameter. Certain materials are permanent magnets or attracted to magnets, this chareteristic is known as ferromagnetism and the reason for this is the automatic ordering of spin and orbital magnetic moments, this process is known as ferromagnetization. Certain materials have spontaneous electric polarization and this property is called ferroelectricity, if external electric field is applied this effect can be reversed .In case of ferroelasticity it is spontaneous strain.

Multiferroics unite the properties of ferroelectrics and magnets. The magnetization of a ferromagnet in a magnetic field show the usual hysteresis (blue), and ferroelectrics have this kind of response to an electric field (yellow). Multiferroics are simultaneously ferromagnetic and ferroelectric (green), in multiferroics there is a magnetic response to an electric field, or, vice versa, the modification of polarization by magnetic field.

Dong et al. studied the magnetic properties of multiferroic $Bi_{4.2}K_{0.8}Fe_2O_{9+\delta}$ nanostructures with different morphologies. Different $Bi_{4.2}K_{0.8}Fe_2O_{9+\delta}$ nanostructures with controllable morphologies were prepared by hydrothermal technique. They were successful in developing a facile one-pot synthesis method for preparing the urchin-like $Bi_{4.2}K_{0.8}Fe_2O_{9+\delta}$ nanostructures on a large scale with a higher magnetization [1] . Achary et al. studied about the materials having more than one ferroic polarization known as multiferroics. Ferric polarization stands for spontaneous magnetization, spontaneous electric polarization or spontaneous strain. They state that multiferroic materials have the possibility to produce tetrahertz radiation. Internal electric field of the ferroelectric material affect the dipole of incident radiation , this produces a tetrahertz pulse even if any voltage is not present there , as the radiation is created in picoseconds , it can lead to the rapid readout of ferroelectric memories[2]. Jyoti Ranjan Rao et al. studied the multiferroic properties of $BiFeO_3$ after substituting Fe by Mn and Bi by La. They observed that the magnetization of the compound was increased also the dielectric properties. As an increase in the Mn doping, the dielectric constant also increased to a greater value. At low frequencies the values of dielectric constant are high, as the frequency is increased the value of dielectric constant was decreased and at high frequencies it is nearly constant [3]. Saha, Rana Shireen, et al. studied that GaFeO3, $AlFeO_3$ and related oxides are ferromagnetic and these show magnetodielectric effect also. They have taken pyroelectric measurements to study the ferroelectricity from these measurements they found that in these oxides ferroelecticity occurs at low temperatures below the Neel temperature [4]. Pal, Madhuparna et al. studied the multiferroic materials at nano-scale. Piezoresponse force microscopy (PFM) has been used to study the ferroelectric domain at the nanoscale level. Single crystals have been studied. The natural domain properties are lost if sample goes through any fabrication process [5]. Zhai, et al. studied the effect of magnetic correlation on the electric properties in multiferroic materials. Here the phase transition temperature of the electric subsystem Te is higher than that of magnetic subsystems Tm. Ferromagnetic subsystem is described by a Heisenberg-type Hamiltonian and a ferroelectric subsystem by a transverse Ising Model. Above Tm electric properties can be altered because of magnetic correlation [6]. W.Wang et al.

studied magnetic properties of multiferroic materials. Magnetic hysteresis loops were formed of produced multiferroic materials. As we increase the ferroelectric phase the Curie temperature of the produced multiferroic materials shifts toward higher temperature [7]. Moure et al. studied that after milling of $Bi_{0.60}Sr_{0.40}FeO_{2.8}$, highly reactive ceramics precursors are produced. Owing to the preparation of such a material the temperature is lowered by 50-100 degree celcius. Due to the presence of Sr in structure, the prevoskite phase is further stabilized. The dielectric permittivity of such material is enhanced w.r.t. pure bismuth ferrite. The conductance is more for Sr doped ceramics[8]. Martin et al. studied some exciting developments in the area of thin-film multiferroics and magnetoelectrics thin film technique has huge effect on perovskite multiferroics and one example for this is $BiFeO_3$,it has spontaneous polarization also it can be morphed into number of polymorphs and all polymorphic mixtures were prepared using epitaxial films [9]. Tokura et al. studied that topological behavior spin and their electronic states important for multiferroicity. Magnetism can sustain at higher temperatures. Thus the topological properties of electrons implement themselves in multiferroics. Thus multiferroics offer rich content yet to be discovered [10]. Vopson et al. studied the fundamentals of multiferroics and their possible applications . The materials having two or more than two magnetic orders are known as multiferroics. These materials are very useful as external electric and magnetic fields can alter the shape of the material .Maxwell was the first who demonstrated the relation between electricity and magnetism by Maxwell equations. Possible applications of multiferroics are magnetic sensors ,multiferroic microwave phase shifter ,multiferroic microwave signal delay line and Memories [11].

In the present research work, we have prepared samples of rare earth element doped bismuth ferrite using Sol gel Method. Characterization of prepared samples have been using XRD, FTIR, and FE-SEM, VSM .

Synthesis of multiferroics

$Bi_{(1-x)}Nd_xFe_{(1-x)}Mg_xO_3$ (x=0.15, 0.25, 0.35) has been synthesized by sol-gel method using citric acid as fuel and then heated at a temperature $550^{O}C$ for 2 hours .

Results and Discussions

XRD Study

The X-Ray diffraction patterns were taken at room temperature. The X-Ray patterns of $Bi_{(1-x)}Nd_xFe_{(1-x)}Mg_xO_3$ shows that the sample is crystalline in nature. The diffraction patterns consist of prominent peaks corresponding to crystallographic planes (104) and (110) in samples having composition variation (x=0 to x=0.4) (Fig.1). It was found that the peaks of XRD pattern for the doped samples of BFO are at the same place but have different intensities. Parameters like cell constants (a and c), cell volume (V), crystalline size (D) were calculated by using the formula:

$$\frac{1}{d_{hkl}^2} = \frac{4}{3}\left[\frac{h^2 + hk + k^2}{a^2}\right] + \frac{l^2}{c^2}$$

$$V=0.866a^2c$$

$$D = \frac{K\lambda}{\beta \cos\theta}$$

Here λ is the wavelength, β is the half width full maxima, K= 0.89, the constant.

The values of these parameters are listed in the table 1.

Table 1: Lattice constants and grain size (having citric acid as fuel)

Sample	2Θ(deg)	d(Å)	β(^{0})	a(Å)	c(Å)	D(nm)	Vol (Å^3)
Kc0	32.1122	2.78741	0.1771	4.55	16.117	7.745	289.15
Kc1	32.2838	2.77298	0.2362	4.52	15.686	5.810	278.74
Kc2	32.2845	2.77293	0.1968	4.52	17.625	5.804	313.32
Kc3	32.3512	2.76736	0.1574	4.51	17.673	5.804	312.74

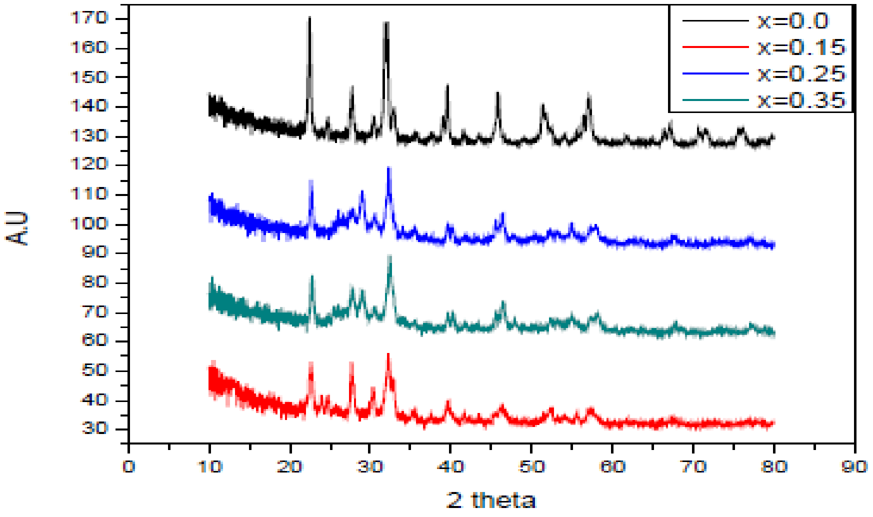

Fig.1: XRD pattern of $Bi_{(1-x)}Nd_xFe_{(1-x)}Mg_xO_3$ (citric acid)

FTIR Study

Absorption band near to 550 cm^{-1} is attributed to Fe-O stretching vibrations of octahedral FeO_6 group n the peroveskite compounds . Absorption band at 1574 cm^{-1} correspond to the bending vibrations of H-C-H. On the other hand, nitrile formation is observed at 2354 cm^{-1} , while a band at 1628 cm^{-1} and 737 cm^{-1} atrributed to the stretching vibrations of C=O and C-C in citric acid (Fig. 2).

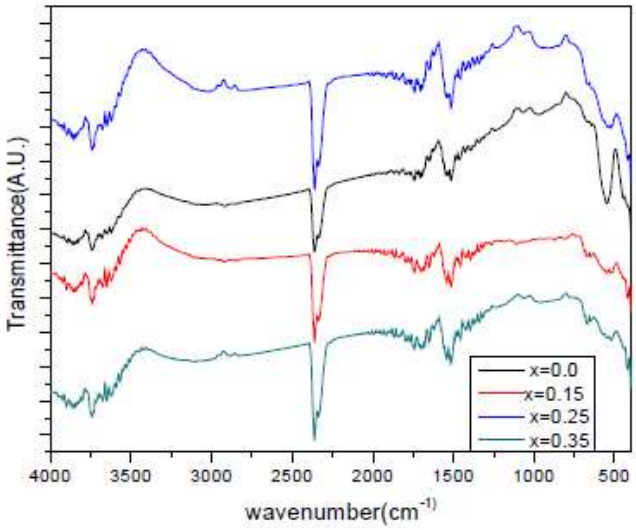

Fig. 2: FTIR spectra of $Bi_{(1-x)}Nd_xFe_{(1-x)}Mn_xO_3$ (Citric acid)

SEM Study

The SEM micrographs have been obtained to study the shape and morphology of the particles of the sample. Shape of particles almost spherical in case of glycine. SEM micrographs are shown in Fig. 3.

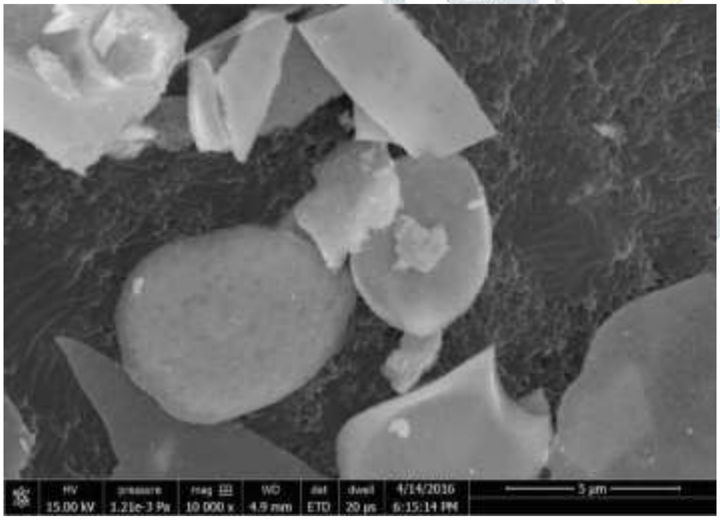

Fig. 3: SEM of $Bi_{0.75}Nd_{0.25}Fe_{0.75}Mg_{0.25}O_3$ obtained after sintering for 2 hours at 550^{O}C

VSM Study

We have plotted the M-H curves (Fig.4) and calculated the magnetic properties like retentivity, coercivity and saturation magnetization and reported in Table 2 . In case of x=0.25, there is enhancement in saturation magnetization, retentivity and coercivity.

Table 2:Saturation magnetization, coercivity and retenvity

Sample name	Sample code	Ms	Mr	Mc
$BiFeO_3$	Kc0	3.11	0.83	271.6
$Bi_{0.85}Nd_{0.15}Fe_{0.85}Mg_{0.15}O_3$	Kc1	2.849	0.20	52.23
$Bi_{0.75}Nd_{0.25}Fe_{0.75}Mg_{0.25}O_3$	Kc2	3.13	1.35	313.41
$Bi_{0.65}Nd_{0.35}Fe_{0.65}Mg_{0.35}O_3$	Kc3	1.34	0.47	167.15

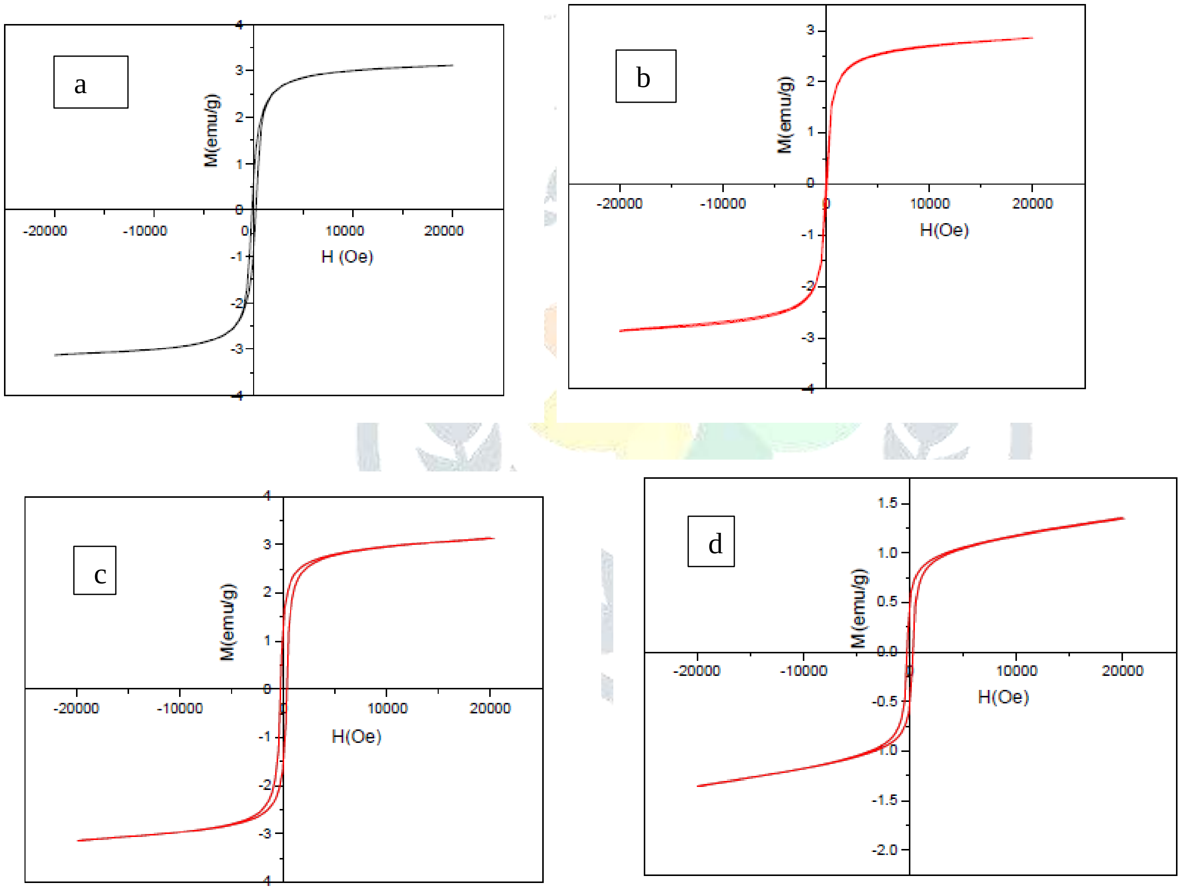

Fig. 4: VSM of (a) Kc0 (b) Kc1 (c) Kc2 (d) Kc3 samples obtained after sintering for 2 hours at 550oC

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