Low temperature magnetic properties of erbium doped Bismuth nano-ferrites

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Abstract

Nano-crystalline Pure and Erbium(Er) substituted Bismuth ferrite nano-particles were synthesized by the citrate-gel auto combustion method. Synthesized powders were sintered at 500°C for five hours in an air and characterized by XRD, TEM and HR-TEM. X-ray diffraction (XRD) analysis showed distorted rhombohedral structure of the ferrites. The surface morphology and particle size of the samples was observed by high resolution transmission electron microscopy. The lattice parameter, crystalline size, X-ray density has been calculated from d-spacing. The perceived results can be explained depending on doping concentration. Temperature dependence of magnetic properties of Bi-Er nano-particles were carried out by using vibrating sample magnetometer (VSM). The magnetization as a function of applied field at ± 100 Oe was carried out at 3K and 300K. Zero field cooled and (ZFC) and Field cooled (FC) magnetization measurements under an applied of 100 Oe in the temperature range of 3-360K. These measurements give the results of blocking temperature (T\textsubscript{b}) at around 350K.

1. Introduction

Multiferroics has the coexistence of two or more orders in a material. Multi ferroic material possess the coupling of electric and magnetic ordering, that has the potential applications such as spintronics, electromagnetic switching, sensors etc [1]. The multiferroic BiFeO3 combines ferroelectricity and ferromagnetism in a single phase. Among all the multiferroic materials, BiFeO3 is the only material having ferroelectric ordering high temperature T\textsubscript{c} = 1003K and G-type antiferromagnetic ordering with Transition temperature of T\textsubscript{N} = 643K [2,3]. At room temperature BiFeO3 is crystallized in ABO3 type pervoskite structure with space group R3c. A and B are the cations of different sizes and O is an anion that bonds both [4,5]. BFO has helical magnetic spin cycloid structure with period length of 62nm cancels out the net net magnetization due to the canted magnetic moment rotating in a spiral direction [6]. Previous reports suggest that electromagnetic properties of BFO strongly depend on nanoscale structure. Decrease in particle size exhibits high magnetization due to the suppression of the spin cycloid structure [7]. Doping of Rare earth ions in BFO enhances the structural magnetic properties.. This work investigates structural and magnetic properties of pure and 10% Erbium doped BiFeO3.

2. Experimental Procedure

Required amount of Bismuth nitrate, Iron nitrate, and Erbium nitrate were mixed in deionized water under continues stirring. Citric acid in 3:1 molar ratio with respect to precursors was added to the solution as gelating agent and stirred for 2 hours to get homogeneous mixture of metal nitrates. Ammonia was added to the above solution to maintain the pH – 7. The resultant solution was continuously heated on hot plate at 100°C up to dryness with continuous stirring. A viscous gel has resulted. Increasing the temperature up to 200°C lead the ignition of gel. The dried gel burnt completely in a self propagating combustion manner to form a loose powder. Finally the grinded powder was calcinated at 500°C for 5 hours.
The formation of $\text{Bi}_{1-x}\text{Er}_x\text{FeO}_3$ nanocrystals was confirmed by X-ray diffraction study using Cu-Kα radiation in 2θ range from 20 to 80°. The transmission electron microscopy (TEM), SEM and EDAX study was performed to obtain the particle size, morphology and elemental analysis respectively. The magnetic properties of nanoparticles were measured with the vibrating sample magnetometer (VSM).

3. Results And Discussion

Fig.1 shows the XRD pattern of $\text{Bi}_{1-x}\text{Er}_x\text{FeO}_3$ ($x=0, 0.1$) nano particles. XRD reveals that the samples are well crystallized. From the fig it can be observed that the pure $\text{BiFeO}_3$ sample has rhombohedral distorted pervoskite structure with space group R3c. by doping of erbium in $\text{BiFeO}_3$ the structural transition occurs, there exist a mixed phase of Rhombohedral and orthorhombic. With 10% substitution of Er all the peaks are shifted towards higher angles side because smaller ionic radius of $\text{Er}^{3+}$ than $\text{Bi}^{3+}$.

The structural variations can be determined by the tolerance factor, which is defined as

$$\tau = \frac{r_A + r_o}{\sqrt{2(r_B + r_o)}}$$

Where $r_A$ is ionic radius A-site cations, $r_B$ is the ionic radius of B-site cations and $r_o$ is the ionic radius of O anions in $\text{ABO}_3$ structure [8,9].tolerance factor is less than 1 for Rhombohedral structure, and $0.80 < \tau < 0.89$ for orthorhombic structure. Tolerance factor decreases with the addition of $\text{Er}^{3+}$ in $\text{Bi}^{3+}$ because of the ionic radius of Er is less compare with Bi, causes the reduction in volume of the unit cell. The average crystallize, lattice parameters of the sample decreases and micro strain increases with the doping because of difference in ionic radius. The average crystalline size can be calculated from the Debye Scherrer formula,

$$D = \frac{0.91\lambda}{\beta \cos \theta}$$

Where $\lambda$ is the wavelength of X-ray, $\beta$ is the peak width at the half maxima and $\theta$ is the peak position.

The calculated values of lattice parameter $a, c$, $c/a$ ratio, volume of the unit cell, tolerance factor ($t'$), X-ray density and Crystalline size for $\text{Bi}_{1-x}\text{Er}_x\text{FeO}_3 (x=0, 0.1)$ Nano-ferrite Partiles are given in table 1. It can be seen from the table that the values of lattice parameter $a, c$, volume, tolerance factor and crystal are decreases with the decrease of erbium composition. The values of $c/a$ is constant and X-ray density is increases with the composition.

Fig 2.represents the Scanning electron microscopy and elemental analysis of pure and 10%Er doped samples. The average grain size of the sample decreased from $\sim 200$nm to $\sim 100$nm on doping of 10%Er in pure $\text{BiFeO}$.Reduction of grain size due to Er suppresses the oxygen vacancies which lead to the low
oxygen ion motion. The decrease in grain size may also be due to the smaller ionic radius of Er compared to Bi.

Fig (3) shows the TEM and High resolution TEM images of 10%Er doped sample. From the figure it can be observed that the average diameter of the particle is ~47nm and the average inter planner spacing between the adjacent lattices is ~0.28nm.

The variation of magnetization with magnetic field of \( \text{Bi}_{1-x}\text{Er}_x\text{FeO}_3(x=0.1) \) sample measured at 3K and 300K with the maximum magnetic field of ±100kOe represented in Fig.4 (a) & (b). Fig shows that the sample exhibits the with enhanced saturation magnetization and ferromagnetic behavior. The improved magnetism attributed to the non zero magnetic moments of \( \text{Er}^{3+} \) ions creates a magnetic exchange coupling between magnetically active \( \text{Er}^{3+} \) and \( \text{Fe}^{3+} \) ions (f-d exchange interaction) [10,11,12]. The appearance of ferromagnetism may also be due to the suppression of the cycloid spiral spin structure caused by the smaller ionic radius of \( \text{Er}^{3+} \) ion doped in comparatively larger ionic radius of \( \text{Bi}^{3+} \). The observed values from the hysteresis loops are recorded in table 2.

Fig.(5). Indicates the variation of magnetization with temperature for \( \text{Bi}_{1-x}\text{Er}_x\text{FeO}_3(x=0.1) \) sample shows FC and ZFC curves with the applied field of 100 Oe. ZFC curve decreases with decrease in temperature and the moments of Er ions decreases with increase in temperature. The FC and ZFC splitting increases with decrease in temperature; this confirms the spin glass behavior. The spin glass behavior is due to the structural phase transition from rhombohedral to orthorhombic and nano size effect[13].

Conclusions

The Pure and Er doped BiFeO\(_3\) nanoparticles were synthesized by citrate gel auto combustion method. The structural, magnetic, electrical properties was investigated. The Pure BFO Is Crystallized in rhombohedrally distorted pervoskite structure, By doping of Er in Bi site the structural transformation occurs from rhombohedral to orthorhombic, and the average grain size decreased. For Er doped sample, as per the TEM results, the average particle size is less than 62nms. The enhanced ferromagnetism in Er doped sample is due to the suppression of the spiral spin structure.

Declarations

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Tables

| composition | a(nm) | c(nm) | c/a | V (nm$^3$) | Tolerance factor $\tau$ | X-ray density | Crystalline size (nm) |
|-------------|-------|-------|-----|------------|-------------------------|---------------|----------------------|
| 0           | 0.56468 | 1.383179 | 2.44948 | 0.038194 | 0.88772 | 8.15907804 | 14.71339 |
| 0.1         | 0.55835 | 1.367673 | 2.44949 | 0.036924 | 0.878778 | 8.429587404 | 11.79839 |

Table 1 : lattice parameter a, c, c/a ratio, volume of the unit cell, tolerance factor ($\tau$), X-ray density, Crystalline size calculated for Bi$_{1-x}$Er$_x$FeO$_3$ (x=0, 0.1) Nano-ferrite Partiles

| Saturation magnetization $M_s$ (emu/g) | Remanent Magnetization $M_r$ (emu/g) | Coercivity $H_c$(Oe) | Remanence ratio $= M_r/M_s$ | Anisotropy Constant(K) (erg/Oe) | Magnetic Moment (BM) |
|---------------------------------------|--------------------------------------|----------------------|-----------------------------|---------------------------------|-------------------|
| 3k                                    | 14.2363639                           | 2.51691448           | 521.23626                   | 0.176795                       | 1338.681          |
| 300k                                  | 6.1601226                            | 1.50118072           | 248.384358                  | 0.243693                       | 1561.304          |

Table.(2) : Saturation magnetization $M_s$, Remanent Magnetization, Coercively, Remanence ratio, Anisotropy Constant, Magnetic Moment of Bi$_{1-x}$Er$_x$FeO$_3$ (x=0.1) ferrite nano-particles

Figures
Figure 1

XRD patterns of the nano crystalline of Bi$_{1-x}$Er$_x$FeO$_3$($x=0, 0.1$) samples.
Figure 2

SEM and EDX images of Bi1-xErxFeO3(x=0, 0.1) ferrite nano-particles.
Figure 3

TEM and HR-TEM images of the Bi1-xErxFeO3(x=0.1) nano-ferrite particles.
Figure 4

M-H hysteresis curve of Bi1-xErxFeO3(x=0.1) ferrite nano-ferrite particles measured at (a) 3K and (b) 300K
Figure 5

Field cooled (FC) and Zero-field cooled (ZFC) curves for Bi1-xErxF3O3(x=0.1) Nano ferrite particles under an applied field of 100 Oe