

Influence of Ce - Co Substitution on Properties of BiFeO₃ Nanoparticles via sol-gel Auto Combustion Method

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Abstract—In present study, Ce - Co substituted bismuth ferrite (Bi_{1-x}Ce_xFe_{1-x}Co_xO₃; x = 0.00, 0.02 and 0.04) nanoparticles were synthesized via sol-gel auto – combustion method. The structural and magnetic properties of powder samples have been investigated using X ray diffraction (XRD), using X ray diffraction (XRD), Fourier Transform Infra-red spectroscopy (FT-IR), Mossbauer spectroscopy and vibrating sample magnetometer (VSM). The synthesized materials are found to have structural distortion in the rhombohedral R3c structure as observed by X-ray diffraction (XRD). In all samples, there was a negligible second phase, i.e. Fe rich compounds Bi₂Fe₄O₉. Fourier transform infra-red spectra of Bi_{1-x}Ce_xFe_{1-x}Co_xO₃ (x = x = 0.00, 0.02 and 0.04) contain two peaks between 440-590 cm⁻¹. The presence of two strong peaks between 440 cm⁻¹ to 590 cm⁻¹, attribute to bending and stretching of Fe-O bond, is the characteristic of the octahedral FeO₆ group in perovskite structure. All samples showed sextet with minor doublets lead to superparamagnetic nature and weak ferromagnetism. The presence of weak doublet along with a sextet pattern in Mossbauer spectra indicate the secondary phase. Also, M-H loops of these materials demonstrate that Ce - Co doping in BiFeO₃ enhances retentivity, coercivity and saturation magnetization. Due to soft magnetic nature of Ce-Co doped BiFeO₃, it can be suitable for storage device applications.

Keywords: Multiferroic properties; Mossbauer spectroscopy; Magnetic properties.

1. INTRODUCTION

Development of modern electronic devices which are based on semiconductor materials are increasingly pointing towards improved performance, multi-functionality and miniaturization. The frequency, operating bandwidth, power handling, power consumption, gain and loss etc are related with multi-functionality. The discovery and refinement of distinct materials and processing help to develop the enhanced devices, assemblies and systems [1]. Multiferroic materials require coexistence and coupling of the ferromagnetic property and the ferroelectric property. The ferroelectric and ferromagnetic properties are mutually exclusive [2]. The bismuth ferric oxide, also known as BFO, is the few one among the example of single multiferroics. BFO shows strong

magnetic and ferroelectric properties at room temperature. The structure of BFO is perovskite rhombohedral at room temperature and it has space group R3c. In its unit cell, rhombohedral angle at room temperature have been reported as ($\beta_{\text{rhombohedral}}$) = 89.3° and lattice parameter as ($a_{\text{rhombohedral}}$) = 3.965 Å. [3]. The rhombohedral unit cell have lattice parameters as $a=5.58\text{Å}$ and $\alpha=89.5^\circ$ (BFO single crystal) [4]. In order to achieve considerable improvement in the multiferroic properties of BiFeO₃, several researchers have investigated BiFeO₃ by doping rare earths (RE) and transition metals (TM).

2. EXPERIMENTAL

2.1 Material

Bi_{1-x}Ce_xFe_{1-x}Co_xO₃; x = 0.00, 0.02 and 0.04 was synthesized using sol-gel auto combustion method at room temperature. The starting materials are AR grade Bi(NO₃)₃ · 5H₂O, Ce(NO₃)₃ · 6H₂O, Fe(NO₃)₃ · 9H₂O and Fe(NO₃)₃·9H₂O (Loba Chemie; 98% purity), Co(NO₃)₂·xH₂O (Sigma Aldrich; 98% purity) and citric acid (C₆H₈O₇·H₂O) (Loba Chemie; 99.5% purity). Aqueous solution of iron and metal salts was prepared separately in stoichiometric ratios by dissolving them in 50ml distilled water making the salt solution. Citric acid was added to the salt solution with cations to citric acid molar ratio of 1:1.5. The mixture was placed on a hot plate with constant and continuous magnetic stirring at 80-86°C for 3-4 hours to evaporate the water and obtain the brownish viscous gel solution. The gel was place on a hot plate at 280-300°C for 30 minute to completely remove the water and obtain the precursor material. Then the precursor material was heat-treated at 550 °C temperatures.

X-ray diffraction pattern (obtained in the range 20°-80° using Cu-K α radiation operating at 40 kV and 35 mA with step size 0.02°) was used to study the structural properties of the prepared sample (Bruker AXS D8 advance diffractometer). Field emission scanning electron microscope (FE-SEM) (Joel

6390LV) operating at a voltage of 20 kV was used to study the surface features. FTIR spectra are recorded at room temperature in the 500-4000 cm⁻¹ range using Shimadzu FTIR-8700.

3. RESULTS AND DISCUSSION

3.1 XRD - Analysis

Figure 1 shows the XRD pattern of nano-crystalline Bi_(1-x)Ce_xFe_(1-x)Co_xO₃ (x = 0, 0.02 and 0.04) compound. From XRD data, all the peaks are well matched with the standard pattern of JCPDS (Card No. 71-2494). The material possesses R3c space group with the distorted rhombohedral structure of the average crystallite size (D) were estimated from X-ray diffraction data using Scherrer relation [5]

Parameters like cell constants (a and c), cell volume (V), crystalline size (D) were calculated by using the formula:

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

$$V = 0.866a^2c$$

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

where *k* is the grain shape factor, *λ*, *θ* and *β* are the X-ray wavelength, Bragg diffraction angle, and FWHM of the diffraction peak respectively. Here *λ* is the wavelength, *β* is the half width full maxima, *K*= 0.89, the constant. Variation of lattice constant *a* and *c* with concentration which shows that Ce - Co are well incorporated into BiFeO₃ lattice.

Table 1: Lattice parameters of Bi_(1-x)Ce_xFe_(1-x)Co_xO₃.

Sample	a(A ⁰)	c(A ⁰)	D(nm)
X = 0.00	5.595	13.90	47
X = 0.02	5.584	13.86	25
X = 0.04	5.582	13.83	17

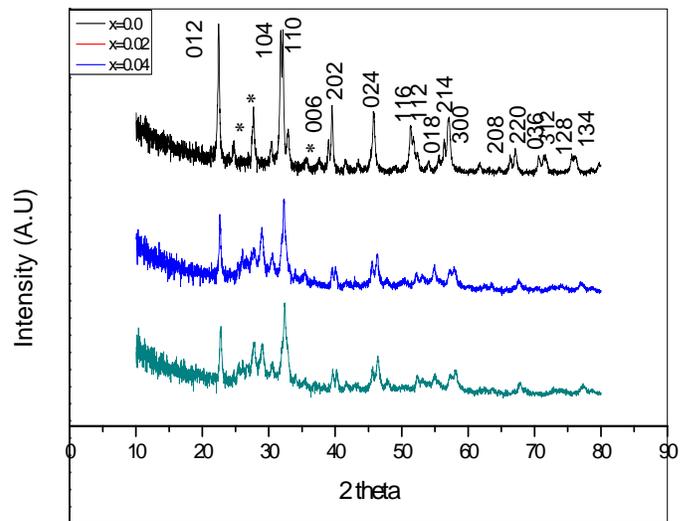


Figure 1: XRD pattern of Bi_(1-x)Ce_xFe_(1-x)Co_xO₃.

3.2 FTIR Analysis

1. The molecular bands and attached functional groups of the samples have been investigated by Fourier transform infrared spectrometer (FTIR). Absorption band near to 550 cm⁻¹ is attributed to Fe-O stretching vibrations of octahedral FeO₆ group in the perovskite compounds. Absorption band at 1574 cm⁻¹ correspond to the bending vibrations of H-C-H. The band at 1560 cm⁻¹ matches with C-N stretch and C-N-H bending vibrations and -CO-NH- vibrations are visible at 1640 cm⁻¹. The bands at 939 cm⁻¹ is assigned to C-CO stretching and the bands at 1235 and 1450 cm⁻¹ correspond to wagging and bending vibrations, respectively of CH₂ group [6].

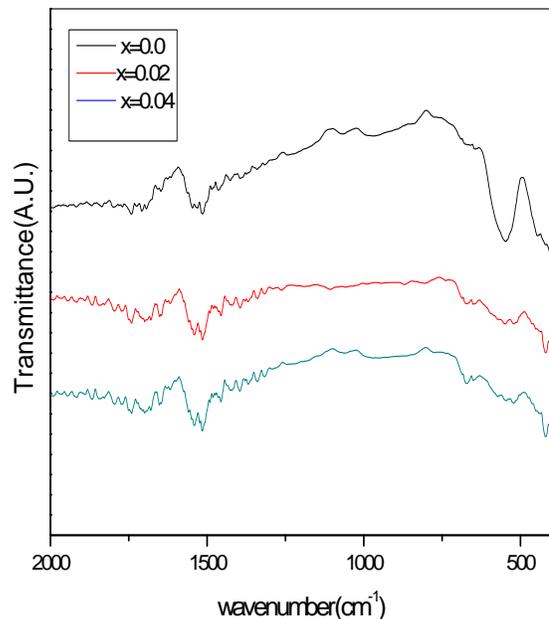


Figure 2: FTIR spectra of Bi_(1-x)Ce_xFe_(1-x)Co_xO₃

3.3 Mossbauer Spectroscopy

Mossbauer spectra show a strong sextet pattern due to antiferromagnetic ordering and weak doublet attributed to a fraction of the super-paramagnetic behavior of finer particles. The doublet in fitted data may be due to the presence of paramagnetic compound $\text{Bi}_2\text{Fe}_4\text{O}_9$. Rietveld refined XRD patterns also support the presence of small amount $\text{Bi}_2\text{Fe}_4\text{O}_9$ in synthesized multiferroics [7]. The Sextet in Mossbauer spectra corresponds to the presence of ferric ions at different sites.

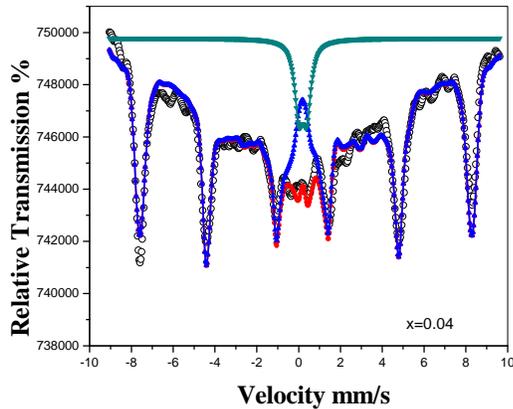


Figure 3. Mossbauer spectra of ^{57}Fe relative transmission for $\text{Bi}_{1-x}\text{Ce}_x\text{Fe}_{1-x}\text{Co}_x\text{O}_3$ ($x = 0.04$) at RT.

3.4 Magnetic Property

The magnetic properties of synthesized samples have been investigated by plotting M-H curves (Figures 4, 5 and 6). The Coercivity, saturation magnetization and retentivity of the samples are reported in Table 2. In case of $x=0.04$, There is enhancement in saturation magnetization, retentivity and coercivity

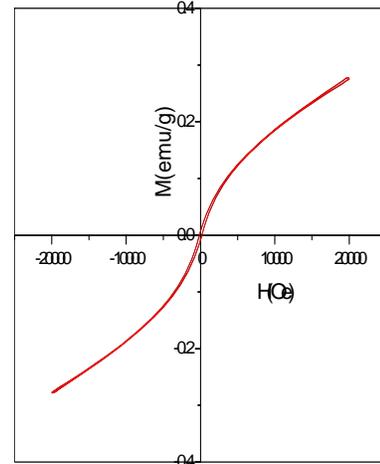


Figure.4: Magnetic Hysteresis loop of BiFeO_3

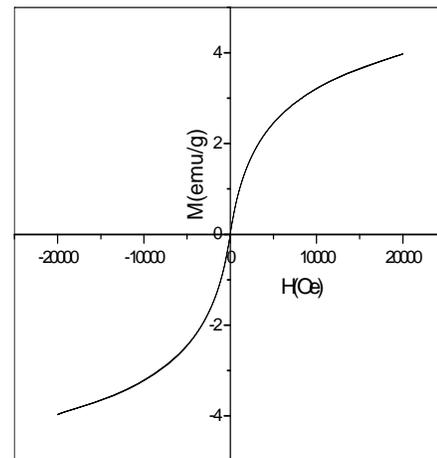


Figure 5: Magnetic Hysteresis loop of $\text{Bi}_{0.98}\text{Ce}_{0.02}\text{Fe}_{0.98}\text{Co}_{0.02}\text{O}_3$.

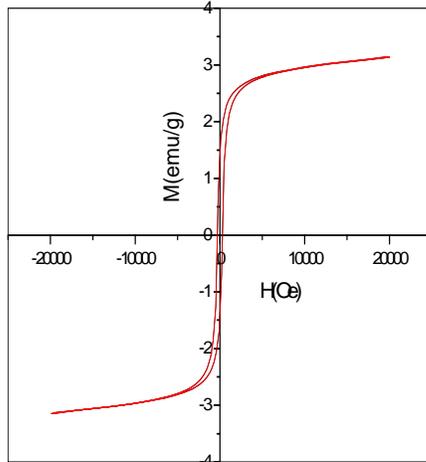


Figure 6: Magnetic Hysteresis loop of Bi_{0.96}Ce_{0.04}Fe_{0.96}Co_{0.04}O₃.

Table 2: Saturation magnetization, coercivity and retentivity for all samples:

Sample name	Ms	Mr	Mc
X = 0.00	0.2	0.01	309
X = 0.02	3.97	0.14	114
X = 0.04	3.13	1.7	417.41

4. CONCLUSION

In summary, Bi_(1-x)Ce_xFe_(1-x)Co_xO₃ (x = 0, 0.02, and 0.04) nanoparticles were successfully synthesized by the sol-gel route. X-ray diffraction, FTIR applied to investigate the structure-dependent evolution of properties of perovskite rare earth and transition metal ion doped BiFeO₃ nanoparticles, Also, Mossbauer and VSM applied to investigate the magnetis properties of pure and undoped BiFeO₃. The formation of the distorted rhombohedral perovskite structure of synthesized compounds has been observed from XRD. Enhancement in saturation magnetization and coercivity of Ce-Co doped multiferroics as compared to BFO have been observed. This enhancement is useful in memory device applications.

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