

Enhanced multiferroic properties in Cerium doped BiFeO_3

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ABSTRACT:

Cerium doped BiFeO_3 nanoparticles were successfully synthesized by auto combustion technique. The prepared samples were characterized by X-ray diffraction (XRD), Scanning electron Microscopy (SEM), Transmission electron microscopy (TEM), Vibrating sample magnetometer (VSM) and dielectric studies. The samples were confirmed to have perovskite type rhombohedral structure with space group $R3C$. SEM micrograph of Ce doped samples exhibits fine grained structure with sharp grain boundaries with almost uniform diameter. The average particle size is found to decrease with Ce doping. Magnetization measurement for all the samples exhibited ferromagnetic ordering at room temperature. Ce doping has strengthened the magnetic properties of BiFeO_3 significantly. The existence of magnetoelectric coupling was indicated by the observation of the dielectric anomaly in the dielectric constant and dielectric loss near antiferromagnetic Neel temperature. All these properties make Cerium doped BiFeO_3 promising for future device applications.

Key words: Powder diffraction, Crystal structure, Magnetic properties and Dielectric properties.

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INTRODUCTION

Multiferroics are classified as materials that have coupled ferroelectric and magnetic order parameters over a certain range of temperature. Multiferroics possess all the potential applications of both ferroelectric and ferromagnetic materials. A lot of novel devices can be brought into application by employing this coupling of electric and magnetic polarization of multiferroics [1-3]. This additional degree of freedom due to coupling between electric and magnetic polarization opens door for designing devices such as multiple state memory elements, in which data is stored both in the electric and the magnetic polarizations, or novel memory media, which might allow the writing of a ferroelectric data bit and the reading of the magnetic field generated by association [4]. Motivated by the potential of coupled ferroelectric and magnetic properties in applications, this study aims to further elucidate the behavior of cerium doping on the magnetic and electric order at the room temperature on multiferroic BiFeO_3 system.

However, there are very few materials that exhibit the multiferroic characteristics at room temperature. BiFeO_3 is one of the most widely studied multiferroic materials over the last few years, largely because it is the only single-phase multiferroic material that is simultaneously both antiferromagnetic and ferroelectric at room temperature (Neel temperature (T_N) ~ 643 K

and ferroelectric Curie temperature (T_C) ~ 1103 K)[5,6]. Besides this, BiFeO_3 has a rhombohedral distorted perovskite structure with space group $R3C$ [7]. A revived interest in the research activities on BiFeO_3 is seen in recent years because of its robust multiferroic properties which would surely replace the commercially available toxic ferroelectric devices containing lead materials [8]. However BiFeO_3 suffers from several major issues like high leakage current, spiral spin structure, large difference in transition temperature (T_C and T_N). The leakage current arises in BiFeO_3 due to its nonstoichiometry. This is particularly because of the difficulty in obtaining stoichiometric single phase BiFeO_3 materials. Hence it allows current to pass through when a high voltage is applied.

Attempts to improve the electrical properties have been made by doping it with rare earth elements such as Lanthanum (La), Samarium (Sm), Gadolinium (Gd) and Dysprosium (Dy) etc [9,10]. Difficulties also prevail in practical realization of BiFeO_3 on account of weak ferromagnetism exhibited by BiFeO_3 , as the spiral spin modulation, superimposed on G-type antiferromagnetic spin ordering [11, 12], cancels out any possible net magnetization. One of the ways of suppressing spiral spin modulation in BiFeO_3 is the chemical substitution in the A-sublattice [13-18]. Diamagnetic substitution at A-site in BiFeO_3 has been shown to enhance the net magnetization of parent material on account of the kind of diamagnetic dopant element [19, 20]. However, the peculiarity of the correlation between the kind of diamagnetic dopant and the magnetic properties of the samples is still an issue of intensive discussion. Motivated by the above discussed facts, we have tried to obtain a single phase multiferroic system by auto-combustion method. In view of furnishing this thought, Cerium is chosen to substitute at A-site of BiFeO_3 because very less attention is paid to this lanthanide. Also the ionic radius of Ce^{3+} is comparable with that of Bi^{3+} . The partial substitution of Bi^{3+} ions by rare earth ions are reported to improve multiferroic properties of BiFeO_3 [21-25].

MATERIALS AND METHODS

The samples with the composition $\text{Bi}_{1-x}\text{Ce}_x\text{FeO}_3$ ($x=0.05, 0.1, 0.15, 0.2$) were prepared by autocombustion method using Urea as fuel. The prime basis of autocombustion method depends on the proficiency of highly exothermic reactions to be self-sustaining and, therefore, energetically efficient. The precursor materials used for the synthesis of $\text{Bi}_{1-x}\text{Ce}_x\text{FeO}_3$ ($x=0.05, 0.1, 0.15, 0.2$) by the autocombustion route were analytical reagent grade Bismuth Nitrate Pentahydrate ($\text{Bi}(\text{NO}_3)_3 \cdot 5\text{H}_2\text{O}$), Iron Nitrate Nona hydrate ($\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$), $\text{Ce}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ Cerium nitrate hexahydrate with a purity of more than 99%. Analytical grade Urea from Sigma Aldrich in a powder form with purity more than 99 % was used as fuel in the synthesis of the BiFeO_3 powder. Appropriate quantities of materials were weighed in microbalance according to the stoichiometry to obtain (0.05, 0.1, 0.15, 0.2) Ce^{3+} dopant concentrations. Stoichiometry of the redox mixture for combustion is calculated based on the total oxidizing and reducing valencies of oxidizer and fuel. So that the equivalence oxidizer to fuel ratio becomes unity which results in release of maximum heat [26, 27].

Thus, a mixture of ($\text{Bi}(\text{NO}_3)_3 \cdot 5\text{H}_2\text{O}$), ($\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$), $\text{Ce}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ and Urea in an appropriate molar proportion were thoroughly mixed by grinding using agate mortar and pestle to form a homogeneous mixture. This homogeneous mixture was then poured into a crucible and was introduced into a muffle furnace preheated to 500°C which undergoes self-propagating, gas producing combustion reaction to yield voluminous metal oxide in less than 5 minutes, which is a porous and foamy product [28]. The porous powder was ground in a mortar and pestle to obtain a fine powder. The ground powder was again placed into the

furnace for calcination at 400°C for 3 hours. The synthesized powders were characterized by using various techniques. X-ray powder diffraction data was collected using a XPERT-PRO diffractometer with Cu α radiation ($\lambda = 0.154056$ nm) at step of 0.02 in the range $2\theta = 20^\circ$ to 80° . The morphology and surface characterization of our samples were observed using Scanning Electron Microscope (JEOL MODEL JSM-6390 LV). The magnetic properties were measured by a vibrating sample magnetometer (Lakeshore VSM 7410) at room temperature. Dielectric measurements were performed on an impedance analyzer (Weynn Kerr 6500 B)

RESULT AND DISCUSSION: Structural Analysis

Room temperature powder x-ray diffraction was then carried out on $\text{Bi}_{1-x}\text{Ce}_x\text{FeO}_3$ ($x=0.05, 0.1, 0.15, 0.2$). Rhombohedral perovskite structure is retained even after substituting Ce^{3+} ions for Bi^{3+} in BiFeO_3 . The profile fits for the Rietveld refinement of $\text{Bi}_{1-x}\text{Ce}_x\text{FeO}_3$ ($x=0.05, 0.1, 0.15, 0.2$) samples are shown in Fig [1&2].

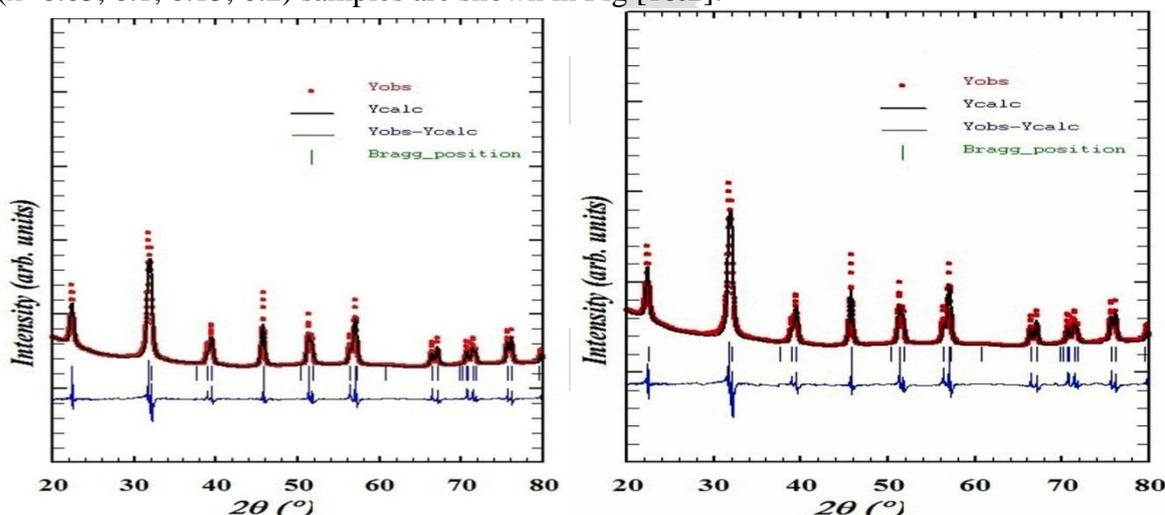


Fig [1]: The fit for the Rietveld refined profile of $\text{Bi}_{0.95}\text{Ce}_{0.05}\text{FeO}_3$ & $\text{Bi}_{0.9}\text{Ce}_{0.1}\text{FeO}_3$ sample

Ce doping causes the peaks to shift toward lower 2θ value. This indicates that Ce is getting substituted in the BiFeO_3 lattice. The lattice parameters are found to increase with Ce doping because ionic radii of Ce^{3+} is more than that of Bi^{3+} ion. The crystallite sizes of all the samples $\text{Bi}_{1-x}\text{Ce}_x\text{FeO}_3$ ($x=0.05, 0.1, 0.15, 0.2$) were found to be 16nm, 19nm, 22nm and 27nm respectively obtained by considering the most intense diffraction peak in the pattern using Scherrer's formula.

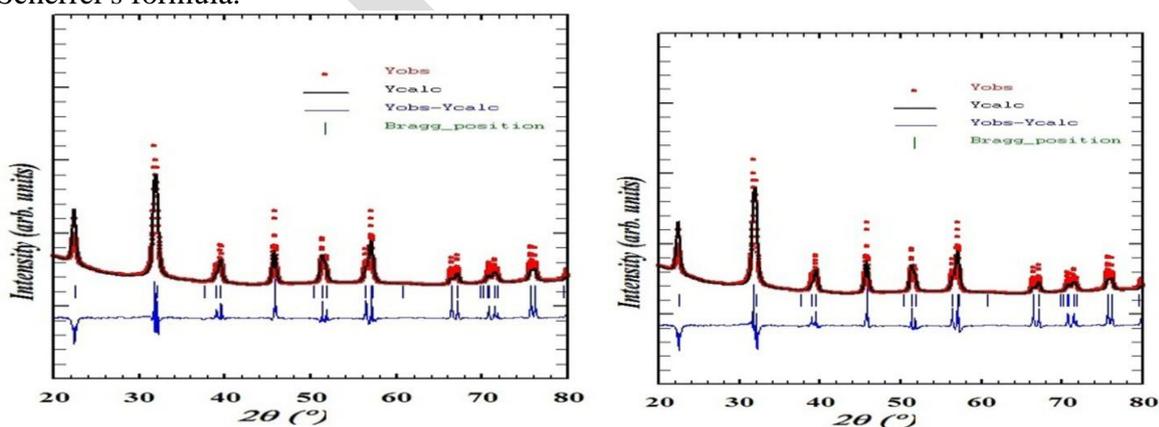


Fig [2]: The fit for the Rietveld refined profile of $\text{Bi}_{0.85}\text{Ce}_{0.15}\text{FeO}_3$ & $\text{Bi}_{0.8}\text{Ce}_{0.2}\text{FeO}_3$ sample.

Microstructural Analysis:

SEM micrograph of Ce doped samples exhibits fine grained structure with sharp grain boundaries with almost uniform diameter. The micrographs of the samples showed relatively greater homogeneity in the microstructure. Also the grain size of the samples decreases with increasing Cerium in BiFeO_3 as shown in Fig 3, which is a clear indication of incorporation of Ce into BiFeO_3 .

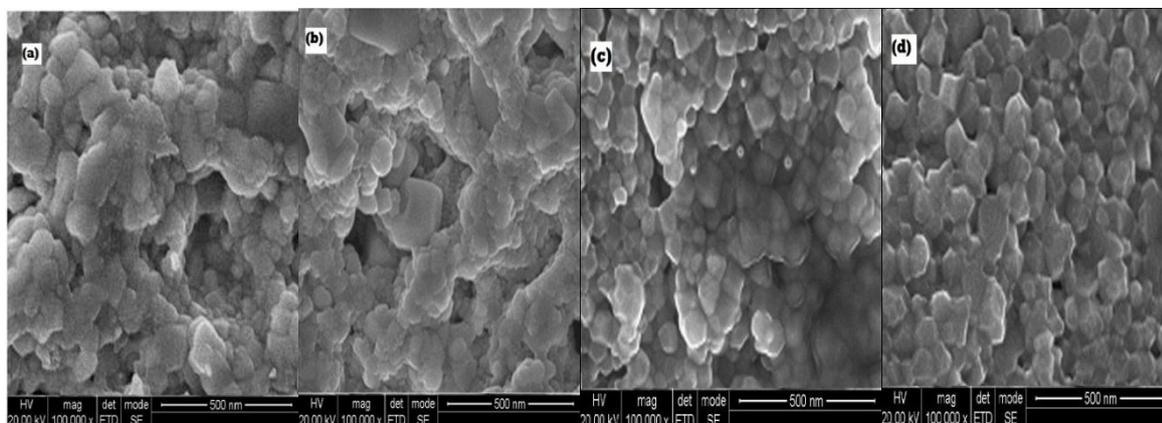
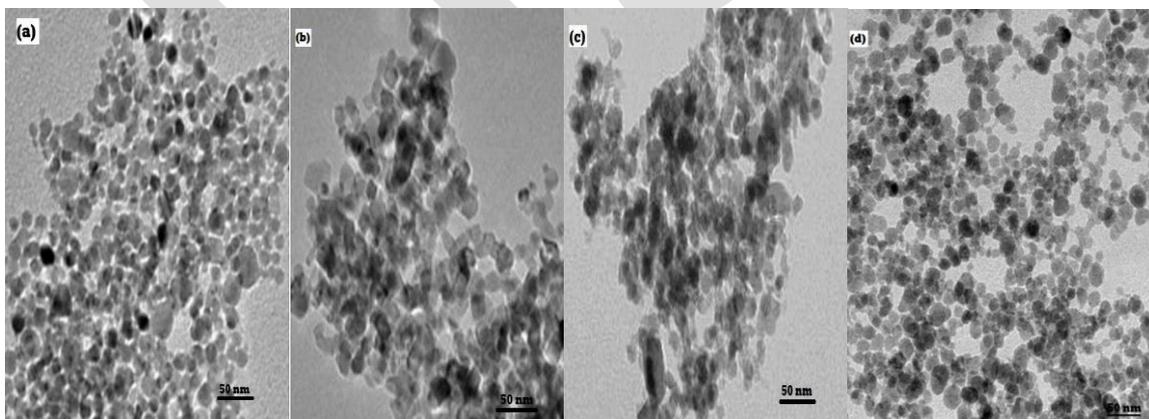


Fig [3] SEM micrograph of $\text{Bi}_{1-x}\text{Ce}_x\text{FeO}_3$ ($x=0.05, 0.1, 0.15, 0.2$) ceramic.

TEM Analysis:

Typical TEM images of the $\text{Bi}_{1-x}\text{Ce}_x\text{FeO}_3$ ($x=0.05, 0.1, 0.15, 0.2$) sample prepared by the autocombustion method is shown in figure [4] respectively. The particles are well connected with each other and are found to be approximately spherical in shape. The average particle size is found to decrease with Ce doping. Thus we can conclude that the substitution of Bismuth by rare-earth in multiferroic material BiFeO_3 is accompanied by a significant decrease of particle size [29].



Fig[4].TEM images of $\text{Bi}_{1-x}\text{Ce}_x\text{FeO}_3$ nanoparticles, (a) $x=0.05$, (b) $x=0.1$ (c) $x=0.15$ and (d) $x=0.2$

Magnetic properties:

The magnetic behavior study of $\text{Bi}_{1-x}\text{Ce}_x\text{FeO}_3$ nanoparticles was carried out through dc magnetization measurements of all the samples at room temperature. Figure [5] displays hysteresis loops of all the samples recorded at 300 K. It is noted that saturation is achieved in

all the samples for an applied field of $<10\text{KOe}$. All the samples exhibited ferromagnetic ordering at room temperature. Owing to finite size the nanoparticles usually show unusual magnetic behaviors distinct from that of their bulk counterparts. In antiferromagnetic nanoparticles, due to the large surface to volume ratio, the contribution of uncompensated spins at the surface becomes higher. Apart from uncompensated spins at the surface, canting of spins in antiferromagnetic sublattices also plays an important role in the magnetic properties of the nanostructures [30,31]. Ce doping could have increased the canting angle, which in turn has resulted in enhanced magnetic properties. Another reason for the observed ferromagnetism is the suppression of spiral spin structure characteristic of BiFeO_3 . When the particle size is of the order of or $<62\text{ nm}$, this spiral spin structure changes so as to result in enhancement in magnetic properties. It is clear that Ce doping has strengthened the magnetic properties of BiFeO_3 significantly.

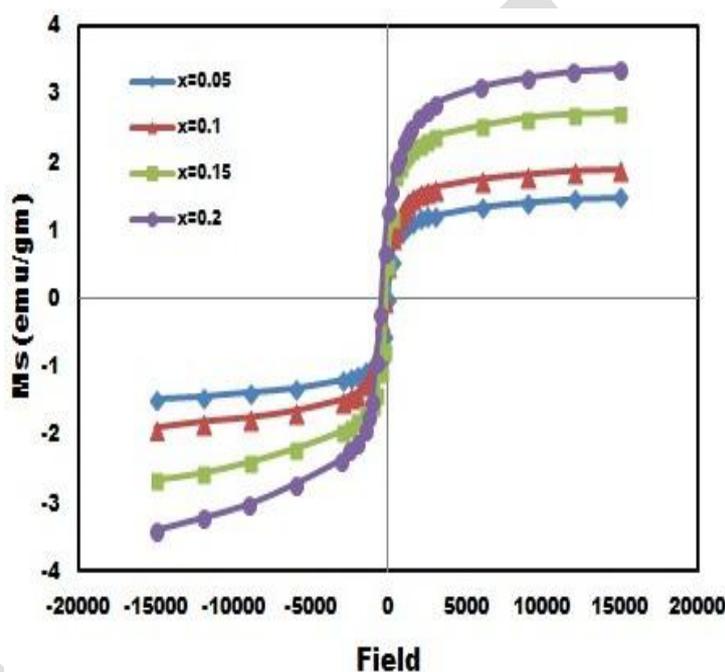


Fig [5] The M-H plot of $\text{Bi}_{1-x}\text{Ce}_x\text{FeO}_3$ ($x = 0.05, 0.1, 0.15, 0.2$) at 300K .

Dielectric properties:

The measured temperature dependence of dielectric constant ϵ and loss for $\text{Bi}_{1-x}\text{Ce}_x\text{FeO}_3$ ($x=0.05, 0.1, 0.15$ and 0.2) samples at 100Hz frequency are shown in figure [6]. Dielectric constant and $\tan\delta$ both show anomaly peak near antiferromagnetic Neel temperature. This phenomenon is a signature of magnetoelectric coupling. The Landau-Devonshire theory of phase transitions predicted this type of dielectric anomaly in magnetoelectrically ordered systems as an effect of diminishing magnetic order on the electric order [32]. Here the peaks show a diffuse nature. The substitution of Cerium, shifts the dielectric peak to low temperature region and a diffuse dielectric peak results. The peak shift may be attributed to the slightly larger ionic radii of Ce^{3+} which replaces Bi^{3+} due to which tolerance factor decreases which in turn reduces the Neel temperature. Another significant result is the peak broadening with increase in Cerium concentration.

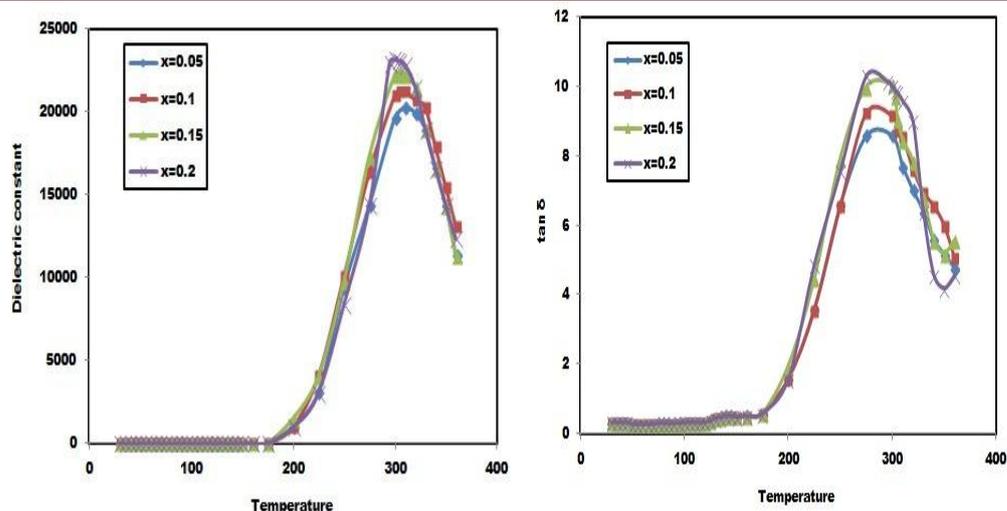


Fig [6] Temperature dependent dielectric constant & $\tan \delta$ of $\text{Bi}_{1-x}\text{Ce}_x\text{FeO}_3$ ($x=0.05, 0.1, 0.15, 0.2$) at 50Hz.

CONCLUSION

It can be concluded from the present work that auto-combustion synthesis technique can be an advantageous method to prepare single phase Cerium doped BiFeO_3 . The XRD pattern showed rhombohedrally distorted perovskite structure for Cerium doped BiFeO_3 . Magnetization is found to increase considerably in all doped samples than in pure BiFeO_3 due to canting of spins and particle size below the periodicity of BiFeO_3 . Temperature dependent dielectric anomaly is observed for all the samples near the vicinity of Néel temperature, which is a signature of magneto-electric coupling.

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