

STRUCTURAL, MORPHOLOGICAL AND MAGNETIC PROPERTIES OF Nd AND Co CO-DOPED BiFeO₃ CERAMICS AT ROOM TEMPERATURE

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ABSTRACT

Synthesis and characterization of BiFeO₃ samples, co-doped with rare earth Nd and Co in place of Bi and Fe respectively were investigated at room temperature (RT). The formula of the four samples are Co-doped BiFe_{1-x}Co_xO₃ (x = 0.05-0.10) and Nd and Co co-substituted Bi_{0.95}Nd_{0.05}Fe_{0.95}Co_{0.05}O₃ and Bi_{0.90}Nd_{0.10}Fe_{0.90}Co_{0.10}O₃. These ceramic samples were synthesized by conventional solid state reaction method. The X-ray diffraction patterns clearly reveal that the secondary impurity phases were eliminated significantly due to the simultaneous substitution of Nd and Co in place of Bi and Fe respectively of BiFeO₃ ceramics. The surface morphology of the synthesized samples was found to improve due to the simultaneous substitution of Nd and Co in place of Bi and Fe in BiFeO₃. The average grain size of the first sample with 5% doping of Co in place of Fe was 1.5µm. In the second sample with 10% Co doping in place of Fe, the average grain size became 1.25 µm. In presence of 5% Nd in place of Bi as well as with 5% doping of Co in place of Fe, grain size reduced to 0.75µm. The sample with 10% doping of Nd and Co in place of Bi and Fe respectively, average grain size decreased to 0.5µm. The EDX spectroscopy ensured the presence of Bi, Nd, Fe, Co and O in these samples and their percentage of mass and atoms. Magnetic properties of the samples were also investigated at room temperature by measuring magnetization versus magnetic field (M-H) hysteresis loops. The wider loop clearly demonstrates the significant improvement of the magnetic behavior in 10% Nd and Co doped Bi_{0.90}Nd_{0.10}Fe_{0.90}Co_{0.10}O₃ sample. The enhanced magnetic properties might be attributed to the substitution induced suppression of spiral spin structure of BiFeO₃. The outcome of this investigation suggests the potentiality of the simultaneous doping of Nd and Co in BiFeO₃ ceramics to improve their structural, morphological and magnetic characteristics.

Key words : Multiferroics, XRD, Grain size, M-H Hysteresis Loop

INTRODUCTION

The materials exhibiting ferroelectric, ferromagnetic and ferroelastic behaviors or at least two out of the three behaviors simultaneously are known as multiferroics (Hill, 2000). In recent years, a source of huge interest has grown up in developing multiferroics possessing ferroelectric polarization and magnetic ordering in the same phase. Coupling between the magnetic and ferroelectric order parameters in these materials can give rise

to a magnetic effect, which might be used in numerous technological applications. These materials have gained tremendous attention on account of their potential applications in various fields. It proves its necessity in digital recording (Qin *et al.* 2012), sensor, multiple state memory element, electro ferromagnetic resonance device (Shami *et al.* 2011), thin film capacitor, non-volatile memory (Garcia *et al.* 2010), optoelectronics, solar energy device, high density ferroelectric and magnetic random access memory. Ferrites are also used in camouflaging military aircrafts and missiles against radar detection (Bhuiyan *et al.* 2015).

Among the various types of multiferroics, BiFeO₃ has attained much attention of researchers due to its promising potential applications in the fields of electromagnetic coupling, spintronics, sensors and data storage devices (Wang *et al.* 2003). In BiFeO₃, dielectric properties can be controlled by applied magnetic field and magnetization can be controlled by varying electric field (Belik *et al.* 2009). It implies that in BiFeO₃, ferroelectric and anti-ferromagnetic ordering coexist in a single phase at room temperature. BiFeO₃ has rhombohedrally distorted ABO₃ type perovskite structure with space group R3c (Demidov *et al.* 2007). Its Curie temperature (T_C) is 1103°K (high ferroelectric) and G-type anti-ferromagnetic Neel temperature (T_N) is 643°K (Liu *et al.* 2009). Ferro electricity appears in pure BiFeO₃ due to off centered distortion of Fe³⁺ ions, caused by ⁶S₂ ion pairs of Bi³⁺ ions in its non centrosymmetric rhombohedral structure (Khomchenko *et al.* 2007). In BiFeO₃, localized antiferromagnetism is generated by canted spins structure which is suppressed by the spiral spin structure at macroscopic level (Uniyal and Yadav. 2008). In BiFeO₃, magnetic ordering is of antiferromagnetic type, having a spiral modulated spin structure (SMSS) with an incommensurate long-wavelength period of 62 nm (Agarwal *et al.* 2012). This spiral spin structure cancels the macroscopic magnetization and prevents the observation of the linear magneto electric effect. Apart from this, the bulk BiFeO₃ is characterized by serious current leakage problems due to the existence of a large number of charges centers caused by oxygen ion vacancies (Agarwal *et al.* 2012). These problems make the use of BiFeO₃ for fabrication of multifunctional devices narrower (Yuan *et al.* 2006). However, BiFeO₃ has serious problems as a ferroelectric material because of its quite large leakage current density at room temperature, which is mainly attributed to the oxygen vacancy and oxidation state of Fe. Therefore, the higher conductive nature of BiFeO₃ makes it harder to get excellent ferroelectric property. To overcome this problem, various approaches have been investigated. The efforts have been made to reduce the leakage current density by either introducing dopants or using different fabrication methods (Dho *et al.* 2006).

For this reason, we explore in this work the structure and morphology and the magnetic properties of the compounds Co doped BiFe_{1-x}Co_xO₃ (x = 0.05-0.10) and Nd

and Co co-substituted $\text{Bi}_{0.95}\text{Nd}_{0.05}\text{Fe}_{0.95}\text{Co}_{0.05}\text{O}_3$ and $\text{Bi}_{0.90}\text{Nd}_{0.10}\text{Fe}_{0.90}\text{Co}_{0.10}\text{O}_3$. Therefore, nominal compositions of $\text{Bi}_{1-y}\text{Nd}_y\text{Fe}_{1-x}\text{Co}_x\text{O}_3$ (i. $y = 0, x = 0.05$; ii. $y = 0, x = 0.10$; iii. $y = 0.05, x = 0.05$; iv. $y = 0.10, x = 0.10$) ceramics were synthesized by conventional solid state reaction technique and their structural, morphological and magnetic properties were investigated.

EXPERIMENTAL DETAILS

The nominal compositions of Co doped $\text{BiFe}_{1-x}\text{Co}_x\text{O}_3$ ($x = 0.05-0.10$) and Nd and Co co-substituted $\text{Bi}_{0.95}\text{Nd}_{0.05}\text{Fe}_{0.95}\text{Co}_{0.05}\text{O}_3$ and $\text{Bi}_{0.90}\text{Nd}_{0.10}\text{Fe}_{0.90}\text{Co}_{0.10}\text{O}_3$ were of high purity. For synthesizing, synthesized by conventional solid state reaction technique oxides of Bi_2O_3 , Nd_2O_3 , Fe_2O_3 , and Co_2O_3 powders were carefully weighed in stoichiometric proportion mixed thoroughly with acetone and grounded in an agate mortar until a homogeneous mixture was formed. The compact mixtures of reagents were 800 calcined at $^{\circ}\text{C}$ for 1.5 hours in a programmable furnace. The powders were pressed into pellets of thickness 1 mm and diameter 12 mm by using a uniaxial hydraulic press and sintered at 825°C for 5 hours at heating rate 10°C per minute. The crystal structure and phase purity of the samples (sintered powder) were determined from X-ray diffraction (XRD) data. XRD patterns were obtained at room temperature using a diffractometer ((3040 Phillips Pro XRD system PW with $\text{CuK}\alpha$ ($\lambda = 1.5406 \text{ \AA}$) radiation.

The comparative grain size was observed using a field emission Scanning Electron Microscope ((LA6490 Jeol JSM equipped with the Energy Dispersive X-ray (EDX). The EDX analysis has been used to determine the overall chemical homogeneity and composition of the samples. The magnetic properties of the samples were characterized by using a Vibrating Sample Magnetometer ((Micro sense 9EV

RESULTS AND DISCUSSION

Structural Characterizations

The XRD patterns of the samples $\text{BiFe}_{0.95}\text{Co}_{0.05}\text{O}_3$ and $\text{BiFe}_{0.90}\text{Co}_{0.10}\text{O}_3$ and Co and Nd co-doped sample $\text{Bi}_{0.95}\text{Nd}_{0.05}\text{Fe}_{0.95}\text{Co}_{0.05}\text{O}_3$ and $\text{Bi}_{0.90}\text{Nd}_{0.10}\text{Fe}_{0.90}\text{Co}_{0.10}\text{O}_3$ sintered at temperature of their optimum density is shown in Fig. 1. There are some small traces of secondary phases of $\text{Bi}_2\text{Fe}_4\text{O}_9$ appeared in doped samples. This unavoidable formation of secondary phases during the solid state synthesis of BiFeO_3 based materials have been reported in several articles (Basith *et al.* 2014). This phase was reported to form during the synthesis of BFO (Qiet *et al.* 2005 (Uniyal *et al.* 2009) (Mishra *et al.* 2008), and could not be removed even by longer calcination times which could also lead to more volatilization of Bi_2O_3 . However the presence of secondary phases do not affect ferroelectric and magnetic properties of the samples because these phases are neither magnetic nor ferroelectric at room temperature.

The Miller indices (hkl) of the diffraction peaks in Fig. 1 were referred to hexagonal axes rather than rhombohedral axes.

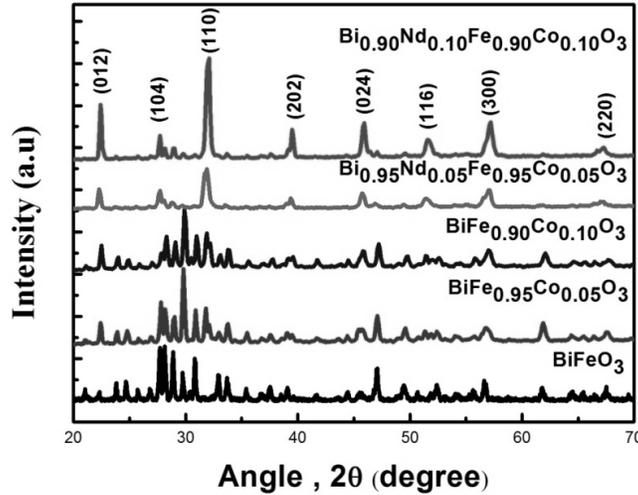


Fig. 1. X-ray diffraction patterns of BiFeO_3 and Co doped $\text{BiFe}_{1-x}\text{Co}_x\text{O}_3$ ($x=0.05-0.10$) and Nd and Co co-substituted $\text{Bi}_{0.95}\text{Nd}_{0.05}\text{Fe}_{0.95}\text{Co}_{0.05}\text{O}_3$ and $\text{Bi}_{0.90}\text{Nd}_{0.10}\text{Fe}_{0.90}\text{Co}_{0.10}\text{O}_3$ ceramics.

Morphological Studies

To investigate the microstructure of the surface of the pellets, SEM imaging was carried out for all the samples. Fig. 2 demonstrates the surface morphology of the pellet of the $\text{BiFe}_{0.95}\text{Co}_{0.05}\text{O}_3$ and $\text{BiFe}_{0.90}\text{Co}_{0.10}\text{O}_3$ and Co and Nd co-doped sample $\text{Bi}_{0.95}\text{Nd}_{0.05}\text{Fe}_{0.95}\text{Co}_{0.05}\text{O}_3$ and $\text{Bi}_{0.90}\text{Nd}_{0.10}\text{Fe}_{0.90}\text{Co}_{0.10}\text{O}_3$ samples respectively. The average grain size is reduced from $\sim 1.5 \mu\text{m}$ to $\sim 0.5 \mu\text{m}$ with increasing Co and Nd substitution. Previous investigations demonstrates that undoped BiFeO_3 had a dense microstructure with an average size of ~ 5 to $\sim 15 \mu\text{m}$ (Makhdoom *et al.* 2012). However, the grain distribution is mostly homogeneous.

Previous investigation suggested that the grain growth depends upon the concentration of oxygen vacancies and diffusion rate of the ions (Brinkman *et al.* 2007). Large number of oxygen vacancies generate in pure BiFeO_3 due to highly volatile nature of Bi. An increment of the Co and Nd concentration in $\text{BiFe}_{1-x}\text{Co}_x\text{O}_3$ and $\text{Bi}_{1-x}\text{Nd}_x\text{Fe}_x\text{O}_3$ decreased the average grain size significantly because Co and Nd possess a higher valance then Fe and suppresses the formation of oxygen vacancies. The decreased oxygen vacancies lead to a lower grain growth rate which is actually a consequence of slower oxygen ion motion.

By EDX spectroscopy we intended to know the amount of mass and atoms in synthesized samples. In these multiferroic samples Bi, Nd, Fe, Co and O are present.

The EDX spectrum confirms the presence and amount of mass of the presented atoms in the synthesized samples.

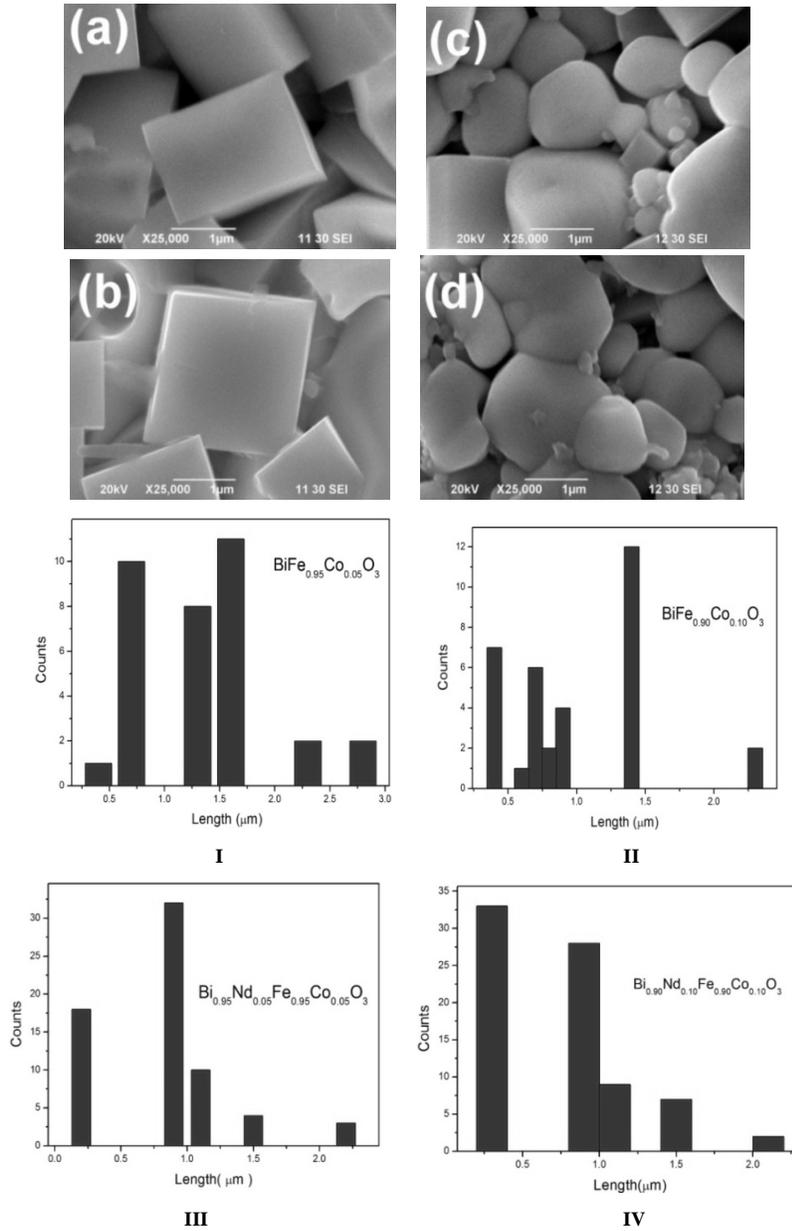


Fig. 2(a-d) represents the SEM micrograph and (I-IV) represents the histogram of $\text{BiFe}_{0.95}\text{Co}_{0.05}\text{O}_3$ and $\text{BiFe}_{0.90}\text{Co}_{0.10}\text{O}_3$ and Co and Nd co-doped samples $\text{Bi}_{0.95}\text{Nd}_{0.05}\text{Fe}_{0.95}\text{Co}_{0.05}\text{O}_3$ and $\text{Bi}_{0.90}\text{Nd}_{0.10}\text{Fe}_{0.90}\text{Co}_{0.10}\text{O}_3$ respectively.

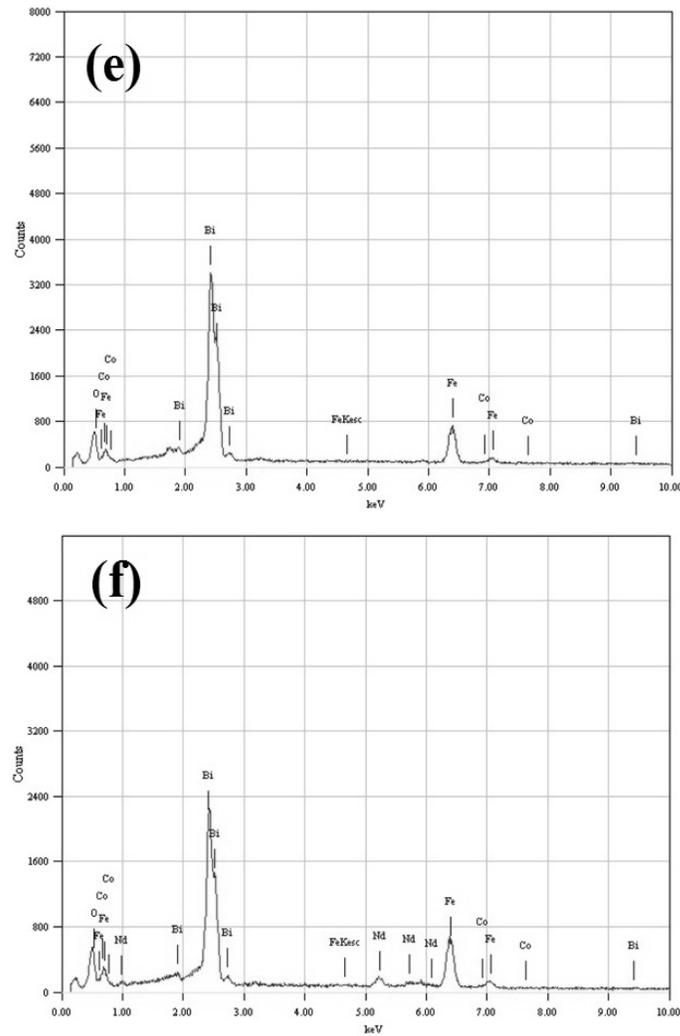


Fig. 2(e-f) shows the EDX spectrum of the $\text{BiFe}_{0.95}\text{Co}_{0.05}\text{O}_3$ and $\text{Bi}_{0.90}\text{Nd}_{0.10}\text{Fe}_{0.90}\text{Co}_{0.10}\text{O}_3$ samples respectively.

Magnetic Properties

The magnetic behaviour properties of the synthesized Co co-doped $\text{BiFe}_{0.95}\text{Co}_{0.05}\text{O}_3$ and $\text{BiFe}_{0.90}\text{Co}_{0.10}\text{O}_3$ and Co and Nd Co-doped sample $\text{Bi}_{0.95}\text{Nd}_{0.05}\text{Fe}_{0.95}\text{Co}_{0.05}\text{O}_3$ and $\text{Bi}_{0.90}\text{Nd}_{0.10}\text{Fe}_{0.90}\text{Co}_{0.10}\text{O}_3$ were carried out at Room Temperature. Fig. 3(a) shows the M-H hysteresis loop of undoped BiFeO_3 as well as Co doped $\text{BiFe}_{0.95}\text{Co}_{0.05}\text{O}_3$, $\text{BiFe}_{0.90}\text{Co}_{0.10}\text{O}_3$ and Co and Nd co-doped sample $\text{Bi}_{0.95}\text{Nd}_{0.05}\text{Fe}_{0.95}\text{Co}_{0.05}\text{O}_3$ and $\text{Bi}_{0.90}\text{Nd}_{0.10}\text{Fe}_{0.90}\text{Co}_{0.10}\text{O}_3$ recorded at Room Temperature (RT). Fig. 3(b) shows the enlarged view of undoped BiFeO_3 ; and Fig. 3(c) shows an enlarged view of M-H

hysteresis loops of Co doped $\text{BiFe}_{0.95}\text{Co}_{0.05}\text{O}_3$, $\text{BiFe}_{0.90}\text{Co}_{0.10}\text{O}_3$ and Co and Nd co-doped sample $\text{Bi}_{0.95}\text{Nd}_{0.05}\text{Fe}_{0.95}\text{Co}_{0.05}\text{O}_3$ and $\text{Bi}_{0.90}\text{Nd}_{0.10}\text{Fe}_{0.90}\text{Co}_{0.10}\text{O}_3$ obtained at Room Temperature (RT).

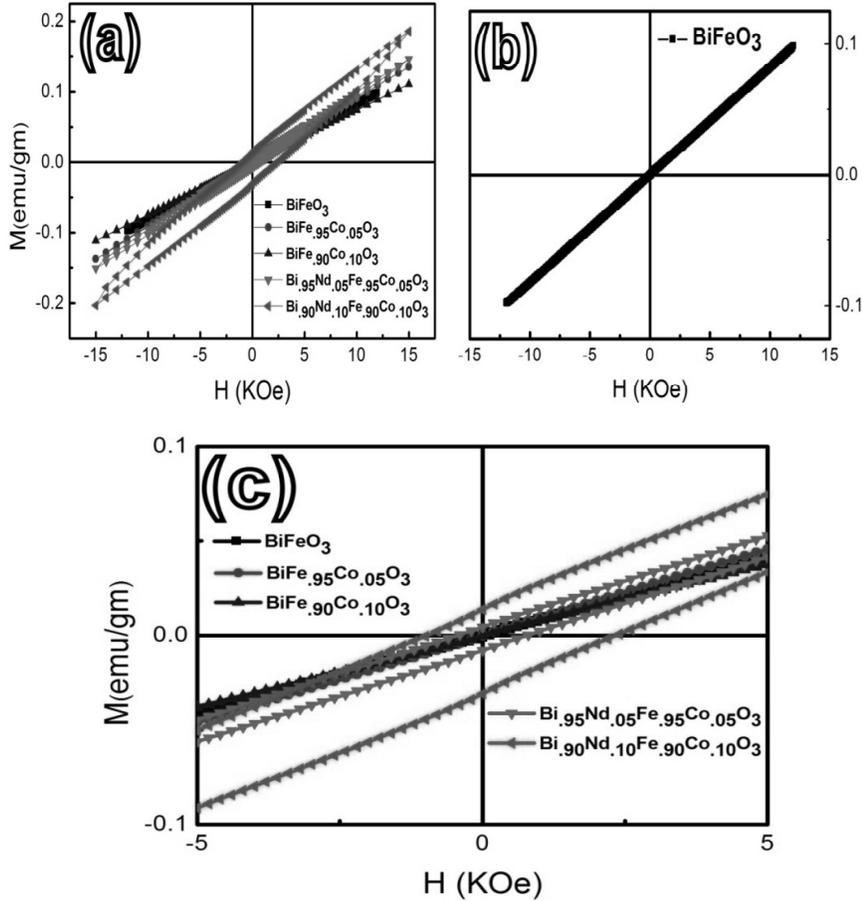


Fig. 3(a) M-H hysteresis loop of undoped BiFeO_3 as well as co doped $\text{BiFe}_{0.95}\text{Co}_{0.05}\text{O}_3$, $\text{BiFe}_{0.90}\text{Co}_{0.10}\text{O}_3$ and Co and Nd Co-doped sample $\text{Bi}_{0.95}\text{Nd}_{0.05}\text{Fe}_{0.95}\text{Co}_{0.05}\text{O}_3$ and $\text{Bi}_{0.90}\text{Nd}_{0.10}\text{Fe}_{0.90}\text{Co}_{0.10}\text{O}_3$ recorded at Room Temperature (RT) (b) shows the enlarged view of undoped BiFeO_3 (c) An enlarged view of M-H hysteresis loops of Co doped $\text{BiFe}_{0.95}\text{Co}_{0.05}\text{O}_3$, $\text{BiFe}_{0.90}\text{Co}_{0.10}\text{O}_3$ and Co and Nd co-doped sample $\text{Bi}_{0.95}\text{Nd}_{0.05}\text{Fe}_{0.95}\text{Co}_{0.05}\text{O}_3$ and $\text{Bi}_{0.90}\text{Nd}_{0.10}\text{Fe}_{0.90}\text{Co}_{0.10}\text{O}_3$ obtained at Room Temperature (RT).

Due to the doping of Co and Nd, the hysteresis loop became wider and thus the magnetic property is improved in BiFeO_3 sample. This enhancement of the magnetization at RT was attributed to the structural distortion in the perovskite with the change in Fe-O-Fe angle (Uniyal and Yadav 2008). It was expected that this structural distortion could lead to suppression of the spin spiral and hence enhanced the magnetization in the doping

system.

the grain size was smallest and ,sample 3 doping In BiFeO-Nd and Co co %10 For .magnetic properties were improved

CONCLUSION

The nominal compositions of Co co-doped $\text{BiFe}_{0.95}\text{Co}_{0.05}\text{O}_3$ and $\text{BiFe}_{0.90}\text{Co}_{0.10}\text{O}_3$ and Co and Nd co-doped $\text{Bi}_{0.95}\text{Nd}_{0.05}\text{Fe}_{0.95}\text{Co}_{0.05}\text{O}_3$ and $\text{Bi}_{0.90}\text{Nd}_{0.10}\text{Fe}_{0.90}\text{Co}_{0.10}\text{O}_3$ samples were synthesized and their structural ,morphological and magnetic properties at room temperature were investigated. The compounds of co-doped ceramic samples were found to have the rhombohedral perovskite like structure, accompanied by a small residual $\text{Bi}_2\text{Fe}_4\text{O}_9$ impurity phase. The combined effects of Co and Nd doping in BiFeO_3 inhibit grain growth of the sample. Our investigation revealed that for the 5% and 10% Co doped $\text{BiFe}_{0.95}\text{Co}_{0.05}\text{O}_3$ and $\text{BiFe}_{0.90}\text{Co}_{0.10}\text{O}_3$ and 5% and 10% Co and Nd doped $\text{Bi}_{0.95}\text{Nd}_{0.05}\text{Fe}_{0.95}\text{Co}_{0.05}\text{O}_3$ and $\text{Bi}_{0.90}\text{Nd}_{0.10}\text{Fe}_{0.90}\text{Co}_{0.10}\text{O}_3$ samples, the average grain size becomes smallest. The investigation . the hysteresis loop became wider ,%10 to %5 also revealed that after doping of Co and Nd by .,3 and had improved the magnetic properties of BiFeO

Therefore, it may be concluded that in these co-doped ceramics, 5% to 10% Co and Nd doping in BiFeO_3 is optimum to have better multiferroic properties. And it can be used in multifunctional devices, thin film capacitors, optoelectrics etc. It can avail multipurpose characteristics of being a scientific and easier medium to make multifunctional devices which will make the technology more vast and helpful.

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