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Ferroelectric and magnetic properties of Nd-doped $\text{Bi}_{4-x}\text{FeTi}_3\text{O}_{12}$ nanoparticles prepared through the egg-white method

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Abstract

Multiferroic behavior of $\text{Bi}_{4-x}\text{Nd}_x\text{FeTi}_3\text{O}_{12}$ ($0.0 \leq x \leq 0.25$, $x = 0.05$) ceramic nanoparticles prepared through the egg-white method was investigated. The dielectric properties of the samples show normal behavior and are explained in the light of space charge polarization. Room temperature polarization-electric field (P - E) curves show that the samples are not saturated with maximum remanence polarization, $P_r = 0.110 \mu\text{C}/\text{cm}^2$, and a relatively low coercive field, $E_c = 7.918 \text{ kV}/\text{cm}$, at an applied field of $1 \text{ kV}/\text{cm}$ was observed for 5% Nd doping. The room temperature M-H hysteresis curve shows that the samples exhibit intrinsic antiferromagnetism with a weak ferromagnetism. These properties entitle the grown nanoparticles of BNFT as one of the few multiferroic materials that exhibit decent magnetization and electric polarization.

Keywords: Nanoparticles, Multiferroic, Dielectric constant, dc magnetization

Background

Recently, there has been an extensive study in the direction of search for the materials possessing magnetic as well as the ferroelectric properties because of the richness of physics involved in the system as well as their potential applications in memory devices and functional sensors [1-6]. These materials exhibit phenomena such as the control of electrical polarization by the application of an external magnetic field or vice versa, providing an additional degree of freedom for the design of new devices. Materials can be considered as multiferroic where ferroelectricity and ferromagnetism make mutually exclusive group [3] with the interaction of electric and magnetoelectric effects [4,7] and the effect of mutual influence of the polarization and magnetization. These phenomena are of practical interest for microelectronics, magnetic memories, sensors, and nonvolatile ferroelectric random access memory applications [3,8,9]. In order to be used as microelectronics and sensor techniques, magnetoelectric materials should satisfy this criterion: the magnetic and electric ordering temperature must

exceed the room temperature. However, up to now, multiferroic materials for room temperature applications are very few [10]. Taking into account the recent literature, most of the published articles are referring to perovskite structures as potential multiferroics [3,11]. However, only BiFeO_3 has proved multiferroic properties at room temperature [7,12], and its complex properties are not yet well understood. Numerous studies for the search of multiferroic properties of BiFeO_3 system substituted with PbTiO_3 , La, Co, Nd, and Gd have been carried out in order to improve its ferroelectric and ferromagnetic properties [13,14]. In the light of continued search for the multiferroic materials, the substitution of Nd was used to enhance the electrical resistivity of $\text{Ba}_4\text{Ti}_3\text{FeO}_{12}$ (BNTF) system. This paper reports the synthesization of Nd-substituted nanomaterials through the egg-white method and their dielectric, ferroelectric, and magnetic studies.

Methods

Material preparation

Nanoparticles of BNTF were prepared through egg-white method. The starting materials $\text{Bi}(\text{NO}_3)_3 \cdot 5\text{H}_2\text{O}$, $\text{Nd}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$, TiCl_3 , and FeCl_3 were mixed together in proper stoichiometric proportions. Extracted egg

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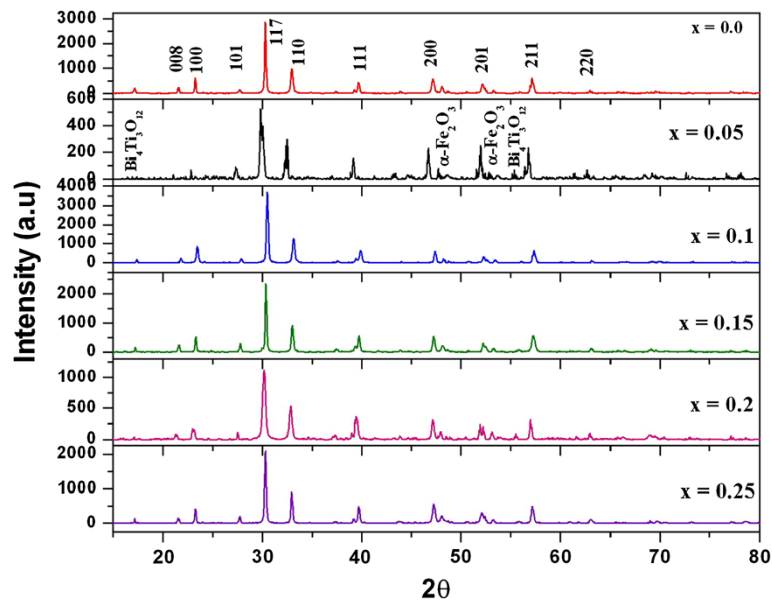


Figure 1 XRD pattern for $\text{Bi}_{4-x}\text{Nd}_x\text{Ti}_3\text{FeO}_{12}$ ($0.0 \leq x \leq 0.25$, $x = 0.05$) nanoparticles.

white (60 ml), dissolved in 40 ml of double distilled water through vigorous stirring, was added to the metal mixture at room temperature. After constant stirring for 30 min, the resultant sol-gel was evaporated at 80°C until a dry precursor was obtained. The dried precursor was sintered at 700°C for 10 h. The final material obtained was ground for 1 h using mortar and pestle.

The powder samples obtained were characterized for structural phase and nanosize formation using PANalytical X'Pert Pro X-ray diffractometer (The Netherlands) with $\text{Cu K}\alpha$ ($\lambda = 1.54 \text{ \AA}$) in the range of 20° to 80° with a sweeping rate of 2°/min.

The microstructural and morphological analysis of the samples were carried out using a field emission scanning

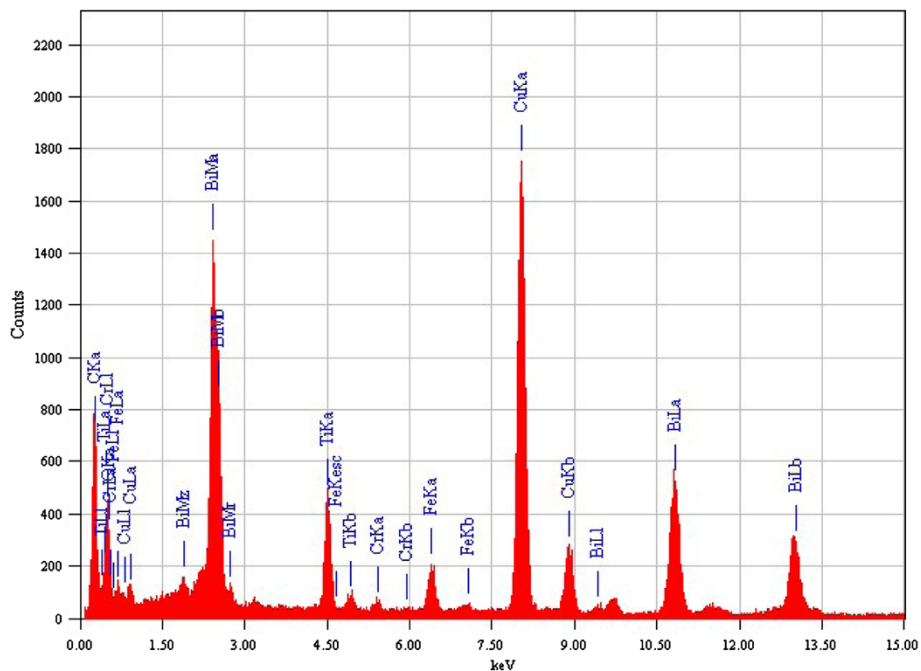
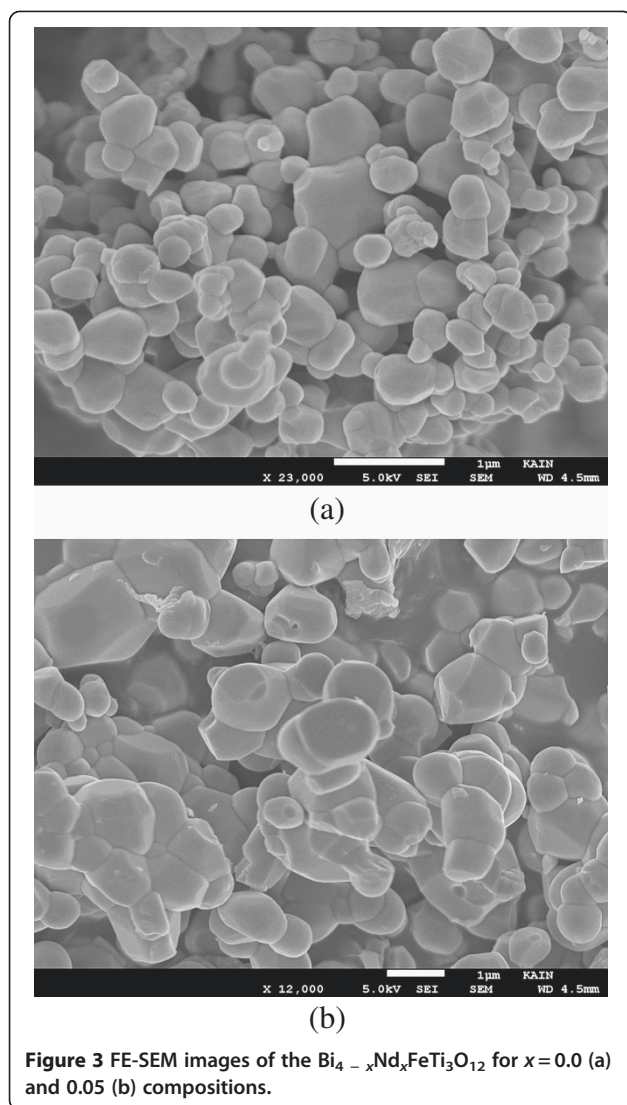


Figure 2 EDX pattern for the pure ($x = 0.0$) composition.



electron microscope (FESEM, JSM 7600 F, JEOL Ltd., Akishima, Tokyo, Japan) and field emission transmission electron microscope (HRTEM, JEOL 2010 F, JEOL Ltd.) with the energy dispersive X-ray (EDX) facility attached.

For electrical measurements, a fixed amount of powder sample was taken, and a few drops of PVA were added to it. The mixture was left over night, dried at room temperature, and pressed into disc-shaped pellets (12 mm \times 12 mm) with the help of hydraulic press. The pellets were heated at 500°C for 1 h, and silver paste coating was applied on opposite flat faces of the pellets to make parallel plate capacitor geometry. The dielectric measurements were performed in the frequency range 1 kHz to 1 MHz using Wayne Kerr 6500B impedance analyzer (Wayne Kerr Electronics Ltd., Woburn, MA, USA). The polarization versus electric field hysteresis measurements were carried out at 1 kV/cm field using P-E loop tracer of Marine India, New Delhi, India. Room

temperature magnetic hysteresis measurements were carried out using Lake Shore VSM (Lake Shore Cryotronics Inc., OH, USA) with a field of 20 kOe.

Results and discussion

Structural and morphological studies

The powder samples of BNTF were characterized for structural and phase analysis through X-ray diffraction shown in Figure 1. The XRD patterns for annealed samples reveal the characteristic well-crystallized pattern with a few signatures of secondary phase corresponding to pure $\text{Bi}_4\text{Ti}_3\text{O}_{12}$ compound and $\alpha\text{-Fe}_2\text{O}_3$. Figure 2 shows the EDX pattern of the pure sample confirming the chemical formation of the polycrystalline BNTF nanoparticles. Figure 3a,b shows the FE-SEM microstructure of the fracture surfaces of pristine and 5% doped Nd sample. Interestingly, with Nd doping, the densification is promoted in the grown nanoparticles. Figure 4a shows the FE-TEM micrograph with inset showing the average grain size plot and selective area electron diffraction pattern for the composition $x = 0.0$. The micrograph shows irregular-shaped highly agglomerated nanoparticles with an average grain size of 50 nm for the composition $x = 0.05$. The average crystallite sizes calculated through FE-TEM show a broad size distribution from 50 to 72 nm as shown in Figure 5. A high crystalline order is observed in the grown nanoparticles. Figure 4b shows lattice pattern for the composition $x = 0.05$ with inset showing the d spacing value of 0.240 Å. The d value obtained collaborated well with the value obtained from X-ray diffraction pattern.

Dielectric study

The high resistivity and low dielectric loss ($\tan\delta \approx 1.6$ at 42 Hz at RT) in Nd-substituted specimens allowed the dielectric constant (ϵ') to be determined, as shown in Figure 6. The room temperature dielectric constant was found 515 at 1 kHz maximum for 5% Nd concentration. The obtained dielectric constant is higher than the values of thin films (≈ 107) [15,16] and Nb-doped BiFeO_3 ceramics [17] reported earlier. Both the dielectric constant and loss tangent (Figure 7) are found to decrease rapidly in low-frequency region and show frequency independent response above 22 kHz. These variations can be explained in the light of space charge polarization as discussed by Maxwell [18] and Wagner [19] and is in good agreement with Koop's phenomenological theory [20]. At low frequencies, the space charges are able to follow the frequency of the applied field, while at high frequencies, they may not have time to build up and undergo relaxation. The low loss values at higher frequencies show potential applications of these materials in high-frequency microwave devices. Moreover, the dielectric loss factor also depends on a number

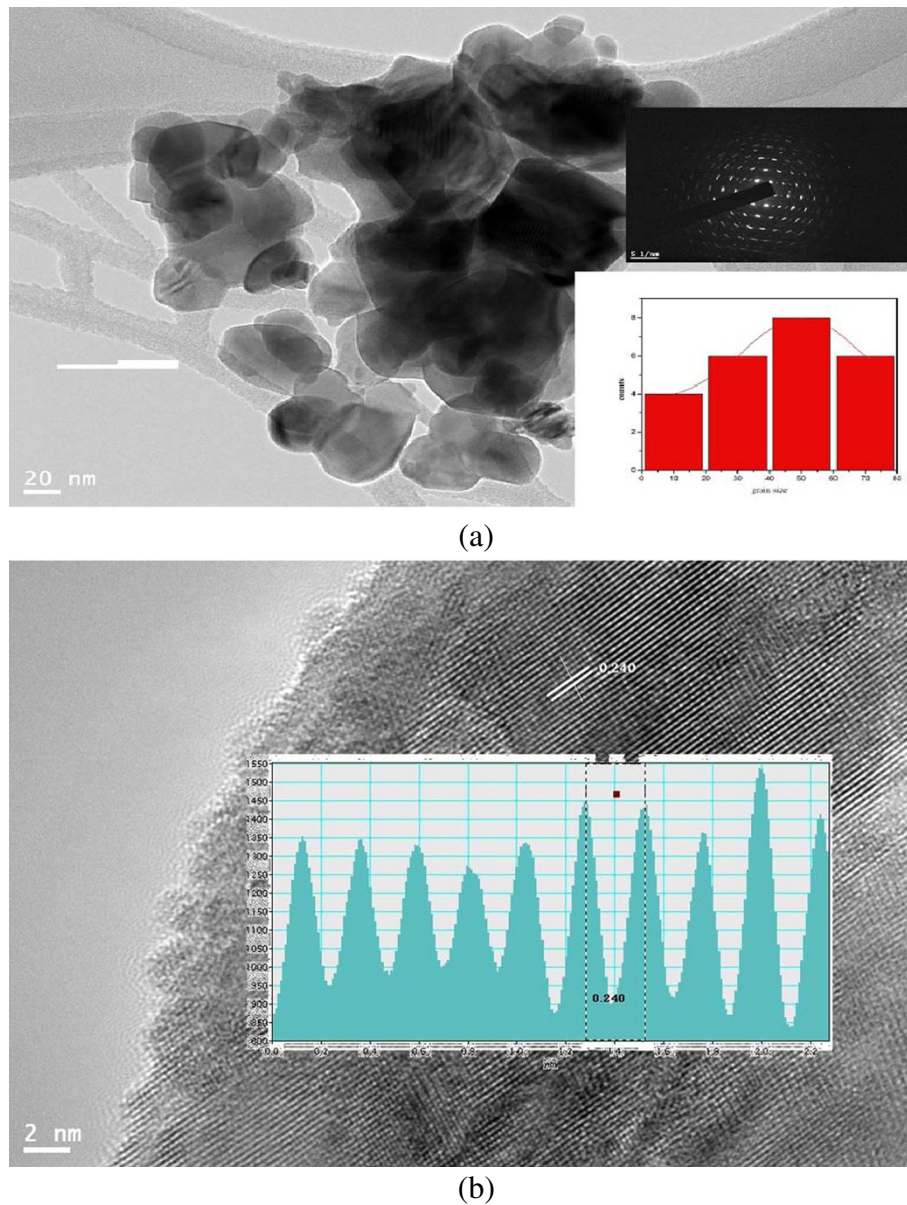


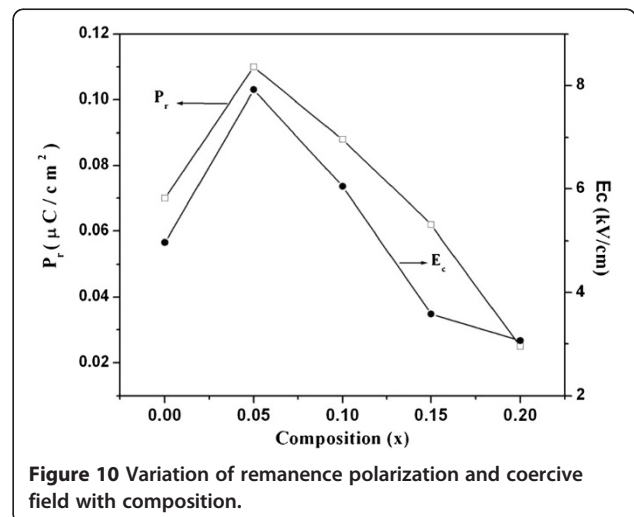
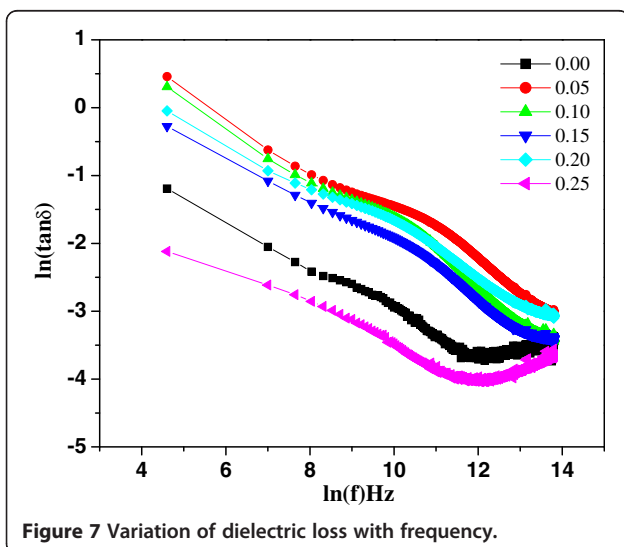
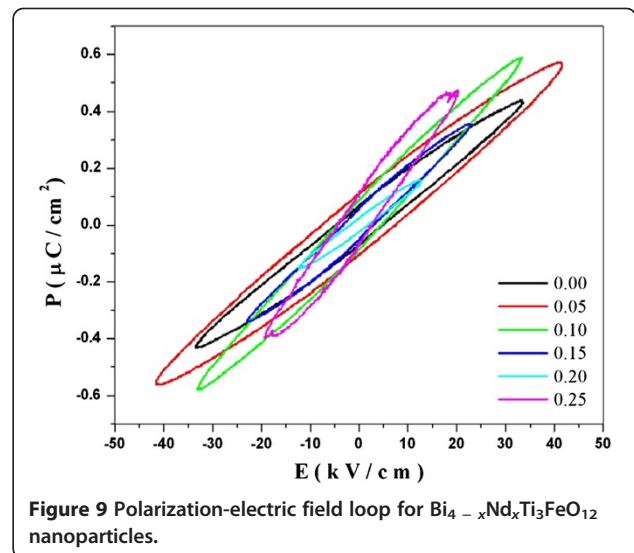
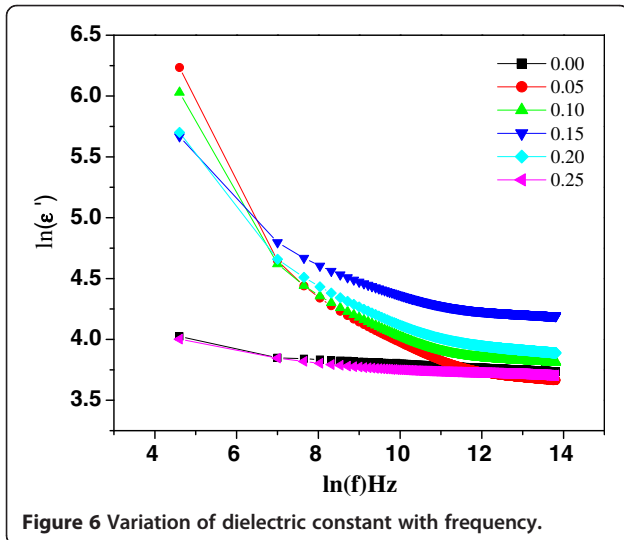
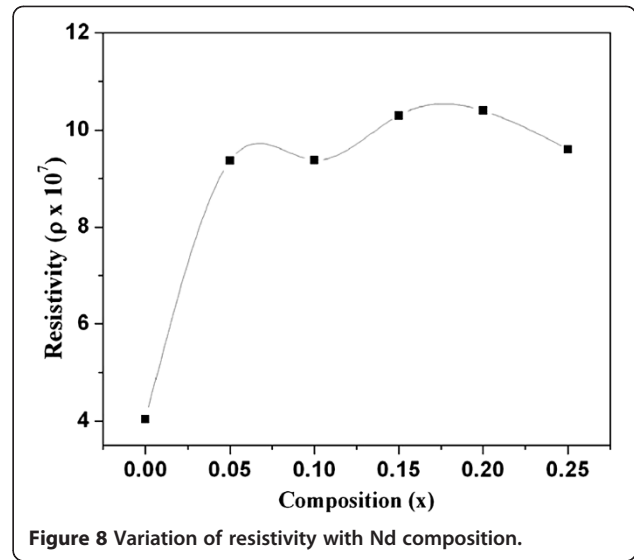
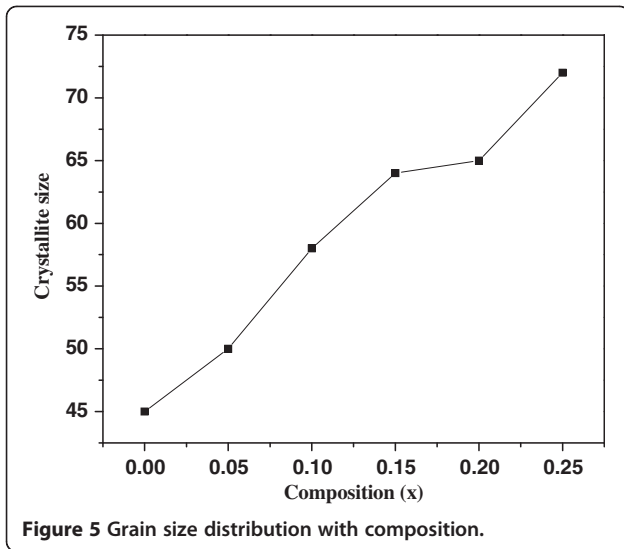
Figure 4 FE-TEM micrograph and lattice planes. (a) FE-TEM micrograph. Lower inset, grain size distribution; upper inset, selective area electron diffraction pattern. (b) Lattice planes. Inset, lattice plane spacing for the composition $x=0.05$.

of factors, such as stoichiometry and structural homogeneity, which in turn, depend upon the composition and sintering temperature of the samples [21]. The room temperature resistivity measurements as a function of composition x are presented in Figure 8. It is seen that the resistivity of the samples increases with the increasing percentage Nd doping. The behavior may be attributed to the decreasing number of the conduction ions.

Ferroelectric hysteresis

The ferroelectric hysteresis loop measurement is always hampered by the high leakage current. Because of low

resistivity of the samples, it is difficult to apply high electric fields to the bulk samples. The ferroelectric polarization hysteresis loops at room temperature for Nd-doped $\text{Bi}_{4-x}\text{FeTi}_3\text{O}_{12}$ samples measured under an applied field (E) of about 10 kV/cm are presented in Figure 9. The loops are not really saturated and represent a partial reversal of the polarization almost elliptical-shaped [22,23]. The P_r and E_c values of the BNTF nanoparticles as a function of Nd composition are shown in Figure 10. The remanence polarization, P_r increases first and then decreases with an increasing value of x . The highest value of $P_r=0.110 \mu\text{C}/\text{cm}^2$ and



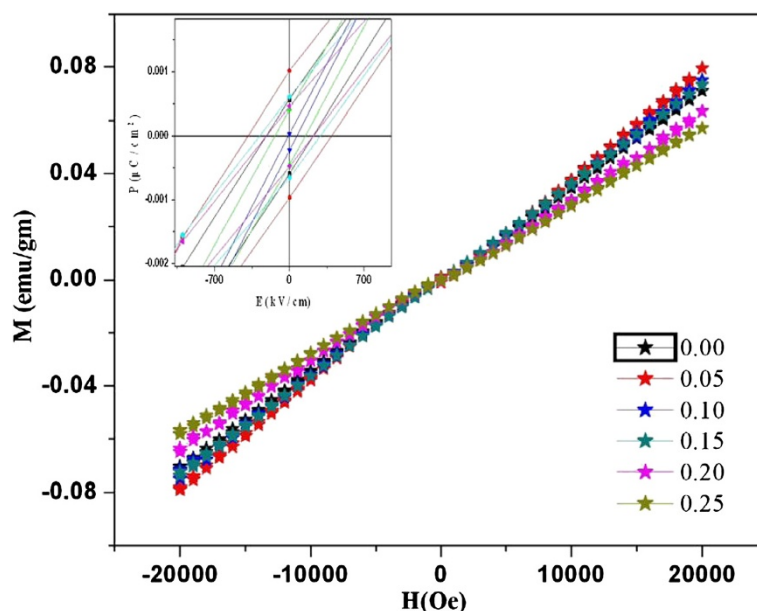


Figure 11 Room temperature hysteresis magnetization. With inset showing the magnified plot showing the ferromagnetic character of the grown nanoparticles.

a relatively low coercive field (E_c) of 7.918 kV/cm were observed for 5% Nd concentration. Similar behavior in E_c is also observed where it increases first and then follows a decreasing trend with increasing Nd content [24,25]. The remnant polarization of the samples is not too high. It is well known that most magnetic materials usually have high electrical conductivity. Thus, few multiferroic materials could exhibit the ferroelectric response properly. It is very critical for magnetic materials with high insulating resistivity to possess both ferroelectric and ferromagnetic properties simultaneously. Otherwise, an applied electric field would cause an increase in current for conducting samples rather than inducing electrical polarization.

M-H hysteresis

Figure 11 shows the magnetization versus magnetic field ($M-H$) hysteresis loops for the BNFT nanoparticles at room temperature for the maximum applied field (H) of 20 kOe. It is seen that all the samples show intrinsic antiferromagnetism and a weak ferromagnetism with a maximum value of remnant magnetization (M_r) of 0.00107 emu/gm for sample $x=0.05$. Various authors have reported earlier similar results [24-26]. The M_r value decreases with increasing Nd doping percentage. The substitution of Nd at Bi site may lead to the effective suppression of the spiral spin structure of BNTE, resulting in the appearance of magnetization. In order to verify and evaluate further the source of magnetism in the grown nanoparticles, room temperature Mossbauer spectroscopy measurements were tried on the present

samples, but due to low percentage of Fe^{57} in the pure and doped samples, no clear Mossbauer peaks were observed.

Conclusions

In summary, a series of nanoparticles of polycrystalline system $Bi_{4-x}Nd_xFeTi_3O_{12}$ were prepared through the egg-white method to investigate the presence of multiferroic properties. The dielectric properties show normal behavior with respect to the frequency. Room temperature unsaturated multiferroic properties were observed for the grown nanoparticles. All the samples show the intrinsic antiferromagnetism with very weak ferromagnetism. The remanence polarization (P_r), and remanence magnetization (M_r) values were found maximum for 5% Nd concentration. These properties entitle the grown nanoparticles of BNFT as one of the few multiferroic materials that exhibit decent magnetization and electric polarization.

Competing interests

The authors declare that they have no competing interests.

Authors' contributions

The work in this paper has been mutually carried out by all authors. RS along with MS prepared and carried out the electrical and magnetic measurement of the samples. JPL carried out the FESEM, EDX, and FE-TEM measurements for the present work. KMB carried out the analysis of the data and write up of the paper. All authors read and approved the final manuscript.

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