Structural, dielectric and magnetic properties of $x$Ni$_{0.50}$Zn$_{0.40}$Mn$_{0.10}$Fe$_2$O$_4$ + $(1-x)$Bi$_{0.90}$La$_{0.10}$Fe$_{0.93}$Eu$_{0.07}$O$_3$ multiferroic composites

A Kaiyum, M A Hossain, A A Momin, R Rashid, F Alam, M A Hakim and M N I Khan

1 Department of Physics, Jahangirnagar University, Dhaka, Bangladesh
2 Department of Physics, Jagannath University, Dhaka, Bangladesh
3 Materials Science Division, Atomic Energy Centre, Dhaka, Bangladesh
4 Department of Physical Sciences, Independent University, Bangladesh, Dhaka, Bangladesh
5 Department of Glass and Ceramics Engineering, BUET, Dhaka, Bangladesh

E-mail: ni_khan77@yahoo.com

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Abstract

Multiferroic composites with chemical formula $x$Ni$_{0.50}$Zn$_{0.40}$Mn$_{0.10}$Fe$_2$O$_4$ + $(1-x)$Bi$_{0.90}$La$_{0.10}$Fe$_{0.93}$Eu$_{0.07}$O$_3$ were prepared by solid state reaction technique. These composites are a mixture of ferrite and ferroelectric phases confirmed by X-ray diffraction (XRD). The phases are crystalline in nature as concentrated and strident peaks were observed in XRD patterns. Elongating and twisting ambiences of various bonds are existing in the composites which are observed from FTIR studies. The surface morphology of the prepared samples was studied by Field Emission Scanning Electron Microscope and detected that materials are dense but there is inhomogeneity in grain size distribution. It was established by the Energy Dispersive X-ray Spectroscopy that all the elements existing in the composition were at an appropriate ratio. The magnetic hysteresis loops of the composite materials were investigated by using Physical Property Measurement System at room temperature. Magnetic properties have been enhanced significantly due to the assimilation of NZMFO in the composites. To understand the ferroelectric strength of the composites, electrical properties of the composite material were studied by P-E hysteresis loop analyses in an external electric field. From P-E hysteresis loops it is observed that the 0.2Ni$_{0.50}$Zn$_{0.40}$Mn$_{0.10}$Fe$_2$O$_4$ + 0.8Bi$_{0.90}$La$_{0.10}$Fe$_{0.93}$Eu$_{0.07}$O$_3$ composite have shown better ferroelectric nature. Dielectric constant decreases with the increase of ferrite content. The ac resistivity was to be decreased with ferrite content which indicates the reduction of eddy current loss with the increase of ferrite content. The maximum value of $\alpha_{\text{ME}}$ (178 × 10$^3$ Vm$^{-1}$ T$^{-1}$) is found for 0.2NZMFO + 0.8BLFEO composite.

1. Introduction

Multiferroic materials have drawn great research interest to the scientific community for their fascinating physical, structural, electrical and magnetic properties and enormous potential technological applications, such as: multistate memory storage, spintronics, heterogeneous read or write devices, memory devices, magnetic field sensors, etc [1, 2]. Moreover, the existence of both ferroelectric and ferromagnetic orders simultaneously in a single-phase material is exceptional. Typically, it exposes ferroelectric shift at room temperature as well as show feeble ferromagnetism. At present BiFeO$_3$ (BFO) is considered one of the promising multiferroic material that shows anti-ferromagnetism below the Neel temperature ($T_N$ ≈ 643 K) and ferroelectricity below the Currie temperature ($T_C$ ≈ 1103 K) [1]. But, owing to the weak ferromagnetism, weak magnetoelectric (ME) responses, low resistivity, high leakage current, and high dielectric loss in BFO impedes it from probable device uses [1, 3]. It exhibits distorted perovskite structure with rhombohedral symmetry R3c while developing spiral spin cycloid...
with a periodicity of 640 Å as reported by Dhanalakshmi et al [4]. The ferroelectric mechanism in BFO is initiated by the high-fidelity chemically active 6s² single pair electrons of Bi³⁺ ion, whereas its G-type anti-ferromagnetic spin arrangement leads only to weak magnetic properties [5–7]. Many researchers have shown that better-quality electrical resistivity, dielectric and magnetic properties as well as magnetoelectric coefficients can be achieved by the replacement of various transition and rare earth components on A and B sites of BFO [8–10]. Sandhya Jangra et al [11] have reported boosted excellent magnetization and coercive field of 0.0581 emu g⁻¹ and 4.7505 kOe respectively in Nb doped BFO compared to that of Mn co-substituted BFO, later demonstrated by Kumari et al [12]. But, standards of magnetic parameters and ME coefficients are quite-stumpy for device applications. Therefore, it is essential to design materials having large ferroelectricity and strong ferromagnetism to accomplish the required standard of those magnetic and magnetoelectric coefficients for device applications.

Different approaches have been taken for further improvement of magnetic moments and producing strong ME coupling. These can be done either by doping for A/B sites in BFO or mixing with other strong ferrimagnetic phases such as Ni or Zn ferrites (NZFO) which not only suppress the spin cycloid but also improve the magnetic moment further and produce strong ME coupling [4, 13]. ME effect is created as a product property of magnetostriuctive and piezoelectric composite sheets in composite materials which was first anticipated by Suchtelen [14]. Composite materials may show sum property as like density, magnetization and dielectric properties [14, 15]. In individual phases, this product property is missing but present in their composites. In previously, composite materials have extraordinarily been used in devices like, switches, actuators, sensors and memory devices but have attracted great care in the recent ages in the arena of magnetoelectric material research [16–18]. In the past few years, numerous ME composites have been advanced; few of them are as follows:

\[(1-x)Bi_{0.85}La_{0.15}FeO_3 + xBaFe_{1-x}O_3 [19], (1-x)Bi_xPr_xFeO_3 + xNi_{0.5}Zn_{0.5Fe}_O_4 [13] \]
\[Ni_{0.75}Zn_{0.25}Fe_2O_4 + BiFeO_3 [20], (1-x)BiFeO_3 + xNi_{0.9}Zn_{0.1}Fe_2O_4 [21], xLi_{0.3},Ni_{0.7}Mn_{0.6}Fe_{2.1}O_4 + (1-x)BiFeO_3 [16], 0.5BiFeO_3 + 0.5Ni_{0.9}Co_{0.1}Zn_{0.1}Fe_2O_4 [22], PbFe_{0.5}Nb_{0.5}O_2 + xNi_{0.5}Zn_{0.5}Fe_2O_4 [23], (1-y)Bi_{0.8}Dy_{0.2}FeO_3 + y(Ni_{0.5}Zn_{0.5}Fe_2O_4) [24]. \]

Among these materials, Pb based multiferroic composites exhibit the higher value of ME coefficient. There are a few composites that have been claimed as good multiferroic materials. For these, it is essential to find out a Pb free multiferroic that will be free from any health hazard.

In this article, spinel type Ni_{0.50}Zn_{0.40}Mn_{0.10}Fe_2O_4 (NZMFO) has been chosen as a ferromagnetic part and perovskite type Bi_{0.90}La_{0.10}Fe_{0.65}Eu_{0.35}O_4 (BLFEO) has been taken as the ferroelectric part. Multiferroic composites xNZMFO + (1-x) BLFEO have been synthesized successfully and their structural, morphological, magnetic, electrical and magnetoelectric properties were carried out thoroughly.

2. Experimental details

2.1. Sample preparation

Multiferroic xNZMFO + (1-x) BLFEO (where x = 0.0, 0.2, 0.5, 0.7, and 1.0) composites were prepared by the solid state reaction technique. Powders of Ni_{0.50}Zn_{0.40}Mn_{0.10}Fe_2O_4 and Bi_{0.90}La_{0.10}Fe_{0.65}Eu_{0.35}O_4 were mixed in an appropriate proportion. To make BLFEO powders, analytical grade raw materials of Bi₂O₃, Eu₂O₃, La₂O₃ and Fe₂O₃ from Sigma Aldrich, Germany were assorted in an appropriate proportion in a mortar. It was crushed with a pestle for 6 h using acetone as a mixing medium. Assorted powder of BLFEO was then calcined and sintered orderly at 600 °C for 3 h and 850 °C for 6 h respectively. Analytical grade raw materials of Ni₂O₃, MnCO₃, ZnO and Fe₂O₃ were mixed thoroughly at appropriate proportion to produce NZMFO in the same method as the BLFEO. To prepare the composites, NZMFO and BLFEO powders with proper ratios have been mixed. From the grounded powders, pellet and toroid-shaped samples were prepared at a pressure of 60 MPa where PVA was used as a binder. The composite samples were finally sintered at 950°C for 6 h.

2.2. Characterization

To understand the phase and structural behavior, all the composite samples were subjected to XRD. The XRD analysis was performed using a Philip’s X′Pert PRO PW 3040 Powder x-ray Diffactrometer with Cu Kα (λ = 1.54056 Å) radiation where 2θ range from 20° to 70°. Room temperature FTIR spectroscopy of all the specimens was measured using the PerkinElmer FTIR Spectrometer in the range of 350–3000 cm⁻¹ wavenumber. Field Emission Scanning Electron Microscopy (FESEM), JEOL JSM- 7600F model with 10 keV of electron beam energy was used to witness the surface morphology. EDX analysis was performed by using the EDX system supplied with the FESEM. PPMS, Quantum Dynamic Dyna Cool at ambient conditions were used for magnetic property measurements. To study dielectric and permeability of proposed specimens, a Wayne Kerr precision impedance analyzer (Model 6500B) was used.
The bulk density ($\rho_B$) of the specimen was calculated using the following relation:

$$\rho_B = \frac{m}{\pi r^2 t}$$

where, $m$ is the mass, $r$ is the radius and $t$ is the thickness of the pellet.

The x-ray density ($\rho_x$) of the composite is expressed as:

$$\rho_x = \frac{M_1 + M_2}{V_1 + V_2}$$

where, $M_1$ is $(1-x)$ times molar mass of BLFEO and $M_2$ is $x$ times molar mass of NZMFO, $V_1 = \frac{M_1}{\rho_1}$ (BLFEO) and $V_2 = \frac{M_2}{\rho_2}$ (NZMFO), $x$ is the mass ratio of NZMFO in the composite.

$\rho_x$ was calculated by the general formula:

$$\rho_x = \frac{ZM}{N_A a^3} \frac{ZM}{N_A a^3}$$

where, $Z$ is the number of available atoms in a unit cell, $M$ is the Molar mass of the specimen, $N_A$ is the Avogadro’s number and $a$ is the lattice constant.

The average grain size has been estimated using the following formula:

$$D = 1.56L\bar{D}$$

where, $L$ is the average linear intercept over a large number of grains as measured on the plane of the specimen.
The porosity of the compositions was determined following the relation as:

\[
P = \left(1 - \frac{\rho_B}{\rho_x}\right) \times 100\%
\]

(5)

For the measurements of dielectric and magnetic properties, specimens were tinted with conducting silver paste on both sides to ensure good electrical contacts.

The dielectric constant was calculated using the relation:

\[
\varepsilon = \frac{Ct}{\varepsilon_0 A}
\]

(6)

where, \(C\) is the capacitance of the disk shaped sample, \(t\) is the thickness of the disk, \(A\) is the cross sectional area of the electrode and \(\varepsilon_0\) is the permittivity in the free space.

The real part of initial permeability was calculated using the following equation:

\[
\mu_r' = \frac{L_s}{L_0}
\]

(7)

where, \(L_s\) and \(L_0\) are the self-inductance of the sample core and the inductance of the winding coil without the sample core respectively. \(L_0 = \mu_0 N^2 S/\pi d\) is measured geometrically where \(N\) is the number of turns of the coil (for our case \(N = 5\)), \(S\) is cross sectional area, \(d = (d_1 + d_2)/2\) is the average diameter of the toroid shaped sample respectively.

The ac resistivity was calculated as:

\[
\rho_{ac} = \frac{RA}{L}
\]

(8)

where, \(R\), \(A\), and \(L\) are resistance, cross sectional area and the thickness of the pellet respectively.

The \(\alpha_{ME}\) was determined by the formula

\[
\alpha_{ME} = \frac{dE}{dH}_{Hac} = \frac{V_0}{h_0 d}
\]

(9)

where, \(V_0\) is the ME voltage across the sample surface and \(h_0\) is the amplitude of the ac magnetic field.

### 3. Results and discussion

#### 3.1. Structural analysis, density and porosity

From the XRD patterns of BLFEO, NZMFO and \(x\)NZMFO + (1-\(x\))BLFEO at room temperature phase of the composites are confirmed which has been displayed in figure 1. Figure 1(a) exhibits the XRD pattern of BLFEO that shows the rhombohedral perovskite structure with Phmn space group [11, 25, 26]. Figure 1(b) represents the XRD pattern for NZMFO which confirms the formation of single phase cubic spinel structure with Fd3m space group [27]. From figure 1(c), it is clearly observed that ferrite (NZMFO) and ferroelectric (BLFEO) phases coexist in the composites [21]. The ferroelectric and ferrite phases were marked as ‘*’ and ‘●’ signs respectively [28].

Lattice parameters for the two phases in the composites have been calculated and are tabulated in table 1.

| Content (x) | Lattice parameter (Å) | Grain size (μm) | X-ray density, \(\rho_x\) (g cm\(^{-3}\)) | Bulk Density, \(\rho_B\) (g cm\(^{-3}\)) | Porosity, \(P\) (%) |
|------------|----------------------|-----------------|---------------------------------|---------------------------------|------------------|
| 0.00       | A  5.882  c  13.828 a — | 4.03            | 6.496                           | 6.166                           | 5                |
| 0.2        | A  6.149  c  13.831 a 8.670 | 1.31            | 6.112                           | 5.377                           | 9                |
| 0.5        | A  6.161  c  13.713 a 8.282 | 1.65            | 5.655                           | 5.116                           | 10               |
| 0.7        | A  6.172  c  12.576 a 7.7819 | 1.54            | 5.381                           | 4.781                           | 11               |
| 1.0        | A —  c — a 7.814 | 0.331            | 4.874                           | 4.165                           | 15               |

Table 1. Lattice parameter, average grain size, x-ray and bulk density, and porosity of \(x\)NZMFO + (1-x)BLFEO composites.
in the lattice parameters of the composites from that of their single phase constituents are found. This variation may arise due to the induced stress exerted on each other by their component parts and also due to the existence of inter diffusion of some unreactive sorts into the two phases [29].

The variation of x-ray density ($\rho_X$), bulk density ($\rho_B$) and porosity ($P$) of the composites as a function of ferrite content has been studied and are shown in figure 2. As some pores are generated during the sintering process of the composites. Both $\rho_B$ and $\rho_X$ decrease with the increase in ferrite part, this is because the density of ferrite part is smaller than that of the ferroelectric part. Both the theoretical and bulk densities decline linearly obeying the sum rule [30]. The porosity of the composites increase with ferrite content as the porosity of the ferrite phase is higher than that of the ferroelectric phase.

Figure 2. X-ray and bulk density, and porosity as a function of ferrite content of various xNZMFO + (1-x) BLFEO composites.

Figure 3. FTIR spectra of various xNZMFO + (1-x) BLFEO composites.
3.2. FTIR analysis

FTIR analysis can be used to characterize new materials or classify and confirm known and unknown samples. The FTIR spectrum of various xNZMFO + (1-x) BLFEO composites at room temperature has been measured which are shown in figure 3.

Table 2. Tetrahedral A site ($\nu_1$) and octahedral B site ($\nu_2$) band position, force constant with average force constant of xNZMFO + (1-x) BLFEO composites.

| Content (x) | $\nu_1$ (cm$^{-1}$) | $\nu_2$ (cm$^{-1}$) | $F_{CT} \times 10^5$ (dynes cm$^{-1}$) | $F_{CO} \times 10^5$ (dynes cm$^{-1}$) | $K_{av} \times 10^9$ (dynes cm$^{-1}$) |
|------------|----------------------|----------------------|-------------------------------------|-------------------------------------|-------------------------------------|
| 0.00       | 548                  | 368                  | 2.199                               | 1.418                               | 1.808                               |
| 0.2        | 564                  | 380                  | 2.329                               | 1.057                               | 1.693                               |
| 0.5        | 586                  | 376                  | 2.515                               | 1.035                               | 1.775                               |
| 0.7        | 568                  | 368                  | 2.363                               | 1.003                               | 1.683                               |
| 1.0        | 570                  | 394                  | 2.379                               | 1.137                               | 1.758                               |

Figure 4. FESEM images of various xNZMFO + (1-x) BLFEO composites.
The FTIR spectra show different absorption bands which describe the existence of characteristic functional groups and bonds in our studied specimens. FTIR spectra of our studied compositions in which the peaks are observed at expected positions confirmed the completion of solid state reaction. In each sample, two unlike major absorption bands are seen in the bands. The first one is in the high frequency range for the elongating vibrations of Metal-Oxygen (M-O) bonds in the tetrahedral A sites as denoted by \( \nu_1 \) and the second band \( \nu_2 \) in the low frequency range in octahedral B sites [31, 32]. These two bands \( \nu_1 \) and \( \nu_2 \) are observed in A and B site around wavenumber of 568 cm\(^{-1}\) and 368 cm\(^{-1}\) respectively [32, 33]. The high and low frequency absorption bands and their corresponding force constants for all the specimens of the composite series are tabulated in table 2.

However, the peaks around 1052 and 1380 cm\(^{-1}\) correspond to the existence of C–O–C bonds [31]. Force constant, \( F_c = 4\pi^2c^2\nu^2m \) specifies the interatomic bonding strength where \( \nu \), \( c \), \( m \) represent the vibrational frequency, the speed of light in free space, the reduced mass of the metal and oxygen system respectively and \( \text{Fe}^{3+} \text{N} \) and \( \text{O}^{2-} \) ions which are equivalent to \( 2.061 \times 10^{-23} \) gm [33]. This experimental absorption exclusivity is well supported by the existing reviews and hence the phase conformation of all the specimens can also be inferred from the FTIR studies as identified by XRD analysis. No remarkable phase shifting is observed here in the study with the addition of NZMFO in BLFEO [20].

### 3.3. Microstructural and EDX investigation

The FESEM images of various xNZMFO + (1-x)BLFEO composites is represented in figure 4. It is witnessed from the best possible FESEM photographs of different composites samples that fine crystallites are formed but non uniform, contain some pores in it and randomly oriented. This non-uniformity in grain growth may be due to the different growth rates of each stage [33]. As the percentage of ferrite content increases, the average grain size of the composites decreases considerably. The quantity of smaller grains of ferrite phase (insufficient sintering temperature) increase as a result the average grain size of the composites decreases.

The FESEM image with the corresponding EDX spectra for 0.2NZMFO + 0.8BLFEO composite is shown in figure 5. The EDX configuration illustrates the well matching of the mass percentage of phase elements to the thought composition except the oxygen gets into at the time of calcination and sintering process as there is an oxygen deficiency at high temperatures. Figure 5(a) represents the FESEM image for 0.2NZMFO + 0.8 BLFEO composite. Figure 5(b) represents the EDX spectra for 001 point, and figure 5(c) represents the EDX spectra for 002 point.
002 point. The EDX bands shown here qualitatively explain the existence of constituent elements i.e., Fe, Ni, Zn, Mn, Bi, La, Eu and O in the studied composites and the FESEM image confirms the formation of grains with fine crystallites. It was anticipated that the employed sintering temperature in the present work should be kept comparatively low to minimize Bi vitalization and to maintain the stoichiometric balance.

3.4. Frequency dependence of permeability

The frequency dependent real part of initial permeability, \( \mu'_i \), of various \( x \)NZMFO + (1-\( x \))BLFEO composites has been analyzed that is shown in figure 6(a). The increase of \( \mu'_i \) with increase of NZMFO content is observed because of increasing \( M_r \). It is clearly observed that the \( \mu'_i \) for \( x = 0.0 \) and 0.2 is to be almost constant all over whole frequency range and their resonance frequency may stretch out the measurement frequency range but for other samples resonance frequency (\( f_r \)) decreases with the increase in ferrite content as presented in figure 5(a). Globus model [34] relates the resonance frequency (the frequency at which the transition occurs) with permeability as

\[
(\mu'_i - 1) f_r = \text{const.}
\]

From this relation, as the permeability increases, resonance frequency decreases and vice versa.

The variation of magnetic loss (\( \tan \delta_M \)) with frequency for various composites is shown in figure 6(b) which measures of energy dissipation of magnetic system. The \( \tan \delta_M \) shows high value at low-frequency region; however, after a particular frequency it remains almost constant and then increases for further increasing frequency. In this higher frequency region, the domain wall motion becomes random and unable to follow the frequency. In the composites, \( \tan \delta_M \) decreases with the increasing ferrite content due to fewer defects in grain.

Practically, Relative Quality Factor, RQF, of a material tells about its performance. Figure 6(c) shows the frequency dependent RQF as measured following, \( RQF = \mu'_i / \tan \delta_M \). From the figure, it is observed that RQF increases with increase in frequency, reaches its maximum and then decreases with further increase in frequency. As the content of NZMFO increases the maximum RQF shifts to the lower frequency which is the consequence of Globus model.

Figure 6. Frequency dependent (a) \( \mu'_i \), (b) \( \tan \delta_M \) and (c) RQF of various \( x \)NZMFO + (1-\( x \))BLFEO composites.
3.5. M–H hysteresis loop
The magnetic hysteresis loops of various $x$NZMFO + $(1-x)$BLFEO composites have been depicted in figure 7. The NZMFO and composites show usual ferrimagnetic behavior while BLFEO (inset figure 8) shows weak ferro/antiferromagnetic nature. Due to local spin ordering of Fe$^{3+}$, the parent compound bismuth ferrite (BFO) is classified as G-type anti-ferromagnetic material at room temperature [35].

At the same time, due to impurity or having a canted structure, BFO has been reported as ferromagnetic [36, 37]. The comparatively large saturation magnetization ($M_s$) is observed ($M_s \sim 50.989$ emu g$^{-1}$) for NZMFO. The $M_s$ increases with the increase of ferrite content and this relatively large value of $M_s$ (50.989 emu g$^{-1}$) for NZMFO can be described on the basis of A-B interaction. The measured values of magnetic parameters ($M_s$, coercivity, $H_c$, remanent magnetization, $M_r$, and anisotropy constant, $K_v$) from hysteresis loops are tabulated in table 3. As Fe$^{3+}$ prefers B-site, it migrates to B-site and as non magnetic Zn$^{+2}$ prefers to travel to A site. This migration of Fe$^{3+}$ to B site increases the net magnetic moment of B site and magnetization increases [24].

3.6. Dielectric behavior

Different types of polarization in materials result in dielectric constant in the material. Namely, these polarizations are: dipolar, electronic, ionic and interfacial. Interfacial defects, different types of pores, grain structure those are generated during calcination and sintering processes, result in inhomogeneity of the samples and there by originates interfacial polarization. In composites, the polarization is due to space charge carriers and also reliant on the conductivity of the material and electron hopping mechanism between Fe$^{2+}$ ⇔ Fe$^{3+}$ [38]. Figure 8(a) shows the variation of dielectric constant ($\varepsilon'$) as a function of frequency of various xNZMFO + (1-x)BLFEO composites. It is seen that $\varepsilon'$ declines abruptly up to the frequency of $10^5$ Hz and then almost constant at higher frequency region, showing the typical dispersion. This dielectric dispersal may be due to the Maxwell-Wagner type of interfacial polarization in accordance with Koop’s phenomenological theory. So, the decrease in $\varepsilon'$ with the increase of frequency may be for two reasons. Initially, the electron hopping...
mechanism between Fe^{2+} \leftrightarrow Fe^{3+} cannot trail the variation of an externally applied field after a specific frequency level. Secondly, the dipoles formed in different polarization taking place in this process cannot counter at higher frequencies and \( \varepsilon' \) does not depend on frequency anymore \[20\]. The \( \varepsilon' \) of the composites decreases with increasing ferrite content. The low value of \( \varepsilon' \) of the ferrite rich composites is because of high porosity.

Figure 8(b) shows the variation of dielectric loss (tan\( \delta_E \)) with frequency which decreases with the increase of ferrite content. The value of tan\( \delta_E \) decreases with increase of ferrite content due to decrease mobility of charge carriers. These low tan\( \delta_E \) composite materials can be used for microwave applications.

### 3.7. P-E Loops

The P-E loops of various xNZMFO + (1-x)BLFEO composites are measured at different voltage (range 200 V to 1000 V) which has been represented in figures 8(a)–(e). The composites sample evidently shows that due to the addition of NZMFO content, the ferroelectric properties of BLFEO have been improved significantly.

Improvement in ferroelectric properties occurs owing to the reduction of grain sizes in BLFEO-NZMFO composite as compared to that of untainted BFO. Consequently, in the composite materials, grain boundaries intensified which are witnessed from FESEM micrographs. Domain wall movement becomes easier as the grains become larger compared to the dimension of the domain \[39\]. Ultimately, there is an effective growth in the ferroelectric response of the BLFEO-NZMFO composites for the increase in grain boundaries. The low value of electric polarization is observed for \( x = 1 \) to the cubic structure of spinel ferrite, which is not advantageous for ferroelectric strength \[40\].
3.8. Frequency dependent ac resistivity

Microstructure, the distribution of grains and the porosity mainly determine the ac resistivity of a material. The variation of ac resistivity ($\rho_{ac}$) as a function of frequency for various $x$NZMFO + (1-$x$)BLFEO composites is shown in figure 10.

The $\rho_{ac}$ has been decreased quickly at $10^5$ Hz and then remains almost constant. It is observed that the resistivity of various $x$NZMFO + (1-$x$)BLFEO composites have maximum value for $x = 0.0$ which is fully ferroelectric and lowest for $x = 1.0$ which stands for ferromagnetic. As described above it is clearly found that the contribution of conduction and dielectric properties of NZMFO is lower than of BLFEO which can be described with the help of resistivity. The resistivity of multiferroic composite has decreased with increasing frequency. In this case, the optimum compositions had to obtain both ferroelectric and ferromagnetic orders to contribute on developing successful multiferroic material. It could be concluded, it is not possible to provide strong multiferroic parameters by a single ferroic ordered material. So in BLFEO content, the dielectric properties were improved by adding La$^{3+}$ content on A-site of BFO which shows a good agreement with the higher value of dielectric parameters and the resistivity was minimized due to BFO. On the other hand, the addition of Mn content improves the magnetization of NZMFO which is also known as a better ferromagnetic material. So the combination of BLFEO as ferroelectric content and NZMFO as ferromagnetic content are contributing to form useful multiferroic parameters. The maximization of the resistivity is useful to minimize the eddy current loss [41].
3.9. Magnetoelectric effect

In composites, the ME coupling originates due to the interaction of ferroelectric and ferrite phases. Magnetostriction coefficient, piezoelectric coefficient, mechanical coupling, dielectric constant and weight fraction of the constituent phases determine the ME effect in composites [42].

The variation of $\alpha_{ME}$ with the magnetic field have been depicted in figure 11 (a). The $\alpha_{ME}$ increases with an increase in magnetic field up to 0.3 T and then decreases. This initially increase in $\alpha_{ME}$ is ascribed to the development in elastic interaction, which is obvious from the magnetic hysteresis loop measurements. The decrease in $\alpha_{ME}$ with increase in magnetic field may be due to the fact that the magnetization reaches its saturation value after 0.3 T and hence the magnetization and connected strain produce a constant electric field in the ferroelectric phase beyond the saturation limit. For this reason, the $\alpha_{ME}$ decreases at higher magnetic fields [43]. The variation of the maximum value of $\alpha_{ME}$ with ferrite content has been plotted that is shown in figure 11 (b). It is observed that the $\alpha_{ME}$ is maximum $(178 \times 10^3 \text{ Vm}^{-1} \text{T}^{-1})$ for 0.2NZMFO + 0.8BLFEO composite due to the stronger coupling between ferroelectric and ferromagnetic phases. The decrease of $\alpha_{ME}$ with the increase of ferrite content can be ascribed to the enlarged porosity of the sample. The existence of the pores hampers the ME coupling between the grains and reduce the ME interactions in the composites [44–46].

4. Conclusions

Multiferroic xNZMFO + (1-x)BLFEO composites were synthesized by standard solid state reaction technique. Phase identification and structural study have been performed by XRD and FTIR respectively. Average grain size decreases with the increase of ferrite content in the composite. The real part of initial permeability and RQF increases with the increasing in ferrite content. The $M_s$ also increased with the increase of ferrite content. The $M_s$ was found to be 50.99 emu g$^{-1}$ for $x = 1.0$. The value of $\varepsilon$ decreases with the increase in ferrite content. The AC resistivity also decreases with the rise of ferrite content which indicates the lowering of eddy current loss. The maximum value of $\alpha_{ME}$ is found $(178 \times 10^3 \text{ Vm}^{-1} \text{T}^{-1})$ for 0.2NZMFO + 0.8BLFEO composite. For $x = 0.2$ suitable values of $\alpha_{ME}$, $M_s$, $\varepsilon$ and electrical polarization have been obtained which suggests the composition can be used as a room temperature multiferroic material.

Data availability statement

The data that support the findings of this study are available upon reasonable request from the authors.

ORCID iDs

A A Momin  https://orcid.org/0000-0002-3170-7493

M N I Khan  https://orcid.org/0000-0001-8239-4493

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