Research Article

Ferromagnetic-Dielectric $Ni_{0.5}Zn_{0.5}Fe_{1.9}O_{4-\delta}/PbZr_{0.52}Ti_{0.48}O_3$ Particulate Composites: Electric, Magnetic, Mechanical, and Electromagnetic Properties

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Novel ferromagnetic-dielectric particulate composites of $Ni_{0.5}Zn_{0.5}Fe_{1.95}O_{4-\delta}$ (NZF) and $PbZr_{0.52}Ti_{0.48}O_3$ (PZT) were prepared by conventional ceramic method. The presence of two phases in composites was confirmed by XRD technique. The variations of dielectric constant (ε) with frequency in the range of 100 kHz–1 MHz at room temperature and also with temperature at three different frequencies (50 kHz, 100 kHz, and 500 kHz) were studied. Detailed studies on the dielectric properties were done confirming that the magnetoelectric interaction between the constituent phases may result in various anomalies in the dielectric behaviour of the composites. It is proposed that interfaces play an important role in the dielectric properties, causing space charge effects and Maxwell-Wagner relaxation, particularly at low frequencies and high temperatures. The piezoelectric d_{33} constant was studied at room temperature, and the d_{33} constant value decreased with ferrite content. Magnetic properties like *B-H* loops traces were studied to understand the saturation magnetic (M_s) and magnetic moment (μ_B) of the present particulate composites. The magnetoelectric (ME) output was measured by varying dc bias magnetic field. A large ME output signal of 2780 mV/cm Oe was observed in the composite having 50% ferrite. The temperature variation of longitudinal modulus (L) and internal friction (Q^{-1}) of these particulate composites at 104 kHz was studied in the temperature range 30°C–420°C by the composite oscillator technique. Longitudinal modulus showed a sharp minimum, and internal friction exhibits a sharp peak at ferroelectric-paraelectric phase transition. These ferroelectric-dielectric particulate composites were prepared with a view to using them as ME sensors and transducers.

1. Introduction

Multifunctional or smart materials combining several properties in the same structure in order to produce new or enhanced phenomena have stimulated much scientific and technological interest within the scientific community in the last years. One of the most interesting categories of multifunctional system is the magnetoelectric, that is, materials showing magnetoelectric effects. Having simultaneous magnetic and ferroelectric activity, possible attractive functionalities caused by the interactions between electric polarization and spontaneous magnetization can be envisaged. The primary magnetoelectric (ME) effect is defined as the appearance of an electric polarization under a magnetic field $P(H)$: ME output or a magnetization at the application of an electric field. The ME of second order (or secondary ME) consists on variation of the permittivity under magnetic field $\varepsilon(H)$ or the magnetic permeability at the application of an electric field $\mu(E)$. Materials exhibiting ME properties can be single phase and composites (di- or poliphasic systems).

A ferroic system has an order parameter switchable by an adequate driving force or field (phenomena normally

accompanied by hysteresis). Ferroelectric, ferromagnetic, and ferroelastics are typical examples of ferroics. The electric polarization, magnetic moment, and strain can be switched from one ordered state to opposite one by means of an electric, magnetic, or stress field, respectively. If the same system possesses two or more ferroic properties in the same phase, it is called multiferroic [1]. Thus, the ferromagneto-dielectrics are multiferroic materials.

The history of the ME effect dates back to early 1894, when Pierre Curie stated that it would be possible for an asymmetric crystalline body to polarize directionally under the influence of a magnetic field [2]. Based on crystal symmetry considerations, Landue and Lifshitz [3] demonstrated that a linear ME can occur in magnetically ordered crystals, while Dzyaloshinskii [4] predicted the existence of the ME effect in antiferromagnetic Cr_2O_3. This was the first system proved as showing ME coupling, measuring the electric field induced magnetization [5] or detection of the magnetic field-induced polarization [6]. One of the first prepared ferromagnetic ferroelectric material was the weakly ferromagnetic nickel iodine boracite, $Ni_3B_7O_{13}I$ [7]. The simultaneous presence of ferroelectricity and ferromagnetism is coexistence with ferroelasticity in nickel boracite $Ni_3B_7O_{13}I$ activities coupling between the spontaneous polarization, spontaneous magnetization and spontaneous deformation. It has been found that a field-induced 180° reversal of the spontaneous polarization causes a symmetry-conditioned 90° reorientation of the spontaneous magnetization (and conversely, a magnetic field-induced 90° reorientation of the spontaneous polarization causes a 180° reversal of the spontaneous polarization [8, 9]). Another case of early discovered ME materials were the antiferromagnetic-ferroelectrics perovskite ceramics $Pb(Fe_{1/2}Nb_{1/2})O_3$ (PFN) [10] and $Pb(Fe_{1/2}W_{1/3})O_3$, (PFW) [11]. The ME effect has been found in numerous compounds in the last few decades [12, 13], in materials with the perovskite structure, rare earth manganites, yttrium iron garnets, pseudoilmenites, $BaMeF_4$ (Me = Mn, fe, Co, Ni), Cr_2BeO_4, and inverted spinels [13, 14]. The discovery of a linear ME effect in the antiferromagnetic-ferroelectric $BiFeO_3$ [15] and in its solid solutions with Bismuth or Barium titanate led to a new class of ME in which the ferroelectric and magnetic phase coexist up to high temperatures [16–20]. Among single-phase ME materials, particularly strong ME effects, as initially envisioned, have not so far been measured, so that they have not yet found large scale applications in technology. In order to increase the ME response, a large number of di- or poliphasic composites in various forms have been investigated, as summarized by Ryu et al. [13].

The primary requirement for the observance of ME effect is the coexistence of magnetic and electric dipoles. Single-phase materials exhibiting ME effect have an ordered structure and require the presence of a ferroelectric/ferrielectric/antiferroelectric state. They are described by both a dipolar (electric) and a magnetic order parameter. These materials should show two types of phase transitions: one from ferroelectric to paraelectric state and the other one from a magnetic ordered state (ferromagnetic/ferromagnetic/antiferromagnetic) to a nonordered paramagnetic state. The ME effect arises due to the local interaction between the ordered magnetic and ferroelectric sublattices. The conditions for the occurrence of ferroelectricity and magnetic order in the same material requires (i) the presence of adequate structural building blokes permitting ferroelectric-type ionic movements, that is, off-centre displacement associated to the spontaneous polarization in ferroelectrics, (ii) magnetic interaction pathways for the magnetic order, usually of the superexchange type, and (iii) to satisfy symmetry conditions [13].

To be technologically viable, ME materials must exhibit high ME coefficients, so that an intense activity was dedicated to look for new materials or structures in order to enhance the ME effect. The possible applications include magnetic-electric sensors in radioelectronics, optoelectronics and microwave electronics and transducers in instrumentation. Apart from the properties of the parent phases (ferro/antiferro/ferroelectric and ferro/antiferro/ferrimagnetism), the ME effect adds a supplementary freedom degree in designing materials for new application. The coupling between the ferroelectric and magnetic activity in multiferroics opens the possibility to manipulate the magnetic properties through electric fields and vice versa, giving to these materials large potential for applications in spintronics, multiple state memory elements or novel memory devices which might use electric and/or magnetic fields for read/write operations. Although highly exciting for potential applications the single-phase ferromagnetic-dielectric multiferroism is quite rare, being restricted to only few systems. The ME multiferroism already put to the scientific community very interesting problems from the point of view of fundamental physics.

The choice of ferroelectric and ferrite phases depends on their Curie temperatures, good piezoelectric properties of piezoelectric phase and sufficiently high-piezomagnetic property of the magnetostrictive phase, high electromechanical and magnetomechanical coupling coefficients and structural comparability. A highly piezomagnetic insulator should be chosen as the magnetostrictive component in these particulate composites. The resistivity of the magnetostrictive phase should also be as high as possible in order to avoid short circuit path for the ME voltage developed in the ME composite through the ferrimagnetic phase. In view of this in the present work, a highly magnetostrictive ferrite generally used for high-power ultrasonic applications, that is, $Ni_{0.5}Zn_{0.5}Fe_{1.9}O_{4-\delta}$ (T_c = 290°C) [21] as a piezomagnetic component, was chosen. Lead Zirconate Titanate ($PbZr_{0.52}Ti_{0.48}O_3$) is a most suitable piezoelectric material for its use in the magnetoelectric composites because of its high-piezoelectric properties and high resistivity of the order of 10^{12} Ohm cm. In view of this, in the present investigation, PZT was chosen as the ferroelectric component and was chosen as ferrite phase for the particulate magnetoelectric composites. In this work, ferromagnetic ferrite phase was made intentionally nonstoichiometric (with respect to iron) in order to increase the electrical resistivity of the NiZn ferrite [22, 23].

Literature survey reveals that the particulate composites PZT + NiCoCuMn ferrite [24], $NiFe_2O_4$ + PZT [25, 26],

PZT + Ni ferrite [27], and Bunget and Raetchi have reported observation of the ME effect in PZT + NiZn ferrite [28] composites, and its dependence on the applied magnetic field have already been studied by various researchers. The ME output voltages, reported by them vary significantly. Keeping in view, the various factors, we have reexamined the dielectric behaviour, piezoelectric coefficient, magnetic properties, magnetoelectric effect, and mechanical properties (longitudinal modulus and internal friction) of PZT + NZF particulate composites and the results are as follows.

2. Experimental Details

2.1. Preparation of Ferrimagnetic Phase $Ni_{0.5}Zn_{0.5}Fe_{1.95}O_{4-\delta}$ (NZF). The piezomagnetic phase was prepared by using the analytical grade NiO (97%), ZnO (99%), and Fe_2O_3 (99%). Stoichiometric amounts of these oxides were weighed and mixed thoroughly. These constituents were ball milled (RETCH PM 200, Germany) in agate bowls with agate balls in acetone medium for 20 h. The slurry was dried, and the dried powders were loosely packed in the form of cakes. These cakes were calcined in a closed alumina crucibles at 800°C for 2 h. After the calcinations, these cakes were crushed and powdered. These powders were ball milled once again with the same conditions in acetone medium for 8 more h to obtain fine particle size.

2.2. Preparation of Ferroelectric Phase $PbZr_{0.52}Ti_{0.48}O_3$ (PZT). The piezoelectric phase $Pb(Zr_{0.52}Ti_{0.48})O_3$ was prepared from the starting materials as the analytical grade PbO (98%), ZrO_2 (99%) and TiO_2 (99%) as starting materials. These constituents were weighed in stoichiometric proportion and mixed thoroughly. These powders were ball milled (RETCH PM 200, Germany) in tungsten carbide bowls with tungsten carbide balls in acetone medium 20 h. The slurry was dried and the dried powders were loosely packed in the form of cakes, and then calcined in a closed alumina crucibles at 700°C for 2 h. After calcination, these cakes were crushed and powdered. These powders were ball milled once again with the same conditions in acetone medium for 8 more hours to obtain fine particle size. Both ferrite and ferroelectric green powders were sieved to obtain uniform particle size. These fine green powders thus obtained were employed for the preparation of the ME composites.

2.3. Preparation of Particulate Composites. The piezomagnetic phase and the piezoelectric phase $Pb(Zr_{0.52}Ti_{0.48})O_3$ (PZT) green powders were mixed in stoichiometric proportion with generic formule $(1-x)Pb(Zr_{0.52}Ti_{0.48})O_3 + xNi_{0.5}Zn_{0.5}Fe_{1.95}O_{4-\delta}$ (where $x = 0, 0.1, 0.3, 0.5,$ and 1) in different batches. The individual batches of powders were ball milled (RETCH PM 200, Germany) using high-purity tungsten carbide balls in acetone media for 3 h. The slurry obtained was dried and used for preparation of samples of desirable shapes. Pellets of 1 cm diameter and 0.2 cm thickness (Figure 1) were pressed in high-chromium high-carbon hardened steel die using a uniaxial hydraulic press. These pellets were finally sintered at 1100°C for 2 h in
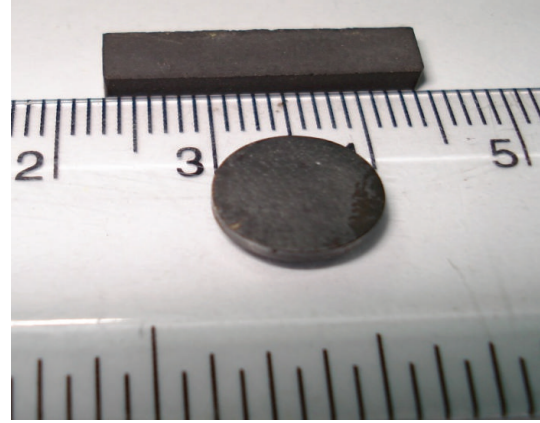

FIGURE 1: Schematic illustration of PZT + NZF composite, bar and pellet.

a programmable furnace (324/PTL-INDFUR, India) with PZT atmosphere powder bed and were cooled to room temperature at the rate of 80°C/h. An enough care was taken for volatization of zinc and lead from the ceramics at sintering processes.

2.4. Characterization. The densities of the sintered particulate composites were examined with Archemedies liquid immersion method by using Xylene. The resistivity of the ME particulate composites were measured using Keithley Electrometer (No. 6514, U.S.A). The XRD patterns of the sample were obtained using a PW 1730 X-ray diffractometer with CuKα radiation. The electrodes required for the electrical measurements were applied on both faces of the samples by applying conducting silver paint (Du Pont). Dielectric measurements as a function of temperature on different samples were performed employing the pellets from 30–550°C using a computer controlled LCR meter (Model 3532-50, HIOKI, Japan). Capacitance and dielectric loss were measured as a function of frequency in the range 100 Hz–1 MHz. The dielectric constant was calculated by using the formula $\varepsilon = Cd/\varepsilon_o A$, where C is the capacitance of pellet, d the thickness of pellet, A the cross sectional area of the flat surface of the pellet, and ε_o is the permittivity of free space $(8.854 \times 10^{-12} F/m)$.

All the traces of space charges in ME output developed by the poling are removed by proper grounding. The ME output was measured by using applied dc magnetic field at room temperature. To get better ME signal, the samples have to be poled both electrically and magnetically. For electrical poling, the samples were heated approximately 50°C above the ferroelectric curie transition temperature and then allowed to cool slowly in presence of an electric field 2 KV/cm. The magnetic field of 5 kOe was applied across the sample in the direction of electric field.

Composite resonator technique [29] was employed for the measurement of internal friction (Q^{-1}) and longitudinal modulus (L) behaviour. By determining the resonant frequency, f_s, of the composite system and logarithmic decrement, δ, the internal friction (Q^{-1}) and the longitudinal

TABLE 1: Data on lattice parameters and magnetization of present particulate composites.

| Composition x | Lattice parameters of the phases (Å) | | | | Saturation magnetization (M_s) |
| | Ferrite | ferroelectric | | | |
	a	a	c	c/a	
0	8.34	—	—	—	—
0.1	8.34	4.11	4.06	0.99	29.89
0.3	8.34	4.11	4.06	0.99	35.88
0.5	8.35	4.11	4.06	0.99	42.12
1	—	4.11	4.06	0.99	—

modulus (L) were evaluated using the standard relations [29]. The powders were mixed with 2% polyvinyl alcohol as binder and pressed into bars of square cross section 3.5×10^{-3} m $\times 3.5 \times 10^{-3}$ m and 2.05×10^{-2} m long (Figure 1) using a hydraulic press and the sintering temperature was $1100°C$ for 2 h. Q^{-1} and L data obtained in the present investigation were accurate to 5 and 2%, respectively. The x-cut quartz transducer used in the present investigation had a length of 2.001 cm, width of 3.32 mm, natural frequency, 104 kHz, and mass of 0.663 g. The electrode faces were painted with conducting silver paint. The composite oscillator was formed by cementing the quartz transducer to the specimen of identical cross-section. The adhesive used in the present work was a paste containing one part by weight of calcium carbonate and five parts by weight of sodium metasilicate in a small quantity of distilled water. The composite system worked satisfactorily after it was kept at room temperature for 24 h.

In order to study the effect of temperature on internal friction and longitudinal modulus on the ferrite-ferroelectric composite specimens, the composite resonator system with the holder was placed at the centre of a tubular electric furnace. All the internal friction measurements were performed with a strain amplitude of 10^{-6}, after the specimen had attained thermal equilibrium.

3. Results and Discussion

3.1. XRD Analysis. Figure 2(a) shows the X-ray diffractogram of the composites with composition $x = 0.1$, 0.3 and 0.5, respectively. All the peaks can be identified for both perovskite and spinel phases. It can be noticed from the figure that the intensity of the peaks corresponding to ferrite phase gradually increases with increase in concentration of the ferrite in the composites. It is clear that there is no intermediate phase or inter phase formed in both the composites, no structural change is observed for both the phases in the composites. The PZT and $Ni_{0.5}Zn_{0.5}Fe_{1.9}O_{4-\delta}$ phases retain their tetragonal structure in composites. The occurrence of peaks with specific indices characteristics of spinal and perovskite structure confirms cubic spinel structure in ferrite phase and tetragonal perovskite structure in ferroelectric phase of the composites. There are no structural changes observed for both the phases in the composites. The lattice parameters for both phases in these

composites vary with the composition as given in Table 1. Figure 2(b) shows the scanning electron micrograph (SEM) of the particulate composite with $x = 0.5$ mole fraction of ferrite. From the figure, it is clear that two different phases distinctly; white region, PZT and dark particles are ferrite. SEM microstructure of the particulate composites did not show any third phase caused by chemical reaction or interdiffusion between two phases.

3.2. Dielectric Measurements with Frequency. The variation of dielectric constant with frequency at room temperature is shown in Figure 3(a). The dielectric constant initially decreases with frequency and then after reaches a constant value at higher frequencies. At lower frequencies, the dispersion is large, while it is independent of frequency. As the frequency increases, ionic and orientation polarization decreases and finally disappears due to the inertia of the molecules and ions. Due to the relaxation time for charge transport, the dielectric constant also depends on the applied frequency. All the samples reveal dispersion due to Maxwell-Wagner type interfacial polarization in agreement with Koop's phenomenological theory [30]. The dispersion at low frequencies suggests that there is a prominent contribution of space change polarization also at the electric polarization process. As the content of ferrite increases beyond the percolation limit, there is a sharp fall of resistivity resulting in the exchange of electrons between $Fe^{2+} \leftrightarrow Fe^{3+}$ in ferrite phase, which gives local displacement of electrons in the direction of applied electric field there by inducing polarization in ferrites. The variation of loss tangent with frequency is shown in Figure 3(b). According to N. Rezlescu and E. Rezlescu [31], the abnormal behaviour of two type of charge carriers, that is, p-type and n-type to the polarization. It is reported that the local displacement of p-type charge carries takes place in opposite direction to that of n-type charge carriers which decreases the polarization at lower frequencies. The oxygen content in the samples during sintering can form both types of charge carriers [32].

3.3. Dielectric Measurements with Temperature. The experimental data recorded on the variation of dielectric constant ε with temperature at different frequencies 50 kHz, 100 kHz and 500 kHz in the temperature range 30–550°C are diagrammatically represented in Figures 4(a)–4(c) of $x = 0.1$, 0.3, and 0.5 particulate composites, respectively. In case of composites, the dielectric constant slowly increases with temperature, reaches a maximum value (ε_{max}), and then it decreases. The sharp and well defined peak corresponding to the transition from ferroelectric phase to paraelectric phase of the ferromagnetic-dielectric particulate composites of the present study. It is also observed that the dielectric constant decreases with increase in frequency and a broad peak is observed. The broad nature of peak corresponding to diffuse phase transition [32]. This might be due to diffuse of zinc ions to the perovskite structure from spinal ferrite phase due to high-volatile nature of zinc ions. However, the Curie transition temperature is not much affected by the presence of the spinal ferrite phase. As the ferrite content increases
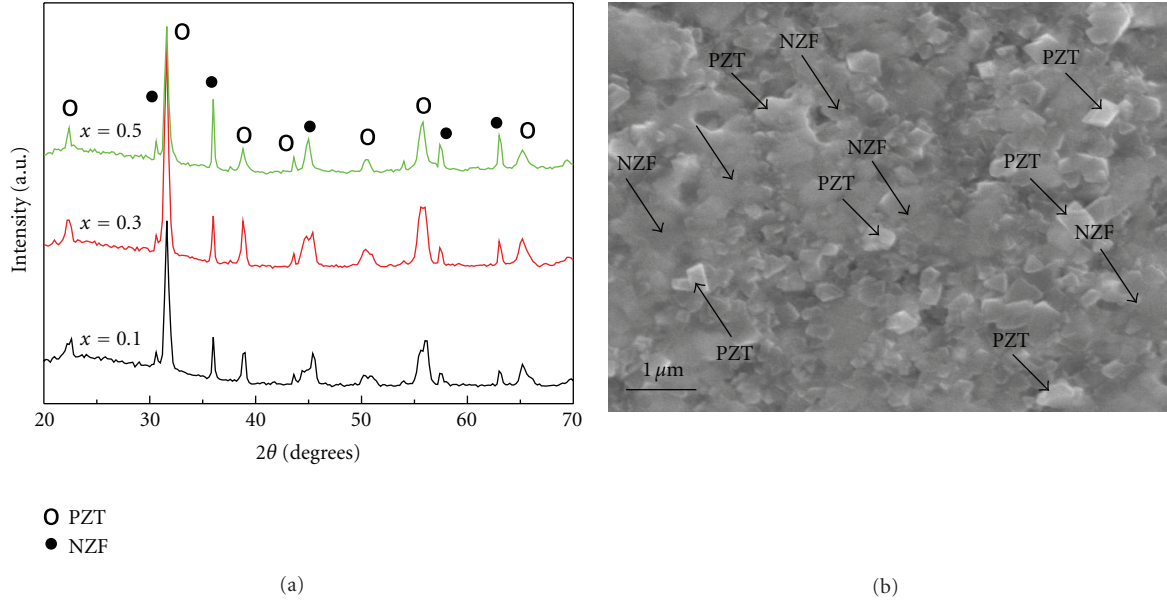
FIGURE 2: (a) XRD patterns of ME particulate composites with $x = 0.1$, 0.3, and 0.5. (b) Scanning electron micrograph of particulate composite with $x = 0.5$.
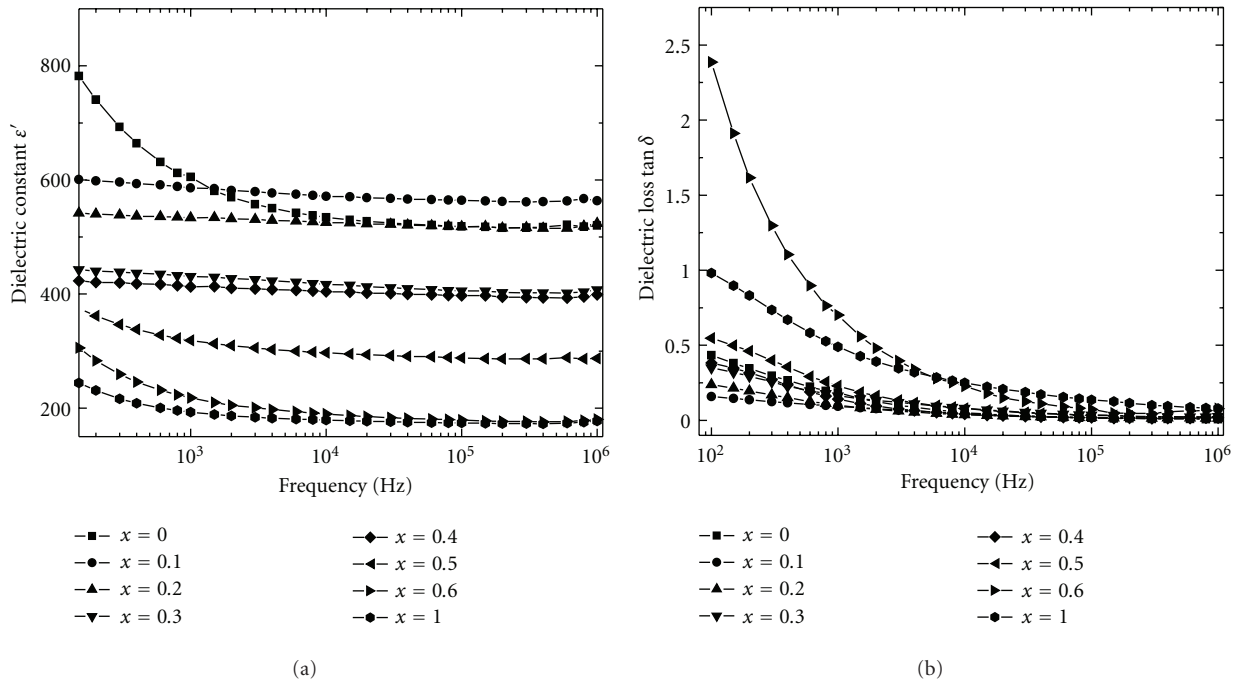

FIGURE 3: (a) Dielectric constant properties of $(1 - x)PZT - xNZF$ magnetoelectric composites with frequency at room temperature. (b) Dielectric loss of $(1 - x)PZT - xNZF$ magnetoelectric composites with frequency at room temperature.

in the composite, the room temperature and T_c dielectric constant decrease. Similar type of decrease in dielectric constant with addition of ferrite to ferroelectric phase was reported by Lopatine et al. [33] and Gelyasin and Laletin [34] in NiCoFe$_2$O$_4$ + BaTiO$_3$ composites and NiCoFe$_2$O$_4$ + PZT composites. This decrease in dielectric constant with addition of ferrite to the ferroelectric is attributed to the high resistivity of ferrite phase.

Patankar et al. [32], Gelyasin and Laletin [34], in various ME composites reported that the broadening of peak in one of the most important characteristic of a disorder perovskite structure with diffuse phase transition. The broadening of the transition has been attributed to disorder in the arrangement of cation on one or more crystallographic sites in the structure, leading to a microscopic hetero-geneity in composites and thus in distribution of different
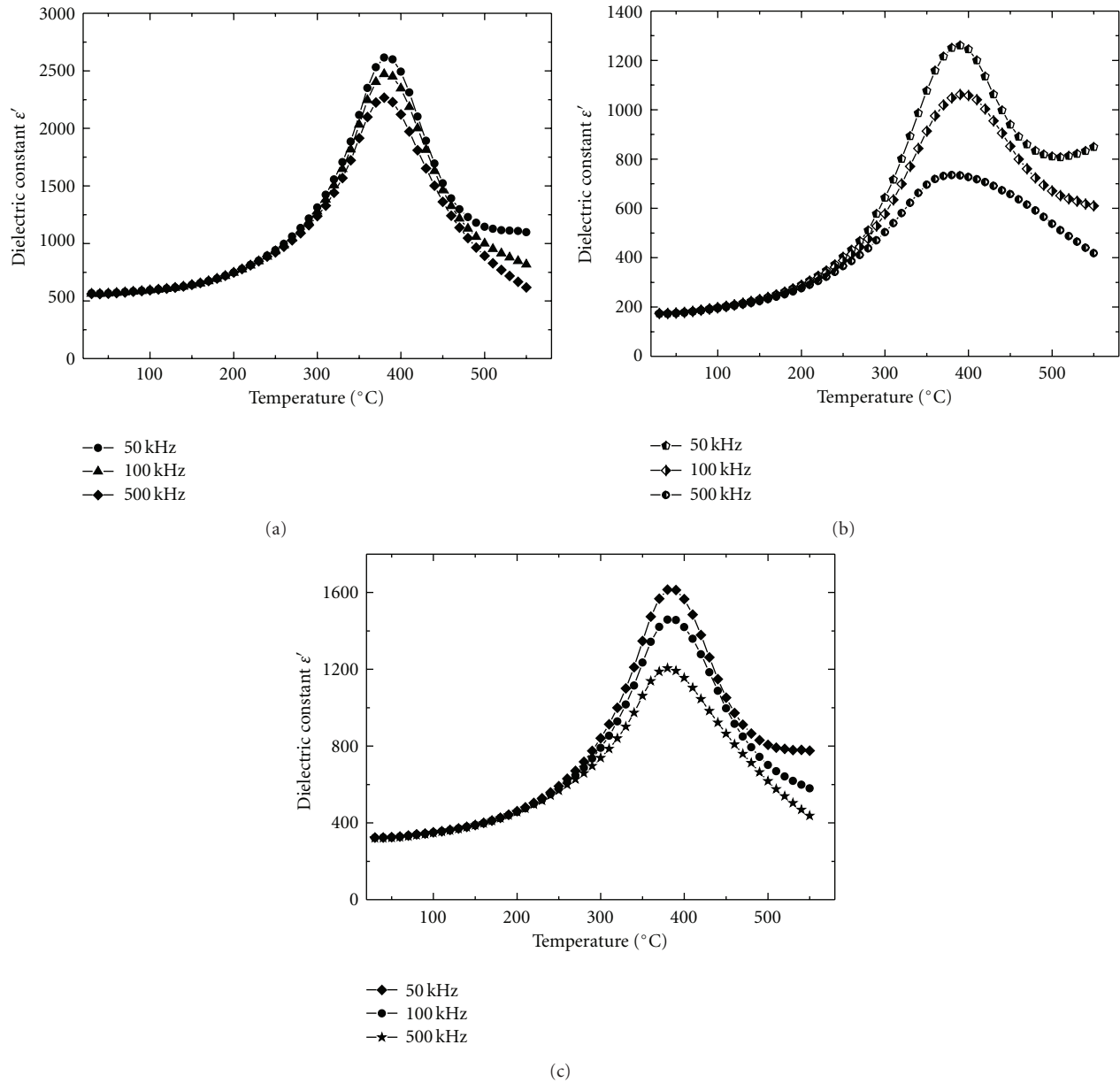
(a)

(b)

(c)

FIGURE 4: Dielectric properties of (a) $x = 0.1$, (b) $x = 0.3$, and (c) $x = 0.5$ of $(1 - x)$PZT + xNZF particulate composites.

localized Curie points. It is related to the nanoscale ordered microregions existing in the material acting as locations of spontaneous polarization [35].

3.4. Piezoelectric Constant d_{33}. Each sample was poled at $150°$C for 2 h in silicon oil bath, which allows higher poling fields than those used in air due to the increase in breakdown voltage, and then cooled to room temperature with continuously applied electric field: this gives balanced poling processes to enable observations of any change in piezoelectric properties of poling levels. Figure 5 shows the piezoelectric property d_{33} for the present particulate composites. The piezoelectric property of these composites decreased with the amount of ferrite phase, as similar to

the dielectric constant. From the figure PZT shows high piezocoefficient (350 pC/N) [36] and with the addition of 10% of ferrite resulted in drastic fall in piezocoefficient (40 pC/N), and further increase in ferrite content shows nominal variation in d_{33}. There are some possibilities for the reduction of the piezoelectric property in the particulate ME composites, First, no chemical reaction should occur between the piezoelectric and magnetostrictive materials during the sintering process. The chemical reaction may reduce the piezoelectric or magnetostrictive properties of each phase. Second, the resistivity of magnetostrictive phase should be as high as possible. If the resistivity of magnetostrictive phase is low, the electric poling becomes very difficult due to leakage current. Also, the leakage current
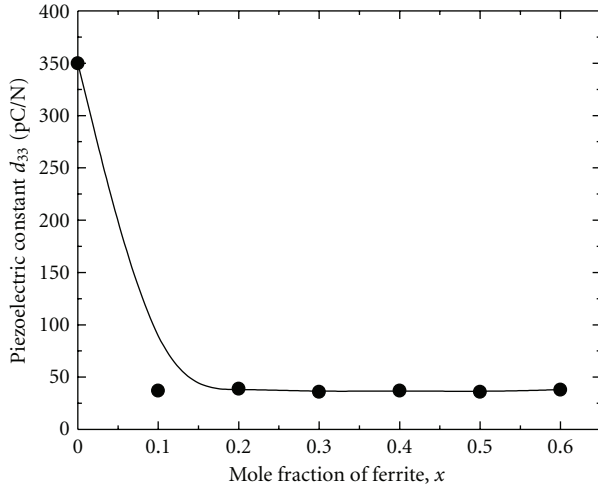
FIGURE 5: Piezoelectric constant d_{33} as a function of ferrite mole fraction of ME composites.

reduces the magnetoelectric properties of the composites. When the ferrite particles make connected chains, the electric resistivity of composites is reduced significantly because of the low resistivity of ferrite. Therefore, good dispersion of the ferrite particles in the matrix is highly required in order to sustain sufficient electric resistivity of the composite. Third, mechanical defects such as pores in the interface between two phases should not exist in the composite for good mechanical coupling.

3.5. Magnetic Properties.

Once the pure biphasic compound obtained, it is important to know if the intrinsic properties of the magnetic and ferroelectric phases maintained, without major changes of the interaction mechanisms due to the foreign phase, particularly, the magnetic properties. Figure 6 shows the typical hysteresis loops for particulate composites (x = 0.1, 0.3, and 0.5). If the PZT presence of the PZT phase does not cause intimate changes of the magnetic interactions, we expect in the magnetic properties to be diluted (proportional reduction of the magnetization, M) with reducing amount of magnetic phase (by increasing the PZT phase). From the Figure 6, it follows that the spontaneous magnetization of the composites originates from the unbalanced antiparallel spins, as in the pure NZF material, giving rise to small values of the coercivity [37, 38]. The saturation magnetization and magnetic moment of the composites increases with ferrite content due to the fact that the individual ferrite grains act a centers of magnetization and the saturation magnetization of the composites is the vector sum of all these individual contributions. The magnetic content increase with ferrite content and result in increase of the net magnetization. Ferroelectric materials incorporated into the ferrite phase acts as pores in the presence of applied magnetic field and brake the magnetic circuit, resulting in the decrease of these magnetic parameters with increasing ferroelectric concentration. The magnetic behavior of ferrite depends on the number of

parameters like cation distribution, site preference energies, covalency of bonds, and the molecular field.

3.6. Magnetoelectric Properties.

The ME voltage coefficient of the samples with different NZF content as a function of dc magnetic bias field is shown in Figure 7, the frequency of the ac magnetic field is 80 kHz. From the Figure 7, we can see that the ME coefficient values increases with increase in ferrite content. Stress transfer through the interface between these phases achieves the magnetoelectric coupling. Hence, magnetomechanical and electromechanical resonance in ferrite and ferroelectric phases assume importance. The ME voltage coefficient depends on the mechanical coupling, resistivity, and mole fraction of the constituent phases. The resistivity of the composites is a temperature-dependent property, which decreases in high-temperature regions, making the polarization of the samples more difficult. Hence, the ME voltage coefficient was measured at room temperature. The magnetoelectric effect in composite materials is determined by magnetostrictive deformation of one phase and piezoelectric effect in the other phase. For this reason, the magnitude of magnetoelectric sensitivity $(dE/dH)_H$ should depend in a complicated way on the composition of the materials [39]. It is well-known fact that in the spinel ferrites the magnetostriction coefficient reaches its saturation value with magnetization at a certain value of the magnetic field. Hence, the strain produced in the ferrite phase would produce a constant electric field in the piezoelectric phase. From Figure 7, the ME voltage coefficient dE/dH increases with dc magnetic field in the range 0–$0.05T$, and saturated after $0.05T$ for a samples with x = 0.1, 0.2, 0.3, 0.4, and 0.5. The maximum ME voltage coefficient of 2780 mV/cm Oe was observed in the composite containing 0.5 NZF + 0.5 PZT. As it is well known, ME effect of the composites depends on the piezoelectricity of the ferroelectric phase and magnetostriction of the ferrite phase. The dependence of the magnetic field exhibited similar behavior for all the composites. The magnetoelectric voltage coefficients of all the composites were increased with increase d.c. bias and saturated around 2 kOe. Ryu et al. [40], Cai et al. [41] also observed this type of behavior in PZT + Terfenol-D, PZT + Terfenol-D + PZT laminated composites, respectively. Srinivas et al. [42] evaluated the electromechanical coupling coefficients in 50% PZT + 50% $CoFe_2O_4$ composites. Corral-Flores et al. [43] also evaluated the highest magnetoelectric effect in the composition of 50% of ferrite. To achieve maximum product property, good mechanical coupling is required between the phases. At the same time, it is desired that no chemical reaction occur between the phases. In the sintered composites or the unidirectional solidified composites of piezoelectric materials and piezomagnetic materials, the temperature of processing is too high to avoid any chemical reaction of the phases. Also, small deviation in compositions while sintering may cause a reasonable drop in the piezoelectric or magnetostrictive properties of the component phases. The connectivity pattern of the component phases in the composites is of important for the electrical properties such as resistivity, dielectric constant, piezoelectric coefficient, and hence the ME constant. The
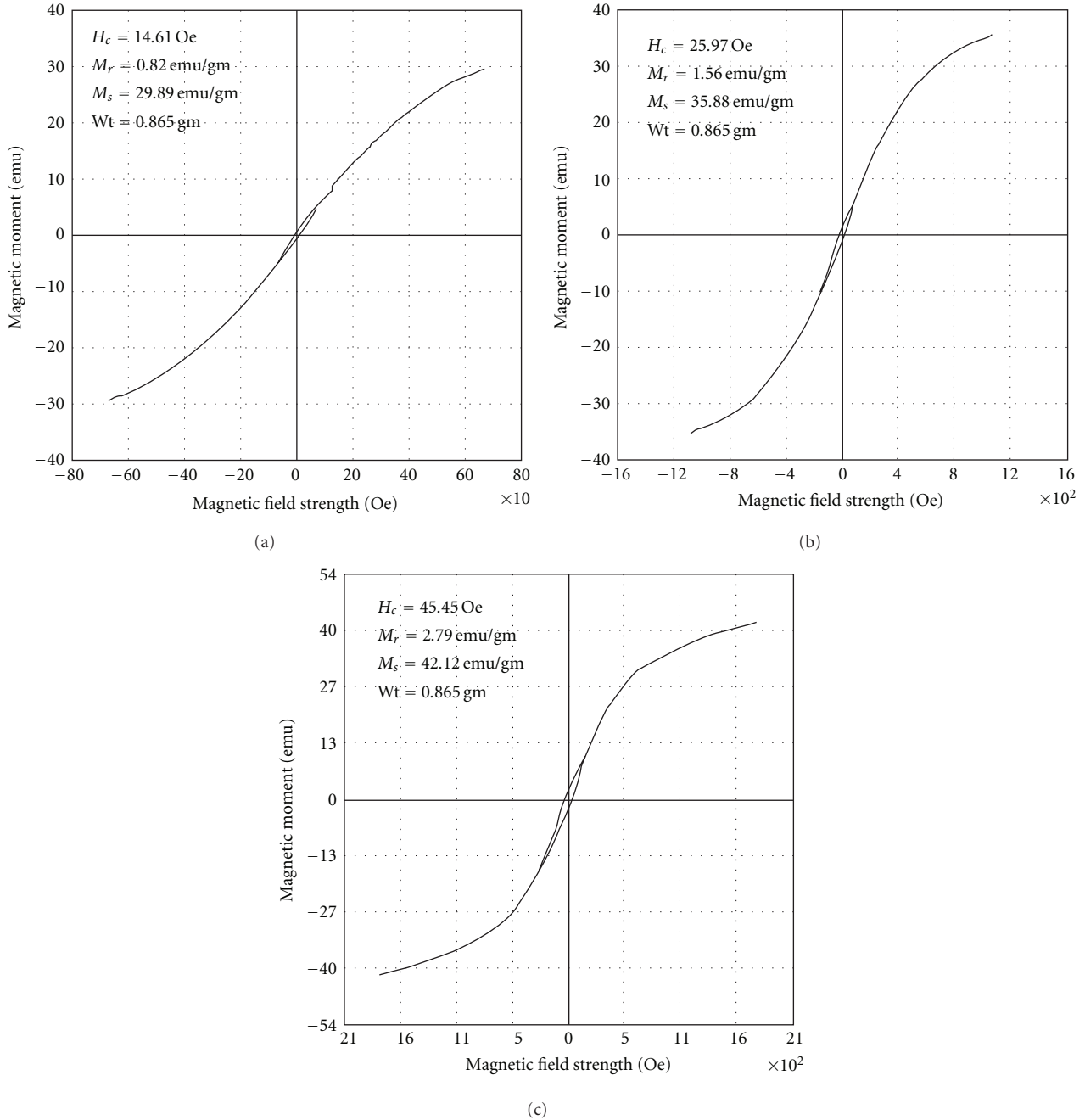
(a)

(b)

(c)

FIGURE 6: Magnetic properties of the composites with $x = 0.1$, 0.3, and 0.5.

comparative study on various ME composites are listed in Table 2, which is comparable to the best values of reported bulk composites, such as ferrite/ferroelectric composites.

3.7. Mechanical Properties

3.7.1. Variation of Longitudinal Modulus with Temperature. In order to examine the dielectric, piezoelectric, and magnetoelectic properties, measurements on longitudinal modulus (L) and internal friction (Q^{-1}) were also carried out on these particulate composites. L and Q^{-1} versus temperature from 30°C–420°C for some selected samples of $(x)\mathrm{Ni_{0.5}Zn_{0.5}Fe_{1.9}O_{4-\delta}} + (1-x)\mathrm{PZT}$ (where $x = 0, 0.1, 0.3, 0.5,$ and 1) studied in the present work are presented in Figures 7 and 8 (i.e., both L and Q^{-1} data). In pure PZT (Figure 7(a)), the ferroelectric-paraelectric phase transition at 390°C can be very clearly seen as a sharp fall in the modulus at the ferroelectric Curie transition temperature (θ_E) [36]. This type of sharp kink in the modulus was reported by Dai et al. [44], Jamenez and Vicente [45], and Bourim et al. [46] in pure PZT. In addition to this kink at 390°C, a broad minimum can be noticed at 230°C. A similar
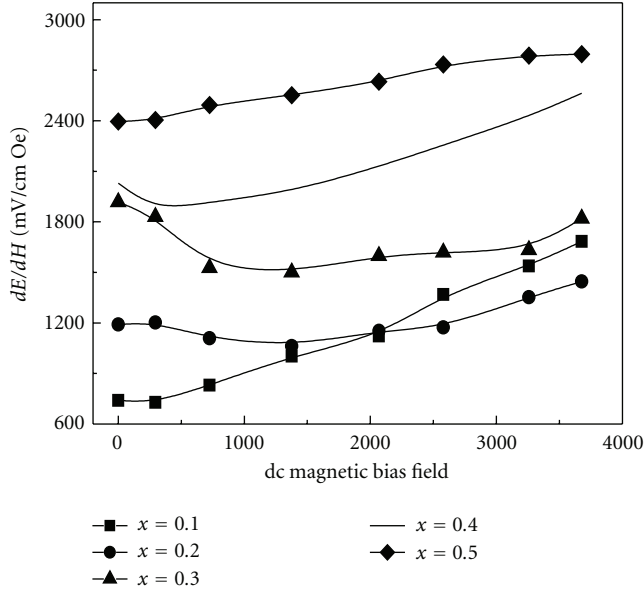
FIGURE 7: ME voltage coefficient as a function of applied dc magnetic bias field for the composites $(1 − x)PZT − xNZF$.

type of behaviour was also noticed by Dai et al. [44] in pure PZT. This was attributed to the movement of domain walls and point defects in the sample.

An examination of Figure 7(b), for the ME particulate composite with $x = 0.1$, reveals that the temperature variation of the longitudinal modulus (L) shows a flat response over a wide temperature range and shows a sharp minimum at 380°C. This temperature coincides with the ferroelectric to paraelectric phase transition of the ferroelectric phase in the composite which is characterized by θ_E. However, no anomalous variation in longitudinal modulus could be observed around 230°C unlike in pure the PZT sample [57]. This type of sharp fall in modulus and sharp peak in internal friction was reported by Koster et al. [58]. As the ferrite component in the composite increased (Figures 7(c) and 7(d)), the minimums shifted to lower temperature side. The shift in the minimum to lower temperature side is found to be linear with ferrite content in the composites. It proves that, Ni ions can lead to a strong decrease if the phase transition temperature and smearing of the phase transition of ferroelectric [59]. Volk et al. [60] have reported the similar phenomena in Ni-doped $Sr_{0.61}Ba_{0.39}Nb_2O_6$ crystals. In case of pure ferrite, (Figure 7(e)), that is, $Ni_{0.5}Zn_{0.5}Fe_{1.9}O_{4−\delta}$, no anomalies behavior was noticed in the longitudinal modulus versus temperature. Moreover, the longitudinal modulus is found to be almost independent of temperature within the temperature range studied in the present work.

3.7.2. Variation of Internal Friction with Temperature. Figure 8(a) represents the temperature variation of the internal friction (Q^{-1}) in pure PZT. The internal friction shows a sharp peak corresponding to the ferroelectric Curie transition temperature (θ_E) at 390°C. In addition to this, one can notice a small but distinct peak at around 230°C

corresponding to the minimum obtained in the longitudinal modulus (L) behaviour with the temperature of pure PZT. As explained earlier, Jamenez and Vicente [45] and Bourim and Tanaka [46] have attributed the minor peak to the domain wall motion and point defects in the sample.

Figure 8(b) shows the temperature variation of the internal friction in the ME particulate composite with $x = 0.1$, where only one sharp peak can be noticed at the ferroelectric Curie transition temperature θ_E. Internal friction measurements also exhibit a systematic variation with temperature in the composites studied in the present work. Corresponding to the ferroelectric Curie transition temperature, sharp peaks are exhibited by these composites, in the temperature variation of internal friction behaviour exhibit in pure ferrite sample. In the case of pure ferrite (Figure 8(e)), that is, $Ni_{0.5}Zn_{0.5}Fe_{1.9}O_{4−\delta}$, there ought to have a transition present at 290°C due to ferromagnetic-paramagnetic Curie transition temperature. However, in the present work, no anomalous behaviour could be noticed in the longitudinal modulus and internal friction behaviour with temperature.

Generally in ferroic materials, the density of the domain walls increases when the temperature approaches the Curie transition temperature. With the increase in temperature the increase in mobility and density of domain walls result in an increase in the internal friction. If the density of the domain walls is so large, such that the interaction of domain walls affects the mobility of domain walls, the internal friction decreases. These two opposing tendencies lead to the formation of an internal friction peak [61].

In the absence of any phase transition, generally, in solids, the elastic modulus decreases with the increase in temperature. However, in the present investigation, the composites studied contain both ferroelectric (PZT) and ferrimagnetic (NZF) phases. In the temperature range studied, that is, 30°C–420°C, the pure ferroelectric component, $PbZr_{0.52}Ti_{0.48}O_3$, transforms from ferroelectric to the nonferroelectric phase at 390°C. Hence, there should be anomalous behaviour in both elastic and anelastic properties near the phase transition, because these are lattice-related properties. Hence, there should be anomalous behaviour near the phase transition. In the present work, in the temperature variation of longitudinal modulus, L, this bahaviour is depicted. The stress induced relaxation peaks observed in the temperature variation of internal friction, Q^{-1}, in the pure ferroelectric and its composites also confirm this phase transition. The Curie transition temperature is found to be linearly decreasing with increasing ferrite content in the composites as mentioned earlier. Even though there is only mechanical contact between the ferroelectric and ferrite phases, the effect of $Ni_{0.5}Zn_{0.5}Fe_{1.9}O_{4−\delta}$ phase on $PbZr_{0.52}Ti_{0.48}O_3$ phase in the composites is to shift the Curie transition temperature linearly to lower temperature side. However, the lowering of Curie transition temperature in the case of composites containing $Ni_{0.93}Co_{0.02}Mn_{0.05}Fe_{1.95}O_{4−\delta} + Ba_{0.80}Pb_{0.20}TiO_3$ [62] is not very much appreciable compared to the present system. Hence, the lowering of Curie transition temperature may be attributed to the presence of diamagnetic $ZnFe_2O_4$ present in these composites.
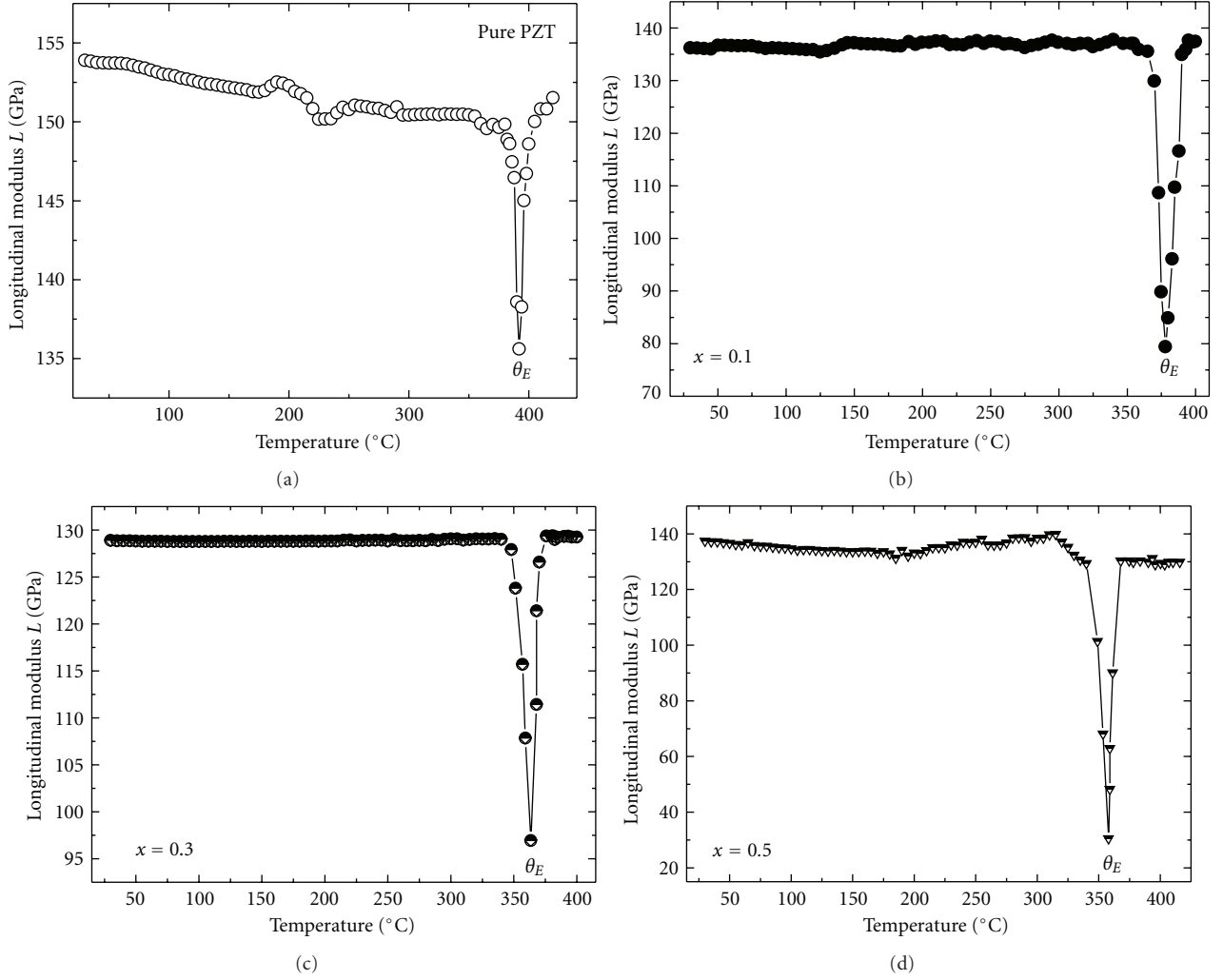
(a)

(b)

(c)

(d)

FIGURE 8: Temperature variation of the longitudinal modulus, (L) of (a) pure PZT and of ME composites with (a) $x = 0.1$, (b) $x = 0.3$, (c) $x = 0.5$, and (d) pure NZF.

TABLE 2: Comparative study of magnetoelectric voltage of particulate composites.

| S. no.	ME composite	ME output mV/cm Oe	Reference
1	$BT + NiCoFe_2O_4$	1–4	[47]
2	$BaTiO_3 + NiCoMnFe_2O_4$	80	[48]
3	$BaTiO_3 + CuCr_{0.4}Fe_{1.6}O_4$	9.56	[49]
4	$Ba_{0.8}Pb_{0.2}TiO_3 + CuFe_2O_4$	0.23	[32]
5	$PZT + Ni\,Fe_2O_4$	25	[26]
6	$PZT + NiFe_2O_4$	115	[24]
7	$PZT + Co\,Fe_2O_4$	100	[50]
8	$PZT + NiCo\,Fe_2O_4$	5	[51]
9	$PbZr_{0.8}Ti_{0.2}O_3 + Ni_{0.8}Co_{0.1}Cu_{0.1}Fe_2O_4$	625	[52]
10	$PZT + Ni_{0.8}Co_{0.1}Cu_{0.1}Fe_2O_4$	776	[53]
11	$PZT + Ni_{0.5}Zn_{0.5}Fe_2O_4$	0.06	[54]
12	$PZT + NiZnFe_2O_4$	40	[55]
13	$PZT + NiZn\,Fe_2O_4$	300	[56]
14	$PZr_{0.52}Ti_{0.48}O_3 + Ni_{0.5}Zn_{0.5}Fe_{1.95}O_{4-\delta}$	2400	Present study

(a)

(b)

(c)

(d)

(e)
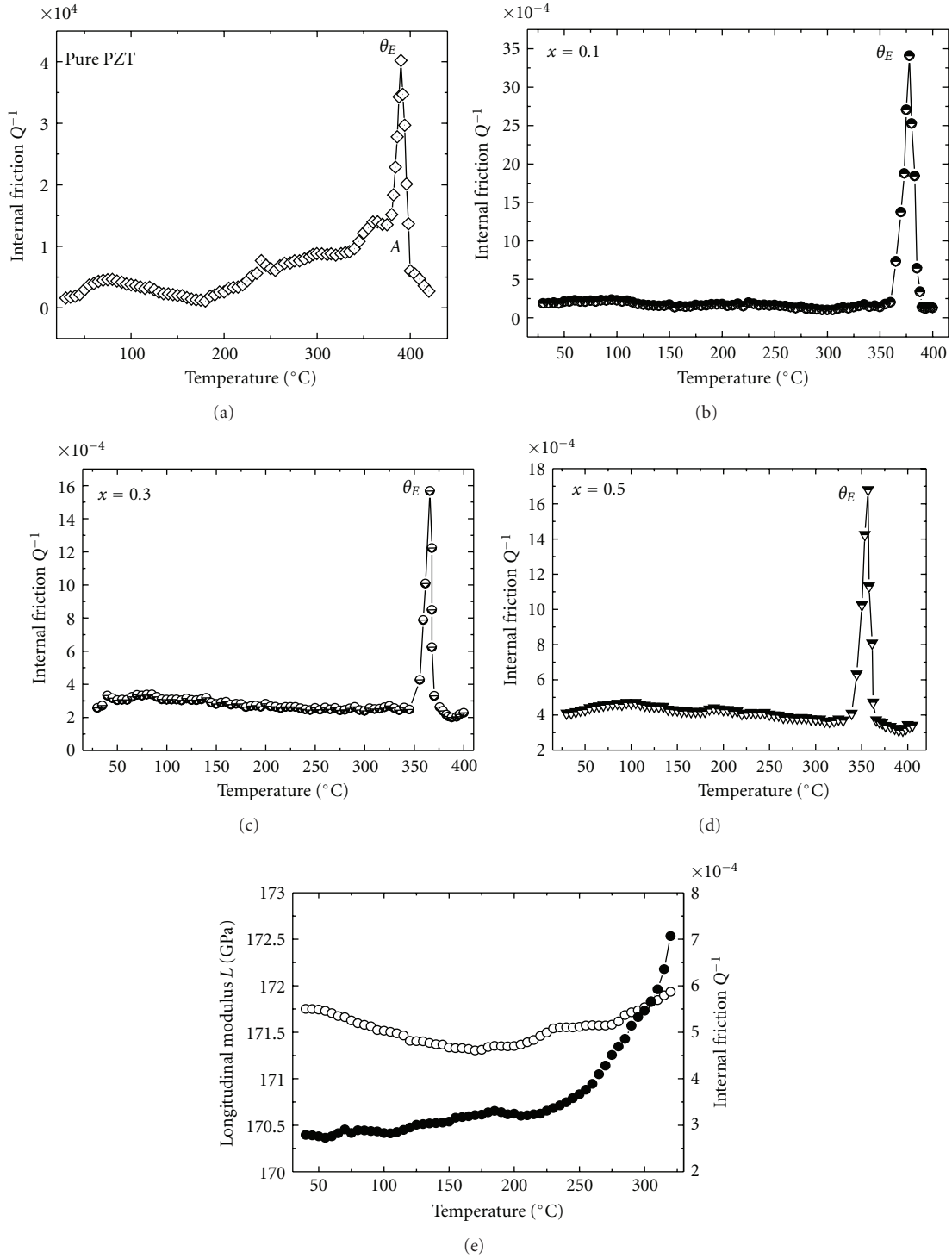
FIGURE 9: Temperature variation of the internal friction, (Q^{-1}) of (a) pure PZT and of ME composites with (a) $x = 0.1$, (b) $x = 0.3$, (c) $x = 0.5$, and (d) pure NZF.

In principle, the ME composites should show two Curie transition temperatures, namely, one due to ferromagnetic-paramagnetic phase transition (θ_M) and the other due to ferroelectric-paraelectric phase transition (θ_E). In our present work, we could found the ferroelectric-paraelectric phase transition only.

4. Conclusions

The Ferroelectric-dielectric particulate composite with $Ni_{0.5}Zn_{0.5}Fe_{1.95}O_{4-\delta}$ as a ferrite phase and $PbZr_{0.52}Ti_{0.48}O_3$ ferroelectric phase were prepared by standard ceramic method. XRD patterns reveal the presence of the ferrite

and ferroelectric phases without any intermediate phase in the composite. XRD patterns confirm the formation of both ferroelectric phase tetragonal perovskite and ferrite phase with spinel structure, respectively. The number of ferrite peaks increases with increases in ferrite content in the composites. Both dielectric constant and dielectric loss shows dispersion in the low-frequency region. The dielectric constant explained in terms of heterogeneity of the sample and the electron exchange between Fe^{2+} and Fe^{3+}. The variation of dielectric constant with temperature shows a sharp peak indicates the transition from ferroelectric to paraelectric phase. With the ferrite content, the d_{33} of the composite descend to low, when the ferrite content is equal to PZT content. Its reason is that the resistance of ferrite is much smaller than that of the PZT. The ME effect is strongly dependent on ferrite content, and the maximum ME output was observed in the composite with $x = 0.5$. The interface effects play an important role in modifying the dielectrics and ME property, causing space charge effect and Maxwell-Wagner relaxation at the interface of the ferroelectric and ferromagnetic phases, particularly at low frequencies and higher temperatures. The ME output was observed linear in the low field range which may apply in the linear ME devices. The longitudinal modulus shows a sharp minimum at the ferroelectric Curie transition temperature in the composites. Internal friction measurements exhibit a sharp peak at ferroelectric-paraelectric phase transition. The longitudinal modulus of pure ferrite phase is found to be temperature independent. No ferrimagnetic-paramagnetic phase transition is noticed in these composites.

These ferroelectric-dielectric composites were prepared with a view to using them as magnetoelectric sensors and transducers. In order to study the ferroelectric and ferrimagnetic domain interaction in these composites, and the work on the effect of the magnetic field on these composites, further investigations are necessary.

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