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The Ferroelectric Dependent Magnetoelectricity in Composites

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1. Introduction

Ferroelectric materials (dielectric materials) attracted the attention of many researchers because of their important applications in the field of science and technology. Ferroelectrics are stable materials having spontaneous polarization and can be switched hysteretically by an electric field; but antiferroelectric materials possess ordered dipole moments that cancel each other completely within each crystallographic unit cell. (The stable ferromagnetic materials possess a spontaneous magnetization and can be switched hysteretically by an applied magnetic field but antiferromagnetic materials possess ordered magnetic moments that cancel each other completely within each magnetic unit cell). Ferroelectrics are similar to ferromagnetic materials but ferromagnetic materials exhibit a permanent magnetic moment. In 1921, J. Valasek discovered the phenomenon of ferroelectricity during the study of the anomalous dielectric properties of Rochelle salt ($NaKC_4H_4O_6 \cdot 4H_2O$) and in 1935 a second ferroelectric material (KH_2PO_4) was investigated followed by some of its isomorphs. In 1944, the third major substance ($BaTiO_3$) was reported by A. Van Orippel, since then his small group suggested many more mixed crystal systems. The dielectric materials are sub divided into 32 crystal classes/ point groups [1] and they get polarized under the influence of an electric field. Out of these 32 classes, 20 classes are piezoelectric, in which a charge can be induced upon the application of mechanical stress. However, out of twenty piezoelectric classes ten exhibits a finite and permanent polarization known as spontaneous polarization in the presence or absence of an applied electric field or stress and such piezoelectrics are known as polar materials. Polar materials possess domain structure and show Curie-Weiss behavior near their phase transition temperature/ Curie temperature. An important and interesting features of the ferroelectrics are the anomalous dielectric properties, non-linearities, reversible polarization and disappearance of ferroelectricity above a certain temperature called transition temperature/ Curie temperature (T_C). At the transition temperature/ Curie temperature the permittivity increases sharply to a very high peak value where as the dielectric constant becomes maximum near the transition temperature. Some general features of ferroelectric materials are as follows

- Ferroelectrics exhibits transition at certain temperature called Curie temperature and lead to high symmetrical structure. At Curie temperature the ferroelectric phase transitions are associated either with anomalous behavior of specific heat or the latent heat.

- Ferroelectric crystal possesses domain structure but at the transition temperature there is a sudden appearance of surface charge and below Curie temperature these materials show piezoelectric and pyroelectric properties.
- Ferroelectrics possess high dielectric constant [2] along the polarization axes as a function of temperature and it reaches to a peak value at the Curie temperature.

$BaTiO_3$ is an important ferroelectric material widely used in ceramic technology. Ferroelectric materials possesses polycrystalline structure with perovskite crystal structure (tetragonal/rhombohedral structure very close to cubic) and has general formula $A^{2+} B^{4+} O_3^{2-}$ in which A denotes divalent or trivalent ion such as barium or lead and B denotes a tetravalent or pentavalent metal ion such as zirconium or titanium.

These crystallites exhibit simple cubic symmetry above the Curie temperature. The crystal structure is centro symmetric with coincidence of positive and negative charge sites as there are no dipoles present in the materials (as it exhibits paraelectric behavior) however, below Curie temperature, the crystallites have tetragonal symmetry in which the positive and negative charge sites no longer coincide.

Lead zirconate titanate (PZT) [3] and barium lead zirconate titanate (BPZT) ferroelectrics are the members of pervoskite family. These ferroelectrics are most widely used in various materials applications. PZT has the cubic pervoskite structure (paraelectric) at high temperature and on cooling below the Curie point the structure undergoes phase transition to form a ferroelectric tetragonal structure. For specific requirements (for certain applications), piezoelectric ceramics are modified by doping them with ions which have a valency, different from that of ions in the lattice. Depending on the doping process, PZT's, are classified into soft PZT's and hard PZT's. The soft PZT's have higher piezoelectric coefficient and are easy to pole and depole, compared to hard PZT's. Barium doped PZT's show good piezoelectric properties, dielectric properties and better ME properties, while lead and zirconium doped $BaTiO_3$ (BPZT) is used to enhance the piezoelectric and mechanical properties. Barium lead zirconate titanate (BPZT - $Ba_{0.8}Pb_{0.2}Zr_{0.8}Ti_{0.2}O_3$) and lead zirconate titanate (PZT- $PbZr_{0.8}Ti_{0.2}O_3$) are chosen as the ferroelectric phases. BPZT is an important piezoelectric material having high dielectric permeability, high dielectric constant and good piezoelectric effect. The induced piezoelectric properties are maintained to obtain maximum piezoelectric conversion factor. Also the PZT has high piezoelectric coefficient, dielectric constant, permittivity and better coupling factor.

2. Methods of preparation

In ceramic technology several methods have been used for the preparation of magnetoelectric composites. The standard double sintering solid state reaction method is one among them (ceramic method) and has been extensively used to study the properties of resulting materials [4, 5]. Magnetoelectric effect is a structure dependent property [6], and at the same time the presence of impurity or intermediate phases in the composite will affect the ME signal [7]. However, the preparation of the ME composites without impurity is a challenging task, as the microstructural mismatching between two phases results in energy loss. Thus care has been taken to prepare the composites to reduce the energy loss. The said method is easier and much cheaper compared to other methods and offers several advantages over the choice of mole fraction of constituent phases, control of grain size and sintering temperature etc. The microstructural aspects such as grain size, pore concentration and grain shapes depend on the purity of the starting materials, mixing condition, sintering temperature, sintering time etc., [8, 9].

In the present work standard double sintering ceramic method is used for the preparation of homogeneous ferrite /ferroelectric phases and their composites of fine particles. In this method it is possible to maintain the stoichiometry of the final product even at large scale production. The method involves the following steps,

1. High purity oxides/ carbonates are mixed together (stoichiometry is maintained) in acetone medium by constant milling for longer period in an agate mortar to form homogenous mixture.
2. In the second stage "Presintering" (heating of the homogenous mixture) process is used to decompose carbonates and higher oxides from the raw materials to remove absorbed gases, moistures and to make oxides to react partially.
3. In the intermediate stage, presintered powder is ground to fine powder to reduce the particle size, which helps for the mixing of unreacted oxides if any. Later on fine powder is mixed with binder and pressed by using a die and a hydraulic press to get the desired shapes.
4. The "Final sintering" (final stage) increases the density of pellets by reducing the porosity. Infact sintering temperature and time affect the microstructure, oxygen content and cation distribution. In this stage uniform grain size, granular grains and other requirements are to be achieved.

The electric and magnetic phases such as ferroelectric and ferrites were prepared separately and then their proper molar proportions are mixed together to form a composites.

3. Structural characterization by XRD measurements

X-ray diffraction (XRD) technique is used for materials characterization (ferrites, ferroelectrics and composites etc) as it provides important information about the internal structure of matter such as grain size (crystallite size), nature of the solid sample (amorphous or crystalline) and crystal structure.

3.1 Ferroelectric phase

The XRD patterns of the ferroelectric systems $Ba_{0.8}Pb_{0.2} Zr_{0.8} Ti_{0.2}O_3$ and $Pb Zr_{0.8} Ti_{0.2}O_3$ (fig 1 & 2) with well defined peaks and highest intensity line (101/110) without intermediate phase

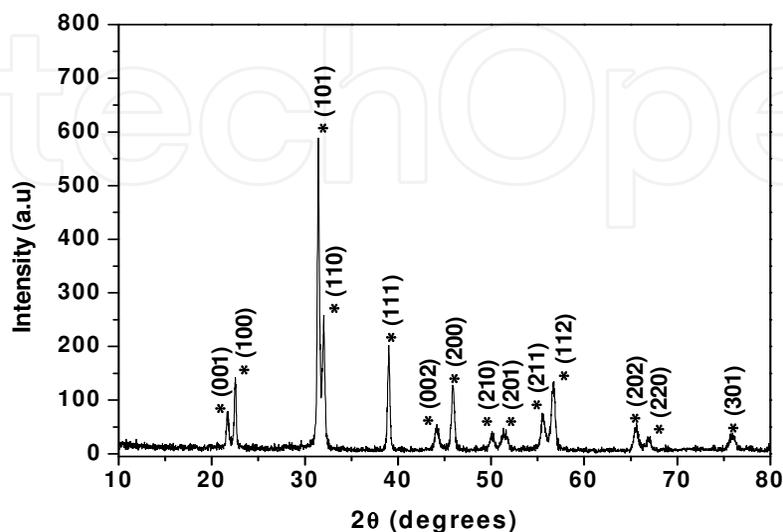Fig. 1. XRD pattern of $Ba_{0.8}Pb_{0.2} Zr_{0.8} Ti_{0.2}O_3$ ferroelectric phase

formation confirms the tetragonal perovskite structure. The prominent peaks are indexed with the help of JCPDs data. The observed and calculated 'd' values are good agreement with each other. The lattice parameters of $Ba_{0.8}Pb_{0.2}Zr_{0.8}Ti_{0.2}O_3$ (a = 4.031 Å and c = 4.032 Å) and $Pb\,Zr_{0.8}Ti_{0.2}O_3$ (a = 4.128 Å and c = 4.129 Å) are in good agreement with the earlier reports[10].
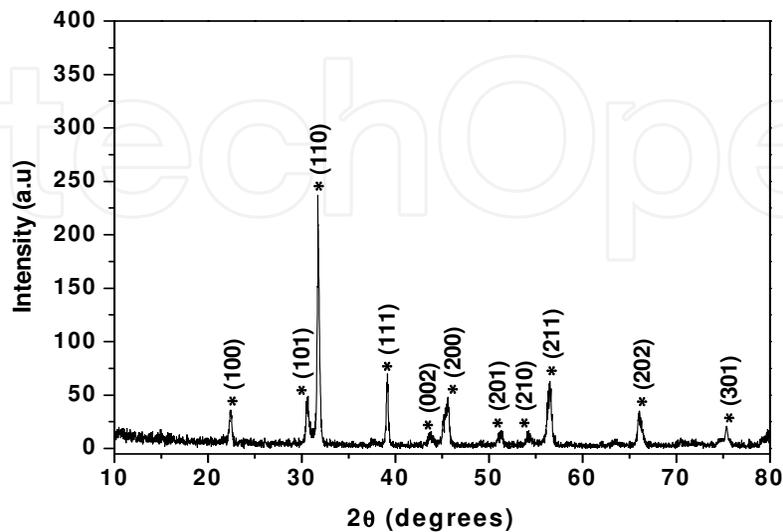
Fig. 2. XRD pattern of $Pb\,Zr_{0.8}Ti_{0.2}O_3$ ferroelectric phase

The scanning electron micrographs of two ferroelectric systems are shown in figs (3 & 4). The average grain diameter for each phase is calculated and is well with experimental results. The ferroelectric systems show fine grains with larger grain diameters than ferrite systems. In ceramics the dependence of grain growth mechanism was explained by Paulus [11] with particle size, composition and sintering temperature. However, the small grain size is important in domain geometry for the study of magnetic properties as well as ME properties.
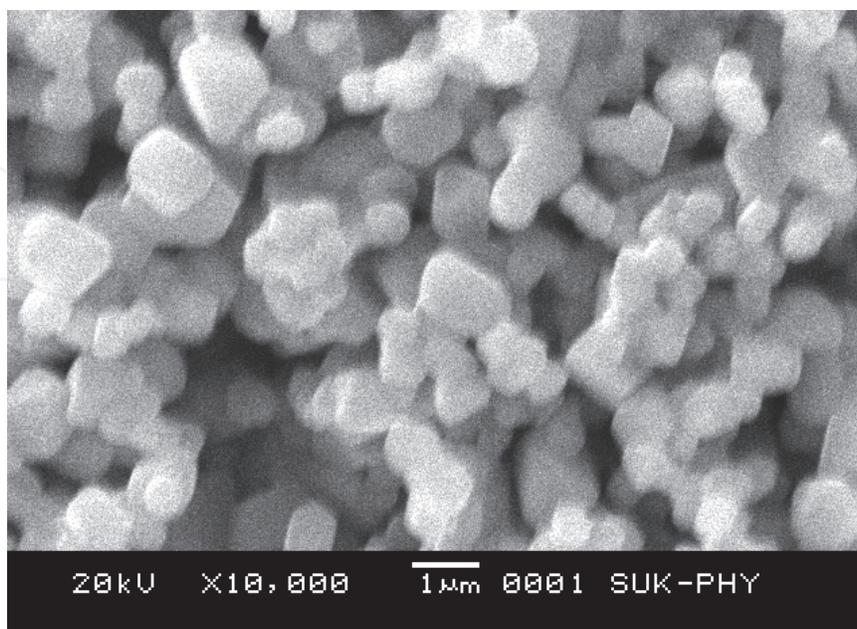

Fig. 3. SEM micrograph of $Ba_{0.8}Pb_{0.2}Zr_{0.8}Ti_{0.2}O_3$ ferroelectric phase
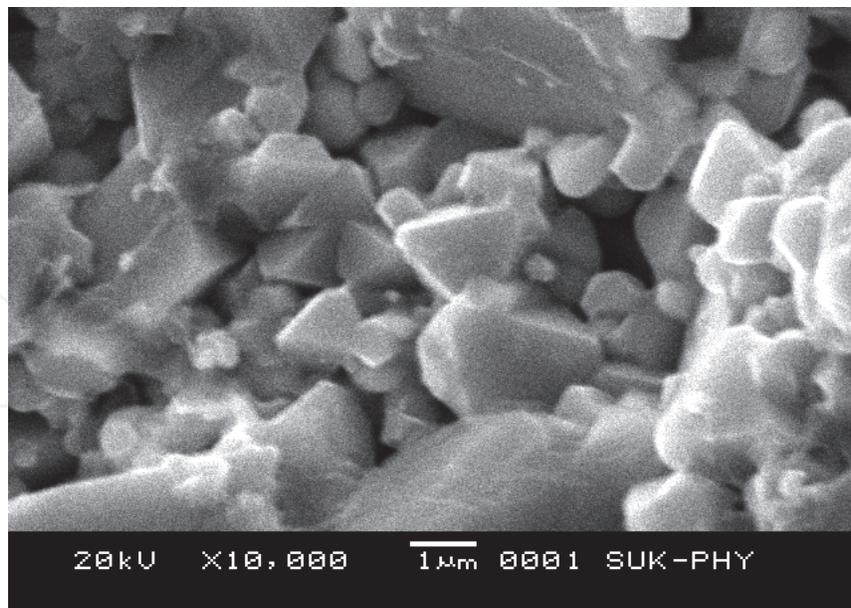
Fig. 4. SEM micrograph of $Pb\,Zr_{0.8}\,Ti_{0.2}O_3$ ferroelectric phase

5. DC electrical resistivity

The DC electrical resistivity of the samples are measured by two probe method. For good electrical contacts, the polished surfaces of pellets are silver coated on both sides and mounted in the sample holder. Afterwords it is placed in the digital temperature controlled muffle furnace and a constant voltage about 5 volts is applied using stabilized power supply unit and the current at different temperature is measured using digital nano ammeter. The resistivity of all the samples ρ_{DC} (ohm-cm) was estimated by measuring the current at the fixed voltage (ohm's law).

$$\rho_{DC} = \frac{R\,r^2\,\pi}{t} \tag{1}$$

Where   t - thickness of the pellet (cm), r - radius of the pellet (cm) and R- resistance (ohm).
The variation of DC resistivity with temperature for (x) $Ni_{0.2}\,Co_{0.8}\,Fe_2O_4$ + (1-x) $Ba_{0.8}Pb_{0.2}\,Zr_{0.8}\,Ti_{0.2}O_3$ composites (with x = 0.0, 0.15, 0.30, 0.45 and 1.0) are presented elsewhere [12]. The first region among the two regions of conductivity, observed at lower temperature is attributed to ordered states of the ferroelectric phase and the second region observed at higher temperature due to polaron hopping is attributed to the disordered para electric states of the composites. However, the impurities present in the system are almost minimized at higher temperature. Polaron hopping is valid in ferroelectrics as well as in composites containing ferrite and ferroelectrics [13]. According to hopping conduction mechanism the resistivity of composites are found to decrease with increase in ferrite content (due to its low resistivity compared to ferroelectric phase). The ferrite particles disperse throughout the composites and make connected chains with the ferroelectric particles which reduces resistivity significantly. Good dispersion of the ferrite particles are required to obtain high electrical conductivity in the composites. The electrical conductivity in ferrites are explained on the basis of Verwey de Boer mechanism, as it involves the electron exchange between ions of same element which are already present in more than one

valance state and distributed randomly over the crystallographic equivalent lattice sites. The resistivity of the composite is the sum of the resistivities of their constituents [14] and the decrease in resistivity with increase in temperature is attributed to the increase in drift mobility of charge carriers. During the process of preparation, the formation of Fe^{2+} and Fe^{3+} ions depends on the sintering condition. But large drop in resistivity is observed on the addition of a ferrite phase to the composites, it is due to the partial reduction of Fe^{2+} and Fe^{3+} ions at elevated firing temperatures. While preparing the mixtures of two phases to get high ME response in the composites the control of the resistivity of the ferrite phase is necessary compared to ferroelectric phase. Similar results have been identified in the temperature dependent resistivity plot for the (x) $Ni_{0.2}$ $Co_{0.8}$ Fe_2O_4 + (1-x) Pb $Zr_{0.8}$ $Ti_{0.2}O_3$ composites with x = 0.0, 0.15, 0.30, 0.45 and 1.0 [15].

The variation of DC electrical resistivity with temperature for (x) $Ni_{0.5}$ $Zn_{0.5}$ Fe_2O_4 + (1-x) $Ba_{0.8}Pb_{0.2}$ $Zr_{0.8}$ $Ti_{0.2}O_3$ composites with x = 0.0, 0.15, 0.30, 0.45 and 1.0 is also presented earlier [16]. The resistivity of the composites decreases with increase in ferrite content and the increase in resistivity with temperature is due to the increase in drift mobility of the charge carriers. However, the conduction in ferrite may be due to the hopping of electron from Fe^{2+} and Fe^{3+} ions. The number of such ion pairs depends upon the sintering conditions and which accounts for the reduction of Fe^{3+} to Fe^{2+} at elevated temperatures. That is the resistivity of ferrite is controlled by the Fe^{2+} concentration on the B-site. In Ni-ferrite, Ni ions enter the lattice in combination with Fe^{3+} ions resulting in a lower concentration of Fe^{2+} ions with higher resistivity and which is one of the prime requirements for getting higher values of ME output. According to theoretical predictions the plots of ferroelectric phase and composites show two regions of conductivity and the change in slope is due to the transition of the sample from the ferroelectric state to para electric state. However, the regions observed above and below the Curie temperature may be due to the impurities and small polaron hopping mechanism.

The mobility is temperature dependent quantity and can be characterized by the activation energy. But at the grain boundaries, the highly disturbed crystal lattice may cause a drastic decrease in the activation energy. The activation energy in the present case is obtained by fitting the DC resistivity data with the Arrhenius relation $\rho = \rho_o \exp(\Delta E/KT)$, where ΔE is the activation energy and K is Boltzmann constant. It is well known that the electron and hole hopping between Fe^{2+}/Fe^{3+} and Zn^{2+}/Zn^{3+}, Ni^{2+}/Ni^{3+}, Ba^{2+}/Ba^{3+}, Ti^{3+}/Ti^{4+} ions is responsible for electrical conduction in the composites. The estimated activation energies for the composites in the higher and lower temperature regions suggest temperature dependent charge mobility and activation energy of paraelectric region greater than 0.2 eV (above Tc), reveals polaron hoping in composites. Similar behavior is observed for (x) $Ni_{0.5}$ $Zn_{0.5}$ Fe_2O_4 + (1-x) $PbZr_{0.8}Ti_{0.2}O_3$ composites (with x = 0.0, 0.15, 0.30, 0.45 and 1.0). In case of composites, the temperature dependent variation of resistivity is very important for the measurements of ME conversion factor, because the conduction in composites being thermally activated mechanism, alters the polarization of the ferroelectric phase as temperature increases. Thus the ME measurements are carried out only at the room temperature [17].

6. Dielectric properties and AC conductivity

6.1 AC conductivity measurements

The temperature dependent AC conductivity (σ_{AC}) are related to the dielectric relaxation caused by the localized electric charge carriers. And the frequency dependent AC conductivity is estimated from dielectric constant and loss tangent (tanδ) using the relation

$$\sigma_{AC} = \varepsilon' \, \varepsilon_o \, 2\pi f \tan \delta \qquad (2)$$

Where, ε' is real dielectric constant, ε_o is the permittivity of free space, $\tan\delta$ is the loss tangent at real ε' (at dielectric constant) and f is the frequency of applied field. However, the conduction mechanism in composites are obtained from the plots of frequency response of the dielectric behavior and AC conductivity.

6.2 Variation of dielectric constant (ε´) and loss tangent (tanδ)

The variation of dielectric constant with frequency at room temperature for the four composite systems shows good response and are reported elsewere [12]. The dielectric constant decreases with increase in test frequency indicating dispersion in certain frequency region and then reaches a constant value. The high values of dielectric constant at lower frequency region and low values at higher frequency region indicate large dispersion due to Maxwell-Wagner [18, 19] type of interfacial polarization in accordance with Koop's theory. At lower frequencies the dielectric constants of ferrites, ferroelectrics and their composites vary randomly. It is due to the mismatching of grains of ferrites and ferroelectrics in the composites and hence it is difficult to estimate the effective values of dielectric constant of composites.

The decrease in dielectric constant with increase in frequency indicating dielectric dispersion due to dielectric polarization. Dielectric polarization is due to the changes in the valence states of cations and space charge polarization mechanism. At higher frequencies, the dielectric constant is independent of frequency due to the inability of the electric dipoles to follow up the fast variation of the applied alternating electric field and increase in friction between the dipoles. However, at lower frequencies the higher values of the dielectric constant are due to heterogeneous conduction; some times it is because of polaron hopping mechanism resulted in electronic polarization contributing to low frequency dispersion. In composites due to the friction, the dipoles dissipate energy in the form of heat which affects internal viscosity of the system and results in decrease of the dielectric constant; this frequency independent parameter is known as static dielectric constant. The dielectric behavior in composites can also be explained on the basis of polarization mechanism in ferrites because conduction beyond phase percolation limit is due to ferrite. In ferrites, the rotational displacement of $Fe^{3+} \leftrightarrow Fe^{2+}$ dipoles results in orientation polarization that may be visualized as an exchange of electrons between the ions and alignment of dipoles themselves with the alternating field. In the present ferrites, the presence of Ni^{2+}/Ni^{3+}, Co^{2+}/Co^{3+} and Zn^{2+}/Zn^{3+} ions give rise to p-type carriers and also their displacement in the external electric field direction contributes to the net polarization in addition to that of n-type carriers. Since the mobility of p-type carriers is smaller than that of n-type carriers, their contribution to the polarization decreases more rapidly even at lower frequency. As a result, the net polarization increases initially and then decreases with increase in frequency. The transport properties such as electrical conductivity and dielectric dispersion of ferrites are mainly due to the exchange mechanism of charges among the ions situated at crystallographic equivalent sites [20]. Iwauchi [21] and Rezlescu et al have established inverse relation between conduction mechanism and dielectric behavior based on the local displacement of electrons in the direction of applied field.

The variation of dielectric loss factor (tanδ) with frequency was also explained. At lower frequencies loss factor is large and it goes on decreasing with increase in frequency. The loss factor is the energy dissipation in the dielectric system, which is proportional to the imaginary part of the dielectric constant (ε''). At higher frequencies, the losses are reduced due to serial arrangements of dipoles of grains which contribute to the polarization. The losses can also be explained in terms of relaxation time and the period of applied field.

When loss is minimum, then relaxation time is greater than period of applied field and it is maximum when relaxation time is smaller than the period of applied field.

6.3 Ferroelectric phase

The variations of dielectric constant with temperature for two ferroelectric systems (BPZT and PZT) are shown in figs (5 & 6). The dielectric constant increases with increase in temperature and becomes maximum at Curie temperature (T_c) and there after it decreases. For BPZT and PZT ferroelectrics, the observed T_c are nearly 160 ºC and 410 ºC, slightly greater than the reported values and can be attributed to constrained grains. Hiroshima et al [22] have reported a close relation between the Curie temperature and internal stresses developed in the constrained grains at the phase transition temperature. The internal stress can shift T_c to higher temperature sides in case of larger grains (diameter greater than 1 μm).
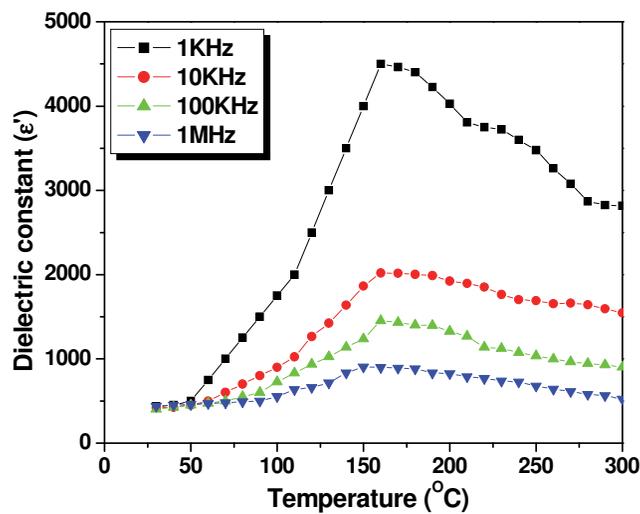
Fig. 5. Variation of dielectric constant with temperature for $Ba_{0.8}Pb_{0.2}Zr_{0.8}Ti_{0.2}O_3$ ferroelectric phase
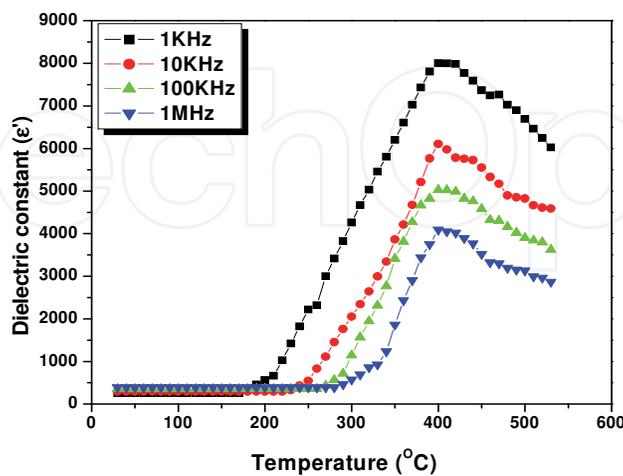
Fig. 6. Variation of dielectric constant with temperature for $PbZr_{0.8}Ti_{0.2}O_3$ ferroelectric phase

The larger grained structure and changes in internal stresses are expected in the pellets due to higher sintering temperature. The large grained ferroelectrics have considerable internal

stress concentration which is enough to form micro cracks at the grain boundaries and hence induced internal stresses are relieved. But in small grain sized ceramics, increased grain boundaries form less micro cracks which reduce the internal stress concentration. Usually the ferroelectric materials have high dielectric constant compared to ferrite; hence dielectric property is enhanced with the increase in ferroelectric content, which is very important in the study of ME output [12]. The nature of variation of dielectric loss tangent with temperature for all the series of composites and their constituent phases shown in figures (7 & 8), almost the same as that of the variation of dielectric constant with temperature. The observed dispersion behavior of the loss tangent is attributed to higher domain mobility near the Curie temperature.
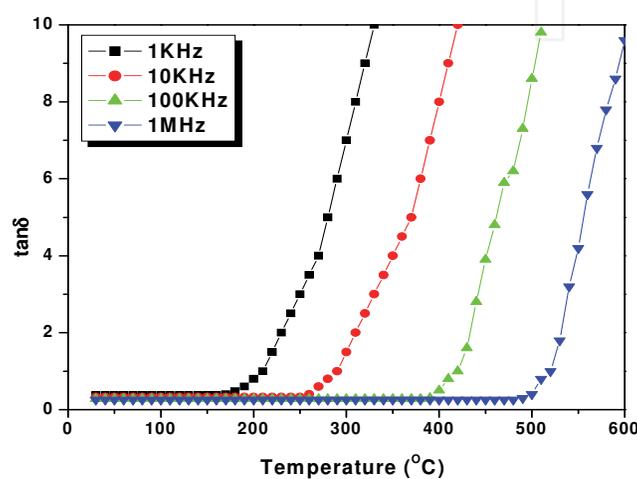
Fig. 7. Variation of dielectric loss tangent with temperature for $Ba_{0.8}Pb_{0.2}Zr_{0.8}Ti_{0.2}O_3$ ferroelectric phase
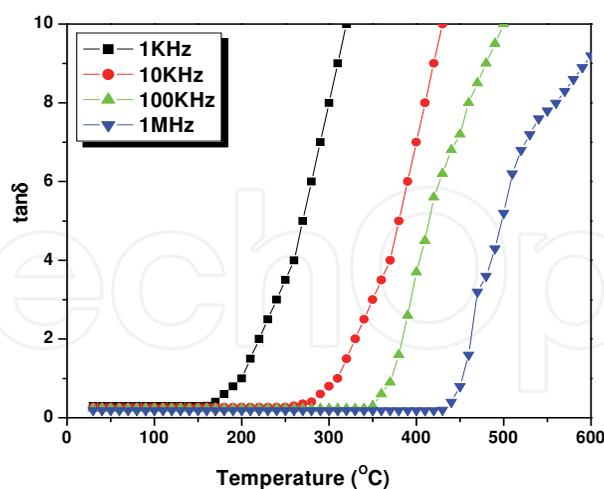
Fig. 8. Variation of dielectric loss tangent with temperature for $PbZr_{0.8}Ti_{0.2}O_3$ ferroelectric phase

6.4 Variation of AC conductivity with frequency at room temperature

The variation of AC conductivity (σ_{AC}) as a function of frequency was presented in figures (9 - 12). From AC conductivity one can retrieve at the behaviour of thermally activated conduction mechanism and the type of polarons responsible for the conduction mechanism.
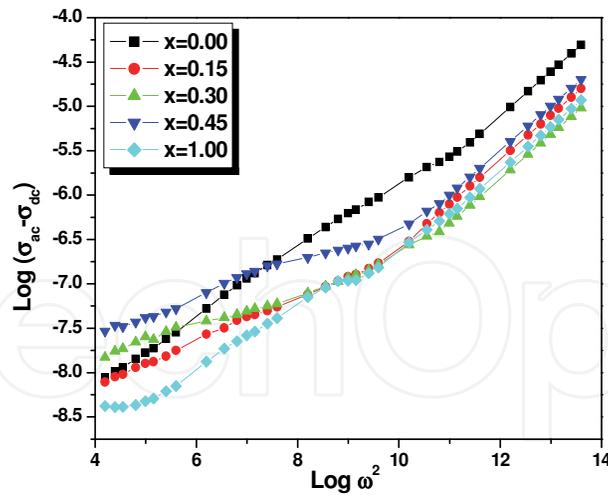
Fig. 9. Variation of AC conductivity with frequency for (x) $Ni_{0.2}Co_{0.8}Fe_2O_4$+ (1-x) $Ba_{0.8}Pb_{0.2}Zr_{0.8}Ti_{0.2}O_3$ composites

Infact the polaron type of conduction was reported by Austin and Mott [23] and Appel et al. According to Alder and Feinleib [24] the direct frequency dependence conduction due to small polarons is given by the relation

$$\sigma_{AC} - \sigma_{DC} = \frac{\omega^2 \tau^2}{\left(1 - \omega^2 \tau^2\right)} \qquad (3)$$

Where ω is the angular frequency and τ is the staying time (10^{-10} s), for all the ceramics $\omega^2 \tau^2$ < 1. The plots of log (σ_{AC} -σ_{DC}) against Log ω^2 are linear in nature indicating small polaron type of conduction. However, a slight decrease in the conductivity at a certain frequency is attributed to mixed polaron (small/large) type of conduction and similar results are reported by various workers. In the present case, the AC conductivity of the composites caused by small polarons is responsible for the good ME response.
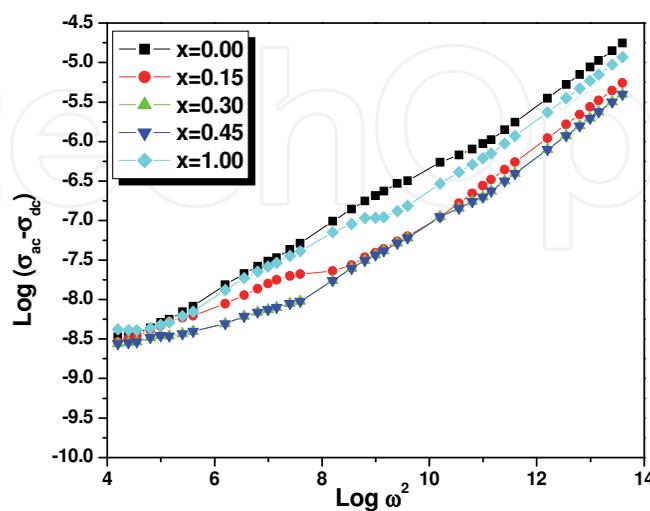
Fig. 10. Variation of AC conductivity with frequency for (x) $Ni_{0.2}Co_{0.8}Fe_2O_4$+ (1-x) $Pb Zr_{0.8}Ti_{0.2}O_3$ composites
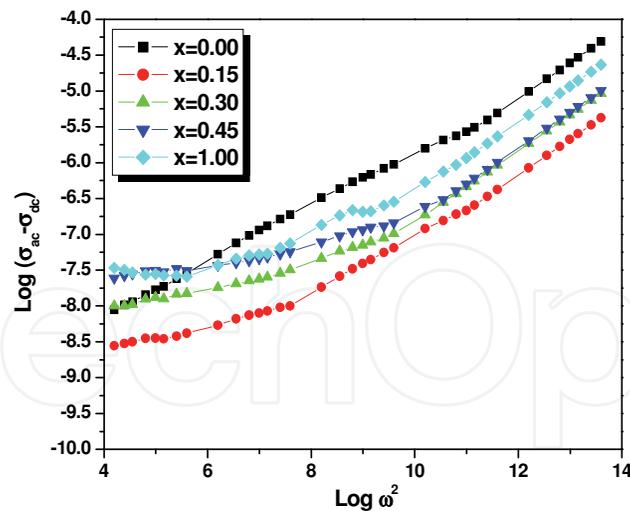
Fig. 11. Variation of AC conductivity with frequency for (x) $Ni_{0.5} Zn_{0.5} Fe_2O_4$+ (1-x) $Ba_{0.8}Pb_{0.2} Zr_{0.8} Ti_{0.2}O_3$ composites
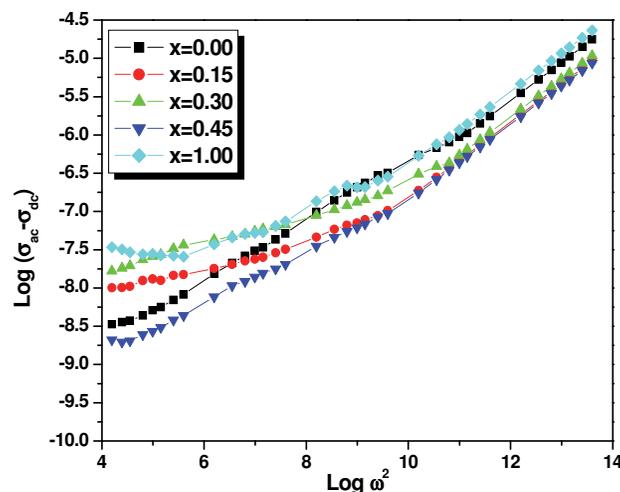
Fig. 12. Variation of AC conductivity with frequency for (x) $Ni_{0.5} Zn_{0.5} Fe_2O_4$+ (1-x) $Pb Zr_{0.8} Ti_{0.2}O_3$ composites

7. Magnetoelectric effect- A product property

Magnetoelectricity, the product property, requires biphasic surrounding to exhibit the complex behaviour. The primary magnetoelectric (ME) materials can be magnetized by placing them in electric field and can be electrically polarized by placing them in magnetic field [25]. The magnetoelectric effect in the composites having ferrite and ferroelectric phases depends on the applied magnetic field, electrical resistivity, mole percentage of the constituent phases and mechanical coupling between the two phases. The resistivity of the composites is a temperature dependent property which decreases in high temperature region, making the polarization of the samples more difficult. In the present studies the ME voltage coefficient is measured at room temperature. The ME coupling can be obtained by electromechanical conversion in the ferrite and ferroelectric phases by the transfer of stress through the interface between these two phases. Infact magneto mechanical resonance in the ferrite phase and electromechanical resonance in ferroelectric phase are responsible for the origins of ME peaks.

For the composite systems (x) $Ni_{0.2}Co_{0.8}Fe_2O_4$ + (1-x) $Ba_{0.8}Pb_{0.2}Zr_{0.8}Ti_{0.2}O_3$ (with x = 0.15, 0.30 and 0.45) the variation of static magnetoelectric conversion factor with applied DC magnetic field is shown in fig. 13. From the figure it is clear that magnetoelectric voltage coefficient $(dE/dH)_H$ increases slowly with applied magnetic field and after attaining a maximum value again it decreases. The constant value of $(dE/dH)_H$ indicates that the magnetostriction reaches its saturation value at the time of magnetic poling and produces constant electric field in the ferroelectric phase. The static ME conversion factor depends on mole % of ferrite and ferroelectric phases in the composites, however with further increase in mole fraction of ferrite phase, the maganetoelectric voltage coefficient $(dE/dH)_H$ decreases. The lower values of static ME output are due to low resistivity of ferrite phase compared to that of ferroelectric phase. At the time of poling, charges are developed in the ferroelectric grains through the surrounding of low resistivity ferrite grain and leakage of such charges is responsible for low static ME output. However, the static magnetoelectric voltage coefficient $(dE/dH)_H$ decreases with increase in grain size of the ferrite and ferroelectric phases in the composites. The large grains are (polydomain) less effective in inducing piezomagnetic and piezoelectric coefficients than that of the smaller ones [26]. Motagi and Hiskins reported the variation of piezoelectric property of ferroelectric phase with grain size. Infact the ME conversion factor also depends on porosity and grain size. In the present experimental investigation it is found that small grains with low porosity are important for getting high ME out put in the composites. A maximum static ME coefficient of 536 µV/cm Oe is observed in the composite containing 15 % $Ni_{0.2}Co_{0.8}Fe_2O_4$ + 85 % BPZT (table. 1). The observed results for the composite system (x) $Ni_{0.2}Co_{0.8}Fe_2O_4$ + (1-x) $Pb Zr_{0.8}Ti_{0.2}O_3$ (with x = 0.15, 0.30 and 0.45) are shown figure. 14. The high ME out put of 828 µV/cm Oe is observed for the composite containing 15 % $Ni_{0.2}Co_{0.8}Fe_2O_4$ + 85 % $Pb Zr_{0.8}Ti_{0.2}O_3$ (table 1). High magnetostriction coefficient and piezoelectric coefficient of the ferrite and ferroelectric phases are responsible for high ME out put in these composites.
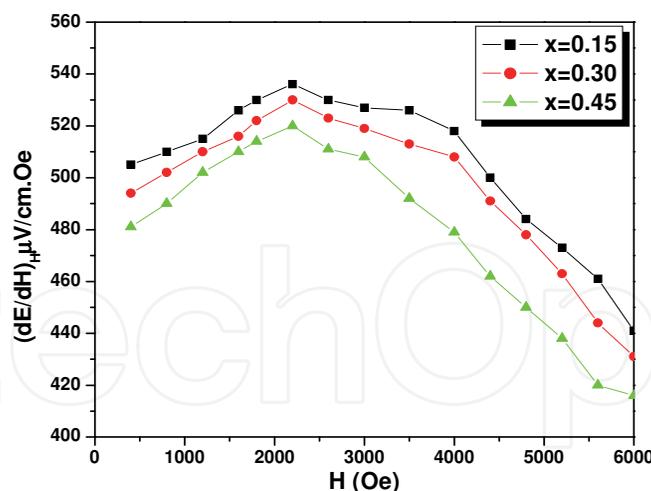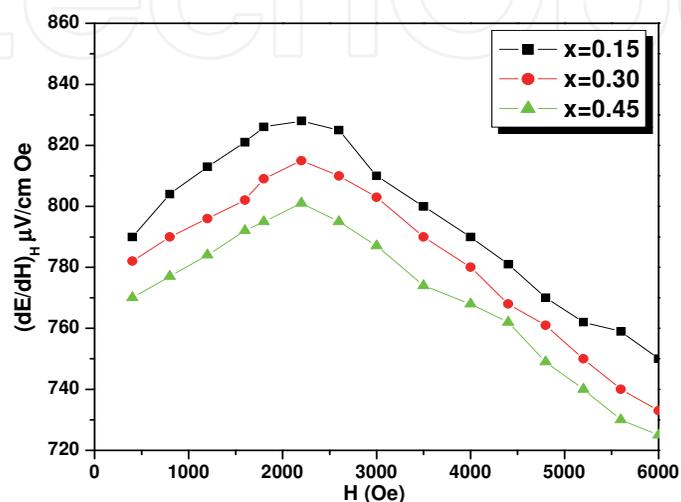

Fig. 13. Magnetic field dependent variation of ME voltage coefficient at room temperature for (x) $Ni_{0.2}Co_{0.8}Fe_2O_4$ + (1-x) $Ba_{0.8}Pb_{0.2}Zr_{0.8}Ti_{0.2}O_3$ ME composites.

From the investigation it is observed that increase in ferrite content in the composites leads to the enhancement of elastic interaction. But there is a limit to the addition of ferrite in the composite because further increase in ferrite content in the composites leads to the decrease in the resistivity of composites. Therefore the additions of ferrites in the composites are restricted to only 0.15, 0.30 and 0.45, because at these values there is a resistivity matching

between ferrite and ferroelectric phases. Many workers studied Ni, Co and Zn ferrite with BaTiO$_3$ ferroelectric by ceramic method and reported very weak ME response inspite of high resistivity of the ferrites. But in the present composites better ME voltage coefficients are obtained, which may be due to the presence of cobalt ions (Co^{+2}) in ferrites, as it causes large lattice distortion in the ferrite lattice and induces more mechanical coupling between the ferrite and ferroelectric phases, leading to the polarization in the piezoelectric phases. Similarly substitution of Zn in nickel also enhances the magnetostriction coefficient and hence shows good ME response.

Fig. 14. Magnetic field dependent variation of ME voltage coefficient at room temperature for (x) Ni$_{0.2}$Co$_{0.8}$Fe$_2$O$_4$ + (1-x) Pb Zr$_{0.8}$Ti$_{0.2}$O$_3$ ME composites.

The magnetic field dependent variation of the ME voltage coefficient with magnetic field for the composite system (x) Ni$_{0.5}$Zn$_{0.5}$Fe$_2$O$_4$ + (1-x) Ba$_{0.8}$Pb$_{0.2}$Zr$_{0.8}$Ti$_{0.2}$O$_3$ is shown in fig 15. The ME coefficient increases linearly with applied magnetic filed (< 1.0 K Oe) and after acquiring a maximum value decreases linearly. The initial rise in ME output is attributed to the enhancement in the elastic interaction, which is confirmed by the hysteresis measurements.
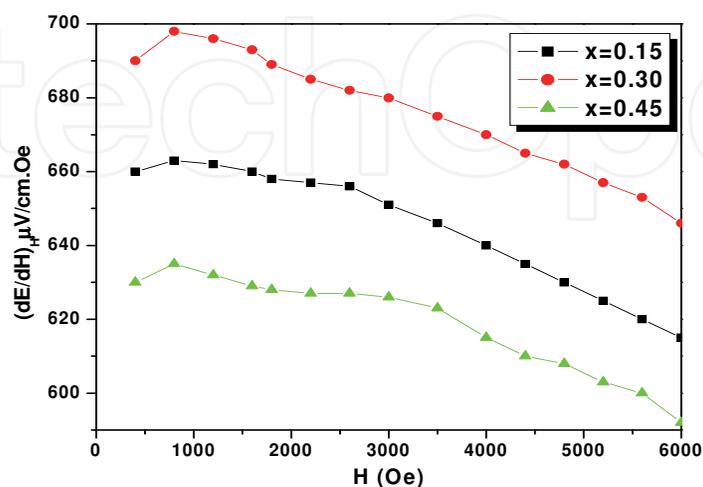

Fig. 15. Magnetic field dependent variation of ME voltage coefficient at room temperature for (x) Ni$_{0.5}$Zn$_{0.5}$Fe$_2$O$_4$ + (1-x) Ba$_{0.8}$Pb$_{0.2}$Zr$_{0.8}$Ti$_{0.2}$O$_3$ ME composites.

The intensity of the magnetostriction reaches saturation value above 1.0 K Oe and hence, the magnetization and associated strain produce a constant electric field in the ferroelectric phase beyond the saturation limit. The maximum ME voltage coefficient of 698 µV/cm Oe is observed for the composites containing 30 % $Ni_{0.5}Zn_{0.5}Fe_2O_4$ + 70 % $Ba_{0.8}Pb_{0.2}Zr_{0.8}Ti_{0.2}O_3$ (table. 1). It is well known that the ME response of the composites depends on the piezoelectricity of the ferroelectric phase and the magnetostriction of the ferrite phase. The composites prepared with a lower content of the ferrite or ferroelectric phase results in the reduction of piezoelectricity or magnetostriction respectively, leading to a decrease in the static ME voltage coefficient as predicted theoretically. The increase in ME output at x = 0.30 (table. 1) may be attributed to the uniform distribution of small grains in both the phases. However, the uneven particle size of the phases reduces the mechanical coupling between them and causes significant current loss in the sample [27]. The similar results have been observed for the composite system (x) $Ni_{0.5}Zn_{0.5}Fe_2O_4$ + (1-x) $Pb Zr_{0.8}Ti_{0.2}O_3$ (with x = 0.15, 0.30 and 0.45) shown in fig. 16.

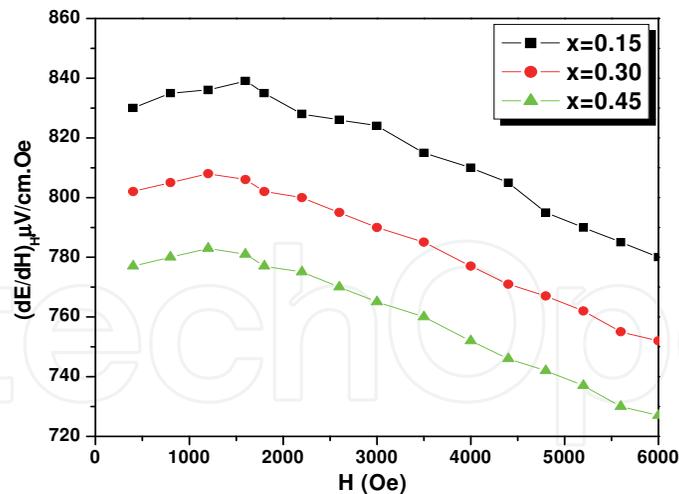| Composition (x)	ME Voltage Coefficient $(dE/dH)_H$ (µV/cm Oe)
(x) $Ni_{0.2}Co_{0.8}Fe_2O_4$ + (1-x) $Ba_{0.8}Pb_{0.2}Zr_{0.8}Ti_{0.2}O_3$	
0.15	536
0.30	530
0.45	520
(x) $Ni_{0.2}Co_{0.8}Fe_2O_4$ + (1-x) $Pb Zr_{0.8}Ti_{0.2}O_3$	
0.15	828
0.30	815
0.45	801
(x) $Ni_{0.5}Zn_{0.5}Fe_2O_4$ + (1-x) $Ba_{0.8}Pb_{0.2}Zr_{0.8}Ti_{0.2}O_3$	
0.15	663
0.30	698
0.45	635
(x) $Ni_{0.5}Zn_{0.5}Fe_2O_4$ + (1-x) $Pb Zr_{0.8}Ti_{0.2}O_3$	
0.15	839
0.30	808
0.45	783

Table. 1. Variation of ME Voltage Coefficient with composition

Fig. 16. Magnetic field dependent variation of ME voltage coefficient at room temperature for (x) $Ni_{0.5}Zn_{0.5}Fe_2O_4$ + (1-x) $Pb\,Zr_{0.8}\,Ti_{0.2}O_3$ ME composites

8. Conclusion

In the study of ME effect, initially ME voltage coefficient $(dE/dH)_H$ increases with the increase in applied DC magnetic field and thereafter decreases linearly. It is attributed to the increase in elastic interaction caused by magnetostriction and piezoelectric effect aswell as low leakage of currents and high degree of polarization.

1. ME output depends on the resistivity and mole percentage of ferrite/ferroelectric phases and maximum ME output is observed for high resistivity composites. The decrease in dielectric constant with frequency shows the dielectric dispersion at lower frequency region.
2. ME output increases with decrease in the grain size of the individual phases. However, large particles are less effective in inducing piezoelectric and piezomagnetic effect compared to smaller grains. The composites having high porosity exhibit better ME response, because the pores provides resistance to the electrons.
3. The present ME composites having large ME response vary linearly with DC electric field in the low and high magnetic field regions and are attractive for technological applications for ME devices.

The content of ferroelectric is very important for getting high ME voltage coefficient. But in order to obtain still better ME response, one can use layered (bilayer layer and multilayer) composites of two phases (ferrites and ferroelectrics) and it requires minimum deficiencies with particles of nano size.

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10. References

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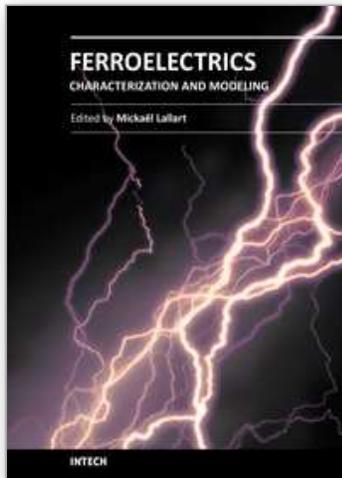
Ferroelectrics - Characterization and Modeling
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Ferroelectric materials have been and still are widely used in many applications, that have moved from sonar towards breakthrough technologies such as memories or optical devices. This book is a part of a four volume collection (covering material aspects, physical effects, characterization and modeling, and applications) and focuses on the characterization of ferroelectric materials, including structural, electrical and multiphysic aspects, as well as innovative techniques for modeling and predicting the performance of these devices using phenomenological approaches and nonlinear methods. Hence, the aim of this book is to provide an up-to-date review of recent scientific findings and recent advances in the field of ferroelectric system characterization and modeling, allowing a deep understanding of ferroelectricity.

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