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## Mechanical properties of $\text{Ni}_{0.83}\text{Co}_{0.15}\text{Cu}_{0.02}\text{Fe}_{1.9}\text{O}_{4-\delta} + \text{PbZr}_{0.52}\text{Ti}_{0.48}\text{O}_3$ particulate composites by composite oscillator technique and the correlation with the results of magnetoelectric properties

M. Venkata RAMANA

*Shenzhen Key Laboratory of Advanced Materials, Department of Materials Science and Engineering, Shenzhen Graduate School, Harbin Institute of Technology, Shenzhen 518055, China*

M. Penchal REDDY

*Department of Physics, Changwon National University, Changwon, Republic of Korea*

N. Ramamanohar REDDY

*Ceramic Composite Materials Laboratory, Department of Physics, Sri Krishnadevaraya University, Anantapur 515003, India*

B. S. MURTY

*Nanotechnology Laboratory, Department of Metallurgical and Materials Engineering, Indian Institute of Technology, Chennai 600036, India*

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K. V. SIVA KUMAR

*Ceramic Composite Materials Laboratory, Department of Physics, Sri Krishnadevaraya University, Anantapur 515003, India*

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**Mechanical properties of  $\text{Ni}_{0.83}\text{Co}_{0.15}\text{Cu}_{0.02}\text{Fe}_{1.9}\text{O}_{4-\delta} + \text{PbZr}_{0.52}\text{Ti}_{0.48}\text{O}_3$  particulate composites by composite oscillator technique and the correlation with the results of magnetoelectric properties**

**Authors**

M. Venkata RAMANA, M. Penchal REDDY, N. Ramamanohar REDDY, B. S. MURTY, K. V. SIVA KUMAR, and Shenhua SONG

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M. Venkata RAMANA<sup>a,\*</sup>, M. Penchal REDDY<sup>b</sup>,  
N. Ramamanohar REDDY<sup>c</sup>, B. S. MURTY<sup>d</sup>, K. V. SIVA KUMAR<sup>c</sup>, Shenhua SONG<sup>a</sup>

<sup>a</sup>Shenzhen Key Laboratory of Advanced Materials, Department of Materials Science and Engineering, Shenzhen Graduate School, Harbin Institute of Technology, Shenzhen 518055, China

<sup>b</sup>Department of Physics, Changwon National University, Changwon, Republic of Korea

<sup>c</sup>Ceramic Composite Materials Laboratory, Department of Physics, Sri Krishnadevaraya University, Anantapur 515003, India

<sup>d</sup>Nanotechnology Laboratory, Department of Metallurgical and Materials Engineering, Indian Institute of Technology, Chennai 600036, India

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**Abstract:** The  $x\text{Ni}_{0.83}\text{Co}_{0.15}\text{Cu}_{0.02}\text{Fe}_{1.9}\text{O}_{4-\delta}$  (NCCF) +  $(1-x)\text{PbZr}_{0.52}\text{Ti}_{0.48}\text{O}_3$  (PZT) particulate magneto ferroelectric composites with  $x = 0, 0.1, 0.2, 0.3, 0.4, 0.5$  and  $0.6$  mole fraction were prepared by conventional ceramic double sintering method. The presence of two phases (perovskite structure of ferroelectric phase and spinel structure of ferromagnetic phase) was confirmed by X-ray diffraction. The magnetoelectric (ME) property of the particulate composites was determined at room temperature as a function of intensity of magnetic field. The temperature variation of the longitudinal modulus ( $L$ ) and the internal friction ( $Q^{-1}$ ) of these particulate composites at 104.3 kHz was studied in the wide temperature range 30-420 °C. The temperature variation of the longitudinal modulus in each composition of these particulate composites showed two abrupt minima. One minimum coincided with the ferroelectric – paraelectric Curie transition temperature ( $\theta_E$ ) and the other with the ferromagnetic-paramagnetic Curie transition temperature ( $\theta_M$ ). The internal friction measurement also showed two sharp peaks in each composition corresponding to those temperatures where the minima were noticed in the temperature variation of the longitudinal modulus behaviour.

**Key words:** X-ray diffraction; magnetoelectric effect; piezoelectric coefficient; internal friction; Curie transition temperature

## 1 Introduction

Composite materials of the type piezoelectric-

magnetostrictive ferrite are of interesting transducers which transform changes in a magnetic field into electric signals and vice-versa magnetoelectricity (ME) is a product property and needs biphasic surrounding to exhibit the complex behaviour [1]. Few single phase materials are magnetoelectric, but the ME effect is

\* Corresponding author.

E-mail: materialphysics.ramana@gmail.com

usually weak [2]. A much stronger ME effect could be realized in a composite of ferrimagnetic and ferroelectric phase in which the ME coupling is mediated by mechanical stress. The resistivity of the piezoelectric phase should be high compared with the ferromagnetic and the mechanical coupling between the two phases is perfect. The stronger piezoelectric activity is observed in materials of the type of Lead Zirconate Titanate,  $\text{Pb}(\text{Zr}_{0.52}\text{Ti}_{0.48})\text{O}_3$  (PZT), and for this reason these materials are promising for the use in magnetoelectric composite materials in order to obtain magnetoelectric sensitivity. The piezoelectric phase in the magnetoelectric composite materials ensures that they are sensitive to vibration, which must be taken into account when these materials are used in magnetic-field pickups.

In reality, the problem of material choice is more complicated as a result of interdoping between piezoelectric and piezomagnetic materials in the sintering process. Because of the uncontrolled composition changes, it is impossible to predict the best combination of the material being only the mechanical approach. On the other hand, the enhanced conductivity of the ferrite particles gives rise to the problems of complete polarization in ferroelectric phase. The interdoping degree and the bulk conductivity depend on the composite connectivity pattern. That is why the concept of connectivity may be considered as a key point of the further improvement of magnetoelectric composite properties [3]. Such multiferroic composites are highly useful as sensors, wave guides, modulators, switches, phase invertors and rectifiers [4].

The data availability in the literature on investigation of properties like elastic, anelastic, piezoelectric, and magnetostrictive in nature on these multiferroic particulate composites are scanty. As reported by many works [5-7] from our own observations [8,9], elastic modulus and internal friction measurements are very sensitive properties to identify the phase transitions, point defects, oxygen ion vacancies and domain wall motions, since they are lattice related properties. In view of this, in the present work, magnetoferroelectric particulate composite containing PZT was chosen as a ferroelectric material, because of its excellent dielectric, pyroelectric and piezoelectric properties. Similarly, a highly magnetostrictive material such as  $\text{Ni}_{0.83}\text{Co}_{0.15}\text{Cu}_{0.02}\text{Fe}_{1.9}\text{O}_{4-\delta}$  (NCCF) was chosen as piezomagnetic component. NCCF is generally used in ultrasonic

applications such as radiators and hydrophones [10]. The temperature variation of the elastic behaviour ( $L$ ) and internal friction ( $Q^{-1}$ ) of  $x$  NCCF+(1- $x$ ) PZT ( $x=0, 0.1, 0.2, 0.3, 0.4, 0.5$  and  $0.6$  mole fraction) multiferroic particulate composites were prepared and studied in the wide temperature range 30-400 °C. The results were reported in this paper and they were discussed in the light of structural phase transitions.

## 2 Experimental details

The piezomagnetic phase ( $\text{Ni}_{0.83}\text{Co}_{0.15}\text{Cu}_{0.02}\text{Fe}_{1.9}\text{O}_{4-\delta}$ ) was prepared by using the analytical grade NiO, CoO, CuO and  $\text{Fe}_2\text{O}_3$ . Stoichiometric amounts of these oxides were weighed and mixed thoroughly. These constituents were ball-milled (RETSCH PM-200, Germany) in agate bowls with agate balls in an ethyl alcohol 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 closed alumina crucibles at 800 °C for 2 h. After calcination, these cakes were crushed and powdered. These powders were ball-milled once again under the same conditions in ethyl alcohol medium for 8 more hours to obtain fine particle size. The piezoelectric phase  $\text{Pb}(\text{Zr}_{0.52}\text{Ti}_{0.48})\text{O}_3$  was prepared from the starting materials such as the analytical grade PbO,  $\text{ZrO}_2$ , and  $\text{TiO}_2$ . These constituents were weighed in stoichiometric proportion and mixed thoroughly. This mixture was ball-milled (RETSCH PM-200, Germany) in tungsten carbide bowls with tungsten carbide balls in ethyl alcohol medium for 20 h. The slurry was dried and the dried powders were loosely packed in the form of cakes and then calcined in closed alumina crucibles at 700 °C for 2 h. After calcination, these cakes were crushed and powdered. These powders were ball-milled once again under similar conditions in ethyl alcohol medium for 8 more hours to obtain a fine particle size. Both ferrite and ferroelectric green powders were sieved to obtain a uniform particle size. These fine green powders thus obtained were employed for the preparation of the composites. Employing these ferroelectric and ferrite green powders, ME particulate composites with a generic formula  $x\text{Ni}_{0.83}\text{Co}_{0.15}\text{Cu}_{0.02}\text{Fe}_{1.9}\text{O}_{4-\delta} + (1-x)\text{PbZr}_{0.52}\text{Ti}_{0.48}\text{O}_3$  ( $x=0, 0.1, 0.2, 0.3, 0.4, 0.5$  and  $0.6$  mole fraction) were prepared. These powders were ball-milled (RETSCH PM 200, Germany) using high

purity tungsten carbide balls in tungsten carbide bowls in ethyl alcohol for 3 h. The slurry obtained was dried and used for the preparation of samples of the desired shapes. The powders were mixed with 2% polyvinyl alcohol as binder and pressed into pellets of 1 cm diameter and 0.2 cm thickness, for magnetoelectric effect measurements and for internal friction properties, the powders were pressed into bars of square cross section  $(3.5 \times 10^{-3} \text{ m}) \times (3.5 \times 10^{-3} \text{ m})$  and  $2.05 \times 10^{-2} \text{ m}$  long using a hydraulic press. These bars and pellets were finally sintered at  $1130 \text{ }^\circ\text{C}$  for 2 h with a PZT atmosphere powder bed and were cooled to room temperature at the rate of  $80 \text{ }^\circ\text{C/h}$ . The composite resonator technique [11] was employed in the present work 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,  $\delta$ , the internal friction and the longitudinal modulus were evaluated using the standard relations.  $Q^{-1}$  and  $L$  data obtained in the present investigation are accurate to 5% and 2%, respectively. The  $x$ -cut quartz transducer used in the present investigation has a length of  $2.653 \times 10^{-2} \text{ m}$ , width of  $3.32 \times 10^{-3} \text{ m}$ , natural frequency 104.3 kHz and a mass of  $1.0316 \times 10^{-3} \text{ kg}$ . The electrode faces were painted with conducting silver paint (Du Pont). The composite oscillator was formed by cementing the quartz transducer to the specimen of identical cross-section. The adhesive used in this work was a paste containing one part by weight of calcium carbonate and five parts by weight of sodium meta silicate in a small quantity of distilled water. The composite system works satisfactorily after it has been kept for 24 h at room temperature. In order to study the effect of temperature on internal friction and longitudinal modulus of the multiferroic composite specimens, the composite resonator system with the sample holder was placed at the centre of a tubular electric furnace. The details of the furnace and temperature controller assembly were given elsewhere [12]. All the internal friction measurements were performed with strain amplitude of  $10^{-6}$ , after the specimen had attained thermal equilibrium. Electroded pellets were poled in silicone oil at  $150 \text{ }^\circ\text{C}$  by applying a DC field of 5 kV/cm for 2 h. This gives balanced poling processes to enable observations of any changes in the piezoelectric properties independent of poling levels. The piezoelectric coefficient ( $d_{33}$ ) was measured using a piezo  $d_{33}$  meter. The magnetoelectric effect

(ME) was measured in terms of the variation of the coefficient ( $dE/dH$ ) as a function of DC magnetic bias field. The coefficient was measured directly as the response of the sample to an AC magnetic input signal frequency of 80 kHz and 10e amplitude superimposed on the DC bias field and both the fields were arranged parallel to the sample axis.

### 3 Results and discussion

Figure 1(a), shows the XRD patterns of the particulate composites of  $x\text{Ni}_{0.83}\text{Co}_{0.15}\text{Cu}_{0.02}\text{Fe}_{1.9}\text{O}_{4-\delta} + (1-x)\text{PbZr}_{0.52}\text{Ti}_{0.48}\text{O}_3$  with  $x=0.1, 0.3$  and  $0.5$ , respectively. All the XRD peaks could be identified for both the perovskite and the spinel phases. All the patterns were almost similar to each other except for the intensity of the peaks. An examination of the figure shows that the diffraction patterns contain both ferroelectric and ferrite peaks. It can be seen from the figure that the

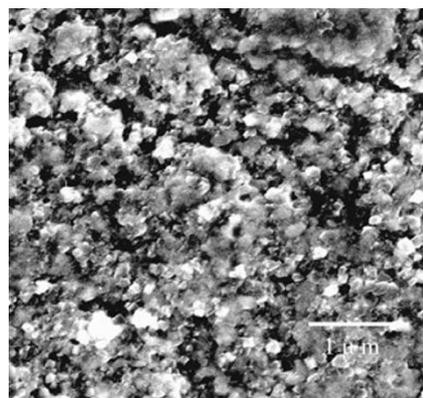
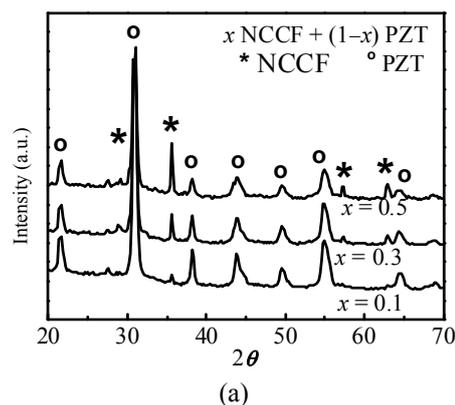


Fig. 1 (a) XRD patterns of the ME composites with  $x = 0.1, 0.3$  and  $0.5$ ; (b) SEM pattern of composite  $x = 0.5$ .

intensity of the ferrite peaks increases with the increase in the ferrite composition. However, the intensity of the peaks corresponding to the ferroelectric phase decreases with the increase in the ferrite concentration. The scanning electron microscopy pattern of composite  $x=0.5$  mole fraction of ferrite is shown in Fig. 1(b). It is evident from the figure that, two different phases distinctly; white region, PZT and dark particles are ferrite. As indicated by XRD patterns, SEM microstructures of the particulate composites did not show any third phase caused by chemical reaction or interdiffusion between two phases (NCCF/PZT).

The densities of the present particulate composites were studied by the Archimedes water immersion method was shown in Fig. 2. From Fig. 2, it reveals that, the pure ferroelectric material shows high density [13], as the ferromagnetic component increases in the composite the density of the present composites decreases.

### 3.1 Piezoelectric and magnetoelectric properties

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 3 shows the piezoelectric coefficient for particulate composites. From the figure PZT shows high piezocoefficient (350 pC/N) [13] and with the addition of 10% of ferrite resulted in drastic fall in piezocoefficient (50 pC/N) and further increase in ferrite content shows nominal variation in  $d_{33}$  (Table 1). Its reason is that the resistance of the ferrite is much smaller than of the PZT. When a composite contains too much ferrite, it can not be poled at a high voltage for its low resistance and can not get good piezoelectric effect. 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

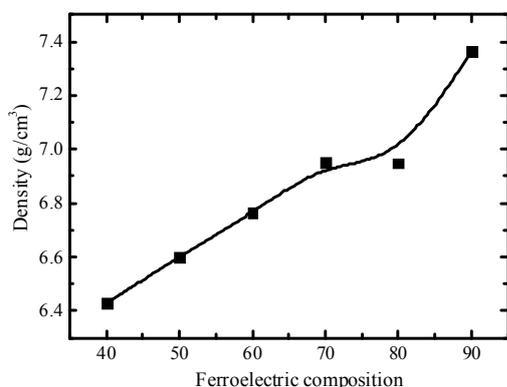


Fig. 2 Dependence of density on mole fraction of ferroelectric.

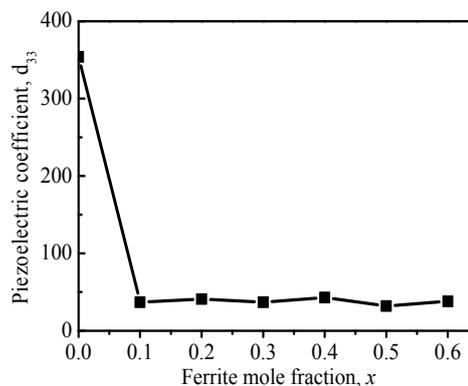


Fig. 3 Piezoelectric coefficient of ME particulate composites.

**Table 1** Data on density, piezoelectric coefficient, magnetoelectric voltage, phase transition temperatures on longitudinal modulus and internal friction studies

Composition	Density $\rho$ (g/cm <sup>3</sup> )	$d_{33}$ (pC/N)	$dE/dH$ (mV/Oe)	Longitudinal modulus		Internal friction	
				$\theta_E$ (°C)	$\theta_M$ (°C)	$\theta_E$ (°C)	$\theta_M$ (°C)
Pure PZT	7.6	255	–	390	–	390	–
$x = 0.1$	7.4	57	1360	392	236	392	236
$x = 0.2$	6.9	44	1360	394	170	394	172
$x = 0.3$	6.9	38	1446	388	120	388	120
$x = 0.4$	6.7	37	1982	396	98	398	100
$x = 0.5$	6.6	34	3151	398	145	398	148
$x = 0.6$	6.4	32	–	404	264	404	264

as possible. If the resistivity of magnetostrictive is low, the electric poling becomes very difficult due to leakage current. Also, the leakage current 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.

The variation of  $dE/dH$  of the ME particulate composites as a function of applied magnetic field (80 kHz)  $H$  bias is shown in Fig. 4. From Fig. 4, we can observe that the ME coefficient values increases with increase in ferrite content. Stress transfer through the interface between these phases achieves the magnetoelectric coupling. This initial rise in ME output is attributed to the enhancement in elastic interaction and was confirmed by the hysteresis measurements [14]. 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 [15]. 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 [16]. Hence the strain produced in the ferrite phase would produce a constant electric field in the piezoelectric phase. From Fig. 4, the ME voltage

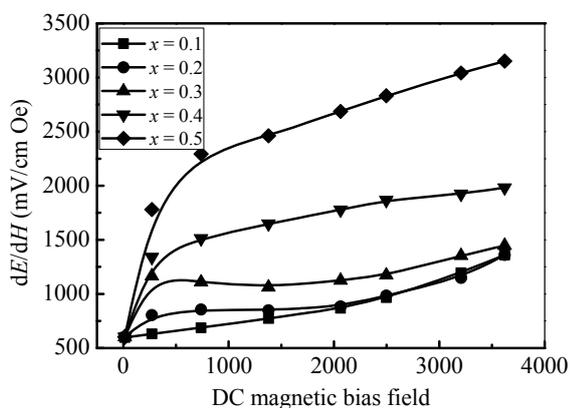


Fig. 4 ME voltage coefficient as a function of applied DC magnetic bias field for the composites  $(1-x)$  PZT+ $x$  NCCF.

coefficient  $dE/dH$  increases with DC magnetic field in the range 0-0.05 T, and saturated after 0.05 T for a samples with  $x = 0.1, 0.2, 0.3$  and  $0.4$ . Whereas, the  $0.5$  sample showed the higher ME output voltage. The maximum ME voltage coefficient of  $3.15$  V/cm Oe was observed in the composite containing  $0.5$ NCCF+ $0.5$  PZT. As is well known that ME effect of the composites depends on the piezoelectricity of the ferroelectric phase and magnetostriction of the ferrite phase. ME coupling mainly arises from the magnetic-mechanical-electric transform through the stress-mediated transfer in the interface. The dynamic magnetoelastic coupling which is caused by the magnetostriction of the ferrite phase is involved in the ME effect. 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 DC (Table 1) bias and saturated around 2 kOe. Ryu *et al.* [17], Cai *et al.* [18] also observed this type of behavior in PZT+Terfenol-D, PZT+Terfenol-D+PZT laminated composites respectively. Srinivas *et al.* [19] evaluated the electromechanical coupling coefficients in 50% PZT+50%  $\text{CoFe}_2\text{O}_4$  composites. As shown in the microstructure [14], the distribution of ferrite particles become more uniform and less connected when the amount of ferrite was low. The effective ME voltage coefficient of the composites can be strongly influenced by the connectivity, the volume fraction and aspect ratio of particles. The reason for the large ME coefficient of the composite may be explained as follows, Co and Cu with John-Teller effect can induce more mechanical coupling and PZT has superior piezoelectric properties. A higher content of ferrite will induce the accumulated charge leaking through the composite. In present ferrite the presence of  $\text{Ni}^{2+}/\text{Ni}^{3+}$ ,  $\text{Co}^{2+}/\text{Co}^{3+}$ , and  $\text{Cu}^{1+}/\text{Cu}^{2+}$  ions give rise to  $p$ -type carriers and their displacement in the external electric field direction contributes to the net polarization in additional  $n$ -type carriers. However, the  $p$ -type carrier contribution is smaller than that from the electronic exchange between ions and opposite in sign.

## 3.2 Mechanical properties

### 3.2.1 Longitudinal modulus measurements

The temperature variation of the longitudinal modulus,  $L$ , and the internal friction, ( $Q^{-1}$ ), for various samples of  $x\text{Ni}_{0.83}\text{Co}_{0.15}\text{Cu}_{0.02}\text{Fe}_{1.9}\text{O}_{4-\delta} + (1-x)\text{PbZr}_{0.52}\text{Ti}_{0.48}\text{O}_3$

( $x=0, 0.1, 0.2, 0.3, 0.4, 0.5$  and  $0.6$ ) are shown in Fig. 5 and Fig. 6, respectively. An examination of the data presented in Fig. 5 shows that there is a systematic variation of the longitudinal modulus as a function of temperature. In pure PZT (Fig. 5(a)), the ferroelectric – paraelectric phase transition at  $390\text{ }^\circ\text{C}$  can be very clearly seen as a sharp fall in the modulus at the ferroelectric Curie transition temperature ( $\theta_E$ ) [11]. This type of sharp kink in the modulus was reported by Dai *et al.* [5], Jamenez and Vincent [6] and Bourim and Tanaka [7] in pure PZT. In addition to the kink at  $390\text{ }^\circ\text{C}$ , a broad minimum can be noticed at  $230\text{ }^\circ\text{C}$ . A similar type of behaviour was also noticed by Dai *et al.* [5] in pure PZT. This was attributed to the movement of domain walls and point defects in the sample.

An examination of Fig. 5(b), for the ME particulate composite with  $x=0.1$ , reveals that the temperature variation of the longitudinal modulus ( $L$ ) shows two sharp minima at  $230\text{ }^\circ\text{C}$  and  $380\text{ }^\circ\text{C}$ . This temperature ( $380\text{ }^\circ\text{C}$ ) coincides with the ferroelectric to paraelectric phase transition of the ferroelectric phase (PZT) in the composite which is characterized by  $\theta_E$ . However the other minimum at  $230\text{ }^\circ\text{C}$  could be observed with the ferromagnetic-paramagnetic phase transition of the ferromagnetic phase in the composite which is characterized by  $\theta_M$ . Figs. 5(c)-(g) show the temperature variation of the longitudinal modulus ( $L$ ) in ME particulate composites with  $x=0.2, 0.3, 0.4, 0.5$  and  $0.6$ , respectively. These figures show two sharp minima “A” and “B” in each case, unambiguously

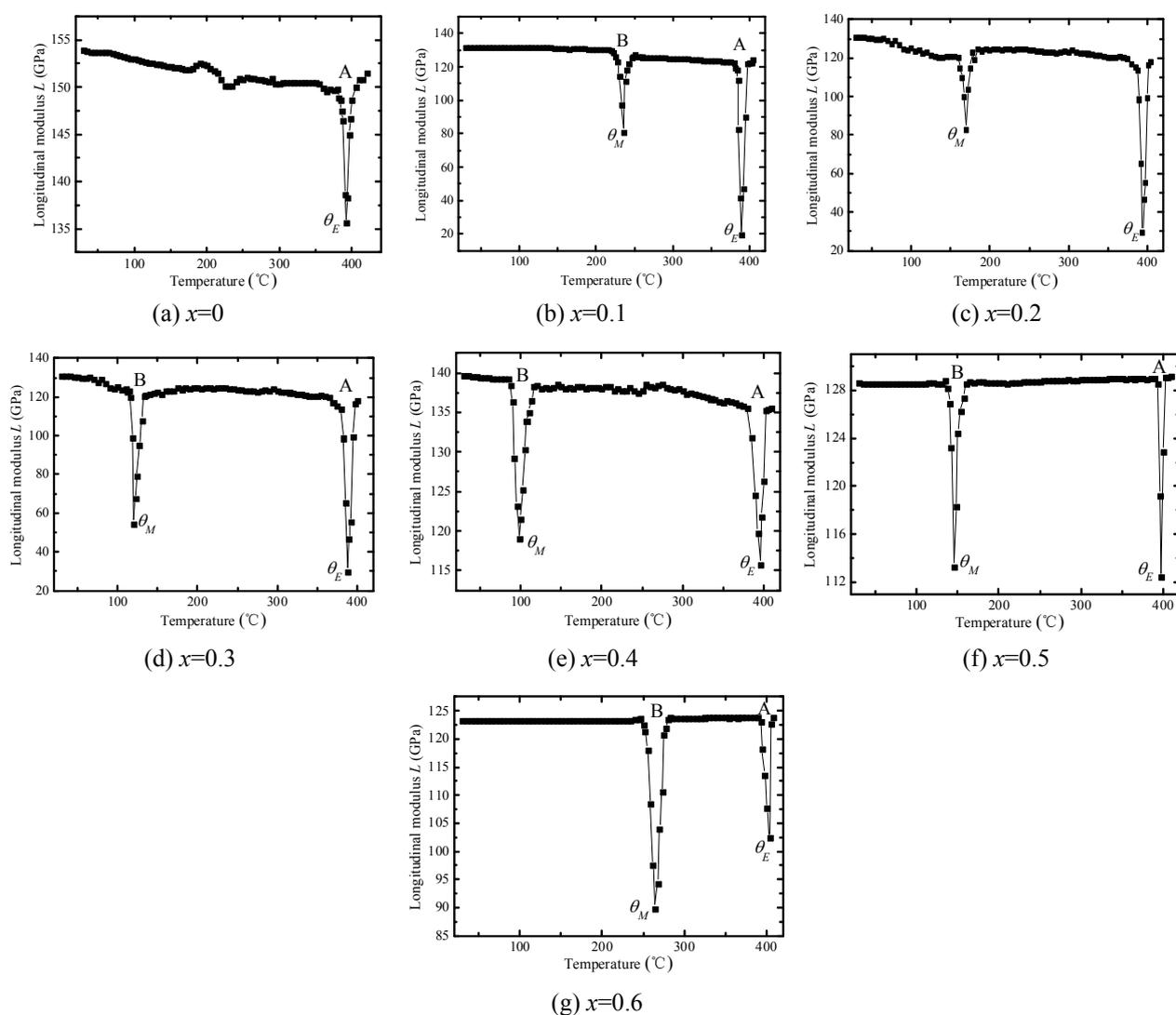


Fig. 5 (a) Temperature variation of longitudinal modulus,  $L$  of pure PZT; (b) Temperature variation of longitudinal modulus,  $L$  of ME composite with  $x=0.1$ ; (c)-(g) Temperature variation of longitudinal modulus,  $L$  of ME composites with (c)  $x=0.2$ , (d)  $x=0.3$ , (e)  $x=0.4$ , (f)  $x=0.5$  and (g)  $x=0.6$ .

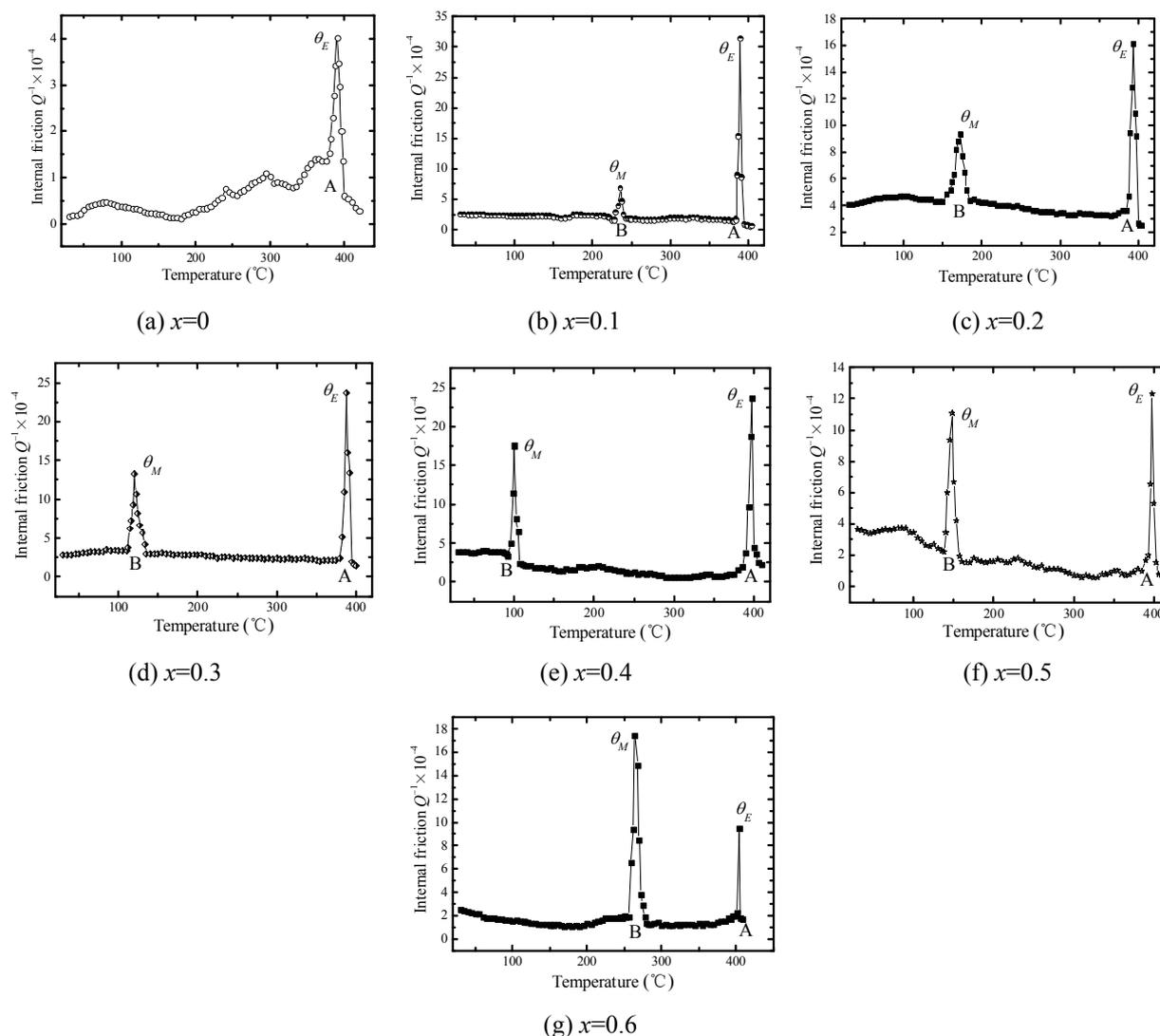


Fig. 6 (a) Temperature variation of internal friction ( $Q^{-1}$ ) of pure PZT; (b) – (g) Temperature variation of internal friction loss ( $Q^{-1}$ ) of ME composites with (b)  $x = 0.1$ , (c)  $x = 0.2$ , (d)  $x = 0.3$ , (e)  $x = 0.4$ , (f)  $x = 0.5$  and (g)  $x = 0.6$ .

indicating two phase transitions. The minimum “A” obtained around 390 °C coincides with the ferroelectric – paraelectric phase transition at the ferroelectric Curie transition temperature [20]. However, the position of second minimum “B” was obtained around 200 °C in the composites studied in this work. This type of sharp fall in modulus and the sharp peak in internal friction was reported by Koster and Bangert [21] in Hume-Rothery alloys in the neighbourhood of solidus temperature. In order to confirm this phase transition, the ferromagnetic Curie transition temperature ( $\theta_M$ ) was studied in these composites using the technique employed by Loria and Sinha with a few modifications [22]. The minimum “B” obtained in the temperature variation of longitudinal modulus plots in each

composite coincides with the corresponding ferromagnetic-paramagnetic phase transition temperature ( $\theta_M$ ) of that ME composite (Table 1). The magnitude of longitudinal modulus at  $\theta_M$  and  $\theta_E$  was observed to be same for the composite with  $x = 0.5$ .

### 3.2.2 Internal friction measurements

Figure 6(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 ( $\theta_E$ ) 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 [11]. As explained earlier,

Jamenez and Vincent [6] and Bourim and Tanaka [7] have attributed the minor peak to the domain wall motion and point defects in the sample. Figure 6(b) shows the temperature variation of the internal friction in the ME particulate composite with  $x=0.1, 0.2, 0.3, 0.4, 0.5$  and  $0.6$ , respectively, (Figs. 6(b)-(g)) we can find two sharp peaks “A” and “B” at two different temperatures. The sharp peak “A” obtained around  $390\text{ }^\circ\text{C}$  coincides with the ferroelectric – paraelectric phase transition temperature characterized by  $\theta_E$  [20]. The sharp peak “B” obtained in the temperature variation of anelastic behaviour of these multiferroic particulate composites (Figs. 6(b)-(g)) coincides with the ferromagnetic Curie transition temperature ( $\theta_M$ ) characteristic of the magnetic component of the ME composites. From Fig. 5 and Fig. 6, it can be noticed that, the height of the peak increases with the increase in ferrite content in the magnetoferroelectric particulate composites. As in the case of longitudinal modulus, the magnitude of internal friction was found to be same at  $\theta_M$  and  $\theta_E$  for the composite with  $x=0.5$  (Table 1). These types of observations are made by Dai *et al.* [23] in  $\text{CuFe}_2\text{O}_4 + \text{PbZr}_{0.53}\text{Ti}_{0.47}\text{O}_3$  composites at lower frequencies.

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 [24]. The Curie transition temperature,  $\theta_M$ , of pure NCCF was found to be  $520\text{ }^\circ\text{C}$ . The variation of the ferromagnetic-paramagnetic phase transition temperature of the ferrite component in the composites with increasing mole fraction of the ferrite component is shown in Fig. 7. It can be noticed that the addition of 10% of ferrite to ferroelectric resulted in a  $240\text{ }^\circ\text{C}$  fall in  $\theta_M$  and with the further increase in the ferrite content the  $\theta_M$  variation is found to be very nominal. The second peak “B” in the ME composite with  $x=0.1$  is not perceptible due to low ferrite content present in the composite. 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)

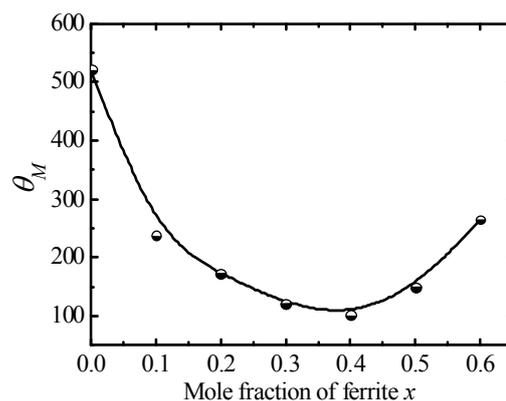


Fig. 7 Variation of  $\theta_M$  with mole fraction of ferrite.

and ferrimagnetic (NCCF) phases. In the temperature range studied, i.e.,  $30\text{--}420\text{ }^\circ\text{C}$ , the pure ferroelectric component,  $\text{PbZr}_{0.52}\text{Ti}_{0.48}\text{O}_3$ , transforms from ferroelectric to the paraelectric phase at  $390\text{ }^\circ\text{C}$ . Hence, there should be anomalous behaviour in both elastic and anelastic properties near the phase transition, because these are lattice-related properties. The peaks observed in Figs. 6(a)-(g) also confirm this phase transition  $\theta_E$ . Similarly an examination of Fig. 5 and Fig. 6 reveals that there is another transition due to ferromagnetic to paramagnetic transformation at the ferrimagnetic Curie transition temperature  $\theta_M$ . It appears that in the lowering of  $\theta_M$  with the ferrite content in these composites indicates that the presence of the ferroelectric perovskite phase affects the ferrimagnetic spinel structure appreciably. However, the ferroelectric Curie transition temperature ( $\theta_E$ ) is not much affected by the presence of spinel ferrite phase in the composites, because the shift in  $\theta_E$  is not appreciable.

In principle, the ME composites should show two Curie transition temperatures [25], namely, one due to ferromagnetic-paramagnetic phase transition ( $\theta_M$ ) and the other due to ferroelectric – paraelectric phase transition ( $\theta_E$ ). In our previous studies on the dielectric behavior of these particulate composites [12], we could identify the ferroelectric – paraelectric phase transition only. In this work on the temperature variation of elastic and anelastic behaviour of the multiferroic particulate composites both  $\theta_E$  and  $\theta_M$  could be identified unambiguously since these properties are lattice related properties. Generally speaking, for the composite structure, the ME effect originates from a product coupling between the magnetostrictive effect from the magnetostrictive phase and piezoelectric effect from the piezoelectric phase in the particulate

composites. So, the ME effect is sensitive with the phase structure and phase distribution. As mentioned above, the internal friction technique can be used to detect the phase distribution, interaction, defect state, phase transitions and so on. Both ME property and internal friction technique are structural sensitive. There must be some relation between them, thus we are trying to establish a linkage between the ME effect and the internal friction. In order to study the ferroelectric and ferromagnetic domain interaction in these composites, the work on the effect of the magnetic field on these phase transitions is in progress.

#### 4 Conclusions

The studies on the temperature variation of elastic and anelastic behaviour of ME particulate composites containing piezoelectric (PZT) and piezomagnetic (NCCF) phases throw considerable light on the phase transitions present in these composites, since they are lattice related properties. The XRD analysis of the particulate ME composites studied in this work reveals that the composites contain a ferroelectric component with perovskite structure and a ferrite component with spinal structure. We obtained the highest magnetoelectric voltage coefficient at 1 kHz of 3.15 V/cm Oe at room temperature from the sample 0.5 NCCF+0.5 PZT. The temperature variation of the longitudinal modulus ( $L$ ) study shows two sharp minima corresponding to ferroelectric and ferrimagnetic Curie transition temperatures  $\theta_E$  and  $\theta_M$ , respectively, in all the composites. The temperature variation the internal friction ( $Q^{-1}$ ) exhibits two peaks corresponding to the two minima obtained in the temperature variation of longitudinal modulus ( $L$ ). There is no noticeable effect of ferrite phase on the ferroelectric phase. However, the effect the ferroelectric phase on the ferrite phase is quite noticeable.

#### References

- [1] Suchtelen V. Magnetoelectric effect in composites of piezoelectric and piezomagnetic phases. *Philipp Res Rep* 1972, **22**: 28-37.
- [2] Astrov DN. Magnetoelectric effect in chromium oxide. *Sov Phys JETP* 1961, **13**: 729-733.
- [3] Newnham RE. Composite electroceramics. *Ferroelectrics* 1986, **68**: 1-31.
- [4] Suryanarayana SV. Magnetoelectric interaction phenomena in materials. *Bull Mater Sci* 1994, **17**: 1259-1270.
- [5] Dai YR, Bao P, Shen HM, *et al.* Internal friction study on low-temperature phase transitions in lead zirconate titanate ferroelectric ceramics. *Appl Phys Lett* 2003, **82**: 109-111.
- [6] Jamenez B, Vincent JM. The low-frequency young modulus and internal friction in Pb-Ca and Pb-Zr titanate ceramics. *J Phy D Appl Phy* 1998, **31**: 130-136.
- [7] Bourim EM, Tanaka H. Domain wall motion effect on the anelastic behavior in lead zirconate titanate piezoelectric ceramics. *J App Phy* 2002, **91**: 6662-6669.
- [8] Ramamanohar Reddy N, Rajagopal E, Siva Kumar KV, *et al.* Effect of temperature on the elastic and anelastic behaviour of magneto-ferroelectric composites  $\text{Ba}_{0.8}\text{Pb}_{0.2}\text{TiO}_3+\text{Ni}_{0.93}\text{Co}_{0.02}\text{Mn}_{0.05}\text{Fe}_{1.95}\text{O}_{4-\delta}$  in the ferroelectric rich region. *J Electroceram* 2003, **11**: 167-172.
- [9] Ramamanohar Reddy N, Venkata Ramana M, Krishnaveni K, *et al.* Dielectric, elastic, anelastic and conductivity behaviour of ferroelectromagnetic composites,  $\text{Ni}_{0.5}\text{Zn}_{0.5}\text{Fe}_{1.95}\text{O}_{4-\delta}+\text{Ba}_{0.8}\text{Pb}_{0.2}\text{TiO}_3$ . *Bull Mater Sci* 2007, **30**: 357-363.
- [10] Kaczkowski Z. Piezomagnetic properties of the Nickel Based Ferrites. In: *Proc 5th Conf on Ferrites*. Bombay, India, 1989, **1**: 279-286.
- [11] Venkata Ramana M, Sreenivasulu G, Ramamanohar Reddy N, *et al.* Internal friction and elastic modulus behaviour of multiferroic  $\text{PZ}_{0.52}\text{Ti}_{0.48}\text{O}_3+\text{Ni}_{0.93}\text{Co}_{0.02}\text{Mn}_{0.05}\text{Fe}_{1.95}\text{O}_{4-\delta}$  particulate composites. *J Phys D: Appl Phys* 2007, **40**: 7565-7571.
- [12] Venkata Ramana M. Studies on Certain Magnetoferroelectric composites. Ph.D. Thesis. Anantapur (India): Sri Krishnadevaraya University, 2007.
- [13] Jaffe B, Cook WJ, Jaffe H. *Piezoelectric Ceramics*. London (UK): Academic Press, 1971.
- [14] Venkata Ramana M, Sreenivasulu G, Ramamanohar Reddy N, *et al.* Enhanced magnetoelectric voltage in multiferroic particulate  $\text{Ni}_{0.83}\text{Co}_{0.15}\text{Cu}_{0.02}\text{Fe}_{1.9}\text{O}_{4-\delta}/\text{PbZr}_{0.52}\text{Ti}_{0.48}\text{O}_3$  composites – dielectric, piezoelectric and magnetic properties. *Current Applied Physics* 2009, **9**: 1134-1139.
- [15] Lupeiko TG, Lopatin IB, Kozyrev IV, *et al.* Electrophysical and magnetoelectric properties of ceramic materials. *Inorg Mater* 1992, **28**: 481.
- [16] Hanumaiah A, Bhimasankaram T, Suryanarayana SV. Dielectric behavior and magnetoelectric effect in cobalt ferrite – barium titanate composites. *Bull*

- Mater Sci* 1994, **17**: 405-409.
- [17] Ryu J, Carzo AV, Uchino K, *et al.* Magnetolectric properties in piezoelectric and magnetostrictive laminate composites. *Jpn J App Phys* 2001, **40**: 4948-4951.
- [18] Cai N, Zhai J, Nan CW, *et al.* Dielectric, ferroelectric, magnetic, and magnetolectric properties of multiferroic laminated composites. *Phys Rev B* 2003, **68**: 224 103-224 109.
- [19] Srinivas K, Prasad G, Bhimasankaram T, *et al.* Electromechanical coefficients of magnetolectric PZT - CoFe<sub>2</sub>O<sub>4</sub> composite. *Mod Phys Lett B* 2002, **14**: 663-674.
- [20] Chaisan W, Yimmirun R, Ananta S, *et al.* Phase development and dielectric properties of (1-x) PbZr<sub>0.52</sub>Ti<sub>0.48</sub>O<sub>3</sub>-xBaTiO<sub>3</sub> ceramics. *Mater Sci Eng B* 2006, **132**: 300-306.
- [21] Koster W, Bangert L. *Z Metallk* 1951, **42**: 391.
- [22] Loria KK, Sinha APB. *Indian J Pure Appl Phys* 1963, **1**: 115-165.
- [23] Dai YR, Bao P, Zhu J S, *et al.* Internal friction study on CuFe<sub>2</sub>O<sub>4</sub>/PbZr<sub>0.53</sub>Ti<sub>0.47</sub>O<sub>3</sub> composites. *J App Phy* 2004, **96**: 5687-5690.
- [24] Liu Z, Chen X, Shen H, *et al.* Ferroelectric domain wall motion and related internal friction in TGS crystal. *Phys Status Solidi* 1989, **116**: K199-K203.
- [25] Smolenskii GA, Chupis IE. *Problems in Solid State Physics*. Moscow: Mir Publishers, 1984: 81.