Dielectric, elastic, anelastic and conductivity behaviour of ferroelectromagnetic composites, $Ni_{0.5}Zn_{0.5}Fe_{1.95}O_{4-\delta} + Ba_{0.8}Pb_{0.2}TiO_3$

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Abstract. Ferroelectromagnetic composites with compositions, X $Ni_{0.5}Zn_{0.5}Fe_{1.95}O_{4-\delta} + (1 − X)$ $Ba_{0.8}Pb_{0.2}TiO_3$, in which X varies as 0, 0·005, 0·010, 0·015, 0·020, 0·040, 0·060, 0·080 and 1 in mole %, were prepared by conventional ceramic double sintering process. The presence of two phases was confirmed by X-ray diffraction. The temperature variation of dielectric constant, ε', dielectric loss, $\tan \delta$, d.c. conductivity, a.c. conductivity, elastic and anelastic behaviour of ferrite–ferroelectric composites were studied in the temperature range 30–350°C. The a.c. conductivity measurements on these composites in the frequency range 100 Hz–1 MHz at room temperature reveal that the conduction mechanism is due to small polaron hopping. The dielectric and elastic data were discussed in the light of phase transitions.

Keywords. Ferroelectromagnetic; dielectric properties; elastic behaviour; internal friction loss; electrical conductivity; polaron hopping.

1. Introduction

Magnetoelectric (ME) effect is the behaviour of a material to generate electric polarization when it is subjected to magnetic field or to generate magnetization when it is placed in electric field. Single phase materials, in which magnetic and ferroelectric ordering exist simultaneously, suffer from the drawback that the ME effect is considerably weak even at low temperatures, limiting their applicability in practical devices (Smolenskii and Chupis 1984). The alternatives are ferroelectromagnetic composites that exhibit fairly large magnitudes of ME voltage coefficient.

Ferroelectromagnetic composite materials consisting of piezoelectric and piezomagnetic phases show ME effect (van Suchtelen 1972). These are of great interest because they can be exploited as wave guides, frequency doublers, phase inverters, microwave field detectors, Hall sensors etc (Wood and Austin 1974; Bracke and van Vliet 1981; Ryu et al 2001a). These composites employ the product property of the materials. Till to date, ME effect on various composites such as $NiCoMnFe_2O_4$–$BaTiO_3$ (Boomgaard and Born 1978), $CoFe_2O_4$–$BaTiO_3$ (Boomgaard et al 1974), $NiFe_2O_4$–$BaTiO_3$ (Gelyasin et al 1988), $LiFe_5O_8$–$BaTiO_3$ (Suryanarayana 1994), $CuFe_{1.6}Cr_{0.4}O_4$–$BaTiO_3$ (Patankar et al 2000), $NiCoFe_2O_4$–$BaTiO_3$ (Lupeiko et al 1992), $CoFe_2O_4$–PZT (Laletin 1991), $NiFe_2O_4$–PZT (Laletin

1991), $NiCoFe_2O_4$–PZT (Lupeiko et al 1991), $NiFe_2O_4$–PBZT (Laletin 1992), $CoFe_2O_4$–PBZT (Laletin 1992), $NiZnFe_2O_4$–PZT (Bunget and Reatchi 1981) and $CuFe_2O_4$–$Ba_{0.8}Pb_{0.2}TiO_3$ (Patankar et al 2001), have been reported. Recent studies on the magnetoelectric effect in three composites containing PZT samples (viz. APC 840, APC 841 and PZT–5A) with Terfenol-D showed fairly high ME voltage coefficient (Ryu et al 2001b). In $\langle 001 \rangle$ oriented single crystalline layer laminated with Terfenol-D, sandwiched transducer enhanced ME effect was reported (Ryu et al 2002). Recently, a template method of preparation of ferromagnetic and ferroelectric nanocomposites containing colossal magneto-resistance materials, i.e. $La_{0.7}Ca_{0.3}MnO_3$–$BaTiO_3$, $La_{0.7}Ca_{0.3}MnO_3$–PZT and $La_{0.7}Ca_{0.3}MnO_3$–$Bi_4Ti_3O_{12}$, was reported (Kim et al 2003).

The data available in the literature on investigation of properties like elastic, anelastic, piezoelectric and magnetostrictive nature on these ferroelectromagnetic composites are scanty. In view of this, in the present work, ferroelectromagnetic composites containing $Ba_{0.8}Pb_{0.2}TiO_3$ ($T_c = 225°C$) as ferroelectric component and highly magnetostrictive ferrite generally used for high power ultrasonic applications viz. $Ni_{0.5}Zn_{0.5}Fe_{1.95}O_{4-\delta}$ ($T_c = 290°C$) (Golyamina 1969) as piezomagnetic component, were chosen. This has been done with a view to identify both ferroelectric and ferrimagnetic Curie temperatures simultaneously. Further, the temperature variation of dielectric constant, ε', dielectric loss ($\tan \delta$), d.c. conductivity, a.c. conductivity, elastic and anelastic behaviour of X $Ni_{0.5}Zn_{0.5}Fe_{1.95}O_{4-\delta} + (1 − X)$

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$Ba_{0.8}Pb_{0.2}TiO_3$ (with $X = 0$, 0·005, 0·010, 0·015, 0·020, 0·040, 0·060, 0·080 and 1) ferrite–ferroelectric composites, has been studied and the results are reported. The results are discussed in the light of conduction mechanism and structural phase transitions in these composites.

2. Experimental

The ferrite phase ($Ni_{0.5}Zn_{0.5}Fe_{1.95}O_{4-\delta}$) was prepared by using the analytical grade NiO, ZnO and Fe_2O_3. Stoichiometric amounts of these oxides were weighed and mixed thoroughly. These constituents were ball milled (Retsch PM-200, Germany) in acetone medium for 10 h, and calcined in a closed alumina crucible at 800°C for 2 h. After calcination, powders were ball-milled once again in acetone medium for 4 h and then dried.

The ferroelectric phase, BPT ($Ba_{0.8}Pb_{0.2}TiO_3$), was prepared by using the analytical grade $BaCO_3$, PbO and TiO_2 in stoichiometric proportion. These constituents were weighed and mixed thoroughly. The ball-milling in acetone medium was carried out for 10 h, and then calcined in a closed alumina crucible at 700°C for 2 h. After calcination, the powders were ball-milled once again in acetone medium and then dried. Both ferrite and ferroelectric green powders were sieved to obtain uniform particle size. The fine green powders thus obtained were employed for the preparation of the composites.

Polycrystalline ferrite–ferroelectric composites with generic formula, X $Ni_{0.5}Zn_{0.5}Fe_{1.95}O_{4-\delta} + (1-X)$ $Ba_{0.8}Pb_{0.2}TiO_3$ (with $X = 0$, 0·005, 0·010, 0·015, 0·020, 0·040, 0·060, 0·080 and 1), were prepared by mixing them with 2% polyvinyl alcohol as binder and pressed into tablet shaped pellets of 1 cm diameter and 0·2 cm thickness, for electrical conductivity and dielectric measurements. For internal friction loss and elastic modulus measurements, the powders were pressed into bars of 0·35 × 0·35 × 2 cm using a hydraulic press. These bars and pellets were finally sintered at 1250°C for 2 h in a programmable furnace, under PbO and ZnO protected atmosphere and were cooled to room temperature at the rate of 80°C/h. The XRD patterns of the sample were obtained using a PW 1730 X-ray diffractometer with CuK_α 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 30–350°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 a.c. conductivity was evaluated from the dielectric data. The d.c. conductivity of these samples was measured in the temperature range 150–300°C using a two-probe method with a guard ring arrangement employing a million megohm-meter (Model RM 160 MK III

A, BPL, India) with an applied voltage of 5 V per mm under ambient atmosphere.

The composite resonator technique (Schwartz 1977) with a few modifications (Komalamba *et al* 1997) was employed in the present work for the measurement of internal friction loss (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 loss (Q^{-1}) and the longitudinal modulus (L) were evaluated using the standard relations (Marx 1951; Schwartz 1977; Ramamanohar Reddy *et al* 2003). 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, 142·387 kHz and mass of 0·6628 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 loss 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. The details of the furnace and temperature controller assembly were described elsewhere (Komalamba *et al* 1997; Ramamanohar Reddy *et al* 2003). All the internal friction loss measurements were performed with a strain amplitude of 10^{-6}, after the specimen had attained thermal equilibrium.

3. Results and discussion

Figures 1a–d depict X-ray diffractograms of pure ferroelectric, two typical composites with $X = 0.020$ and 0·080 and pure ferrite, respectively. From the XRD patterns of the composites it is clear that both $Ba_{0.8}Pb_{0.2}TiO_3$ and $Ni_{0.5}Zn_{0.5}Fe_{1.95}O_{4-\delta}$ phases are present. All the peaks could be identified for both perovskite and spinel phases. It can be noticed from figures 1b and c that the intensity of peaks corresponding to ferrite phase are very low due to the low concentration of ferrite in the composites. Ferroelectric phase has a tetragonal structure with lattice constants, $a = 3.9826$ Å and $c = 4.0424$ Å and pure ferrite has a cubic spinel structure with lattice constant, $a = 8.4181$ Å.

The compositional variation of d.c. conductivity, $\sigma_{d.c.}$, dielectric constant, ε', and dielectric loss, tan δ, at room temperature is shown in figure 2. At low concentration of ferrite, the dielectric constant and d.c. conductivity increased while tan δ decreased with increasing X up to ~0·01 and thereafter all the parameters gradually de-
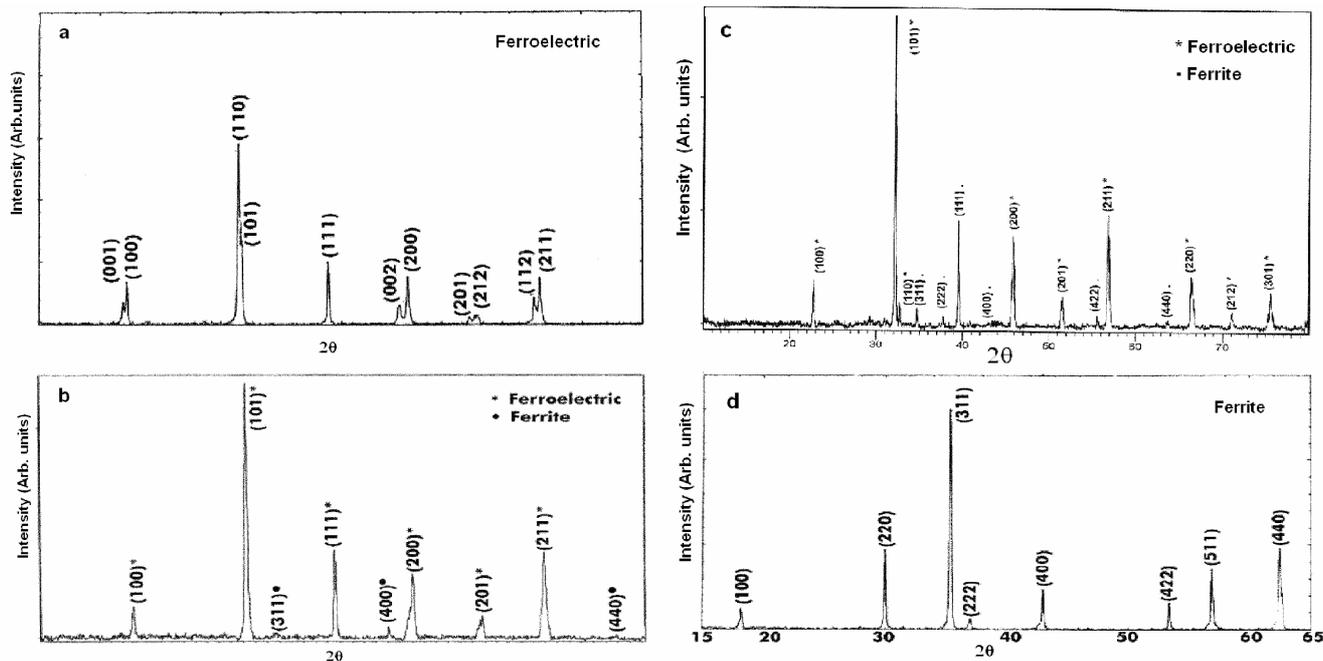
Figure 1. X-ray diffractograms of **a**. pure $Ba_{0.8}Pb_{0.2}TiO_3$, **b**. $X = 0.020$, **c**. $X = 0.080$ and **d**. pure $Ni_{0.5}Zn_{0.5}Fe_{1.95}O_{4-\delta}$
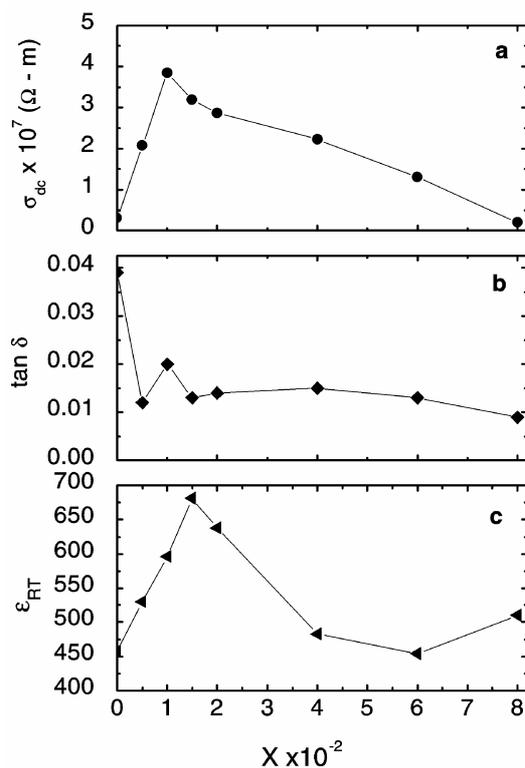

Figure 2. Variation of **a**. d.c. conductivity, **b**. dielectric loss and **c**. dielectric constant of magnetoferroelectric composites with composition at room temperature.

creased with increasing X. A similar type of anomalous behaviour in dielectric measurements on barium titanate and nickel ferrite composites at low concentrations of

nickel ferrite was reported (Gelyasin and Laletin 1988). They attributed this to some sort of eutectic formation at low concentrations of nickel ferrite in the composite.

The temperature variation of d.c. conductivity is shown in figure 3 and the values of activation energies ($\Delta E_{d.c.}$) calculated are given in table 1. These plots are similar to those of doped ferroelectric materials (Prakash *et al* 1994). The plots indicate that the conductivity increases with increase in temperature suggesting a semiconductor behaviour. The temperature variation of conductivity in these composites studied in the present work conform to the Arrhenius law

$$\sigma = \sigma_0 \exp(-\Delta E_{d.c.}/kT), \tag{1}$$

where $\Delta E_{d.c.}$ is the activation energy required for the hopping process. The magnitudes of the activation energies (table 1) are greater than 0.2 eV for the samples under study. This suggests that the conduction mechanism is due to hopping (Lalitha Sirdeshmukh *et al* 1998). Thermoelectric power measurements on similar composites (Patankar *et al* 2000) reveal that the conduction is due to polaron hopping.

To study the mechanism of hopping, a.c. conductivity was measured at room temperature in the frequency range 100 Hz–1 MHz. The conductivity is observed to increase with frequency for all the composites studied in this work. In figure 4, the variation of $\log(\sigma_\omega - \sigma_{d.c.})$ with $\log \omega^2$ is shown. In large polaron model, a.c. conductivity decreases with frequency, while in small polaron hopping mechanism, the conductivity increases with frequency (Austin and Mott 1969). An examination of figure 4 indi-

Table 1. The ε'_{RT}, ε'_{max}, T_c, s, γ, $\sigma_{d.c.RT}$ and $\Delta E_{d.c.}$ of the composites with composition of ferrite.

Composition, x	100 kHz data					$\sigma_{d.c.} \times 10^{-7}$ (Ω-m)	
	ε'_{RT}	ε'_{max}	T_c (°C)	s	γ	$\sigma_{d.c.RT}$	$\Delta E_{d.c.}$ (eV)
0·000	458	4010	225	0·975	1·386	0·30	0·375
0·005	553	1447	200	0·994	1·353	2·08	0·315
0·010	534	1655	180	0·995	1·467	3·85	0·290
0·015	681	1958	170	0·995	1·726	2·89	0·428
0·020	638	1402	160	0·808	1·772	2·87	0·363
0·040	466	805	145	0·994	1·738	2·86	0·329
0·060	454	748	135	0·989	1·733	1·50	0·334
0·080	575	863	125	0·980	1·762	0·20	0·365
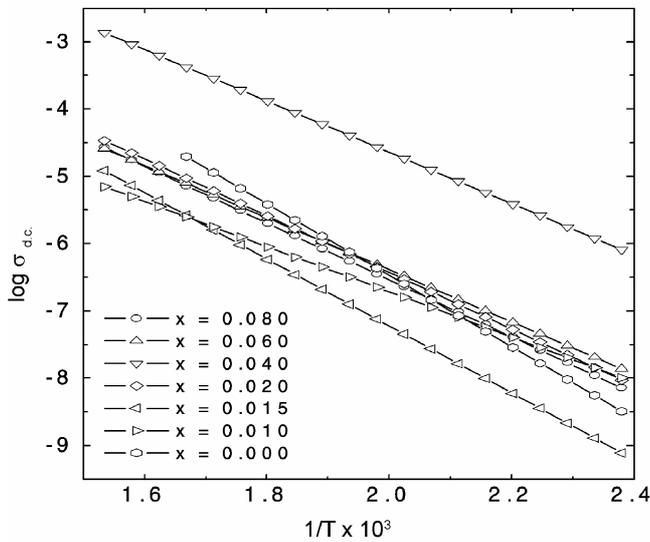
Figure 3. Variation of $\log \sigma_{d.c.}$ with $10^3/T$ in the composites.
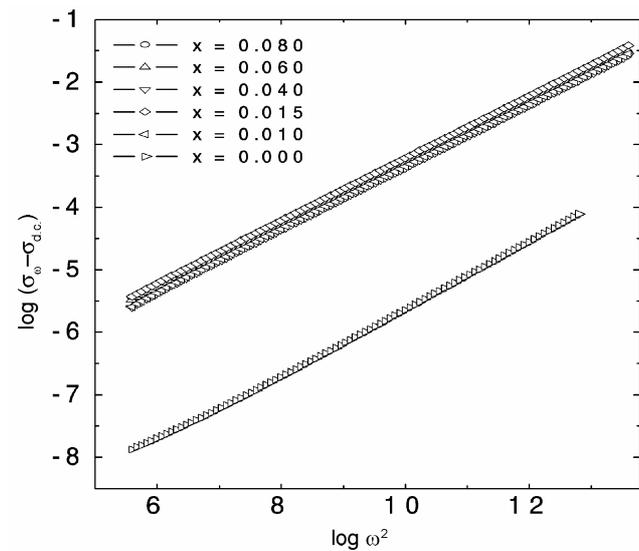
Figure 4. Variation of $\log (\sigma_\omega - \sigma_{d.c.})$ vs $\log \omega^2$ in the composites.

cates a perfect linear behaviour between $\log (\sigma_\omega - \sigma_{d.c.})$ and $\log \omega^2$ indicating that the conduction mechanism in these composites is due to small polaron hopping.

The variation of dielectric constant, ε' and dielectric loss, $\tan \delta$, in the temperature range 30–350°C at 100 kHz is presented in figures 5 and 6, respectively for all the samples studied in the present work. In the case of pure $Ba_{0.8}Pb_{0.2}TiO_3$, the ferroelectric–non-ferroelectric phase transition is sharp and is noticed at 225°C (Nomura and Sawada 1951; Shirane and Suzuki 1951). It is clear from figure 5 that as the ferrite component in the composite is increased, the Curie temperature transition becomes broader and shifts to lower temperature side. The diffusivity of the peak is estimated using the following expression

$$\varepsilon^{-1} = \varepsilon^{-1}_{max} + A'(T - T_c)^\gamma, \qquad (2)$$

where γ is the diffusivity parameter, a measure of broadness in diffuse phase transition which varies between $\gamma = 1$ for normal Curie Weiss law and $\gamma = 2$ for typical diffuse transition type (Kuwata *et al* 1982; Alemany *et al* 1984) and A' is a constant. The diffusivity parameter is given in table 1. An examination of data shown in table 1 indicates that the diffusivity parameter, $\gamma > 1$. The a.c. conductivity data obtained in this work on ferroelectromagnetic composites is found to obey the relation

$$\sigma_{a.c.} = A\omega^s, \qquad (3)$$

where A is a constant. The magnitude of exponent, s, is evaluated for all the composites and are presented in table 1. It tends to unity in all the composites studied in the frequency range 100 Hz–1 MHz, indicating a linear dependence of a.c. conductivity on ω (Prakash *et al* 1994). Figure 6 shows the dielectric loss vs temperature curves for various values of X and they show diffusivity indicating diffused phase transition.

The longitudinal modulus, L, and the internal friction loss, Q^{-1} vs temperature from 30–350°C for some selected samples of X $Ni_{0.5}Zn_{0.5}Fe_{1.95}O_{4-\delta} + (1 - X)$ $Ba_{0.8}Pb_{0.2}TiO_3$ (where $X = 0$, 0·005, 0·010, 0·015, 0·020 and 1) studied in the present work are presented in figure 7. An examination of the data presented in figure 7 (i.e. both L and Q^{-1} data)
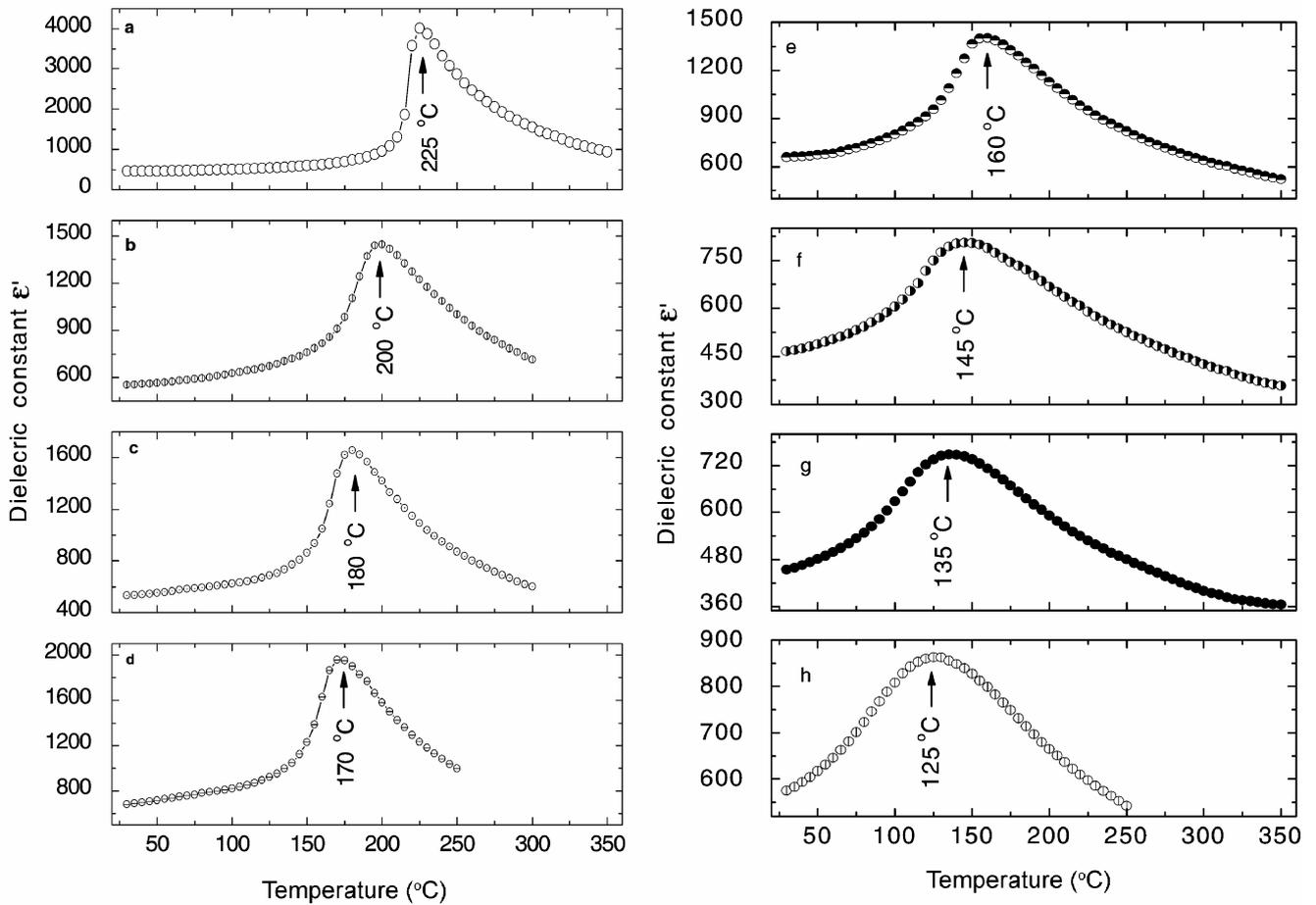
Figure 5. Temperature variation of dielectric constant ε' of **a**. pure BPT, **b**. $X = 0.005$, c. $X = 0.010$, **d**. $X = 0.015$, **e**. $X = 0.020$, **f**. $X = 0.040$, **g**. $X = 0.060$ and **h**. $X = 0.080$.
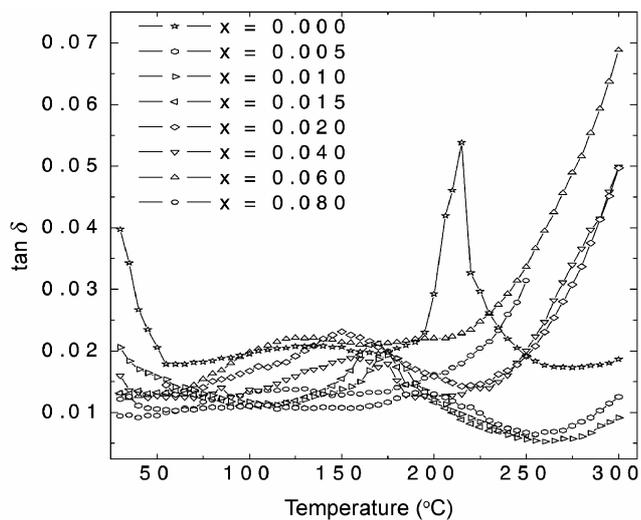

Figure 6. Variation of dielectric loss, tan δ, with temperature in the composites.

indicates that there is a systematic variation of longitudinal modulus and internal friction loss as a function of temperature as the ferrite composition is increased in the

composites. In pure Ba$_{0.8}$Pb$_{0.2}$TiO$_3$, the ferroelectric–non-ferroelectric phase transition at 225°C, can be very clearly seen as a sharp minimum in the longitudinal modulus vs temperature. This type of anomalous behaviour in the modulus was reported in PZT and PCT (Jamenez and Vincent 1998) samples near the phase transition temperature. As the ferrite component in the composite is increased, this minimum shifted to low temperature side. The shift in the minimum to low temperature side is found to be linear with ferrite content in these composites. In the case of pure ferrite, i.e. Ni$_{0.5}$Zn$_{0.5}$Fe$_{1.95}$O$_{4-\delta}$, no anomalous behaviour was noticed in the longitudinal modulus vs temperature. Moreover, the longitudinal modulus is found to be almost independent of temperature within the temperature range studied in the present work. Internal friction loss (Q^{-1}) measurements (figure 6) also exhibit a systematic variation with temperature in the composites studied in the present work. Corresponding to the ferroelectric Curie temperature, sharp peaks are exhibited by these samples, in the temperature variation of anelastic behaviour except in pure ferrite sample. In the case of pure ferrite, i.e. Ni$_{0.5}$Zn$_{0.5}$Fe$_{1.95}$O$_{4-\delta}$, there ought to have been a transition present at 290°C due to ferromagnetic–
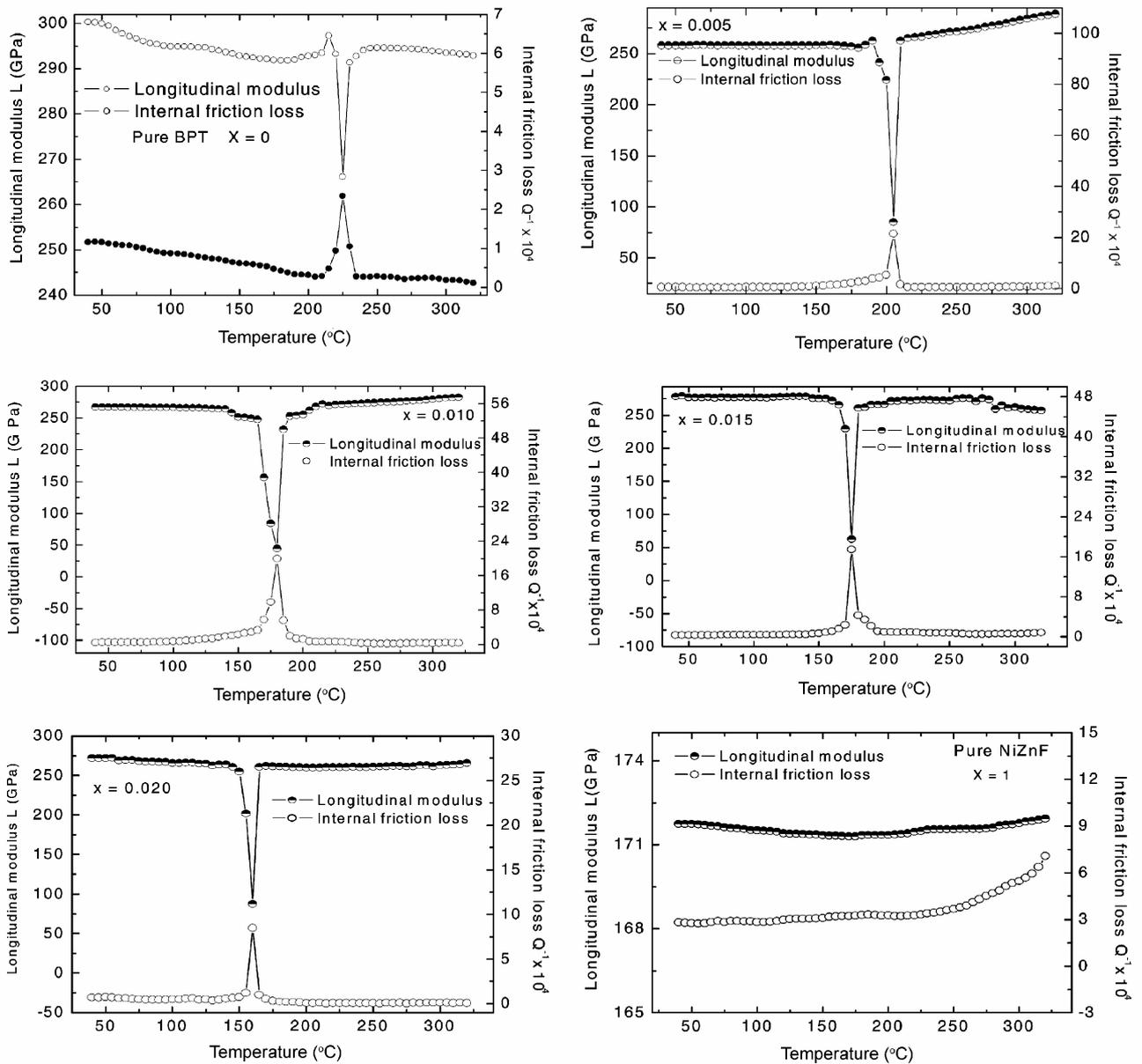
Figure 7. Temperature variation of elastic modulus (L) and internal friction loss (Q^{-1}) of magnetoferroelectric composites with $X = 0.000, X = 0.005, X = 0.010, X = 0.015, X = 0.020$ and $X = 1.000$.

paramagnetic Curie transition. However, in the present work, no anomalous behaviour could be noticed (figure 7) in the longitudinal modulus or internal friction loss behaviour with temperature.

In the absence of any phase transition, generally in solids, the elastic modulus decreases with increase in temperature. However, in the present investigation, the composites contain both ferroelectric and ferrimagnetic phases. Moreover, in the temperature range studied i.e. 30–350°C, the pure ferroelectric component, $Ba_{0.8}Pb_{0.2}TiO_3$, transforms from ferroelectric to non-ferroelectric phase at 225°C. Hence, there should be anomalous behaviour near the phase transition. In the present work, in the tempera-

ture variation of longitudinal modulus, L, this behaviour is depicted. The stress induced relaxation peaks observed in the temperature variation of internal friction loss, Q^{-1}, in the pure ferroelectric and its composites also confirm this phase transition. The Curie temperature is found to be linearly decreasing with increasing ferrite component in the composites as mentioned earlier. Even though there is only mechanical contact between the ferroelectric and ferrite phases, the effect of $Ni_{0.5}Zn_{0.5}Fe_{1.95}O_{4-\delta}$ phase on $Ba_{0.8}Pb_{0.2}TiO_3$ phase in the composites is to shift the Curie temperature drastically to lower temperature side. However, the lowering of Curie temperature in the case of composites containing $Ni_{0.93}Co_{0.02}Mn_{0.05}Fe_{1.95}O_{4-\delta} + Ba_{0.8}Pb_{0.2}TiO_3$

(Ramamanohar Reddy *et al* 2003) is not very much appreciable compared to the present system. Hence, the drastic lowering of Curie temperature may be attributed to the presence of diamagnetic $ZnFe_2O_4$ present in these composites.

4. Conclusions

The present work on magnetoferroelectric composites reveals that the effect of ferrite on the ferroelectric in the composites is to shift the ferroelectric–non-ferroelectric phase transition to lower temperature side. The addition of ferrite to the ferroelectric in the composite is to broaden the Curie temperature transition. The a.c. electrical conductivity is found to vary linearly with frequency in these composites within the frequency range studied. The conduction mechanism in these ferroelectromagnetic composites is found to obey small polaron hopping. The longitudinal modulus shows a sharp minimum at the ferroelectric Curie temperature transition in these composites. Internal friction loss exhibits a sharp peak at the 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 due to the low concentration of ferrite phase.

Acknowledgements

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