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Effect of Temperature on the Elastic and Anelastic Behaviour of Magneto-Ferroelectric Composites $Ba_{0.8}Pb_{0.2}TiO_3$ + $Ni_{0.93}Co_{0.02}Mn_{0.05}Fe_{1.95}O_{4-\delta}$ in the Ferroelectric Rich Region

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Abstract. Composites with composition $x Ba_{0.8}Pb_{0.2}TiO_3 + (1-x)\, Ni_{0.93}Co_{0.02}Mn_{0.05}Fe_{1.95}O_{4-\delta}$ in which x varies as 1.0, 0.9, 0.7 and 0.5 in molar percent have been prepared by the conventional ceramic double sintering process. The presence of the two phases has been confirmed by X-ray diffraction. These composites were prepared for their use as magnetoferrolectric devices. Variation of longitudinal modulus (L) and internal friction loss (Q^{-1}) of these samples with temperature at 142 kHz has been studied in the wide temperature range 300 to 630 K. The elastic behaviour (L) showed a break at the ferroelectric Curie temperature (498 K) in the case of pure ferroelectric material ($Ba_{0.8}Pb_{0.2}TiO_3$). This break shifted to lower temperature side as the ferrite component increases in the composite. The temperature variation of internal friction loss (Q^{-1}) showed a corresponding stress induced relaxation peak at the ferroelectric-non-ferroelectric phase transition. This behaviour is explained in the light of structural phase transition.

Keywords: composites, Curie temperature, ferrite, ferroelectric, internal friction loss, longitudinal modulus, magnetoferroelectric, phase transition

Introduction

Composite materials consisting of piezoelectric and piezomagnetic phases show magnetoelectric (ME) effect. The ME effect is a coupled, two field effect in which the application of electric field induces magnetisation and magnetic field produces electric polarisation. ME effect is a property of the composites which is absent in their constituent phases [1]. The deformation of ferrite phase causes polarisation of piezoelectric particles in the composite and on the other hand the electrical polarisation of piezoelectric material causes change in magnetisation of ferrite phase due to mechanical coupling of the piezomagnetic (ferrite) and piezoelectric (ferroelectric) phases [2]. Such magnetoferrolectric composites are exploited as sensors, wave guides, modulators, phase inverters, rectifiers, transducers etc. [3]. Though these composites find lot of applications in radioelectronics, optoelectronics, microelectronics and as transducers in instrumentation, the work available in literature is mostly confined to the measurement of ME effect in composites containing a ferroelectric as the first component and Ni [4–6], Co [7–9], Ni-Co-Mn [10], Ni-Co-Cu-Mn [11] Cu [12, 13] ferrites, the second component, as magnetostrictive component. The data available in literature on the investigation of properties like elastic, anelastic, piezoelectric and magnetostrictive nature on these magnetoferroelectric composites are scanty. In view of this, in the present investigation, it is intended to study the temperature variation of elastic and anelastic behaviour of $x Ba_{0.8}Pb_{0.2}TiO_3$ + $(1-x)Ni_{0.93}Co_{0.02}Mn_{0.05}Fe_{1.95}O_{4-\delta}$ (where $x = 1.0$, 0.9, 0.7 and 0.5) composites in ferroelectric rich

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*To whom all correspondence should be addressed. E-mail: sivani_atp@yahoo.co.in region. The results are discussed in the light of structural phase transition.

Materials and Methods

The ferrite phase ($Ni_{0.93}Co_{0.02}Mn_{0.05}Fe_{1.95}O_{4-\delta}$) was prepared by using the analytical grade NiO, $MnCO_3$, CoO and Fe_2O_3 in stoichiometric proportion. These oxides and carbonate were mixed intimately using agate mortar for 8 h and the mixture was pre-sintered at 1073 K for 10 h in the form of a cake. After pre-sintering, the cake is once again crushed and ground in agate mortar to obtain fine particle size. The powder is sieved to obtain uniform particle size.

The ferroelectric phase ($Ba_{0.8}Pb_{0.2}TiO_3$) was prepared using the starting materials $BaCO_3$, PbO and TiO_2 by thoroughly mixing and grinding for nearly 8 h. The mixture was compressed in to a cake and pre-sintered at 873 K for 12 h by taking enough care to avoid the evaporation of lead. The pre-sintered cake was crushed, ground and sieved. The fine green powder obtained was employed for the preparation of the composites.

Employing the pre-sintered ferrite and ferroelectric green powders, polycrystalline ferroelectric and ferrite composites with generic formula $x Ba_{0.8}Pb_{0.2}TiO_3 + (1-x)Ni_{0.93}Co_{0.02}Mn_{0.05}Fe_{1.95}O_{4-\delta}$ ($x = 1.0$, 0.9, 0.7 and 0.5) were prepared by mixing them with 2% polyvinyl alcohol as binder and pressed into bars of square cross section 3.5×10^{-3} m $\times$ 3.5×10^{-3} m and 2.05×10^{-2} m long using hydraulic press. These bars were finally sintered at 1523 K for 2 h in a programmable furnace, and were cooled to room temperature at the rate of 80 K/h [14, 15]. XRD analysis revealed the presence of both the phases in the composites. No additional or intermediate phases were noticed.

Experimental Details

The experimental technique employed in the present study for the measurement of internal friction loss and the elastic behaviour is similar to the one developed by Schwartz [16] with a few modifications. By determining the resonant frequency of the composite system and the logarithmic decrement, the internal friction (Q^{-1}) and the longitudinal modulus (L) has been evaluated using the standard relations as detailed in literature [16–18]. Q^{-1} data and L data obtained in the present work are accurate to 5 and 2% respectively.

The x-cut quartz transducer used in the present investigation has a length of 2.001×10^{-2} m, width of 3.32×10^{-3} m , natural frequency 142.387 kHz and mass of 0.6628×10^{-3} kg. 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 works satisfactorily after it has been kept for 24 h at room temperature.

In order to study the effect of temperature on internal friction loss and longitudinal modulus in the ferroelectric—ferrite composite specimens, the composite resonator system with the holder is placed at the centre of a tubular electrical furnace. The details of the furnace and temperature controller assembly were described elsewhere [14, 19]. All the internal friction measurements have been performed with a strain amplitude of 10^{-6}, after the specimen had attained thermal equilibrium.

Results and Discussion

Figures 1(a) and (b) show the typical X-ray diffractograms of composites with $x = 0.9$ and 0.5 respectively. All the peaks could be identified for both perovskite and spinel phases. It can be noticed from the figures that the intensity of the peaks corresponding to ferrite phase increases with increase in ferrite composition. The lattice parameters of pure ferroelectric ($Ba_{0.8}Pb_{0.2}TiO_3$) and pure ferrite ($Ni_{0.93}Co_{0.02}Mn_{0.05}Fe_{1.95}O_{4-\delta}$) are $a = 4.0424$ Å, $c = 3.9826$ Å and 8.3958 Å respectively.

The longitudinal modulus, L, and the internal friction loss, Q^{-1}, versus temperature from 300 to 630 K for various samples of $x Ba_{0.8}Pb_{0.2}TiO_3 + (1-x) Ni_{0.93}Co_{0.02}Mn_{0.05}Fe_{1.95}O_{4-\delta}$ ($x = 1.0$, 0.9, 0.7 and 0.5) studied are presented in Figs. 2 and 3 respectively.

An examination of the data presented in Fig. 2 indicates that there is a systematic variation of longitudinal modulus as a function of temperature as the ferrite composition is increased. In pure $Ba_{0.8}Pb_{0.2}TiO_3$ the ferroelectric—non-ferroelectric phase transition at

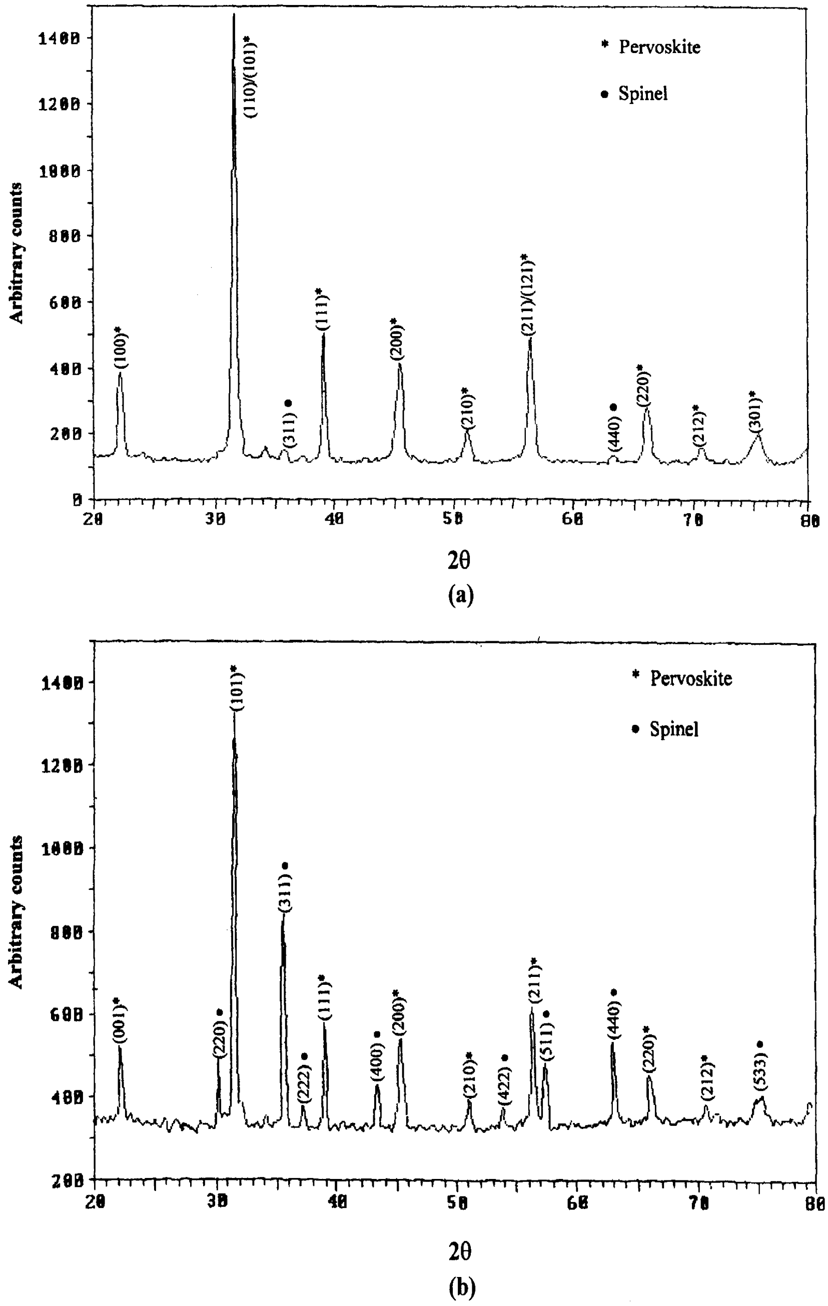

Fig. 1. XRD patterns of magneto-ferroelectric composites: (a) $0.9Ba_{0.8}Pb_{0.2}TiO_3 + 0.1Ni_{0.93}Co_{0.02}Mn_{0.05}Fe_{1.95}O_{4-\delta}$ and (b) $0.5Ba_{0.8}Pb_{0.2}TiO_3 + 0.5Ni_{0.93}Co_{0.02}Mn_{0.05}Fe_{1.95}O_{4-\delta}$.

498 K, can be very clearly seen as a sharp discontinuity at the ferroelectric Curie temperature [20, 21]. This type of discontinuous behaviour in modulus was reported by Koster and Bangert [22] in Hume-Rothery alloys in the neighbourhood of solidus temperature. As the ferrite component in the composite is increased this discontinuity becomes broader and shifts to the low temperature side. This is in conformity with the X-ray studies carried out on these samples where the tetragonal phase of the pure ferroelectric, i.e., $Ba_{0.8}Pb_{0.2}TiO_3$,

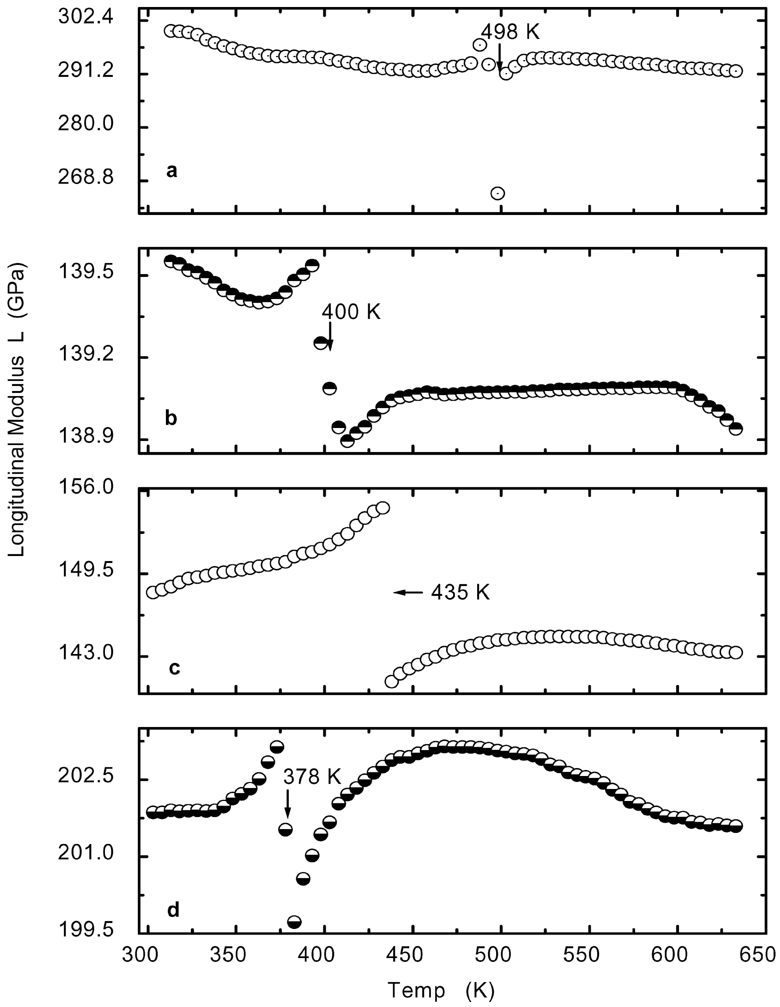

Fig. 2. Variation of longitudinal modulus L as a function of temperature T in magneto-ferroelectric composites $x\mathrm{Ba_{0.8}Pb_{0.2}TiO_3} + (1-x)$ $\mathrm{Ni_{0.93}Co_{0.02}Mn_{0.05}Fe_{1.95}O_{4-\delta}}$: (a) $\mathrm{Ba_{0.8}Pb_{0.2}TiO_3}$, (b) $0.9\mathrm{Ba_{0.8}Pb_{0.2}TiO_3} + 0.1\mathrm{Ni_{0.93}Co_{0.02}Mn_{0.05}Fe_{1.95}O_{4-\delta}}$, (c) $0.7\mathrm{Ba_{0.8}Pb_{0.2}TiO_3} +$ $0.3\mathrm{Ni_{0.93}Co_{0.02}Mn_{0.05}Fe_{1.95}O_{4-\delta}}$, and (d) $0.5\mathrm{Ba_{0.8}Pb_{0.2}TiO_3} + 0.5\mathrm{Ni_{0.93}Co_{0.02}Mn_{0.05}Fe_{1.95}O_{4-\delta}}$.

transforms to cubic as $x = 0.5$ is reached and thereafter remains in the cubic phase [14].

Figure 3 depicts that there is also a systematic variation of internal friction loss with temperature in the composites studied in the present work. Corresponding to the ferroelectric Curie temperatures (Fig. 3) sharp peaks are exhibited by all the samples in the temperature variation of anelastic behaviour of these ferroelectric and ferrimagnetic composites. The arrows in Figs. 2 and 3 indicate the ferroelectric-non-ferroelectric phase transitions.

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 chosen contain both ferroelectric and ferrimagnetic phases and moreover in the temperature range studied i.e., 300–630 K, the pure ferroelectric component, $\mathrm{Ba_{0.8}Pb_{0.2}TiO_3}$, transforms from ferroelectric to non-ferroelectric phase at 498 K [20]. Hence there should be anomalous behaviour near the phase transition. In the present work, of temperature variation of longitudinal modulus L, this 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. However in the composite with

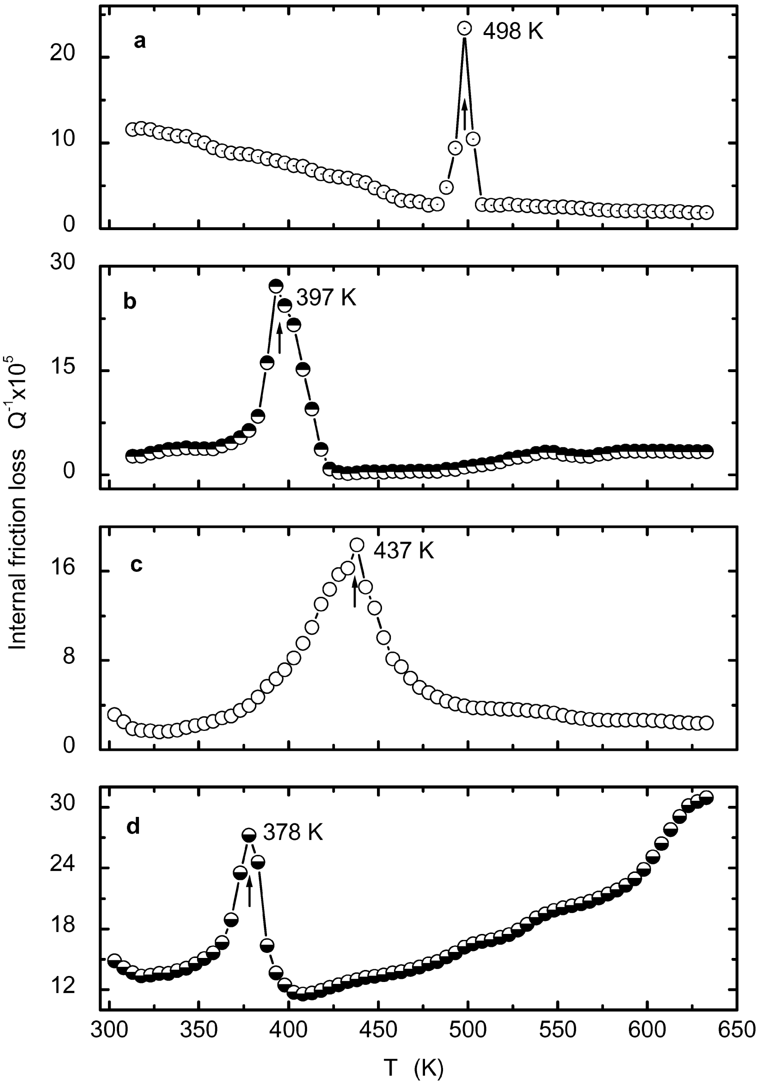

Fig. 3. Variation of internal friction loss Q^{-1} as a function of temperature T in magneto-ferroelectric composites $x\mathrm{Ba_{0.8}Pb_{0.2}TiO_3} + (1-x)\mathrm{Ni_{0.93}Co_{0.02}Mn_{0.05}Fe_{1.95}O_{4\text{-}\delta}}$: (a) $\mathrm{Ba_{0.8}Pb_{0.2}TiO_3}$, (b) $0.9\mathrm{Ba_{0.8}Pb_{0.2}TiO_3} + 0.1\mathrm{Ni_{0.93}Co_{0.02}Mn_{0.05}Fe_{1.95}O_{4\text{-}\delta}}$, (c) $0.7\mathrm{Ba_{0.8}Pb_{0.2}TiO_3} + 0.3\mathrm{Ni_{0.93}Co_{0.02}Mn_{0.05}Fe_{1.95}O_{4\text{-}\delta}}$, and (d) $0.5\mathrm{Ba_{0.8}Pb_{0.2}TiO_3} + 0.5\mathrm{Ni_{0.93}Co_{0.02}Mn_{0.05}Fe_{1.95}O_{4\text{-}\delta}}$.

$x = 0.9$ the shift in Curie temperature is more than the other composites studied in the present work. Gelyasin and Laletin [23] reported this type of anomalous behaviour in their dielectric measurements on $\mathrm{BaTiO_3} + \mathrm{NiFe_{1.96}O_{4\text{-}\delta}}$ composites for small additions of nickel ferrite.

This was attributed by them to the fact that there is some type of eutectic formation in the low concentration range of ferrite compositions in the composites containing nickel ferrite. Since the composites studied in the present work also contain nickel ferrite as the second component, relatively large shift in the Curie temperature for the composition $x = 0.9$ is attributed to the above fact.

Conclusions

The longitudinal modulus, L, shows a break at Curie temperature in all the composites studied in the present investigation. The internal friction loss, Q^{-1}, exhibits stress induced relaxation peak at Curie temp. The effect of ferrite phase on the ferroelectric phase is to shift the Curie temperature to lower temperature side. Thus studies on the elastic and anelastic behaviour of composites containing piezoelectric and piezomagnetic phases throw considerable light on the phase transitions present in the composites since they are lattice related properties.

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