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Magnetoelectric effect in cobalt ferrite–barium titanate composites and their electrical properties

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Abstract. $CoFe_2O_4$–$BaTiO_3$ composites were prepared using conventional ceramic double sintering process with various compositions. Presence of two phases in the composites was confirmed using X-ray diffraction. The dc resistivity and thermoemf as a function of temperature in the temperature range 300 K to 600 K were measured. Variation of dielectric constant (ε') with frequency in the range 100 Hz to 1 MHz and also with temperature at a fixed frequency of 1 kHz was studied. The ac conductivity was derived from dielectric constant (ε') and loss tangent ($\tan\delta$). The nature of conduction is discussed on the basis of small polaron hopping model. The static value of magnetoelectric conversion factor has been studied as a function of magnetic field.

Keywords. X-ray diffraction; $CoFe_2O_4$–$BaTiO_3$, dielectric constant; ac conductivity; hopping model; magnetoelectric effect.

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1. Introduction

Composite materials containing piezoelectric (ferroelectric) and piezomagnetic (ferrite) phases exhibit magnetoelectric effect (ME) [1]. These composites have ME property which is absent in their constituent phases. The ME effect couples two field effects: (1) magnetization due to application of electric field and (2) electric polarization due to the application of magnetic field. The magnetoelectric effect is due to the mechanical coupling between piezomagnetic (ferrite) and piezoelectric (ferroelectric) phases [2]. From literature it is clear that the work on these magnetoelectric composites is limited to measurement of ME effect only. Hanumaiah *et al* [3] have studied ME effect in $NiFe_2O_4$–$BaTiO_3$ and $CoFe_2O_4$–$BaTiO_3$ composites. Gelyasin *et al* [4] have measured the ME coefficient with ac magnetic field for $NiFe_2O_4$–$BaTiO_3$ composites. The ME coefficient was attributed to relaxation process and resistivity of the materials. However, the conductivity behavior in $CoFe_2O_4$–$BaTiO_3$ composites has not been studied. In this paper we report the dc electrical conductivity and thermoelectric power (TEP) as a function of temperature for this system. Dielectric behavior is also studied to understand the conduction phenomenon.

2. Experimental

Ferrite–ferroelectric composites were prepared by standard ceramic method. Ferrite phase chosen was cobalt ferrite, and ferroelectric phase was barium titanate. Cobalt ferrite was prepared by conventional solid-state reaction route taking CoO and Fe_2O_3 in molar ratios. Similarly, ferroelectric phase was prepared from BaO and TiO_2. These raw materials were mixed thoroughly. The constituent phases were presintered at 750°C for 6 h, separately. After presintering these were ground to fine powder. The composites were prepared by dispersing 75, 50 and 25 mole% of ferrite phase ($CoFe_2O_4$) into the matrix of ferroelectric phase ($BaTiO_3$) and labeled as c2, c3 and c4, respectively. The single phase $CoFe_2O_4$ and $BaTiO_3$ were labeled as c1 and c5, respectively. They were mixed thoroughly and presintered at 950°C for 6 h. Once again these compositions were mixed thoroughly and pressed into pellets of diameter 10 mm and thickness of about 4 mm. The pelletized samples were sintered at 1200°C for 12 h and slow-cooled to room temperature.

The samples were characterized using Cu-K_α radiation. The dc resistivity and thermoelectric power measurements were carried out in the temperature range 300–800 K using laboratory designed sample holders. The thermoelectric power (α) was calculated using the relation $\alpha = \Delta E/\Delta T$, where ΔE is the measure of voltage across the sample. The electrical contacts for these measurements were made ohmic by applying silver paste on the faces of the pellets. Dielectric measurements were carried out by using LCR bridge model HP 4284A in the frequency range 100 Hz to 1 MHz. For ME measurements electrical poling was performed by heating the samples to 150°C, which is 30°C above the transition temperature of $BaTiO_3$. The applied field was 2.5 kV/cm. The samples were held at this temperature for 45 min and then cooled to room temperature in the presence of the field. For ME measurements a specially designed perspex sample holder having copper electrodes was used [4].

3. Results and discussion

The X-ray diffraction pattern (figure 1) shows that the composites consist of cobalt ferrite and barium titanate as predominant phases. Some other unidentified peaks are also observed. The intensity of ferrite peaks decreases with increasing $BaTiO_3$ content. The lattice constants of the individual phases do not vary much. Cobalt ferrite has cubic spinel structure whereas $BaTiO_3$ retains the perovskite structure. The lattice parameters of individual phases are listed in table 1.

Variation of dc resistivity with temperature in the range 300–800 K is shown in figure 2. It is observed that ρ_{dc} increases with increase in $BaTiO_3$ content. The plots show that there are three regions indicating different types of conduction. The variation of Seebeck coefficient (α) with the temperature is shown in figure 3. At lower temperature all the samples show positive Seebeck coefficient (α) which indicates that the charge carriers are of p-type. There is p–n transition observed in all the compositions at higher temperature. The p–n transition temperature decreases with the increase in $BaTiO_3$ content and approaches to Curie temperature of $BaTiO_3$. Above 500 K the Seebeck coefficient is almost independent of temperature. The variation of drift mobility (μ_d) with temperature is shown in figure 4. The drift mobility increases with temperature.

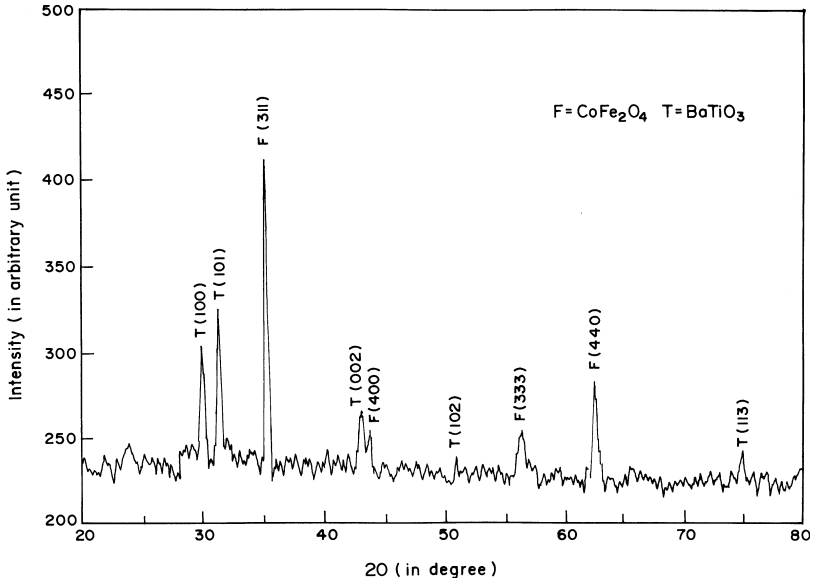


Figure 1. X-ray diffractogram of c3 composite.

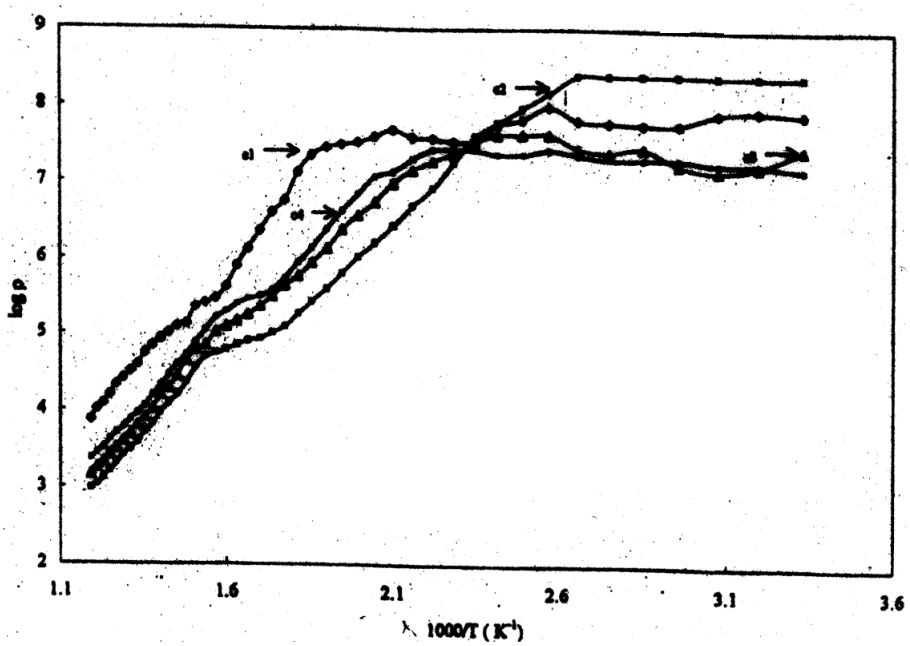


Figure 2. Variation of dc resistivity (log ρ) with temperature (1000/T) for c1, c2, c3 and c4.

Table 1. Electrical and structural data for the $CoFe_2O_4$–$BaTiO_3$ system.

composition	Lattice parameter: Ferrite phase (Å)	Lattice parameter: Ferroelectric phase (Å)	ρ (Ω cm) at 100°C	α (μV/K) at room temp.	ΔE (eV) from: Resistivity	ΔE (eV) from: mobility	$(dE/dH)_H$ (μV/cm Oe)
(c1) $CoFe_2O_4$	$a = 8.3529$	–	6.5×10^7	3000	1.4	1.23	–
(c2) 75% $CoFe_2O_4$ + 25% $BaTiO_3$	$a = 8.3824$	$a = 4.0015$ $c = 4.1896$	2.47×10^8	1920	0.79	0.73	110
(c3) 50% $CoFe_2O_4$ + 50% $BaTiO_3$	$a = 8.389$	$a = 3.992$ $c = 4.0127$	2.8×10^7	1500	0.66	0.6	130
(c4) 25% $CoFe_2O_4$ + 75% $BaTiO_3$	$a = 8.3608$	$a = 3.994$ $c = 4.018$	2.3×10^7	900	0.93	0.91	140
(c5) $BaTiO_3$	–	$a = 3.998$ $c = 4.05$	1.9×10^8	34	–	–	–

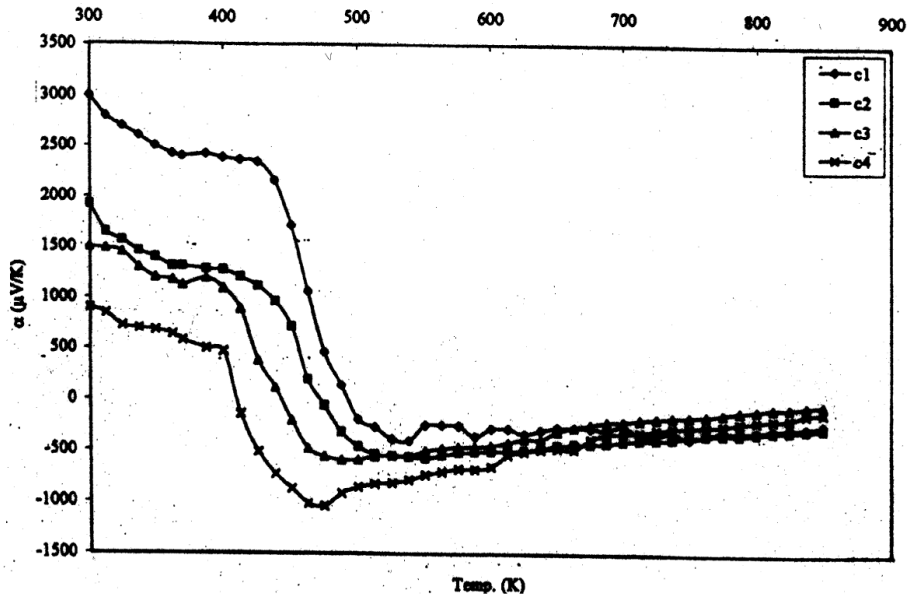


Figure 3. Variation of Seebeck coefficient (α) with temperature (T) for c1, c2, c3 and c4.

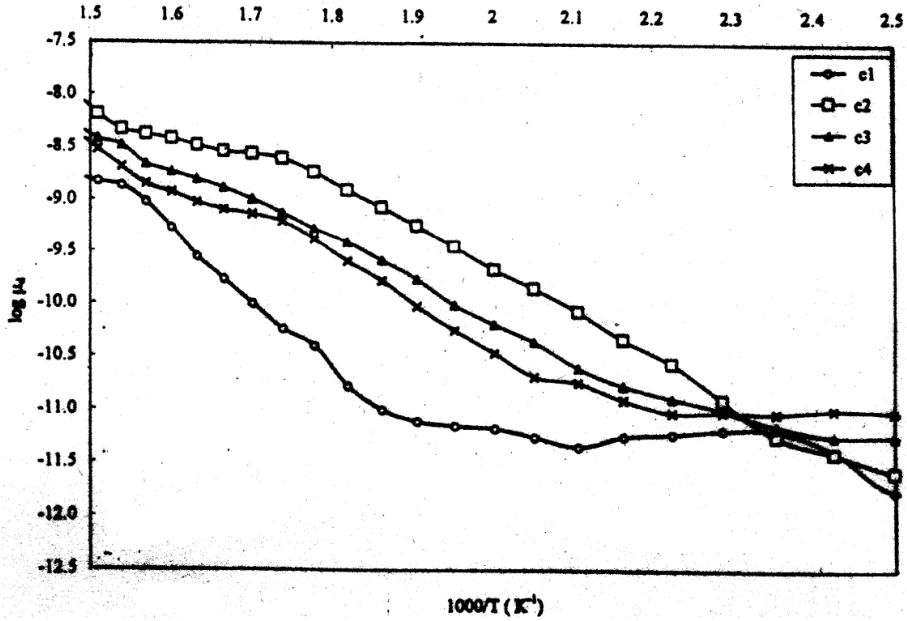


Figure 4. Variation of mobility (log μ_d) with temperature (1000/T) for c1, c2, c3 and c4.

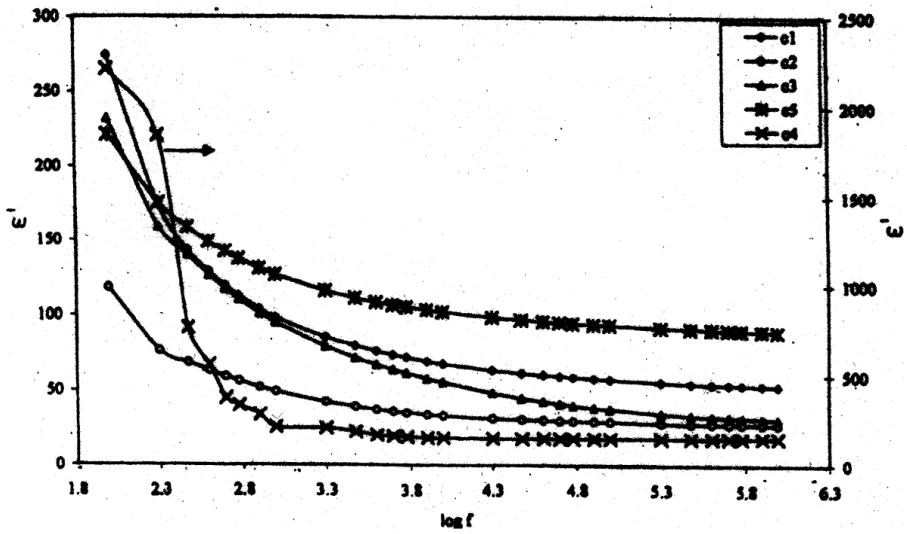


Figure 5. Variation of dielectric constant (ε') with frequency for c1, c2, c3, c4 and c5.

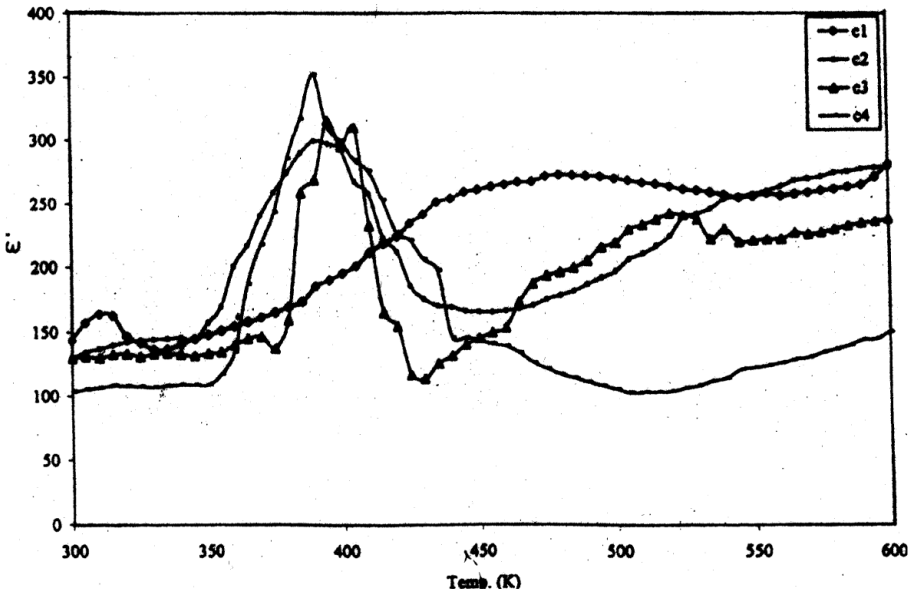


Figure 6. Variation of dielectric constant (ε') with temperature (T) for c1, c2, c3 and c4.

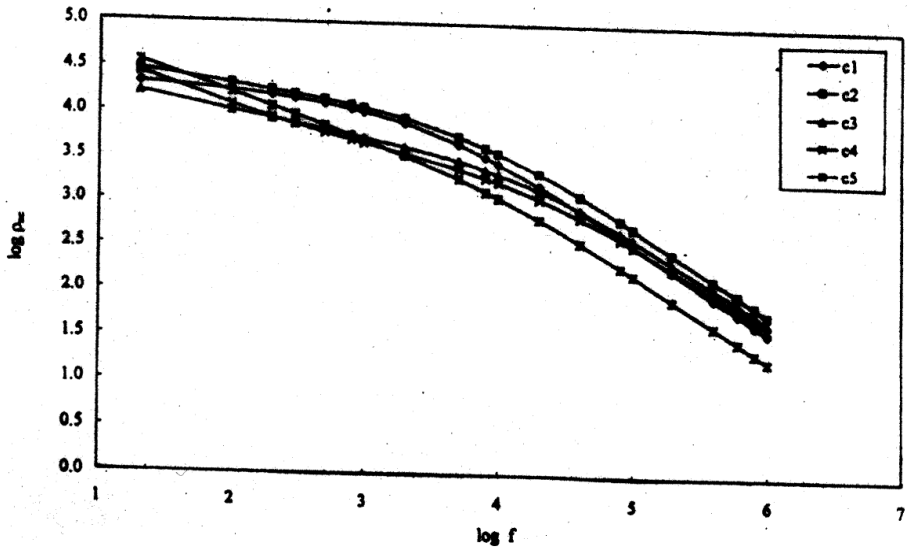


Figure 7. Variation of log ρ_{ac} with log frequency for c1, c2, c3, c4 and c5.

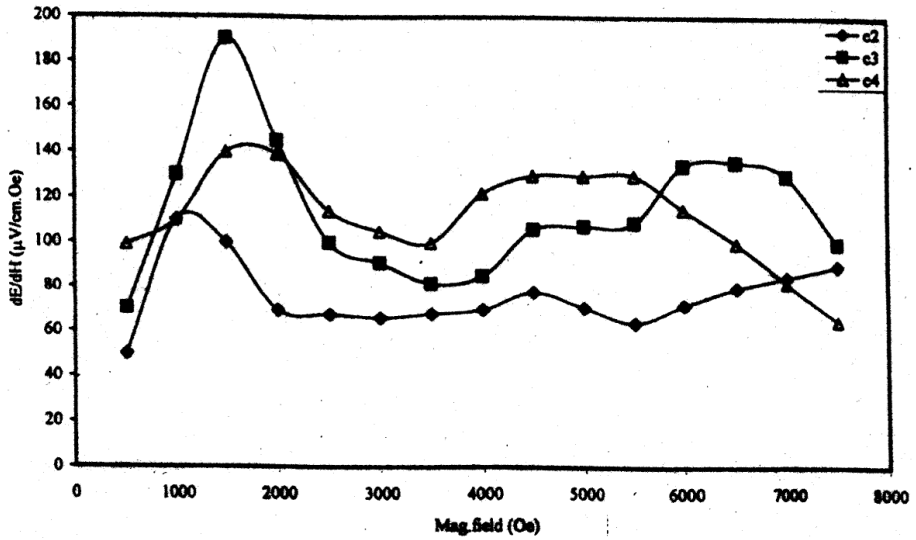


Figure 8. Variation of $(\mathrm{d}E/\mathrm{d}H)_{\mathrm{H}}$ with dc magnetic field for c2, c3 and c4.

Frequency variation of dielectric constant (ε') for the present composites at room temperature is shown in figure 5. It may be noted that as the frequency is increased ε' falls rapidly to a low value and remains almost constant afterwards. Similar behavior is observed for the loss tangent (tan δ). Also it is noted that the dielectric constant (ε') increases with the content of $BaTiO_3$. The dependence of ε' on temperature for the present system at 1 kHz is shown in figure 6. A peak in the ε' vs. T curve is observed which is associated with Curie temperature of $BaTiO_3$, and as the content of $BaTiO_3$ increases the peak intensity increases. The plots of ρ_{ac} with frequency are shown in figure 7. The ac resistivity increases with the decrease in frequency.

Figure 8 shows variation of magnetoelectric coefficient with applied dc field. The magnetoelectric (ME) coefficient is a measure of changes in the resulting electric field in the magnetoelectric composites due to the applied external magnetic field [5]. It is observed that the ME coefficient increases approximately up to 1.5 kOe and decreases thereafter.

Many workers [6,7] observed three regions in the conductivity plots for mixed ferrites, which have been attributed to different types of conduction processes. Accordingly, in the present study the first region in the conductivity plot at low temperature (< 450 K) indicates conduction due to impurities while the second region is due to thermally activated polaron hopping and the third region is due to magnetic disordering. In the case of the composites, the electron hops between two states by absorbing phonon according to Boltzmann statistics. If ΔE is the barrier energy between two states then only the fraction $\exp(\Delta E/kT)$ of the number of charge carriers can cross the barrier per second [8]. From this consideration the temperature variation of resistivity can be represented as

$$\rho = \rho_0 \exp(\Delta E/kT)\,, \tag{1}$$

where ρ is the resistivity at temperature T and ΔE is the activation energy for electrical process. The activation energies are noted in table 1.

For cobalt ferrite the conduction phenomenon is described as $Co^{2+} + Fe^{3+} \Leftrightarrow Co^{3+} + Fe^{2+}$. Cobalt occupies only the octahedral site. Therefore, the predominant conduction at lower temperature in the present composites is mainly due to $Co^{2+} \rightarrow Co^{3+}$, which gives p-type conduction. The conduction mechanism is due to the hopping of holes between Co^{3+} and Co^{2+}. This type of process requires higher energy. At higher temperature, due to the oxidation–reduction process the majority charge carriers are electrons. Thus at higher temperature the conduction is mainly due to $Fe^{3+} \rightarrow Fe^{2+}$. Hence, there is a p–n transition [9].

Drift mobility μ_d was calculated using the data of α and ρ with the help of equation given by Austin and Mott [10]

$$\mu_d = \exp(\alpha/2 \cdot 3k/e)/2N_0 \cdot e \cdot \rho \tag{2}$$

the notations have their usual meaning.

Plots of $\log \mu_d$ vs. $1/T$ (figure 4), are nearly linear supporting the polaron hopping model for the conduction. The activation energies calculated from resistivity and that from mobility are tabulated in table 1. There is a close agreement between the activation energies indicating localized model of charge carriers. These activation energies are much larger than the ionization energy $E_i = 0.1$ eV of donors or acceptors; and hence, the possibility of band type of conduction is ruled out. The values are also higher than those for $Fe^{2+} \leftrightarrow Fe^{3+}$ transition. This indicates that the polaron hopping mechanism is more favored. According to the localization model, electrons are strongly localized on the cations. Localization may be attributed to electron–phonon interaction. An additional localization of electrons at Fe^{2+} ions may arise from inhomogeneous distribution of ions over octahedral and tetrahedral sites.

All samples reveal dispersion in dielectric constant and loss tangent (tan δ) due to Maxwell–Wagner interfacial polarization in agreement with Koops phenomenological theory [11]. The observed variation in dielectric constant can be explained on the basis of space-charge polarization due to inhomogeneous dielectric structure. The high ε', often observed at low frequencies, has been ascribed to the effect of heterogeneity of the sample, viz. pores, grain boundaries etc. Many workers [12,13] have explained the behavior of dielectric constant by assuming that the mechanism of dielectric polarization is similar to that of conduction electron exchange interaction. In normal dielectric behavior ε' decreases with increasing frequency and reaches a constant value depending on the fact that beyond a certain frequency of electric field the electron exchange does not follow the alternating field. This is the reason why ε' remains constant beyond a certain frequency in the case of present composites.

The dielectric constant with temperature plots (figure 6) show peaks at Curie temperature of ferroelectric phase. This temperature in these composites on average is around 117°C, which is close to Curie temperature of $BaTiO_3$. It is also noted that the phase transition temperature T_c remains constant for different frequencies. A broad peak-like trend is noticed in the temperature range 400–550 K for $CoFe_2O_4$ (c1). A slope change in conductivity vs. temperature plot (figure 2) is also noted in the same temperature region. This anomaly may be due to the clustering of Co^{3+} ions.

Variation of resistivity with frequency shows that the contribution to the dc resistivity comes from grain boundary resistivity and grain resistivity. According to Volger [14] the

parameters of electrical conductivity vs. frequency spectrum are related to the material characteristics. The resistivity at lower frequency is considered as grain boundary resistivity and at higher frequency due to grains. The value of ρ_{ac} at 1 kHz is of the order of 10^4 whereas it is 10 for 1 MHz. Therefore, it can be concluded that the main contribution to ac resistivity comes from the grain boundary. The decrease of ac conductivity with frequency and temperature independent nature of thermoelectric power (α) indicate that the conduction is due to small polaron hopping mechanism [15].

The ME coefficient (dE/dH)) for the present composites was measured as a function of dc magnetic field. The maximum value of dc $(ME)_H$ is observed for 50% $BaTiO_3$ content. This may be due to the stiffnesses of the two phases which are comparable in magnitude and the elastic interaction between the two phases is strongest near the volume ratio $f=0.5$. The maximum value of (dE/dH) observed was 140 μV/(cm Oe). It is observed that the value of (dE/dH) increases from 1 kOe up to 1.5 kOe and then decreases with increasing magnetic field. This decrease in ME coefficient is due to the saturation magnetization in $CoFe_2O_4$.

4. Conclusion

From the variations of the resistivity, Seebeck coefficient and drift mobility with temperature it can be concluded that the conduction in the present composites is due to thermally activated polaron hopping. This is also confirmed from variation of ac conductivity with frequency. The maximum magnetoelectric coefficient is observed for 75 mole % of $BaTiO_3$.

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