



Electrical Conduction and Magnetoelectric Effect in $\text{CuFe}_{1.8}\text{Cr}_{0.2}\text{O}_4\text{--Ba}_{0.8}\text{Pb}_{0.2}\text{TiO}_3$ Composites

K.K. PATANKAR,¹ V.L. MATHE,¹ A.N. PATIL,¹ S.A. PATIL,¹ S.D. LOTKE,¹
Y.D. KOLEKAR² & P.B. JOSHI²

¹Composite Materials Lab., Physics Department, Shivaji University, Kolhapur 416004, India

²Shivaji University P.G. Center, Solapur 413003, India

Submitted March 29, 2000; Revised November 21, 2000; Accepted November 30, 2000

Abstract. Magnetoelectric composites of $\text{CuFe}_{1.8}\text{Cr}_{0.2}\text{O}_4\text{--Ba}_{0.8}\text{Pb}_{0.2}\text{TiO}_3$ were prepared using high temperature solid-state reaction technique. X-ray structural analysis of these composites confirms the presence of both the phases in the composite. Detailed studies of dielectric properties (ϵ' , $\tan \delta$ and σ_{ac}) as a function of frequency (100 Hz to 1 MHz) and temperature (30°C to 250°C) show that these compounds exhibit diffuse ferroelectric phase transitions. Results of ac conductivity, dc resistivity and thermoelectric power measurements show that conduction occurs by hopping of charge carriers. The magnetoelectric effect has been studied as a function of intensity of magnetic field. The electrical polarisation was induced in piezoelectric ($\text{Ba}_{0.8}\text{Pb}_{0.2}\text{TiO}_3$) phase as result of strain induced in the ferrite ($\text{CuFe}_{1.8}\text{Cr}_{0.2}\text{O}_4$) phase by the applied magnetic field. The Jahn-Teller distortion caused in the ferrite lattice by Jahn-Teller ions like Cu^{2+} and Cr^{3+} is also responsible for the elastic coupling of strain to the $\text{Ba}_{0.8}\text{Pb}_{0.2}\text{TiO}_3$ phase.

Keywords: magnetoelectric effect, electric conduction and diffuse phase transition

Introduction

The possibility of existence of magnetoelectric effect was first discussed by Landau and Lifshitz [1]. In materials having both electric and magnetic ordering, an application of magnetic field induces electrical polarisation, while an external electric field causes change in magnetisation. Such a phenomenon is called as magnetoelectric (ME) effect [2–5]. It occurs due to the interaction between electric and magnetic dipoles [2]. ME effect in composites is due to the strain, induced in piezomagnetic (ferrite) phase by the applied magnetic field, being mechanically coupled to stress induced in the piezoelectric (ferroelectric) phase; the coupling resulting in an electrical voltage [5]. However, a selection of suitable combination of piezoelectric and piezomagnetic material with a view to achieve ME effect itself is a challenging task. The reasons being: (1) the ferrite phase is required to have high piezomagnetic coefficient and its resistivity must be comparable to that of

the ferroelectric phase; (2) the piezoelectric coefficient of ferroelectric phase should also be high and its resistivity should be at least of the order of $10^7 \Omega\text{-cm}$ and (3) the mechanical coupling between ferrite and ferroelectric phase must be perfect. Hence, with all these stringent requirements, search for a suitable combination of ferrite and ferroelectric leads to hardly a handful number of such materials that can be put to the study of ME effect and the calculation of ME conversion factor (dE/dH) in them. The ME conversion factor is a measure of changes in the resulting electrical field in the magnetoelectric composite due to the applied external magnetic field, as measured on the flux of the constant magnetic field [6]. This first order derivative results from the terms proportional to $E.H$ in the expression for the free energy of the crystal [6]. As aforesaid, the ME effect being a product of piezomagnetic and piezoelectric effect of the constituent phases, the ME conversion factor is obviously the product of piezomagnetic coefficient and the piezoelectric coefficient.

$$\begin{aligned}
& \text{Mathematically, } (dE/dH)_{\text{composite}} \\
& = (dl/dH)_{\text{composite}} \times (dE/dl)_{\text{composite}} \\
& = (dl/dH)_{\text{ferrite,bulk}} \times f \times (dE/dl)_{\text{ferroelectricbulk}},
\end{aligned}$$

where f is the volume fraction of ferrite. But this is true only in the ideal case, i.e., when there is a perfect coupling between the phases. In reality, the two phases may make a poor mechanical contact, so that a slip may occur at the interfaces and energy may be dissipated in friction [3].

Suryanaryana and his group investigated LiFe_5O_8 – BaTiO_3 , NiFe_2O_4 – BaTiO_3 and CoFe_2O_4 – BaTiO_3 systems prepared by ceramic method and have reported that no ME signal was observed in the first of these while in the other two the ME signal was of the order of $\mu\text{V}/(\text{cm Oe})$ [6]. It is rather surprising that though the ferrites phases in these composites have high resistivity and giant magnetostriction, the resulting ME signal was weak. We have reported ME conversion factor of the same order of magnitude in $\text{CuFe}_{1.6}\text{Cr}_{0.4}\text{O}_4$ – BaTiO_3 and CuFe_2O_4 – BaTiO_3 systems, though our chosen ferrites were less magnetostrictive but still preferred, as they could produce larger Jahn-Teller distortion in the ferrite lattice, which will in turn induce more mechanical coupling between the ferroelectric and ferrite phases (since Cu^{2+} and Cr^{3+} being Jahn-Teller ions) [7, 8]. In the present study we communicate the ME effect in $\text{CuFe}_{1.8}\text{Cr}_{0.2}\text{O}_4$ – BaTiO_3 system. In addition, we report the study of effect of temperature, frequency and composition on the dielectric properties of the system; temperature dependence of dc resistivity and thermoelectric power. As such, the system is considered here to provide a unique opportunity for the study of properties of materials when in composite form. Moreover, it is learnt that magneto-electric interactions introduce a number of peculiarities in ferroelectric phase transition besides exhibiting ME effect and the study on electro-physical properties in two-phase systems is relatively scant.

Experimental

These composites contain two individual phases, one ferroelectric and the other ferrimagnetic. The ferrimagnetic phase chosen is $\text{CuFe}_{1.8}\text{Cr}_{0.2}\text{O}_4$. It was prepared through normal solid state reaction taking CuO , Cr_2O_3 and Fe_2O_3 in appropriate molar proportion. The ferrite was presintered at 800°C for 10 hrs. Similarly, the

same route starting with BaO , PbO , and TiO_2 taken in appropriate molar proportion and presintered at 850°C for 4 hrs also prepared $\text{Ba}_{0.8}\text{Pb}_{0.2}\text{TiO}_3$ phase. After presintering, the constituent phases were thoroughly mixed together and the mixtures were presintered at 900°C for 12 hrs to prepare magnetoelectric composites of varying compositions of $\text{Ba}_{0.8}\text{Pb}_{0.2}\text{TiO}_3$ and $\text{CuFe}_{1.8}\text{Cr}_{0.2}\text{O}_4$. The $\text{CuFe}_{1.8}\text{Cr}_{0.2}\text{O}_4$, taken in 15, 30 and 45 mole percent, was dispersed in the matrix of 85, 70 and 55 mole percent of $\text{Ba}_{0.8}\text{Pb}_{0.2}\text{TiO}_3$ respectively to prepare composites labeled as 85% BPT, 70% BPT and 55% BPT respectively. The pure ferroelectric phase was abbreviated as 100% BPT. These composites were then shaped to cylindrical pellets and subjected to final sintering at 1050°C for 24 hrs to yield the final materials.

Powder X-ray diffraction patterns of the samples were recorded using Phillips X-ray diffractometer (PW 1710 model). For the measurement of dielectric properties, the pellet surfaces were polished and silver coated for electroding the samples. Capacitance and dielectric loss were measured as a function of temperature (25 – 225°C) in the frequency range 100 Hz – 1 MHz using LCR meter (HP 4284A). AC conductivity was derived from the dielectric data. Thermoelectric power of these samples was measured by producing a thermal gradient ($\Delta T = 25^\circ\text{C}$) across the sample by a small heater attached to the end of one of the hard electrodes of the sample holder. Sufficient time was let for thermal stabilization. The thermoemf (ΔE) was measured at different ambient temperatures of the samples. The thermoelectric power was determined by using the relation:

$$\alpha = \Delta E / \Delta T \quad (1)$$

To realise ME signal in composites, the samples were poled electrically and magnetically separately following Boomgaard et al. [4]. ME coefficient was measured as a function of static magnetic field. For this a specially designed sample holder having two perspex sheet of an area nearly 17 cm^2 were used in which two copper electrodes were brazed to the electrical leads separately and were kept on the either side of the poled sample. The whole sample holder assembly was then kept between the two pole pieces of a DC electromagnet. All stray pick-ups were avoided by proper grounding of experimental set-up. The leads from the two ends of the sample were connected to multimeter (Kiethley) through a shielded cable. The

resulting voltage was then measured as a function of intensity of magnetic field. The ME conversion factor was then obtained at different values of magnetic field by calculating the slopes at different points on the curve of voltage (electric field) versus magnetic field [6].

Results and Discussions

Figure 1 indicates the XRD of 55% BPT composite. From the XRD, it is clear that both $\text{CuFe}_{1.8}\text{Cr}_{0.2}\text{O}_4$ and $\text{Ba}_{0.8}\text{Pb}_{0.2}\text{TiO}_3$ phases are present. Both the phases have tetragonal type of crystal structure. The lattice constants for $\text{CuFe}_{1.8}\text{Cr}_{0.2}\text{O}_4$ phase are $a = 8.0337 \text{ \AA}$ and $c = 8.62554 \text{ \AA}$ ($c/a = 1.073$) and for $\text{Ba}_{0.8}\text{Pb}_{0.2}\text{TiO}_3$ phase, the values are $a = 3.9787 \text{ \AA}$ and $c = 4.345 \text{ \AA}$ ($c/a = 1.092$). Particle size in all the composites were calculated using a few reflections widely spaced in 2θ range according to Scherrer's formula:

$$P_{\text{hkl}} = (k\lambda) / (\beta_{1/2} \cos \theta_{\text{hkl}}) \quad (2)$$

where $k = 0.89$ and $\beta_{1/2}$ = half peak width. The average particle size for $\text{CuFe}_{1.8}\text{Cr}_{0.2}\text{O}_4$ phase is $0.0569 \mu\text{m}$ and for $\text{Ba}_{0.8}\text{Pb}_{0.2}\text{TiO}_3$ phase is $0.0671 \mu\text{m}$.

The variation of dc resistivity with temperature is shown in the Fig. 2. The values of activation energy (ΔE_{ac}) calculated in the ferroelectric region and ferroelectric transition temperatures (T_c) are given in Table 1. These plots are similar to those of the doped ferroelectrics [9]. Plots depict that resistivity decreases with increase in temperature suggesting semiconductor type of behaviour. The linear variation in the ferroelectric phase suggest that Arrhenius law:

$$\rho = \rho_0 \exp(\Delta E_{\text{ac}}/kT) \quad (3)$$

is obeyed in the present ceramics, where ΔE_{ac} is the activation energy required for hopping of charges. The values of ΔE_{ac} greater than 0.2 eV in the present ceramics suggests that conduction is due to hopping of charges [9]. Variation of the Seebeck coefficient (α) with temperature for the composites is shown in the Fig. 3. The figure reveals that α decreases with temperature in the ferroelectric phase as the transition point is approached and becomes negative in the paraelectric state. In the paraelectric phase, α remains fairly constant. The transition temperatures are noted in Table 1. Since α is positive in the ferroelectric region the majority charge carriers are holes and is negative in the paraelectric state indicating electrons are the

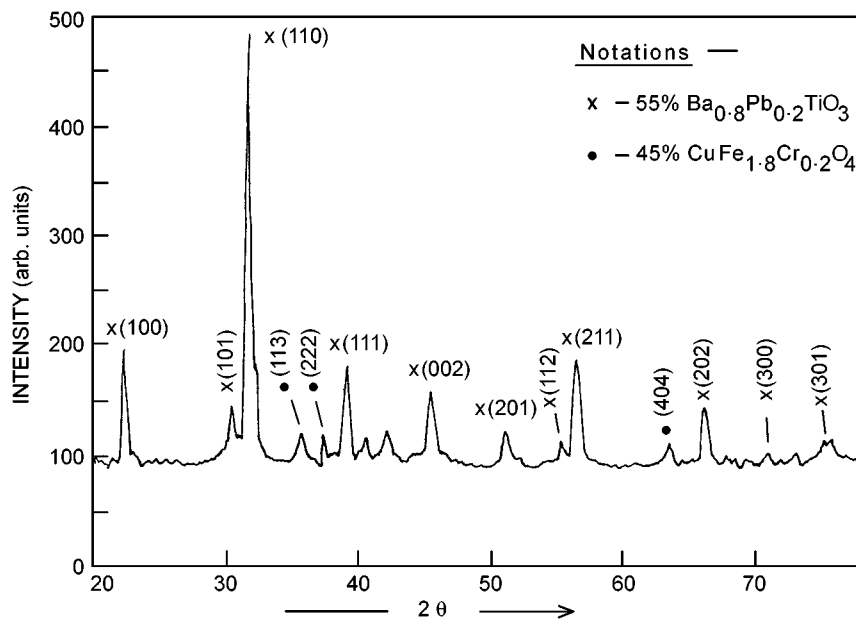


Fig. 1. XRD of 55% $\text{Ba}_{0.8}\text{Pb}_{0.2}\text{TiO}_3$ composite.

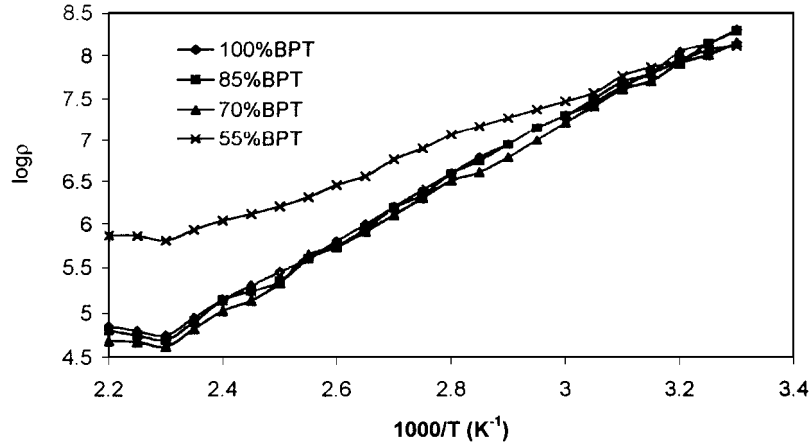


Fig. 2. Variation of dc resistivity with temperature.

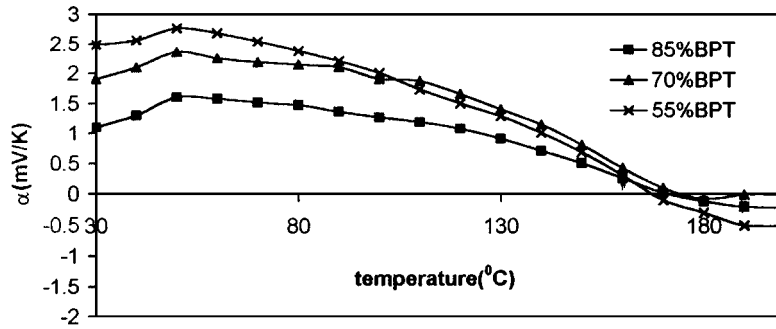
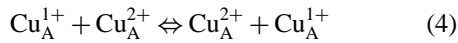


Fig. 3. Variation of Seebeck coefficient with temperature.

majority charge carriers. The results are similar to those obtained for the other ferroelectrics [10]. The conduction mechanism in the present case can be explained on the basis of the following reaction mechanism [11]:

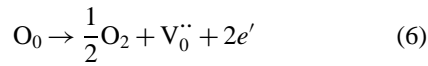
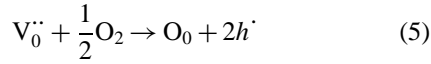


In the present composites of $\text{CuFe}_{1.8}\text{Cr}_{0.2}\text{O}_4$ – $\text{Ba}_{0.8}\text{Pb}_{0.2}\text{TiO}_3$, p-type conductivity increases with increase in $\text{CuFe}_{1.8}\text{Cr}_{0.2}\text{O}_4$ content (Fig. 3). This is due to release of holes as a result of transform of $\text{Cu}^{2+} \rightleftharpoons \text{Cu}^{1+}$. It is also well known that oxido-reduction process appears in air atmosphere in accordance with the following reactions, where all the

Table 1. Electric data on composites.

Composition	For 1 kHz				From σ_{ac} . S	α (mV/K)	ρ_{dc} ($10^7 \Omega - \text{cm}$)		
	ϵ'_{RT}	ϵ'_{max}	T_c	γ			ρRT ($10^7 \Omega - \text{cm}$)	E_{ac} (ev)	dE/dH ($\mu\text{V}/(\text{cm}^* \text{Oe})$)
100%BPT	173.4	323.32	160	1.3	0.43	1.04	20.36	0.695	–
85%BPT	352.3	413.4	165	1.4	0.76	1.1	19.68	0.595	Not detected
70%BPT	165.4	180.31	160	1.45	0.47	1.9	14.45	0.397	184.32
55% BPT	177.3	435.64	160	1.2	0.62	2.48	13.12	0.298	194.3

species are written in accordance with Kroger-Vink notation of defects [12].



The n-type conductivity in the paraelectric state is accounted by traces of Fe^{2+} ions, which may be present because of loss of oxygen occurring during sintering of these materials at high temperatures in accordance with the reaction (6). The electrons released in the reaction (6) are captured by Fe^{3+} to generate Fe^{2+} ions. In general, the large values of α ($\geq 100 \mu V/K$) are related to the localised electronic state for the oxide ceramics while small values of α ($\leq 30 \mu V/K$) indicate that the electronic state is metallic [13]. The values of α in the present samples are much greater than $100 \mu V/K$ suggesting polaron hopping type of conduction.

The frequency variation of ϵ' at room temperature for $Ba_{0.8}Pb_{0.2}TiO_3$ and its composites is shown in the Fig. 4. An examination of the figure reveals that all the samples exhibit dielectric dispersion. The ϵ' and $\tan \delta$ decrease rapidly at low frequencies and remain fairly constant at high frequencies, that is, beyond 10 kHz. The large values of dielectric constant at low frequencies in case of ionic crystals are due to voids, dislocations and other defects. In case of ceramic materials (ferrite and ferroelectric), this large value of ϵ' has been attributed to the effect of heterogeneity of the samples like pores and layered structures. However, in case of composites, the high value of ϵ' is ascribed to the fact that ferroelectric regions are surrounded by

non-ferroelectric regions similar to that in case of relaxor ferroelectric materials [7, 14]. This gives rise to interfacial polarisation which is reflected by sharp fall in ϵ' upto 10 kHz. Polaron hopping mechanism resulting in electronic polarisation also contributes to low frequency dispersion. These spurious effects cease to influence beyond a certain frequency. The static value of dielectric constant in the present samples lies in the range 75–130 and it is almost frequency independent beyond 10 kHz in case of composites. It is also noted from the figure that the value of ϵ' at 100 Hz increases with increase in $CuFe_{1.8}Cr_{0.2}O_4$ content (Fig. 4).

All the samples exhibit anomaly in the variation of their dielectric constant, ϵ' with temperature. Typical variation of ϵ' and $\tan \delta$ for 55% BPT at four different frequencies namely, 1 kHz, 10 kHz, 100 kHz and 1 MHz are shown in Fig. 5 and 6 respectively. Dielectric behaviour of all other samples is similar to this composition. ϵ' at room temperature, ϵ' at transition temperature (T_c) and T_c at 1 kHz frequency are given in Table 1. From Fig. 5, it is seen that the region around dielectric peak was broadened at all the frequencies. The broadening of the peak may be due to the microscopic heterogeneity in the composite [7]. A distribution of different local curie points results as different regions have different curie points. Thus the transition is of diffuse type [15].

In order to understand the conduction mechanism, ac conductivity was measured as a function of frequency in the range 100 Hz–1 MHz at 30°C. It is noted that the conductivity obeys the relation as given below [16, 17]:

$$\sigma_{ac} = A\omega^s \quad (7)$$

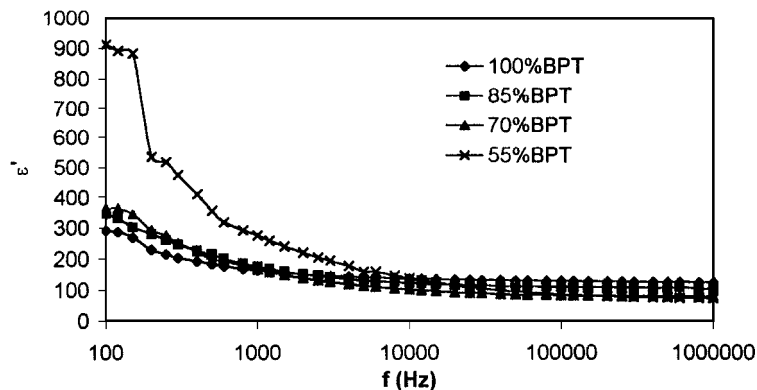


Fig. 4. Variation of dielectric constant versus frequency.

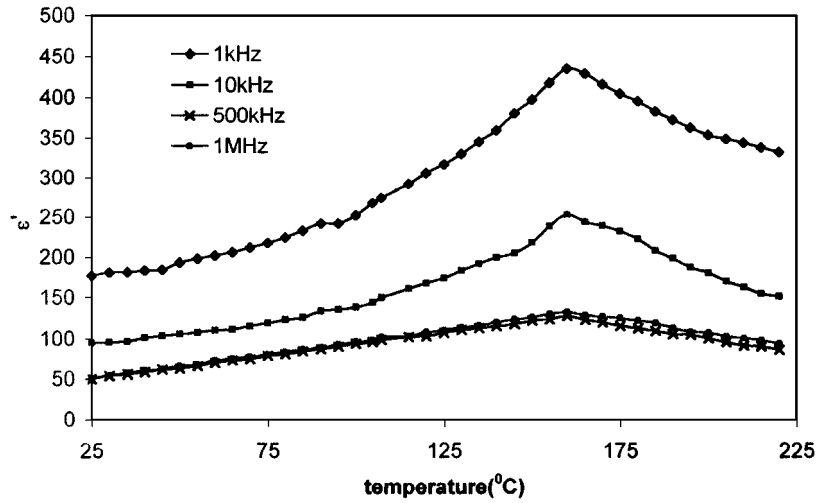


Fig. 5. Dielectric constant versus temperature for 55% Ba_{0.8}Pb_{0.2}TiO₃ composite.

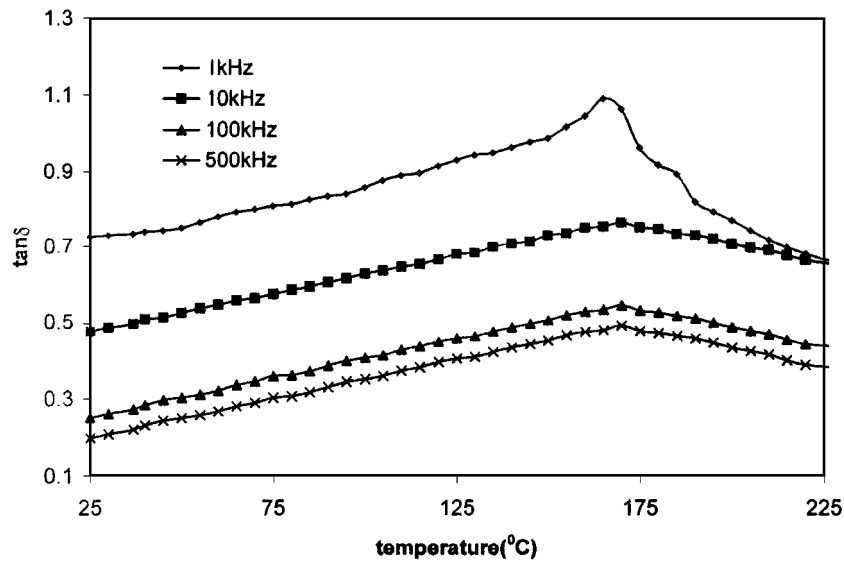


Fig. 6. Variation of loss tangent with temperature for 55% Ba_{0.8}Pb_{0.2}TiO₃ composite.

Value of s found by least square fitting of data is given in Table 1. Frequency dependence of ac conductivity in these samples show that conduction occurs by hopping of charges among localised states [18, 19]. Moreover, Adler and Fienleib [20] have shown that for conduction by small polarons the conduction increases with increase in frequency and following relation holds good.

$$\sigma_{ac} - \sigma_{dc} = (\omega^2 \tau^2) / (1 + \omega^2 \tau^2) \quad (8)$$

where ω is the angular frequency and τ is the staying time ($\sim 10^{-10}$ sec). Therefore for the frequencies $\omega^2 \tau^2 < 1$ the plot of $\log(\sigma_{ac} - \sigma_{dc})$ vs. $\log \omega^2$ should be a straight line. For the present samples the plots are straight lines as shown in the Fig. 7. This indicates the conduction is due to small polarons in the present ceramics.

The variation of static magnetoelectric conversion factor (dE/dH) as a function of magnetic field is shown in the Fig. 8. In case of 15% CuFe_{1.8}Cr_{0.2}O₄

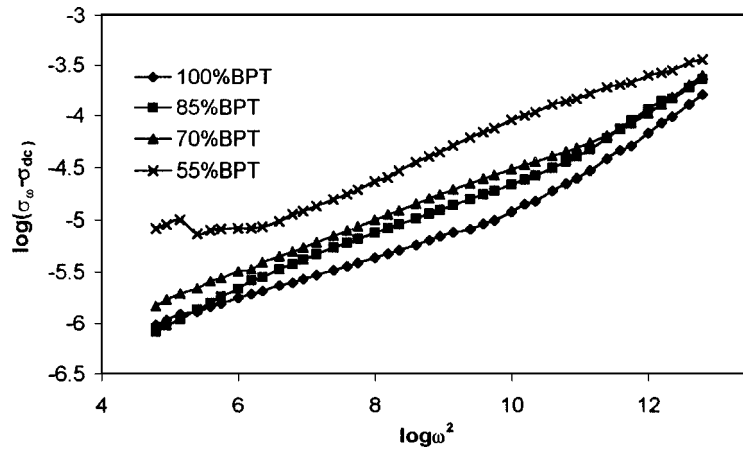


Fig. 7. Variation of $\log(\sigma_{ac} - \sigma_{dc})$ with $\log \omega^2$ at room temperature.

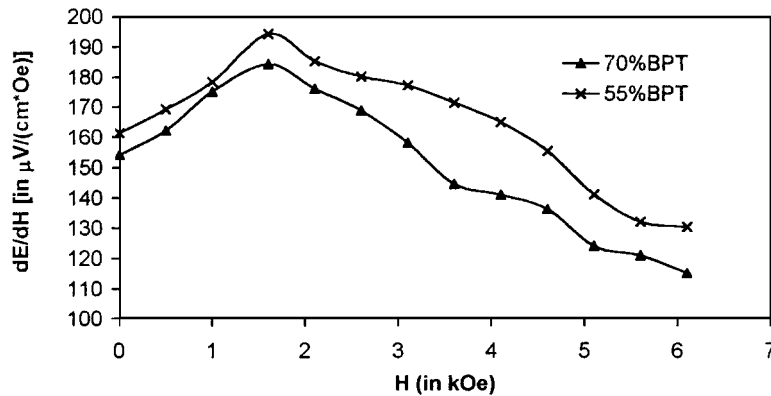


Fig. 8. Variation of static magnetoelectric conversion factor with intensity of static magnetic field.

composite no ME signal was detected. This is due to very weak magnetoelectric interactions in this composite [4, 5]. However in case of 30% and 45% $\text{CuFe}_{1.8}\text{Cr}_{0.2}\text{O}_4$ composite, ME signal resulted, which is due to the enhancement in elastic interaction with increase in $\text{CuFe}_{1.8}\text{Cr}_{0.2}\text{O}_4$ content [21]. The order of the magnitude of ME signal (dE/dH) is akin to $\text{NiFe}_2\text{O}_4 - \text{BaTiO}_3$ composites, though NiFe_2O_4 is highly magnetostrictive ferrite when compared with the present ferrite [6]. In the present system we attribute the appearance of ME signal to the strain induced by lattice distortion in ferrite phase by the Jahn-Teller ions like Cu and Cr [7]. Hence asserting the fact that Jahn-Teller effect in the ferrite can lead to the polarisation in the piezoelectric phase. From figure it is also clear that initial rise in dE/dH with increase in magnetic field is due to the enhancement in electric polarisation caused by the

magnetic strain developed by the increasing magnetic field. At 1.6 kOe, the magnetisation reaches its saturation confirmed from the hysteresis loop measurement studied by us. Therefore beyond this field the magnetostriction and strain thus produced would produce a constant electric field in the piezoelectric phase. This leads to decrease in dE/dH with increase in magnetic field beyond 1.6 kOe [6].

Conclusions

The present composites prepared by ceramic method have only ferrite ($\text{CuFe}_{1.8}\text{Cr}_{0.2}\text{O}_4$) and ferroelectric ($\text{Ba}_{0.8}\text{Pb}_{0.2}\text{TiO}_3$) in them. Hence the possibility of impurity phases being present and affecting the signal adversely is ruled out. The ferroelectric phase transitions are of diffused type. The transition temperature

of ferroelectric phase is not affected due the presence of other phase in the present composites, which is not similar to that reported earlier [7]. This indicates that the magnetoelectric interaction between the two phases in the present system is weak to cause any change in the ferroelectric phase transition. This may also be one of the reasons for the low output in ME signal. However the value of ME conversion factor is slightly higher compared to $\text{CuFe}_{1.6}\text{Cr}_{0.4}\text{O}_4\text{-BaTiO}_3$ system wherein a drastic change in ferroelectric phase transition. We attribute it to higher resistivity of present ferrite compared to $\text{CuFe}_{1.6}\text{Cr}_{0.4}\text{O}_4$, to impede the leakage of developed charge carriers in ferroelectric phase. Hence the choice of ferrite component is logical. Though no conclusive theory has yet been formulated to explain conduction in such samples, attempts have been made in the present paper to interpret the conduction phenomenon in terms of polaron hopping model.

Acknowledgment

The authors are grateful to DST, New Delhi for lending the financial support. One of the authors (KKP) offers her sincere thanks to DST for providing the senior research fellowship. The authors acknowledge their thanks to Prof. R.N. Patil, the former Head of physics Dept. Shivaji University Kolhapur for his constant encouragement and valuable suggestions.

References

1. I.P. Getman, *Sov. Phys. Dokl.*, **36**(3), 233 (1991).
2. M. Mahesh Kumar, A. Srinivas, S.V. Suryanaryana, G.S. Kumar, and T. Bhimasankaram, *Bull. Mat. Sci.*, **21**, 251 (1998).
3. A.M.J.G Van Run, D.R. Terrel, and J.H. Scholing, *J. Mater. Sci.*, **9**, 1710 (1974).
4. J. Vanden Boomgaard and R.A.J. Born, *J. Mater. Sci.*, **13**, 1536 (1978).
5. V.M. Laletin, *Sov. Tech. Phys. Lett.*, **17**, 1342 (1991).
6. S.V. Suryanaryana, *Bull. Mat. Sci.*, **17**, 1259 (1994).
7. K.K. Patankar, S.A. Patil, K.V. Sivakumar, Y.D. Kolekar, and M.B. Kothale, *Mat. Chem. Phys.*, **65**, 97 (2000).
8. R.P. Mahajan, K.K. Patankar, M.B. Kothale, and S.A. Patil, *Bull. Mater. Sci.*, **23**, 273 (2000).
9. O. Prakash, K.D. Mandal, C.C. Christopher, M.S. Sastry, and D. Kumar, *Bull. Mat. Sci.*, **17**, 253 (1994).
10. A.J. Kulkarni, S.P. Rasal, T.S. Magdum, and S.H. Chavan, *Bull. Mat. Sci.*, **16**(4), 297 (1993).
11. B.M. Kulkarni, M. Phil Thesis, Physics Dept. Shivaji University, Kolhapur, (1995).
12. I. Burn and S. Neirman, *J. Mater. Sci.*, **17**, 3150 (1982).
13. J.B. Goodenough, *Prog. Solid State Chem.*, **5**, 145 (1971).
14. S. Upadhyay, D. Kumar, and O. Prakash, *Bull. Mat. Sci.*, **19**, 513 (1996).
15. R.N.P. Choudhary, S.R. Shannigrahi, and A.K. Singh, *Bull. Mat. Sci.*, **22**(6), 75 (1999).
16. A. Jonscher, *Dielectric Relaxations in Solids* (Chelsea Dielectric Press, London, 1983).
17. Y. Yamazaki and M. Satou, *J. Appl. Phys.*, **12**, 988 (1973).
18. N.F. Mott and E.A. Davis, *Electronic Processes in Non-Crystalline Solids*, 2nd eds. (Clarendon Press, Oxford, 1979).
19. I.G. Austin and N.F. Mott, *Adv. Phys.*, **18**, 41 (1969).
20. D. Adler and J. Fienleib, *Phys. Rev.*, **B2**, 3112 (1970).
21. Ce-Wen Nan, *Phys. Rev. B.*, **50**, 6082 (1994).