

Electrical Behavior of $(y)\text{Cd}_{1-x}\text{Ni}_x\text{Fe}_2\text{O}_4+(1-y)\text{BaZr}_{0.2}\text{Ti}_{0.8}\text{O}_3$ Composites

G. N. Chavan¹, P. B. Belavi², L.R. Naik¹, B. K. Bammannavar³, K. P. Ramesh⁴

Abstract— The particulate composites of Cadmium Nickel ferrite (CNFO) and Barium-Zirconate-Titanate (BZT) ferroelectric were prepared by conventional solid state reaction technique. The presence of both phases in the composite were confirmed from XRD Analysis. The purity and stoichiometry of constituent phases of the composition were confirmed from Energy Dispersive X-ray (EDX) technique. The variation of dielectric constant (ϵ') and loss tangent in the frequency ranging from 40Hz up to 10MHz at room temperature and as a function of temperature (ranging from 30°C up to 650°C) at four different fixed frequencies (1kHz, 10kHz, 100kHz, 1MHz) were studied. Some irregular behavior of dielectric properties in the ME composites due to magnetoelectric interaction between ferromagnetic and piezoelectric phases were observed. The plot of dielectric constant with temperature shows a peak at the transition temperature. The AC conduction in the composites is due to hopping of charges between localized states. The DC resistivity of the ME composites were studied as a function of temperature, ranging from room temperature up to 800°C.

Index Terms— Ferrite, piezoelectric, composites, EDX, dielectric constant, loss tangent.

1 INTRODUCTION

Ferroelectromagnetic composite materials consisting of piezomagnetic and piezoelectric phases show magnetoelectric (ME) effect [1]. The ME effect is an induced dielectric polarization of a material in an applied magnetic field, and/or the induced magnetization in an applied external electric field. ME materials can be used as magnetic sensors for DC or AC magnetic field measurements, transducers or actuators, microwave field measurements, radio electronics etc. [2-3]. The ME effect was first observed in antiferromagnetic single crystal, Cr_2O_3 in 1961 and latter many single phase crystal families were found which have a smaller ME effect. Astrov confirmed it by measuring the induced electric field due to magnetization, and Rado by measuring the magnetic field due to induced polarization [4-6].

In last few decades, there is a thrust to overcome the problems of single phase magnetoelectric materials, which show low ME voltage and requires low temperature condition. Thus in order to overcome this problem, many particulate composite materials have been developed using piezoelectric and magnetostrictive materials, which show higher ME voltage [7-8]. Most of the single phase ME compounds have a complicated crystal structure and show output at low temperatures where as these composites, show a product property due to the effect of both ferrite and ferroelectric phases, which cannot be shown by their constituent phases alone. The ME (Piezoelectric/ferrite) ceramic composites are found to have larger ME output due to the magnetic - mechanical - electrical interaction between the piezoelectric and ferrite phases. Boomgaard et al [9-10] in 1978, stated that the ME effect in these

composites mostly depend on:

- i. chemical equilibrium of individual phases
- ii. molar percentage of ferrite and ferroelectric phase
- iii. magnetostriction coefficient of ferrite phase and piezoelectric coefficient of ferroelectric phase
- iv. resistivity of the sample and
- v. mechanical coupling between the grains

There are many factors based on which ferrite and ferroelectric phases are selected. The main factors are that the constituent ferrite phase should have high magnetostrictive coefficient and the ferroelectric phase should have high piezoelectric coefficient and high dielectric constant. In the present work, we have selected Ni substituted Cd ferrite since it is one of the well known ferrite having high magnetostriction coefficient [11]. The ferroelectric $\text{BaZr}_{0.2}\text{Ti}_{0.8}\text{O}_3$ (BZT) is one of the constituent phases of ME composites. The most popularly studied ferroelectric material is barium titanate (BaTiO_3), since it has high dielectric constant and low loss tangent. In the present case we have substituted zirconium in barium titanate to get the required ferroelectric phase. The substitution of Zr^{4+} was carried out as it is chemically more stable than Ti^{4+} [12-13]. The principal motivation of the present work is to investigate the overall electrical properties of such simple CNFO/BZT particulate composites.

2 EXPERIMENTAL DETAILS

2.1 Preparation of composites

The individual phases of ferrite and ferroelectric were prepared by conventional solid state reaction technique. The ferrite phase chosen was $\text{Cd}_{1-x}\text{Ni}_x\text{Fe}_2\text{O}_4$, was prepared by taking AR grade of CdO, NiO and Fe_2O_3 powders. The oxides were weighed in the required molar proportions and milled in an agate mortar for several hours to get a homogeneous mixture of the oxides. Further, this mixture was pre-sintered at 800°C for 8 hours in a furnace. Similarly, the ferroelectric

- L. R. Naik, G. N. Chavan, Department of studies in Physics, Karnatak University, Dharwad - 580003, India. PH-01123456789. E-mail: naik_36@rediffmail.com
- P. B. Belavi, Gogte college of Engineering, Belgaum, India.
- B. K. Bammannavar, Govt Polytechnic college, Joida, India
- K. P. Ramesh, Department of Physics, Indian Institute of Science, Bangalore, India.

phase $BaZr_{0.2}Ti_{0.8}O_3$ was prepared separately by milling AR grade of $BaCO_3$, ZrO_2 , and TiO_2 in required molar proportions and sintered at $800^\circ C$ for 8 hours. After pre-sintering the individual phases, the constituent phases were thoroughly mixed together with the general formula $(y)Cd_{1-x}Ni_xFe_2O_4 + (1-y)BaZr_{0.2}Ti_{0.8}O_3$ where y varies as 0.1, 0.2, 0.3 mol% to get the ME composites. The mixtures were sintered at $800^\circ C$ for 8 hours. The sintered mixture were mixed with 10% of polyvinyl alcohol (PVA) as a binder agent and were pressed into pellets of 1.1 cm diameter and 2-3 mm thickness using hydraulic press by applying pressure of 7 tons/cm². The pellets were finally sintered at $1150^\circ C$ for 12 hours in a furnace and cooled to room temperature in air to get the final ME composites.

2.2 Characterization

X-ray Diffractometer of type XPERT PRO with $CuK\alpha$ ($\lambda = 1.5424 \text{ \AA}$) radiations was used to characterize and confirm the presence of constituent phases in the prepared composites. The purity and stoichiometry of the composition of the constituent phases after final sintering were confirmed using Energy Dispersive X-ray (EDX) technique (ESEM Quanta 200, FEI). Agilent 4294 A impedance analyzer was used to study the AC parameters such as capacitance (C) and dissipation factor (D) as a function of frequency (40 Hz to 110 MHz) at room temperature and as a function of temperature for four different fixed frequencies (1kHz, 10kHz, 100kHz, 1MHz). The variation of dielectric constant and loss tangent with frequency and with the temperature were recorded. The disk shaped samples were coated with silver paste on both sides for good electric contact.

3 RESULTS AND DISCUSSION

3.1 Phase determination

Figure (1) shows XRD patterns of the particulate composites with $(y)Cd_{0.9}Ni_{0.1}Fe_2O_4 + (1-y)BaZr_{0.2}Ti_{0.8}O_3$ with $y = 0.1, 0.2$ and 0.3 . All the peaks were identified and indexed using standard XRD data.

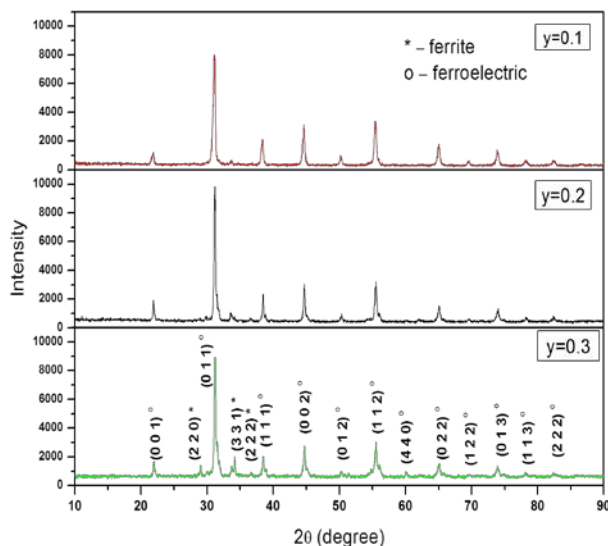
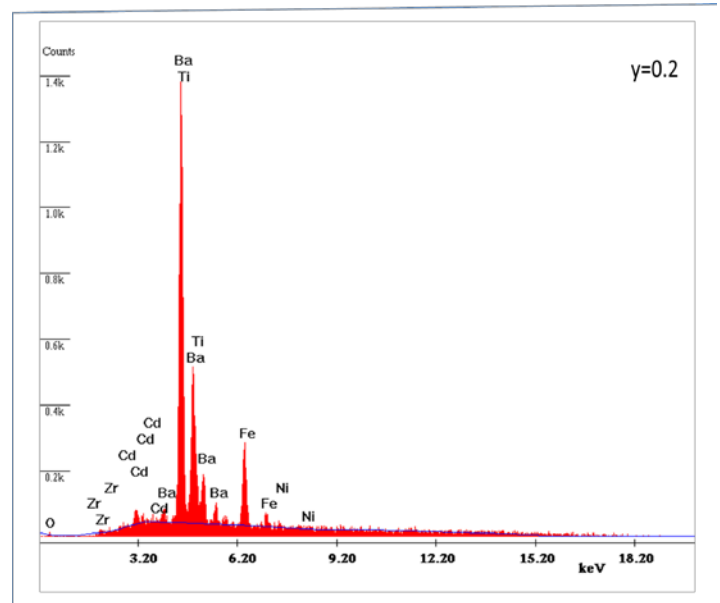
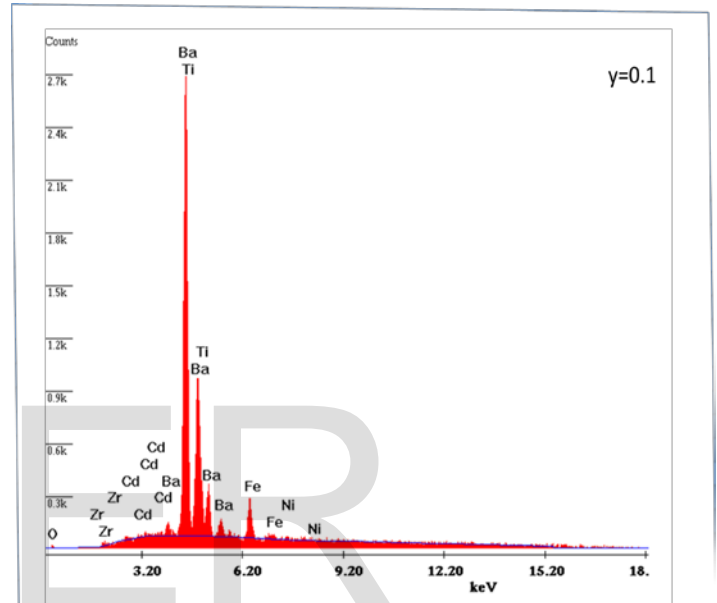


Figure 1: XRD of $(y)Cd_{0.9}Ni_{0.1}Fe_2O_4 + (1-y)BaZr_{0.2}Ti_{0.8}O_3$

The diffraction peaks are the characteristics of constituent phases, confirming the spinel cubic ferrite and tetragonal perovskite crystal structure. It is observed that there exist two sets of well defined reflections in the composite. The intense $(3\ 1\ 1)$ reflection peak is due to spinel cubic ferrite and $(0\ 1\ 1)$ reflection peak is due to tetragonal perovskite structure. No unidentified or impurity peaks were observed, which suggests that no chemical reaction or structural changes occurred between ferrite and ferroelectric phases during the final sintering of composites [13-14].



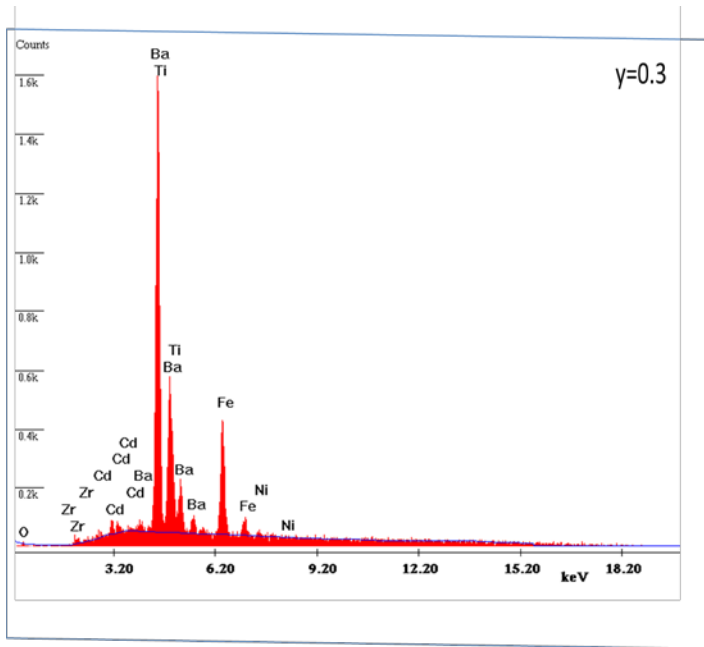


Figure 2: EDX of $(y) \text{Cd}_{0.9}\text{Ni}_{0.1}\text{Fe}_2\text{O}_4 + (1-y) \text{BaZr}_{0.2}\text{Ti}_{0.8}\text{O}_3$

A comparison of XRD pattern of all the samples show that the intensity of the (0 1 1) reflection peak of ferroelectric phase decreases whereas the intensity of the (3 1 1) peak of ferrite phase increases with an increase in the mol% of ferrite in the composites [4]. The Energy Dispersive X-ray (EDX) of the samples is shown in Figure (2). The EDX spectrograph reveals no trace of any peak other than the elemental peaks of the constituent phase elements confirming purity and stoichiometry of the composition of the constituent phases after final sintering.

3.2 Dielectric properties

a. As a function of frequency

The variation of dielectric constant (ϵ') as a function of frequency at room temperature is shown in Figure (3). In the higher frequency range, the dielectric constant decreases rapidly with increase in frequency. This suggests dispersion due to Maxwell - Wagner [15-16] type of interfacial polarization and which is in good agreement with Koop's phenomenological theory [17]. The dielectric constant attains a constant value at higher frequencies and becomes independent of frequency beyond 10 kHz. As that in case of relaxor ferroelectric samples, ferroelectric regions are surrounded by non-ferroelectric/ferrite regions and the space charge polarization in composites is attributed for the high dielectric constant at lower temperature. The dielectric behavior in the composite samples is due to the polarization mechanism in ferrites. The dipolar oscillations in ferrites are due to the presence of Fe^{3+} ions and minority Fe^{2+} ions which are also responsible for the conduction mechanism. The conduction in composites beyond phase percolation limits was due to the ferrite phase. Orientational polarization was due to the rotational displacement of

dipoles in ferrite phase. In the ferrites, the rotation of $\text{Fe}^{2+} \leftrightarrow \text{Fe}^{3+}$ dipoles may be due to the exchange of electrons between the ions so that dipoles align themselves with the applied alternating field [18]. The charge moment would cause a relaxation to the polarization in the direction of applied field.

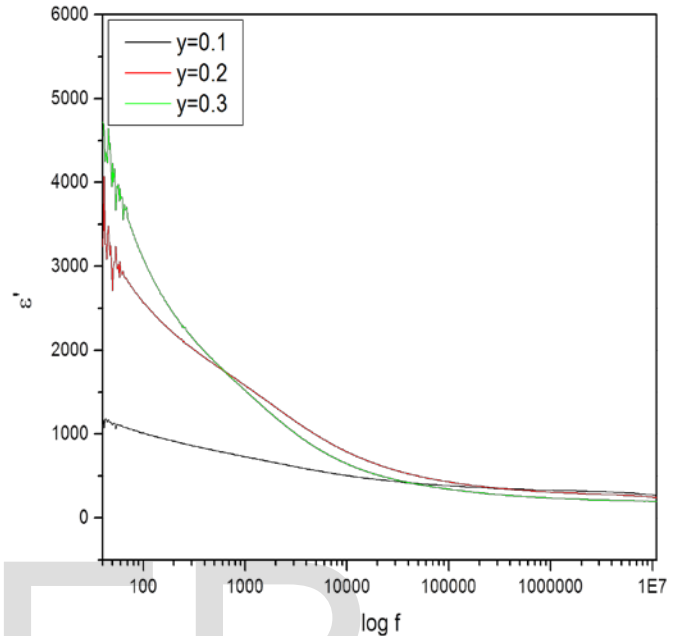


Figure 3: Variation dielectric constant with frequency for $(y) \text{Cd}_{0.9}\text{Ni}_{0.1}\text{Fe}_2\text{O}_4 + (1-y) \text{BaZr}_{0.2}\text{Ti}_{0.8}\text{O}_3$

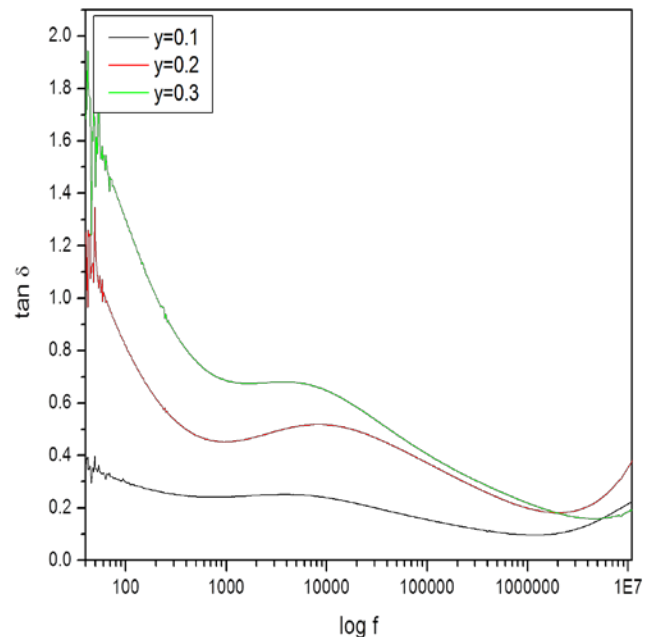


Figure 4: Tangent loss with frequency for $(y) \text{Cd}_{0.9}\text{Ni}_{0.1}\text{Fe}_2\text{O}_4 + (1-y) \text{BaZr}_{0.2}\text{Ti}_{0.8}\text{O}_3$

The decrease in the value of dielectric constant may attribute

to the fact that the electron exchange between Fe^{2+} to Fe^{3+} does not follow the alternating field [19]. The dielectric constant is found to increase with the increase of mol% of ferrite content in the composites. The $\tan \delta$ variation with frequency shown in Figure (4) shows similar behavior as of ϵ' with frequency. However in all the composites the loss tangent increases with temperature, irrespective of ferrite or ferroelectric transition temperature.

b. As a function of temperature

Figure (5) shows the variation of ϵ' with temperature in the range of 30°C to 650°C at fixed frequency of 1kHz for $(y)\text{Cd}_{0.9}\text{Ni}_{0.1}\text{Fe}_2\text{O}_4 + (1-y)\text{BaZr}_{0.2}\text{Ti}_{0.8}\text{O}_3$ with $y = 0.1, 0.2$ and 0.3 . Some irregular variation was observed in dielectric constant with temperature.

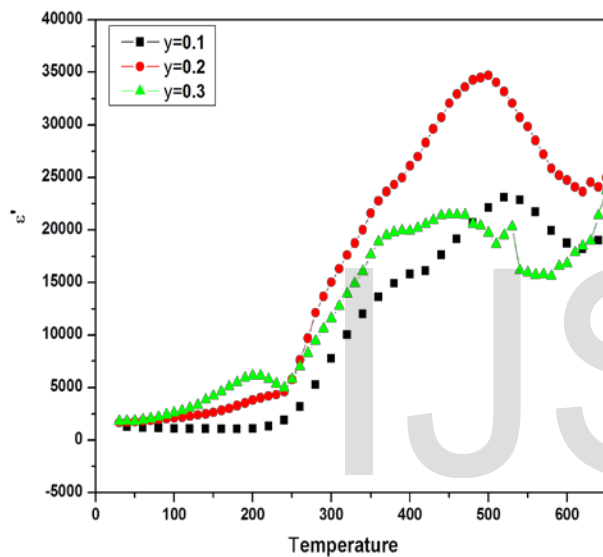


Figure 5: Variation of dielectric constant with temperature for constant frequency of $(y)\text{Cd}_{0.9}\text{Ni}_{0.1}\text{Fe}_2\text{O}_4 + (1-y)\text{BaZr}_{0.2}\text{Ti}_{0.8}\text{O}_3$

The dielectric constant remains unvaried from room temperature to 220°C and then attains a maximum value (23081) at 520°C followed by a decreasing trend with increase in temperature indicating phase transition. The broad diffused peaks are observed and the transition temperatures are very near to that of antiferromagnetic transition temperature. It is to be noted that hopping of electrons causes the conduction in ferrite and also hopping causes local displacement in the direction of external field, influencing dielectric polarization in ferrites. The hopping of electron between Fe^{2+} to Fe^{3+} ions and hopping of hole between Ni^{3+} and Ni^{2+} ions in B sites in the spinel structure are responsible for electrical conductivity. The increase of AC conductivity with temperature was due to the increase in drift mobility of thermally activated electrons, thus the dielectric polarization increases causing an increase in dielectric constant and loss tangent. In addition, as ferrites are basically ionic solids, there is an inherent ionic polarization. Hence there is a net increase in dielectric constant with temperature. The dielectric constant decreases after passing through the

transition temperature as the further rise in temperature will result in increase in relative vibrational motions of the ions and electrons which fail to align themselves with the alternating field [20]. The dielectric constant observed at transition temperature (for 1 kHz fixed frequency) are 23081, 34497 and 21447 for $y = 0.1, 0.2$ and 0.3 respectively. The phase transition temperature shifts towards lower temperature as the ferrite content increases in composites. It can also be observed that the dielectric constant is maximum for $y = 0.2$ of ferrite in the composites. This can be explained on the fact that the dielectric constant for the constituent ferrite and ferroelectric phases alone with their composites vary in a random fashion at low frequencies. There are 10 possible ways of connectivities of diphase in composites, as the ferrite and ferroelectric grains are randomly mixed together in parallel and series mode. This makes it difficult to calculate the effective value of dielectric constant of the composite and also to predict a sum rule or rule of mixture do to the random variation in ϵ' . Thus earlier workers [19-22] have ignored dependence of ϵ' with y .

The Figure (6-8) shows variation of ϵ' with temperature for all composites ($y = 0.1, 0.2$ and 0.3) at four fixed frequencies (1 kHz, 10 kHz, 100 kHz and 1 MHz). It is observed that the dielectric constant in all the samples increases slowly and reaches to maximum value at Curie temperature. The dielectric constant starts decreasing with further increase in temperature for all values of y . The dielectric constant is maximum at 520°C for 1 kHz frequency. The peak becomes broader and shifts towards higher temperature at high frequencies.

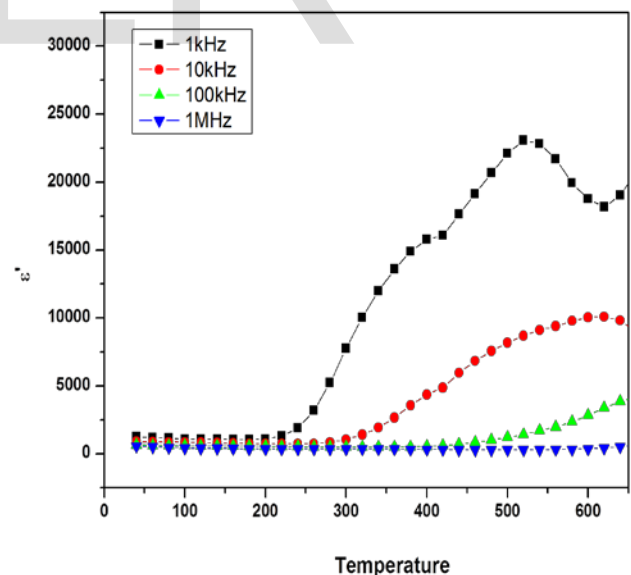


Figure 6: Variation of dielectric constant with temperature of $(0.1)\text{Cd}_{0.9}\text{Ni}_{0.1}\text{Fe}_2\text{O}_4 + (0.9)\text{BaZr}_{0.2}\text{Ti}_{0.8}\text{O}_3$

At 1 MHz and beyond the peak is likely to occur beyond the investigation range of temperature. Due to the rise in temperature the electrons are thermally activated and this increases the electron hopping between Fe^{2+} and Fe^{3+} ions. This electron

hopping causes local displacement in the direction of the applied external field.

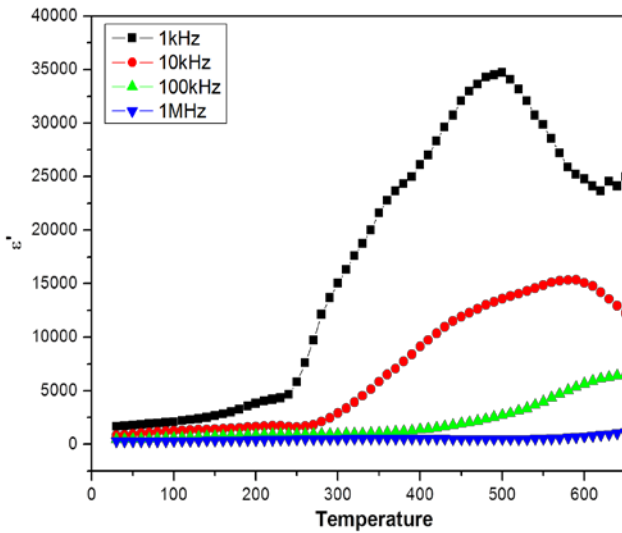


Figure 7: Variation of dielectric constant with temperature of (0.2) $\text{Cd}_{0.9}\text{Ni}_{0.1}\text{Fe}_2\text{O}_4$ + (0.8) $\text{BaZr}_{0.2}\text{Ti}_{0.8}\text{O}_3$

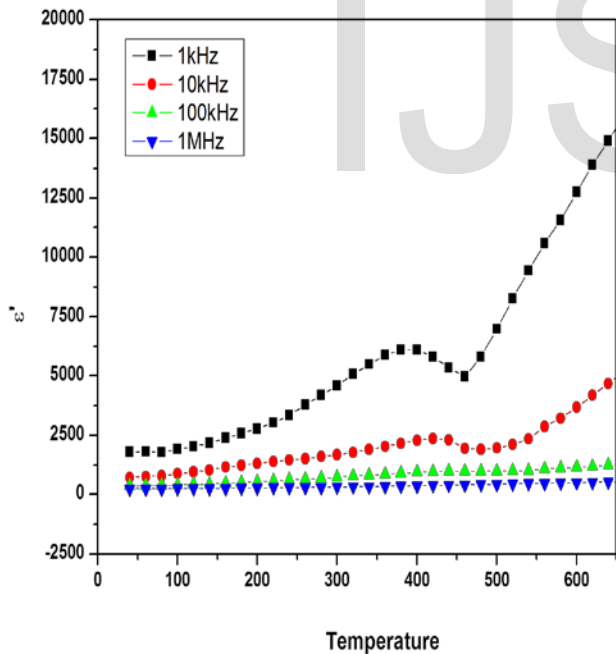


Figure 8: Variation of dielectric constant with temperature of (0.3) $\text{Cd}_{0.9}\text{Ni}_{0.1}\text{Fe}_2\text{O}_4$ + (0.7) $\text{BaZr}_{0.2}\text{Ti}_{0.8}\text{O}_3$

On increase in temperature beyond 520°C at 1 kHz, the vibrational motion of ions become random and fails to align in the field direction, and hence, the dielectric constant decreases [20, 22]. The shift in the diffused maxima towards higher temperature with the increase in frequency is analogous to the behavior

observed in relaxor ferroelectric. One cannot rule out the possibility of such variation as ceramic ferrites have heterogeneous microstructure [23]. These transition temperatures are close to the ferrite transition temperature. The ME interaction in composites exhibits shift in magnetic transition due to an external field. Thus the transition temperature in the composites shift towards lower temperature as ferroelectric content increases in the composites, since the transition temperature of the ferroelectrics is very low than that of ferrites.

3.3 AC conductivity

The frequency dependence of AC conductivity is shown in Figure (9). The AC conductivity is observed to increase with increase in frequency for all the composites. The plots of σ_{ac} with frequency are linear attributing to the fact that the conduction occurs due to the hopping of charge carriers between localized states. In all the

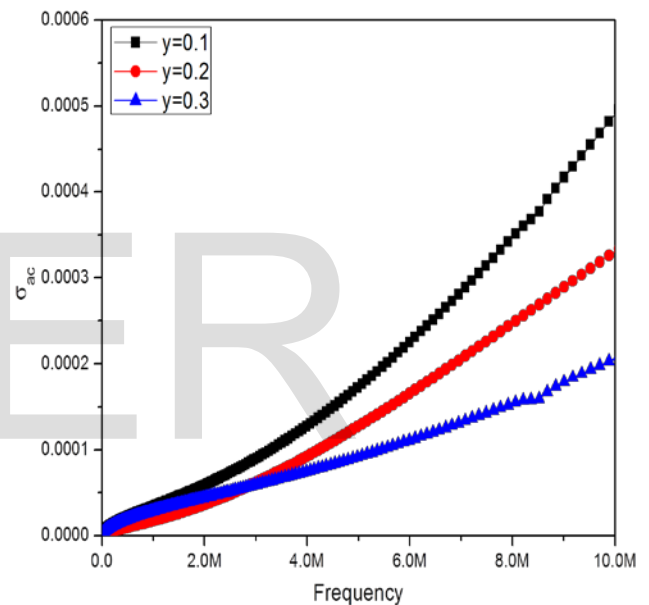


Figure 9: Variation of AC conductivity with frequency for (y) $\text{Cd}_{0.9}\text{Ni}_{0.1}\text{Fe}_2\text{O}_4$ + (1-y) $\text{BaZr}_{0.2}\text{Ti}_{0.8}\text{O}_3$

composites, the linearity of plots confirms the small polaron type conduction.

3.4 DC conductivity

The Figure (10) shows the DC resistivity as a function of temperature ranging from room temperature to 800°C. The variation of resistivity with temperature in the present case is

obtained using the Arrhenius relation

$$\rho = \rho_o \left(\frac{\Delta E}{kT} \right)$$

Where ρ is resistivity, ρ_o is temperature independent constant,

ΔE is the activation energy, k is the Boltzmann constant and T is absolute temperature. The resistivity decreases with the increase in temperature and is attributed to the increase in the drift mobility of the charge carriers. It is also observed from the graphs that the resistivity decreases with increase of ferrite content in the composites. According to conduction mechanism, decrease in the resistivity with the increase in ferrite content is due to the low resistivity value of ferrite phase compared to that of ferroelectric phase. All the samples show a break in the conduction at the transition temperature. There are two mechanism involved in the conduction process in the ME composites.

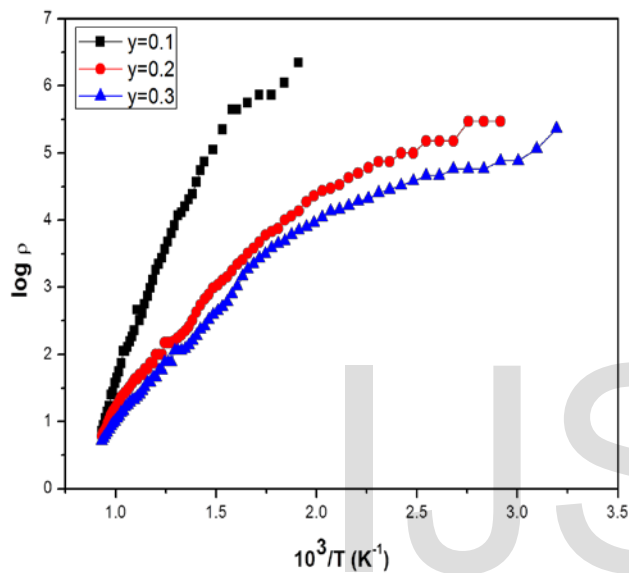


Figure 10: Variation of resistivity with temperature for (y) $\text{Cd}_{0.9}\text{Ni}_{0.1}\text{Fe}_2\text{O}_4 + (1-y)\text{BaZr}_{0.2}\text{Ti}_{0.8}\text{O}_3$

The conduction below the transition temperature ($T < 230^\circ\text{C}$) is due to the impurities and that of above the transition temperature ($T > 230^\circ\text{C}$) is attributed to the hopping of charges between $\text{Fe}^{2+} \leftrightarrow \text{Fe}^{3+}$, $\text{Ti}^{3+} \leftrightarrow \text{Ti}^{4+}$, $\text{Zr}^{3+} \leftrightarrow \text{Zr}^{4+}$, $\text{Ba}^{2+} \leftrightarrow \text{Ba}^{3+}$. It is also observed that the transition temperature decreases with increase in the ferrite content in the composites. The activation energies calculated for the ME composites for $y=0.1, 0.2$ and 0.3 were 0.289 eV , 0.205 eV , 0.132 eV respectively. The electrons and holes keep hopping and which is responsible for the conduction in the composites. As the temperature increases the hopping phenomenon between the ions increases which results the decrease in resistivity. The activation energy decreases with the increase in the ferrite content in the composites.

4 CONCLUSION

Magetoelectric particulate composites consisting of $\text{Cd}_{1-x}\text{Ni}_x\text{Fe}_2\text{O}_4$ ferrite and $\text{BaZr}_{0.2}\text{Ti}_{0.8}\text{O}_3$ ferroelectric phases were prepared by ceramic method. The presence of constituent phases in the composites was confirmed by XRD analysis.

The EDX spectrographs show no trace of occurrence of chemical reaction in final sintering process. The variation of dielectric constant with mole ratio and with temperature at four different frequencies show the variation of phase transition with the variation of mole ratio of the constituent phases. The dielectric study also reflects the interaction between electric and magnetic phases of the composites. The linearity of AC conductivity confirms the small polaron type of conduction. The DC resistivity decreases with increase in temperature and it was due to the increase in the drift mobility of the charge carriers in the ferrite phase and also the transition temperature decreases with increase in ferrite content in the composites.

ACKNOWLEDGMENT

One of the authors G. N. Chavan is thankful to Sunil kumar, Department of Physics, IISc, Bangalore for his help during AC measurement and also acknowledges UGC for providing financial help as RFSMS research fellowship.

REFERENCES

- [1] J. Van Suchtelen, Phillips, Res. Rep.27, 28 (1972).
- [2] Junyi Zhai, Ning Chai, Zhan Shi, Yuanhua Lin and Ce-Wen Nan, J. Phys D: Appl. Phys. 37, 823-827 (2004).
- [3] Jung-ho Ryu, Shashank Priya, Kenji Uchino and Hyoun-EE Kim, Journal of electroceramics 8, 107-119 (2002).
- [4] S. S. Chougule and B. K. Chougule, Smart Materials and Structures 16, 493-497 (2007).
- [5] B. K. Bommanavar, G. N. Chavan, L. R. Naik, B. K. Chougule, Materials Chemistry and Physics 117, 46-50 (2009).
- [6] G. Srinivasan, E. T. Ramussen and R. Hayes, Physical Review B, 67, 014418-1-9 (2003).
- [7] S. R. Kulkarni, C. M. Kanamadi and B. K. Chougule, Journal of Physics and Chemistry of solids 67, 1607-1611 (2006).
- [8] N. Cai, J. Zhai, C. W. Nan, Y. Lin and Z. Shi, Physical Review B, 68, 224103-1-7 (2003).
- [9] J. V. Boomgaard, R. A. J. Born, J. Mater Sci 13, 1538-1548 (1978).
- [10] R. S. Devan, S. A. Lokare, D. R. Patil, S. S. Chougule, Y. D. Kolekar, B. K. Chougule, Journal of Physics and Chemistry of Solids 67, 1524-1530 (2006).
- [11] K. B. Modi, M. K. Rangolia, M. C. Chhantbar, H. H. Joshi, J. Mater Sci. 41, 7308-7318 (2006).
- [12] W. Zhang, X. G. Tang, K. H. Wong, H. L. W. Chan, Scripta Materialia 54, 197-200 (2006).
- [13] P. B. Belavi, G. N. Chavan, L. R. Naik, R. K. Kotnala, International journal of Nanoscience 11, 1240007-12 (2012).
- [14] R. C. Kambale, P. A. Shaikh, K. Y. Rajpure, P. B. Joshi and Y. D. Kolekar, Integrated Ferroelectrics, 121, 1-12 (2010).
- [15] J. C. Maxwell, Electricity and Magnetism, Oxford Univ. Press London, 1973.
- [16] K. W. Wagner, Ann. Phys. 40, 818 (1993).
- [17] C. G. Koop, Phys. Rev. 83, 121 (1951).
- [18] R. S. Devan, B. K. Chougule, Journal of Applied 101, 014109-14 (2007).
- [19] R. S. Devan, S. A. Lokare, D. R. Patil, S. S. Chougule, Y. D.

- Kolekar, B. K. Chougule, Journal of Physics and Chemistry of Solids 67, 1524 – 1530 (2006).
- [20] D. R. Patil, S. A. Lokare, R. S. Devan, S. S. Chougule, Y. D. Kolekar, B. K. Chougule, Journal of Physics and Chemistry of solids 68, 1522-1526 (2007).
- [21] V. L. Mathe, K. K. Patankar, R. N. Patil, C. D. Lokhande, Journal of Magnetism and Magnetic materials 270, 380-388 (2004).
- [22] K. K. Patankar, S. S. Joshi, B. K. Chougule, Physics Letters A 346, 337-341 (2005).
- [23] Jiang li Chen, Zhuo Xu, J. Mater Sci. Mater Electron 1007/s,10854-009-9938-8.

IJSER