CHAPTER VI

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SUMMARY AND CONCLUSIONS

A material composed of two or more phases as its constituent parts may be considered as a composite material. Piezomagnetic - piezoelectric composites have recently attracted considerable attention owing to their wide range of practical applications. They are useful as sensors, phase inverters, optical modulators, ferroelectromagnetic wave generators, optical wave-guides, etc. One of the most important scientific applications of these composites is that they give us precious information for determining the magnetic point groups and space groups and also the determination of magnetic and electric field induced phase transitions [1]. Some other important scientific applications are -

1) Accurate determination of magnetic phase transition temperatures and critical exponents.
2) Study of defects in magnetic phases.
3) Study of switching and poling of antiferromagnetic domains by simultaneous application of electric and magnetic fields
4) Magnetic and electric field induced phase transitions.

The above applications of magnetoelectric composites are due to the phenomenon of magnetoelectric effect (ME effect). Following the concept of product property as suggested by Van Suchtelen [2], a suitable combination of ferrite (piezomagnetic) and ferroelectric (piezoelectric) can give rise to magnetoelectric effect. The composites exhibiting ME effect are termed as 'magnetoelectric composites'. ME effect is due to the strain induced in the ferrite phase i.e. mechanically coupled to a stress induced in the ferroelectric phase. The coupling results in an electric voltage [2,3,4]. This effect results from the interaction between different properties of the two phases in the composites [5]. It is important to note that neither the ferrite nor the ferroelectric phase on its own exhibits ME effect, but suitable combination of these two phases can exhibit a remarkable magnetoelectric effect [2,5,6].

The recent interest and development of ferrite-ferroelectric composites results from the recognition of the potential for enhanced performance and the increasing need for a combination of desired material properties that often cannot be obtained in single phase materials. These composites having high values of magnetoelectric conversion factor are of practical interest because of their use in electronic devices [7].

The studies on ME composites in which (Ni, Co)Fe_2O_4 is ferrite phase and $BaTiO_3$ is a ferroelectric phase have been carried out by many workers [4,8-12]. This composite is most widely used because of its high value of magnetoelectric conversion factor. Although there has been an emphasis on the practical development of such composite materials, work related to electrical conduction is relatively scant. Moreover, the available work is confined to the measurement of magnetoelectric conversion factor (dE/dH) having ferrite phases highly magnetostrictive, especially Ni, Co or Ni-Co-Mn ferrites. Hence it was decided to carry out studies on preparation, characterization and electrical properties of $Ni_{1-x}Co_xFe_2O_4$ + $Ba_{0.8}Pb_{0.2}TiO_3$ ME composites with x = 0.5, 0.75 and 1. The composites prepared by us have higher content of ferroelectric phase. By substituting the value of x we get three composite series as, $Ni_{0.5}Co_{0.5}Fe_2O_4$ + $Ba_{0.8}Pb_{0.2}TiO_3$, $Ni_{0.25}Co_{0.75}Fe_2O_4$ + $Ba_{0.8}Pb_{0.2}TiO_3$ and $CoFe_2O_4$ + $Ba_{0.8}Pb_{0.2}TiO_3$. The samples were prepared for each composite series using the relation $xBa_{0.8}Pb_{0.2}TiO_3$ + (1-x) $Ni_{0.5}Co_{0.5}Fe_2O_4$ for the first series, where x = 1, 0.85, 0.70, 0.55 and 0. The work is presented in six chapters.

Chapter - I is introductory. It includes definition and classification of composites, need and advantages and magnetoelectric composites. It also includes historical background and applications. A review of literature and orientation of the problems is also included. The references are given at the end of the chapter.

Chapter - II deals with constituent phases viz. ferrite and ferroelectric. It has been divided into two sections. Section A includes ferrite phase in which introduction, historical developments and structure of spinel ferrite is given. It also includes theory of ferrimagnetism and applications of ferrites.

Section B includes ferroelectric phase in which introduction, definition and classification etc. are given. The crystal structure of $BaTiO_3$ and ferroelectric domain structure is explained. It includes dielectric properties, theory and application of ferroelectrics etc.

Chapter III deals with the preparation and characterization of ferrite - ferroelectric composites by XRD and SEM techniques. It has been subdivided into three sections for the sake of presentation. Section A includes the methods of preparation and actual preparation of the samples. The ferrite phase was prepared by standard ceramic method using AR grade $NiCo_3$, $CoCo_3$ and Fe_2O_3 powders. The ferroelectric phase was prepared using AR grade BaO, PbO and TiO_2 powders. The ferrite was presintered at 700^0C and ferroelectric at 900^0C for 12 hrs. After presintering, the individual phases were grounded in an agate mortar to fine powder. The ME composites were prepared by thoroughly mixing 85, 70 and 55 mole % of ferroelectric with 15, 30 and 45 mole % of ferrite respectively. The composite mixture was presintered at 800 ^{0}C again. The powders were ground to a fine powder and pressed into pellets (1cm diameter and 2-3 mm thickness). The compacts so prepared were finally sintered at 1100 ^{0}C for 24 hrs. The furnace was cooled at the rate of 80 ^{0}C per hour.

Section B deals with the XRD studies. The diffractogram were recorded on Phillips X-ray Diffractometer (Model PW 1710) using CuK_α (λ = 1.5418 Å) radiation. Indexing of the patterns was done by comparing the present data with the standard ASTM data. The lattice parameters and interplanar distances were calculated using the standard relations. The lattice parameters of the ferroelectric phase in composites match fairly well with the reported values [13,14]. Also, the lattice parameter of ferrite phases in composites match fairly well with the reported values [12]. The calculated and observed 'd' values are in good agreement with each other. The composites results with cubic spinel structure for ferrite phase and tetragonal perovskite structure for ferroelectric phase [12,15,16]. Similar is the case with the present composites.

The lattice parameters and the c/a ratios are found to vary slightly with change in mole % of either phase. Similar observations have been made earlier [17]. The porosity of the samples lies in the range of 10-15 %.

Section C deals with Scanning Electron Microscopy (SEM) studies of composites. The SEM micrographs were obtained from C-MET, Pune. The ME coefficient measured in different composites has shown that high ME effect is observed only when the mole ratio is 15% ferrite. Hence, microstructure of only composites having 15% ferrite and 85% ferroelectric phase was studied. The grain size is maximum for composite having $Ni_{0.5}Co_{0.5}Fe_2O_4$ and minimum for $Ni_{0.25}Co_{0.75}Fe_2O_4$ as ferrite phase. It is also observed that ME coefficient, resistivity and porosity is larger for the composite having $Ni_{0.25}Co_{0.75}Fe_2O_4$ as ferrite phase. The average grain size was calculated using the line intercept method. The grain growth for both the phases in the composite is less compared to that observed if the same phases exists separately, i.e., as single phases. It is obvious because the presence of two phases in the composite indicates that a grain of one phase is more probable to have a grain of the other phase as its neighbour. Hence the grain growth is hampered as the grain of a particular phases grows at the cost of the small grains of same kind by diffusion phenomenon.

Chapter IV deals with the 'sum' properties of the composites. It is divided into three parts. The first part deals with the measurement of the dielectric properties and ac conductivity, second part gives the measurement of dc resistivity and third part the TEP measurements. The nature of electrical conduction in these composites can be understood with the help of this study.

AC conductivity measurements were carried out in the frequency range 100 Hz to 1 MHz on LCR meter bridge HP 4284 A. The dielectric constant decreases with increase in frequency showing dispersion in a certain lower frequency range. This variation reveals that dispersion is due to Maxwell- Wagner type interfacial polarization [18,19] in agreement with Koop's theory [20]. Dispersion is large in compositions with large values of ε' in comparison to those with smaller values of ε'.

The values of dielectric constant for the constituent ferrite, ferroelectric phases along with their composites vary in a random fashion at lower frequencies. It is obvious as the ferrite and ferroelectric grains are randomly mixed together in parallel and series modes. Hence it would be difficult to calculate the effective value of the dielectric constant of composite and also to predict a sum rule or rule of mixtures due to random variations in ε'. The high values of dielectric constant observed at lower frequencies are explained on the basis of space charge polarization due to inhomogeneous dielectric structure and resistivity of the samples. The inhomogenities in the present system are impurities, porosity and grain structure. However, in case of composites, the high value of ε' is ascribed to fact that ferroelectric regions are surrounded by non ferroelectric regions similar to that in case of 'relaxor' ferroelectric materials [21]. This again gives rise to interfacial polarization.

The plots of tan δ versus frequency show that, for all the samples, it decreases continuously with frequency. All the samples show dispersion in tan δ at lower frequencies. The results are similar to those reported by other workers for other composites [22,23].

To know the nature of polarons (large or small) responsible for conduction, a study on variation of ac conductivity combined with dc conductivity with frequency at room temperature is undertaken. The plots are almost linear indicating that the conductivity increases with increase in frequency. It confirms the small polaron hopping mechanism of conductivity [24].

The variation of dielectric constant with temperature at four different test frequencies viz. 1 kHz, 10 kHz, 100 kHz and 1MHz was studied. The dielectric constant decreases with increasing test frequency. For $Ba_{0.8}Pb_{0.2}TiO_3$ i.e. for 100% ferroelectric sample, dielectric constant initially increases with increase in temperature, reaches a maximum value at the transition temperature (T_C = 195°C) and thereafter decreases. The transition temperature does not show any frequency dependence but the dielectric constant exhibits decrease in values for higher frequencies. For 100% ferrite samples, the value of dielectric constant is less as compared to the ferroelectric. It is obviously due to Verwey type of electron exchange mechanism in ferrite on one hand and polarization being an inherent property of ferroelectrics on the other. The polarization in ferrite can be explained on applying Koop's model [20]. The Tc observed for 100% $Ni_{0.5}Co_{0.5}Fe_2O_4$, 100% $Ni_{0.25}Co_{0.75}Fe_2O_4$ and 100% $CoFe_2O_4$ are 550°C, 540°C and 520°C respectively.

Anomalies are observed in all the composite series for 15% ferrite + 85% ferroelectric phase. There is only one sharp dielectric maximum is obtained at the ferroelectric Curie temperature (195^{0}C) for all test frequencies. The absence of a dielectric maximum at the ferrite curie temperature for this composite is a result of the relatively small amount of ferrite content in the composite available for initiation of the Verwey mechanism. This is supported by the fact that the X-ray diffractogram shows only three characteristic peaks of very low intensities corresponding to ferrite phase, in contrast to the much more intense peaks characteristic of the ferroelectric phase.

In all the three composite series for 30% & 45% ferrite phase samples there is one more dielectric maximum at 1 kHz and 10 kHz frequencies corresponding to the ferrite Curie temperature in addition to the dielectric maximum corresponding to ferroelectric Curie temperature. The absence of dielectric maximum for the 100 kHz & 1 MHz test frequencies can be explained on the basis that the electron exchange mechanism can not follow the applied electric field above a certain frequency [25,26]. The electric field induced magnetic phase transition depends on the strength of interaction between electric and magnetic ordering, which in turn depends on the molar ratio of the phases.

In all the three composite series, the loss tangent increases with increase in temperature, irrespective of ferrite ferroelectric transition temperature. Thus polaron hopping mechanism holds good for this type of variation.

The dc resistivity was measured using two probe method, from room temperature to 600^{0}C. It is observed that resistivity is maximum for 100% ferroelectric (i.e $Ba_{0.8}Pb_{0.2}TiO_3$) phase and minimum for 100% ferrite phase in all the three composite series. The resistivity of composites decreases with increase in ferrite content. There are two regions in the resistivity plots The first region at low temperature is attributed to the ordered state of ferroelectric phase in the composite while the second region is for paraelectric state of the composite. Hence the change in the activation energy is observed when transition from ferroelectric to paraelectric state takes place. Activation energy is maximum for pure ferroelectric phase and minimum for pure ferrite phase. The activation energy decreases as the ferrite content in the composition increases. The conduction in ferrite and ferroelectric phases is due to polaron hopping.

The thermoelectric power measurements of the samples were carried out from room temperature to 600 ^{0}C keeping the temperature difference of 20^{0}C across the cold and hot junctions. This study was done mainly to know the type of charge carriers responsible for conduction. At lower temperatures all the samples show positive values of Seebeck coefficient, which indicates that the charge carriers are of p-type. A p-n transition is observed in all the composites (i.e. in 15%, 30% and 45% ferrite phases) and in pure ferrite (i.e. 100% ferrite phase). The observed p- type conduction in pure ferroelectric and p-n transition for other samples in all the composite series are explained in terms of ions of variable valency. It is welknown that the evidence for polaron hopping conduction is the occurrence of p-n transition and the temperature independence of Seebeck coefficient [27].

Chapter V is concerned with the introduction to magnetoelectric effect as a 'product property' of composites, experimental setup for the measurement of ME conversion factor along with the brief description of electric poling and magnetic poling. The measurement of ME conversion factor as the function of magnetic field and mole ratio of the constituent phases for all the three composite series is carried out. There is a gradual decrease in dE/dH with increase in magnetic field. Also dE/dH decreases with increase in volume fraction of ferrite at all the field strength. The variation is similar to that obtained by other workers for different composites [4,9,15]. The maximum value of dE/dH is obtained for 15% ferrite + 85% ferroelectric phase in all the composite series. This is a result of decreased polarisability of ferroelectric phase in composite with higher ferrite content.

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