CHAPTER I

Magnetoelectric composites

Chapter I

MAGNETOELECTRIC COMPOSITES

SECTION A: MAGNETOELECTRIC COMPOSITES

1A.1 Introduction

The composite is a material which is composed of two or more physically distinct components, each of which by virtue of its own scientific properties plays main role in the functioning of the material. The development of composites is known for last 45 years and has been exploited for a number of applications. The study of composite materials has led to the development of a variety of devices which have found applications in man's everyday life. Presently composite materials assume various manifestations.

Most of the composite materials have been created to improve mechanical properties such as stiffness, toughness and strength. However, recently the interest has been shifted to use the composites for the electrical applications [1]. The magnetoelectric effect and magnetoelectric composites have gained much importance at present [2].

1A.2. Magnetoelectric Composites

The magnetoelectric (ME) effect is defined as an induced dielectric polarization of a material in an applied magnetic field and / or an induced magnetization in an external electric field [3]. The composites which exhibit ME effect are known as the "magnetoelectric (ME) composites". Composite materials containing piezoelectric (ferroelectric) and piezomagnetic (ferrite) phases exhibit ME effect [4]. The ME effect is however absent in the constituent phases. The mechanical coupling between magnetostrictive and piezoelectric phases is the origin of ME effect [5]. This process takes place under the application of magnetic field. When the magnetic field is applied to the ME composite, the mechanical deformation in ferrite phase induced by magnetostriction is mediated by mechanical stress and results in electric fields being induced due to the piezoelectric effect [6, 7]. So that suitable combination of constituent phases helps to obtain good ME effect. According to Boomgaard [ref] the following conditions are necessary for that.

1) The two phases must be in equilibrium.
2) The mechanical coupling between the two phases must be perfect.
3) The values of magnetostriction coefficient of piezomagnetic phase and piezoelectric coefficient of piezoelectric phase must be high.
4) The resistivity of the constituent phases must be high to avoid leakage current during poling.
5) To realize high ME output in composite proper poling strategy is to be adopted [8, 9].
6) The transition temperature (Tc) of either phase must be greater than the room temperature.

1A.3 Literature Survey

After the first observation of ME effect by Curie [10], Landau and Lifshitz [3] came to conclusion that the ME effect can exist in magnetically observed crystals. Though Dzyaloshinskii predicted the ME effect, Astrov [11] and Folen [12] reported the experimental evidence for both magnetoelectric and electromagnetic effects in Cr_2O_3 an antiferromagnetic. Afterwards a few single phase crystal family such as $Ni_3B_7O_{13}I$ were reported to exhibit ME effect at low temperature [13]. During this period the introduction of product property by Suchetelene [4] followed by Boomgaards [14] conceptual points for the preparation of ME composites, made researchers to think on the composite materials. Boomgaard et al. observed high ME output (130 mV/cm.Oe) in unidirectionally cooled Ni (Co, Mn) Fe_2O_4 and $BaTiO_3$ ME composites prepared by double sintering ceramic method. The coupling between ferroelectric and magnetic order parameter in a nanostructured $BaTiO_3$-$CoFe_2O_4$ ferromagnet is reported by Zheng et al. [15]. Considerable progress has been reported towards noticeable giant ME voltage coefficients in layers systems [16]. The systems studied so far include laminated thick films of lithium Zinc ferrite and lead zirconate titanate ME composites. The maximum ME output obtained was about 250 mV/cm.Oe.

In recent years particulate level composites have been attempted. Such materials are interesting from the stand point of production. Jun Yi Zhai et al. [2003] have studied the magnetoelectric properties of PZT/ Co Ferrite particulate composites using conventional solid state reaction method. The ME output value of 30.2 mV/cm.Oe has been obtained. Mahajan et. al. have studied Cobalt ferrite–Barium titanate composites and reported a maximum ME coefficient of 140 μV/cm. Oe [17]. ME composites of (x) $Ni_{0.8}Cu_{0.2}Fe_2O_4$ + (1-x) $Ba_{0.8}Pb_{0.2}Ti_{0.8}Zr_{0.2}O_3$ were studied by Kanamadi and observed Maximum ME coefficient 0.431 mV/cm/Oe [18]. The subsequent researches are done on systems such as (x) $Ni_{0.8}cu_{0.2}Fe_2O_4$ + (1-y) $Ba_{0.9}Pb_{0.1}Ti_{0.8}Zr_{0.2}O_3$, $Ni_{0.8}Co_{0.1}Cu_{0.1}Fe_2O_4$ + PZT, (x) $BaTiO_3$ + (1-x) $Ni_{0.94}Co_{0.01}Cu_{0.05}Fe_2O_4$, (x) $Ni_{0.8}Zn_{0.2}Fe_2O_4$ + (1-y) PZT etc. [19, 20, 21].

SECTION B: FERRITES

1B.1 Introduction

Mixed metal oxides with iron (III) oxides as their main component are known as ferrites [22]. Ferrites are industrially important ferrimagnetic materials. The structural, magnetic and electrical properties of these materials have been the subject of tremendous interest to physicist, chemist and materials scientists. Ferrites are semiconductors by nature and possess resistivity in the range 10^2 to 10^{11} Ω/cm.

After 1996, the development of ferrites had an enormous impact. Due to the property to stand at higher frequencies they are used in vast applications from microwave to radio frequencies. The advantage with ferrite is that they yield higher efficiency, low cost, greater uniformity and easier manufacture than that can be obtained with metals.

1B.2 Classification of ferrites

The classification of ferrites is done mainly on the basis of two concepts as,

a) Chemical composition

b) Crystal structure.

a) On the basis of chemical composition, ferrites are classified as,

I. Simple ferrites

In such ferrites ferrous ion in Fe_3O_4 is replaced by divalent metal ion like Co, Ni, etc. e.g. $NiFe_2O_4$, $CoFe_2O_4$

II. Mixed ferrites

In these types of ferrites ferrous ion in Fe_3O_4 is replaced by two other divalent metal ions like Ni, Co, Cd etc. without altering the stoichiometry of the system. e.g. $Co_{1-x}Cd_xFe_2O_4$, $Co_{1-x}Zn_xFe_2O_4$.

III. Substitutional ferrites

When divalent as well as trivalent iron ions are replaced by other magnetic or non magnetic ions in Fe_3O_4 then it forms substitutional ferrites.
e.g. $Zn_xMg_{1-x-y}Zr_yFe_{2-2y}O_4$.

b) Based on their crystal structure, ferrites have been classified into three main types viz.

i) Spinels
ii) Garnets
iii) Magnetoplumbites

Of these spinel and garnet ferrites have cubic structure while magnetoplumbites have hexagonal crystal structure.

1B.3 Spinel ferrites

Originally spinel ferrite is derived from mineral spinel $MgAl_2O_4$. The cubic structure of spinel ferrites was first determined by Bragg [23]. The unit cell consists of eight subcells of AFe_2O_4 where A is divalent metal ion. Due to face centered cubic lattice formed by 32 oxygen ions the lattice contains 96 interstitial sites of which 64 tetrahedral (A) and 32 octahedral (B) sites. The schematic diagram of the adjacent octants of a single unit cell of spinel ferrite is as shown in Fig1.1.

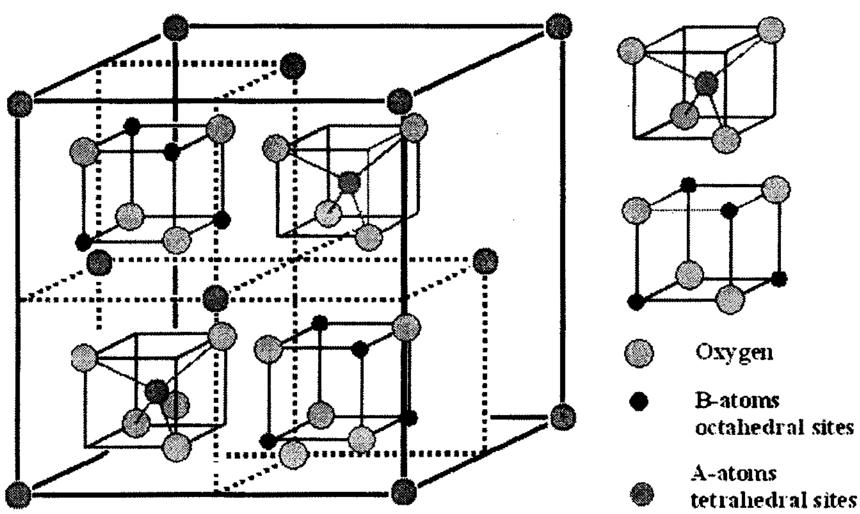

Fig.1.1 Position of the A site ions, B site ions and oxygen ions in spinel ferrite

Classification of spinel ferrites

On the basis of cation distribution in spinel ferrites they are classified as

i) Normal spinel ferrites

ii) Inverse spinel ferrites

iii) Random spinel ferrites

I Normal spinel ferrites

In these types of ferrites all divalent metal ions occupy A sites and all trivalent iron ions occupy B sites.

The cation distribution is $[M^{2+}]^A$ $[Fe^{3+}$ $Fe^{3+}]^B O_4^{2-}$, e.g. $CdFe_2O_4$

II Inverse spinel ferrites

In these spinels all 8 divalent metal ions and 8 out of 16 trivalent ions occupy B site and remaining 8 trivalent ions occupy A site.

The cation distribution is $[Fe^{3+}]^A$ $[M^{2+}$ $Fe^{3+}]^B O_4^{2-}$

e.g. $CoFe_2O_4$

III Random spinel ferrites

When divalent and trivalent metal ions get randomly distributed over A and B sites, then it results random spinel.

The cation distribution is $[Fe_{1-\delta}^{3+} M_{\delta}^{2+}]^{A} [M_{1-\delta}^{2+} Fe_{1+\delta}^{3+}]^{B} O_4^{2-}$
e.g. $CuFe_2O_4$

1B.4 Applications of ferrites

Ferrites play a useful role in many magnetic applications because their electrical conductivity is relatively low in comparison with that of magnetic metals. The most important application of non conducting ferrites is as square loop memory cores in computers. Semiconducting magnetic oxides are widely used as thermistors.

At present there is much interest in devices based on magneto-optical phenomena especially the Faraday Effect in garnets. High permeability ferrites find important applications in increasing the recording efficiency of magnetic heads stopples.

1B.5 Literature survey on Co-Cd Ferrites

Jonker [24] studied electrical conductivity of a series of ferrites $Co_{1-x}Fe_{2+x}O_4$ and observed two regions of conductivity. Josyulu and Shobhanadri [25] have investigated dc conductivity and dielectric properties of $CoxZn_{1-x}Fe_2O_4$(x = 0.32, 0.49, and 0.79) as a function of temperature and frequency. Petit and forester [26] investigated the mossbauer effect in Co-Zn ferrites and derived the cation distribution formula $[Zn_xFe_{1-x-y}Co_y]^A [Co_{1-x-y}Fe_{1+x+y}]^BO_4$

Currently there has been a fairly extensive amount of work directed towards the ferrites. Study of the cation distribution and susceptibility of Cd-Co and Cr^{3+} substituted Cd-Co ferrites has done by Vasambekar et.al. [27]. Vladmir Sepelak and Klara Tkacova have studied mechanically induced structural disordering in spinel ferrites. They concluded that in the process of mechanical activation of normal two basic structural phenomena take place. One is mechanically induced inversion and deformation of octahedron geometry [28]. Hemeda and Barakat have studied the effect of hopping rate and jump length of hopping electron on the conductivity and dielectric properties of Co-Cd ferrite. In which they studied effect of Cd additives on jumping rate, hopping length and diffusion of oxygen vacancies [29]. The structural and electrical transport phenomena of Co ferrite substituted by Cd have been studied by Abdeen, Hemeda, Assem and Elsehly [30].

SECTION C: FERROELECTRICS

1C.1 Introduction

Ferroelectrics are dielectric materials possessing spontaneous polarization which can be reversed by applying suitable electric field [31]. The dielectric materials are classified into 32 crystal classes or point groups, twenty of them are piezoelectric in which polarization can be induced by an applied mechanical stress [32]. Ferroelectric materials are analogous to ferrimagnetic materials may display permanent magnetic dipole behaviour. Ferroelectric materials exhibit hysteresis properties similar to that of the ferrimagnetic materials [33]. Ferroelectric materials are smart materials [34].

1C.2 Crystal structure of ferroelectrics

The ferroelectrics crystallize in the perovskite crystal structure [34]. They have the general formula $A^{2+}B^{4+}O_3^{2-}$, in which A denotes a large divalent metal ion such as barium and lead, B denotes a tetravalent metal ion such as titanium or zirconium [15].

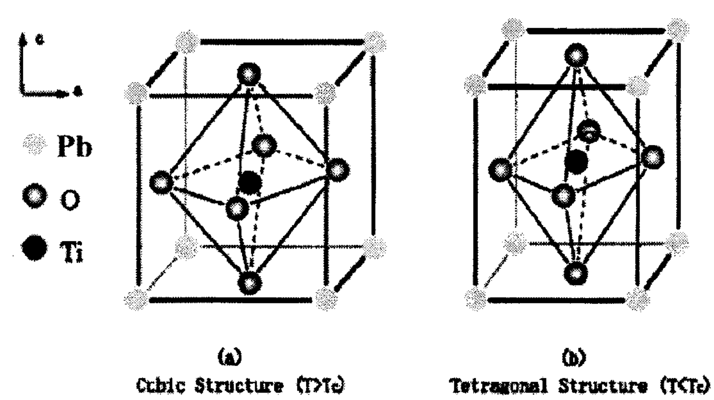

Fig. 1.2Crystal structure of PZT

The structure may be described as simple cubic unit cell with large cation (A) on the centres of the faces as shown in Fig 1.2. In this structure the smaller cation fills the octahedral holes and the large cation fills the dodecahedral holes.

1C.3 Applications of ferroelectrics

Due to the effective properties such as dielectric constant, electro optical coefficients, piezoelectric coefficient etc. ferroelectrics are used in various applications. The very large dielectric constant makes them useful in ceramic form to make high capacity condensers. Their large piezoelectric coefficients make them particularly suitable as transducers [35]. Ferroelectric ceramics are presently being used in a broad range of applications including sonar, fuel injector for high efficiency low emission diesel engines, actuators for active control of helicopter rotor blades and ultrasonic rotary inchworm motors with high power torque densities. By definition, an electromechanical device or material converts an input of electrical energy to an out put of mechanical energy (actuating applications) or an input of mechanical energy to an output of electrical energy (sensing application). Hence there exists a fundamental coupling between the electrical and mechanical fields in these materials [36]. The piezoelectrics are widely used due to their good resolution, good mechanical durability, high speed high output force and low power consumption sensors and actuators [37]. The energy dissipated in ferroelectrics during switching can be stabilized accurately at it's transition temperature. This effect can be used in frequency multipliers, dielectric amplifiers, thermostat etc. It is possible to use ferroelectrics as memory devices as they show hysteresis of square loop.

1C.4 Orientation of problem

Currently the magnetoelectric composites composed of ferrite and ferroelectric materials have attracted much attention as they exhibit good ME effect.

The present work involves the synthesis, characterization and property measurements of magnetoelectric composites consisting of Cd substituted cobalt ferrite and $PbZr_{0.52}Ti_{0.48}O_3$ as a ferroelectric phase. PZT has high Tc (390°C) [38], high dielectric constant and exhibits good piezoelectric effect. Co ferrite has large magnetostrictive effect. As Cd is non magnetic, it is substituted for Co to enhance the resultant magnetization. During the present work following studies have been carried out,

1) Preparation of constituent phases and their ME composites in required molar proportions (i.e. y = 0.15, 0.30, 0.45) by ceramic method.
2) Confirmation of ferrite and ferroelectric phases and presence of these phases in their respective composites by x-ray diffraction method.
3) Studies on microstructural details by SEM technique.
4) Measurement of electrical properties viz. ac conductivity and dielectric properties.
6) Measurement of magnetic properties viz. hysteresis, ME effect etc.

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