

Smart material composites for magnetic field and force sensors

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ABSTRACT

Piezoelectric material based sensors are widely used in applications such as automobiles, aircraft, and industrial systems. In past decade, attention has been focused on synthesizing composites that can provide multifunctional properties, i.e., same material exhibits two or more properties. In this group of composites, magnetoelectric materials are particularly interesting as they provide the opportunity of coupling magnetic and electric field. Another class of composite materials that are being actively pursued is piezoresistive materials. Piezoresistivity refers to change in resistance with applied stress and these materials are promising for enhancing the sensitivity of current generation pressure sensors based on silicon.

In this study, we focus on two composites systems: ferrite / Terfenol-D / nickel – lead zirconate titanate (magnetoelectric); and lanthanum strontium manganate (LSMO) – carbon nanotube (CNT) – silicon carbonitride (SiCN) (piezoresistive). Recently, Islam et al. have reported a magnetic field sensor based on a piezoelectric transformer with a ring-

dot electrode pattern. In this thesis, this design was further investigated by synthesizing Terfenol-D / PZT laminate. The fabricated sensor design consists of a ring-dot piezoelectric transformer laminated to a magnetostrictive disc and its working principle is as follows: When a constant voltage is applied to the ring section of the piezoelectric layer at resonance, a stress is induced in the dot section. Then, if an external magnetic object is introduced in the vicinity of the dot section, the effective elastic stiffness is increased, altering the resonance frequency (f_r). The variation of resonance frequency and magnitude of output voltage with applied magnetic field was characterized and analyzed to determine the sensitivity. The sensor showed a shift of $\sim 1.36\text{Hz/Oe}$ over the frequency range of $137.4 < f_r < 144.2\text{ kHz}$ with increasing magnetic bias from $1 < H_{dc} < 6\text{kOe}$.

Next, in order to overcome the need of magnetic DC bias in current magnetoelectric composites, a metal – ceramic core-shell composite structure was investigated. Metal-ceramic composite particles were synthesized at room temperature and their magnetic properties were investigated. The particles constitute a core-shell structure where the core is nickel-metal, while the shell is manganese zinc ferrite (MZF). Coprecipitation was used for synthesis of MZF nanoparticles comprising the shell, whereas nickel was synthesized by hydrazine assisted reduction of nickel ions in aqueous media. A core shell structure was then obtained by hetero-coagulation to form a shell of MZF around the nickel particles. Electron microscopy and x-ray diffraction confirmed nickel cores coated by MZF shells. Magnetization studies of MZF nano-particles revealed that they were not super-paramagnetic at room temperature, as expected for such particle

sizes of 20nm in size. Sintered composites of metal-ceramic particles core-shell exhibited a magnetostriction of 5ppm.

Lastly, the thesis investigates the piezoresistive properties of LSMO – CNT – SiCN composites that were synthesized by the conventional ceramic sintering technique. Recent investigations have shown that CNTs and SiCN have high piezoresistive coefficient. DSC/TGA results showed that pure CNTs decompose at temperatures of ~600°C, however, SiCN was found to sustain the sintering temperature of 1300°C. Thus, LSMO – SiCN composites were used for the final analysis. A fractional resistivity change of 4% was found for LSMO – 12.5 vol% SiCN composites which is much higher compared to that of unmodified LSMO.

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CHAPTER 1 – INTRODUCTION

Recently, magnetoelectric materials have attracted significant attention from the scientific community as evidenced by the rising number of publications in the last five years. Figure 1.1 shows the results of a simple search on the INSPEC database using the two key words together “magnetoelectric” and “piezoelectric”. The results of this search clearly highlight the revival of interest in this phenomenon. Materials exhibiting the ME effect can be classified in two classes: single phase and composites. Single phase materials exhibiting ME effects should show two coupled-transitions: one from ferroelectric to paraelectric states, and another from ferro/ferri/antiferro-magnetic to paramagnetic states: the ME effect then arises due to coupling between the magnetic and polar sublattices. Recent investigations of single phase multiferroics have revealed that the origin of the ME effect is often associated with a particular exchange mechanism for various families of compounds. Orbital ordering, Jahn – Teller distortion, super/double exchange, and/or geometric magnetic frustration have been cited as the origin source of ME effects.

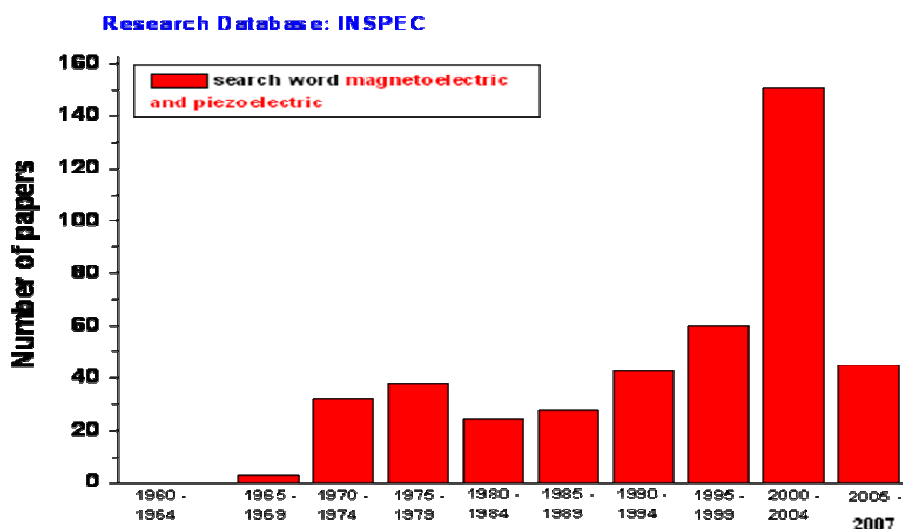


Figure 1.1: Search results on the INSPEC database using the two key words together “magnetoelectric” and “piezoelectric”.¹

1.1 Magnetic sensors background:

Magnetic sensors detect changes in magnetic fields that have been created or modified and provide direct information on magnitude and directionality or indirect information on electric current. Table 1.1 lists some of the current magnetic field sensing technologies and a brief discussion is provided below:

1.1.1 Search coil: When search coil or solenoid moves through the magnetic field, the magnetic flux linked through the coil changes, which induces current in the coil. This induced current is proportional to the magnetic field strength.

1.1.2 Fluxgate magnetometer: As shown in Fig.1.2, the construction consists of two sets of coils where one set is driven by an input current which saturates the core in one direction. The changes in magnetic field are sensed by the other coil whose output changes in proportion to the external magnetic field.

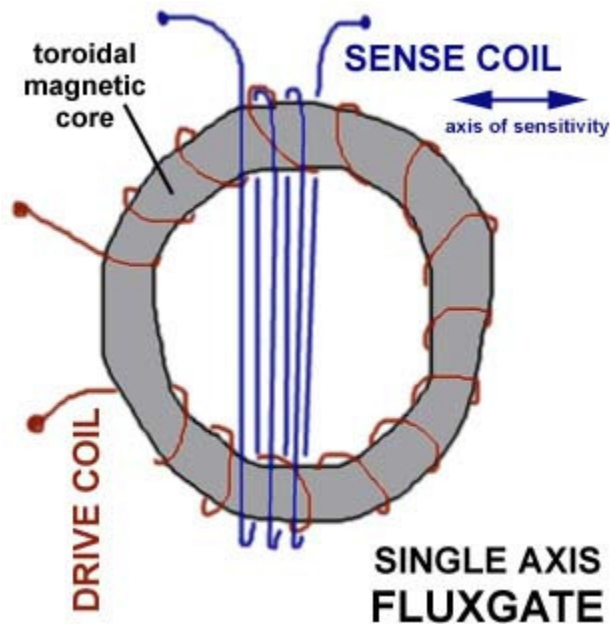


Figure 1.2: Fluxgate magnetic field sensor. From ref-2

1.1.3 Optically pumped Magnetometer (OPM):

Magnetic field causes change in precession frequency of magnetic atoms which are magnetized by irradiation with circularly polarized light of a suitable wavelength. During the last decade, progress has been made with OPM of the following three types: (1) The narrow-line potassium M_x -OMP with the highest shot-noise-limited resolution (about $10 \text{ fT/Hz}^{1/2}$) and with an absolute accuracy better than 0.1 nT ; (2) The "tandem" M_x - M_z -type magnetometer with a narrow line potassium M_z unit of enhanced absolute accuracy (of about 10 pT); (3) The laser pumped ^3He free-precession magnetometer of highest absolute accuracy and lowest energy consumption. Detailed description on these developments is available in the reference³..

1.1.4 Nuclear precession magnetometer:

Nuclear precession magnetometers polarize the atomic nuclei of an element causing the nuclei to precess temporarily around a new axis. The frequency of precession of the nuclei is measured, and can be correlated to magnetic flux density. A proton precession magnetometer uses hydrogen as the precession atom. An Overhauser magnetometer is an improvement upon the proton precession. It utilizes RF power to excite the electrons of a special chemical dissolved in the hydrogen-rich liquid. The electrons pass on their excited state to the hydrogen nuclei, altering their spin state populations, and polarizing the liquid.

1.1.5 SQUID Magnetometer:

It utilizes Josephson junction, consisting of two superconducting coils separated by thin insulating layers. The changes in magnetic flux are recorded by the changes in voltage phase. One period of voltage variation corresponds to an increase of one flux quantum ($\sim 2.0678 \times 10^{-15} \text{ T.m}^2$).

1.1.6 Hall effect sensor:

A current-carrying conductor when placed in the magnetic field will generate voltage perpendicular to both conductor and field. Figure 1.3 schematically describes the Hall-effect.

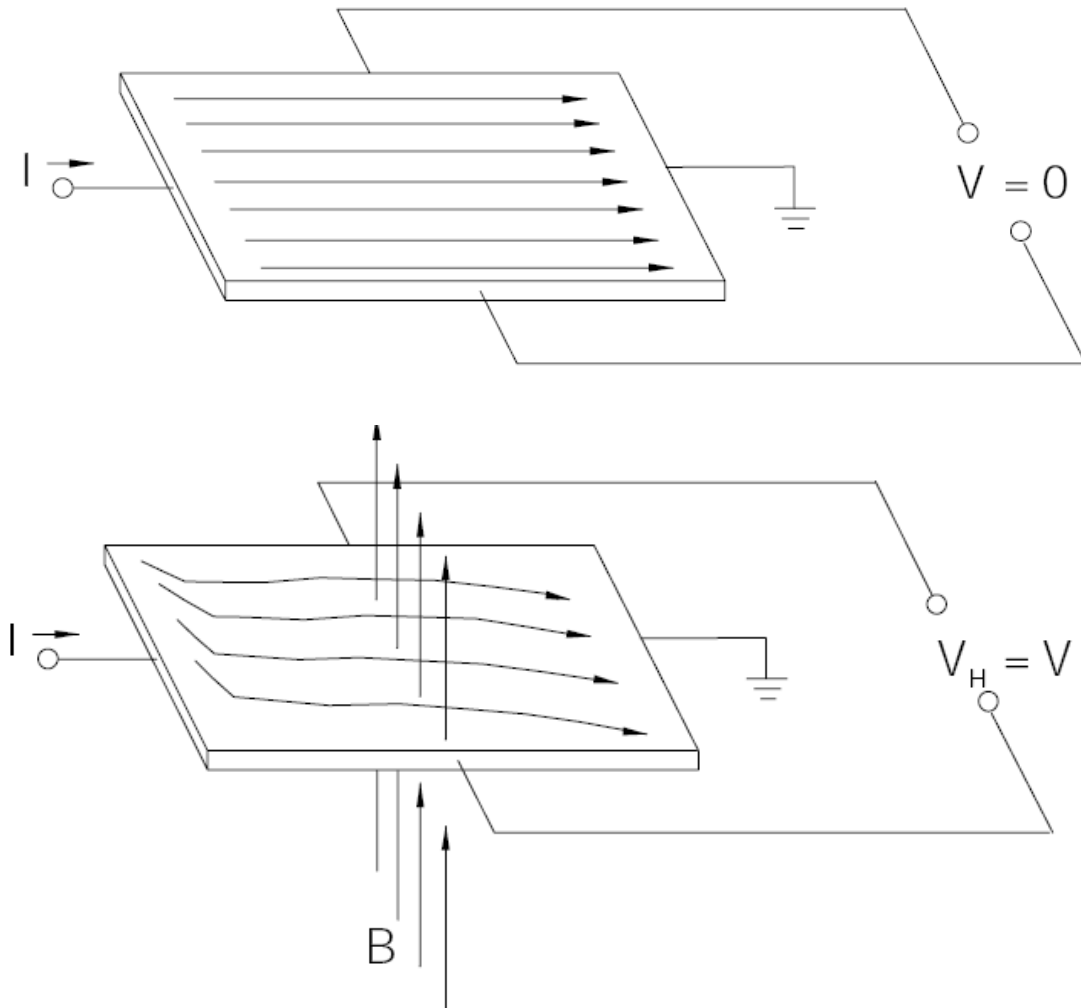


Figure 1.3: Hall effect sensor schematics (a) For $B = 0$, the current distribution is uniform and no potential difference is observed. (b) For non-zero magnetic field, a Lorentz force is exerted on the current which results in potential difference ($V_H \propto I \times B$) (Schematics from Honeywell)

1.1.7 Magneto resistive magnetometer:

Anisotropic magnetoresistive (AMR) sensor⁴ consists of a Wheatstone bridge of four AMR thin-film elements. The differential output voltage of the bridge is proportional to the supply voltage and the component of local magnetic field along a given direction. Sensitivity of AMR sensor is in the vicinity of $10 \text{ mV V}^{-1} \text{ mT}^{-1}$ with a minimum detectable field on the order of 1 nT or less, while the measurement bandwidth covers the interval from 0 to 1 MHz. Figure 1.4(a) shows the sensor with a single strip directed along the anisotropic axis⁵ and Fig. 1.4(b) shows the encapsulated design. The parameters for this sensor are: $t = 50 \text{ nm}$, $w = 20 \text{ }\mu\text{m}$, $R = 18 \text{ }\Omega$, and $I = 10 \text{ mA}$. Figure 1.4(c) shows the transfer characteristic. Fig. 1.4(d) shows the transfer characteristic for magnetoresistor used in high-density read heads with parameters $t = 59 \text{ nm}$, $w = 4.6 \text{ }\mu\text{m}$, $l = 279 \text{ }\mu\text{m}$, $R = 229 \text{ }\Omega$, and $I = 10 \text{ mA}$ ⁶.

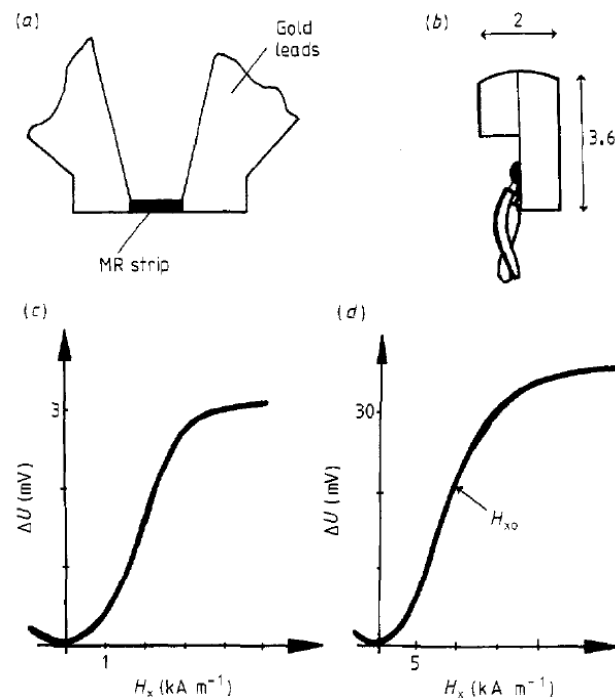


Figure 1.4: Single axis magnetoresistor and examples of transfer characteristics. From C. H.

Bajorek, C. Coker, L. T. Romankiw, D. A. Thompson, Nov 1974, IBM Journal of Research and development, © IBM. Reproduced with permission

1.1.8 Magneto diode:

Figure 1.5 shows the construction of the magnetodiode magnetic field sensor⁷. The sensing mechanism is based on the change in resistance between the metal contacts due to application of magnetic field perpendicular to direction of travel of charge carriers. Under forward bias condition, the recombination occurring near the silicon / silicon – dioxide and silicon / sapphire interface increases the overall resistance. This magnitude is further increased or decreased upon application of magnetic field due to change in recombination rate.

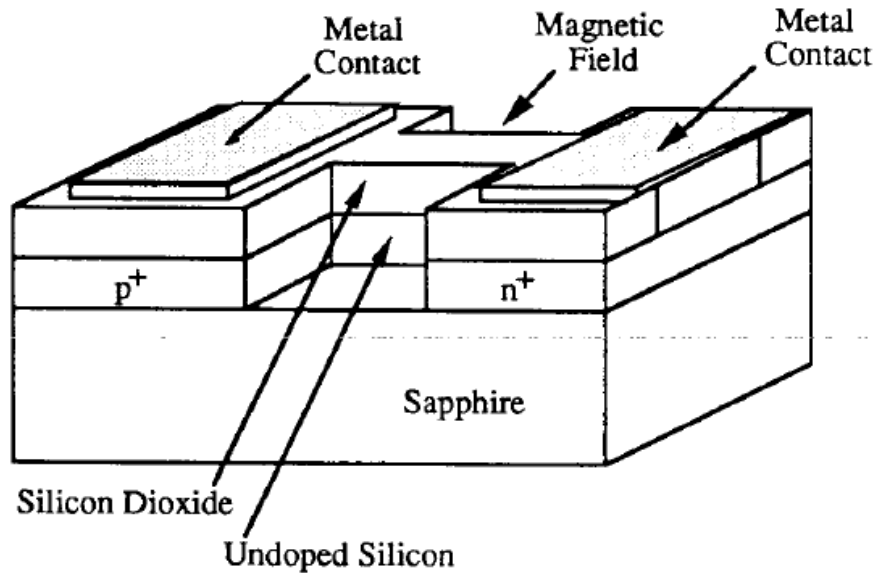


Figure 1.5: Schematic description of the magnetodiode sensor . James E. Lenz , Proceedings of the IEEE, Vol. 78, No. 6, June 1990, © 1990 IEEE

1.1.9 Magneto transistor:

First magnetotransistor proposed by Hudson consisted of two collector bipolar transistor where applied magnetic field (B) changes the collector current (I_C)⁸. The relative sensitivity (S) of the collector current to magnetic field induction B is given as:

$$S = \frac{1}{I_C} \left(\frac{\partial I_C}{\partial B} \right)$$

The reported sensitivities range from $10^{-2}T^{-1}$ to $10T^{-1}$. Figure 1.6 shows the cross-section of recently proposed lateral magnetotransistor where emitter – base junctions are forward biased

and both collector – base junctions are reverse biased ⁹. The external magnetic field causes the change in the ratio of collector to substrate current (I_C/I_S).

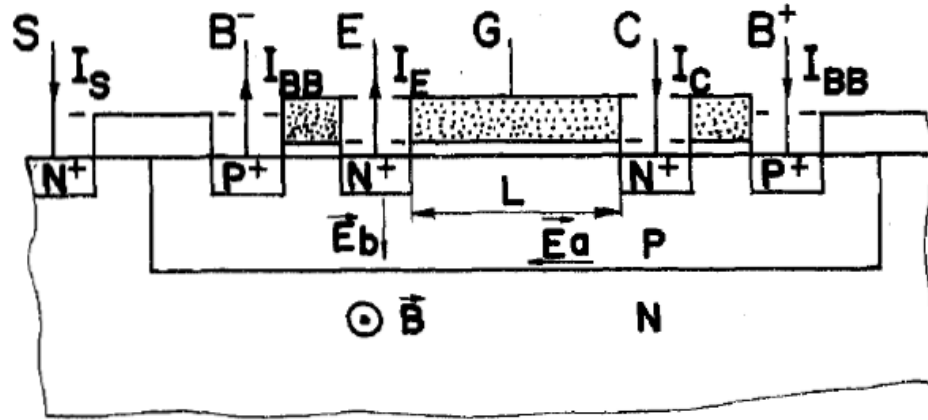


Figure 1.6: Cross-section of then-p-n magnetotransistor proposed by R. S. Popovic et al; R. S. Polovic and Rolf Widmer, IEEE Transactions on Electron devices, Vol ED-33, No-9, September 1986, © 1986 IEEE. Reproduced with permission

1.1.10 Fiber optic magnetometer:

Recent design proposed by Sato and Saito shown in Fig. 1.7 improves the functioning of fiber-optic magnetometer by using laminated magnetostrictive films and optical fibers.¹⁰

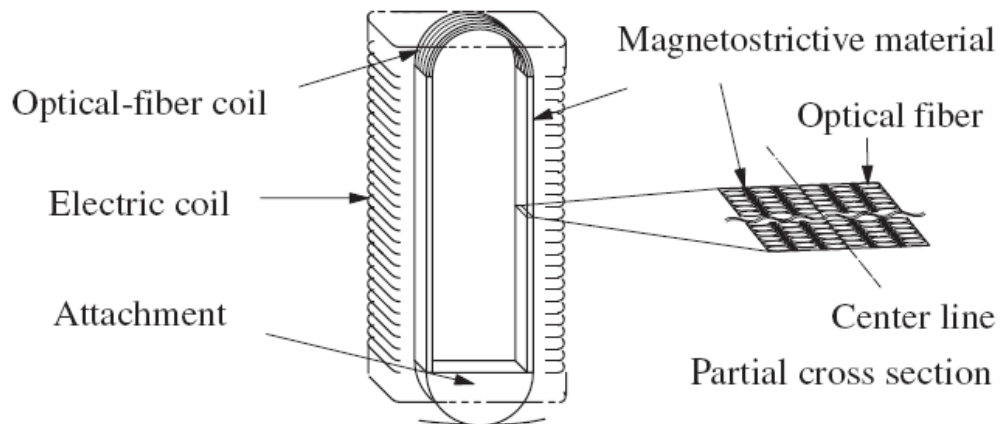


Figure 1.7: Structure of sensor for fiber-optic magnetometer proposed by Sato and Saito¹From R. Sato and S. Sato Japanese Journal of Applied Physics, Vol. 46/No.2, pp. 817-820 (2007), ©2007, JJAP. Reproduced with permission

On application of the external magnetic and dither magnetic field, the change in magnetostriction can be measured by fiber-optic interferometer with an AM modulation at the dither frequency. The proposed design accounts for the demagnetizing field.

1.1.11 Magneto optical sensor:

Optical current sensors (OCSs) have several advantages over conventional current transformers including no-contact, good insulation, insensitivity to electromagnetic interference, large dynamic range, high-speed measurements and operation in harsh environments. A popular configuration of OCSs is to use bulk glass as a magnetic field sensor and an air-gapped core surrounding the conductor as a field concentrator. According to the Faraday effect, the polarization azimuth of a linearly polarized light beam propagating inside a magnetooptically active medium is rotated by an angle ϕ under the influence of a magnetic field B generated by an electric current, and is given by:

$$\phi = V_d B_{eff} L_{opt}$$

where V_d is the Verdet constant of the magneto-optic sensing medium, L_{opt} is the total geometrical path length along the direction of the applied magnetic field and B_{eff} is the effective magnetic field, which is proportional to the current and dependent on the size and shape of the air gap. Thus, the sensitivity of the sensor is dependent upon the product $B_{eff}L_{opt}$.

1.1.12 Magnetoelectric detector:

Magnetoelectric composite sensors work on the following principle: An external AC magnetic field creates strain in the magnetostrictive layer which is elastically transferred to the piezoelectric layer which produces electric charge. The sensitivity of such sensor is proportional to the permeability and permittivity of the composite material.

Table 1.1: List of current magnetic field sensing technologies

Magnetic sensor Type	Detection principle	Sensitivity (G)	Frequency limits	Power	Size	T (°C)
Search coil	Faraday's law	10^{-6} - 10^{-10}	1Hz-1MHz	1-10mW	2"-5"	
Flux gate magnetometer	magnetic induction and ferromagnetic hysteresis	10^{-6} - 10^{-2}	Max 10 KHz	5-50mW	1" or less	
Optically pumped Magnetometer	Zeeman effect	10^{-8} -1		~10W	12-20"	
Nuclear precession magnetometer	Gyro magnetic resonance	10^{-7} -1		0.5W	12-20"	
SQUID Magnetometer		10^{-10} - 10^{-4}		~		-273 to 200
Hall effect sensor	Lorentz force	10 - 10^3	1MHz	0.2W		-273 to 200
Magneto resistive magnetometer	Magneto-resistive effect	10^{-2} -50	1GHz	0.1-0.5mW		-55 to 200
Magneto diode		10^{-1} - 10^4			0.25"	-100 to 100
Magneto transistor	Hall and Suhl effect	10^{-2} - 10^4				

Fiber optic magnetometer	Magnetostricti on and optical interference	10^{-7} - 10	Below 60 Hz		4''	~
Magneto optical sensor	Faraday polarization effect	10 - 10^8			~	~
Magnetoelectric detector	Magnetoelectr ic effect	10^{-3} - 10^3	10^5 Hz- 10^{-2} Hz		~	-75 to 70

As seen from the table above, SQUID has highest sensitivity but they need coolant to keep the superconducting material operating in its superconducting phase hence are quite expensive. ME sensors are relatively new entry in the magnetic sensing materials and have moderate to high sensitivity. Fig 1.8 summarizes the detection range of various magnetic field sensors (taken from Ref. 11)

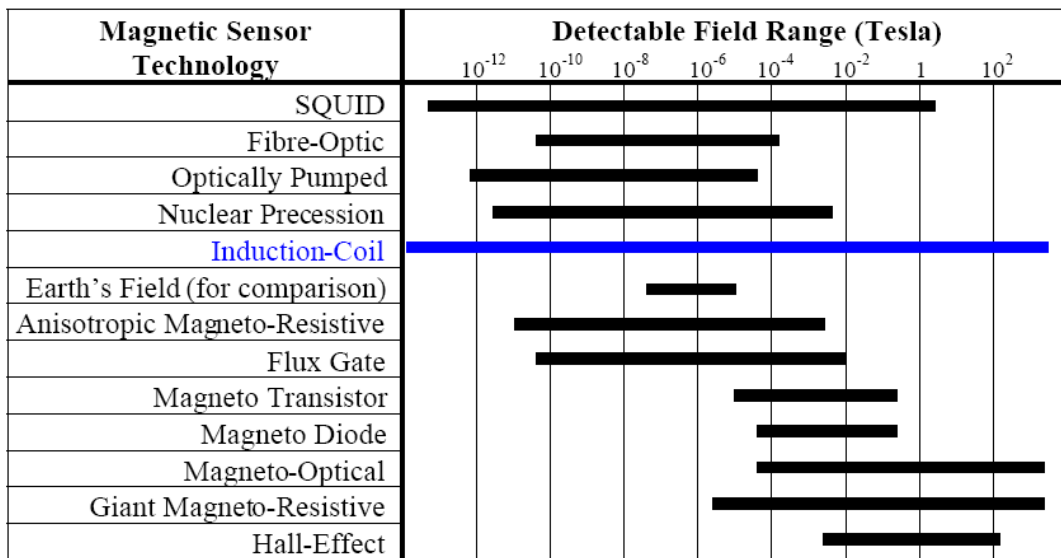


Figure 1.8 Detection range of various magnetic field sensors

1.2 Composites theory:

Composites with one piezoelectric phase and second phase like rubber, polymer⁵, metal^{6,7} are synthesized for improving mechanical properties (fracture toughness), permeability, and sensing capability (multi-layering). Composites of PZT-PVDF are used for underwater transducers⁵, and vibration damping. Functionally graded PZT-Ag composite⁶ and BaTiO₃ – Ni composite are used for high permittivity applications⁷.

For n phases the number of connectivity patterns is given as $(n + 3)!/3!n!$, which for two phase composites comes out to be 10, for three phases as 20, and 35 for four phase pattern. There are numerous possibilities for synthesizing ME composite as there can be several material states (amorphous, ceramic, metal, polymer, etc.), shapes (disk, cylinder, plate, toroid, sphere, etc), and sizes (number of layers, layer thicknesses, length and width can be varied differently) for obtaining the magnetoelectric properties. Further, in each of these shapes there is the possibility of orienting the polarization along different axes and applying the electric (E) and magnetic (H) fields along different axes. In addition there are several choices for materials depending on magnetostriction constant, resistivity, permeability, permittivity, piezoelectric strain and voltage constant, sintering temperature, and chemical reactivity (Magnetostrictive – MnFe₂O₄, CoFe₂O₄, NiFe₂O₄, ZnFe₂O₄, YFe₅O₁₂, SmFe₅O₁₂, YIG, Terfenol-D, Metglas 2605SC, Ni, Co, etc. ; Piezoelectric – PZT, BaTiO₃, PMN – PT, PVDF, SrBi₄Ti₄O₁₅, (Na_{0.5}K_{0.5})NbO₃) etc.).

1.3 Magnetoelectric composites- a product property

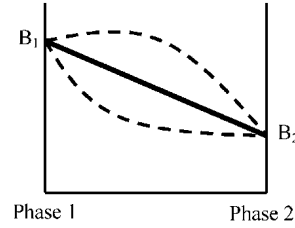
A suitable combination of magnetostrictive and piezoelectric phases can yield dramatically enhanced ME effects, relative to single phase materials. Magneto-elastic interactions are known to be high in only a few magnetostrictive materials: accordingly,

investigations of ME composites have focused on magnetostrictive layers, rather than piezomagnetic ones. In magnetostrictive materials, the strain induced by applied magnetic field is proportional to square of the magnetic field. An effective linear operational range can be achieved by applying a DC magnetic bias across the structure; i.e., by DC biasing the magnetostrictive layer to an effective piezomagnetic state.

Magnetoelectric composites utilize ‘product’ property of two phase combination as shown in Fig. 1.9.^{8,9,10} In a biphasic composite material, if one phase exhibits a property $A \rightarrow B$ (application of an independent variable A resulting in an effect B) with a proportionality tensor $dB/dA = X$ (may be a constant or dependent on A or B) and the second phase exhibits a property $B \rightarrow C$ with a proportionality tensor $dC/dB = Y$, then the composite will exhibit a property $A \rightarrow C$ which is absent in either of the initial phases. The property $A \rightarrow C$ is called as product property of the composite. The proportionality tensor dC/dA is the product of the proportionality tensor of the phases, i.e. $dC/dA = (dC/dB)(dB/dA) = YX$. A ‘sum’ property of composite depends on the sum of the property of each component proportional to its weight/volume fraction given by “rule of mixtures”. Physical quantities like density and resistivity are sum properties. In certain cases, the averaged value of the output, A^* , of a composite does exceed the magnitude of end components A_1 and A_2 . This enhanced output refers to an effect A/B which depends on two parameters A and B. Suppose that A and B follow convex and concave type sum effects, respectively, as illustrated in fig. 1.9(c), the combination value A/B will exhibit a maximum at an intermediate ratio of phases. This is called a “combination effect”.

(a) Sum Properties

Phase 1 : $A \rightarrow B_1$
Phase 2 : $A \rightarrow B_2$ $\bigcup$ $A \rightarrow B^*$



(b) Product Properties

Phase 1 : $A \rightarrow B$
Phase 2 : $B \rightarrow C$ $\bigcup$ $A \rightarrow C$ New Function

(c) Combination Properties

Phase 1 : $A \rightarrow B_1/C_1$
Phase 2 : $A \rightarrow B_2/C_2$ $\bigcup$ $A \rightarrow (B/C)^*$

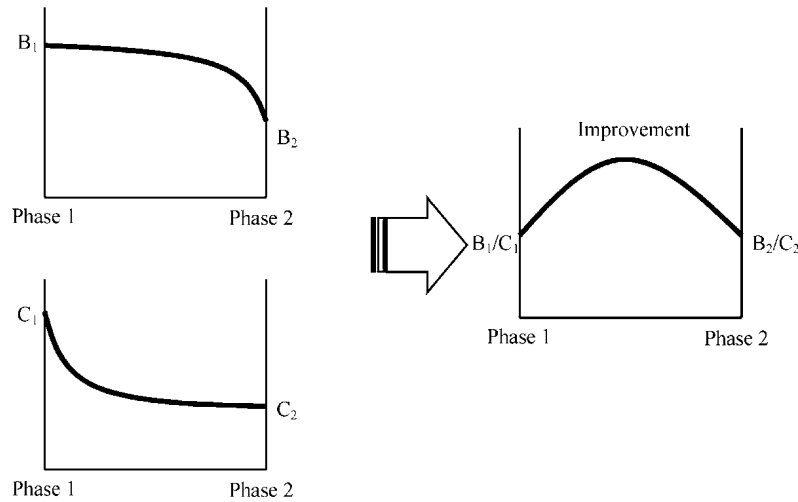


Figure. 1.9: Composite properties; (a) sum properties, (b) product properties, and (c) combination properties From J. Ryu, S. Priya, K. Uchino, H-E. Kim, Journal of Electroceramics, Vol. 8, 2, pg 107-119 (2002),© Springer science. Reproduced with permission

1.3.1. Symmetry requirements for composites:

The importance of symmetry in the design of magnetoelectric composites has been discussed in detail by several researchers.^{1,12-14} The induced magnetization B_i (axial first rank tensor) is proportional to the applied electric field E_j (polar first rank tensor) through the

magnetoelectric susceptibility coefficient α_{ij} which is an axial second rank tensor. The transformation of the ME coefficient is given as following:

$$\alpha'_{il} = \pm |a| a_{ij} a_{ik} \alpha_{jk}$$

In matrix form the transformation can be written as:

$$(\alpha') = \pm |a| (a)(\alpha)(a)_t$$

The magnetoelectric tensor has nine independent coefficients. The effect vanishes for all symmetry groups containing time reversal symmetry ($1'$) and inversion ($\bar{1}$) while space inversion along with time inversion ($\bar{1}'$) is allowed. It can be shown that the effect is non-zero for 58 of the 90 magnetic point groups.

Sintered polycrystalline ceramics consisting of ferroelectric grains in the vicinity of ferromagnetic ones illustrates the importance of symmetry. For example, combining the magnetized CoFe_2O_4 ceramic having symmetry group ∞/mm' with poled BaTiO_3 ceramic having symmetry group $\infty ml'$ results in magnetoelectric $\text{CoFe}_2\text{O}_4 - \text{BaTiO}_3$ ceramic having symmetry group $\infty m'$.¹³ Both BaTiO_3 and CoFe_2O_4 by themselves are not magnetoelectric. Thus, the ME effect can be realized by incorporating materials of suitable symmetry in a composite.

1.3.1.1 Single phase materials:

A simple equation for ME coupling in single phase composites can be stated as:¹²

$$H_i = \alpha_{ik} E_k$$

where, H_i is induced magnetization (Wb/m^2) that is linearly proportional to the applied electric field E_k (V/m) and α_{ik} is the magnetoelectric coefficient. There are 80 or more single phase materials found to exhibit ME effect¹⁵. Suryanarayana has reviewed the ME effect for the

family of compounds represented by the general formula $\text{Bi}_4\text{Bi}_{m-3}\text{Ti}_3\text{Fe}_{m-3}\text{O}_{3m+3}$, where compounds with $m = 4, 5, 6, 7$ and 8 have been successfully synthesized.^{16,17} The maximum magnitude of the ME coefficient for $\text{Bi}_5\text{FeTi}_3\text{O}_{15}$ was found to be 17mV/cm.Oe under a DC bias of 8000Oe ; while for $\text{Bi}_6\text{Fe}_2\text{Ti}_3\text{O}_{12}$, it was 3.2mV/cm.Oe under 4000Oe .¹⁶⁻¹⁸ Recent investigations of $\text{Bi}_8\text{Fe}_4\text{Ti}_3\text{O}_{24}$ have reported a ME coefficient of 0.35mV/cm.Oe at room temperature.¹⁹ In general, it has been found that as the Fe content increases in these compounds that the magnitude of the ME coefficient decreases.

Recently, the ferromagnetoelectric material BiFeO_3 has been investigated in thin film form.^{20,21} First, it is relevant to mention that BiFeO_3 -based bulk materials have previously been reported to exhibit extremely small ferroelectric polarization and ferromagnetic magnetization: which might possibly be due to low resistivities and high coercive fields in crystals and ceramics. The magnitude of the ME coefficient of bulk materials has been reported to be on the order of 0.064mV/cm.Oe under a magnetic bias of 9500Oe .¹⁶ Unfortunately, single phase materials suffer from the drawback that the ME effect is extremely small at room temperature. For example, the highest ME coefficient has been reported for antiferromagnetic Cr_2O_3 crystals, which is $2.67 \times 10^{-12}\text{s/m}$ at a Neel temperature of 34°C .

1.3.1.2 Bulk and co-fired composites:

Particulate and co-fired composites consisting of magnetostrictive and piezoelectric phases have been synthesized by using the mixed-oxide sintering process. Table 1.2 lists some of the examples of piezoelectric materials that can be used for this purpose and Table 1.3 lists the magnetostrictive materials. Sintered composites exhibit small magnitude of magnetoelectric coefficient due to inter-diffusion of ions reducing the individual properties, low resistivity due to

connectivity of magnetic phase and microstructural defects due to different crystal structure. Co-fired composites reduce these problems by eliminating the direct contact between the piezoelectric and magnetostrictive phase. Recent results by Islam et al. has shown improved performance for both bilayer and multi-layer geometries.²²

Table 1.2: Example of piezoelectric materials that can be used for sintered magnetoelectric composites.¹

Material	d_{33} (pC/N)	d_{31} (pC/N)	ϵ_r (@ 1 kHz)	k_{33}	T_c (°C)
BaTiO ₃	190	-78	1700	0.49	120
APC 850 (soft PZT)	400	-175	1750	0.72	360
APC 855 (soft PZT)	630	-276	3300	0.76	250
APC 840 (hard PZT)	290	-125	1250	0.72	325
PZT – Pb(Ni _{1/3} Nb _{2/3})O ₃	600	-250	3900	0.69	205
SrBi ₄ Ti ₄ O ₁₅	20	-3	150	0.2	550
(Na _{0.5} K _{0.5})NbO ₃	120	-40	400	0.4	350

Table 1.3 Saturation magnetostriction of some representative magnetic oxides at 20 °C¹.

Material	λ_s (x 10 ⁻⁶)
MnFe ₂ O ₄	-5
Fe ₃ O ₄	40
CoFe ₂ O ₄	-110
MgFe ₂ O ₄	-6

$\text{Li}_{0.5}\text{Fe}_{2.5}\text{O}_4$	-8
NiFe_2O_4	-26
CuFe_2O_4	-9

1.3.1.3.Laminate composites:

In general, laminated composites consist of piezoelectric (PE) and magnetostrictive (MS) phases bonded via epoxy in various configurations. The constitutive equations for describing magneto-mechano-electrical coupling across the PE and MS phases approximated to linear range in tensorial notations can be represented as: ²³

$$\sigma = cS - e^T E - q^T H,$$

$$D = eS + \epsilon E + \alpha H$$

$$B = qS + \alpha^T E + \mu H$$

where, σ , D and B are respectively stress, electric displacement and magnetic field which are individually related to strain S , electric field E and magnetic field H via tensors for stiffness c , piezoelectric e , piezomagnetic q and mangetoelectric α coefficients. The superscript T stands for transpose of the tensors. For individual MS phase, e and α is zero, while for PE phase q and α is zero, but for ME composites the effective ME co-efficient α^* is non zero and depends on composite microstructure. Direct ME effect in composites can also be represented ²³

$$\delta P / \delta H = \alpha = k_c \cdot e \cdot q$$

where, piezoelectric coefficient $e = \delta P / \delta S$ and piezomagnetic coefficient $q = \delta S / \delta H$ are related by the ME coefficient α . A coupling factor k_c ($0 \leq |k_c| \leq 1$) between the two phases takes into consideration for interfacial losses. Till date laminate composites have shown highest ME output. The advantages are simple fabrication and greater freedom on selection of MS and PE phases.

The disadvantages being stability only close to ambient temperature and difficulty of miniaturization. In general, the ME coefficient of bulk/ particulate sintered composites is less than the sintered bilayer/tri-layer composite and that in turn is less than the laminate composites.

1.4 ME Coupling coefficient

The upper limit for the value of the ME susceptibility can be given as:²⁴

$$\alpha_{ij}^2 < (\kappa_{ii}^e \chi_{jj}^m) \quad (1)$$

where κ^e and χ^m are the electric and magnetic susceptibilities respectively. A similar relationship can be derived based on the thermodynamic considerations given as:²⁵

$$\alpha_{ij} < (\epsilon_{ii} \mu_{jj})^{1/2} \quad (2)$$

where ϵ and μ are the electric permittivity and magnetic permeability respectively. The magnetoelectric coupling coefficient has been defined as:

$$k_{ME} = \frac{U_{mutual}}{(U_{electric} \cdot U_{magnetic})^{1/2}} \quad (3)$$

where $U_{mutual} (= \frac{1}{2} \alpha_{ij} E_i H_j, \text{ where } H_j \text{ is the magnetic field})$ is the mutual energy, $U_{electric} (= \frac{1}{2} \epsilon_{ii} E_i E_i)$ is the electric energy and $U_{magnetic} (= \frac{1}{2} \mu_{jj} H_j H_j)$ is the magnetic energy. In order to evaluate the efficiency of energy conversion from magnetic to electric forms, or vice-versa, a working definition of the coupling coefficient can be written as:

$$k_{me}^2 = k_{ij, piezo}^2 k_{ij, magnetic}^2 \quad (4)$$

where $k_{ij, piezo}$ is the coupling coefficient of the piezoelectric phase, and $k_{ij, magnetic}$ is the coupling coefficient of the magnetic phase.

1.5. Magnetic sensors:

Working principle of ME magnetic sensors is based on direct effect. The strain in the magnetostrictive-MS phase due to external magnetic field is transferred to the Piezoelectric-PE phase where it is converted into proportional charge. Composites with high ME effect can be used to measure ac or dc fields up to 10^{-8} G at resonance frequency. Fig 1.10²⁶ The key to high magnetic sensitivities is higher ME effect and a design that eliminates various kinds of noise. For example a bimorph composed of two oppositely poled PZT stacked one over other in push-pull mode has better sensitivity at lower frequencies as compared to unimorph composed of a PZT and Terfenol-D.¹⁵ Still higher sensitivity at ultra low frequency (10 mHz) is achieved in multilayer stacking of ME laminates due to higher ME charge coupling and large capacitance as shown in figure 1.11.²⁷ Both of these designs take advantage of high ME effect and thermal noise cancellation.

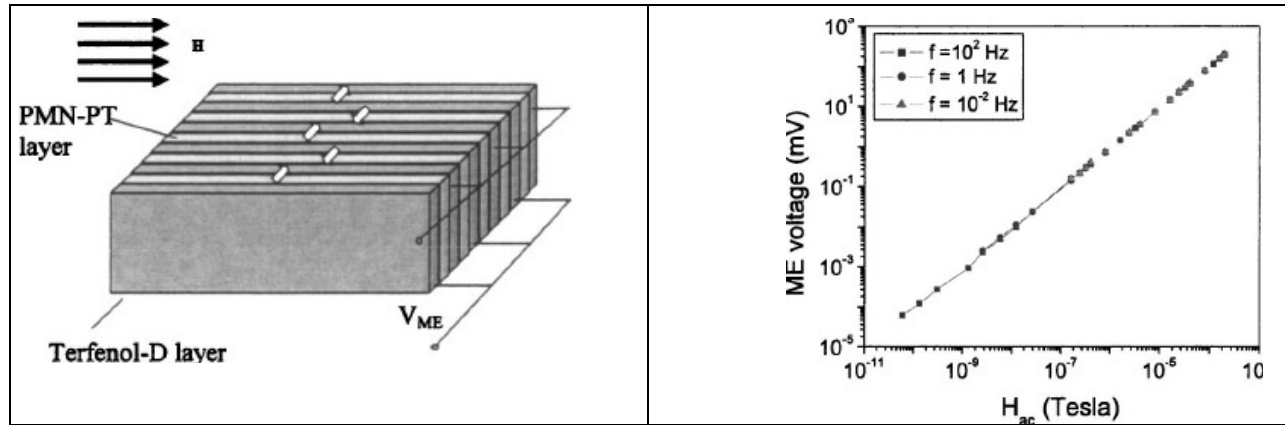


Figure.1.10: (a) Multilayer Terfenol-D/PMN-PT laminates in L-T mode and (b) its response especially at low frequency at 0.04 T DC magnetic bias. From S. X. Dong, J. Y. Zhai, J. F. Li, and D. Viehland, Appl. Phys. Lett. 88, 082907 (2006) “Small dc magnetic field response of magnetoelectric laminate composites, (C) ”American institute of Physics. Reproduced with permission²⁹

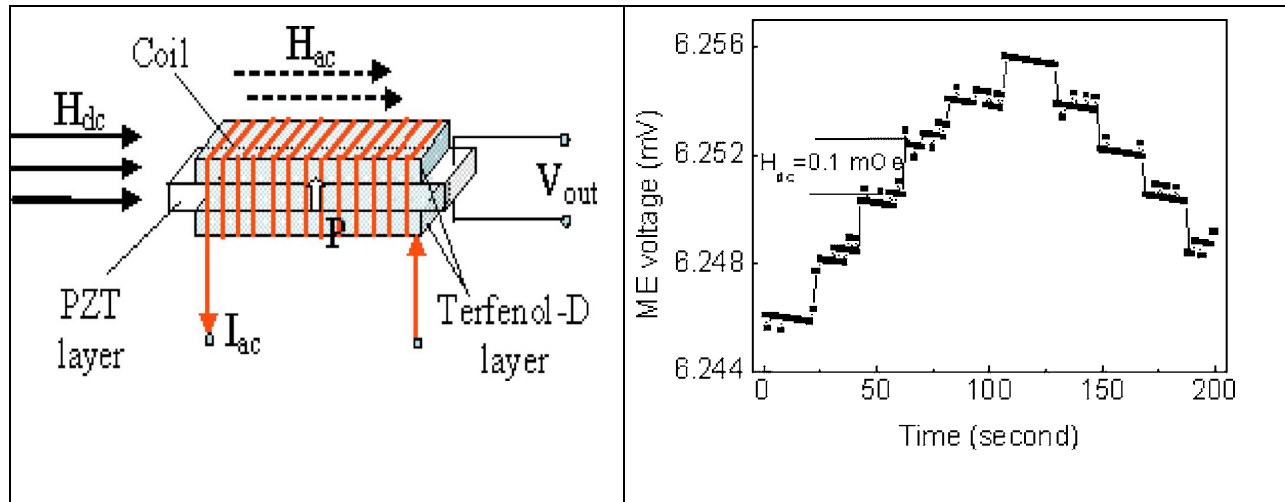


Figure 1.11: (a) DC magnetic field sensor and (b) sensitivity limit of small dc magnetic field changes for LT laminate. From S. X. Dong, J. Y. Zhai, Z. P. Xing, J. F. Li, and D. Viehland, Appl. Phys. Lett. 86,102901 (2005), ©American institute of Physics. Reproduced with permission²⁸

1.5.1 DC magnetic field requirement:

All the ME composites based on MS – PS combination require a DC- bias. This represents one of the challenge in miniaturization of ME composites and their integration with electronics. Table X provides some examples of DC bias required by various ME composites reported in literature.

Table 1.4: List of ME material systems with highest ME voltage and DC bias required for the same²⁸⁻³⁸

ME material system	ME output (mV/cm.Oe)	DC bias (Oe)	Reference
BaTiO ₃ -CoFe ₂ O ₄ uni-directionally solidified eutectic	130	500	28
PZT-NiFe ₂ O ₄ co-sintered particulate composite	1250	115	29
BaTiO ₃ -CoFe ₂ O ₄ nano-pillar thin film nanostructure	700	-	30
Fe-20%Ga-PZT epoxy glued laminate	345	750	31

PZT-Terfenol-D epoxy glued laminate	30	30	32
PZT-Permendur epoxy glued laminate	600	150	35
MnZnFe ₂ O ₄ /Terfenol-D-PZT epoxy glued laminate	3000	56	33
FeBSiC alloy ribbons-PZN-7PT epoxy glued laminate	10500	2	34
PZT-5- Terfenol-D	5	0	36

Thus, a new approach for designing ME composite is required that can eliminate the need of DC bias in MS – PE composites. One of the concept investigated in this thesis utilizes converse ME effect for generating magnetic field in the MS phase by electromagnetostriction. That is increasing the eddy currents generated in MS phase (which has higher conductivity as compared to PE phase) by incorporating metal particles shells surrounding ferrite grains. This gives higher magnetostrictive strains on the PE ³⁹ phase and consequently higher ME output at low or zero external bias magnetic field. The key to such synthesis is discussed in the third chapter of nanoparticle synthesis and core-shell self assembly by hetero-coagulation.

1.6 Carbon Nanotubes:

Walls of a CNT can be single or multiple and categorized as single walled nanotubes SWNT or multiwall MWNT respectively and length of CNT is manufacturing process dependent but lengths approaching a few centimeters have been reported⁴¹. Commonly used CNT synthesis methods are arc plasma discharge, CVD and laser ablation. Owing to their unique geometry and bonding structure, CNTs have interesting thermal, mechanical, and electrical properties. Chemical bonding in nanotubes is composed of sp² bonds like graphite⁴⁰. SWNT or MWNT's are found resilient to chemical or thermal decomposition. Manipulation of single CNT is difficult and hence their use as conducting paths for large scale chip manufacturing has not yet realized. In the present study, CNT's were used as a dopant in LSMO – SiCN composite.

1.7 Silicon Carbonitride:

Silicon carbide- SiC or Silicon Nitride- Si_3N_4 are known carbides and nitrides of silicon and have high refractory properties. They are also used in wide band gap semiconductor technology because of their good thermo-chemical resistance. Composites of SiC nanoparticles in Si_3N_4 have shown better toughness properties than monolithic SiC or Si_3N_4 and exhibit super plastic behavior, high strength and fracture toughness.⁴² Silicon Carbonitride - SiCN is newer ternary compound which has better thermo mechanical characteristics than the SiC/ Si_3N_4 nanocomposite. It also has better optoelectronic properties and possess metal like electrical conductivity.⁴³⁻⁴⁵ This compound has been produced by various methods like CVD, RF plasma, laser pyrolysis, polymer precursor pyrolysis. The properties were found to be sensitive to the synthesis techniques since it affects the extent of Si-C, C-C and C-N bonds.⁴⁶⁻⁵⁰ The synthesis of SiCN from pyrolysis of its polymer precursor is an easy way and commonly is used to make SiCN on large scale.⁵¹ In present study, SiCN was coated on CNT for protecting them from high temperature sintering with LSMO and was also used as second phase in composites with LSMO.

CHAPTER 2 - MAGNETOELECTRIC LAMINATE BASED DC MAGNETIC FIELD SENSOR

2.1 Piezoelectric transformer design:

The piezoelectric transformer design considered here is ring-dot type⁵² where both input and output sections have same direction of polarization. An AC voltage applied at the input section at electromechanical resonance frequency causes radial vibrations in the output-dot section.⁵³⁻⁵⁵ Figure 2.1 shows the schematic of unipoled piezoelectric transformer. On applying the electrical excitation to the external ring (input), the radial extensional vibration is generated through converse piezoelectric effect which is propagated to the center dot (output). The ring and dot are separated from each other by an insulation gap (un-electroded area). At the output, the mechanical vibrations are again converted into electrical voltage through direct piezoelectric effect. Since this transformer design utilizes radial mode for both input and output parts which are built-in on the same ceramic disk, it has much higher bandwidth as compared to other designs (since $k_{33} > k_p > k_{31}$).⁵³

Combining a MS phase with PE phase in a bulk sintered composite would provide the advantages of both PE transformer and ME particulate composite. In this prior design shown in Fig. 2.1, a voltage is applied to the ring section at the resonance frequency which induces a magnetic field in the dot section. If an external magnetic object is then brought in the vicinity of the dot section, the change in magnetic field will induce a change in the voltage gain of the transformer via the magnetoelectric (ME) effect. Particulate ME composites of composition $0.8 \text{ Pb}(\text{Zr}_{0.52}\text{Ti}_{0.48})\text{O}_3 - 0.2 \text{ Ni}_{0.8}\text{Zn}_{0.2}\text{Fe}_2\text{O}_4$ were used in this prior design. It is well-known that the ME effect in sintered composites is small because of: (i) reduced piezoelectric and

magnetostrictive constants due to inter-diffusion, (ii) interfacial defects, and (iii) low resistivity. Various investigations have shown that the ME effect is an order of magnitude or more higher in laminate composites.^{18,55-58} Thus, the previously reported design was modified to include a laminate configuration. Our findings demonstrate enhanced sensitivity to small changes in DC magnetic field and reduced input voltages to the piezoelectric transformer.

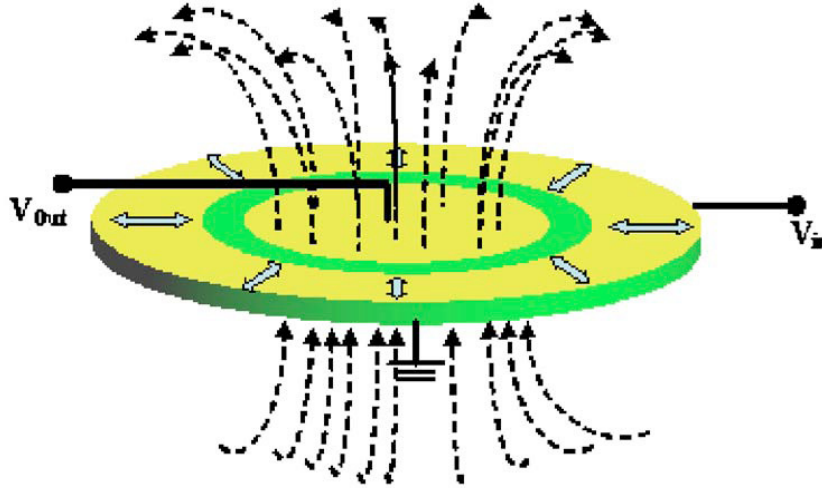


Figure 2.1: ME particulate composite of composition $0.8 \text{ Pb}(\text{Zr}_{0.52}\text{Ti}_{0.48})\text{O}_3 - 0.2 \text{ Ni}_{0.8}\text{Zn}_{0.2}\text{Fe}_2\text{O}_4$ with transformer design. Induced magnetic field is shown by dotted arrows. From R. Islam, H. Kim, S. Priya, H. Stephanou, *Appl. Phys. Lett.* 89, pg 152908 (2006), © American institute of Physics. Reproduced with permission⁵²

2.2 Design Approach

Figure 2.2 shows a schematic of our magnetic field sensor made of a $\text{Pb}(\text{Zr}_x\text{Ti}_{1-x})\text{O}_3$ or PZT disc type transformer and an attached magnetostrictive Terfenol-D disc. The output electrode ring and center electrode dot on the PZT act as input and output ports of the transformer, respectively. The attached magnetostrictive disc will alter the output voltage of the piezoelectric transformer once a magnetic field H is applied, via a ME coupling. On application

of a DC magnetic field, the magnetostrictive layer applies a mechanical force on the piezoelectric transformer which will alter its voltage gain.

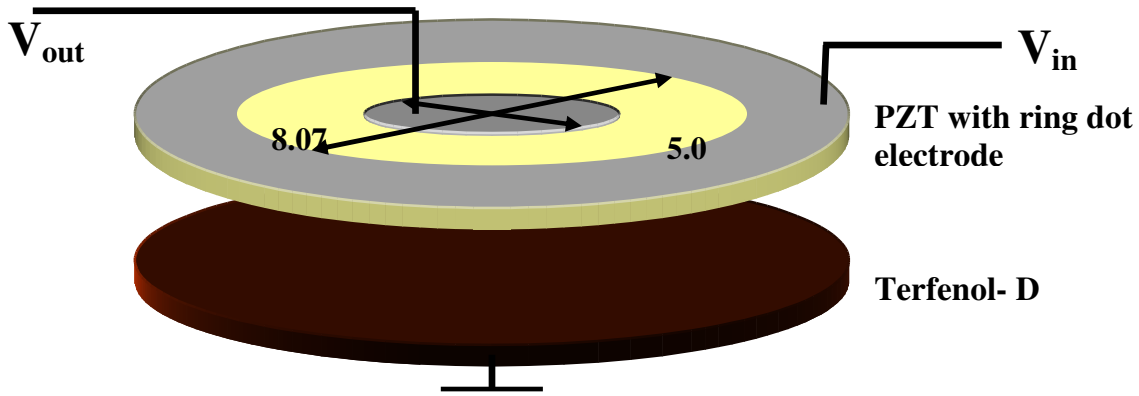


Figure 2.2: Schematic diagram of the DC magnetic field sensor. M. Karmarkar, S. X. Dong, J-F.Li, D. Viehland, S. Priya, *phys. stat. sol. (RRL)* 2, No. 3, 108 (2008), © Wiley-VCH Verlag GmbH & Co.KGaA. Reproduced with permission.⁶⁰

2.3 Experimental⁶⁰

A soft piezoelectric PZT composition was used, which was synthesized using a conventional mixed-oxide process. The samples were electroded with a ring and dot pattern on the top and bottom surfaces with a silver paste (Dupont 7713), and poled using an electric field of $E=25\text{kV/cm}$ for 30 minutes. Each face of the poled PZT discs was of dimensions $15.25 \times 0.85\text{mm}^2$. The diameter of the inner dot was 5.04mm and that of outer ring was 8.07mm, where the ratio of outer to inner electrode area was 6.59. The PZT discs were bonded with Terfenol-D discs of the same diameter by using epoxy resin (West System 105) and hardener (West System 206) in a 5:1 ratio. The input section of the sensor (i.e., outer ring) was excited by a HP3325B function generator using a frequency close to that of the piezoelectric transformer's

resonance, and the output response was measured as a function of applied voltage and applied magnetic field using an Agilent 54624A oscilloscope. In order to find the working frequency range, frequency sweeps were performed using a peak-to-peak voltage of 1Volt: which was determined to be 133 – 145 kHz. At these low voltage drives of $V^{PP}=1\text{Volt}$, no significant temperature rise was observed in the PZT. In addition, we also performed magnetoelectric measurements using a lock-in amplifier method (SR950 DSP).

2.4 Results and Discussion:⁶⁰

Figure 2.3(a) shows the variation of the output voltage as a function of frequency at various AC drives. The applied DC magnetic bias was kept constant at 1 kOe. The data shows the shift in the frequency of the maximum amplitude of vibration towards lower values and a widening of the resonance spectrum with increased AC drives. The increased asymmetry of the resonance curve with a bending towards lower frequencies upon increased excitation is typical of an elastic nonlinearity in elastically soft material. The widening of the resonance peak indicates that the mechanical damping factor increases with increased excitation.

Figure 2.3(b) shows the variation of the output voltage as a function of frequency and applied DC magnetic bias (H_{dc}) for an applied input voltage of $1V^{PP}$. There is a strong shift in the resonance frequency (f_r) over the range of $137.4 < f_r < 144.2$ kHz with increasing bias from $1 < H_{dc} < 6\text{kOe}$: i.e., a shift of $\sim 1.36\text{Hz/Oe}$. The output voltage from the transformer decreased from about 8.5 to 6.5Volts with increasing H_{dc} . Since $g = V_{dot}/V_{ring}$ where V_{ring} is constant, similar decreases in the gain of the transformer will occur with increasing H_{dc} .

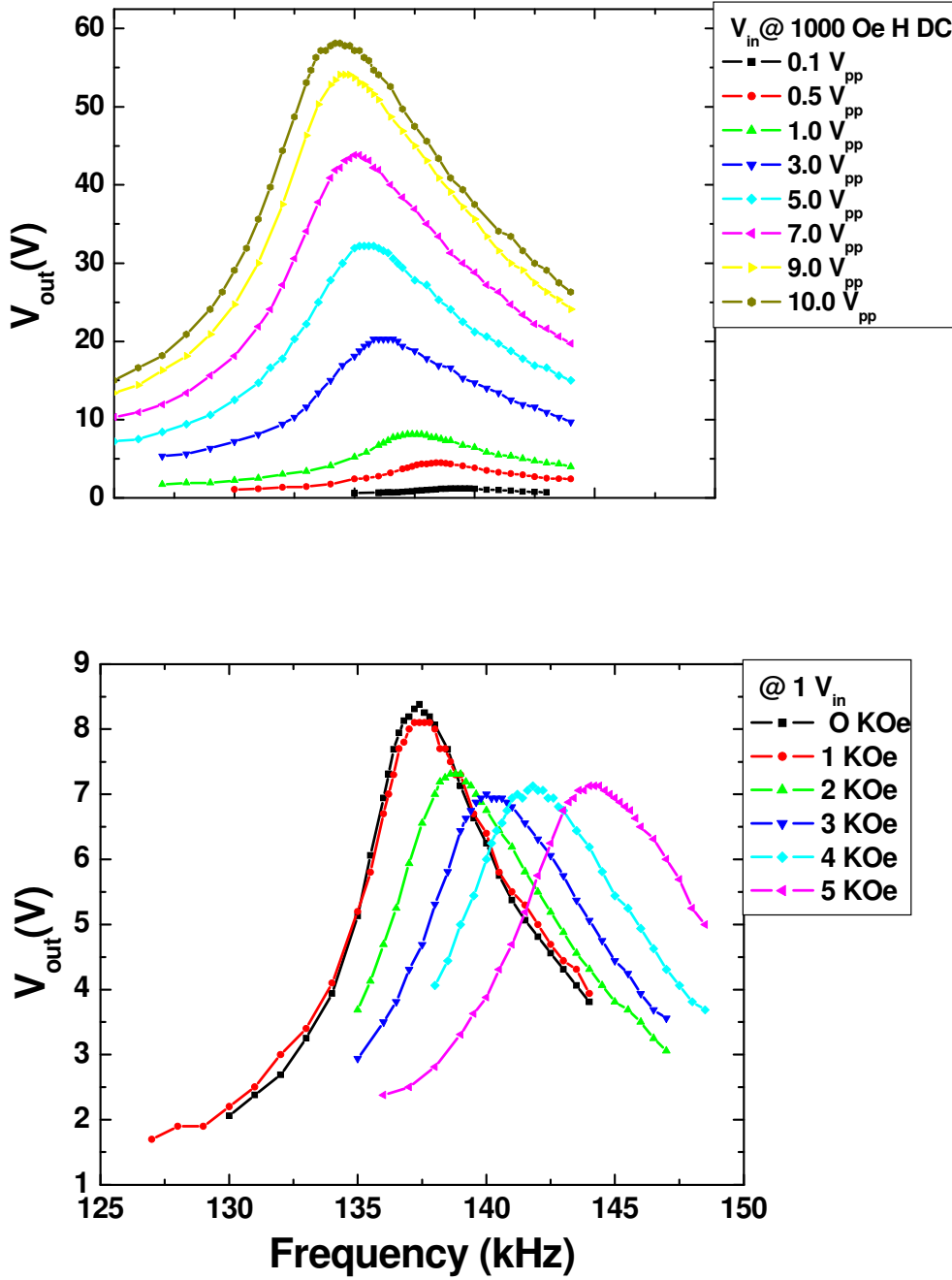


Figure 2.3: Resonance measurement on the bilayer sensor. (a) Variation of the output voltage as a function of input voltage and frequency at constant DC magnetic field of 1kOe, and (b) Variation of the output voltage as a function of the frequency DC magnetic field at constant input

voltage of $1V^{pp}$ M. Karmarkar, S. X. Dong, J-F.Li, D. Viehland, S. Priya, phys. stat. sol. (RRL) 2, No. 3, 108 (2008), © Wiley-VCH Verlag GmbH & Co.KGaA. Reproduced with permission.⁶⁰.

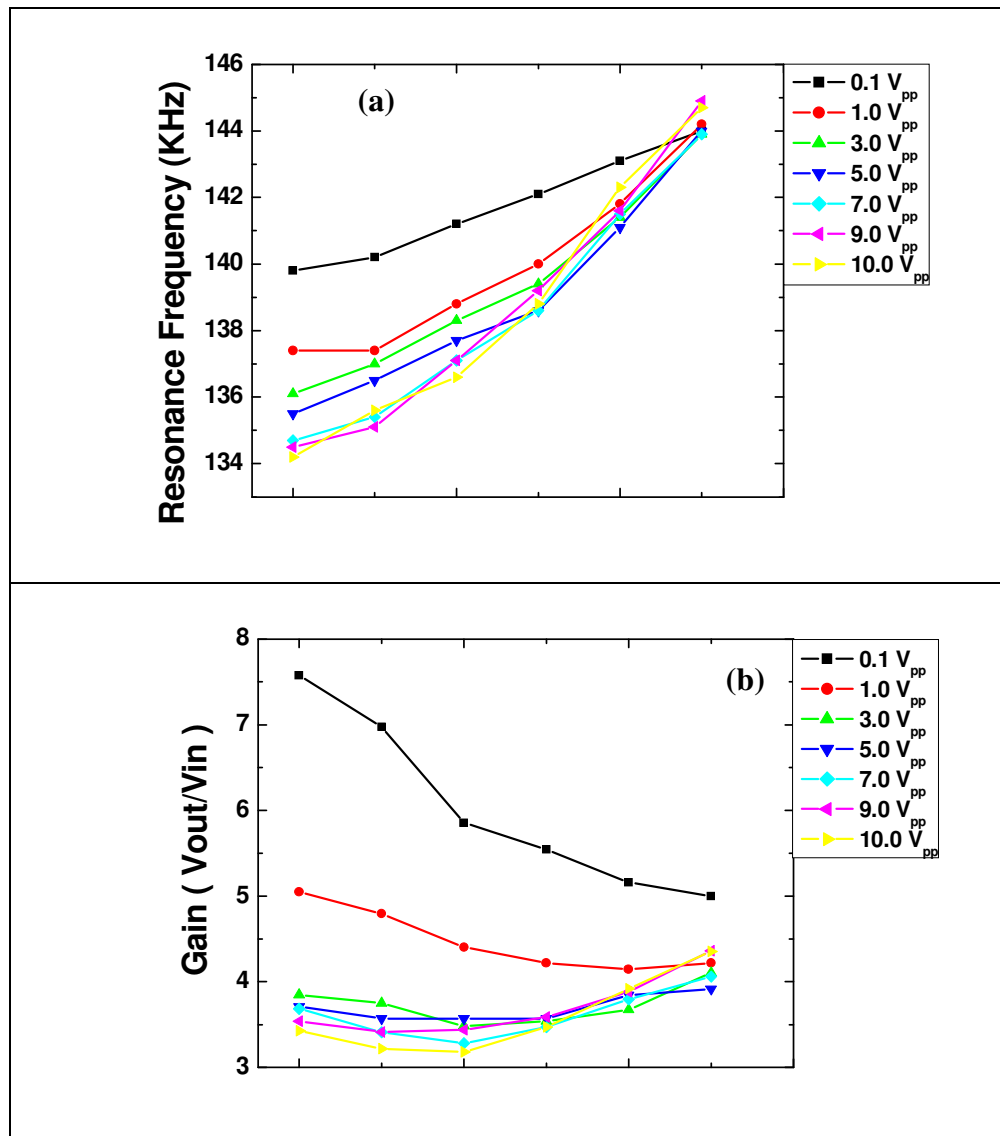


Figure 2.4: (a) Variation of the resonance frequency as a function for DC magnetic field for various input voltages, (b) Variation of the transformer gain as a function of the DC magnetic field for various input voltages,

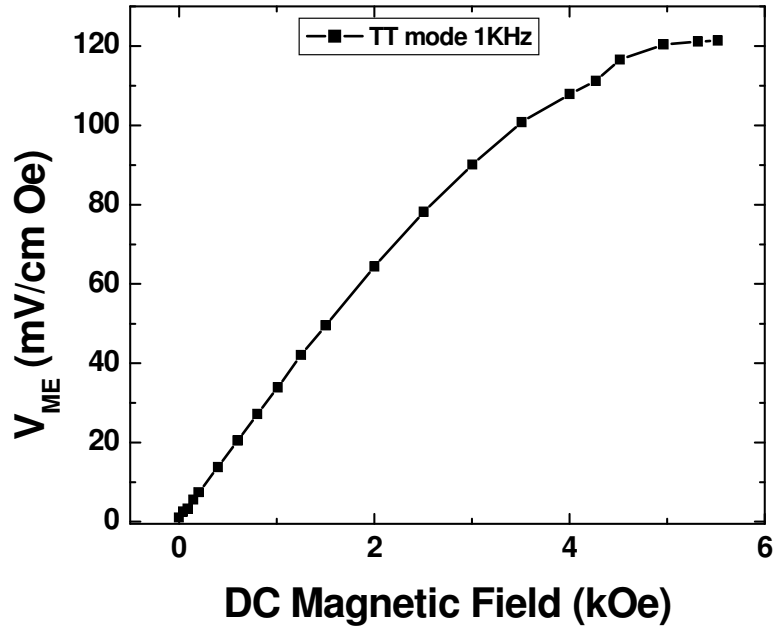


Fig 2.4 (c) Magnetolectric voltage coefficient as a function of DC magnetic bias at 1kHz From M. Karmarkar, S. X. Dong, J-F.Li, D. Viehland, S. Priya, phys. stat. sol. (RRL) 2, No. 3, 108 (2008), © Wiley-VCH Verlag GmbH & Co.KGaA. Reproduced with permission.⁶⁰

Figures 2.3 (a) and (b) summarize the shift in f_r and the decrease in transformer gain with increasing H_{dc} . A linear increase in f_r can be seen with increasing H_{dc} , where increasing input voltage results in a significant softening of f_r . Please note by comparing these two figure parts that the largest input voltage (~ 10 V) resulted in the largest change in f_r , whereas the smallest input voltage (~ 0.1 V) provided the largest change in the gain. At higher biases, the values of f_r and g were found to converge for the various input voltages, reflecting saturation. Figure 2.4(c) shows the ME voltage coefficient (V_{ME}) as a function of H_{dc} . For $H_{dc} > 4$ kOe, the ME voltage coefficient saturated at a maximum value of $V_{ME} \approx 0.12$ V/cm-Oe.

We can understand the linear shift in f_r of the composite disc with H_{dc} , by considering the effect of magnetoelectricity on the elastic constant of the piezoelectric phase, via electrostriction. Let's assume the disc laminate operates in a radial vibration mode, the resonance frequency can then be expressed as

$$f_r = \beta \frac{\bar{v}}{2\pi a} = \beta \frac{\sqrt{C_{ijkl}^{eff}}}{2\pi a} \frac{1}{\rho} \quad (1)$$

where β is a constant related to mean Poisson's ratio of the laminate disc, a is radius of the disc, $\bar{v}$ is the mean velocity, C_{ijkl}^{eff} is the effective elastic constant, and ρ is the average density. The elastic constant of soft piezoelectrics has been shown to be dependent on electrostriction, given as:

$$C_{ijkl}^{eff} = C_{ijkl}^{eff}(0) + C_{ijklmn}^{eff} Q_{mnop} \Delta P_o \Delta P_p \quad (2)$$

where the first term on the left is the effective elastic stiffness under zero field, and the second is the nonlinear elastic stiffness contribution due to electrostrictive strain; where ΔP is the induced polarization change and Q_{mnop} the electrostriction constant. An applied magnetic field will induce a shape change in the Terfenol-D disc, via magnetostriction. This strain will then be elastically coupled to the piezoelectric disc, resulting in an induced polarization change within that layer and an induced voltage across it. The polarization change induced by a magnetic field in a ME composite material is $\Delta P = \alpha_{me} H_{dc}$ where α_{me} is the magnetoelectric charge coefficient: which is related to the ME voltage coefficient (α_{ME}) by $\alpha_{ME} = \chi_{eff} \alpha_{me}$, where χ_{eff} is the effective dielectric constant. Equation (2) can then be modified to be

$$C_{ijkl}^{eff} = C_{ijkl}^{eff}(0) + C_{ijklmn}^{eff} Q_{mnop} \frac{\alpha_{me}^2}{\chi_{eff}^2} H_{dc}^2. \quad (3)$$

By placing (3) into equation (1), we can then predict that f_r is linearly proportional to H_{dc} . The resonance frequency linearly increases because the effective linear elastic constant is increased by the magnetoelectric-induced polarization.

The magnitude of the ac electrical voltage (V_{ac}) used to drive the piezoelectric transformer also had an effect on the resonance frequency, as illustrated in Figs.2.3(a) and 2.3(b). However, in this case the elastic stiffness was decreased with increasing V_{ac} , opposite the effect of H_{dc} . Prior investigations of piezoelectrically-driven and mechanically-driven perovskite ferroelectrics have revealed a dependence of the resonance frequency on the amplitude of excitation, where the resonance frequency shifts to lower frequencies with increasing [9,10], as given by:

$$f_r(eff) = f_r^{lin} + \frac{3}{8} \left(\frac{\gamma \epsilon^2}{f_r^{lin}} \right) \pm \sqrt{\left(\frac{K}{f_r^{lin}} \right)^2 - \delta^2} ; \quad (4)$$

where $f_r(eff)$ is the effective resonance frequency defined by the maximum displacement amplitude, f_r^{lin} is the amplitude independent linear resonance frequency, γ is the nonlinear elastic constant, δ is the mechanical damping factor, K is the external excitation, and ϵ is the rms strain amplitude of the vibration of the sample. Previous investigations have shown significant dynamic nonlinear effects in soft PZTS: in fact, α / f_r^{lin} is about 40x higher for soft PZTs relative to hard ones⁶¹⁻⁶².

To summarize, following our data and equations (1) and (4), we report a design for a DC magnetic field sensor that detects a change in H_{dc} by a shift in the resonance frequency. The sensitivity of such a dc magnetic field sensor would depend on (i) the ME coefficient, (ii) the saturation magnetic field, and (iii) the amplitude of excitation via elastic nonlinearity. A large

ME coefficient with lower saturation fields will provide higher sensitivity. To lower power consumption, it would be best to drive the piezoelectric oscillators as weakly as possible.

CHAPTER 3 - MAGNETIC PROPERTIES OF METAL-CERAMIC COMPOSITE CORE-SHELL STRUCTURES SYNTHESIZED USING COPRECIPITATION AND HETERO-COAGULATION

3.1 Introduction: applications of core shell particles

This chapter focuses on one of the method of making composite structures in core-shell form. Core and shell metal–ceramic composite particles are of significant research interest for novel properties that could be enabling to various applications. Recently, magnetic core-shell particles have been synthesized with metal –metal oxide structures such as Co-CoO^{63,64}, FePt-Fe₂O₃⁶⁵, CoFe-Fe₃O₄⁶⁶, Ni-Fe₂O₃^{67,68} and FeNi₃-NiZnFe₂O₄⁶⁹; and with all metal oxide structures such as CoFe₂O₄-ZnFe₂O₄.⁷³ These particles are considered prospective candidates for high capacity magnetic memory device,⁷⁰ microwave, EMI shielding^{67,68,71} and biomedical applications.⁷²⁻⁷⁴

One way to synthesize core-shell structures is by combining the process of co-precipitation with hetero-coagulation⁷⁵⁻⁷⁸. This would allow co-synthesis of two dissimilar material systems. The process of hetero-coagulation consists of coagulation of particles with opposite surface charges dispersed in a solution^{77,78}. At a specific pH value, one of the species has positive surface charge density, and the other a negative one: this corresponds to the average iso-electric points of the two powders. The zeta potential is both a function of dispersing media and of pH, and accordingly can be tailored by additives. The individual particles to be hetero-

coagulated can be synthesized by various means. For example ferrite particles can be synthesized by coprecipitation⁷⁹⁻⁸², sol-gel⁸³, spray pyrolysis⁸⁴ and hydrothermal⁸⁵ methods. Coprecipitation followed by hetero-coagulation of two dissimilar types of magnetic particles offers the possibility to develop, for example, exchange-biased core-shell composite particles that have superior magnetic and electrical properties.

In this chapter, we synthesized metal-ceramic magnetic composite material systems with a core-shell structure by using co-precipitation and hetero-coagulation techniques. We have synthesized core-shell structures that (i) have Ni particles of μm size which are near-fully coated with nano particles of MZF; (ii) have Ni particles of sub-micron size which are fully coated with nano-particles of MZF; and (iii) have resultant magnetic properties superior to those of either core or shell. The core-shell particles were subsequently sintered in a ($\text{N}_2 + \text{H}_2$) atmosphere at high temperature to achieve dense magnetostrictive metal-ceramic composites. MZF was selected as the magnetic oxide system because of its high permeability, high resistivity and potential for electromagnetostriction (i.e., electric field controlled magnetostriction); whereas, Ni was selected as the metal system because of its ability to be co-sintered with ceramics, and its high conductivity and magnetostriction. Nickel has an anisotropic magnetostriction ($\lambda_{111}=-25 \times 10^{-6}$ and $\lambda_{100}=-46 \times 10^{-6}$) with a $\langle 111 \rangle$ easy axis, and its electrical resistivity is of the order of $6 \times 10^{-6} \Omega \cdot \text{cm}$.

3.2 Experimental Procedure

Ammonium hydroxide, $\text{MnSO}_4 \cdot \text{H}_2\text{O}$, $\text{ZnSO}_4 \cdot 7\text{H}_2\text{O}$ and $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ (Alfa Aesar), were used as starting reagents for synthesis of MZF. Nano particles were synthesized by a coprecipitation route using individual metal salts. The initial steps consisted of hydrolysis of the metal salts (sulfates, chlorides, nitrates) into their respective hydroxides; as a subsequent step,

the metal hydroxide precipitates form the spinel ferrite structure on heating between 85-95 °C under constant stirring:



Salts of the metal sulfates ($\text{MnSO}_4 \cdot \text{H}_2\text{O}$, $\text{ZnSO}_4 \cdot 7\text{H}_2\text{O}$ and $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$) were dissolved in stoichiometric proportion (0.05M, 0.05M, 0.2M respectively) in deionized water and mixed with a 1M 35% aqueous NH_4OH solution preheated at 85 °C under constant stirring. A higher concentration of the precipitating base was intentionally added to achieve faster reaction time and a larger precipitate size. The stoichiometry of the resulting MZF particles is sensitive to the process parameters. It has been reported that for pH values > 10 and for an alkalinity > 2 that stoichiometric MZF is obtained.⁸⁶⁻⁸⁸ Accordingly, the resulting mixture was continuously stirred, at a pH of 10 and a temperature of 85 °C, for two hours. During which time the metal hydroxides reacted to form spinel ferrite. The precipitates were magnetically decanted and washed repeatedly (5 times) in deionized water until the supernatant was close to 7. The powders were dried in air at 70 °C for 5 hours.

Spinel phase formation was confirmed by X-ray diffraction (Powder XRD D500, Siemens Kristalloflex 810), using Cu K α radiation ($\lambda = 1.54 \text{ \AA}$) at a scan speed of $0.01^\circ \text{sec}^{-1}$, and a dwell time of 0.5 sec. The as-synthesized MZF particles were confirmed to have the spinel structure, as shown in Fig. 3.1(a). However, after repeatedly storing freshly synthesized particles over a period of 3 days, we found that the particles exhibited a change in chemical composition, as quantified by elemental analysis using energy dispersive analysis by X-rays or EDAX (Supra 55VP Leo). The reason for this change may be related to a room temperature decomposition of the particles into iron oxide (although XRD did not reveal a new phase formation), or the leaching of ions from samples stored under wet conditions.

Zeta potential measurement was done by using Malvern Nano ZS ZEN3500 zetasizer. The sample solution was synthesized by dispersing 1-5 mM of particles under consideration in 1mM of NaCl and DI water followed by automated stirring at 80 rpm. Concentration of particles in the solution was decided by utilizing the phase data, standard deviation of zeta potential and stability of particles against self agglomeration. The magnitude of pH was varied from basic to acidic scales by addition of 1M NaOH and 0.1M HCl solutions.

Nickel powders were procured from a commercial source (Inframat Advanced Material Inc.), which were determined to have a multimodal size distribution. Hetero-coagulation was performed by ultrasonically mixing solutions of filtered MZF precipitates and nickel particles (1% and 5% by volume, respectively) for 10 minutes in an inert atmosphere to avoid oxidation of nickel. This procedure was repeated at various pH levels over the range of $2 < \text{pH} < 12$, which was controlled by HNO_3 (EM Science) or tetra ethyl ammonium hydroxide (TEAOH, Alfa Aesar) in deionized water. To get better coating of MZF particles and to have stable zeta potential values, Ni particles were synthesized in lab with hydrazine reduction of nickel sulphate powders. Once core-shell particles were obtained and characterized, they were mixed in different ratios with nano sized MZF particles and were sintered in slightly reducing atmospheres

3.3 Results and Discussion:

3.3.1: X-ray, Electron microscopy analysis:

Figure 3.1(b) shows XRD patterns for the core-shell composite particles. In this figure, the Ni peaks over shadow the MZF ones. The crystallite sizes of the MZF shells is too small to yield sharp peaks and hence are quite broadened, whereas the Ni particles are larger and well-crystallized. Please note in this figure that the presence of MZF which coated Ni was magnified by a log intensity plot. Nickel particles synthesized by aqueous hydrazine reduction were used

for hetero-coagulation with MZF using the same procedure. The core-shell structure was directly confirmed by transmission electron microscope or TEM and by selected area electron diffraction pattern or SAED (JEOL 1200EX).

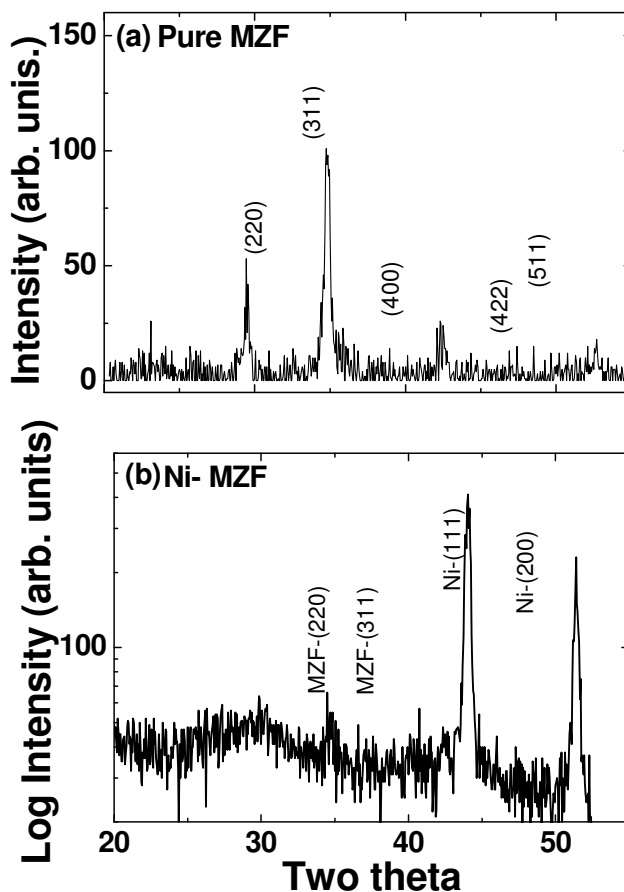


Figure. 3.1: X ray diffraction pattern of pure (a) MZF precipitates and (b) Ni coated with MZF

SEM/TEM characterization:

The extent of hetero-coagulation was monitored at each pH by SEM/ EDAX analysis and TEM/SAED. Figure 3.2 shows SEM images that illustrate the effect of pH on the extent of MZF coating over the nickel cores. It can be seen that a pH=10 yields the most uniform MZF coating.

EDAX analyses of the particles in the images of Fig. 3.2(a) – (d) was then performed by EDAX. Studies of uncoated particles (Fig. 3.2a) revealed the presence of only nickel, whereas coated ones had signatures of both MZF and Ni, via their respective electron excitation energies. The structure of the core-shell composite particles was then characterized by TEM

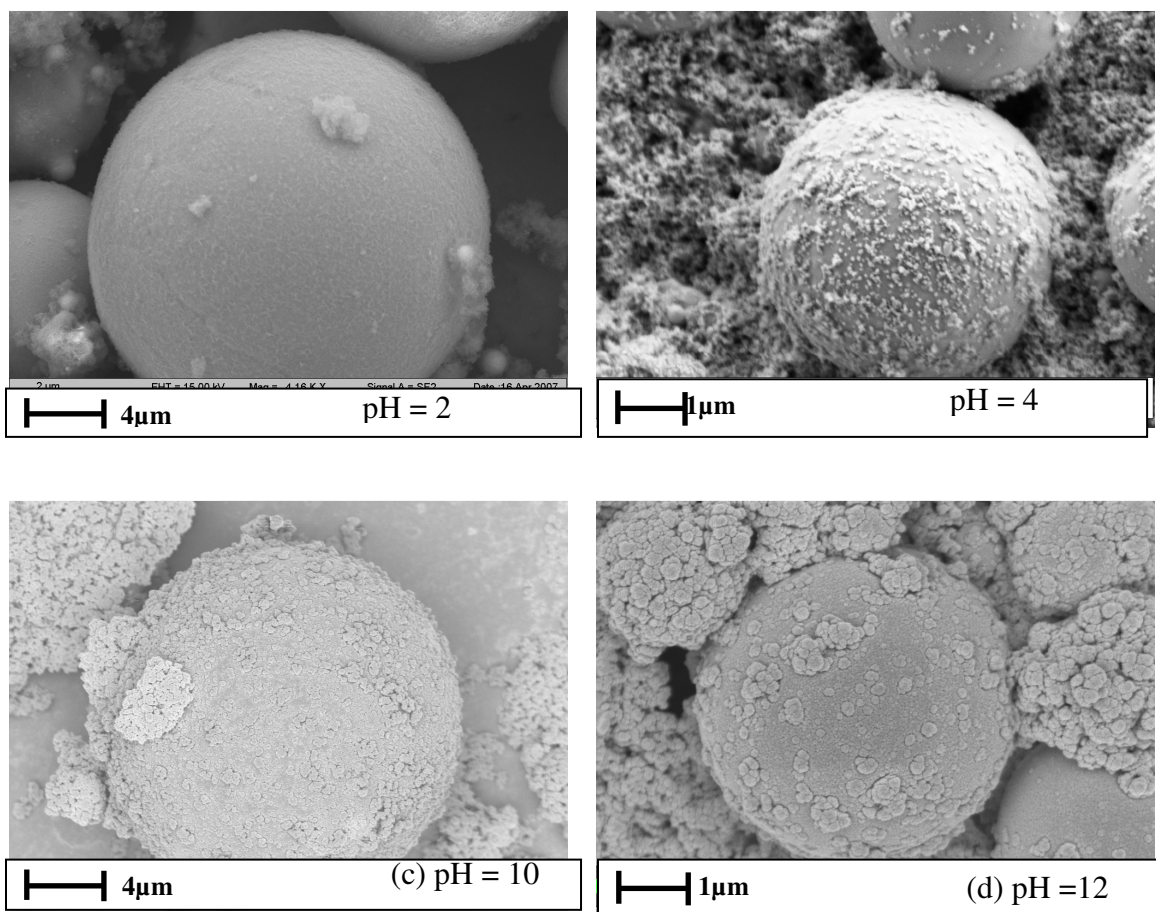


Figure 3.2: SEM micrographs of extent of composite coating of MZF shell over Nickel core as a function of pH; (a)pH=2,(b)pH=4,(c)pH=10 and (d) pH=12

Figure 3.3 shows a TEM image for fully MZF coated Ni particles: the dark spherical regions are the nickel cores, whereas, the lighter areas are the MZF shell coatings. The MZF shell particle size can be seen to be ~20 nm, and an electron diffraction pattern taken from a

region containing only MZF particles (marked by an arrow in Fig. 3.3) is shown in the inset. This diffraction pattern revealed rings, which is consistent with the broad XRD peaks, reflecting the finite size of the nano-particles. The zones of the various rings are identified in the inset. The ring of the strongest intensity was indexed to be $2.56 \text{ \AA}$, which corresponds to the (311) reflection of the MZF spinel structure.

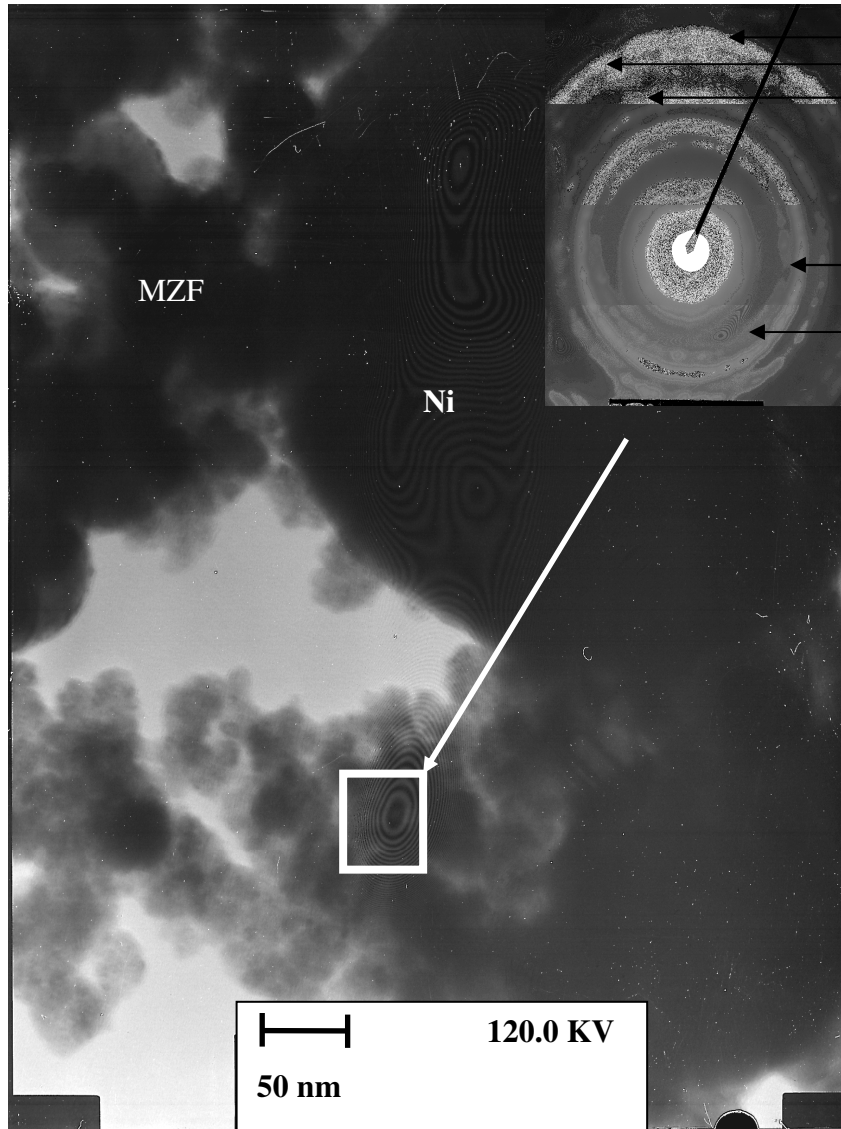


Figure 3.3: TEM image of Ni coated with MZF with inset showing indexed SAED pattern of MZF and the area corresponding to the SAED

3.3.2 Zeta potential measurements:

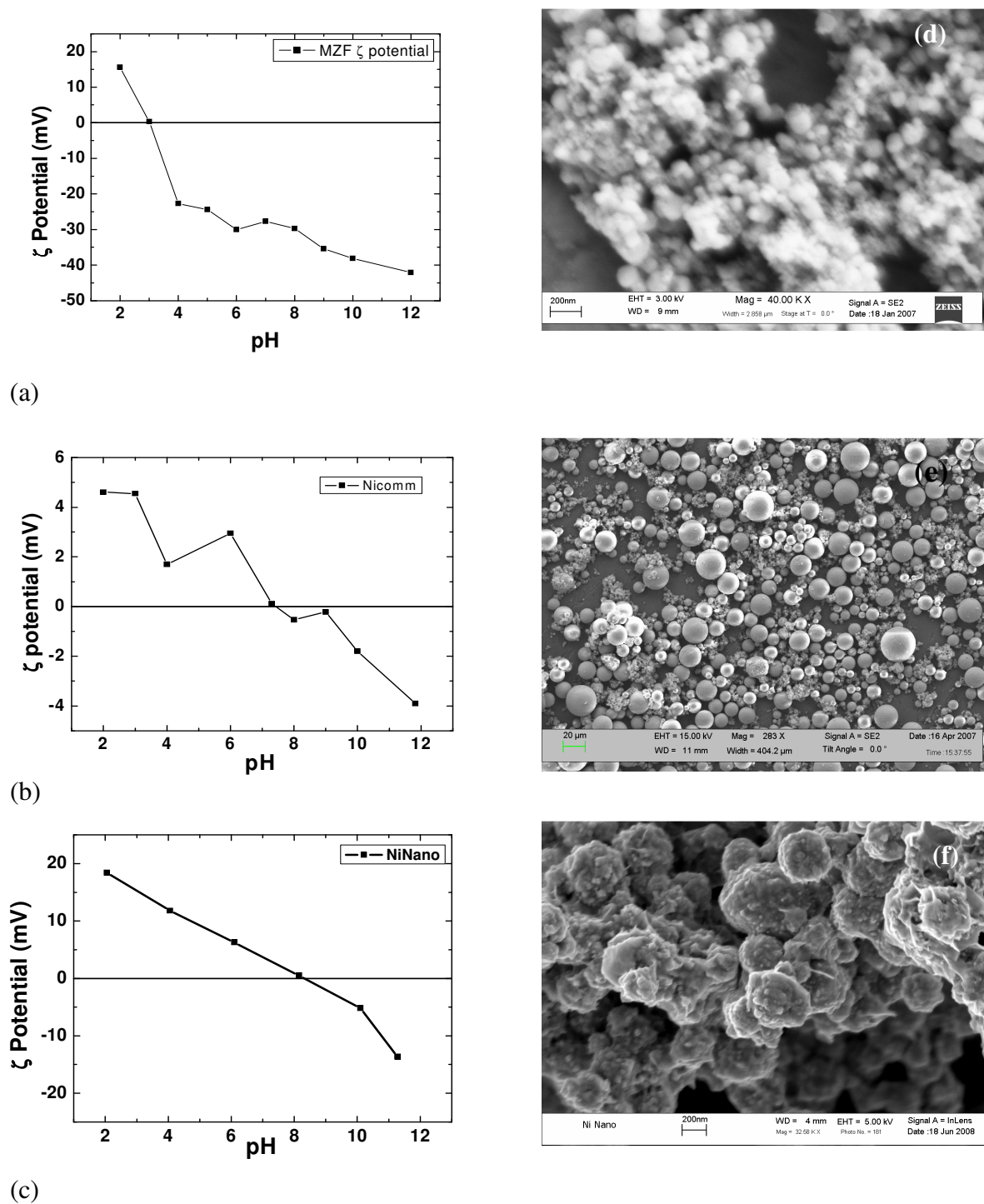


Figure 3.4: Zeta potential of synthesized (a)MZF, (c)Ni and commercial(b)Ni particles

The combinations of Figs 3.3 and 3.4 directly confirm that MZF nanoparticles can be near uniformly coated on larger Ni particles, forming a magnetic oxide / metal core-shell structure.

The as-obtained commercial nickel particles were found to have a large particle size variation by SEM particle size analysis: from $50 < d < 20,000$ nm. Such a wide variation of particle size can have a direct influence on hetero-coagulation with MZF: hence, submicron size nickel particles were synthesized in the lab by reduction of nickel ions (nickel sulfate hexa hydrate- 98%) with hydrazine monohydrate and NaOH in aqueous solution[34,35] The resulting particles size distribution were narrower and had smaller average size $300 < d < 500$ nm, as can be seen in the SEM image of Fig. 3.5(a). The roughness of nickel particle surfaces is characteristic of hydrazine and nitrogen reductions of particles formed in the solution.

Ni commercial contains large particles which act as centers to attract other small Ni particles making large agglomerate and giving rise to small zeta potential values. In contrast the lab synthesized Ni particles have close size range giving higher mobility and zeta potential. Also, they can be dispersed in the solution for longer times than commercial Ni particles. Zeta potential follows the equation $\zeta = q/4\pi\epsilon\epsilon_0 a$, where a is the radius of particle and q is the charge. The result is visible in the zeta potential graphs in Fig3.4 (b) and (c) where commercial nickel powders show unstable zeta potential values as compared to lab synthesized particles. To get an idea of the particle size and size distribution each zeta potential graph is shown with an SEM micrograph showing the particles. Higher zeta potential values for MZF can be explained by the basic conditions of MZF synthesis ($\text{pH} > 10$), unreacted metal hydroxides and possible presence of OH bonds on the surface and of particles. Due to large difference in surface charge between

MZF and commercial Ni at a range of pH from 7 to 12, hetero-coagulation is seen in this region but at higher pH values MZF has very high zeta potential which would explain the agglomerated MZF particles still attached on lower surface charged Ni. At lower (acidic) pH values both MZF and Ni have low surface charge and have no driving force for agglomeration.

3.3.3 Heterocoagulation with nanosized Ni particles:

Fig3.5 shows similar heterocoagulation experiment done with lab synthesized Ni particles. Similar to results in fig 3.5(b) they too was found to be coated with MZF at pH 10. The SEM image in Fig 3.5(b) shows composite particles synthesized by hetero-coagulation with Ni. Following the steps described above, an optimum coating was found for pH=8: the MZF coating is nearly complete although its topology is not uniform. It can be seen that the surface roughness of the particles is accentuated by hetero-coagulation, as can be seen in the TEM image of Fig 3.5(c). Please note that the nickel particles were too thick for electron transmission, hence the diffraction pattern reveals inter-planar spacing (rings) only for the MZF coatings.

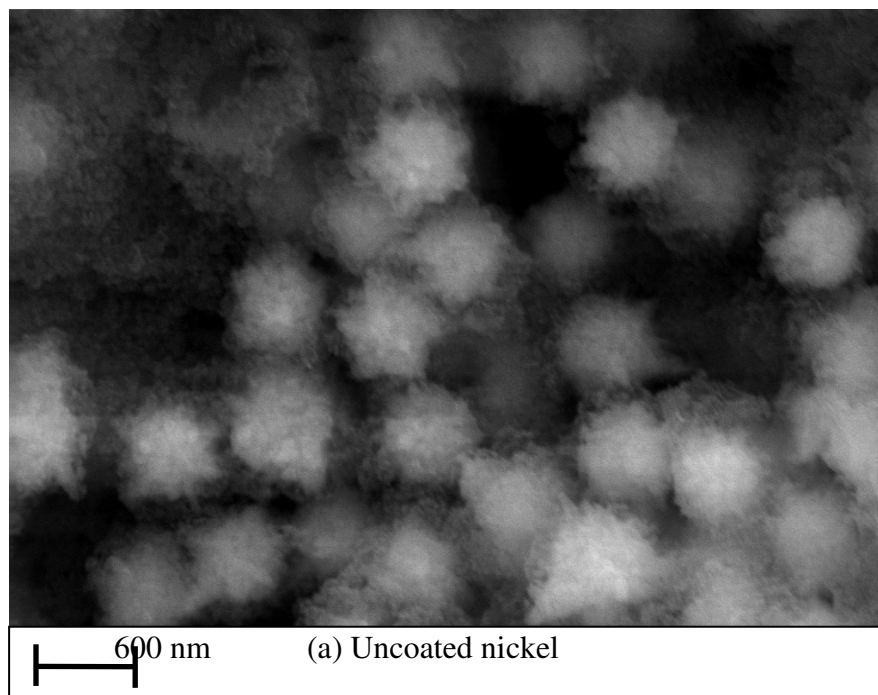


Figure 3.5: (a) Pure nickel particles synthesized by hydrazine reduction of nickel ion.

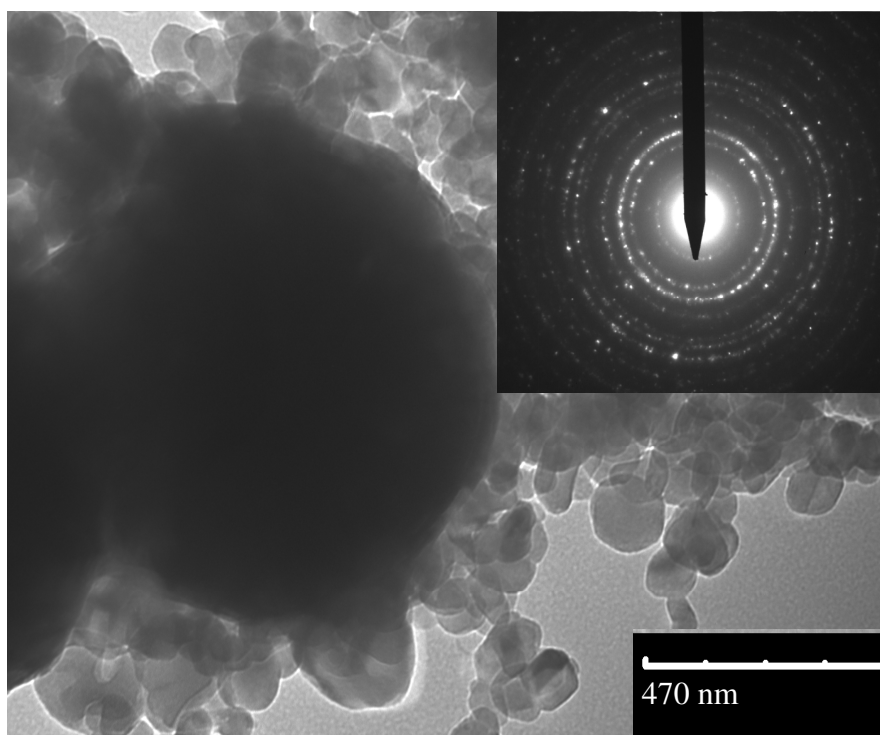
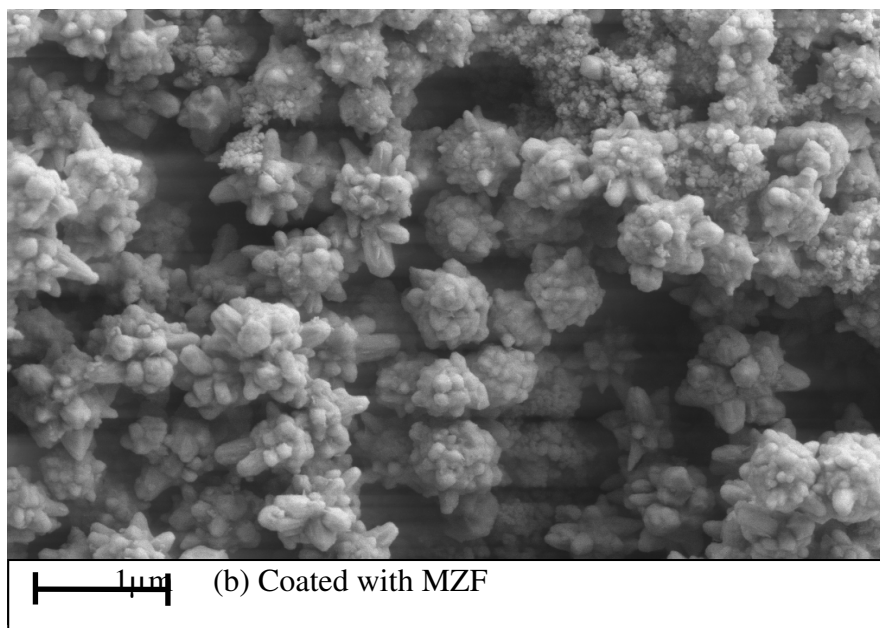


Figure 3.5: (b) Hetero-coagulated nickel MZF particles at pH 8. (c) TEM image of MZF coated Ni with inset showing SAED pattern of MZF.

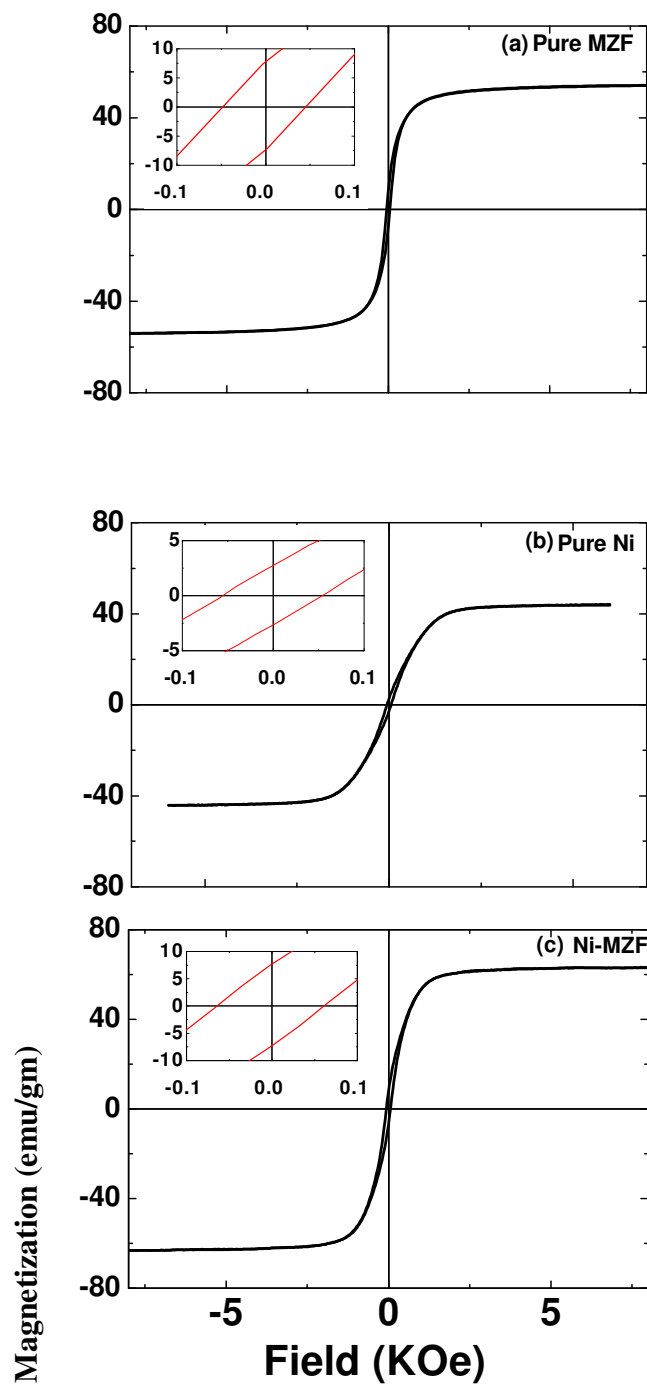


Figure 3.6: Magnetization measurement of (a) pure MZF precipitates (b) Pure Ni particles and (c) composite MZF coated Ni. Inset in each figure shows the magnified loop at low fields to read coercivity and remanence magnetization

3.3.4 Magnetic Charecterization:

The magnetic properties of as-synthesized particles were then studied after drying using an alternating gradient magnetometer or AGM (Princeton Measurements Corporation, Micromag 2900). The MZF particles were found to have a coercivity, of $H_c=45\text{Oe}$, which is higher than that of sintered bulk MZF $H_c=1\text{Oe}$,⁸⁸⁻⁹⁰ as seen in Fig. 3.6(a). The saturation magnetization of coprecipitated MZF was $M_s=54\text{emu/gm}$, which is lower than that for bulk samples (milled, calcined and sintered), where $M_s=60-80\text{ emu/gm}$: possible reasons mentioned below. The magnetization of pure nickel is given in Fig. 3.6(b), and is similar to previously reported values⁹¹. Since MZF is an iron based nanocrystallite, it has a higher normalized saturation magnetization, relative to pure Ni. Next, we show the magnetic properties of Ni-MZF core-shell structures. In Fig.3.6(c), it can be seen that these composite particles had lower values of H_c than pure Ni, while having an M_s comparable to that of MZF. Furthermore, the magnetic properties of these core-shell structures were found to be dependent on the volume fraction of the Ni and MZF phases; although, we have yet to perform a detailed investigation to determine the form of any composite rule of mixing.

The lower magnetizations for MZF nano particles may be attributed to (i);ower magnetic ions in smaller particles (ii) non–stoichiometry: if MZF deviates from ideal stoichiometry, as the magnetization will be reduced by Fe_2O_3 2nd phase precipitates; (iii) moisture: since our particles were dried at $100\text{ }^\circ\text{C}$, there may be up to 10wt% residual H_2O that does not dehydrate until heating above $250\text{ }^\circ\text{C}$; and /or (iv) small particle size: decreasing particle size has been previously reported known to reduce the magnetization⁹². In addition, formation of surface dead layers⁹³, non-saturation effects due to a random particle size distribution⁹⁴, and changes in normal cation distribution⁹⁵ have all been reported to reduce the magnetization of nanoparticles.

It should be noted that MZF particles are nanosized but are not superparamagnetic, since they do show coercivity ⁹⁴.

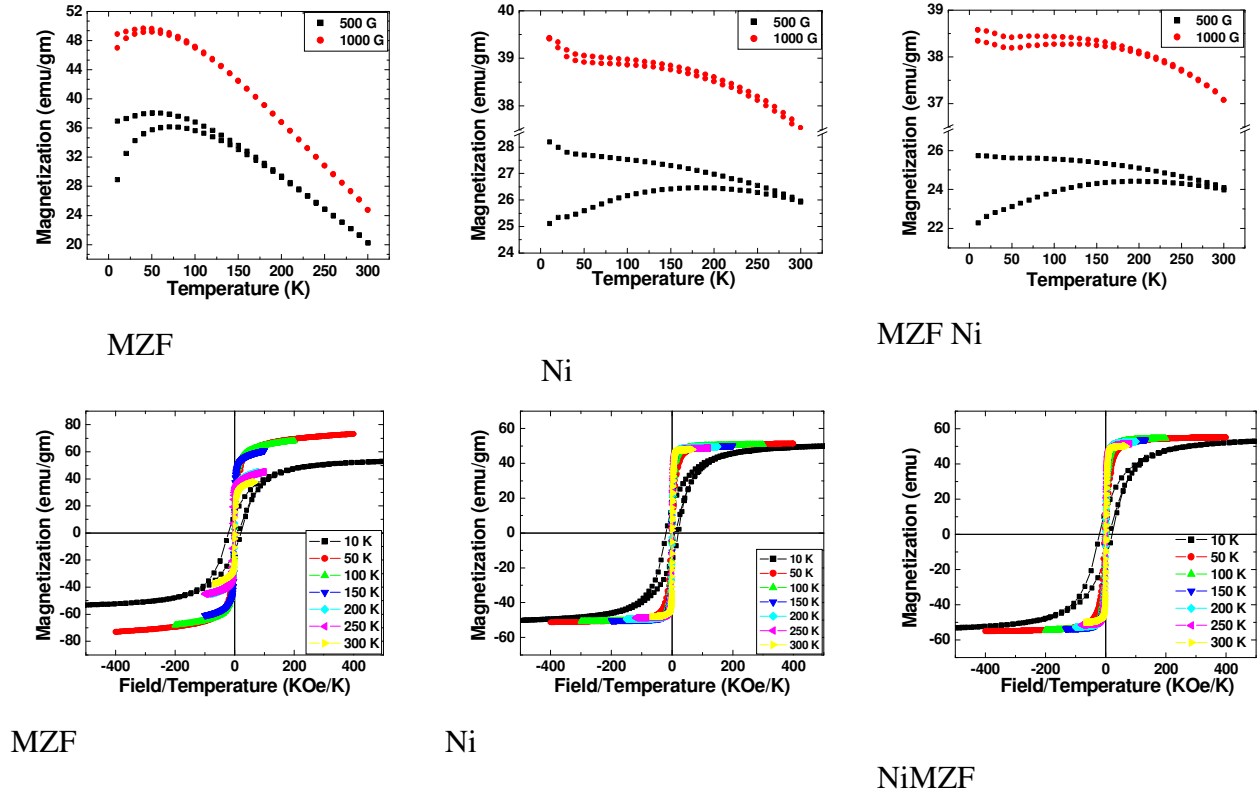


Figure 3.7: Magnetic characterization of Ni-MZF particles and composite

The magnetic properties of these composite particles were then measured by AGM as shown in Fig. 3.7. These data revealed similar trends as for Ni-MZF core-shell particles hetero-coagulated with Ni particles that we synthesized. The coercivity of the composite particles was larger than those of pure nickel, whereas the magnetization was comparable to that of MZF.

3.3.5 Sintering experiment results:

With a view of sintering core-shell particles of Ni-MZF, with a piezoelectric matrix like $0.8\text{Pb}(\text{Zr}_{0.52}\text{Ti}_{0.48})\text{O}_3$ - $0.2\text{Pb}(\text{Zn}_{0.33}\text{Nb}_{0.66})\text{O}_3$, initially Ni-MZF particles were sintered in different sintering atmospheres. Pellets of the size 5.6mm diameter and 1mm thickness were uniaxially pressed at 1000 lbs and subjected to various sintering cycles in controlled atmosphere in a tube furnace. Optimized sintering temperature and atmosphere (1050 °C and 2 vol % Hydrogen in Nitrogen atmosphere) was found for sintering Ni-MZF. This temperature and mildly reducing atmosphere was able to prevent Ni oxidation at higher temperature while preventing MZF from decomposing to any other constituent oxides or change of valence. Sintering results for PZT and NiMZF are given in appendix since they need to be optimized.

Finally, magnetostriction measurements were performed on sintered samples containing 20wt% MZF-Ni composite particles and 80 wt% co-precipitated MZF as shown in Fig. 3.9(a). The samples were discs that were 5.6mm in diameter, with a thickness of 0.60mm. A strain gage (120ohm: EA-06-060LZ-120) was bonded to the polished surfaces of sintered samples, and the strain gage response was measured via a wheatstone bridge circuit as shown in Fig. 3.9(b). The value of magnetostriction was found to be 5.2ppm which is on the high end of that typical for $(\text{Mn,Zn})\text{Fe}_2\text{O}_4$ bulk materials (.02-5ppm)^{89,98}, but lower than that of pure nickel (-40 ppm)⁹⁹. However, our samples had high MZF particle fractions. These results demonstrate success in synthesizing metal-ceramic core-shell composite structures, which are also attractive for electromagnetostrictive structures. A dense microstructure with a more homogenous phase distribution might help in enhancing the magnetostriction. As discussed in experimental part,

initial sintering tests were done on Ni-MZF particles with varying proportion of core-shell Ni MZF in MZF matrix.

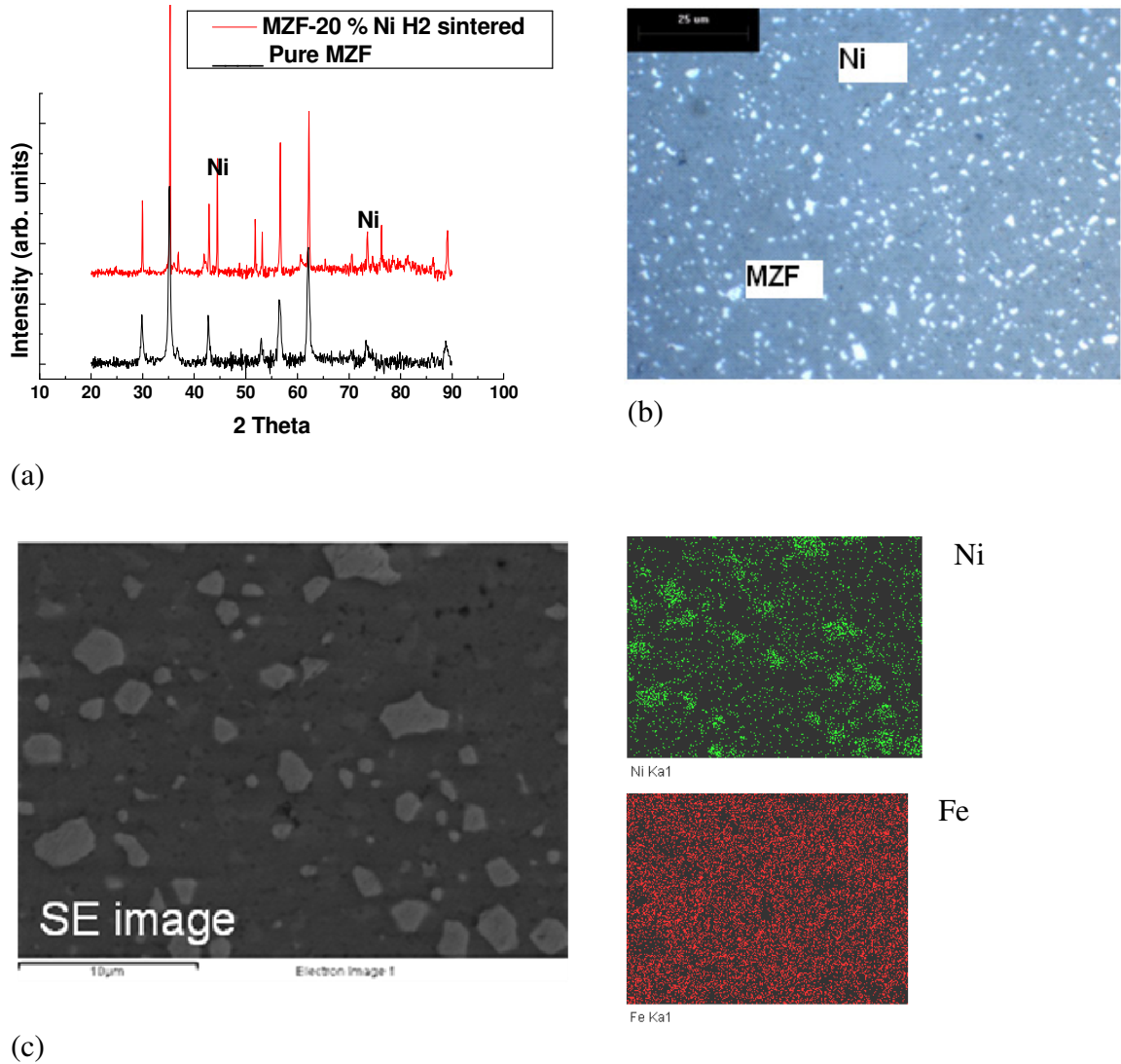


Figure 3.8: Sintered (b) optical and (c) SEM microstructure of Ni-MZF composite, (a) x-ray diffraction from polished surface showing pure Ni and MZF peaks from sample compared with pure MZF peaks with (d) Ni and Fe EDAX maps confirming presence of unoxidized Ni

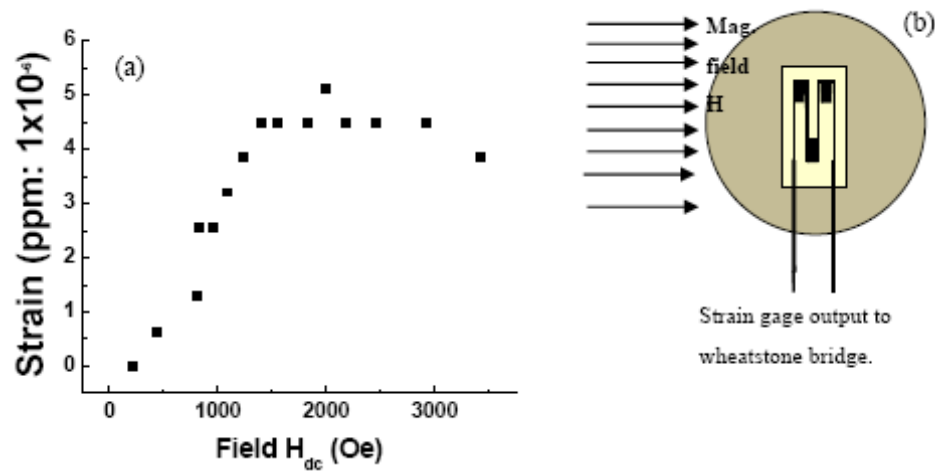


Figure 3.9: Strain measurement on sintered pellet and schematic of measurement method

Sintering the core-shell particles with PZT matrix was not successful because of thermodynamically instable region for PZT based materials in inert or reducing atmosphere. The results of sintering are presented in appendix A where inert atmosphere of nitrogen was not able to prevent Ni oxidation (characterized by X-ray and SEM) since Ni particles were surrounded by MZF and PZT. As a solution to this problem, sintering with BaTiO_3 as a matrix in the core shell structure was proposed and initial sintering tests with Ni- BaTiO_3 were conducted. The results of the same are shown in the appendix A.

CHAPTER 4 - PIEZO-RESISTIVE FORCE SENSOR

4.1 Piezoresistance: definition and history

Piezoresistivity is the linear coupling between mechanical stress and electrical resistivity of a material and is characterized by change in electrical resistivity due to applied mechanical stress. Derived from the Greek word “piezein” which means to squeeze or press, and combined with “resistivity”, which is the inherent property of any material.¹⁰⁰ The effect is seen in metals, ceramics, cermets, conducting polymers and some of their composites. The effect was first discovered by Lord Kelvin in 1856, in metals like copper and iron where he observed that the electrical resistance of these metals changed under an applied external mechanical stress.²³ This effect is predominantly geometric piezoresistance and depends on the Poisson’s ratio of the metal. Later in 1954, Smith in Bell Labs, discovered piezoresistivity in semiconducting silicon and germanium.¹⁰¹ Today’s sensors employ both geometric and pure piezoresistivity to detect pressure, force or changes in the same.

In 1959, Sauer, Flaschen and Hoesterey at Bell Labs reported an extremely large hydrostatic piezoresistive response of 6450Pa^{-1} in semiconducting positive temperature coefficient of resistance ceramics (PTCR) near Curie temperature (e.g. $(\text{Ba,Sr})\text{TiO}_3$ and $(\text{Pb,Ba})\text{TiO}_3$).¹⁰² Later, piezoresistance effect was discovered in Ruthenium Oxide (ReO_2) ‘Metal-Insulator-Metal’ (MIM) structures by Canali et al. in 1980.¹⁰³ Manganites such as lanthanum strontium manganese oxide (LSMO) exhibit piezoresistivity and magnetoresistivity in both doped and undoped compositions. Recently, piezoresistivity has been reported in polymer

thick film (PTF) resistors¹⁰⁴ that are screen printed and cured on epoxy glass or polyamide substrate. The effect has also been reported in carbon nanotubes (CNT) and polymer derived ceramics such as silicon carbonitride (SiCN). This chapter studies the piezoresistive effect in LSMO-CNT-SiCN composites.

4.2 Piezoresistance coefficient tensor description: ^{104,23}

The figure of merit generally used for comparing various piezoresistive materials is a dimensionless quantity, strain gage factor or simply gage factor, G . In terms of material coefficients piezoresistance is represented as a fourth rank tensor, π . Deformation sensitivity is expressed by gage factor:

$$G = (\Delta\rho/\rho)/(\Delta l/l) \quad \dots\dots\dots(1)$$

where, l is resistor length and ρ is resistivity. The resistivity (ρ) change is related to stress by the piezoresistance tensor as:

$$\Delta\rho/\rho = \pi.T \quad \dots\dots\dots(2)$$

where, π is piezoresistivity coefficient. This coefficient is a fourth rank tensor property. The change in electric field with current density and stress can be expressed in expanded form of McLaurin series as:

$$dE = \left(\frac{\partial E_i}{\partial J_j}\right) dJ_j + \left(\frac{\partial E_i}{\partial X_{kl}}\right) dX_{kl} + \frac{1}{2}\left(\frac{\partial^2 E_i}{\partial J_j \partial J_m}\right) \partial J_j \partial J_m + \frac{1}{2}\left(\frac{\partial^2 E_i}{\partial X_{kl} \partial X_{no}}\right) \partial X_{kl} \partial X_{no} + \frac{1}{2}\left(\frac{\partial^2 E_i}{\partial J_j \partial X_{kl}}\right) \partial J_j \partial X_{kl} + \dots\dots\dots(3)$$

The first term in this series is electrical resistivity ρ_{ij} , a second rank tensor, second term is piezoelectric voltage coefficient g_{ikl} which is a third rank polar tensor. The third term represents

the change in electrical resistivity with current density. The fourth term represents stress dependence of piezoelectric voltage coefficient. The fifth term is the piezoresistive coefficient. It is a fourth rank polar tensor and is represented as π_{ijkl} in tensor form and π_{ij} in matrix form. For centrosymmetric point groups the odd ranked tensors disappear and the above expression reduces to:

$$dE = \rho_{ij} dJ_j + \pi_{ijkl} \epsilon_{kl} \quad \dots\dots\dots(4)$$

Integrating the above equation we get,

$$E = \rho_{ij} J_j + \pi_{ij} \epsilon_j \quad \dots\dots\dots (5)$$

Hence, change in resistivity under stress is given as:

$$\Delta\rho = \frac{E_i - \rho_{ij} J_j}{J_j} = \pi_{ij} \epsilon_j \quad \dots\dots\dots (6)$$

For cubic point groups $m\bar{3}m$ or 432 , there are just three independent coefficients, $\pi_{11}, \pi_{12}, \pi_{44}$.

$$\begin{pmatrix} \Delta\rho_1 \\ \Delta\rho_2 \\ \Delta\rho_3 \\ \Delta\rho_4 \\ \Delta\rho_5 \\ \Delta\rho_6 \end{pmatrix} = \begin{pmatrix} \pi_{11} & \pi_{12} & \pi_{12} & 0 & 0 & 0 \\ \pi_{12} & \pi_{11} & \pi_{12} & 0 & 0 & 0 \\ \pi_{12} & \pi_{12} & \pi_{11} & 0 & 0 & 0 \\ 0 & 0 & 0 & \pi_{44} & 0 & 0 \\ 0 & 0 & 0 & 0 & \pi_{44} & 0 \\ 0 & 0 & 0 & 0 & 0 & \pi_{44} \end{pmatrix} \quad \dots\dots\dots(7)$$

For polycrystalline materials belonging to curie group $\infty\infty m$ only two coefficients are needed to be measured as $\pi_{44} = \pi_{11} - \pi_{12}$. This implies that experiments are required to measure only transverse and longitudinal coefficients for a polycrystalline material. Table X provides the list of gage factors for common materials.¹⁰⁶

4.3 Comparison of various piezoresistive materials:

Table 4.1: Piezoresistive materials overview

Type	Gage factor	TCR (ppm/°C)	Stability	Cost
Metals (e.g. Au,Ag,Ni,Cr)	2	20	Excellent	High
Thin films (polysilicon)	50	0-20	Very good	High
Semiconductors	50	1500	Good	Medium
Thick films (polymer)	10	50	Very good	Medium
LSMO	2-4	5	Good	Low
SiCN	1000-4000	-	-	Very expensive
CNT	40-3000	-	-	Medium

In addition to gage factor, temperature sensitivity should also be considered for selection of material in applications such as force or pressure sensor. Generally, the sensing elements are arranged in wheatstone bridge or more complex configurations reducing temperature sensitivities.¹⁰⁰

4.3.1 Piezoresistivity in LSMO, CNT and SiCN;

The effect of various doping elements on piezoresistive properties in LSMO has been investigated and summarized in Fig. 4.1 by Sharma et al..¹⁰⁵ It can be seen from this figure that Bi substitution on the A-site and Nb substitution on the B-site provides significant enhancement in the fractional resistivity change. The reason for this enhancement has been attributed to change in the bonding strength.

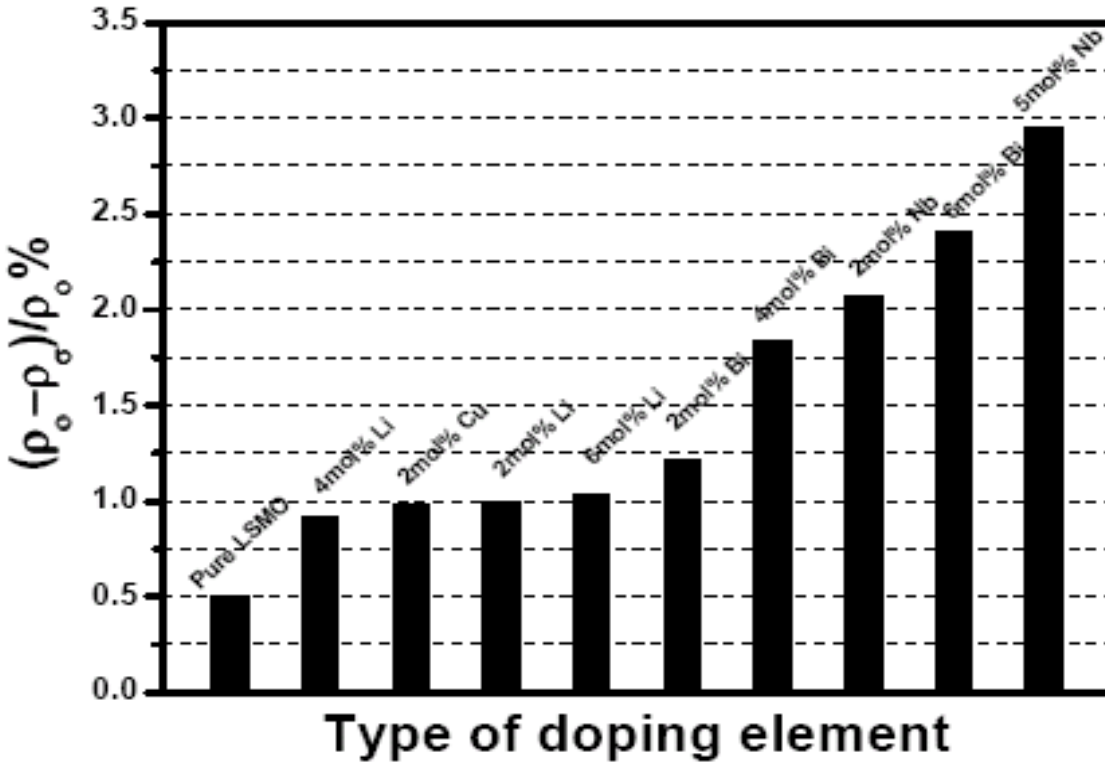


Figure 4.1: Effect of various doping elements in LSMO piezoresistive response plotted with respect to change in resistivity.¹⁰⁵

Various studies have been conducted on piezoresistance effect in CNT. A comparative chart of the reported piezoresistance values in terms of gage factor is plotted in Fig. 4.2 It can be seen from this figure that there is large variation in the reported values which could be associated with the differences in synthesis condition and quality of the tubes. Recent studies on SiCN have shown high gage factor of 2000-4000.^{106,107-} The reason for this large change in resistivity was

attributed to tunnelling percolation mechanism. It is well-known that distribution of nano-domains in SiCN matrix can lead to interesting properties if organized in specific pattern. Based on these prior results, it is expected that a composite of LSMO and SiCN coated CNT may provide large piezoresistivity constants.

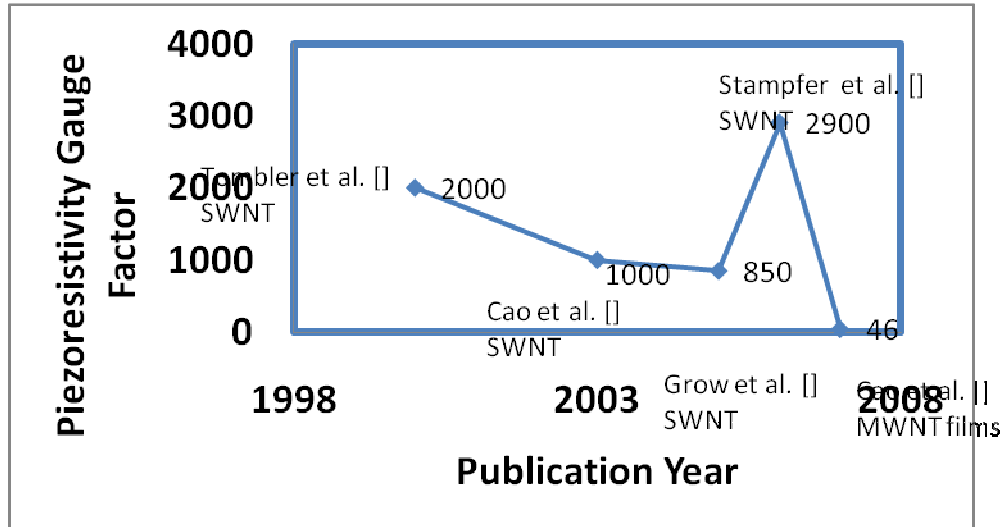


Figure 4.2: Summary of piezoresistivity data for CNT.¹⁰⁷⁻¹⁰⁹

4.4 Experimental Procedure:

The process for synthesis of LSMO-CNT composite can be divided into two steps:

- 4.4.1 LSMO synthesis by conventional ceramic processing and sintering
- 4.4.2 CNT coating with SiCN by pyrolysis of crosslinked polymer cerasetTM.

4.4.1 LSMO synthesis: Ceramic powder processing

All the ceramic samples in the present work were synthesized via the conventional ceramic powder processing technology.

4.4.1.1 Stoichiometric calculations

Powders were obtained from Alfa Aesar Co. Massachusetts, USA. The base composition $\text{La}_{0.8}\text{Sr}_{0.2}\text{MnO}_3$ (LSMO) was modified at the B-site by 5 mol% Niobium (Nb).

4.4.1.2 Powder mixing

The powders were mixed in a polyethylene bottle with ZrO₂ grinding balls of 3, 5 and 10mm diameter. The ZrO₂ grinding media was obtained from Tosoh Corporation, Japan. Ethanol was used as the solvent for ball milling. Ball milling was done two times (before and after calcination) for each composition for 24 – 36 hrs. For the case of ball milling after calcinations, 10 mm diameter ZrO₂ grinding balls were used to ensure complete breakdown of hard agglomerates and the ball milling period was increased to 36 hrs. After each step of ball milling the ceramic powders slurries were dried in an oven in borosilicate glass vessels at 80°C.

4.4.1.3 Calcination, Sintering:

After initial mixing of oxide and carbonate powders as per the composition, the dried powders were calcined in alumina crucible at 1000°C for 4 hrs. X-ray diffraction (XRD) analysis was conducted to determine the formation of the perovskite phase, Fig. 4.3. It was found that a complete perovskite crystal structure was formed above 1000°C. Calcined powders were crushed and ball milled for 24hrs using 10mm diameter grinding media in ethanol. The powders after calcination were ball milled, dried and sieved in a 270 mesh size. The sieved powders ensured uniform starting particle size for better sintering. The sieved powders were pressed into uniform pellets of size 13 mm diameter and 1 mm thickness in a hardened steel die at 15 MPa pressure. These bars were then isostatically pressed at 150 MPa in a cold isostatic press (CIP). The green bodies were sintered by optimizing sintering temperature between 1300°C and 1400°C for 6 hrs. X-ray diffraction (XRD) and SEM analysis was conducted for each sintered sample to detect the presence of any second phase and determination of the parent lattice crystal structure, porosity, and grain size.

4.4.2 CNT coating:

Multiwalled CNT samples were dispersed with a cross-linking polymer ceraset™ in chloroform by ultrasonication for 20 minutes. The Ceraset coated CNT were pyrolyzed in nitrogen atmosphere at 1100°C for 5 hrs in a tube furnace. During pyrolysis, the cross-linked polymer transformed to SiCN coating the entire surface of CNT. This step was essential in preventing oxidation of CNT at higher sintering temperatures. Separately, SiCN was also prepared by pyrolysis of Ceraset and used for fabricating SiCN – LSMO composites. Microstructure of CNT coated with SiCN was observed in SEM and analyzed for oxidation resistance using thermo gravimetric analysis TGA.

4.4.3 Composite sample preparation:

Two types of composites were prepared: (i) LSMO containing SiCN coated CNT, and (ii) LSMO with SiCN. The volume percent of SiCN coated CNT and SiCN was fixed at 3, 6.5 and 12.35% in LSMO (CNT weight = 0.02, 0.04, and 0.08 gm). The mixing was done by dispersing in acetone followed by ultrasonic agitation and manually in mortar pestle. Pellets of the same size as pure LSMO were made from this mixture and sintered at 1300 °C for 3 hours.

4.4.4 Piezoresistivity sample preparation

The samples for piezoresistivity measurements were prepared by cutting a square piece of dimension 5.0 x 5.0 x 1.5 mm³ and painting a high temperature silver electrode Dupont® 6160 on the two opposite edges. The painted electrodes were then fired at 650°C for 1 hr to obtain a good

electrical contact. Two thin wires were then soldered on the opposite smaller faces for the piezoresistivity measurement.

4.5 Results and discussion:

4.5.1 Calcining and sintering optimization of 5 mol % Nb modified LSMO.

Calcining of Nb modified LSMO at 1000°C for 5 hours proved to be enough to form single phase spinel structure as shown in Fig. 4.3. The sintering temperature and time was optimized at 1300°C for 3 hrs based upon the SEM analysis showing dense and uniform grain structure.

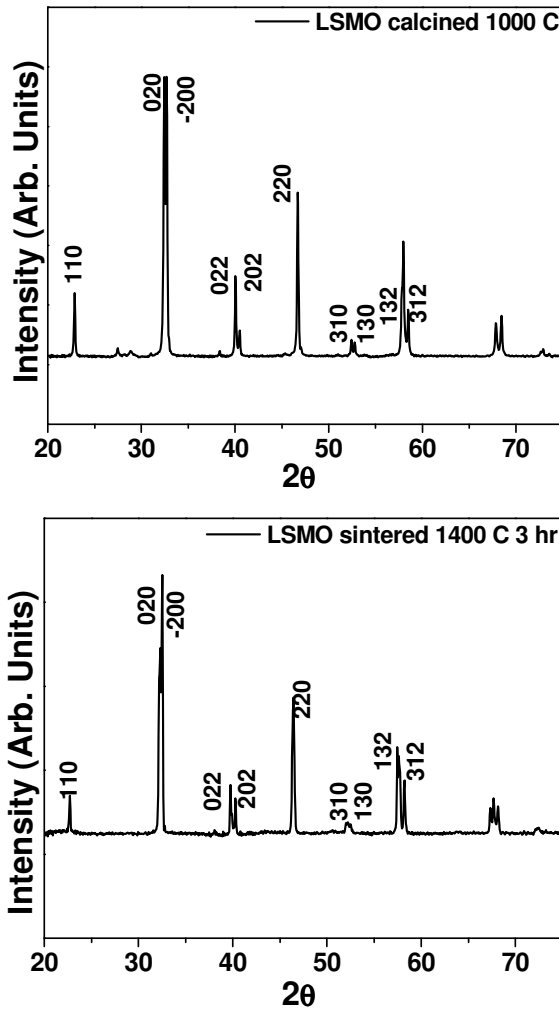


Figure 4.3: XRD peaks for calcined and sintered Nb modified LSMO.

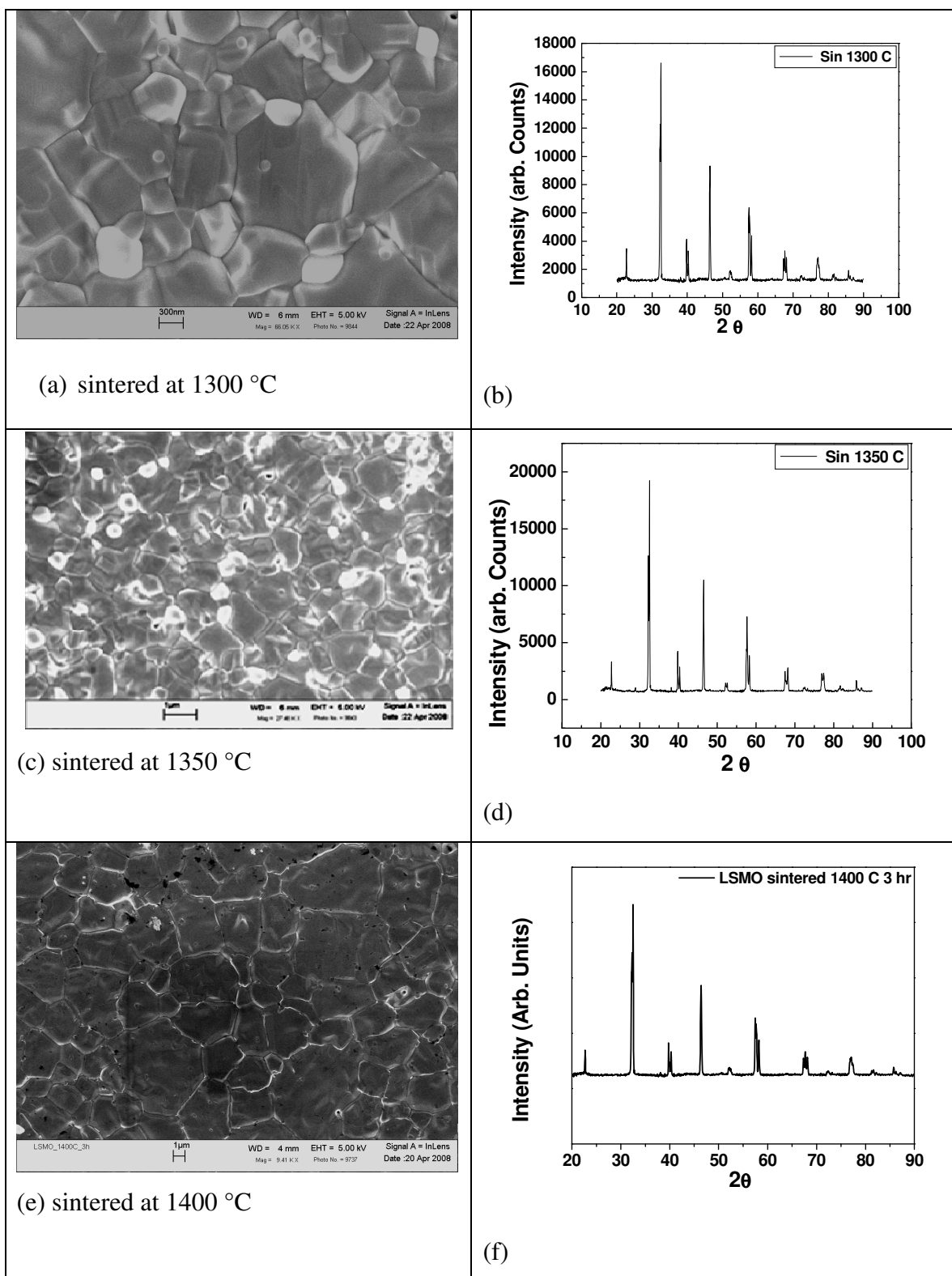


Figure 4.4: Sintering of 5% Nb modified LSMO

. Sintering at higher temperatures resulted in large grains whereas at lower temperatures the sample showed high porosity. To ensure that no second phase is formed, XRD was done after each sintering step and the results are plotted with along with SEM micrographs in Fig. 4.4.

4.5.2 Addition of MWCNT

Multiwall carbon nanotubes were procured from commercial source and were pre-treated by coating with silicon carbonitride (SiCN). SiCN coating was done by dispersing MWCNT in polymer solution precursor of SiCN called Ceraset™ and pyrolysing the MWCNT at 1100 °C in nitrogen atmosphere in tube furnace.

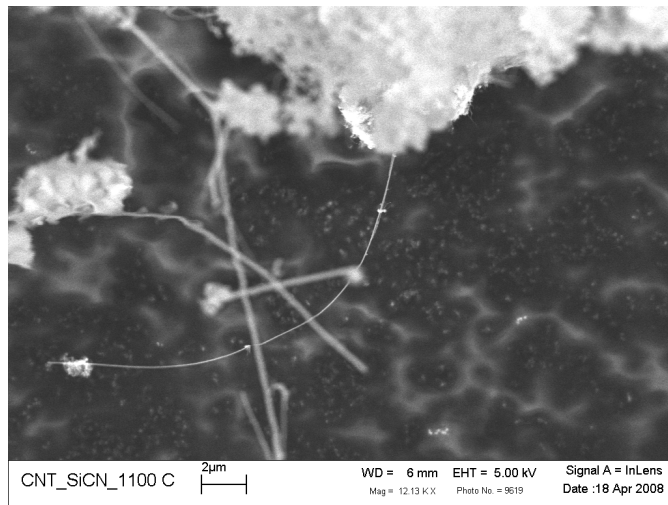
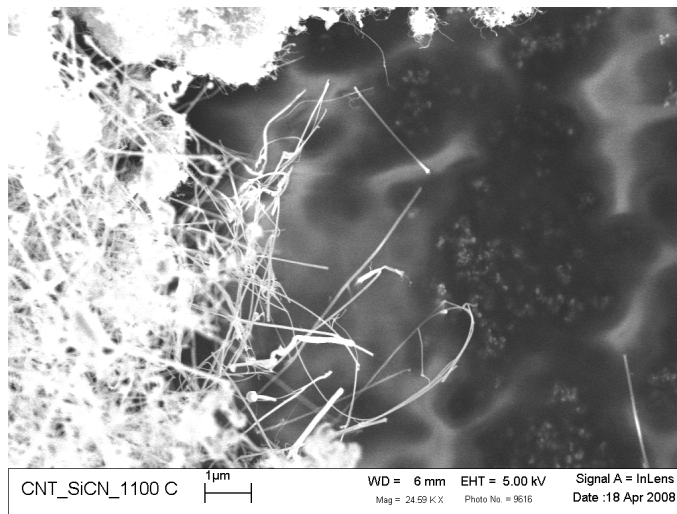


Figure 4.5: SEM micrographs of SiCN coated CNT

Figure 4.5 shows that CNT is fully coated with SiCN. A 3, 6.5 and 12.35 vol % of SiCN coated CNT was mixed with LSMO.

Figure 4.6 shows the sintered surface of the 10vol% pyrolyzed (CNT – SiCN) – LSMO composites (CNT weight = 0.06gm). The microstructure shows porosity distribution throughout the material with inhomogeneous grains. The grain size was found to be in the range of 1 – 10 μm . The color map for Nb and Si in Fig. 4.6(b) demonstrates the distribution of Nb rich grain in LSMO matrix and SiCN in the composite. It seems that the matrix is essentially composed of LSMO grains with SiCN forming along the grain boundaries. This is expected as the interface will provide the site for heterogeneous nucleation. The presence of CNT was not found in the microstructure. This indicates that CNTs are burned-off at this sintering temperature. Figure 4.6(c) shows the XRD of the 10vol% SiCN-LSMO composite (XRD was taken on the polished sample before the SEM analysis). The presence of extra peaks can be seen which may be due to the formation of secondary phases from LSMO and Si- reaction. It is known from the research in sintering of SiO_2 -doped PZT that at high temperature a glassy phase is formed which promotes the sintering. It may be possible that SiCN pyrolyzed at 1100°C decomposes to releases from Si- ion which forms the secondary phase. Since no other analysis was conducted on understanding the nature and composition of this secondary phase, we will assume for the discussion purposes that all the composite studies here have Si-rich glassy phase. Figure 4.6(d) and (e) shows the surface microstructure of 6.5vol% and 12.35 vol% SiCN-CNT – LSMO composite. The surface shows grain structure with presence of some rod-like structures. These rods could be due to the formation of secondary phase as seen in the polished specimens.

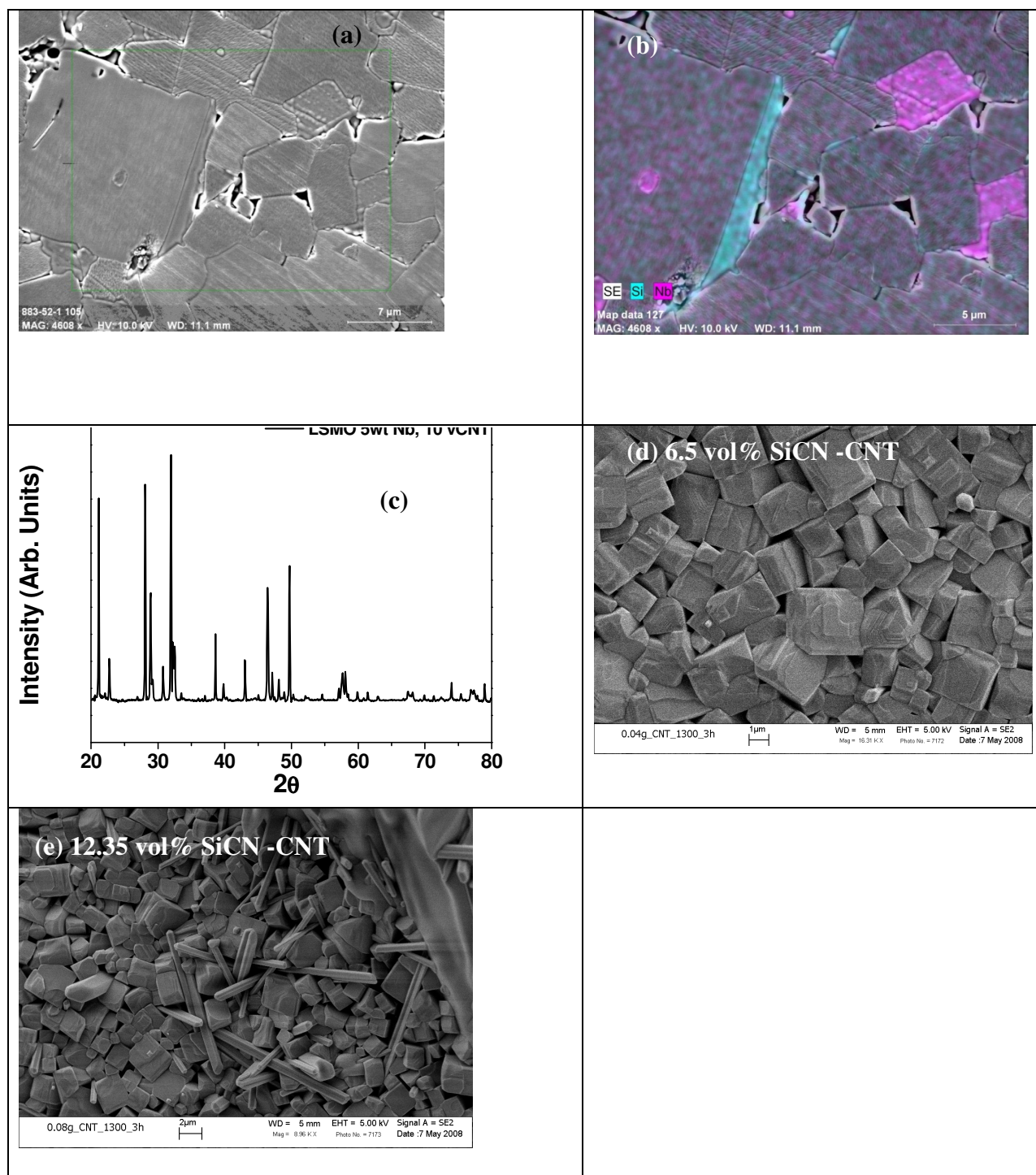


Figure 4.6: (a)SEM micrograph of composite of SiCN coated CNT in LSMO (b) Nb and Si EDAX map superimposed on the secondary image of (a) showing Nb pink hue and Si-blue color rich regions and (c) XRD of the composite of 10 vol.% SiCN coated CNT. (d),(e) sintered surface of LSMO-SiCN coated CNT composite for 6.5 vol % and 12.35 vol % respectively.

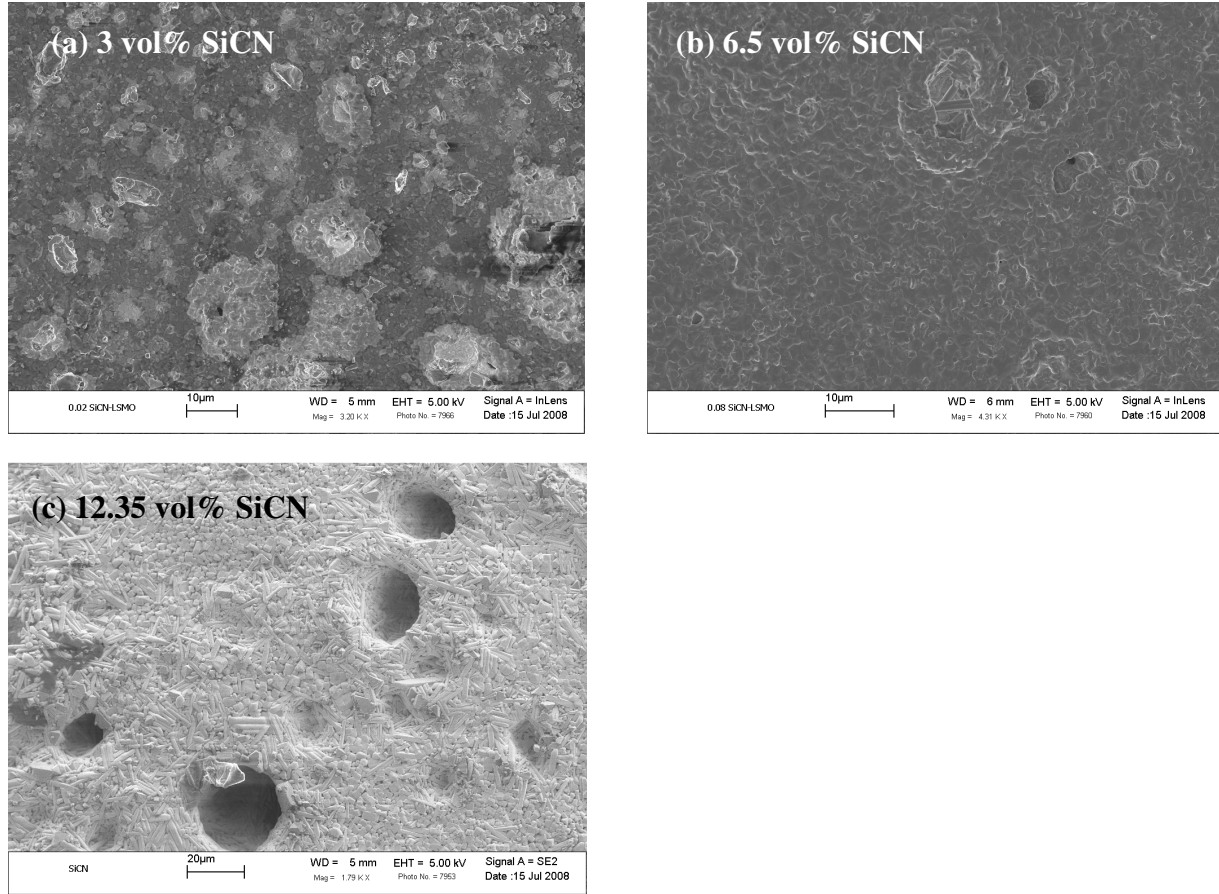


Figure 4.7: SEM micrographs of LSMO- SiCN composite (without CNT). (a) 3 vol% SiCN – LSMO, (b) 6.5vol% SiCN – LSMO, and (c) 12.35vol% SiCN – LSMO.

Figure 4.7 shows the surface microstructure of LSMO – SiCN composites (without CNT). The microstructure shows large pore-like regions which we think is due to the difference in thermal shrinkage of the LSMO and SiCN. The sample did not show any macro-cracks so it is assumed here that the strain generated during sintering is absorbed by forming these defect regions.

4.5.3 Piezoresistivity measurement technique

Transverse piezoresistivity coefficient-- π_{12} measurements were done on the samples by compressing them between two highly polished, flat surfaces using Instron as shown in Fig. 4.8. A compressive load of up to 200 N maximum was applied uniaxially at the rate of 20N/min, onto

the sample. The resistance change in the samples was recorded by an Agilent® 6½ digit multimeter. For each measurement, approximate load intervals of 20 N were chosen, and the load was held constant at that value for 3 min allowing the resistance values to be stabilized. After the 3 min holding time the compressive load was resumed at the same rate.

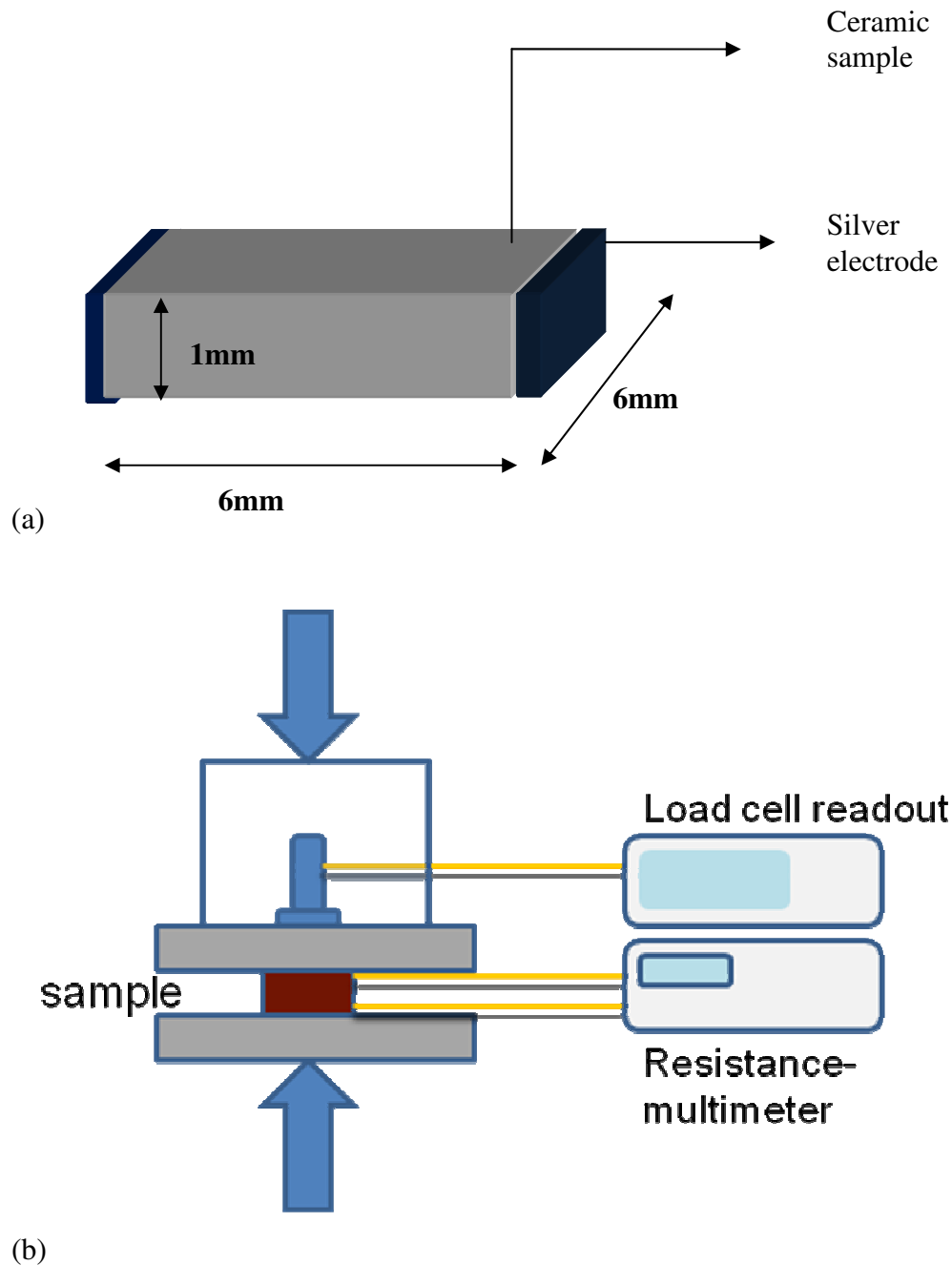


Figure 4.8: Schematic diagrams of (a) sample geometry and (b) testing setup

4.5.4 Piezoresistance results:

As compared to Nb modified LSMO both additives of SiCN coated CNT and SiCN in LSMO increased the resistivity of the material. Figure 4.8 comprehensively lists the resistivity values of all the composite samples

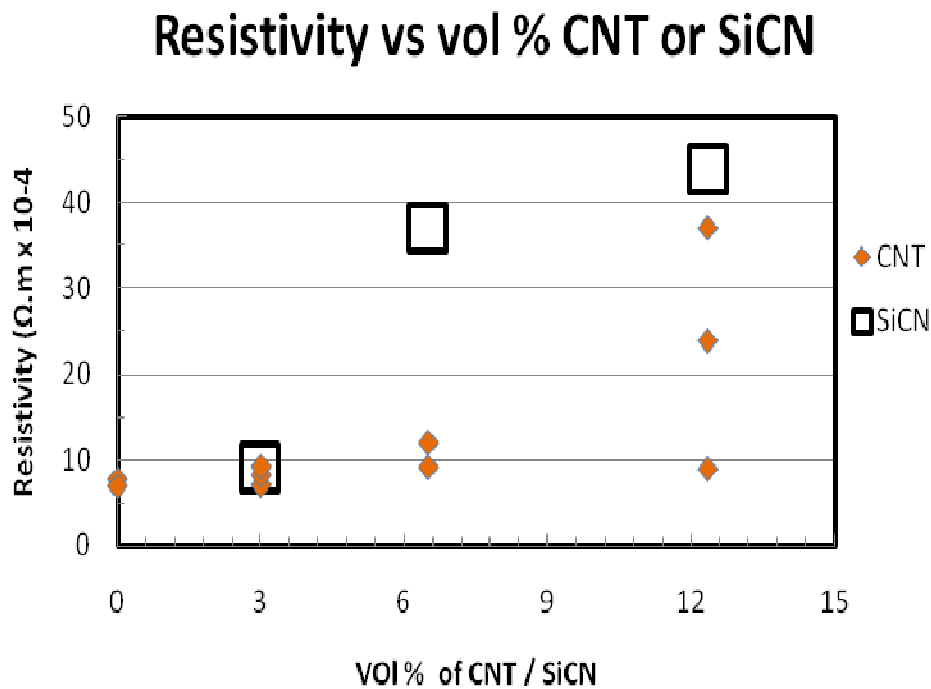


Figure 4.9: Resistivity values of 5% Nb modified LSMO- 0 vol % additive and those of composites of LSMO and SiCN coated CNT or LSMO and SiCN.

During testing sample with 6 vol % SiCN coated CNT was broken and hence the fractional resistivity values of that batch were not considered. The data for 3 and 12.35 vol % CNT is as shown in Fig. 4.9 where the change in resistivity is plotted with respect to applied stress. The data shows an order of magnitude increase in the fractional resistivity for CNT

containing composites as compared to 5%Nb modified LSMO. The reason for this enhancement is not clear at this time.

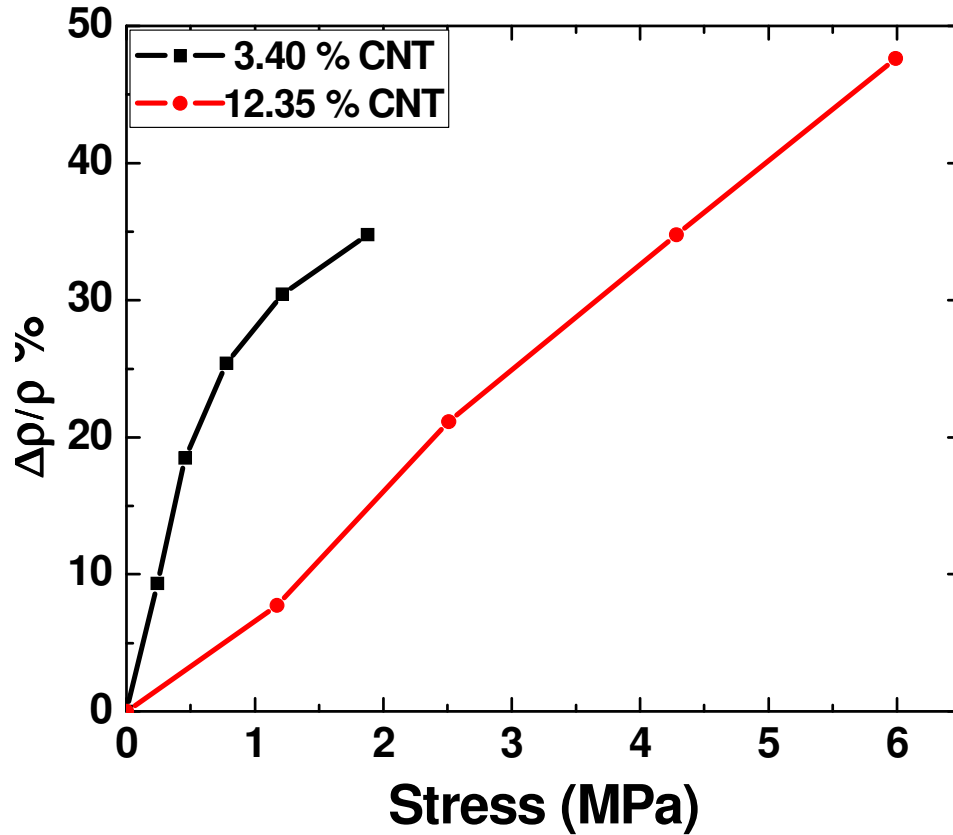


Figure 4.10: Fractional resistivity change in LSMO – SiCN - CNT composites.

Composites containing SiCN coated CNT and SiCN were found to have porosity which was not eliminated even after sintering at 1400°C. The reason for the porosity was associated with partial decomposition of CNT at about 700°C giving rise to porosity. In high magnification SEM and TEM analysis, regions rich in Si were found but CNT was not traced.

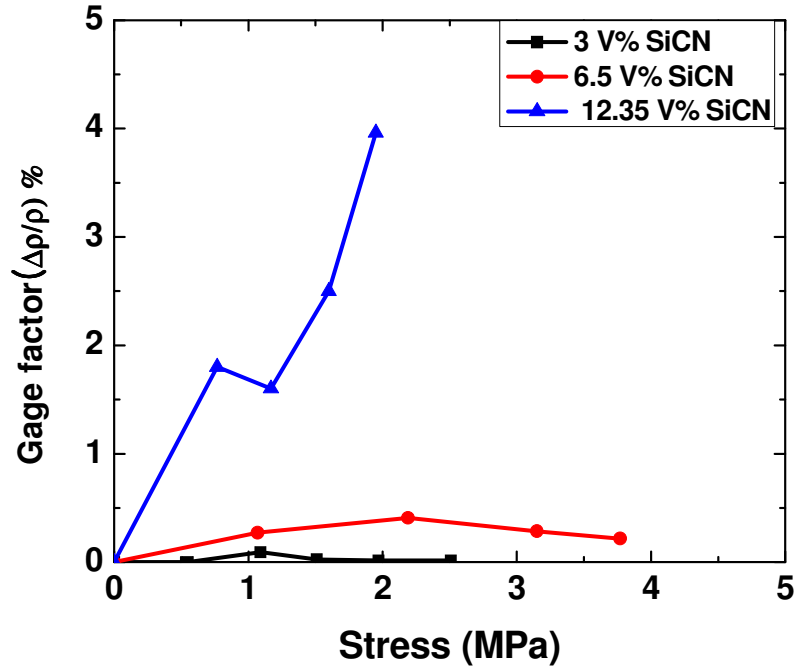


Figure 4.11: Fractional resistivity change vs. stress for composites containing 3, 6.5 and 12.35 vol % SiCN in LSMO.

Fig. 4.11 shows the piezoresistance behavior of SiCN containing composites. Comparing the data with pure LSMO, it can be seen that SiCN containing composites have higher change in resistivity with stress. The reason for this enhancement needs more thorough analysis and more careful sample preparation

4.6 Conclusion:

Preliminary results of LSMO and SiCN coated CNT show improvement in piezoresistance over Nb-modified LSMO. The results prompt further studies in these novel composites using high resolution SEM or TEM. Optimization of sintering is required to yield pore free microstructure for both the composites.

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CHAPTER 6:APPENDIX A
PZT-5wt % NiMZF Sintering results

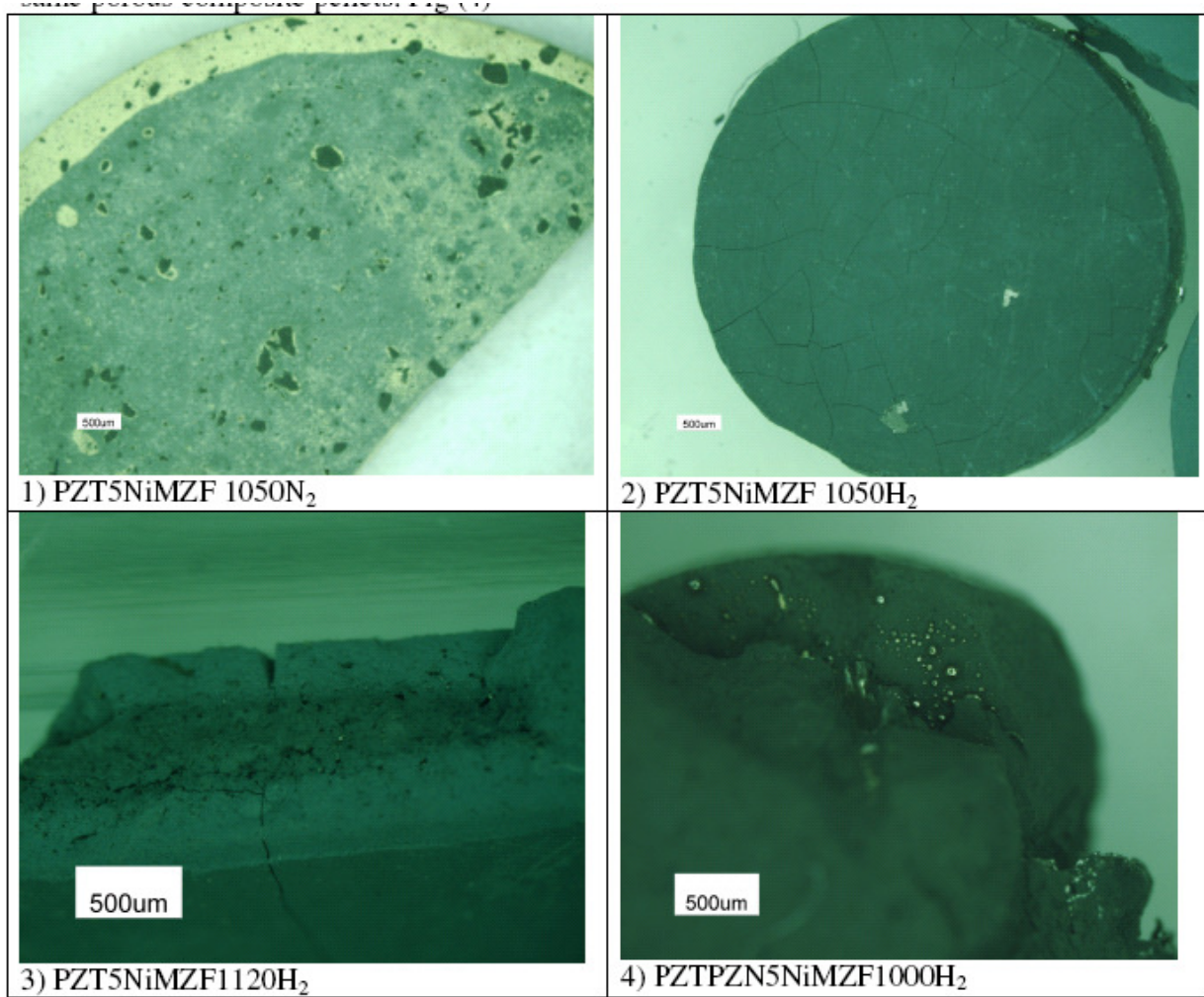


Figure 1: (1) Nitrogen sintered and 2), 3) and 4) 5vol % hydrogen + Nitrogen sintered PZT-5 wt % NiMZF

5wt % of core shell Ni-MZF particles were mechanically mixed in mortar pestle with $\text{Pb}(\text{Zr}_{0.48}\text{Ti}_{0.52})\text{O}_3$ or PZT and sintered in various atmospheres as shown above. At inert atmospheres till 1050 °C PZT showed porous structure and friable nature after sintering. Also, Ni

MZF particles shown here as dark irregular particles in matrix were seen to be oxidized even in inert atmosphere

To avoid Ni oxidation, mildly reducing atmospheres made by 2 vol. % Hydrogen mixed with Nitrogen was purged in the furnace throughout the sintering cycle at a flow rate of 300-450 Standard cubic centimeters per minute (SCCM). Sintering at various temperatures from 1000 - 1120 °C was not successful since the pellets turned out to be more friable and showed cracks with some reduced lead particles on the surface.

It was found from standard literature for free energy diagrams for various oxides in different atmosphere that Barium oxides had higher stability in reducing/inert atmospheres than all forms of lead oxide.

BaTiO₃- Ni co-sintering results:

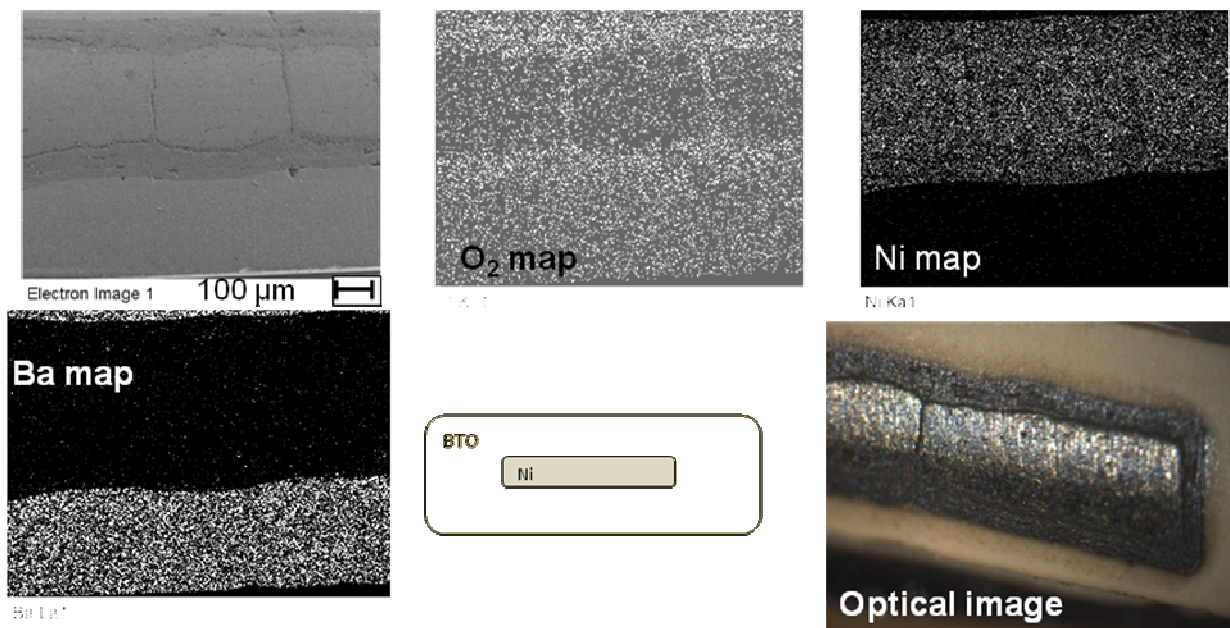


Figure 2: i-BTO sintering experiment. All SEM images represent similar area scanned under various elemental EDAX maps

Hence, to study the stability and of cosintering Ni and BaTiO₃-BTO, a pellet where BTO was completely coating Ni pellet was pressed. Cross-section of such a pellet is represented in fig

2. Since Ni in this pellet was completely surrounded by BTO and not in contact with external atmosphere, this pellet was sintered in normal sintering box furnace without special atmosphere in the furnace. This yielded good results as far as avoiding Ni oxidation was concerned. As shown in the same figure, the Ni pellet in the centre of BTO has some oxidation near the BTO interface but rest of the core of Ni plate is still in metallic state and not oxidized. Thus, core-shell Ni-MZf particles can be sintered in BTO matrix without Ni being oxidized. And as a further work such a system can be used to make a sintered ME composite.