**ADVANCED
MAGNETIC AND DIELECTRIC
NANOMATERIALS**

by

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A thesis submitted to

VICTORIA UNIVERSITY OF WELLINGTON

in fulfilment of the requirements for the degree of

Doctor of Philosophy

in

Chemistry

2020

ABSTRACT

Multiferroics are a novel class of next generation multifunctional materials that exhibit simultaneous magnetic spin, electric dipole, and ferroelastic ordering. It gives an additional degree of freedom to design new devices. Magnetoelectric effect in these materials result in the manipulation of magnetic spins via applied electric field and vice versa, making them suitable for next generation applications. Single phase multiferroics show low magnetoelectric coefficient, hence there is a need to look at composite multiferroic structures with respective magnetic and ferroelectric phase. The magnetoelectric coefficient in the composite structures depends on the magnitude of strain induced by one phase to the other. This requires the need to study suitable magnetic and ferroelectric materials that can be combined to create magnetoelectric multiferroic composite structures. Also, higher surface to volume ratio at the nanoscale should enhance the interaction between the two phases. Here, in we synthesised and studied magnetic and ferroelectric structures that have potential to be used as the respective phases of multiferroic magnetoelectric composites.

Magnetic materials with high magnetostriction and low coercivity are suitable candidates for the formation of multiferroic composite. The size dependent and tuneable magnetic properties of cobalt ferrite and nickel-iron composites, respectively fulfil the above-mentioned criteria. Herein, the properties of the above magnetic materials were explored at nanoscale where efficient techniques such as thermal decomposition and electrospinning were applied. Cobalt ferrite nanoparticles with varying sizes were synthesised at the nanoscale and magnetic studies were performed to study their size dependent suitability to be used as a potential magnetic material in multiferroic composite formation. The nanoparticle synthesis by thermal decomposition of metal oleate precursors displayed reaction time dependent growth. The nanoparticles sized below superparamagnetic limit showed a negligible coercivity fulfilling an essential requirement to display magnetoelectric effect. Alongside, a successful synthesis of novel cobalt iron oxide ($\text{Co}_{0.33}\text{Fe}_{0.67}\text{O}$) nanoparticles was also performed. This displayed a synthesis dependent ferrimagnetic to antiferromagnetic phase transition in Co-Fe-O structure at nanoscale. A controlled oxidation of $\text{Co}_{0.33}\text{Fe}_{0.67}\text{O}$ could lead to the formation of antiferromagnetic-ferrimagnetic core-shell nanostructure that can overcome the superparamagnetic limit in

nanoparticles system. They are potential materials in ME-RAMs. 1-D magnetic nanostructure show a sharp shape anisotropy and hence can be used as magnetic components of composite multiferroic structures. Nickel-iron composites in FCC phase were studied at the nanoscale in the form of fibres. Electrospinning of suitable metal precursors with PVP polymer followed by the reduction of nanofibres in H_2 led to the formation of $Ni_{0.47}Fe_{0.53}$ fibre mats. They were ferromagnetic and displayed high saturation magnetisation along with low coercivity fulfilling the requirement to be used in magnetoelectric applications.

1-D flexible ferroelectric composite structures were studied alongside to be used as the ferroelectric component of multiferroic composites. Polyvinylidene fluoride was doped with DIPAB at varying ratios to study the improvement in the ferroelectric properties of the composite structure in comparison to just PVDF with low dielectric constant. Electrospinning of composite polymer solution led to the formation of DIPAB doped PVDF nanofibres. They displayed improved relative dielectric constant and low loss tangent and find use in composite magnetoelectric materials formation. The ease of processability of DIPAB doped PVDF nanofibres aids in incorporating the above studied magnetic materials.

The studies proved the worth of as-synthesised magnetic and ferroelectric materials at the nanoscale for the formation of magnetoelectric multiferroic composite nanomaterials. The cobalt ferrite nanoparticles doped in DIPAB-PVDF nanofibres can result in core-sheath ME composite structure. A coating of DIPAB-PVDF composite on the formed $Ni_{0.47}Fe_{0.53}$ fibres will result to the formation of 1-D magnetoelectric structures.

Dedicated to the three most beautiful and courageous women in my life.....

My Grandma (late), Maa and Sana

Daadu Papa and Daadi Mummy, I miss you!

ACKNOWLEDGEMENT

My journey during this learning experience would not have been possible without the support, concern and love of few people who always stood by me. I am grateful and will always hope that good things happen to them.

I would like to thank both my supervisors Prof Thomas Nann and Prof Grant Williams for believing in me and supporting me all the way. You have been the two strong pillars who have always guided me and took my research in the right direction. I have learnt a lot from both of you whether it be research or wisdom. This will help me with my career my whole life. I am also thankful to all my group members (past and present) for accepting me and supporting me all the way. All of you have been a crucial part because your suggestions led me to research better and made my journey till the end easier. I want to thank Renee Goreham, Siobhan Bradley, Andreas Zeller, Geoffry Laufersky, Nicolò Canever, Kathryn Schroeder, Fraser Hughson, Shalini Divya, Rohan Borah, Zeineb Ayed, Deanna Dupre, Erin Service, Garima Dobhal, Chunyan Zheng and Jacob Johnston. It would have been difficult without you guys around. I would also like to acknowledge Grant Williams' research group for accepting me. Shen, Joe and Tehreema, thank you for being there and helping me out with all the research related things. I want to acknowledge Prof Martyn Coles and Ryan Schwamm for the collaboration and help related to my project. You have helped me a lot and I want to thank you for that. A sincere thanks to IPT, Wellington team members, John Kennedy, Nick Long, Bill Trompetter, Jérôme Leveneur, Arvid Hunze and Shen Chong for accepting me as a part of the team. I want to thank my fellow PhDs and post-docs who contributed their knowledge and time, naming them- Parth Vashishtha, Mat Anker, Matt Cryer and Sreelakshmi Chandrabose. I also want to acknowledge and thank the collaborators from University of Auckland, Sesha Manuguri and Prof. Jenny Malmstrom for their valuable collaboration. I also want to acknowledge all the other staff members and technicians who resolved my doubts and helped with my research when I needed it. I sincerely want to thank David Flynn who has always helped me and guided me, and Chris Lepper for the help with differential scanning calorimetry. I also want to thank the other staff members, naming a few Sarah Spencer, Mathew Cairns, Andy Edgar, Robin Fulton, Rob Keyzers and Putri Fraser for all the help required during my PhD.

I would also like to thank my family and friends whose love, blessing, strength and motivation made this journey easier to follow. Thank you to my family, Anil (papa), Renu (Maa), Shubham (brother), Aishika (sister), Shiven (brother), Depesh (uncle) and Nikita (aunt) who though being far away from me, never let me feel alone. I am very lucky to have you and I adore you all. I also want to thank my grandma, Late Smt. Krishna Kumari and my grandfather, Late Sh. Manohar Lal Bhugra. They would have been the proudest. Your values and love made me the person I am today. We miss you. I want to thank my partner, Sana for the love that I was showered with and is more than I ever deserve. You make me the happiest person on earth. You are my peace in this world. I want to acknowledge my friends from office and outside- Ashish, Sonali, Sasha, Ronnie, Jordan, Benny, Isabella, Clement, Amanda, Amrita, Howard, Sunil, Putri, Justinas, Valentin, Dani, Yuta and all others. You made my New Zealand experience so much better. I will miss you. I wish you all the very best for your life ahead.

ABOUT THE THESIS:

CHAPTER 1 discusses in detail the basic theory and properties of magnetic and electric materials which are necessary for the formation of magnetoelectric materials. It also discusses the applications of magnetoelectric materials and the role of nanomaterials in enhancing the magnetoelectric coefficient. In the end, it discusses the role of ferromagnetic nanomaterials in wireless charging applications.

CHAPTER 2 explains the important synthesis/fabrication, characterisation and analytical techniques applied for the formation and analysis of nanomaterials to be used as components of magnetoelectric composites. The chapter also contains a detailed literature review useful for respective nanomaterials formation.

CHAPTER 3 discusses the synthesis procedure of formed magnetic nanomaterials during the PhD course. The magnetic properties of the formed materials have been thoroughly discussed pointing out their importance to be used in magnetoelectric composite formation.

CHAPTER 4 gives a detailed information of fabrication procedure of ferroelectric nanomaterials that were formed during the PhD course. The ferroelectric properties of the formed materials have been thoroughly discussed depicting their importance as a ferroelectric component of magnetoelectric composite.

CHAPTER 5 is the conclusion chapter that connects the formed materials based on their importance in magnetoelectric composite structure formation. The chapter also discusses the future work with respect to the results achieved and based on the PhD work.

The thesis ends with an **APPENDIX section** where the side projects performed during the thesis have been discussed. A ligand exchange strategy to synthesise water dispersible ferrimagnetic nanoparticles and formation of polymer bonded soft magnetic composites in the form of toroids has been discussed.

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LIST OF ABBREVIATIONS

Abbreviation	Full form
H	Applied magnetic field
M	Magnetisation
S	Spin quantum number
B	Magnetic induction
μ_0	Permeability of free space
X	Magnetic susceptibility
k_B	Boltzmann constant
T_c	Curie temperature
T_N	Neel Temperature
M_R	Remanence magnetisation
SPM	Superparamagnetism
τ_N	Neel relaxation time
T_B	Blocking temperature
FCC	Face-centred cubic
BCC	Body-centred cubic
MNPS	Iron ferrite nanoparticles
SPIONs	Superparamagnetic iron oxide nanoparticles

B_s	Saturation flux density
χ_e	Electric susceptibility
P	Polarisation
DIPAB	Diisopropylammonium bromide
PVDF	Poly-(vinylidene difluoride)
FeRAMs	Ferroelectric random-access memory
ME-RAM	Magnetoelectric random access memory
PVP	Polyvinylpyrrolidone
PVB	Polyvinyl butyral
TEM	Transmission electron microscopy
EDXS	Energy-dispersive X-Ray spectroscopy
STEM	Scanning transmission electron microscopy
SEM	Scanning electron microscopy
XRD	X-ray diffraction
TGA	Thermogravimetric analysis
FTIR	Fourier transform infrared spectroscopy
nm	Nanometer
Å	Angstrom unit
SQUID	Superconducting quantum interference device
ZFC	Zero field cooled
FC	Field cooled

ϵ_r	Relative dielectric constant
σ_{AC}	AC conductivity
C	Capacitance
$\tan \delta$	Loss tangent

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CHAPTER 1

INTRODUCTION

1.1.MOTIVATION

The interplay between electricity and magnetism has attracted the researchers and engineers since the early 1800s when Hans Christians Oersted accidentally discovered the deflection in magnetic compass needle in the presence of a battery nearby when it was switched on and off simultaneously. This further lead to the classical theory of electromagnetism. Even during the era of Maxwell, the magnetic field, electric fields and the other related phenomenon were considered crucial as they were clearly shown to be unified in the special theory of relativity. There is, however, a class of materials where such coupling is found to be very noteworthy. These materials have simultaneous ferroelectric and ferromagnetic order and are known as multiferroic materials. A magnetoelectric (ME) effect can simply be described as the manipulation of charges by applied magnetic fields and spins by applied voltages. Magnetoelectric multiferroics exhibit both a ferroelectric polarisation and magnetisation in a single-phase. Single-phase multiferroic materials are easy to synthesise and sometimes are also available naturally in abundance, for example, iron ferrite and chromium oxide.¹ The ME effect arises from the coupling between the magnetic and polar sub-lattices in single-phase materials. ME multiferroic allows us to study new physical phenomena and they have numerous possibilities in multi-functional devices.² However, multiferroic composites have ME coupling coefficients several orders of magnitude higher than those of single-phase multiferroics. Single-phase multiferroics provide effective energy conversion between electric and magnetic fields,³⁻⁸ but the magnetoelectric coupling in them is not promising enough to be used for applicative purposes. Alternatively,

synthesising artificial multiferroic materials increase the possibility of tailoring the properties. Using two compounds with different properties, where one is ferromagnetic and other is ferroelectric, composite materials with high magnetoelectric coupling and improved physical properties can be formed. **Figure 1** illustrates the formation of the layered magnetoelectric composite where the change in the applied magnetic field results in the electric signal.

Figure 1: Illustration of the formation of layered magnetoelectric composite where the change in applied magnetic field results in the electric signal.

The importance of the investigation, synthesis, characterisation, and utilisation of nanostructured material was addressed by American theoretical physicist, Richard P. Feynman in 1959 in his article titled “There is plenty of room at the bottom”.⁹ Nanomaterials are characterised by one or more dimensions in the nanometre range (1 to 100 nanometres). They can be in the form of nanoclusters, nanoparticles, nanowires, nanotubes, nanoporous solids, thin films and superlattices.¹⁰ The physical, chemical, magnetic and electric properties of a nanomaterial differ significantly from those at bulk scale. The size and shape dependence of materials drastically change at nanoscale where the properties get affected by increased surface areas and densities of low coordination surface atoms, quantum confinement, changes in miscibility and the phase stability. The last two decades have portrayed tremendous advancement in the field of science and technology. The advances in synthesis, characterisation, and analytical techniques to study the materials have helped in expanding technology at the nanoscale.

The exploration for the respective magnetic and electric properties of nanomaterials to fabricate ME composites³⁻⁴ might allow an additional degree of freedom in the design of

novel ME devices such as magnetic sensors, read head for disk drives, drug delivery and energy harvesting. The thesis discusses the formation, properties and applications of potential nanomaterials for their use as magnetic and electric components of multiferroic composites.

This chapter further discusses the basics of magnetism and ferroelectricity essential for understanding the use of suitable materials for the formation of magnetoelectric composites.

1.2. MAGNETISM AND MAGNETIC MATERIALS

Magnetism is an intrinsic response to an applied magnetic field (H) by a material. In the case of isotropic materials, both the magnetisation (M) and applied magnetic field (H) are uniaxially aligned inside the material. Paramagnetism and ferromagnetism are the results of unpaired electrons with their total spin quantum number (S) being non-zero. An external magnetic field on a magnetic material can result in the interaction of spins with each other that may cause alignment in the magnetic moments. The magnetisation of the material is equal to magnetic dipole per unit volume. It is also the measure of alignment of spins. The magnetic induction (B) relates M and H inside a material by the equation:

$$\vec{B} = \mu_0 \vec{H} + \mu_0 \vec{M} \quad (\text{Eqn. 1})$$

where μ_0 is the permeability of free space and $\mu_0 = 4\pi \cdot 10^{-7} \text{ N/A}^2$.

The magnetic susceptibility (χ) is the ratio between magnetisation (M) and applied magnetic field (H), i.e.

$$\chi = \frac{M}{H} \quad (\text{Eqn. 2})$$

Based on the magnitude and sign of magnetic susceptibility, magnetic materials can be classified in different categories which is discussed in **Section 1.2.1**.

1.2.1. TYPES OF MAGNETISM:

DIAMAGNETISM

Diamagnetism is the outcome of the orbital motion of core electrons in a material. The susceptibility of these materials is always negative ranging from -10^{-6} to -10^{-4} .¹¹ Atoms or molecules of materials such as carbon, copper, water and silicon have no net magnetic moment. A weak opposite magnetisation is only produced under the effect of an external magnetic field.¹² The effect of diamagnetism is so small that it is usually overshadowed by other forms of magnetism.

Figure 2: (a) No net magnetisation is observed in the diamagnetic material in the absence of applied magnetic field; (b) Alignment of the magnetic moment in the direction opposite to the applied magnetic field; (c) M vs H curve portraying a negative susceptibility; (d) Temperature independence of the susceptibility of a diamagnetic material

The susceptibility of a diamagnetic material is given by the equation from Langevin theory of diamagnetism:

$$\chi = \frac{\mu_0 N \mu}{B} = -\frac{\mu_0 N Z e^2}{6m} \langle r^2 \rangle \quad (\text{Eqn. 3})$$

where B is the flux density of the applied field, Z is the number of electrons present. The m , r , N represents the mass, atomic/ionic radius and the number of atoms or ions in the diamagnetic material, respectively. **Figure 2** shows the ordering of the magnetic moments, a general M vs H curve and the dependence of susceptibility on the temperature of a diamagnetic material.

PARAMAGNETISM

Paramagnetism is the result of a non-zero spin quantum number system, i.e. they have unpaired electrons. In a paramagnetic material, the magnetic moments of the electrons are randomly oriented that results in an average zero net magnetisation. The susceptibility of these materials is always positive ranging from 10^{-4} to 10^3 .¹¹

Figure 3: (a) No net magnetisation is observed in the paramagnetic material because of randomly aligned magnetic moments in the absence of applied magnetic field; (b) Alignment of the magnetic moment in the direction parallel to the applied magnetic field; (c) M vs H curve portraying a positive susceptibility; (d) Temperature dependence of the susceptibility of the paramagnetic material showing a decrease with increasing temperature.

The elements and molecules which have unpaired electrons such as aluminium, lithium, tungsten and sodium show paramagnetism. When these materials are subjected to an external magnetic field, the magnetic moments of the paramagnetic material align along the same direction and result in a net magnetisation. This magnetisation is temperature-dependent and decays with increasing temperature. The heating causes thermal agitation of magnetic moments which lowers the alignment inside the material.¹³

The dependence of magnetisation of these materials on temperature can be described by the Langevin equation:

$$M = M_0 \left[\coth(\chi) - \frac{1}{\chi} \right], \quad \chi = \frac{\mu_0 m_0 H}{k_B T} \quad (\text{Eqn. 4})$$

where M_0 is the maximum magnetisation achieved at 0 K, m_0 is the modulus of the magnetic moment, k_B is the Boltzmann constant and T is the temperature of the paramagnetic material. **Figure 3** shows the ordering of the magnetic moments, a positive susceptibility with the applied magnetic field and the dependence of the susceptibility on the temperature of a paramagnetic material.

FERROMAGNETISM

Ferromagnetism is an ability of the materials to exhibit a spontaneous magnetisation which is stable and can be hysterically switched in the presence of an external magnetic field. The susceptibility of these materials is always positive ranging from 10^4 to 10^5 .¹¹ In these materials, there are small regions called domains. Each domain itself has aligned magnetic moments. In the presence of an external magnetic field, the magnetic moments of ferromagnetic materials rotate and align along the direction of the field until the magnetisation saturates. At this point, it is assumed that all the magnetic moments are aligned in the direction of the applied field. Ferromagnetic materials change their magnetic ordering at a characteristic temperature known as Curie temperature (T_c). The T_c for the ferromagnetic materials— iron, cobalt, and nickel, are 1043 K, 1394 K and 631 K, respectively. Below T_c , the magnetic moments of the ions are aligned, and the crystal shows high magnetic orders. For temperatures above T_c , the individual atomic moments are no longer aligned resulting in the loss of ferromagnetic behaviour. The susceptibility of the ferromagnetic material can be described by Curie-Weiss law by the equation:

$$\chi = \frac{C}{T - T_c} \quad (\text{Eqn. 5})$$

where C is the curie constant of a specific material and T is the absolute temperature. **Figure 4** shows the ordering of the magnetic moments in the magnetic domains and the dependence of the susceptibility on the temperature of a ferromagnetic material.

Figure 4: **(a)** A net magnetisation is observed in the ferromagnetic material because of the presence of magnetic domains even in the absence of applied magnetic field; **(b)** Alignment of magnetic moments in the magnetic domains in the direction parallel to the applied magnetic field; **(c)** Aligned magnetic moments in the magnetic domains; **(d)** Temperature dependence of the susceptibility of the ferromagnetic material showing a decrease with increasing temperature above T_c .

ANTIFERROMAGNETISM

Antiferromagnetism is the ability of a material to spontaneously align their magnetic moments antiparallel to neighbouring moments on the application of an external magnetic field. It results in a net-zero magnetisation in the material. Usually, in an antiferromagnetic material, the alternating sublattices have their spins aligned antiparallel to each other.¹⁴ This

phenomenon is observed only below critical temperature known as Neel Temperature (T_N). Above T_N , these materials behave like a paramagnet.

Figure 5: (a) No net magnetisation is observed in the antiferromagnetic material because of randomly aligned magnetic moments in the absence of applied magnetic field; (b) Alignment of the magnetic moment in an antiparallel fashion under the applied magnetic field resulting no net magnetisation; (c) Temperature dependence of the susceptibility of the antiferromagnetic material an increase in susceptibility till T_N followed by the falling value above T_N .

The magnetic susceptibility dependence on temperature below T_N is also explained by Curie-Weiss law:

$$\chi = \frac{c}{T - \theta} \quad \text{(Eqn. 6)}$$

And, the magnetic susceptibility dependence on temperature above T_N is given by:

$$\chi = \frac{c}{T + \theta} \quad \text{(Eqn. 7)}$$

where θ is another curie constant based on temperature, T_N . The T_N for commonly known antiferromagnetic materials such as oxides of manganese, iron, nickel and cobalt are 116 K, 198 K, 523 K and 293 K respectively. **Figure 5** shows the ordering of the magnetic moments in the magnetic domains and the dependence of the susceptibility on the temperature of antiferromagnetic material.

FERRIMAGNETISM

The ferrimagnetism phenomenon is similar to antiferromagnetism, i.e., the magnetic moments are aligned antiparallel to the neighbouring atoms. The antiparallel alignment is observed because of two different sublattices having different number of unpaired electrons. This results in a net magnetisation in the material in a specific direction. These are more complex forms of magnetic ordering and these interactions are known as exchange interactions. This phenomenon usually occurs in transition metal oxide compounds with partially filled d-orbitals. Ferrites with the general chemical formula MFe_2O_4 are the most common materials portraying ferrimagnetism. Here M is a divalent ion such as Fe^{2+} , Co^{2+} , or Ni^{2+} . Ferrimagnetic materials have been extensively used in various technological applications.¹⁵

HYSTERESIS CURVE OF A FERROMAGNETIC / FERRIMAGNETIC MATERIAL

When a ferromagnet or ferrimagnet in an unmagnetised state is exposed to the external magnetic field, an increase in its magnetisation to a point where it saturates, known as saturation magnetisation is observed. This shown in **Figure 6** as point (a). When the field is removed, the curve does not follow the same path, instead, it decreases to the point which is known as remanence magnetisation (M_R). This shown in **Figure 6** as point (b). To bring the induced field to zero, it requires negative external field called a coercive field (H_c).

The hysteresis properties rely on the composition of the materials and the presence of imperfections.^{16,17} Hysteresis loops are important to characterise a ferromagnetic material. For example, in case of an application like magnetic data storage, square-shaped loops having two stable magnetisation states are usually desirable. While a small hysteresis,

which can be cycled easily between states is more suited for a transformer core. The difference between the ferromagnetic and ferrimagnetic material based on the hysteresis curve is that the saturation magnetisation (M_s) value of ferrimagnetic materials is usually lower than the ferromagnetic materials because of the cancellation by the opposing spins in the structure.

Figure 6: B-H Curve for ferromagnetic/ferrimagnetic materials under the influence of an external magnetic field.

SUPERPARAMAGNETISM (SPM)

Superparamagnetism (SPM) is a kind of magnetism occurring in small ferrimagnetic or ferromagnetic nanoparticles. This is applicable for the nanoparticles which are single domain in nature. In the presence of enough thermal energy, the nanoparticles with magnetic crystalline anisotropy can randomly flip the direction of their magnetisation. According to the Neel-Brown equation, when the particle's magnetic moment reverses over a shorter average time (τ_o) than the measurement time scale (τ_N), then the particle is in the superparamagnetic state. τ_N is commonly known as the Neel relaxation time. The average time to perform a flip is described by the equation:

$$\tau_N = \tau_0 \exp\left(\frac{\Delta E}{k_B T}\right) \quad (\text{Eqn. 8})$$

where τ_0 is the length of time specific to the probed material. Often, it is on a scale of around 10^{-9} to 10^{-12} seconds. The ΔE represents the thermal energy or magnetic anisotropic barrier that magnetisation spin must overcome, k_B is the Boltzmann constant and T is the temperature.

Figure 7: B-H curve for a ferromagnetic material based for the temperatures ranging $T \ll T_B$, $T_B < T < T_C$ and $T > T_C$

When $\tau_N \gg \tau_0$, the particle's magnetic moment reverses over a longer time than the measurement time scale, the particles are then in a well-defined or 'blocked' state. When $\tau_N \ll \tau_0$, the particle's magnetic moment reverses over a shorter time than the measurement time scale. At this stage, the particles are in a fluctuating state (unresolved magnetisation spin directions). This is referred to as a superparamagnetic state. A blocking temperature (T_B) for a superparamagnetic material can be defined as the temperature at which the transition from the blocked to superparamagnetic state takes place which is given by the equation:

$$T_B = \frac{\Delta E}{k_B \ln\left(\frac{\tau_m}{\tau_0}\right)} \quad (\text{Eqn. 9})$$

Whilst, the two states can be described as the following:

- The blocked state: $\tau_m \ll \tau$ or $T < T_B$.
- The superparamagnetic state: $\tau_m \gg \tau$ or $T > T_B$

Figure 7 shows the temperature dependence of the magnetic hysteresis curves for superparamagnetic material.

1.2.2. INTERACTIONS IN MAGNETIC MATERIALS

Magnetic moments in a magnetic material tend to couple together which results in long-range magnetic orders. The type of interaction taking place inside a magnetic material are as follows:

MAGNETIC DIPOLE INTERACTION

The energy of interaction of two magnetic dipoles, μ_1 and μ_2 separated by a distance, r can be written as:

$$E = \frac{\mu_0}{4\pi r^3} \left[\mu_1 \cdot \mu_2 - \frac{3}{r^2} (\mu_1 \cdot \hat{r})(\mu_2 \cdot \hat{r}) \right] \quad (\text{Eqn. 10})$$

Equation 10 shows the dependence of mutual alignment of magnetic moments and their degree of separation. However, these interactions are noticeable only at very low temperatures. At higher temperatures, the thermal energy overpowers the magnetic dipole interaction.

DIRECT EXCHANGE INTERACTIONS

Direct exchange interactions are observed when the moments are close enough to have enough overlap of their wavefunctions. They play a significant role in the long-range order of magnetic materials. The two electrons located at certain spatial coordinates respectively will follow Pauli's exclusion principle and they will either have asymmetrical or symmetrical wavefunctions. Usually, an overlap of the magnetic orbitals of the neighbouring atoms is insufficient to control the magnetic properties of the material.

INDIRECT EXCHANGE

The indirect exchange interactions that are observed in ionic solids are known as the superexchange interactions where two non-neighbouring magnetic ions interact by placing a non-magnetic ion in between. The other indirect exchange interaction is the Ruderman, Kittel, Kasuya and Yosida (RKKY) interaction which is seen in metal structures. Here, the conduction band electrons are spin-polarised by the localised magnetic moments. These spin polarised electrons couple with another local environment resulting in RKKY indirect exchange.

1.2.3. MAGNETOSTRICTION

Magnetostriction is a property of a ferromagnetic or ferrimagnetic material which results in their contraction and expansion in the presence of an applied magnetic field (H). With an increase in the intensity of H on a magnetic material, there is an increase in the magnetostrictive strain. It is found to be highest in ferromagnetic materials because of their high magnetic anisotropy. Magnetostriction is the result of strain caused by the movement of domain walls (also known as the Bloch walls) under H to align the magnetic moment inside each domain. Furthermore, upon the application of a stress to the magnetic material, it can result in inverse magnetostriction and a magnetic anisotropy can be observed. The Bloch walls tend to align along the direction of applied stress and that direction becomes the preferred direction of orientation of magnetic moments. This force can be counteracted by the application of the magnetic field perpendicular to the direction of the applied stress on the material. The degree of magnetostriction i.e., magnetostrictive coefficient, λ can be defined as the ratio of strain to the magnetisation observed in the material. The relation between the two is linear until saturation magnetisation is obtained where all the magnetic moments have aligned along the direction of applied stress. On the removal of H , a hysteresis is usually observed because of the residual magnetisation left in the material that directly depends on the crystal anisotropy energy.¹⁸

1.3.DIELECTRICS

A dielectric material is an electrical insulator but can sustain an electric field with a minimum dissipation of power. It means that under the effect of an electric field, a dielectric material can be polarised. The electric charges do not flow through the material but shift from their equilibrium position resulting in a net polarisation inside the material. In short, alteration of electronic distribution and nuclear positions take place inside the dielectric material. The pair of equal and opposite charges (+q and -q) separated by a very small distance (a) can be represented by a vector (p) pointing from -q to +q. This vector is known as electric dipole moment (**Figure 8 (a, b)**).¹⁹

Figure 8: Representation of (a) an electric dipole induced in the presence of an applied electric field; (b) a dipole moment portraying as a vector that points in the direction from -q to +q with the distance of magnitude 'a' in between them.

Since the charges are bound and surrounded by similar electric charges inside a material, the material is electrically neutral in the absence of an applied electric field.¹⁹ In the presence of an applied electric field, the positive charges inside the material tend to displace towards the field while the negative charges move in the opposite direction. It results in the formation of the electric dipole that compensates the applied field inside the material. Polarisation (P) is defined as the number of induced dipole moments present per unit volume of a material. It can be mathematically illustrated by the equation:

$$P = \alpha E \quad \text{(Eqn. 12)}$$

where E is the electric field and α is polarisability. The unit for P is $\left(\frac{C}{m^2}\right)$.

The displacement (D) of charge as defined by Maxwell follows the equation:

$$D = \varepsilon_0 E + P \quad \text{(Eqn. 13)}$$

where ε_0 is the permittivity of free space.

The dielectric material's ability to polarise is defined as electric susceptibility (χ_e). The polarisability (α) can be written as:

$$\alpha = \chi_e \varepsilon_0 \quad \text{(Eqn. 14)}$$

The polarisation (P) of the material can be then be defined based on the electric susceptibility using the equation:

$$P = \chi_e \varepsilon_0 E \quad \text{(Eqn.15)}$$

The electric displacement can then be written as:

$$D = \varepsilon_0 E + \chi_e \varepsilon_0 E = \varepsilon_0 (1 + \chi_e) E \quad \text{(Eqn. 16)}$$

The permittivity of the material can be defined as:

$$\varepsilon = \varepsilon_0 (1 + \chi_e) \quad \text{(Eqn. 17)}$$

If we substitute the above equation in the displacement equation, it gives:

$$D = \varepsilon E \quad \text{(Eqn. 18)}$$

The dielectric constant (ε_r), also known as relative permittivity as mentioned earlier is the measure of polarisation taking place in the dielectric materials. We can define the dielectric constant as the ratio of absolute permittivity and the permittivity of free space and is given by:

$$\varepsilon_r = \frac{\varepsilon}{\varepsilon_0} = (1 + \chi_e) \quad \text{(Eqn. 19)}$$

where ϵ_r is a dimensionless quantity. The value of ϵ_r for air or vacuum is 1. From the equation, we can say that the electrical energy density of the material is directly proportional to the value ϵ_r . It is higher for solid materials in comparison to air or vacuum.²⁰

1.3.1. TYPES OF POLARISATION

There are 3 types of polarisation that are responsible for the overall polarisation in a dielectric material:

ELECTRONIC POLARISATION

Electronic polarisation is common in crystal lattices of covalent solids. In a covalent bond, the valence electrons are shared between the atoms of a material. The shared electrons between the two atoms produce an electron cloud which can tunnel and exchange positions with other electrons. This results in delocalisation of these electrons and their resulting wave functions. The shift of the electron clouds towards the positive end of the electric field leads to a dipole moment. This dipole moment (M_d) increases with increasing field strength, i.e.

$$M_d \propto E \quad \text{(Eqn. 20)}$$

ORIENTATION POLARISATION

Orientation polarisation occurs in molecules that have permanent dipole moments. Initially, the molecules are randomly oriented in all directions. On the application of an electric field, the dipoles in the molecules align along the direction of the applied field.²⁰ Hydrocarbon molecules such as chloroform tend to align in the absence of electric field.²¹ Materials such as plastics usually have randomly aligned dipoles. Their molecules can realign their dipoles in a certain direction by heating and exposing them to an electric field. This way, materials with permanent dipole moments can be produced. The orientation polarisation is temperature dependent and the alignment randomises at high temperatures. The induced orientation polarisation (P_o) per molecule is given by the equation:

$$P_o = \alpha_o E \quad \text{(Eqn. 21)}$$

where α_o is orientation polarisability of the material and E is the applied electric field.

IONIC POLARISATION

Ionic polarisation occurs in crystal lattices of ionic solids. The net dipole moment of these materials is zero. This is because the molecules of these materials are lined up head to head and tail to tail. In an applied electric field, the cations and anions are pushed on opposite sides resulting in a net polarisation in the material. Ionic polarisation is temperature independent. The induced ionic polarisation (P_i) per molecule is given by the equation:

$$P_i = \alpha_i E \quad (\text{Eqn. 22})$$

where α_i is ionic polarisability of the material and E is the applied electric field.

INTERFACIAL POLARISATION

Interfacial polarisation arises because of impurities and defects present in the crystal. The charge carriers, i.e., electrons, holes and ions, can travel inside the material creating boundaries such as grain boundaries or the dielectric-electrode boundaries. It can also be observed in materials which are composites due to the accumulation of charges at the interface of two materials. Under an applied electric field, it results in the movement of free electrons to the surfaces of the material as the surfaces near to negative end acquire positive charge and vice versa. This redistribution of charges contributes to the dielectric constant of the material.

POLARISATION PROCESSES COMPARISON

The total polarisation taking place inside a material can simply be calculated by the addition of all the four kinds of polarisation in a material:²²

$$P_{Total} = P_e + P_i + P_o + P_s \quad (\text{Eqn. 23})$$

1.3.2. FACTORS AFFECTING THE DIELECTRIC CONSTANT

TIME

All the polarisation effects that have been discussed earlier are not based on the time dependence with respect to the applied electric field. They are considered to be in a static environment. When subjected to a static electric field for a prolonged time (t), a dielectric material tends to develop a maximum polarisation ($P_{\max}$) that it can achieve. Particles have masses, hence accelerating and shifting them back and forth with the change in the applied electric field takes time and cannot happen instantaneously. The time taken to return to the original position once the electric field has been removed is known as the relaxation time (t_r). During the relaxation, the ' $P_{\max}$ ' decreases to ' P '. Their relationship is given as:

$$P = P_{\max} \left[1 - e^{\left(\frac{-t}{t_r}\right)} \right] \quad (\text{Eqn. 24})$$

FREQUENCY OF THE APPLIED FIELD

Figure 9: Representation of frequency dependence of the polarisation processes.

Under a time-varying electric field, the dielectric constant relies on the frequency of the applied field. At low frequencies, all kinds of polarisation have enough time to come back to the relaxed state. With increasing frequencies, not all the polarisations can keep up with the frequency of the applied field. For example, the relaxation after ionic polarisation is

slower than that of electronic polarisation since the ions (which result in ionic polarisation) are heavier than the electron cloud (which results in electronic polarisation). In short, slow polarisation processes are not able to contribute to the dielectric constant at higher frequencies.²³ Usually, ionic and orientation polarisation occurs between infrared and audio frequency ranges. **Figure 9** shows the frequency dependence of each of the polarisation processes.

1.3.3. FERROELECTRICITY

Neumann's principle suggests that the symmetry of a crystal structure includes the symmetry of physical properties. 20 out of 32 point groups are found to be non-centrosymmetric and exhibit a piezoelectric effect (discussed later in this section). Among these, 10 of the known non-centrosymmetric groups are pyroelectric, which can develop a spontaneous polarisation. Among these, ferroelectricity is shown by only those materials which display reversible spontaneous polarisation. Ferroelectricity is a property of certain non-conducting materials or dielectric materials which are composed of crystals in which structural units are small electric dipoles i.e. the centre of positive and negative charge are slightly separated in each crystal unit. In short, they exhibit a dipole moment under a suitable electric field. The above spontaneous polarisation can be observed in a certain temperature range and is characterised by the hysteric behaviour in the polarisation vs. electric field curve.

Figure 10: Polarisation vs. electric field curve (hysteresis loop) for ferroelectric materials. P_s and P_r correspond to saturation polarisation and remnant polarisation, respectively.

Figure 10 shows a typical hysteresis loop in ferroelectric materials. On the application of a high enough electric field, there is an increase in polarisation which reaches a saturation value. The removal of the electric field results in a leftover polarisation known as remnant polarisation. On the application of a large enough electric field in the opposite direction of polarisation, the polarisation is reversed creating a ferroelectric hysteresis. As mentioned earlier, a ferroelectric material shows spontaneous polarisation below the Curie temperature (T_C). At T_C , there is a phase transition from the low-temperature ferroelectric state to a higher temperature paraelectric state. The ferroelectric to non-ferroelectric transition and the dielectric constant for the temperature above T_C can be described by Curie-Weiss law²⁴:

$$\epsilon_r = \frac{A}{T - \theta_c} \quad (\text{Eqn. 25})$$

where ' ϵ_r ' is the dielectric constant, ' T ' is the temperature, ' A ' is a constant for a given material and ' θ_c ' is the temperature near to but not same as the T_C . Since the ferroelectric materials become partially or completely depoled (polarisation loss) near T_C , it severely degrades their performance. Hence, the operating temperature of ferroelectric materials is limited to one-half of the T_C .²⁵

The piezoelectric effect is observed in non-centrosymmetric crystal systems. The prefix – 'piezo' is a Greek word that means – 'to press.' It is a direct result of strain applied to a material that further results in the polarisation in the material by the displacement of ions relative to one another. When these materials are subjected to stress along their polarisation axis, it further results in distortion or displacement of opposite charges farther from each other, therefore changing the polarisation strength of the crystal. This is known as the direct piezoelectric effect. On subjecting these materials to an electric field, it also results in a relative shift in the position of the ions, leading to the distortion of the unit cell. This is the source of an inverse piezoelectric effect. In the case of direct piezoelectric effect, the applied stress is directly proportional to the resultant electric field which can be written as:

$$E \propto \sigma \quad (\text{Eqn. 26})$$

$$E = \lambda \sigma \quad (\text{Eqn. 27})$$

where λ is a voltage-output coefficient. In the case of inverse piezoelectric effect, the resultant strain ϵ is proportional to the applied electric field E which can be written as:

$$\varepsilon \propto E \quad (\text{Eqn. 28})$$

$$\varepsilon = P_{coeff} E \quad (\text{Eqn. 29})$$

where P_{coeff} is the piezoelectric constant more commonly known as the piezoelectric modulus of a material. Since the stress applied to the material is directly proportional to the strain created, i.e.

$$\sigma \propto \varepsilon \quad (\text{Eqn. 30})$$

$$\sigma = Y\varepsilon \quad (\text{Eqn. 31})$$

where Y is the modulus of elasticity more commonly known as Young's modulus of the material.

The above equations relate the stress, strain, electric field and Young's modulus of the material:

$$E = \lambda\sigma = \lambda(Y\varepsilon) \quad (\text{Eqn. 32})$$

$$E = \lambda(YP_{coeff}E) \quad (\text{Eqn. 33})$$

$$Y = \frac{e}{\lambda P_{coeff} E} = \frac{E}{\lambda P_{coeff}} \quad (\text{Eqn. 34})$$

All ferroelectric materials are piezoelectric, but not all piezoelectric materials are ferroelectric. The properties of these materials are temperature dependent. With the increasing temperature, the interatomic distances of their crystal structure change asymmetrically. This affects the polarisation which induces a potential difference inside the crystal due to changing interatomic distances. This phenomenon is known as the pyroelectric effect.²²

1.4. MULTIFERROIC AND MAGNETOELECTRIC MATERIALS

Magnetoelectric multiferroics are a particular subclass of the materials that are characterised by the simultaneous presence and coupling between a magnetic and an electric order parameter.²⁶ When a magnetic or an electric field is applied to these materials,

it results to onset, or modify their electric and magnetic properties, respectively. The sensitivity of these complex oxides depends on factors such as strain, stoichiometry, oxidation states, and disorder. At the nanoscale, it can lead to severe modifications in their electronic, magnetic and electric properties. For example, misfit strain in epitaxial thin films may act to enhance the ferroelectric state²⁷ and modify strongly the preferred magnetic orientation axes.

There have been fewer developments in the field of single-phase multiferroic materials because they show low magnetoelectric coupling coefficient. Hence, there is a need for developing alternative approaches like combining dissimilar materials (magnetic and ferroelectric) to form composite structures with improved coupling between electric and magnetic properties. Around 100 compounds have been discovered which have exhibited the magnetoelectric effect.²⁸ However, the coexistence of magnetism (spin order) and ferroelectricity (electric dipole order) of high magnitude is quite rare in a single-phase. A lot of focus is given to thin films and microstructures based on the above effect, but the area of nanoparticles and 1-D nanostructures is still in the early stages of research. **Figure 11** shows the relationship of multiferroic and magnetoelectric materials.

Figure 11: The relationship of multiferroic and magnetoelectric materials with respect to electrically and magnetically polarisable materials.

1.4.1. COMPOSITE MULTIFERROICS

Composites have been used as alloys since the Bronze Age to obtain specific kind of properties²⁹. Composite nanostructures can be categorised based on the structure and atomic ordering. Bimetallic composite structures are of great interest owing to their physicochemical properties different from their monometallic components. Although the properties of these materials can be modified by changing the percentage composition of each component, they are mainly dependent on the ordering of these materials components. Atomic ordering in bimetallic nanostructures can be an ordered arrangement in the case of intermetallic structures (**Figure 12 (b)**) or it can be a random arrangement of atoms in the case of alloys (**Figure 12 (a)**). Segregated structures are formed when two components share an interface and form a subcluster structure (**Figure 12 (c)**). If a metal forms a shell over another metal structure, it results in the formation of a core-shell structure (**Figure 12 (d)**).³⁰ A multi core-shell structure where there are alternating shells of materials present (**Figure 12 (e)**) and multiple small cores coated by a single shell (**Figure 12 (f)**) are also possible.³¹

Figure 12: Interpretation of composite structures: The red and blue spheres represent atoms of two different types of materials for (a) alloyed, (b) intermetallic, (c) subcluster, (d) core-shell, (e) multi-shell core-shell, and (f) multiple core materials coated by a single shell material.

The final structure of a bimetallic compound relies on the thermodynamic and kinetic model of the synthesis reaction. The product with lowest Gibbs free energy is the thermodynamic product whereas the product with the lowest activation energy is the kinetic product. The end product depends on the relative strength of metal-metal bonds, surface energies of both materials in bulk form, charge transfer and relative atomic size of both materials.³²

One dimensional (1-D) nanomaterials such as nanotubes, nanofibres and nanowires show a sharp shape anisotropy. Therefore, 1-D magnetic nanostructures show enhanced anisotropy in coercive force, remanence and the hysteresis shape because of their specific ferroelectric behaviours.³³ 1-D ferroelectric nanostructures have also been extensively studied because of their specific ferroelectric behaviours related to size confinement. They show modifications in phase transition or Curie temperature (T_C), dielectric constants, coercive fields, spontaneous polarisation levels, and piezoelectric response levels. Generally, the specific properties of 1D nanostructures are attributed to the increased surface area.

Intrinsic multiferroics have a low magnetoelectric (ME) coefficient thus it motivates the design of materials which can result in a coupling between ferroelectric and ferromagnetic/ferrimagnetic components' ordered parameter. Strain mediated coupling (via the piezoelectric effect in the ferroelectric phase and magnetostriction effect in ferromagnetic or the ferrimagnetic phase) has been studied intensively.^{34,35} With the ongoing advancements in nano-/micro-electronics technology, the power consumption of the sensor nodes is becoming smaller and smaller, and in that case, the harvested energy may be sufficient to eliminate batteries completely, provided the harvestable energy sources are stable and continuous.

Some multiferroic structures have shown charge sensitivity in the magnetic phase of complex oxides³⁶ and dilute magnetic semiconductors³⁷ where charge modulation was used by scientists to achieve control of spin states using the approach of ferroelectric field. Composite structures offer tailored properties to take advantage of a specific coupling between the individual components that usually lack in the constituent phases. Magnetodielectric measurements are used to characterise the degree of the coupling between magnetic and electric materials. The magnetocapacitive measurements are used to measure the change in dielectric constant with the applied magnetic field and it can be described as:

$$M_D = \frac{(\varepsilon_H \varepsilon_0)}{\varepsilon_H} \cdot 100\% \quad (\text{Eqn. 35})$$

where ε_H and ε_0 are the dielectric constants with and without the application of the magnetic field, respectively. Magnetic and piezoelectric materials with high conversion factors are desired to fabricate composites of high ME coefficients. The magnetoelectric effect in composite structures can be calculated as:

$$\text{Magnetoelectric effect} = \frac{\text{Electric Output/Input}}{\text{Mechanical Input (transfer from/to)}} \times \frac{\text{Mechanical output (transfer to/from)}}{\text{Magnetic (input/output)}} \quad (\text{Eqn. 36})$$

1.4.2. STRAIN MEDIATED MAGNETOELECTRIC MULTIFERROICS

Strain mediated ME effect has been the long-standing path in the field of magnetoelectric multiferroics. In these materials, the indirect ME coupling takes place. Here, the strain induces crystal deformations on the magnetic phase by the converse piezoelectric effect. The other way is to induce strain in the ferroelectric phase by magnetostriction. At first, the applied field is converted to strain and then this strain is converted into polarisation.

Hence, the coupling is a product of two different interactions occurring side by side. Good order in magnetic coupling is determined by various factors like large piezoelectric coefficients in ferroelectric materials and large magnetostriction and resistivity in magnetic materials. Decent chemical stability accompanied by a strong mechanical contact between two phases of the materials also makes a huge difference to coupling. The magnetoelectric effect in these bulk composites is not promising due to the lack of the above factors. Ferroelectrics like BaTiO_3 , $\text{Pb}(\text{Zr,Ti})\text{O}_3$ and PbTiO_3 , and the magnetic systems like CoFe_2O_4 , NiFe_2O_4 and Fe_3O_4 have been studied the most.

The order of ME effect relies on the relative amount of the ferroelectric phase along with the orientation of ferroelectric polarisation. It also depends on the presence or absence of ferroelectric domain walls. The conductivity in composites may also limit the strength of the applied electric field. The coupling interaction may also be affected by residual strains, voids, grain boundaries, dislocations and clamping effects between the phases. Also, the

ferroelectric part can be stressed by the magnetostriction effect (usually termed as pseudo-piezomagnetic effect) and cause piezoelectric signal. Thus, the piezoelectric effect led to the generation of surface charges in them. This effect is reduced at large magnetic fields (above the saturation field) since the spins are then aligned with the magnetic field, which results in the change in magnetic configuration to minimal. Henceforth, the magnetoelectric effect will vary linearly at smaller magnetic fields before summing at a magnetic field value below the saturation field. Alternatively, on applying a voltage to the piezoelectric material (core), the magnetic structure of a film can be altered.³⁸ Recent advancements in nanotechnology have resulted in better magnetoelectric responses but still, a lot of improvement is required to overcome the above-mentioned factors.

1.4.3. MATERIALS FOR MAGNETOELECTRIC COMPOSITE FORMATION

Iron Ferrite (Fe_3O_4) and Cobalt Ferrite

Iron Ferrite (Fe_3O_4) is one of the most studied iron oxide structures because it shows a sharp metal-insulator first-order transition. This transition is known as Verwey transition (T_V). It is observed at 120 K for iron ferrite.³⁹ The electrical conductivity of iron ferrite increases by two orders above T_V . It has inverse spinel structure (**Figure 13**) with the Fe^{2+} ions located in half of the octahedral sites and Fe^{3+} ions filling the rest of the octahedral sites. All the other tetrahedral sites are in the face centred cubic (FCC) lattice which are filled by O^{2-} ions. The length of the unit cell is 0.839 nm. The net moment of Fe^{3+} ions at both sites cancel each other and only the Fe^{2+} ions result in the net magnetic moment.

Figure 13: Unit cell of iron ferrite portraying an inverse spinel structure.

The net measured magnetic moment per formula unit is reported to be $4 \mu_B$ (the unit is Bohr magneton).⁴⁰ It has a high room temperature magnetostriction coefficient (λ_{111}) of 80×10^{-6} which make it suitable for magnetoelectric applications. The T_c of iron ferrite is 858 K and it belongs to space group Fd3m.

Cobalt ferrite is one of the other compounds that belong to the inverse spinel structure family of spinel ferrites. With the length of the unit cell equal to 0.839 nm, the metallic cations (Co^{2+} and Fe^{3+}) occupy 8 out of 64 tetrahedral sites and 16 of 32 octahedral sites (**Figure 14**). Just like iron ferrite, it has a large magnetic anisotropy accompanied by large magnetostriction ($\lambda_{100} = -590 \times 10^{-6}$ and $\lambda_{111} = -120 \times 10^{-6}$).^{41,42} The tetrahedral sites which are filled with 8 Fe^{3+} and Co^{2+} ions in a unit cell, align in antiparallel fashion with 8 Fe^{3+} ions and cancel each other's spin. The Co^{2+} itself results to the net magnetic moment of $3 \mu_B$ per unit cell.⁴³

Figure 14: Unit cell of cobalt ferrite portraying an inverse spinel structure.

However, the saturation magnetisation comes out to be $4 \mu_B$ because Fe^{3+} ions are not aligned perfectly on octahedral and tetrahedral sites and result in a higher value.⁴⁴ The T_c of cobalt ferrite is 789 K and belongs to the same space group as iron ferrite, i.e., Fd3m.

Ferrimagnetic ferrite nanoparticles (MNPs) have found their uses in a variety of research applications because of their attractive magnetic properties. The crystalline structure, shape, size and monodispersity define their magnetic properties. High surface energy results in agglomeration of nanoparticles. Therefore, a coating on the surface of

nanoparticles is usually required to maintain monodispersity in the system. Non-aqueous synthesis results in nanoparticles with smaller particle size distribution with comparatively lower or no agglomeration and are generally preferred over aqueous techniques. In case of the nanoparticles prepared by non-aqueous synthesis, the properties depend on the synthesis parameters such as kind of reagents used,⁴⁵ types of surfactant used,⁴⁶ time of reaction⁴⁷ and temperature of the reaction⁴⁶. A certain size and shape of MNPs can be obtained by adjusting the heating rate and surfactants during the synthesis.

The optimal particle size for most applications is found to be in the range of 5-20 nm. For the particle sizes lower than 10 nm, a single magnetic domain structure is observed which is superparamagnetic.⁴⁸ The exchange interactions in the nanoparticles in close proximity affects the surface spins. The dominating interaction in the system are long range order dipolar interaction which are the result of high magnetic moment of the nanoparticles. The dipolar interaction (E_D) for randomly distributed nanoparticles with a mean interparticle distance (r) and average magnetic moment (μ) can be written as:

$$E_D = \frac{\mu_0 \mu^2}{4\pi r^3} \quad (\text{Eqn.11})$$

The strength of interparticle interaction can be modified by changing the concentration of nanoparticles in a medium. The strong interparticle interactions in a nanoparticle system can result in collective magnetic states at low temperatures which is similar to the properties of spin glasses.⁴⁹ Both cobalt ferrite and iron ferrite nanoparticles have been studied as an important magnetic component of ME composite.⁵⁰⁻⁵⁴

Nickel-Iron (Ni-Fe) Composites

Nickel-iron in alloy form is of great interest because their properties can be modified based on the composition and preparation process. They display a well-defined structure in the range of 35-80 wt% nickel and exists in two stable unordered phases. When the composition of nickel is less than 7 wt%, the Kamacite phase is observed in the crystal with a body-centred cubic (BCC) packing. Above this concentration of nickel, a mixed phase of α and γ is observed which is face-centred cubic (FCC) in nature. At higher nickel concentrations, only the stable taenite phase exists. The ordered taenites are usually observed in meteorites because of slow cooling rates and are known as tetrataenites which

have around 50 wt% nickel content.⁵⁵ Zero crystal anisotropy and zero magnetostriction have been observed in the materials above 80% nickel composition.⁵⁶ They are known as soft magnetic alloys that have low saturation flux density (around 0.8 T) and a high initial permeability that depends on the thickness of the materials and the frequency of the applied magnetic field. When the concentration of nickel is kept between 36 wt% - 48 wt%, they have a high saturation flux density (1.35 T – 1.55 T) and low permeability. The 55 wt% nickel has portrayed relatively higher values for both the initial permeability and saturation flux density (1.5 T).⁵⁷ **Figure 15** shows the phase diagram based on the composition of iron in wt % in nickel-iron alloy structures.⁵⁸

Figure 15: Phase diagram for the lattice constants of the FCC and BCC phases of nickel-iron composites as a function of the Fe content.⁵⁸

The bulk properties of $\text{Fe}_{(1-x)}\text{Ni}_x$ are described by remarkably small magnetocrystalline anisotropy and relatively high saturation moment leading to high magnetic susceptibilities which make them suitable for applications such as magnetic flux guides and magnetic sensors.^{59,60} One of these kinds are permalloys which show excellent magnetic and mechanical properties. They show a high magnetic permeability, low coercivity and near-zero magnetostriction along with notable anisotropic magnetoresistance.⁵⁶ Invar alloy which has a nickel composition of around 35 % has exhibited thermal expansion over a

wide range of temperature.⁶¹ Ferrimagnetic nickel ferrite composites are found to have a high magnetostriction coefficient and has been used as the magnetic component of ME composite.^{62,63} On the other hand, the ferromagnetic Fe-Ni should show even higher magnetostriction coefficient. However, Fe-Ni composites tend to oxidise and cannot be used directly.

Barium Titanate (BaTiO_3)

The crystal structure for most of the crystalline ferroelectric materials is a perovskite-type ABO_3 .⁶⁴ BaTiO_3 is one of the most studied ferroelectric material as it exhibits several structural phase transitions into different crystal systems which have been intensively studied.⁶⁵ In BaTiO_3 , a phase transition occurs from the paraelectric cubic phase to the ferroelectric/piezoelectric tetragonal phase at 130 °C. On cooling below 0 °C, another transition occurs from a tetragonal to an orthorhombic one, which is followed by the final phase transition to a rhombohedral crystal structure occurring at -90 °C. Perovskites are ferroelectric when B-site cations are off-centred. The B-site cation (titanium ion) sits slightly off-centre and hence, an electrical polarity develops inside the unit cell, which effectively turns the unit cell into an electric dipole. They are shifted towards the directions $\langle 100 \rangle$ (tetragonal), $\langle 110 \rangle$ (orthorhombic) or $\langle 111 \rangle$ (rhombohedral). **Figure 16** shows the unit cell structure of BaTiO_3 .

Figure 16: Unit cell of barium titanate.

When mechanical stress is applied to the crystal, it further shifts the position of the titanium ion, therefore changing the polarisation strength of the crystal resulting in a direct piezoelectric effect. The resulting shift of the titanium ions leads to distortion of the unit cell. This makes the structure more (or less) tetragonal resulting in an inverse piezoelectric effect. BaTiO₃ has a piezoelectric coefficient of 199 pc/N and a spontaneous polarisation of 26 $\mu\text{C cm}^{-2}$. The above properties make it a suitable candidate to be used as a ferroelectric component of the ME composite.^{51,53,54} However, it is a heavy metal compound and requires higher temperature processing.

Poly-(vinylidene difluoride) (PVDF)

PVDF has been a material of interest because it shows distinctive piezoelectric, pyroelectric and ferroelectric properties.^{66,67} It is a semicrystalline polymer that is flexible, lightweight, inexpensive and has a high electrical breakdown strength.⁶⁸ It has a low density along with low dielectric permittivity resulting in a very high voltage coefficient. PVDF belongs to the ‘order-disorder’ ferroelectric class in which the phase transition can take place from randomly oriented dipoles (paraelectric phase) to ordered dipoles (ferroelectric phase). PVDF has a crystallinity of ~50% and can be found in five different polymorphs.⁶⁹ The monoclinic α -phase of PVDF is the most commonly occurring polymorph with TGT $\check{G}$ {Trans – Gauche (+) – Trans – Gauche (-)} chain conformation. The β -phase (**Figure 17**) shows piezoelectricity with an all-trans (TTTT) conformation forming an orthorhombic structure with all the fluorine atoms located on the same side of the polymer crystal structure.⁶⁶ The other polymorphs include γ (orthorhombic; TTTGTTT $\check{G}$ conformation), δ and ϵ , which are polar and anti-polar equivalents to α -phase and γ -phase, respectively. The most common α -phase can also be converted easily into β -phase by electrical poling and mechanical drawing.^{70–72} The intrinsic polarisation value of PVDF is 8 $\mu\text{C/cm}^2$. Although the spontaneous polarisation is low, it has still been used as a ferroelectric component of ME composite because of its ease of processability and inertness. This makes PVDF easier to be doped with other ferroelectric materials which can improve the overall property of the structure.

Figure 17: Representation of Poly-(vinylidene difluoride) chain.

Diisopropylammonium Bromide (DIPAB)

Diisopropylammonium bromide is a high temperature, molecular, organic ferroelectric crystal compound having a room temperature polar point group and a high melting point. It exists in two different polymorphs, 1-F and 1-P. The 1-F structure belongs to the monoclinic crystal system at room temperature and is the ferroelectric active phase (**Figure 18**). While 1-P belongs to the rhombohedral crystal system at room temperature which is not ferroelectric. 1-F is needle-shaped, while 1-P has a block shape. The conversion of 1-P form to the ferroelectric 1-F form is done by simply heating to 428 K. Da-Wei Fu et al.⁷³ reported a spontaneous polarisation of $23 \mu\text{C}/\text{cm}^2$ (comparable to that of highly ferroelectric barium titanate (BaTiO_3)) and a high Curie temperature (T_c) of 426 K (above that of BaTiO_3). It has shown a high dielectric constant of 85 and low dielectric loss.⁷⁴ Thus, DIPAB exhibits a good piezoelectric response along with well-defined ferroelectric domains. With such good ferroelectric properties, it may act as a molecular alternative to perovskite/polymer ferroelectrics and thus can be used an important candidate to be used in ME applications. But it is difficult to use DIPAB in practical applications as big crystals of DIPAB have low mechanical strength. Moreover, it is highly hygroscopic which means that it will absorb moisture quickly which will result in structural deterioration; hence it cannot be used in the long run. DIPAB can be doped in a polymer such as Poly-(vinylidene fluoride (PVDF) or bisphenol-A EP matrix that can help overcome the stated problems.⁷⁴

Figure 18: Representation of diisopropylammonium bromide molecule.

1.4.4. APPLICATIONS OF MAGNETOELECTRIC MULTIFERROIC COMPOSITES:

Multiferroic magnetoelectric materials allow us to study new physical phenomena and they have numerous possibilities in multi-functional devices.² For instance, the transducers convert magnetic fields to electric fields and vice versa. Attenuators, filters, field probes and data recording devices are some other devices based on electric control of magnetisation. Multiple order parameters in multiferroic and magnetoelectric coupling can both be exploited in novel types of memory applications. However, there is still a challenge posed by imperfections in the structure. The nature of magnetoelectric (ME) coupling in nanostructures compared to the bulk and layered multiferroic composites are of interest due to a large surface to volume ratio.⁷⁵ Studies to-date on nanocomposites include core-shell nanoparticles, nanopillars, coaxial tubes, and core-shell wires.^{76–78} Ferromagnetism control by electricity in multilayer films of the ferroelectric-ferromagnetic sublayers has been well illustrated.⁷⁹ The electrically driven change in multilayer structures results in the polarisation of a ferroelectric-layer producing mechanical strain that is transmitted to an overlying ferromagnetic/ferrimagnetic thin film. This deformation leads to a preferred orientation of the magnetic dipoles further causing macroscopic magnetisations. Few of the ME applications have been discussed in detail:

ME sensors:

Magnetoelectric (ME) sensors comprise of magnetostrictive and piezoelectric phases that are mechanically coupled. A magnetic field acts on the magnetostrictive material which further stresses the piezoelectric material and in turn, generates a voltage. The room temperature operation of these magnetic sensors with ultrahigh sensitivity enables them for

applications in the field of penetration imaging and tracking or communications. They can be used in medical technology for measuring human magnetic fields. They can be used for magneto-biological reactions (electrical signals of the heart, ferromagnetic inclusions signals of skeletal muscle, brain activity, eye tissue, may also be used for magnetic sensors in ME tomography.⁸⁰ ME sensors can also be applied in the field of motion and metal detectors. They can be used as instruments for measuring the characteristics of the magnetic field and the magnetic properties of materials.

ME-based vibration energy harvesters:

Energy harvesting by collecting the waste energy from the environment or small-scale energy scavenging to freely operate low-power electronic devices, has attracted the research community. It can minimize the dependence of wireless sensor networks (WSNs) on external power sources.^{81–83} ME composites can be configured to harvest energy from mechanical vibrations. The external vibration can change the relative position between the ME composite and permanent magnet and result in an electrical voltage/power (direct ME effect). Alternatively, by converse ME effect, magnetic field or electric power line energy can be harvested using the radiated magnetic energy generated from a power/current line. However, relatively high resonance frequency limits the application of ME materials in energy harvesting from industrial or household electrical devices. Usually, the electric powers are delivered in the range between 50-60 Hz. It requires the ME energy harvesting devices to be tuned to considerably lower frequency ranges to optimize the output power. The effect of magnetic flux concentration needs to be adapted to develop high sensitivity magnetic field sensors using ME composites.

Drug delivery:

The challenges for using nanomaterials in drug delivery depends on their improved biocompatibility and surface modifications for optimum drug loading/migration and tailored electrical-magnetic properties for on-demand drug release.⁸⁴ ME nanoparticles can act as drug-vehicle for the controlled drug release. ME nanoparticles can be functionalised accordingly, to offer the unique capability of field triggered release at the desired location of the body. To achieve target-specific delivery to perform the drug release, ME particles with specific electrical, optical and magnetic properties are required. The external magnets

can guide the drug to the specified location. The electric charges produced as a result of ME effect can change the bond strength of the attached drug. An enough localized field opens up the cell membrane pores for the penetration of nanocarriers and drug release with changing field.⁸⁵ The advantage is that no heat is caused during the delivery. Core-shell M.E nanoparticles have also been used as nuclear magnetic resonance (NMR) sensitive nanoprobes for the detection of the biological cell-based on types of cell and corresponding particle association with the cell.⁸⁶

EM wave absorbers:

EM wave absorption is a process, in which the energy of the electromagnetic wave is depleted and then transformed into other energy, such as thermal energy so that the wave cannot be reflected or permeated through the materials. EM wave absorption materials have the impedance matching between free space and the material surface to prevent wave being reflected. EM wave absorbing material should absorb as many incident waves as possible. This requires materials with strong magnetic and dielectric losses. Moreover, EM wave absorbers should be lightweight, thin and have tuneable absorption frequency.

Magnetic nanomaterials have a higher surface area and more surface atoms. As a result, multireflection can result in larger dielectric or/and magnetic losses. The nanoparticles size is below the skin depth (about 1 micron) at microwave frequencies (10 GHz) range. It induces eddy current losses which enhances the stability of wave absorption properties. The use of ferrite nanoparticles restricts the skin effect at high frequency, therefore making them a suitable candidate as a multiferroic microwave absorbing material.^{87–90} Polymer embedded magnetic nanoparticles form ME composite structures with improved processability and aggregation of nanoparticles is also avoided. It increases the reflection loss of EM wave. The interfaces formed between the components of the composites act as polarised centres that enhance the EM wave absorption properties by the induced interfacial polarisation. The high frequency electromagnetic (EM) waves absorbers can be applied in the field of electronic devices for telecommunication, industrial and medical applications.⁹¹

ME Memory Based Devices

Since ferroelectric polarisation and magnetisation are used to encode binary information, the coexistence of magnetisation and polarisation in a multiferroic material allows the

realisation of four-state logic states (or >4) in Fe-RAM (ferroelectric random access memory) and M-RAM (magnetic random access memory) in a single device, respectively.⁹² The basic principle and operation of magnetoelectric random access memory (ME-RAM) have been studied.² The precise regulation of magnetic domains in a ferromagnetic material through a continuous voltage-driven multiferroic shows true potential to combine the best features of Fe-RAM and M-RAM.

OTHER APPLICATIONS OF MAGNETIC AND FERROELECTRIC NANOMATERIALS

Magnetic nanoparticles find their use in applications such as:

- a. **Catalysis:** Magnetic nanoparticles (MNPs) have been used in the field of catalysis.^{46,93} MNPs act as a catalyst for the preparation of NH₃, natural gas desulphurisation and water-gas shift reaction, Fischer-Tropsch synthesis of hydrocarbons and alcohol oxidation.⁹⁴
- b. **Hyperthermia treatment:** By optimising the size and functionality, the superparamagnetic iron oxide nanoparticles (SPIONs) can be used for *in-vivo* applications such as cancer therapy.^{95–97} These nanoparticles can circulate in the blood for a prolonged time and cross the capillary walls. SPIONs can randomly flip direction in an external magnetic field. This flipping results in heat energy which can be used to kill tumour cells by increasing their temperatures.
- c. **Contrast agents for MRI applications and drug delivery:** MNPs have been used extensively as contrast agents.^{98–101} SPIONs have an advantage of producing an enhanced proton relaxation when compared to paramagnetic MRI contrast agents.
- d. **Data storage and spintronics:** The stable and switchable states can be obtained in MNPs which is the requirement for information storage and spintronics applications. These can represent bits of information that remain unaffected by temperature fluctuations.^{102–106} They have intensively been used for ultra-high density data storage.^{107–110}

Kretschmer and Binder¹¹¹ studied the effects of the varying surface areas of the dielectric materials on the spontaneous polarisation in the thin film structures and found that significant changes are introduced in the dielectric/ferroelectric properties.¹¹¹ Nanostructuring can result in dense arrays of isolated ferroelectric nanostructures and domains which can be used as memory elements bits for data storage applications. On the other hand, a large surface area can result in the existence of depolarising fields because of incomplete compensation polarisation induced surface charges.^{112,113} Hence, it is very important to study the size limitations of these materials so that they can be used for specific applications while taking care that the dielectric/ferroelectric properties are not lost.

Dielectric/ferroelectric nanomaterials find their use in applications such as:

- a. Non-Volatile Memory Storage:** The ferroelectric nanomaterials show reversible polarisation. The switching of this polarisation can be represented as the binary value '0' and '1' which can be used for data storage.¹¹⁴ FeRAMs use switchable remnant polarisation property of ferroelectric materials. PVDF-TrFE polymer has shown their capability to be used in non-volatile memory cells which can decrease the cost and induce flexibility in the device.¹¹⁵ The polarisation reversal in these materials can result in charge transfer properties and find its use in memory storage applications.
- b. Energy Conversion-** The ferroelectric nanomaterials show piezoelectric effect, i.e. they can convert mechanical energy into electrical energy and vice versa. This property can be used in the field of actuators, transducers and MEMs devices.¹¹⁴ The coupling of the ferroelectric polarisation to the channel of a field-effect transistor can be used for ferroelectric field effect transistor formation.
- c. Flexible Electronics-** The flexibility and stretchability of polymer-based dielectrics can result in the addition of extra functionality and efficiency.¹¹⁶ The flexible and wearable nanogenerator devices with embedded piezoelectric nanowires in the polymer matrix have shown an output voltage of 6V and current equal to 45 nA has been reported.¹¹⁷
- d. Energy Storage-** Since these ferroelectric nanomaterials have a high dielectric permittivity, they can be used as capacitors in the field of electronics.¹¹⁸ The dielectric

properties of these materials can be tuned by the functionalisation with suitable organic moieties.¹¹⁹ PZT (lead zirconia titanate) capacitors have shown a capacity of 176 GB/inch² and have found their use in the field of FeRAMs.¹²⁰ Polymers with embedded nanoparticles have been used as flexible dielectric capacitors.¹²¹

1.5. WIRELESS CHARGING OF ELECTRIC CARS BY INDUCTIVE POWER TRANSFER

Wireless power transfer (WPT) can be traced back to the times in the late 19th century when Nicola Tesla designed a wireless lightning bulb. WPT refers to the transfer of electrical power from one point to another through an air gap without any electrical contacts. Wireless power transfer (WPT) is also known as Inductive power transfer (IPT) and find their uses in applications such as handling of materials, charging of batteries and efficient transfer of power.^{122,123} WPT technology has also been applied in the field of electric vehicles (EVs), consumer electronics and biomedical.^{122–124} Inductively coupled wireless power transfer (ICWPT) system are ideally designed power to a movable object. They are a promising candidate for the future of transportation as they are ideally free from huge and costly batteries. They charge directly while moving on a road (dynamic charging). The electric vehicles currently available in the market have limited travel range in comparison to the traditional internal combustion engines. The creation of bigger batteries and the increase of the energy density of batteries increase the range of electric cars. However, the use of bigger batteries results in the addition of extra weight and increasing the energy density of individual batteries requires lots of research. Moreover, it takes a lot of time to charge the batteries which can be problematic when the vehicle is being used every day. The vehicles cannot be driven while they are plugged in for charging. The charging wires also increase the chances of electrocution and are aesthetically unappealing.¹²⁵ The IPT system for wireless charging of electric vehicles have recently been developed as illustrated in **Figure 19**.¹²⁶ A realistic idea for the use of the above technology would require it to be economical and durable.

Figure 19: Illustration of inductive power transfer for wireless charging of vehicles.

The development of the system relies on the integrated system of both magnetic and power electronics. The design of magnetic coupling structure with a small air gap would result in high magnetic coupling coefficient that will increase the power transfer capability. At the same time, realistic use of the above technology would require it to be economical and durable. The charging pads must retain their properties when subjected to the stresses of an active roadway. Hence, there is a need of non-brittle and affordable magnetic materials. IPT systems recently being used have ferrite materials to improve magnetic coupling, and operate between 10 kHz to 500 kHz.^{127,128} Ferrites show good magnetic permeability at high frequencies along with suitable electrical properties.¹²⁹ However, the ferrites are brittle and suffer from high mechanical and thermal stresses. The nanomaterials can be used in IPT applications for higher working frequencies.¹³⁰

The amount of magnetic flux transferred from one end (transmitter) to the other end (receiver) depends on the coupling coefficient.¹³¹ And, the geometry of core material plays a big role. Overall, the effectiveness of WPT in cars depends on:

- a. The geometry of coil structures for improved inductance.
- b. The power transfer capacity.
- c. Airgap, size, weight, and cost of the WPTs.
- d. Operating frequency.

New Zealand's Ministry of Transport's (MoT) latest electric vehicle projections (2017) expect electric vehicles (EV) fleet numbers to at least double every year to reach 64,000 EVs by the end of 2021 and it will make up 40% of the total vehicle fleet by June 2040.

This estimate is in line with global estimates, where Bloomberg expects EVs to account for 54% of sales by 2040. Norway's capital city of Oslo will be the world's first metropolitan area to install wireless, induction-based charging stations for electric taxis, in a bid to make a zero-emission cab system in early 2023. The NZ magnetic minerals studied by the IPT, Wellington team showed a magnetic permeability of 1–5.¹³²

HaloIPT's research and development department is in Auckland. London-based HaloIPT's (from the University of Auckland's commercialisation company) technology has been taken up by UK companies including Rolls-Royce. Wireless charging pads have been designed to transmit power to vehicles ranging from small city cars to trucks and buses. Special charging lanes are being tested so that vehicles can drive along the open road and pick up power en-route. Tech-company, Qualcomm has been looking in developing their technology for charging while driving using their "Dynamic Electric Vehicle Charging" technology. They have claimed to charge the vehicles at the speed of 70 mph on a 100-meter test track.

1-D magnetic materials for wireless charging applications

Following Moore's law, with decreasing sizes, a higher saturation flux density and lower coercivity are required to preserve the necessary flux densities inside the material. This requires a need to study new complex materials with improved morphology and confinement. The magnetic properties rely on the composition of the materials and the presence of imperfections.^{16,17} The geometrical dimensions of magnetic nanostructures compliment the magnetic length scales such as the exchange length and domain wall width.^{107,133} The permeability of magnetic materials depend directly on the aspect ratio and anisotropy in the materials.¹³⁴ The requirements for effective magnetic coupling are high Q-factor and low losses in the operating frequency ranges.¹³⁵ One-dimensional (1D) nanomaterials such as nanotubes, nanofibres and nanowires show a sharp shape anisotropy. 1D nanostructures have received much attention especially due to confined size and anisotropic enhancement in coercive force, remanence and hysteresis shape.³³

The metallic nickel-iron nanofibres were fabricated by electrospinning method and their magnetic properties have been discussed in **Section 3.3** of **Chapter 3**. They were fabricated to be studied as potential magnetic materials for inductive power transfer applications for the wireless charging of cars based on the following desirable reasons:

1. To lower inductive losses as induction system takes a longer time to charge the battery in comparison to wired chargers.
2. To lower material cost as nanofibres fabrication is relatively cheaper in comparison to other physical processes.
3. Less usage of the material per unit area based on higher volume per unit area of the nanofibres in comparison to bulk materials.
4. Altering of morphology by the modification of iron to nickel ratio is very easy as it is based on the amount of added iron precursor to the nickel precursor.
5. Mechanical strength of the nanofibres is higher to withstand shock forces in the portable systems in comparison to bulk materials.

Chapter 2 further discusses the basics synthesis, characterisation and analysis techniques used for the formation of respective materials for magnetoelectric application. **Chapter 3** discusses the synthesis, characterisation and analysis of magnetic nanomaterials produced during the PhD. **Chapter 4** discusses the ferroelectric materials produced during the PhD. In short, the thesis further discusses the techniques and formation of magnetic and ferroelectric materials which find their use as a component of magnetoelectric multiferroic materials.

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CHAPTER 2

SYNTHESIS, CHARACTERISATION AND ANALYTICAL TECHNIQUES

This chapter deals with the synthesis, characterisation techniques and the relevant literature review performed during the PhD. The intention is to give an outline on the type of techniques performed to synthesise the nanomaterials. Cobalt ferrite and iron ferrite nanoparticles were synthesised via thermal decomposition of organic precursors. Iron nickel composites were fabricated in the form of nanofibers by the process of electrospinning. Electrospinning was also applied for the formation of PVDF based composite nanofibres. Also, several characterisation and analytical techniques were performed to study the structural, electrical, and magnetic properties of the synthesised nanomaterials and have been discussed later in this chapter. The chapter also discusses relevant literature review that helped to develop the synthesis/fabrication protocols for the above-mentioned materials.

2.1. NANOMATERIALS SYNTHESIS AND FABRICATION TECHNIQUES

2.1.1. HOT INJECTION TECHNIQUE

The hot injection technique allows for a defined control of nanoparticle's size and shape by separating the nucleation and growth processes during the synthesis. The precursor solution(s) prepared at room temperatures are injected into a reaction media at elevated temperatures in the presence of suitable surfactants. It usually follows the "LaMer

mechanism” as shown in **Figure 20**. Based on LaMer mechanism, there are three stages during the formation of nanocrystals:¹

- a. **Generation of monomer:** The heating up of the initial precursors to their minimum concentration results in the development of monomers.
- b. **Self-nucleation stage:** A rapid self-nucleation process takes place when the mixture’s concentration reaches the critical limiting saturation value. In a short period, the monomer concentration decreases with the formation of nuclei in the solution.
- c. **Nanocrystals growth:** With the decrease in monomer concentration, the nuclei growth rapidly at the slowest rate-determining step of the growth process. Hence, nucleation and growth occur separately resulting in the formation of monodispersed nanocrystals. Eventually, the growth of nanoparticles occurs at lower temperatures than the nucleation process temperature.^{1,2}

Figure 20: Illustration of LaMer mechanism showing three stages of nanoparticles growth.

2.1.2. THERMAL DECOMPOSITION TECHNIQUE

This technique enables us to synthesise a wide range of monodispersed oxide nanoparticles. It uses desired metal compounds with oxygen-containing ligands such as acetates,³ oleates

(M(oleate)_x),⁴⁻⁶ acetylacetonates (M(acac)_n),^{3,7} dispersed in a surfactant solution. The narrow particle size distribution is the result of the separation of nucleation and growth processes with temperature. By modifying the reaction conditions, metal oxide nanoparticles of varying shapes, sizes and crystal structures can be produced. Remarkably, even bigger particles can be obtained without any seeding taking place in the reaction.¹ **Figure 21** shows the reflux tube setup for the preparation of nanomaterials by thermal decomposition or hot injection method.

Figure 21: Illustration of the reflux tube setup for the preparation of nanomaterials by thermal decomposition or hot injection method.

The following procedure is used to produce ferrite nanoparticles that takes place in two steps:

- a. Formation of Metal oleate complexes:** They are prepared using salts of metal and oleic acid. Dewi et.al.,⁶ used ferric chloride hexahydrate as a precursor of iron. Oleic acid was used as a surfactant where OH bonds of the carboxyl groups in the oleic acid get attached to the metal atoms. This increases the dispersion of precursors during oleate complexes formation. A separate washing process is usually performed to get rid of excess and unreacted ions in the solution.

- b. Effective monomer growth of nanoparticles:** In this step, the oleate complexes are decomposed by heating at refluxing temperature of the solvent. In the case above, 1-octadecene was used as solvent which has a boiling point of 318 °C. It was followed by the washing of particles using a suitable solution of anti-solvents and solvents assisted by high-speed centrifugation to remove excess solvents and ligands from the collected precipitate containing nanoparticles.

2.1.3. ELECTROSPINNING

Electrospinning is an adaptable and an efficient method to fabricate continuous fibres with diameters from submicron to nanometer range with a variety of composition and structures.⁸ The latest advances in electrospinning have led to the production of nanofibres with diameters as small as 50 nm.⁹ The controlled composition of nanofibres aids in achieving a particular functionality. The modification of an electrospinning setup based on a controlled fibre deposition technique can result in the alignment in the nanofibres.^{10,11} Electrospinning is similar to the electrostatic spraying process. They are based on the employment of very high voltages that leads to the formation of liquid jets. An electrified jet in the electrospinning process results in the formation of solid fibres in comparison to the electrospraying process that results in the formation of small droplets or particles. High voltages affect the polymer solution that stretches or melts before getting solidified on the collector.

An electrospinning set-up has three main components:

- a. A syringe attached with a needle of small diameter.
- b. A high voltage supply.
- c. A collector that can either be metal collecting screen (for a fibre mat) or a rotating drum (for aligned fibres).

When a high voltage is applied to a polymer solution, an electrically charged polymer solution/melt is formed. This melt stretches itself before reaching the collector. The solvent evaporates as the fibres fly towards the collector. It solidifies on the collector in the form of nanofibres (**Figure 22**).

Figure 22: Representation of a typical electrospinning setup with a rotating collector drum for aligned nanofibres fabrication.

The principle of electrospinning is based on the electrostatic effect that acts on a viscous liquid. A typical electrospinning setup has a metallic needle extruding a viscous polymer solution that is affected by a high voltage source (typically in the range 10 kV to 30 kV). The applied high voltage causes the droplet extruding from needle to stretch and take an elongated conical shape which is known as a “Taylor cone”.¹² A high enough voltage leads to disturbed surface tension and causes the pointed side of the Taylor cone to stretch like a wire and fly towards the surface of the collector. The collector plate can be exchanged with a rotating drum collector to get aligned nanofibres. Alternate ways to induce alignment is by using a parallel plate collector with the application of an external magnetic field using strong permanent magnets. The electrospinning process can be used to prepare nanofibres of metal oxides¹³, metal¹⁰, graphite & amorphous carbon¹¹, and many other crystalline & inorganic structures¹⁴ and semi-crystalline polymers such as PVDF.

Electrospinning process is simple and cost-effective as the whole setup which consists of a syringe pump, a high voltage source and a collector plate can be bought at cheap prices. It

can be up-scaled for industrial processes and can be applied in the field of electronics, pharmaceuticals, etc.¹⁵

PARAMETERS FOR ELECTROSPINNING

The electrospun fibres' morphology depends on a variety of variables:

- a. Ionic strength and conductivity of solution:** An increase in conductivity of the solution results in fibres with decreased diameters. An increased charge increases the electrostatic force. This results in pulling of thinner nanofibres during the extrusion process. The situation can be controlled by modifying the overall ionic strength of the solution by addition of unreactive salts such as NaCl or KCl or by adding acids such as acetic acid.¹⁶
- b. Viscosity of the precursor solution:** With an increase in the viscosity of the precursor solution, there is an increase in the thickness of nanofibres. It is because surface tension increases with increasing viscosity of the solution. This decreases the electrostatic force created by an external electric field. It results in the production of thicker nanofibres. The solution must be viscous enough for electrospinning otherwise discrete particles with large size distribution are produced like electrospraying. The viscosity of polymer solution can be changed by changing the polymer concentration or by using a higher molecular weight polymer.
- c. Applied voltage:** The strength of an applied electric field has a huge impact on the diameter of the fibres. Studies show that an increase in the repulsive electrostatic forces result in higher voltages acting on the polymer jet when moved towards the collector.¹⁷ It results in the formation of thinner nanofibres while counteracting the repulsive forces.¹⁷
- d. Distance between the needle and collector:** An increase in the distance between the collector and needle gives more time to the repulsive forces in the solution to act against the applied voltage. It favours the formation of thinner nanofibres. However, the distance must be kept to a certain limit, otherwise, the jet can become unstable resulting in back and forth whipping that can even cause the breaking up of fibres. If the distance is very small, the solvent in the polymer solution may not get ample time to evaporate. This can lead to the dissolution of fibres on the collector.¹⁸
- e. Temperature during the spinning process:** It has been reported that with the increase in temperature, the fibres during the extrusion process are thinner. It is because of the decreasing viscosity of polymer solution with increasing temperature.¹⁹ Any fluctuation

in temperature can result in wider size distribution of the fibres during the extrusion process.

2.2. CHARACTERISATION AND ANALYSIS TECHNIQUES

2.2.1. TRANSMISSION ELECTRON MICROSCOPY

Imaging of nanomaterials is vital because it helps us to study their particle size, morphology and crystal structure. In transmission electron microscopy (TEM), an electron beam is transmitted through a very thin layer of the specimen. It is advantageous for the analysis of the internal composition of the sample with a high lateral resolution ($1 \text{ \AA}$). The electron diffraction patterns and high-resolution images showing the lattice fringes of the material provide a lot of information related to the crystal properties of the sample. The imaging of the sample by TEM is shown in **Figure 23**.

Figure 23: Illustration of the imaging of the sample by transmission electron microscopy (TEM)

The sample is analysed in an ultra-high vacuum where a beam of high voltage electrons emitted by a filament is focussed and concentrated on the specimen with the help of condenser, objective and projector lenses. The electrons get elastically scattered after passing through the objective lens. It results in the formation of an image of the specimen which is illuminated on a fluorescent screen. This is detected by the charge-coupled device (CCD) camera. The TEM can magnify up to 800,000 times. The instrument can also be loaded with energy-dispersive X-Ray (EDX) detectors that give spatially resolved information regarding the elemental composition of the material. The bulk, point or line patterns along with the elemental maps provide information related to the elemental composition of the materials.

2.2.2. SCANNING ELECTRON MICROSCOPY (SEM)

The imaging through scanning electron microscopy (SEM) requires an intense beam of high energy electrons. This high energy beam is generated by tungsten present inside an electron gun. This beam passes through the electromagnetic lenses and apertures to give a focused beam. It generates a collection of signals interacting with a solid specimen at its surface. The detectors collect these signals to form images of the sample displayed on a cathode ray tube screen. These signals are composed of secondary electrons, backscattered electrons, diffracted backscattered electrons, photons, visible light and heat. The signals in the form of secondary electrons help us to study the morphology of samples. They display the topography of the material's surface features up to few nanometers across. The backscattered electrons help us to see different phases in any multiphase samples. They display the spatial distribution in the top few microns of the sample. The whole process takes place under vacuum. The electron beam is greatly localised which helps to build a detailed picture of the material. The samples must have a conductive nature. The samples with low or no conductivity are made conductive before loading in the machine by applying a thin layer of conductive coating using sputter coating technique. The imaging of the sample by SEM is shown in **Figure 24**.

Figure 24: Illustration of the imaging of the sample by scanning electron microscopy (SEM)

2.2.3. X-RAY DIFFRACTION

The electronic and magnetic properties of a material rely on the crystal structure and phase of the material. X-ray diffraction is an analytical technique for phase identification and crystallographic information of materials. Its principle is based on the constructive interference of monochromatic X-rays and the specimen sample. The material is bombarded with a continuous beam of X-rays which a cathode ray tube generates (**Figure 25**). The rays are monochromatic and collimated to concentrate on the sample. When the conditions satisfy Bragg's Law, the interaction leads to constructive interference, This is shown by the following equation:

$$2d \sin \theta = n\lambda \quad (\text{eqn. 1})$$

In this equation, n is the integer number, λ is the wavelength of the incident rays, d is the lattice spacing between the planes of the material being studied and θ is the angle at which beam is interacting with the sample. This interaction results in loss of energy in a certain number of photons by the process of elastic scattering, also known as Thompson scattering. The diffracted X-rays are directed, processed and counted at different 2θ angles which are recorded by a goniometer.

Figure 25: Illustration of the physical principle of X-ray diffraction following Bragg's law.

An X-Ray diffractometer is used to study the crystal phases of the material as every crystal has a certain set of diffraction peaks. The pattern is known as a diffractogram. It is consistent with the diffraction angles and relative intensities concerning a certain crystallographic compound. The obtained diffractogram from the studied material can be compared with the diffractogram from the database which are the simulated profiles based on predicted crystal structures. Along with the above information, the XRD can predict the degree of crystallinity of the material based on the inverse correlation between the mean size of the sample's crystal domain and diffraction peak's line broadening. Physical properties of the material such as its size can also be predicted by Debye-Scherrer equation:

$$\tau = \frac{K\lambda}{\beta \cos \theta} \quad (\text{eqn. 2})$$

where τ is the crystalline domain's mean size, K is the shape factor that is a dimensionless quantity whose value is 0.9 typically but can depend on real crystallite shape, λ is the wavelength of the X-rays, θ is the Bragg's angle and β is the full width half maximum (FWHM). The Panalytical X-Ray diffractometer records the X-Ray diffraction patterns using Cu-K α radiation at an operating voltage of 45 kV and a current of 40 mA.

2.2.4. FOURIER TRANSFORM INFRARED SPECTROSCOPY

The nanomaterials require surface modification to be used in a variety of applications. Mostly the nanoparticles are stabilised using ligands with organic molecules. This demands a better understanding of the surface functional groups present on the nanomaterials. FTIR technique can analyse the structure as well as the structural composition of organic molecules using infrared rays. Generally, this technique is used to study electromagnetic radiation absorbed by a sample in the range of around 4000 cm^{-1} to 400 cm^{-1} . The absorption is a result of excitation of vibrational energy states. FTIR looks up the signature vibrational modes of organic compound that are produced by specific functional groups. Consequently, the fingerprint information related to the chemical composition of the material can be obtained.²⁰

Figure 26: Illustration of the working principle of Fourier transform infrared spectroscopy (FTIR) setup.

The infrared radiation is applied to the material of interest. **Figure 26** illustrates the working principle of FTIR. The obtained IR spectra are the graph of the infrared light that is absorbed by the material on the Y-axis and frequency (wavelength) on the X-axis. This signal is interpreted using the mathematical technique known as Fourier transformation. It is a computer-generated process that generates a mapping of the spectral data. This spectrum is checked against reference libraries for detection of compounds.

2.2.5. SQUID MAGNETOMETER

A SQUID (Superconducting Quantum Interference Device) magnetometer is a device that measures moments of magnetic materials at a very small level by utilizing the physical phenomenon of flux quantisation and the DC Josephson effect. It can precisely measure magnetic fields as low as 5×10^{-18} T. The technique is based on superconducting loops containing Josephson junctions as shown in **Figure 27**.

Figure 27: Illustration of the working principle of SQUID with the Josephson junction setup.

In a superconducting state, the magnetic flux gets trapped in a superconducting ring. This flux can be trapped in discrete levels resulting in a magnetic quantisation, also known as flux quantisation. When two of these rings are magnetically coupled and an insulating gap is placed between them, a Josephson junction is formed. A gap thin enough can let the electron tunnel from one superconducting ring to the other by quantum tunnelling effect and no current can flow across the insulator. This effect is known as the DC Josephson effect. It demonstrates the superconductor's long range quantum coherence and it is the only method which allows to directly define the overall magnetic moment of a material specimen in absolute units.

The coupling of the external magnetic field with the SQUID loop results in a voltage change across the Josephson junction. With the changing voltage, we can observe the change in magnetic flux and study the magnetic properties of the material.²¹ The time derivative of the changing magnetic flux is correlated with the voltage across the weak current. It can be used to convert magnetic flux into electrical voltage. It is possible to access temperature as low as 1.9 K and as high as 400 K, and field as high as 5 T with the help of the superconducting magnets. The magnetic measurements are based on temperature-dependent magnetisation with fixed external magnetic field and field-dependent magnetisation at fixed temperatures.

The zero-field cooled (ZFC) and field cooled (FC) measurements help to determine the blocking temperature (T_B) and presence of interparticle interactions. For the ZFC-FC measurements, the samples are first cooled down to a very low temperature (5 K) in the absence of an external magnetic field (B_{ext}). Once the above state has been reached, the B_{ext} is applied on the sample with a constant increase in temperature. This gives the zero-field cooled curve (ZFC). Following this, the sample is then cooled down under the effect of B_{ext} and is followed by a constant increase in temperature to give field cooled curve (FC).

When the material is cooled down without B_{ext} , the magnetic moments freeze in a disordered state. At this instance, the magnetic moment is negligible. Then, with the increase in temperature under B_{ext} , the magnetic moments start aligning in the direction of B_{ext} up to T_B . Above T_B , the thermal fluctuations dominate and results in a loss of magnetisation. The peak of the ZFC curve gives the value of T_B . The width of the peak depends on the particles size distribution in the sample.

In comparison to the cooling of material in the absence of B_{ext} resulting in a disordered state, the FC measurements have ordered magnetic moments along the direction of applied B_{ext} which is then cooled down. The material shows the highest magnetisation at the lowest temperatures. Now, with the increase in temperature under B_{ext} , the magnetisation decreases following the Curie law. The place where the ZFC and FC curve coincides is called the irreversibility temperature, T_{irr} or the bifurcation point. The value of T_{irr} is equal to T_B in the case of isotropic materials. In the case of nanoparticles, if the particles size distribution is wide, the value of T_{irr} depends on the largest particles. By ZFC-FC curve, it is possible to predict the strength of interparticle interactions. The interparticle interaction is indicated by the saturation of magnetisation in the FC curve (**Figure 28**).

Figure 28: The ZFC curves and FC curves for (a) monodispersed nanoparticles having negligible interparticle interactions; (b) monodispersed nanoparticles having intermediate interparticle interactions; (c) wide size distribution nanoparticles with strong interparticle interactions.

2.2.6. IMPEDANCE ANALYSER

Electrical impedance can be defined as the resistance to the flow of an alternating current in a circuit. It is represented as a complex quantity which is graphically plotted on the vector plane as shown in **Figure 29**. The impedance vector has a real part (resistance, R) and an imaginary part (reactance, X). Their relation is represented as $Z = R + jX$ (coordinate form) or $|Z| \angle \theta$ (polar form as magnitude and phase angle). Since there is no ideal inductor (L),

capacitor (C), or resistor (R) in reality, the real-world performance of the devices depends on their signal level and working frequency. Since the current and voltage measurements are phase sensitive with the changing frequency, an impedance analyser measures the complex electrical impedance as a function of frequency. It can be used to find out other important parameters such as capacitance (C), loss tangent ($\tan \delta$), admittance magnitude (Y) and phase (θ) of the sample. By further using the recorded values, important properties of materials such as the relative dielectric constant (ϵ_r) and AC conductivity (σ_{AC}) can be calculated using the following formulas:

$$\epsilon_r = \frac{C.d}{\epsilon_0.A} \quad (\text{eqn. 3})$$

$$\sigma_{AC} = \frac{Y.d.\cos(\theta)}{A} \quad (\text{eqn. 4})$$

Here, d and A represent thickness and area of the sample under observation, respectively, and ϵ_0 is the constant vacuum permittivity with a value of 8.854×10^{-12} F/m. An impedance analyser can be used to characterise materials which are used in electronic components and circuits. It can evaluate the permittivity and loss tangent of the dielectric materials such as plastics, ceramics and printed circuit boards. The permittivity, conductivity and current-voltage (C-V) characterisation of semiconductor materials can also be performed.

Figure 29: The Impedance analyser (Agilent 4294A) along with the followed circuit for impedance measurements of the desired nanomaterials.

The Agilent 4294A impedance analyser available for use at Victoria University of Wellington performs measurements in the impedance range of 3 m Ω to 500 M Ω and frequency range of 40 Hz to 110 MHz with a basic accuracy of $\pm 0.08\%$. A parallel RC circuit was used for all the measurements performed on the dielectric materials.

2.3. ROLE OF LIGANDS IN NANOPARTICLES SYNTHESIS

The colloids with high surface to volume ratio have high surface energies which lead them to aggregate together. Hence, a metastable state can be created around these structures. These states act as free energy barriers and prevent aggregation. Ligands adsorbed on the nanoparticles' surface act as the free barriers and stabilise the nanoparticles by steric hindrance. These ligands serve the following significant roles:

1. Surface passivation of nanoparticles to prevent aggregation.
2. Functionalisation of nanoparticles.
3. Act as an interface between the nanoparticles and the environment imparting physical properties of the nanoparticle core.

The energy with which the ligands get attached to the nanoparticles depends on bond strength of the head group and the NP surface and lateral London dispersion forces acting along the neighbouring chains of ligands. High adsorption energy results in ligands not leaving the nanoparticle's surface, thus preventing nanoparticles' growth. On the contrary, low adsorption energy leads to uncontrolled growth and particles aggregate.²²

The thermal decomposition and hot-injection techniques use ligands such as alkyl phosphine oxides, alkyl phosphonic acids, alkyl phosphines, fatty acids, and amines. The ligands can also impart functionality to the nanoparticle.²³ For example, the ligands that are bound to the surface atoms of the semiconductor can passivate the trap states and strongly affect the luminescence efficiency of semiconductor nanoparticles.

Oleic acid is one of the fatty acids that is used as a ligand. It is found naturally in vegetable fats and oils and classified as monounsaturated omega-9 fatty acid, abbreviated with a lipid number of 18 monounsaturated omega-9 fatty acid. With a molecular weight of 282.46, it is categorised as a non-polymer. The length of a single oleate chain is ~ 2 nm. The carboxyl

group on one side of oleic acid attaches to the ferrous and ferric atoms to form ferrous and ferric oleate as shown in **Figure 30**.

Figure 30: Representation of oleic acid ligands attached to the ferric and ferrous ions by its carboxyl groups.

The metal oleate complexes can be thermally decomposed to form metal oxide nanocrystals. The DFT calculations suggest the attachment of 3 oleic acid ligands to one ferric ion.²⁴ The binding energies of the ligands control the nucleation and growth of the nanoparticles. The binding energies for the two ligands are smaller (7.0 and 10.5 eV) in comparison to the binding energy of the third one which is 39.2 eV. The low binding energies can be attributed to the two symmetric ligands with a weak binding to Fe(III) centre. 2 of the Fe(III) carboxylates formed have low dissociation temperatures around 150 °C and one of the three have a higher dissociation temperature of 230 °C.²⁵ This result in the higher nucleation and growth temperatures during nanoparticles synthesis which gives more control over the size and shape of the particles. The particles can then be dispersed in apolar solvents. The nanoparticles can be purified using an antisolvent. Its addition induces aggregation and the nanoparticles precipitate and separate from the solvent. This process is usually assisted by precipitation. The nanoparticles with tightly bound ligands can be resuspended to obtain pure dispersion of the particles in the solvent.

Figure 31: The BF_4^- from the NOBF_4 molecule attached to the surface of the nanoparticles.

NOBF_4 (**Figure 31**) is used as a compound in ligand exchange strategy. It can be used to strip off the oleic acid ligands in a two-phase system. The addition of NOBF_4 to the apolar colloidal solution of oleic acid coated metal/metal oxide nanoparticles leads to an acidic environment formation as NO^+ ions react to form nitric acid. The excess proton state results in the complete stripping of oleic acid. The particles get transferred to the other phase and get stabilised by the BF_4^- ions.²⁶

Figure 32: CM Dextran structure showing the carboxymethyl group attached to dextran backbone.

Dextran is a glucose-based polysaccharide. It is mainly composed of β (1 $\rightarrow$ 6) glucoside linkages. Its neutrality, water-solubility and biocompatibility make it an optimal material to be used as a ligand over nanoparticles for in-vivo applications. However, dextran when used as a ligand for nanoparticles, for example over iron ferrite nanoparticles, they are held together via non-covalent bonding interactions. This can lead to their dissociation under

specific biological conditions. To prevent this, dextran can be functionalised with suitable functional groups to provide better bonding with the nanoparticles. Carboxymethyl dextran is one such example where the dextran backbone is substituted with carboxymethyl substituents and is a polyanionic (**Figure 32**).

2.4. LITERATURE REVIEW ON THE SYNTHESIS OF MAGNETIC AND FERROELECTRIC MATERIALS FOR ME COMPOSITE FORMATION

2.4.1. COBALT FERRITE AND IRON FERRITE NANOPARTICLES

Cobalt ferrite (CoFe_2O_4) and iron ferrite (Fe_3O_4) have high magnetostriction. Their high surface area to volume ratio at the nanoscale make them a suitable candidate for strain mediated coupling in ME nanocomposites. This section introduces important methods which have been used in the past to synthesise CoFe_2O_4 and Fe_3O_4 nanoparticles. A few allow for a good monodispersity and controlled size & shape in the nanoparticles.

The co-precipitation method is a conventional method to synthesise Fe_3O_4 , $\gamma\text{-Fe}_2\text{O}_3$, and CoFe_2O_4 nanoparticles.^{27–30} This method use chlorides, sulphates, perchlorates or nitrates salts of Co^{2+} , Fe^{2+} and Fe^{3+} . Optimised ionic solutions in basic environments result in the formation of ferrite nanoparticles. The size and shape of nanoparticles are highly dependent on synthesis parameters such as ionic strength of reaction mixture, kind of salts used, pH of the solution and reaction temperature.³¹ However, this method results in nanoparticles with wide particle size distribution which is not advantageous. The particles with varying sizes have different magnetic properties at the nanoscale. For example, mixed size magnetic materials display multiple blocking temperatures (T_B). The saturation magnetisation (M_s) value for cobalt ferrite nanoparticles show the increasing value of M_s with increasing annealing temperatures.³² The shape and size distribution can be controlled by controlling the nucleation and growth rates. Some studies show that short burst of nucleation followed by a slow controlled growth result in monodispersity in the nanoparticles.³³ The yield was found to be pH-dependent.³⁴ An increase in the crystallite size was also observed with the increase in pH and calcination temperature.³⁵ Since the nanomaterials agglomerate because of high surface to volume ratio, a surfactant or a stabiliser is required to act as a protective coating over the synthesised nanoparticles. Organic additive such as polyvinyl alcohol with carboxyl groups (1 wt%) are common stabilising agents in aqueous media. The Fe_3O_4

nanoparticles with bulky aliphatic coatings have displayed good stability of nanoparticles though the particles showed some agglomeration with a wide size distribution.^{36,34} Even though oleic acid was used during the reaction as a coating for the nanoparticles, aggregation was unavoidable by co-precipitation method.

Hydrothermal synthesis is an effective way to crystallise substances from high-temperature aqueous solutions at high vapour pressures. A variety of nanostructured materials can be synthesised using this liquid-solid-solution reaction methodology. It is based on the principle of phase transfer and separation mechanisms which occur at the interphase of solid, liquid and solution phases during the synthesis. Uniform iron ferrite and cobalt ferrite nanoparticles of varying sizes have been synthesised using this method previously.³⁷ A general hydrothermal synthesis takes into consideration a reduction of solid, liquid and solution. The reaction takes place in Teflon coated autoclave of the desired size. Researchers have synthesised monodispersed nanoparticles of Fe_3O_4 ³⁸ and CoFe_2O_4 ³⁹ using this method. The basic scheme of hydrothermal synthesis was indicated by Deng et.al.⁴⁰ wherein monodispersed Fe_3O_4 nanoparticles, the addition of surfactants acted as a ligand electrostatic stabiliser maintaining the steric stabilisation during the reaction.

The thermal decomposition technique has come out to be one of the best approaches to synthesise monodispersed nanoparticles of metal oxides because it gives precise control over the size and shape of the particles. Thermal decomposition of organometallic compounds in high boiling point solvents along with stabilising surfactants can result in monodispersed and single-phase nanocrystals. The most commonly used organometallic precursors are metal oleates, metal acetylacetonates, $[\text{M}(\text{acac})_n]$, ($\text{M}=\text{Fe}, \text{Mn}, \text{Co}, \text{Ni}, \text{Cr}$; $n = 2$ or 3 , $\text{acac} = \text{acetylacetonate}$), metal cupferronates $[\text{M}_x\text{Cup}_x]$ ($\text{M}=\text{metal ion}$; $\text{Cup}=\text{N-nitrosophenylhydroxylamine}$, $\text{C}_6\text{H}_5\text{N}(\text{NO})\text{O}$), or metal carbonyl groups.^{41,42} Octadecene and oleic acid have been used as high boiling point solvents along with surfactant hexadecylamine that act as ligands to stabilise nanoparticles in non-aqueous media.⁴³ Synthesis of nanomaterials of specific size and shape by thermal decomposition technique depend on the ratios of surfactants, reagent precursors, solvent, reaction time and heating rates during the reaction. A zero-valent precursor such as metal carbonyl compound results in metal nanoparticles which can further be converted to oxides.^{41,42} The precursors with cationic metal centres can directly result in the formation of metal oxide structures.⁴⁴ Dumestre et. al.⁴⁵ used $[\text{Fe}\{\text{N}[\text{Si}(\text{CH}_3)_3]_2\}_2]$ as a precursor along with oleic acid to form Fe_3O_4 nanocubes. Park et.al.⁵ used the thermal decomposition technique to perform ultra

large scale synthesis of monodispersed nanocrystals of iron ferrite sized 5-20 nm. A metal oleate complex was specially prepared which acted as the reagent precursor for the reaction. The metal oleate complex can be prepared and stored for further reactions. Ferric chloride and sodium oleate were used to make the iron oleate complex paste. Its decomposition with 1-octadecene and oleic acid as solvents at the refluxing temperature of 320 °C resulted in the formation of iron ferrite nanoparticles. Herrera et.al.⁴⁶ synthesised CoFe_2O_4 nanoparticles with narrow size distribution by thermal decomposition using cobalt-iron oleate complex as the precursor.

Although co-precipitation and hydrothermal synthesis prove to be acceptable methods for nanoparticles synthesis, there are many disadvantages of using them in comparison to thermal decomposition which is as the following:

- a. The reaction time taken by few co-precipitation and hydrothermal synthesis is long ranging from hours to even days while the thermal decomposition method takes few hours to synthesise metal oxide nanoparticles.
- b. The reaction for co-precipitation technique takes place in water which doesn't seem to be the right solvent for the reaction since high temperatures cannot be attained. The thermal decomposition reaction in non-aqueous solutions takes place at high temperatures so we have more control over changing the reaction rates and times.
- c. The particles obtained by co-precipitation techniques are not monodispersed which decrease the overall quality of the as synthesised nanoparticles batch. On the other hand, thermal decomposition technique can result in high quality monodispersed nanoparticles. The hydrothermal synthesis can also result in good quality nanoparticles but the problem with this technique is that the way it works for certain reactions is unknown. Hence, the synthesis procedure cannot be modified much. The addition of ligands before the nanoparticle's synthesis by thermal decomposition and hydrothermal technique gives more control over shape and size of nanoparticles in comparison to co-precipitation technique where in-situ addition of ligands is not that effective.

2.4.2. METAL (II) OXIDES OF COBALT AND IRON

The metal (II) oxide structures have recently been studied and are found to be interesting because of their defect-related magnetic properties. These kinds of structures can be

transformed into different phases using chemical and thermal processes.⁴⁷ The wustite type structure of FeO (where the ratio of Fe to O is 0.84-0.95:1) is a non-stoichiometric iron oxide structure. It is unstable in bulk form and exists only above 560 °C.⁴⁸ Below this temperature, it turns to iron ferrite or zero-valent iron because of the ordering of the iron vacancies. The FeO structure can exist at room temperature only at the nanoscale because of high surface energies. FeO has been used for gas-sensing application, heat absorbing glasses, enamels, pigments and cosmetics, as well as catalysis⁴⁹⁻⁵². FeO has been studied along with Fe₃O₄ in the form of core-shell at the nanoscale level. While there are few reports present on FeO nanoparticles synthesis and characterisation, no literature as per our knowledge was present on Co_xFe_{1-x}O. These findings were further used for the knowledge required to synthesise cobalt iron oxide (Co_xFe_{1-x}O) structure which is supposed to be antiferromagnetic and can potentially have a variety of similar applications to FeO.

Thermal decomposition of metal oleate precursor has been studied to synthesise FeO nanoparticles. Their shape was optimised by controlling the growth rate.⁵³ The iron oleate decomposes via the ketonic decarboxylation reaction which involves the release of reductive gases like CO and H₂. In their presence, the metal precursor is reduced from Fe³⁺ to Fe²⁺ in monomer form which results in small crystallites made of FeO.²⁵ Thermal decomposition of metal oleate seem to be a better way to synthesise metal oxide nanoparticles. The mentioned literature suggested the use of solvents with high boiling points such as octadecene. Oleic acid act as a good stabilising agent due to strong coordinate bonding with the surface of nanoparticles. The optimisation of heating rate during the synthesis has shown to produce shape anisotropy during nanoparticles growth. They were applied for the synthesis of cobalt iron oxide nanoparticles.

2.4.3. ANTIFERROMAGNETIC - FERRIMAGNETIC CORE-SHELL NANOPARTICLES

Ferromagnetic(FM)-antiferromagnetic(AFM) systems display interesting exchange bias properties such as loop shifts and coercivity enhancements.⁵⁴ Not only do these systems combine the characteristic properties of each material, but also result in an additional degree of freedom, thus improving the properties and making them useful for a variety of applications.⁵⁵⁻⁵⁸ These are commonly known as inverted structures where the shell is FM and the core is AFM. A representation of the system is shown in **Figure 33**. These systems

have been studied for metal oxides such as Fe, Co, Cr.^{47,53,59,60} FeO-Fe₃O₄ core-shell structures have been studied to gain a better understanding of the origin of exchange bias (EB) in magnetic nanostructures.⁵⁹ Studies have been performed to learn about the nature of coupling between the spins of antiferromagnetic and ferrimagnetic phases at the interface of the core-shell structure of FeO-Fe₃O₄ nanoparticles. The observed exchange bias in these structures can be applied in present technologies such as spin valves and magnetic tunnel junctions. Lee et al.⁶¹ reported the use of the core-shell nanoparticles in the field of magnetic hyperthermia by tuning the effective anisotropy of the nanoparticles. The exchange bias in these structures can be applied in present electronic technologies such as spin valves and magnetic tunnel junctions.⁶²

Figure 33: Representation of antiferromagnetic- ferrimagnetic core-shell nanoparticles.

Lima et al.⁶³ synthesised CoO core-CoFe₂O₄ shell nanoparticles by thermal decomposition of metal precursors. CoO nanoparticles were synthesised by thermal decomposition process taking place at 260 °C. The shell precursors, Co(acac)₂ and Fe(acac)₃, were introduced after the solution was cooled down to room temperature. The reaction was refluxed again to form CoO-CoFe₂O₄ nanoparticles. However, this method did not result in good quality particles as agglomeration and lack of monodispersity was observed. This could be the result of uneven heating rates by two-step thermal decomposition process. Kavich et al.⁴⁷ synthesised FeO-Fe₃O₄ core-shell nanocrystals by thermal decomposition of Fe-oleate at 320 °C in the presence of oleic acid and solvent ODE. Firstly, the synthesis resulted in FeO nanoparticles which were later converted to FeO-Fe₃O₄ core-shell structure by exposure to air. The author also mentioned that the conversion of FeO phase to Fe₃O₄ phase was the result of chemical instability of FeO that converts it to Fe₃O₄. The particles were monodispersed through this technique. The controlled aerial oxidation of nanoparticles resulted in monodispersity which makes this process better than two-step thermal

decomposition process. Khurshid et al.⁵³ synthesised FeO-Fe₃O₄ core-shell nanoparticles by high-temperature reduction of iron-acetylacetonate. Oleylamine and oleic acid were used to stabilise the nanoparticles. The decomposition of the metal precursor at 300 °C under inert atmosphere resulted in core-shell nanoparticles. The varying ratio of oleic acid to oleylamine resulted in faceted nanoparticles of various shapes (rod-shaped, triangular, hexagonal and cubic). The author mentioned that a controlled oxidation process could tune the oxidation content of MO type nanocrystals to create core-shell structures and this system can be used as a model to study the origin of exchange bias (shifting of field-cooled hysteresis loop).

While there are few reports present on FeO-Fe₃O₄ core-shell nanoparticles synthesis and characterisation, we could not find any literature present on Co_{0.33}Fe_{0.67}O-CoFe₂O₄ core-shell nanoparticles. The reported findings have been used for the knowledge required to synthesise the core-shell cobalt iron oxide nanocrystals.

2.4.4. METAL NANOFIBERS

1-D magnetic nanostructures have been used as a magnetic component of magnetoelectric composites. They have exhibited significantly higher ME coefficients in comparison to values observed in thin films⁶⁴ and bulk structures.^{65,66}

Figure 34: Bimetallic nanofibres fabrication by different electrospinning parameters.

Electrospinning can result in the formation of magnetic nanofibres. They can be formed as polymer nanofibres having nanoparticles embedded inside them. They can be formed by *in-situ* growth of nanoparticles in the nanofibres. They can also be of the form of metal or metal oxide nanofibres. **Figure 34** shows the formation of nanofibres by different ways of electrospinning. Magnetic nanofibres fabrication has been achieved by four different ways which have been discussed in this section.

IN-SITU GROWTH OF NANOPARTICLES IN POLYMER SOLUTION

The formation of in-situ grown nanoparticles in the polymer solution requires the doping with inorganic metallic precursors in an appropriate amount before the electrospinning. This method is very reliable if a certain amount of magnetic nanomaterials doping is required which can simply be modified by increasing or decreasing the concentration of metal precursors. Xiang et al.⁶⁷ synthesised carbon nanofibres with ferromagnetic nanoparticles of iron, cobalt and nickel. Wang et al.⁶⁸ fabricated Fe₃O₄-PVA nanofibres by forming an *in-situ* composite with electrospinning technology. Here the mixed solution of Fe(II), Fe(III) and PVA at a pH of 13 resulted in the formation of Fe₃O₄ nanoparticles which were stabilised by PVA.

ADDITION OF MAGNETIC NANOPARTICLES IN POLYMER SOLUTION

In this method, the polymer solution is doped with already synthesised magnetic nanoparticles before electrospinning. The nanoparticles are synthesised beforehand. This is quite advantageous as there is no polymer present during the nanoparticles synthesis which might have caused hindrance in nanoparticles formation and resulted in polydispersed nanoparticles. Effective synthesis techniques can be applied for nanoparticles formation such as the thermal decomposition technique as discussed earlier. This way we can have particles with size and shapes based on the desired applications of magnetic nanofibres. However, this method requires nanoparticles' compatibility with the polymer solution during electrospinning. To ensure a good dispersity of nanoparticles in the nanofibres, there should not be any kind of phase separation taking place in the polymer solution. This can be overcome by using nanoparticles with suitable ligands.⁶⁹⁻⁷¹ The iron ferrite nanoparticles doped nanofibres which are elastic⁷⁰ and non-toxic.⁷² This scheme has

been discussed in **Chapter 4** in detail where we have fabricated multiferroic 1D nanofibres of PVDF nanocomposites and surface functionalised MNPs.

ADSORPTION OR IN-SITU GROWTH OF NANOPARTICLES IN/ON THE NANOFIBRES

Electrospun nanofibres have found their role in a variety of biological applications such as wound dressing,⁷³ tissue engineering scaffolds,⁷⁴ vascular grafts,⁷⁵ drug delivery.⁷⁶ Lin et al.⁷⁷ fabricated chitosan nanofibre composite for hyperthermia treatment of tumour cells. Two different kinds of methods to introduce nanoparticles in the structure. In the first method, the magnetic nanoparticles prepared by the co-precipitation method were adsorbed on the crosslinked chitosan nanofibres by dipping the fibres directly into the solution containing the nanoparticles for 1 hour under continuous mechanical stirring. The nanoparticles have also been grown on the nanofibres by immersing the crosslinked chitosan nanofibres in $\text{Fe}^{3+}/\text{Fe}^{2+}$ solution for 1 h that resulted to the adsorption of Fe-ions.⁶¹

ALL METAL/METAL OXIDE NANOFIBRES

Metal or metal oxide nanofibres require the addition of metals salts. Metal salts with low molecular masses are chosen to accommodate them in the polymer solution in high concentrations. At high temperatures, polymer decomposes, and metal ions oxidise to form metal oxides as 1-D nanofibres. The nanofibres can further be reduced from metal oxides to metals in the presence of reducing gases. The three requirements for the process are:

- a.** The precursor species should have high solubility in the carrier polymer solution to obtain homogeneity in the product that affects the shape and diameter of nanofibres.
- b.** The carrier polymer should be supportive of the chemical reactions subjected to the precursor. In short, the polymer should be inert to reaction conditions.
- c.** The polymers should be completely removed under reaction conditions.

This approach has been applied extensively to produce ferrimagnetic/ferromagnetic metal/metal oxide nanofibres. Li et al.¹³ fabricated magnetic nickel ferrite nanofibres using the ethylhexanoisopropoxide precursors of nickel and iron in polyvinylpyrrolidone (PVP). Favourable electrospinning conditions were chosen to obtain nanofibres with metal precursors inside polymer carriers followed by the calcination in air at 550 °C. The

nanofibres were composed of agglomerated nanoparticles of sizes around 20 nm. Graeser et al.¹⁰ electrospun anisotropic cobalt and iron nanofibres via electrospinning using the nitrates of cobalt and iron along with polyvinyl butyral (PVB). A rotating drum collector was used to enhance the alignment. The annealing at 550 °C under H₂ reduced the nanofibres to their metal '0' oxidation state along with quantitative degradation of the polymer. The resultant nanofibres showed ferromagnetic behaviour with a high saturation magnetisation (M_s). Han et al.⁷⁸ fabricated pure Fe nanofibres using ferric nitrate as a precursor along with PVP dissolved in a combination of solvents containing ethanol and N,N-dimethylformamide. The two-step process to reduce the nanofibres was employed where the α -Fe₂O₃ phase was first obtained at 550 °C. The next involved the reduction of obtained α -Fe₂O₃ nanofibres at 350 °C which resulted in Fe-nanowires. Barakat et al.⁷⁹ used nickel acetate as a precursor for the formation of pure and smooth nickel nanofibres. The author mentioned the importance of acetate precursors based the gases evolved that could assist in the reduction process to obtain pure metal nanofibres. Later Barakat et al.⁸⁰ prepared bimetallic nanofibres of Co-Ni with uniformly distributed Ni and Co along the nanofibres which showed potential of nickel based soft magnetic materials. The acetates of cobalt and nickel in poly-(vinyl alcohol) PVA/H₂O solution were electrospun at favourable conditions followed by calcination at 800 °C for 5 h under argon atmosphere.

2.4.5. PVDF COMPOSITE STRUCTURES

Dielectric/ferroelectric nanomaterials have a huge scope in the emerging electronic applications.^{81–84} Reducing the size of dielectrics means that there will be more space to incorporate components on the integrated circuits. The alignment of the dipoles is influenced by the size and dimensionality of the material which defines the ferroelectric characteristics of the material. The increased surface area in nanostructures influences the ordering of the dipoles both in the short and long-range. This effect can be seen in phase transition temperatures, dielectric constant, and hysteresis curve of the ferroelectric materials.^{85,86} The depolarisation of the field inside the material can also be observed with the changing surface area as it is directly dependent on the ordering of the dipoles. The electric properties of the materials are directly related to its crystallinity, atomic ordering, surface functionalisation and alignment with the field.

The dielectric/ferroelectric nanomaterials have been fabricated by the top-down as well as bottom-up approach. The solution based routes such as sol-gel, thermal decomposition of solution phase and hydrothermal synthesis have been successfully employed.^{87–90} These approaches can result in fine dielectric nanostructures, i.e. nanoparticles and nanowires. The top-down approach involves cutting down of bulk dielectric materials to form coherent and continuous structures at the nanoscale. Since the semicrystalline PVDF can easily be doped with different crystalline and polymer materials, its dielectric/ferroelectric properties can be improved and modified. The following methods based on the formation of PVDF nanostructures have been discussed.

Liu et al.⁹¹ incorporated surface-hydroxylated $\text{Ba}_{0.6}\text{Sr}_{0.4}\text{TiO}_3$ nanotubes (BST NT-OH) with a high-aspect ratio in the polymer solution of PVDF with varying concentrations from 0 wt% to 10 wt%. The perovskite $\text{Ba}_{0.6}\text{Sr}_{0.4}\text{TiO}_3$ showed high ϵ_r , but it is a heavy metal which is toxic and it also requires high-temperature sintering thus increasing the cost of production. The addition of fillers increased the electroactive β -phase and decreased the α -phase of PVDF. It proves that the addition of filler in the PVDF structure enhances the dielectric properties of the material. Mahadeva et al.⁹² studied the effects of poling time and grid voltage on the dielectric properties and phase transition in PVDF. The piezoelectric coefficient (d_{33}) improved with the poling process and grid voltage. Automated stretching and poling machines resulted in enhanced β -phase content ($85 \pm 7\%$). Higher β -phase results in higher ϵ_r till all the dipole moments have been aligned in one direction.

The flexibility and low-temperature processing of PVDF assist the formation 1-dimensional (1D) nanostructures by the process of electrospinning. The result is increased effective β -phase in the nanofibres along the length. The anisotropy in the polarisation of material under an applied electric field affects the dielectric and ferroelectric properties of materials. The alignment of the nanofibres result in enhanced anisotropy in the direction of dipole moments. Shehata et al.⁹³ demonstrated the process of achieving good alignment at the collector during the electrospinning process to create well-aligned PVDF nanofibres using two magnetic bars setup. The doping in PVDF has shown improvement in the mechanical and dielectric properties.⁹⁴

An detailed study on diisopropylammonium bromide (DIPAB) was reported by Da-Wei Fu and co-workers in 2013.⁹⁵ The 1-F monoclinic crystals of DIPAB were grown by the slow

evaporation of the aqueous solution containing equimolar amounts of diisopropylamine and hydrobromic acid. They portrayed spontaneous polarisation (P_s) of $23.9 \mu\text{C}/\text{cm}^2$. A relative dielectric constant (ϵ_r) value of 85 was recorded at the frequency of 400 Hz at room temperature. A small loss tangent of 0.44 was also observed. The loss tangent quantitatively defines the dissipation of the electrical energy which are caused by physical processes such as electrical conduction, dielectric relaxation, and dielectric resonance.⁹⁶ This makes DIPAB a good choice to be used as a dielectric material. Hence, DIPAB is easy to synthesise and can be considered as a good dielectric filler material.

Sui et al.⁹⁷ prepared DIPAB doped PVDF films with enhanced dielectric properties. A 10 wt% solution of PVDF with different amounts of DIPAB along with silicone coupling agent KH-570 were used to form the composite films. DIPAB doped PVDF samples showed higher dielectric constants and lower dielectric losses. The recorded dielectric constant was 27.2 at low frequencies which was about 3.4 times higher in comparison to the pure PVDF but relatively lower in comparison to BST NT-OH and CNT fillers materials as mentioned before. However, this value was quite low if the results of dielectric losses were compared with the original values at high frequency (1×10^4 Hz). The ferroelectric phase transition of DIPAB around 140°C was observed quite clearly in the temperature-dependent dielectric constant measurements. Above 140°C , a sharp rise in the dielectric loss was observed. Yang et al.⁹⁸ prepared DIPAB-PVDF composite films which showed ϵ_r as high as 94 with 5 wt% doping of DIPAB at low frequencies. This value was 12 times higher than bulk PVDF. *In-situ* growth of DIPAB nanoparticles resulted in strong spontaneous polarisation with improved electroactive β -phase (78 %) in the PVDF thin films. The AC conductivity was observed to increase with the increase in the concentration of DIPAB in the film. The dielectric breakdown strength decreased with increasing DIPAB content while the energy density increases till 5 wt%. doping of DIPAB and then it decreased with further loading. The finding proved that DIPAB is a good filler material for PVDF to improve its dielectric properties.

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CHAPTER 3

MAGNETIC MATERIALS FOR MAGNETOELECTRIC APPLICATIONS: SYNTHESIS, CHARACTERISATION AND ANALYSIS

Herein, we synthesised magnetic nanomaterials suitable for magnetoelectric (ME) applications. The nanoparticles of the cobalt ferrite (CoFe_2O_4) with increasing sizes were synthesised. A detailed investigation on the nanoparticles was performed based on their crystal structure, size distribution and magnetic properties. The studies suggested that the above properties rely a lot on the type of method chosen for the synthesis of nanoparticles.¹ The most important finding during the studies reveals that not only the reaction parameters such as heating rate and reaction time but also the atmosphere in which the reaction is being performed made a big difference to the product. The reaction parameters modification resulted in the formation of a new structure of cobalt iron oxide ($\text{Co}_x\text{Fe}_{1-x}\text{O}$) which was antiferromagnetic. Heating-rate dependent thermally unfavoured states were introduced that resulted in faceted nanocrystals. As per our knowledge, this crystal structure has not been synthesised or studied before. These antiferromagnetic nanoparticles cannot be used directly as a magnetic component for a magnetoelectric composite structure. However, an antiferromagnetic-ferrimagnetic core-shell system of these nanoparticles seems to be an interesting candidate for the above role.² The presence of two different magnetic materials in vicinity result in new and interesting exchange properties such as hysteresis loop shifts and improved coercivity.³ The Fe_3O_4 nanoparticles were also synthesised by thermal decomposition technique to be used as a filler in the ferroelectric material matrix to create a multiferroic material with multifunctional applications.⁴ The formation of multiferroic

material has been discussed later in **Chapter 4**. 1-D nickel-iron ($\text{Ni}_x\text{Fe}_{1-x}$) composites were also fabricated as a potential magnetic component for 1-D magnetoelectric composite formation because of their sharp shape anisotropy. Electrospinning of polymer solutions of respective metal precursors and their calcination at high temperatures led to the formation of ferromagnetic ($\text{Ni}_x\text{Fe}_{1-x}$) nanofibres.

3.1 COBALT FERRITE NANOPARTICLES

During the PhD, cobalt ferrite (CoFe_2O_4) nanoparticles (n.p) were synthesised by thermal decomposition of metal oleate precursors. Initial results proved the formation of polydispersed nanoparticles as shown in **Figure 35 (a, b)**. The synthesis parameters such as heating rate and concentration of precursor and surfactant were optimised that resulted in monodispersed nanoparticles of cobalt ferrite. They are further discussed in detail in this chapter.

Figure 35: TEM micrographs of cobalt ferrite nanoparticles obtained during initial trials for by (a) thermal decomposition of metal oleate; (b) co-precipitation of metal nitrate precursors.

Cobalt ferrite nanoparticles with high monodispersity were obtained by thermal decomposition of iron oleate and cobalt oleate pastes. We synthesised cobalt ferrite nanoparticles sized 8 nm and 12 nm. The smaller 8 nm particles fall in the superparamagnetic limit (size below 10 nm) whereas 12 nm size particles are just above the superparamagnetic limit of cobalt ferrite nanoparticles. The synthesis requires the formation of cobalt and iron oleate pastes in advance to be used as precursors in the thermal decomposition reaction. The growth of particles takes place by effective monomer growth

method.¹ The decomposition of metal oleate via the ketonic decarboxylation reaction can be written as:⁵

3.1.1. SYNTHESIS OF COBALT FERRITE NANOPARTICLES

MATERIALS

Cobalt (II) chloride hexahydrate (ACS reagent, 98%), iron (III) chloride hexahydrate (ACS reagent, 97%), 1-octadecene (ODE, 80-90% technical grade) and oleic acid (Technical Grade) were purchased from Sigma Aldrich. Ethyl alcohol and NaOH (AR grade) were purchased from Chem. Supply.

IRON OLEATE COMPLEX FORMATION

The iron oleate complex was prepared by mixing 12 mmol of NaOH in a solution of 60 mL deionised (DI) water and 33.9 g (120 mmol) of oleic acid at room temperature leading to the formation of sodium oleate solution. The formed solution was further dissolved in a mixture of 10.8 g (40 mmol) iron chloride hexahydrate, 80 mL ethanol, and 140 mL n-hexane which was then heated at 70 °C for 4 h. After the reaction, the upper organic layer was washed three times with distilled water using a separating funnel. The leftover solvents were removed by evaporation using a rotary evaporator. The pure iron oleate was collected and dried overnight. It was later stored in a vacuum desiccator. The product obtained was dark brown.

COBALT OLEATE COMPLEX FORMATION

Cobalt oleate complex was prepared in the same way as the iron oleate complex. The only difference between them was the use of cobalt (II) chloride hexahydrate as a precursor for cobalt. All the concentrations and molar ratios were kept the same as that for iron oleate synthesis for all the experiments. Cobalt oleate had a more viscous texture in comparison to iron oleate complex. It was stored in a vacuum desiccator. The product obtained was dark purple.

CoFe₂O₄ NANOPARTICLES FORMATION

0.8 g (1.28 mmol) cobalt oleate and 1.05 g (1.69 mmol) iron oleate and 0.31 g (1.09 mmol) of oleic acid were dissolved in 15 mL of 1-octadecene. The solution was stirred at room temperature till the oleate paste dissolved in octadecene. The temperature of the solution was further increased to 200 °C resulting in the formation of blackish-brown solution which also confirmed the complete dissolution of oleate precursors. The temperature of the reaction was increased to 320 °C at the rate of 5 °C/min. It was controlled using a specially designed temperature controller built at VUW. On reaching the refluxing temperature of the solvent, growth of nanoparticles further took place for the next 15 minutes and 20 minutes, respectively to obtain nanoparticles with increasing sizes. The reaction yielded a brownish-black solution which was cooled down immediately to stop further growth of nanoparticles. The obtained solution was washed two times using the 1:1:2 mixture of toluene, n-butanol and ethanol, respectively. The washing step was assisted by centrifugation of the mixture solution at 10,000 rpm where the supernatant was disposed and the precipitate was collected. The precipitate was dispersed in hexane. **Figure 36** shows CoFe₂O₄ nanoparticles sized 8 nm & 12 nm dispersed in hexane.

Figure 36: (a) CoFe₂O₄ sized 8 nm and (b) CoFe₂O₄ sized 12 nm showing dispersed in hexane forming a very stable colloidal solution with no observed precipitation.

3.1.2. CHARACTERISATION AND ANALYSIS OF COBALT FERRITE NANOPARTICLES

XRD measurements were performed on the synthesised CoFe_2O_4 nanoparticles of varying sizes. A drop casting technique on the glass substrate was used to prepare the XRD samples. The particles were initially dispersed in hexane and then allowed to dry on the glass substrate. **Figure 37** shows the XRD pattern of the above-mentioned nanoparticles. The XRD pattern of CoFe_2O_4 nanoparticles was compared to the JCPDS reference file for CoFe_2O_4 (reference code – 00-022-1086). The particle size of the nanoparticles was calculated using Scherrer's formula:

$$D = \frac{k\lambda}{\beta \cos\theta} \quad (\text{Eqn. 2})$$

where D is the size of particles, k is the grain shape factor with a value of 0.9 and λ is the wavelength of the X-rays with a value of $1.54056 \text{ \AA}$. Since all the synthesised nanoparticles belong to the cubic crystal system, the lattice parameters a , b and c should be equal and were calculated from their respective characteristic 2θ peaks using the equation:

$$\frac{1}{d^2} = \frac{h^2 + k^2 + l^2}{a^2} \quad (\text{Eqn. 3})$$

Figure 37: X-Ray diffraction patterns for (a) 8 nm sized CoFe_2O_4 n.p; (b) 12 nm sized CoFe_2O_4 nanoparticles

The lattice parameters and particle sizes obtained for the synthesised nanoparticles using XRD analysis are mentioned in the **Table 1**. The Gaussian function was applied to the data to find the respective sizes and lattice parameters.

Table 1: Characteristic properties of 8 nm and 12 nm sized CoFe₂O₄ nanoparticles and obtained by XRD analysis.

S. No	Sample	Space group	Property	Size from XRD (nm)	Lattice parameter(nm)
1.	CoFe ₂ O ₄	Fd-3m	Ferrimagnetic	Diameter = 7.1	a = b = c = 0.84
2.	CoFe ₂ O ₄	Fd-3m	Ferrimagnetic	Diameter = 11.2	a = b = c = 0.84

High-resolution TEM (HR-TEM) micrographs show that the particles formed by each method were monodispersed. The nanoparticles dispersed in hexane were drop cast on a 300-mesh carbon coated formvar copper grid and imaged at 200 kV. **Figure 38** and **Figure 39** show high resolution images of CoFe₂O₄ sized 8 nm and 12 nm, respectively. The nanoparticles showed self-assembly as seen in the TEM images. It proved that the surfactant, oleic acid plays an important role in the growth of magnetic nanoparticles. Oleic acid gets chemisorbed on the surface of nanoparticles via carboxyl groups where it is symmetrically coordinated to the Fe³⁺ and Fe²⁺ atoms on the surface of the nanoparticles.⁶ It creates a steric barrier that prevents the agglomeration of nanoparticles. The dependence of the growth of nanoparticles with reaction refluxing time at high temperatures was evident with the increasing sizes of nanoparticles. The inter-fringe distances as for CoFe₂O₄ nanoparticles sized 8 nm was found to be 0.21 nm that corresponds to (400) plane. A representative selected area electron diffraction (SAED) pattern of the nanoparticles is shown in the inset of **Figure 38 (a)**. The pattern displayed the characteristic diffraction rings that are typical of the cubic spinel structure.

Figure 38: (a) TEM micrograph of monodispersed CoFe_2O_4 nanoparticles sized ~ 8 nm (inset- SAED displaying the characteristic diffraction rings); (b) HR-TEM image of CoFe_2O_4 nanoparticles sized ~ 8 nm and their particle size distribution.

CoFe_2O_4 nanoparticles sized 12 nm had an interfringe distance of 0.246 nm that corresponds to the (222) plane. The inset of **Figure 39 (a)** represents selected area electron diffraction (SAED) pattern of these nanoparticles.

Figure 39: (a) TEM micrograph of monodispersed CoFe_2O_4 nanoparticles sized 12 nm (inset- SAED portraying the characteristic diffraction rings); (b) HR-TEM image of CoFe_2O_4 nanoparticles sized 12 nm and their particle size distribution.

The use of iron oleate complex as a precursor resulted in the delay of the nucleation process as the iron oleate releases the metal ions at high temperatures which was indicated by the colour change of the solution from dark brown to black above 200 °C. This delay further resulted in a smaller amount of nuclei formation during the reaction. These nuclei grew to

form larger particles. Octadecene has a high boiling point of 318 °C. The high temperatures during the synthesis allowed for the rearrangement of the atoms inside the nanocrystals that resulted in the highly crystalline nanoparticles. Oleic acid strongly binds with the surface of the nanoparticles which was confirmed by negligible agglomeration after being washed three times by harsh anti-solvents. The surfactants create a steric barrier avoiding agglomeration and played a very important role during the nanocrystal synthesis owing to its stronger bonding with the surface of the nanocrystals in comparison to other weakly bonded ligands such as amines where partial agglomeration was common.⁷

Figure 40: (a, b) MH curve performed at 5 K and 300 K; (c) ZFC/FC measurements; (d) saturation magnetisation (M_s) as a function of temperature for 8 nm sized nanoparticles.

Magnetic characterisation of the particles was performed at 5 K and 300 K to obtain the isothermal magnetisations curves with the maximum applied field of ± 6 Tesla using the SQUID magnetometer. The spinel structure of the CoFe_2O_4 nanoparticles (2 cation sites, 8 tetrahedral ‘A’-sites and 16 octahedral ‘B’-sites) results in possible interactions. The possible interactions that can take place are A-A & B-B (intrasublattice), B-A & A-B

(intersublattice). The last-mentioned A-B interaction occurs from the near neighbouring interactions. These A-B interactions are the result of the coupling which are mediated by the dominant oxygen ion that leads to super exchange interactions.⁸

The 8 nm sized CoFe_2O_4 had a negligible coercivity (H_c) of 0.391 mT at 300 K (**Figure 40 (a, b)**). The presence of superparamagnetism was confirmed from the fact that they displayed low coercivity (H_c) below the blocking temperature (T_B). However, the shape of the M-H curve strongly depends on temperature and time of measurement. The H_c of the sample at 5 K was 1.28 T. Below the critical size limit, the ferromagnetic or ferrimagnetic nanoparticles show the lowest magnetic energy when all the magnetic moments are parallel. This statement is true when the particle size is equivalent to the thickness of Bloch walls.

The saturation magnetisation (M_s) of the samples were 21.4 emu/g and 25.9 emu/g at 300 K and 5 K, respectively. The effective uniaxial anisotropy in magnetic particles can be attributed to surface effects which result in large magnetic anisotropies. The lower value of M_s of 8 nm sized CoFe_2O_4 nanoparticles in comparison to the M_s value of bulk magnetisation (~90 emu/gm) was attributed to a “nanoscale size effect” according to which the magnetic moments present near the surface of the nanoparticles behave differently from that present in the core of the particles and a much higher spin disorder is present on the surface of the particles.⁹ The surface interactions result in exchange fields distribution as a result of the modification in the coordination bonds and bond breaking. The remanence magnetisation (M_r) of 8 nm sized CoFe_2O_4 nanoparticles were 17.95 emu/g and 0.07 emu/g at 5 K and 300 K, respectively. The remanence ratio of the sample was ~0.68 at 300 K. ZFC and FC curves were obtained for 8 nm sized CoFe_2O_4 nanoparticles. The FC curve was obtained by lowering down the temperature from room temperature to 5 K in an applied field of 10 mT. ZFC/FC curves obtained for 8 nm sized CoFe_2O_4 nanoparticles sample had the T_B at ~310 K (**Figure 40 (c)**). The value of T_B higher than 300K indicates that the particles are superparamagnetic above room temperature. The ZFC magnetisation curves for the sample sized 8 nm show a shoulder at ~110 K. The shoulder was indicative of the presence of high surface spins disorder because of high surface to volume ratio of the nanoparticles.

The temperature dependence of magnetisation decay for 8 nm sized CoFe_2O_4 sample was studied. The sample was cooled down from room temperature to 5 K under the applied

magnetic field of 6T. On the removal of the magnetic field at 5 K, the induced magnetisation in the particles was recorded as a function of temperature. The magnetisation decreased with the increasing temperature and the maximum magnetisation was observed at 5 K. Earlier, during the cooling of the sample, the applied magnetic field resulted in the direction of magnetisation of the nanoparticles along the direction of the applied field. At 5 K, the nanoparticles were magnetised even after the removal of the field. With the warming up of the sample, the nanoparticles tend to overcome the energy barrier by building up thermal activation energy.

Figure 41: (a, b) MH curve performed at 5 K and 300 K and; (c) ZFC/FC measurements for 12 nm sized CoFe_2O_4 nanoparticles.

The saturation magnetisations (M_s) of the 12 nm sized CoFe_2O_4 were 52.03 emu/g and 60.22 emu/g at 300 K and 5 K, respectively. The H_c 12 nm sized nanoparticles 17 mT at 300 K. The coercivity at 5 K was found to be 1.29 T which is comparable to the H_c of 8 nm sized CoFe_2O_4 . This indicated that surface anisotropy didn't cause the origin of the H_c in the sample. However, the H_c can also be the result of surface anisotropy and the effective

anisotropy constant in case large values of coercivities are observed. The presence of ligands on the surface of the particles suppress the surface anisotropy of the nanoparticles and this is true for nanoparticles of varying sizes. The oleic acid ligands that were attached to the surface of the nanoparticles via its carboxyl groups decrease the surface spin disorder resulting in the lowering of surface anisotropy. The ZFC/FC curve for 12 nm sized CoFe_2O_4 nanoparticles (**Figure 41 (c)**) did not portray a defined maximum which suggested an average blocking temperature higher than 300 K. The shoulder obtained for 12 nm sized CoFe_2O_4 nanoparticles at ~ 300 K indicated the Neel temperature value (T_N) corresponding to the small amount of antiferromagnetism in the material. However, the related study requires further extensive studies which are not covered in this thesis.

Figure 42: BH curves obtained at 300 K for 8 nm (green) and 12 nm (red) sized nanoparticles showing a difference in saturation magnetisation and coercivity with the changing size.

The total moment of a superparamagnetic particle above the blocking temperature is random for zero applied field. The thermal average moment increases with the increasing magnetic field and follows the Langevin equation. The magnetic crystalline anisotropy

energy (E_A) for the superparamagnetic particles was explained by Stoner and Wohlfarth by the equation¹⁰:

$$E_A = KV \sin^2 \theta \quad (\text{Eqn. 4})$$

where K is the anisotropy constant, V is the volume of nanoparticles and θ is the angle between the field and the easy axis. The easy axis is defined by the two stable orientations (parallel and antiparallel) that show the preferred direction of magnetisation alignment due to magnetic anisotropy in magnetic nanoparticles. Monocrystalline cobalt ferrite structures show high magnetostriction.^{11,12} An even higher magnetostriction should be observed in single domain structures.¹³ Studies have been performed where ferrimagnetic nanoparticles have been used to fabricate ME composites.¹⁴ An increase in the room temperature M_s with the increase in the particle size of CoFe_2O_4 from 8 nm to 12 nm was observed due to the decreasing surface area to volume ratio as a result of spin canting effects (**Figure 42**).¹⁵ The superparamagnetic nanoparticles have near-zero coercive field. A lower coercive field will support higher switching speeds and cause very low hysteresis loss as the magnetic moment disappears on the removal of external magnetic field when used in a ME composite. The 8 nm sized CoFe_2O_4 nanoparticles below the superparamagnetic limit had a negligible coercivity. The H_c was higher for 12 nm sized nanoparticles with a value of 17 mT in comparison to the lower H_c value of 0.391 mT for 8 nm sized nanoparticles at 300 K. The high surface to volume ratio of the CoFe_2O_4 nanoparticles results in higher induced strain in the magnetoelectric composite. The above studies prove that 8 nm sized CoFe_2O_4 nanoparticles which fall in the superparamagnetic limit that were synthesised by thermal decomposition are suitable candidates for ME composite formation owing to their high monodispersity, negligible coercivity, low magnetic anisotropy and high surface to volume ratio.

3.2. $\text{Co}_{0.33}\text{Fe}_{0.67}\text{O}$ NANOPARTICLES AND RELATED STRUCTURES

$\text{Co}_{0.33}\text{Fe}_{0.67}\text{O}$ nanoparticles with the stoichiometric ratio of 1:1 between the metallic precursors (Co & Fe) and oxygen were fabricated. Similar materials (FeO) have shown an antiferromagnetic state in comparison to the ferrimagnetic states observed in spinel ferrite structures.¹⁶ This structure has not been reported before as per our knowledge. We intend

to synthesise monodispersed nanoparticles of $\text{Co}_{0.33}\text{Fe}_{0.67}\text{O}$ using the same procedure applied for cobalt ferrite nanoparticles with minor changes that result in a different product.

3.2.1. SYNTHESIS OF $\text{Co}_{0.33}\text{Fe}_{0.67}\text{O}$ NANOOCTAPODS

The $\text{Co}_{0.33}\text{Fe}_{0.67}\text{O}$ nanooctapods were synthesised in an organic phase by similar methods using oleates of iron and cobalt as precursors in the same ratios used to synthesise cobalt ferrite nanoparticles without excess oleic acid. A precursor solution was prepared by mixing 0.8 g (1.28 mmol) Co-oleate and 1.05 g (1.69 mmol) Fe-oleate in 15 octadecene (ODE). After stirring for an hour at room temperature, the whole solution was degassed under vacuum at 120 °C for 1 hour as aerial oxidation during the synthesis might lead to the formation of ferrimagnetic CoFe_2O_4 structure. The setup was switched to N_2 atmosphere, the temperature was further increased to 200 °C and maintained at this temperature for another 1 hour. The heating rate to reach the refluxing temperature of the solvent was kept at 6 °C/min. This step takes exactly 20 minutes. Once the reflux temperature of the solvent was reached, the growth of nanoparticles took place for the next 15 minutes. The reaction yielded a brownish-black solution which was cooled down immediately to stop the further growth of nanoparticles. The obtained solution was washed three times using the 1:1:2 mixture of toluene, n-butanol and ethanol, respectively. The washing step was assisted by centrifugation of the mixture solution at 10,000 rpm. The resulting particles showed good dispersion in hexane.

3.2.2. CHARACTERISATION AND ANALYSIS OF $\text{Co}_{0.33}\text{Fe}_{0.67}\text{O}$ NANOOCTAPODS

XRD measurements were performed on the as synthesised $\text{Co}_{0.33}\text{Fe}_{0.67}\text{O}$ nanooctapods in the same way as it was performed on CoFe_2O_4 nanoparticles. **Figure 43** shows the XRD pattern of the above-mentioned nanoparticles. The XRD pattern was compared to the JCPDS reference files of CoO (reference code- 00-048-1719) and FeO (reference code- 01-089-0687) since no reference files were available for the Co-Fe monoxide crystal structure. The reference JCPDS files related to FeO and CoO suggested cubic crystal system for all the above-mentioned nanoparticles. The particle size of the nanoparticles as

calculated using Scherrer's formula was 11.9. The lattice parameter was 0.42 and belonged to Fm-3m space group.

Figure 43: XRD pattern obtained for Co_{0.33}Fe_{0.67}O nanooctapods.

Figure 45 shows the high-resolution TEM images of Co_{0.33}Fe_{0.67}O nanooctapods. The particles had a facet length of 12.6 ± 1.1 nm and an edge length of 21.5 ± 1.1 nm. The presence of facets was a result of thermodynamically unfavorable growth of nanoparticles. The heating rate of 6 °C/min when the temperature was increased from 200 °C to 318 °C resulted in the formation of nanooctapods. To compare, spherical nanoparticles were observed when the heating rate was kept at 6 °C/min (**see Appendix**). The synthesis of spherical nanoparticles of Co_{0.33}Fe_{0.67}O which is the thermodynamically favorable state has been shown in the appendix section and it was formed when the heating rate was kept at 4 °C/min. **Figure 44** shows the illustration growth of spherical and octapod shaped nanoparticles.

Figure 44: Illustration of growth of the nanoparticles by thermal decomposition technique resulting in thermodynamically favourable spherical nanoparticles (top) and thermodynamically unfavourable nanooctapods (bottom).

Figure 45: (a) TEM micrographs of Co_{0.33}Fe_{0.67}O nanooctapods (inset- SAED portraying the characteristic diffraction rings); (b) HR-TEM image of Co_{0.33}Fe_{0.67}O nanooctapods and their particle size distribution.

Dewi et al.¹ suggested that the rate of decomposition of metal oleate precursors govern the rate of crystal growth at different crystal facets. The author also mentioned that the metal concentration was inadequate at lower heating rates, whereas self-nucleation inhibits the growth of non-spherical nanoparticles at higher heating rates.

Degassing the solution at 120 °C and performing the reaction in N₂ atmosphere resulted in the formation of Co_{0.33}Fe_{0.67}O structure instead of a spinel ferrite structure which was observed when the reaction took place in air and resulted in the formation of CoFe₂O₄

nanoparticles. SAED presented in the inset of **Figure 45 (a)** showed the characteristic diffraction rings of $\text{Co}_{0.33}\text{Fe}_{0.67}\text{O}$ nanooctapods. The inter-fringe distances as for $\text{Co}_{0.33}\text{Fe}_{0.67}\text{O}$ nanooctapods was found to be 0.215 nm that corresponds to the (200) plane. A very small fraction of spherical nanoparticles was also observed along with nanooctapods.

The use of oleate complexes as precursors resulted in the delay of the nucleation process as the oleates release the metal ions at high temperatures which is also indicated by the colour change in the solution from dark brown to black above 200 °C.

The elemental mapping at high magnification using TEM setup (Jeol 2100F) with energy dispersive X-Ray spectrometry (EDXS) was performed on $\text{Co}_{0.33}\text{Fe}_{0.67}\text{O}$ nanooctapods. **Figure 46** shows that the elemental signals of cobalt, iron and oxygen confirming the formation of cobalt iron oxide instead of cobalt oxide and iron oxide forming separately.

Figure 46: Elemental analysis of $\text{Co}_{0.33}\text{Fe}_{0.67}\text{O}$ nanooctapods by STEM mapping showing the presence of cobalt iron oxide structure formation instead of iron oxide nanoparticles and cobalt oxide nanoparticles separately.

Figure 47 (a, b) show the MH curve for the $\text{Co}_{0.33}\text{Fe}_{0.67}\text{O}$ nanooctapods. The linearity in hysteresis loop is the characteristic of an antiferromagnetic material. The linearity is quite evident in bulk or microstructures. If the size of the material is reduced to nanoscale, MH

loop attains an “S” like shape where the curvature represents the ferrimagnetic part of the sample. The ferrimagnetic part is result of uncompensated moments on the surface of particles which are disordered surface spins. The antiferromagnetic signals are from the core below the surface of the nanoparticles. Uncompensated spins at the surface should increase with the decreasing particle size because of increased surface to volume ratio. This should increase the net magnetisation and hence the coercive force. The increasing net magnetisation also results in the increased static magnetic interactions among the particles and reduced magnetocrystalline anisotropy in small magnetic nanoparticles.

Figure 47: (a, b) MH curve performed at 5 K and 300 K displaying low saturation magnetisation and confirmation of antiferromagnetic phase; (c) ZFC/FC measurements; and (d) M_s as a function of temperature for $\text{Co}_{0.33}\text{Fe}_{0.67}\text{O}$ nanooctapods.

Magnetic measurements of $\text{Co}_{0.33}\text{Fe}_{0.67}\text{O}$ nanooctapods were performed in the same way as for CoFe_2O_4 particles. An H_c of 0.5 T and a low M_s of 3.35 emu/g was observed at 5 K. The presence of ferrimagnetic material in proximity to an antiferromagnetic material increases Neel temperature (T_N) due to exchange interactions.¹⁷ However, this is true only

for very small nanoparticles and becomes negligible with increasing particle size. The obtained magnetic data also suggested the maximum magnetisation value obtained at 300 K was similar to that obtained at 5 K, i.e. it was not saturated. The ZFC/FC curves do not bifurcate even at high temperatures. The sharp decrease in the magnetisation below T_N in the ZFC curve is the characteristic of an antiferromagnetic material. This statement was supported by the sharp decrease in the magnetisation below $T_N = 220$ K in the ZFC curve (**Figure 47 (c)**). The decrease in magnetisation above 220K in the curve is indicative of the small presence of ferrimagnetic phase with T_B higher than 300K. A flat graph in FC curve below T_N shows low or no interparticle interaction because of the pinning of the spins by the dominating AFM phase.

The temperature dependence of magnetisation for $\text{Co}_{0.33}\text{Fe}_{0.67}\text{O}$ has been shown in **Figure 47 (d)**. The sample was cooled down from room temperature to 5 K under the applied magnetic field of 6 T. On the removal of the field at 5 K, the induced magnetisation in the particles was recorded as a function of temperature ($M(T)$). The $M(T)$ showed an increase in the magnetisation from 5 K till 86 K followed by a decrease in magnetisation to the highest measured temperature (300 K). The presence of a ferrimagnetic layer on the surface of the antiferromagnetic nanoparticles can result in a spin disorder which might explain the shape of obtained curve. The increase in magnetisation till below 87 K might be the result of surface effects from the uncompensated spins.

The AFM-FM structures results in exchange coupling between the two systems. The switching modes under an applied magnetic field are affected by the presence of the antiferromagnetic system. It depends on the interface of the core-shell and hence is dependent on the of size of the antiferromagnetic core and is maximum at the critical. The switching of the applied magnetic field from one direction to the exactly opposite direction results in hysteresis loop formation. In the case of AFM-FM system, during the shifting, the spins in FM at the interface of AFM-FM structure do not shift as the spin are locked or blocked by the AFM s surface spins and hence a higher applied magnetic field is required to switch the directions of the interface spins. The overcome the limits of conventional systems and increased coercivities and loops shifts are observed.¹⁸ The Neel temperature of the AFM phase is effected because of the proximity effect of the FM shell.¹⁹ The blocking temperature of the AFM-FM system can be adjusted by changing the size of the AFM core where the T_B is directly dependent on the size of the AFM part of the AFM-FM

structure.¹⁹ The obtained $\text{Co}_{0.33}\text{Fe}_{0.67}\text{O}$ nanooctapods were subjected to controlled oxidation during their synthesis to attain AFM-FM core-shell structure. These factors make them potential magnetic candidate to be used in the magnetoelectric applications such as magnetoelectric-RAMs.²⁰ The synthesis technique and characterisation of this structure has been discussed in the next section.

3.2.3. SYNTHESIS OF $\text{Co}_{0.33}\text{Fe}_{0.67}\text{O}$ - CoFe_2O_4 CORE-SHELL NANOPARTICLES

The core-shell nanoparticles were prepared by using the same method applied for formation of $\text{Co}_{0.33}\text{Fe}_{0.67}\text{O}$ nanooctapods followed by controlled oxidation of the surface of formed nanoparticles. Once the solution was refluxed and maintained at 318 °C for 15 minutes, it was cooled down to 200 °C. The flow of N_2 in the reaction was exchanged with regular air and maintained for next 10 min. The exposure to air resulted in the oxidation of surface metal atoms of the nanoparticles. The solution was cooled down and washed three times using the 1:1:2 mixture of toluene, n-butanol and ethanol followed by centrifugation at 10000 rpm. The particles were dispersed in hexane.

3.2.4. CHARACTERISATION AND ANALYSIS OF $\text{Co}_{0.33}\text{Fe}_{0.67}\text{O}$ NANOOCAPODS

The XRD measurements were performed on the as synthesised nanoparticles which were drop cast on a glass substrate. **Figure 48** shows the XRD diffraction pattern of the above-mentioned nanoparticles. The obtained XRD pattern of core-shell nanoparticles was compared to the JCPDS reference file for CoFe_2O_4 (reference code- 00-022-1086), CoO (reference code- 00-048-1719), FeO (reference code- 01-089-0687) and XRD of previously obtained $\text{Co}_{0.33}\text{Fe}_{0.67}\text{O}$ nanooctapods. The data suggested the presence of 2 cubic crystal systems obtained, i.e. the antiferromagnetic $\text{Co}_{0.33}\text{Fe}_{0.67}\text{O}$ and ferrimagnetic CoFe_2O_4 . The particle size of the nanoparticles was calculated using Scherrer's formula. The lattice parameter $a=b=c$ was calculated from the characteristic 2θ peaks. The XRD data also suggested a proportion of 31% for $\text{Co}_{0.33}\text{Fe}_{0.67}\text{O}$ core and 69% for CoFe_2O_4 shell by comparing the intensities of the characteristic peaks of both systems.

The lattice parameters and particle sizes obtained for the synthesised nanoparticles by their XRD analysis are mentioned in the **Table 2**.

Figure 48: X-Ray diffraction pattern for the two phase nanostructure formation as confirmed by the presence of respective peaks for CoFe_2O_4 (red) and $\text{Co}_{0.33}\text{Fe}_{0.67}\text{O}$ (blue).

Table 2: Characteristic properties of as synthesised $\text{Co}_{0.33}\text{Fe}_{0.67}\text{O}$ - CoFe_2O_4 nanoparticles obtained by XRD analysis

S. No	Sample	Space group	Property	Size from XRD data	Lattice parameter(nm)
1.	$\text{Co}_{0.33}\text{Fe}_{0.67}\text{O}$	Fm-3m	Antiferromagnetic	11.7 nm	$a = b = c = 0.42$
2.	CoFe_2O_4	Fd-3m	Ferrimagnetic	14.9 nm	$a = b = c = 0.85$

High-resolution TEM (HR-TEM) micrographs show the formation of nanoparticles (**Figure 49**). The nanoparticles dispersed in hexane were drop casted on the 300-mesh carbon coated formvar copper grid and imaged at 200 kV. The obtained particles were not monodispersed. The particles were more cubic than being of an octapods shape which was not expected since we formed nanooctapods by our method for $\text{Co}_{0.33}\text{Fe}_{0.67}\text{O}$ by thermal decomposition. The introduction of air at high temperatures led to the formation of uneven nanoparticles. The nanoparticles were not agglomerated owing to strong bonding of oleic

acid on their surface that created a steric barrier. We expected that TEM micrographs would confirm the formation of core-shell nanoparticles based on contrast difference that is usually observed when two materials with different densities are observed. However, distinct core-shell features were not visible. The obtained nanoparticles require more analysis to prove that core-shell structure was formed. We could not further analyse the nanoparticles due to time constraints.

Figure 49: TEM micrograph of as synthesised surface oxidised $\text{Co}_{0.33}\text{Fe}_{0.67}\text{O}$ nanoparticles (inset- HR-TEM micrographs of nanoparticles and particle size distribution). The particles lacked monodispersity and the core-shell formation was not visible in the micrographs.

Hence, we could not confirm the formation of core-shell structures and their potential use in ME material as more analysis is required. The core and shell of the nanoparticles can be distinguished by studying the variation of oxygen content in the core and shell by EDX spectroscopy as the CoFe_2O_4 shell will have a higher oxygen content in comparison to $\text{Co}_{0.33}\text{Fe}_{0.67}\text{O}$ core which will comparatively have a lower oxygen content. The dark field imaging using HR-TEM would help to confirm the core and shell formation based on difference in the density of the CoFe_2O_4 being less than $\text{Co}_{0.33}\text{Fe}_{0.67}\text{O}$ materials.

To summarise, the studies based on cobalt ferrite proved the synthesis dependent structural transition in cobalt iron oxide system at nanoscale. Thermal decomposition technique proved to be a useful way to synthesise monodispersed nanoparticles with different magnetic properties. The dependence of size, shape, and type of crystal structure on the time, heating rate and atmospheric conditions were studied. The control over these

parameters proved to be a useful way to synthesise magnetic nanomaterials with different magnetic properties. The time dependent growth was evident during CoFe_2O_4 synthesis. 8 nm sized nanoparticles were produced when the solution was kept at the refluxing temperature for 15 min and 12 nm size nanoparticles were produced when the solution was kept at the refluxing temperature for 20 min. The atmospheric conditions of the synthesis procedure have considerable effect on the crystal structure of the formed nanoparticles. This can be proven from the fact that when the thermal decomposition synthesis of cobalt oleate and iron oleate was performed in the presence of air (oxygen) it resulted in CoFe_2O_4 (ferrimagnetic) nanoparticles formation. The performing of the same synthesis in the absence of oxygen resulted in $\text{Co}_{0.33}\text{Fe}_{0.67}\text{O}$ nanoparticles formation. The shape of the crystal structure was affected by the heating rate as the heating rate of $4\text{ }^\circ\text{C/h}$ resulted to the formation of spherical nanoparticles and the heating rate of $6\text{ }^\circ\text{C/h}$ resulted to the formation of nanooctapods. Hence, CoFe_2O_4 nanoparticles sized below the superparamagnetic limit were chosen as potential magnetic candidate for ME nanocomposite formation. Novel $\text{Co}_{0.33}\text{Fe}_{0.67}\text{O}$ nanooctapods showed antiferromagnetism and they were oxidised to form core-shell nanoparticles with tuneable magnetic properties to be used in magnetoelectric composite structures.

3.3. NICKEL-IRON NANOFIBRES

Electrospinning of composite metallic materials has not yet been studied intensively but it opens the door to combine multiple materials to produce new uniaxial nanostructures with improved magnetic, electrical and optical properties.^{21–23}

Ni-Fe alloys have been studied in the form of bulk, thin films and nanoparticles but 1-D Ni-Fe nanostructures have not been studied. We have fabricated $\text{Ni}_{1-x}\text{Fe}_x$ nanofibres which collectively form submicron fibre mat. They were synthesised by an electrospinning process followed by heat treatment and reduction in a H_2 atmosphere. Graesar et al.²⁴ fabricated pure iron nanofibres by annealing the polymeric fibres containing ferric precursors in hydrogen atmosphere at $550\text{ }^\circ\text{C}$. Han et al.²⁵ applied similar technique where the electrospun Fe_2O_3 nanofibres were reduced using H_2 . The 95% Ar : 5% H_2 mixture was chosen instead as H_2 is combustible and the smaller ratio of H_2 with inert gas was a safer option when working at high temperatures.²⁶ The structural and magnetic properties

of the formed nanofibres were studied and found to be nanocrystalline and ferromagnetic. The tube furnace setup as shown in the **Figure 50** was later used to reduce nanofibres to their metal '0' oxidation state.

Figure 50: Tube furnace setup to reduce metal precursors-polymer nanofibres to metal nanofibres. The polymeric fibres are introduced into the furnace via the attached glove box and then sealed. The setup is controlled by specially designed temperature controller.

During the PhD, to fabricate Ni-Fe nanofibres, the chosen initial ratio of Fe to Ni was kept near to 1:1 since they show large permeability and low coercivities for effective magnetic coupling in ME nanocomposites. A variety of metal precursors, polymers, solvents were studied. Different approaches were applied which are discussed in **Table 2**.

Table 3: Electrospinning parameters for the synthesis of intermediate polymer-metal precursor nanofibres for Ni-Fe crystalline nanofibres formation.

S. No	Iron precursor	Nickel precursor	Polymer used	Solvent used (mL)	Infusion rate (mL/h)	Voltage applied (kV)	Needle size	Collector Distance
1	2g $\text{Fe}(\text{NO}_3)_3$	1.5g $\text{Ni}(\text{NO}_3)_2$	1g PVB	8 mL IPA	0.25	25	18 gauge	10 cm
2	2g $\text{Fe}(\text{NO}_3)_3$	1.5g $\text{C}_4\text{H}_6\text{NiO}_4$	0.5g PVP	10 mL MeOH	0.75	17.5	18 gauge	10 cm
3	2g $\text{Fe}(\text{NO}_3)_3$	1.5g $\text{C}_4\text{H}_6\text{NiO}_4$	0.5g PVP	10 mL MeOH	0.6	17.5	18 gauge	10 cm
4	2g $\text{Fe}(\text{NO}_3)_3$	1.5g $\text{C}_4\text{H}_6\text{NiO}_4$	0.5g PVP	10 mL MeOH	0.4	10.5	18 gauge	10 cm

5	2g Fe(NO ₃) ₃	1.5g C ₄ H ₆ NiO ₄	0.5g PVP	10 mL MeOH	0.3	20	21 gauge	10 cm
6	2g Fe(NO ₃) ₃	1.5g C ₄ H ₆ NiO ₄	0.75g PVP	10 mL MeOH	0.3	22.5	21 gauge	9 cm
7	2g Fe(NO ₃) ₃	1.5g C ₄ H ₆ NiO ₄	0.75g PVP	10 mL MeOH	1.5	15	21 gauge	10 cm
8	2g Fe(NO ₃) ₃	1.5g C ₄ H ₆ NiO ₄	0.5g PVP	10 mL MeOH	0.4	17.5	21 gauge	9 cm
9	2g Fe(NO ₃) ₃	1.5g C ₄ H ₆ NiO ₄	0.5g PVP	9 mL IPA, 1mL H ₂ O	0.4	13	21 gauge	10 cm
10	2g Fe(NO ₃) ₃	1.5g C ₄ H ₆ NiO ₄	0.5g PVB	8 mL IPA, 2mL H ₂ O	0.6	17.5	18 gauge	10 cm
11	2g Fe(NO ₃) ₃	1.5g C ₄ H ₆ NiO ₄	1.0g PVB	8 mL IPA, 2mL H ₂ O	0.2	22.5	18 gauge	10 cm
12	2g Fe(NO ₃) ₃	1.75g C ₄ H ₆ NiO ₄	0.5g PVB	8 mL IPA, 2mL H ₂ O	0.5	22.5	18 gauge	10 cm
13	2g C ₁₄ H ₂₇ Fe ₃ O ₁₈	2g C ₄ H ₆ NiO ₄	0.5g PVP	10mL CH ₃ COOH 0.5mL HNO ₃	1.2	20	18 gauge	10 cm
14	2g C ₁₄ H ₂₇ Fe ₃ O ₁₈	2g C ₄ H ₆ NiO ₄	0.5g PVP	10mL CH ₃ COOH	1.0	10	18 gauge	10 cm

3.3.1. NICKEL-IRON FIBRES FABRICATION

MATERIALS

All chemicals that were used in the reaction were of analytical grade. The polyvinylpyrrolidone (PVP, $M_w = 1,300,000$ — polymer for electrospinning), iron(III) nitrate nonahydrate (Fe(NO₃)₃·9H₂O), >98% — the precursor for Fe) and nickel(II) acetate tetrahydrate (C₄H₁₄NiO₈·4H₂O), 98% — the precursor for Ni) were purchased from Sigma-Aldrich. Methanol was obtained from Chem. Supply.

Figure 51: (a) The electrospinning setup used for PVP-metal precursor nanofibers formation; (b) top view of the rotating drum collector; (c) The image on the right is the nanofibers sheet obtained on the collector covered with aluminium foil.

FABRICATION PROCEDURE

Figure 51 shows the electrospinning setup with a rotating drum collector at Victoria University of Wellington. In a typical procedure, 2 g of Fe-nitrate tetrahydrate and 1.5 g of Ni-acetate tetrahydrate were mixed in 10 mL of methanol and 0.5 g polyvinylpyrrolidone (PVP). The whole mixture was magnetically stirred overnight and loaded into the plastic syringe fitted with 21-gauge stainless steel needle. The syringe was loaded on the syringe pump (Harvard Apparatus) and its needle was connected to a high-voltage power supply (Gamma High Voltage Research, Ormand Beach, FL). A rotating drum was chosen as a collector which acted as a counter electrode to collect highly charged fibres and causing the alignment of the fibres. The rotating drum was wrapped with aluminium foil before the fibres collection which is advantageous for post electrospinning treatments of the fibres and it also avoids mechanically induced damage. The solution through the needle was pumped at the rate of 0.65 mL/hour. The voltage for electrospinning was set to 17.5 kV and

the distance between the electrodes was fixed to 10 cm. The sample was transferred into a tube furnace after electrospinning and heated in an argon atmosphere at a rate of 10 °C/min till 300 °C and held there for 1.5 hours. This temperature was lower than the decomposition temperature of PVP (380 °C) but high enough to form metal oxides of nickel-iron. This was followed by increasing the temperature of the furnace at a rate of 10 °C/min to 600 °C in H₂ atmosphere and holding for 3 hours where the sample was reduced to pure metal state. This sample was left to cool down to room temperature in the furnace. The resultant sample was black and brittle. We expected our fibres to undergo the following chemical reactions that resulted in the formation of novel Ni-Fe crystal structures:

3.3.2. CHARACTERISATION AND ANALYSIS OF NICKEL-IRON NANOFIBRES

Figure 52 shows the SEM micrograph of electrospun nanofibres of Fe(NO₃)₃/C₄H₆NiO₄/PVP. The nanofibres had a smooth surface and wavy alignment when the solution was spun at the flow rate of 0.6 mL/h and 17.5 kV. The pre-treated ‘wavy’ nanofibres could be beneficial especially in the case of heat treatment for the formation of metal/metal oxide nanofibres synthesis since the fibres tend to shrink along the length at high temperatures. The waviness along the length should give extra spacing during the shrinkage which results in less breakage in the final nanofibres product. Some fused nanofibres were also observed. The sample morphology of the electrospun fibres dramatically changed after processing at 600 °C in 95% Ar / 5% H₂. **Figure 53 (left)** shows

the SEM micrograph of nanofibres with diameters ranging from ~200 nm to ~250 nm. The apparent coalescence in the nanofibres resulted in large, oriented, submicron fibres with diameters ranging from ~600 nm to ~900 nm. These fibres fused at high temperature to create fibre mat with significant voids (**Figure 53 (right)**).

Figure 52: SEM micrographs of electrospun PVP/ Fe precursor/ Ni precursor composite nanofibres showing a wavy alignment and a smooth surface.

Figure 53: SEM micrographs of $\text{Ni}_{0.47}\text{Fe}_{0.53}$ fibres reduced at 600 °C in 95% Ar / 5% H_2 which coalesced with the polymer removal to formed dense fibre mats.

Small branching nanofibres with dimeters the ~110 nm range were also observed in the structure (**Figure 54**).

Figure 54: SEM micrographs of $\text{Ni}_{0.47}\text{Fe}_{0.53}$ single nanofibres. These comparatively thin nanofibers were observed as branches alongside bigger fibres.

EDX spectra showed the formation of fibres of $\text{Ni}_{1-x}\text{Fe}_x$ type with the value of $x = 0.53$, which was the value expected from the initial precursor ratios. The presence of very low oxygen content in the nanofibres proved that $\text{Ni}_{0.47}\text{Fe}_{0.53}$ was the main product after the reaction. Usually, in the pure metals composites especially containing iron tend to oxidise immediately in the air. This oxidation should happen even faster in nanostructures as they have a higher surface area to volume ratio. Since the fibres show a high metallic structure, there should be a protective coating formed on the surface of these fibres which prevent them from getting oxidised. However, it is difficult to prove this using EDXS. STEM mapping was performed on well isolated nanofibres to avoid background signals. They have been shown in **Figure 55** for two of the smaller fibres. Iron and nickel were uniformly distributed within the fibres. **Table 3** shows the mass% and atom% of iron and nickel obtained from the area analysed as shown in **Figure 55**.

Figure 55: (Top) Elemental maps by SEM of reduced $\text{Ni}_{0.43}\text{Fe}_{0.57}$. (Bottom) Energy dispersive X-Ray spectra for Fe-Ni fibre mat showing the presence of (b) iron and (c) nickel. Low oxygen is indicated by the presence of a small antiferromagnetic metal oxide phase alongside the dominant pure metal phase. The small carbon peak is expected from the background because of adhesive present on the tape used for sticking the fibres on the SEM stub.

Table 4: EDXS elemental analysis of FeNi of fibre mat.

Element	(keV)	Counts	Atom%	Mass%
Fe K	6.398	2771.90	53.36	54.60
Ni K	7.471	9026.85	46.64	45.40

Figure 56 shows the XRD pattern $\text{Ni}_{0.47}\text{Fe}_{0.53}$ fibres. The main phase fits to the FCC of $\text{Ni}_{1-x}\text{Fe}_x$ structure that was expected for $x < 0.6$.²⁷ The lattice parameter value of $a = 0.357$ nm was calculated. The literature suggested this was consistent with $x = 0.53$ value.^{28,29} This value of x was close to where the saturation magnetic moment is highest with the FCC crystal structure seen for $x < 0.6$. The x value was comparable for the EDX and XRD data. A very small and broad peak at $\sim 36.5^\circ$ could be the result of the presence of a small fraction of $\text{Fe}_{1-z}\text{Ni}_z\text{O}$ as NiO and FeO structures show (111) peaks in this region. The presence of NiO and FeO can be attributed to the partially oxidised surface of $\text{Ni}_{0.47}\text{Fe}_{0.53}$ fibres. The main (200) peak was hidden under the Ni-Fe (111) peak (JCPDS

file- 00-047-1405). The broadening of XRD peaks in **Figure 22** could be the result of the formation of small nanocrystals or strain.

Figure 56: X-Ray diffraction pattern of $\text{Ni}_{0.47}\text{Fe}_{0.53}$ fibres reduced at 550 °C in 95% Ar/5% H_2 . The sharp peaks indicate the crystallite formation and the absence of polymer peaks confirmed the full removal of polymer.

The magnetic characterisation of the material was performed using magnetic property measurement system (MPMS) from Quantum Design. The fibre mat was sealed in a gelatine capsule before placing in a straw and then into the MPMS.

Figure 57 shows the magnetic measurements performed on $\text{Ni}_{0.47}\text{Fe}_{0.53}$ fibre mats. We have plotted moment per formula as a function of the applied magnetic field (B). Bohr magneton (μ_B) was used as unit for the magnetic moment, $m_{f.u.}$. The data suggested the presence of ferromagnetic order which was expected based on $\text{Ni}_{0.47}\text{Fe}_{0.53}$ structure. The magnetic moment, ($m_{f.u.,sat}$) was large with a value of 0.91 μ_B at 5 K. Comparing it to the bulk value ($m_{f.u.,sat} = 1.78 \mu_B$) of $\text{Ni}_{1-x}\text{Fe}_x$ where $x = 0.53$, the value obtained for the fibre mats is smaller. The value was comparable to the nanoparticles of size ~ 2.7 nm with $x = 0.47$ for a similar structure phase.³⁰ However, the value was in proportion to the nanoscale materials which have portrayed lower $m_{f.u.,sat}$ than bulk.

Figure 57: (a, b) Moment per formula unit, $m_{f.u.}$, as a function of applied magnetic field at 5 K (blue curve) and 300 K (red curve) displaying the their ferromagnetic phase of the fibre mats as confirmed by high saturation magnetisation. (b) An expanded view is plotted in the upper right inset. (c) ZFC and FC plotted for $m_{f.u.}$ vs. temperature for an applied magnetic field of 10 mT.

The enhancement in coercivity was observed in comparison to the bulk $Ni_{0.47}Fe_{0.53}$. The ZFC curve was plotted at 10 mT and 300 K. It suggested that the nanocrystals sizes were too large to be superparamagnetic. Two main significant features were observed. A peak at ~ 230 K suggested the presence of some antiferromagnetic phase. This temperature is too low to be related with the Neel temperature (T_N) of NiO (525 K). The value is large when compared to the T_N of FeO (198 K). Thus, it may have occurred from a $Fe_{1-z}Ni_zO$ phase observed in the XRD data which has a T_N between 198 K and 525 K. The peak at 40 K should be the result of some spin disorder. However, it was dominated by the magnetisation from the major crystal structure, $Ni_{0.47}Fe_{0.53}$.

The magnetic studies and XRD proved the presence of antiferromagnetic part in the structure. This can be attributed to the partially oxidised surface of the fibres. This also explains why the fibres do not oxidise even when exposed to air. The partial oxidation on the surface acts as a protective coating on the fibres thus retaining their dominant

ferromagnetic phase. Studies have shown that 1D ME core–shell nanocomposites exhibit a stronger ME coupling when compared to the other kind of nanocomposite structures as they have higher interfacial contact area between the constituting phases.^{31,32} Also, the use of ferromagnetic 1-D nanostructures should even have higher magnetostriction in comparison to their ferrimagnetic oxide counterparts.^{33,34} The 1-D multiferroic are advantageous because they show uniaxial anisotropy that enhances the magnetostriction coefficient. The combination of $\text{Ni}_{0.47}\text{Fe}_{0.53}$ along with suitable piezoelectric shell or coating can form 1-D multiferroic composite structures that are suitable for applications such as electromagnetic wave absorbers and zero-power magnetic sensors. $\text{Ni}_{0.47}\text{Fe}_{0.53}$ fibres also find their use in magnetic flux guiding applications as a result of their uniaxial anisotropy. Hence, they can be used as the magnetic component of the charging pads for inductive power transfer for the wireless charging applications. RPEVs can make use of the technology as 1-D structures can direct the magnetic flux directly in the direction of cars receiving pad thus decreasing the inductive losses and increasing the efficiency of wireless charging. With the high surface to volume ratio of the fibre mats, it will reduce the cost as less material will be required. However, the ferromagnetic fibre mats cannot be used directly as they are brittle with low mechanical strength.

To summarise, the ferromagnetic mats containing orientated submicron $\text{Ni}_{0.47}\text{Fe}_{0.53}$ fibres were made by electrospinning of polymer solution containing metal precursors followed by reduction at high temperatures. Magnetic measurements suggested a high ferromagnetic order in the fibres. The saturation magnetic moment per formula was less than that found in the bulk but it was similar to that reported in other studies of nanostructured $\text{Ni}_{1-x}\text{Fe}_x$ with similar x values. Temperature dependence of the saturation moment showed that there was some spin-disorder, probably from a thin layer of $\text{Fe}_{1-z}\text{Ni}_z\text{O}$ layer in the surface region of the fibres, with a characteristic spin-freezing temperature of 38K. The coercivity was enhanced when compared with the bulk, which is probably due to the small nanocrystals that lead to a high density of domain wall pinning centres. The high saturation magnetisation and high surface to volume ratio makes them a suitable candidate for the formation of 1-D ME composite structure. The 1-D shape makes them a suitable candidate for flux guiding applications as well as a suitable magnetic component for wireless charging to direct the flux lines towards the receiving pad in the cars for the IPT project.

SUMMARY OF THE CHAPTER

The chapter discussed the formation of magnetic materials suitable for enhanced magnetoelectric effect in comparison to bulk materials. The thermal decomposition of metal oleate precursors resulted in monodispersed cobalt ferrite nanoparticles. The electrospinning strategy followed by reduction in H₂ atmosphere was applied to form pure metal nickel-iron nanofibres. The materials were characterised to study their crystal structure and shape and phase. The magnetic analysis revealed interesting magnetic properties which showed their potential as a magnetic component of magnetoelectric material at the nanoscale. The following properties make cobalt ferrite and nickel-iron nanostructures suitable for magnetoelectric applications:

- i. Their high surface to volume ratio at nanoscale increases the contact surface area with the respective ferroelectric material which should result in a high magnetoelectric coefficient.
- ii. The corresponding ferrimagnetic/ferromagnetic phase showing a high magnetic moment obtained from both the structures. This results in higher magnetostriction which directly corresponds to a high magnetoelectric effect.

Alongside, novel Co_{0.33}Fe_{0.67}O nanoparticles were also synthesised that were found to be antiferromagnetic. The Co_{0.33}Fe_{0.67}O nanoparticles with oxidised surface would lead to the formation of antiferromagnetic-ferrimagnetic core-shell nanostructure where antiferromagnetic core leads to interesting exchange bias properties such as high coercivity and loops shift. Along with this, adjustable blocking and Neel temperature can also be obtained by optimising the size of the AFM and FM shell. These kinds of core-shell nanostructures can directly be used as magnetoelectric-RAMs.

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CHAPTER 4

FERROELECTRIC COMPOSITES FOR MAGNETOELECTRIC APPLICATIONS: FABRICATION AND DIELECTRIC STUDIES

In this chapter, we fabricated 1-D PVDF composite structures. A detailed discussion on the fabrication, characterisation and dielectric analysis of diisopropylammonium bromide doped Poly-(vinylidene fluoride) (PVDF) has been done. The dielectric constant value of PVDF is quite low which results in its limited use in the field of electronics. The alignment of dipoles along the direction of an applied electric field can be obtained by the electric poling of PVDF. PVDF nanofibres with a varying doping concentration of diisopropylammonium bromide have been fabricated by the process of electrospinning. The investigation on the material includes the analysis of their crystal structure, size distribution, homogeneity and dielectric properties. Electrospinning at low temperatures along with fast solvent evaporation results in β -phase formation in PVDF. A detailed dielectric study on all the nanofibre sample was done based on varying frequencies. **Figure 58** is the representation of a typical electrospinning setup for the formation of nanofibres. The studies on the nanofibres have been presented in detail in **Section 4.1**. The next section includes the addition of previously formed iron ferrite nanoparticles into the DIPAB-PVDF composites. These nanoparticles were synthesised by thermal decomposition technique.

Figure 58: Electrospinning setup for DIPAB doped PVDF nanofibres. The extrusion of the polymer solution from the needle results in nanofibres which are collected on the rotating drum.

4.1. DIPAB DOPED PVDF COMPOSITE NANOFIBRES

So far, there has not been any reports on the fabrication of DIPAB doped PVDF composites in the form of 1D nanostructures. The idea behind fabricating the above is automatic poling of PVDF by high electric field electrospinning (resulting in higher β -phase), which is assisted by very good dielectric properties of DIPAB. It improves the dielectric properties of the overall composite structure. Initially, DIPAB was synthesised and loaded to the PVDF polymer solution. The proven high compatibility of the DIPAB with PVDF based on previous literature made the use of this polymer solution favourable for the dielectric nanofibres.^{1,2} Initial electrospinning of the nanofibres was performed at highest DIPAB doping of 35 wt% where it was difficult to obtain good alignment and monodispersity owing to a very high viscosity of polymer solutions at higher concentrations of DIPAB. The same procedure was followed all the way to fabricate the fibres. The electrospinning parameters were manipulated to obtain good quality aligned nanofibres of DIPAB doped PVDF solution.

Figure 59 shows the SEM images of initially obtained DIPAB doped PVDF nanofibres that were fabricated with high concentrations of DIPAB in PVDF. A high voltage of 18 kV, with the 70 rpm rotating drum speed and the infusion rate of 1.5 mL/h resulted to the following DIPAB doped PVDF nanofibres.

Figure 59: DIPAB doped PVDF nanofibres formation at high DIPAB doping percentages (> 30 wt% DIPAB doping). Beading, polydispersity and no alignment was observed at high concentration of DIPAB.

The beading and the size wise non-homogeneity in the fibres were earlier obtained. The fibres were broken and not continuous. This is not preferable as the broken fibres will lead to conductive pathways during the dielectric measurements and affect the dielectric properties of the fibres negatively. The alignment was also not good as the broken fibres were badly oriented. The simultaneous presence of thicker and thinner fibres will hinder the measurements since the dielectric data will be difficult to associate owing to the wide fibre size distribution. The alignment of the nanofibres was greatly dependent on the distance of the extrusion needle to the collector.

Figure 60: SEM micrographs of DIPAB doped PVDF with improved alignment and less beading by the optimisation of electrospinning parameters.

By decreasing the concentration of DIPAB to 24 wt%, the distance between collector and the needle from 10 cm to 7 cm and lowering down the voltage as per DIPAB doping, the alignment of the formed composite nanofibres was greatly improved. It is shown in **Figure 60**. The final studied DIPAB concentrations were kept at 24 wt%, 10 wt% and 5 wt% and the fibres were spun at varying electrospinning conditions resulting in aligned DIPAB doped PVDF nanofibres. All the details have been discussed in the next section.

4.1.1. FABRICATION OF DIPAB DOPED PVDF NANOFIBRES

MATERIALS

All chemicals that were used in the reaction were of analytical grade. The Poly-(vinylidene difluoride) (HSV 900) in powder form was purchased from MTI chemicals, USA. N-N dimethylformamide (DMF), diisopropylamine and hydrobromic acid (HBr) were purchased from Sigma Aldrich.

SYNTHESIS AND CHARACTERISATION OF DIISOPROPYLAMMONIUM BROMIDE

Figure 61: XRD pattern of crushed DIPAB powder (left) in its α -phase or the 1-F (ferroelectric) phase compared with XRD pattern available in the literature (right) confirming the presence of 1-F ferroelectric phase.³

Diisopropylammonium bromide (DIPAB) crystals were obtained by the slow evaporation of the equimolar solution of diisopropylamine and hydrobromic acid in methanol. The

obtained DIPAB crystals were collected and finely ground using mortar and pestle and stored under inert gas atmosphere since DIPAB is hygroscopic.

The obtained X-Ray pattern was compared to the previous literature (**Figure 61**).³ DIPAB displayed the ferroelectric phase at room temperature belonging to monoclinic crystal system and the polar point group C_2 and P_{21} chiral space group. This is the ferroelectric α -phase. The powder X-ray diffraction showed high crystallinity in the DIPAB sample. The α -phase or the 1-F (ferroelectric) phase of DIPAB was visible through the presence of characteristic 2θ peaks in the XRD at 12.5° , 17.0° , 22.4° , 25.2° and 27.6° . The synthesis can also lead to the 1-P phase which is paraelectric and not ferroelectric. This usually occurs when the synthesis is taking place in the presence of some water during the evaporation of the solvent for DIPAB crystals formation. The paraelectric phase (1-P) can be converted to the ferroelectric phase (1-F) by heating the crystals at 426 K for more than 5 minutes. The DIPAB sample was crushed using mortar and pestle to finely ground the crystals before being used as filler material for PVDF structure.

DIPAB DOPED PVDF NANOFIBRES FORMATION:

The formation of PVDF nanofibres requires the viscous PVDF polymer solution using a suitable solvent. PVDF usually has a limited solubility in organic solvents. PVDF is soluble in polar solvents such as dimethyl sulfoxide (DMSO), N-methylpyrrolidone (NMP), dimethylacetamide (DMAc) and N, N-dimethylformamide (DMF).⁴ DMF has a high boiling point and slow rate of its evaporation. Dry DMF was used as the solvent of choice. The temperature for polymer solution formation was kept at 105°C , which is higher than the critical dissolution temperature (40°C) of PVDF. It was done to ensure the achievement of the thermodynamic equilibrium as the low temperature can form small crystallites as a result of the partial dissolution of polymer.⁵ The use of dry DMF prevents the phase separation in the polymer solution.

A 9.8 wt% homogenous solution of PVDF powder in DMF was obtained by heating the mixture at 105°C for 1.5 hours along with constant stirring. Once a clear solution of PVDF was achieved, different amounts of DIPAB powder were then added to the solution. The DIPAB powder was added after the solution cooled down below 40°C . The mixtures were left to stir at room temperature overnight to ensure complete dissolution of DIPAB. The overnight stirring also led to the leftover air bubbles removal in the solutions.

DIPAB doped PVDF solutions (10 mL) with a doping ratio 0%, 5%, 10% and 24% by weight were prepared. All the solutions were clear with no observed haziness even at 24 wt% concentration of DIPAB. The viscosity of the solution increased with the increase in the concentration of DIPAB. The following doping ratios were considered based on the previous studies performed on DIPAB doped PVDF thin film samples where the highest dielectric constant was observed in samples below 10% DIPAB doping.¹ The sample with highest DIPAB loading (24 wt%) was considered based on the improved orientation in doping samples since above this concentration, the polymer solution became too viscous to electrospin well and it was difficult to maintain the fibres' orientation. Each sample was loaded in a plastic syringe fitted with a metallic needle tip (18G). The needle size was kept the same for all the samples to ensure the optimum and relative size distributions in all the sample based on the amount of DIPAB doping. The syringe containing the solution was then loaded on the top of an automatic syringe pump and was connected to the high voltage power source. The solution was fed to the setup at varying infusion rates and electric fields depending on the DIPAB-PVDF ratio. The fibres were collected on an aluminium foil wrapped on a custom-made rotating drum (diameter – 7 cm). The tip of the needle attached to the syringe was kept at a fixed distance of 7 cm. The 7 cm distance was chosen because it resulted in the formation of a good Taylor cone visually. The distance less than 7 cm might lead to improper removal of solvent which may cause the dissolving of nanofibres on the collector. The rotating drum aided in the alignment of the nanofibres. The electrospinning parameters for all DIPAB-PVDF samples have been listed in **Table 1**.

Table 1: Optimised parameters for the electrospinning of PVDF nanofibres with varying DIPAB content by wt%.

S. No	Sample label	DIPAB in PVDF [wt%]	Infusion rate [mL/h]	Voltage applied [kV]
1.	DIPAB 0%	0 %	1	12
2.	DIPAB 5%	5 %	0.85	13
3.	DIPAB 10%	10 %	0.75	13.5
4.	DIPAB 24%	24 %	0.85	15

4.1.2. CHARACTERISATION AND ANALYSIS OF DIPAB DOPED PVDF NANOFIBRES

The X-Ray diffraction (XRD), Fourier-transform infrared (FTIR) spectroscopy and scanning electron microscopy (SEM) were performed on the sheets of aligned PVDF nanofibres with different DIPAB ratios. The dielectric measurements were performed on the same batch of the samples.

Figure 62: XRD patterns of PVDF nanofibres, DIPAB and DIPAB-PVDF nanofibres showing the dominating β -phase of PVDF in DIPAB-PVDF nanofibres sample. Also, the data confirms the retaining of 1-F phase in DIPAB after nanofibres formation.

X-Ray diffraction (XRD) was performed on a Panalytical X-Ray diffractometer using Cu-K α at an operating voltage of 45 kV and current of 40 mA at room temperature to study the crystal structure of the composite nanofibres. **Figure 62** shows the comparison of X-Ray diffraction (XRD) patterns of the obtained PVDF nanofibres, DIPAB powder, and DIPAB-PVDF nanofibres. The XRD of the PVDF nanofibres showed a strong diffraction peak at 20.3°, which corresponds to the β -phase of PVDF. The presence of α -phase was impacted by electrospinning at high electric fields. It resulted in the poling in PVDF. A significant non-polar α -phase peak at 18.3° and γ -phase peak at 38.3° of PVDF were diminished with the increasing amount of DIPAB in the PVDF nanofibres. A significant peak was observed at 18.3° for the PVDF sample without DIPAB. This further proved that DIPAB aids in the formation of higher β -phase content. The peak of the β -phase shifted

slightly to 20.42° when it was loaded with DIPAB powder. It happened due to the interaction of DIPAB with the PVDF structure. These results also confirmed the DIPAB incorporation into the PVDF matrix. The α -phase or the 1-F (ferroelectric) phase of DIPAB was evident through the presence of characteristic 2θ peaks in the XRD at 12.5° , 17.0° , 22.4° , 25.2° and 27.6° . These peaks corresponded to the monoclinic system of DIPAB crystals. The findings highlighted the good compatibility of the DIPAB crystal structure with the PVDF's semi-crystalline structure.

Figure 63: FTIR spectra of DIPAB-PVDF composite films with varying weight ratios 0-24 wt% showing the formation of the dominating electroactive β -phase in electrospun nanofibres.

The crystalline structure and β -phase of PVDF nanofibres with different concentrations of DIPAB were investigated by FTIR spectroscopy. FTIR spectra were recorded over a range of 500 cm^{-1} to 4000 cm^{-1} to study the presence of ferroelectric phase of PVDF. **Figure 63** shows the spectra for all the nanofibre structures in the concerned range of 650 cm^{-1} to 1000 cm^{-1} . The vibration 840 cm^{-1} (CF_2 asymmetric stretching and CH_2 rocking) represent the electroactive β -phase. The electrospinning of nanofibres result in higher β -phase content when it was performed below 80°C along with uniaxial stretching at high electric fields. This was supported by DIPAB's strong spontaneous polarisation during the nanofibres formation. The intense vibration occurring at 840 cm^{-1} confirmed the presence of a very high concentration of the β -phase. The fraction of β -phase was calculated for all the nanofibres sample using the equation:

$$F(\beta) = \frac{A_{\beta}}{(K_{\beta}/K_{\alpha})A_{\alpha} + A_{\beta}} \quad (\text{eqn. 1})$$

where A_{α} and A_{β} are the corresponding wavenumber values at 762 cm^{-1} and 840 cm^{-1} , and the K_{α} and K_{β} are the absorption coefficients for the α - and β -phases with a value of $6.1 \times 10^4 \text{ cm}^2 \text{ mol}^{-1}$ and $7.7 \times 10^4 \text{ cm}^2 \text{ mol}^{-1}$, respectively.⁶ The high β -phase of $\sim 93.8 \text{ wt\%}$ was observed in all the DIPAB doped PVDF samples.

SEM was performed on a Jeol SEM-6500 microscope to study the incorporation and dispersion of DIPAB crystals inside the PVDF nanofibres. The studies were done on four electrospun samples based on the doping of DIPAB. The SEM samples of the nanofibres were prepared by cutting the square sheets of the samples and sticking them on the SEM stub using copper tape to prevent the carbon background resulting in the carbon signal to be confined to the polymer fibres. All the sample were platinum-coated using the Pt coater to prevent the charging of the sample under high voltages in SEM.

Figure 64 (a) shows the SEM micrographs of nanofibres with pure PVDF in DMF. The alignment was not observed in the pure PVDF nanofibres. Even the adjustments of the electrospinning parameters did not result in the enhancement of alignment in the structure. The size distribution of nanofibres was quite high as well. Overall, the uniformity of the structure was not good as the fibres were broken and even resulted in the formation of sheets instead of the nanofibres. **Figure 64 (b, c, d)** showed that the nanofibres were aligned when 5 wt%, 10 wt% and 24 wt% DIPAB doping was applied. The alignment of DIPAB doped nanofibres was improved in comparison to the pure PVDF nanofibres. Further issues in the alignment were corrected by adjusting the parameters such as the distance between needle and collector, and the applied voltage. As observed during their electrospinning, the most important parameters that resulted in the alignment were distance between the needle & collector, and infusion rate. Usually, the electrospinning is performed at 10 cm distance between needle and collector. We found out that for our system when we decreased the distance to 7 cm, a lot of the improvement in the alignment was seen. Decreasing the distance to 7 cm resulted in improved alignment in the nanofibres (probably due to low whipping). Decreasing the distance further results in improper solvent removal from the fibres. Also, the infusion rate was optimised and found to be a critical parameter to form fibres with uniform diameters.

Figure 64 : SEM micrographs of (a) DIPAB 0%, (b) DIPAB 5%, (c) DIPAB 10% and (d) DIPAB 24% representing alignment in PVDF nanofibre samples doped with DIPAB. The alignment was observed in all the DIPAB doped PVDF nanofibres in comparison to pure PVDF fibres.

The alignment was found to be the best in 5 wt% DIPAB doped PVDF sample. The maximum doping of DIPAB in PVDF before to electrospinning was kept around 24.2 wt% after which it became very difficult to obtain aligned nanofibres. Moreover, the increasing viscosity of nanofibres also resulted in difficulty during the spinning of the nanofibres even at high applied voltages.

The elemental mapping was also performed on the DIPAB doped PVDF nanofibres using the same equipment for SEM imaging (**Figure 65**). The study showed that DIPAB was present at the places where the nanofibres were located on the SEM/EDXS sample and not in the background. The signal of nitrogen and bromine confirmed the presence of DIPAB in the 5 wt% sample. This proves that DIPAB was either inside the fibres where it should ideally be to create a good coupling in the nanocomposite structure, or it could be on the surface of nanofibres which is undesirable as the DIPAB is hygroscopic and can degrade with time.

Figure 65: EDXS of DIPAB 5% composite nanofibres sample. The signals from DIPAB having (b) nitrogen and (d) bromine coincides with (c) fluorine from PVDF confirming the presence of DIPAB within the nanofibres.

High-resolution transmission electron microscopy (HR-TEM) was further performed using a Jeol TEM-2100F instrument to confirm the uniform doping of DIPAB and observe the formation of DIPAB nanocrystals inside the fibres. The composite nanofibres were spun directly on carbon-coated lacey copper grids. It was important to confirm whether DIPAB was incorporated inside the nanofibres as it can have a direct impact on its dielectric properties of the composite. **Figure 66** shows the TEM micrograph of a single DIPAB-PVDF nanofibre containing 5 % DIPAB by weight. To prepare the TEM sample of nanofibres on a carbon-coated copper grid, the grid was stuck directly on the rotating drum collector of the electrospinning setup before the electrospinning process. A few seconds of electrospinning of the solution resulted in the spinning of nanofibres on the TEM grid. There should not be many fibres present on the grid as they are long 1-D materials and can hinder the focussing on single nanofibres for clarity during the TEM. Without any further treatment, the grid was loaded directly into the TEM.

The TEM micrograph shows a single electrospun nanofibre where darker contrast material is DIPAB while lighter contrast is portrayed by semicrystalline PVDF. The contrasts are directly based on the density of the material. Since PVDF has a lower density than DIPAB, it gives a comparatively lower contrast image. DIPAB was equally dispersed inside the nanofibres. The DIPAB nanoparticles formation took place *in-situ* with the

evaporation of the solvent before reaching the rotating drum collector. The size of the DIPAB nanoparticles formed was in the range of ~80-250 nm. DIPAB was found to be equally dispersed inside the nanofibres, which should create a large interface between the two materials.

Figure 66: TEM micrograph of single DIPAB-PVDF (DIPAB 5%) nanofibre on a lacey grid. The DIPAB nanoparticles are incorporated inside the PVDF nanofibers with sizes ranging from ~80-250 nm.

DIELECTRIC AND FERROELECTRIC PROPERTIES

The dielectric properties of the nanofibres were measured using a parallel LCR circuit with Agilent 4294A impedance analyser and Agilent 16451B dielectric test fixture at 500 mV for all the measurements. The impedances of nanofibres were measured in the range of 40 Hz to 1 MHz. Since the nanofibres are 1D structures and the electrospinning process and DIPAB addition resulted in enhanced β -phase along the length of the nanofibres, it was important to perform the frequency-dependent measurements parallel as well as perpendicular to the nanofibres' orientation. This would also prove the enhanced performance of nanofibres in the preferred orientation. The measurements parallel to the nanofibres was performed by the formation of a cylinder of standing nanofibres with a height of less than 1 cm which can fit between the two electrodes of the Agilent 16451B

dielectric test fixture — **Figure 67 (a)**. The cylinder of standing nanofibres was formed by stacking multiple sheets of parallel nanofibres on the top of each other. These sheets were obtained by neatly cutting the big electrospun nanofibres sheet into smaller sheets. The characterisation, as well as the measurements were performed on the same sample. Utmost care was taken that the orientation was preserved in the overall cylinder. The nanofibre sheets were held together and packed carefully from the side using Teflon tape. The diameter of the cylinder of standing nanofibres was bigger than that of the electrode. Therefore, the Teflon tape had no impact during the measurement of the dielectric properties of DIPAB doped PVDF nanofibres. The volume fraction measurements were later performed individually on each sample to provide accurate results. The measurements perpendicular to the nanofibres' orientation were done by placing the nanofibre sheets between the two electrodes of the Agilent 16451B dielectric test fixture — **Figure 67 (b)**. **Figure 67 (c)** shows real nanofibres cylinder and sheet made by the above method.

Figure 67: Schematic for electrical measurements, (a) Cylinder of standing electrospun nanofibres in between dielectric test fixture (Agilent 16451B) electrodes for dielectric measurements parallel to the length, (b) sheet of nanofibres for dielectric measurements perpendicular to the length, and (c) real life sample for dielectric measurements (i) nanofibres cylinder (ii) nanofibres sheet.

Care was taken that the nanofibre cylinders retained their shape and alignment during the measurements. This method was chosen to provide more accuracy in the data by using the same electrodes setup for all the frequency dependent measurements. Since all the samples were spun at different infusion rates, we expected them to have different thicknesses when in sheet form. The height of the cylinders was also carefully measured. Smoothing was performed on the collected dielectric data to reduce the noise. The observed noise might have been caused by the improper contact of electrodes with some nanofibres during the measurements. The thicknesses and heights of the film samples and cylinder samples respectively have been presented in **Table 2**.

Table 2: Representation of the thickness (d) in mm for DIPAB-PVDF nanofibres samples for dielectric measurements.

S. No	Sample name	Thickness (d) (mm)
1.	DIPAB 5% film	0.17
2.	DIPAB 10% film	0.12
3.	DIPAB 24% film	0.20
4.	DIPAB 5% cylinder	1.30
5.	DIPAB 10% cylinder	1.22
6.	DIPAB 24% cylinder	6.30

The capacitance (C), loss tangent ($\tan \delta$), admittance magnitude (Y) and phase (θ) of the samples were measured to calculate the relative dielectric constant (ϵ_r) and the AC conductivity (σ_{AC}) using the following equations:

$$\epsilon_r = C \cdot d / (\epsilon_0 \cdot A) \quad (\text{eqn. 2})$$

$$\sigma_{AC} = Y \cdot d \cdot \cos(\theta) / A \quad (\text{eqn. 3})$$

Here, d and A represent the thickness and area of the samples, respectively, and ϵ_0 is the constant vacuum permittivity with a value of 8.854×10^{-12} F/m. The dielectric values were calculated based on the volume fraction of electrospun nanofibres as the nanofibre sheets had voids in them. **Equation 11** was used to calculate the volume fraction of nanofibres

during the measurements and the actual relative dielectric constant was measured using **Equation 12**. These equations were derived using **Equations 2 – 10**. Here, m_f , m_p and m_d are the masses and V_f , V_p and V_d are the volumes of electrospun nanofibres, PVDF and DIPAB, respectively. V_s is the overall volume of the samples. ϵ_{rc} is the corrected relative dielectric constant of the sample.

$$m_f = m_p + m_d \quad (\text{eqn. 4})$$

$$m_p = x(m_s) \quad (\text{eqn. 5})$$

$$m_d = 1 - x(m_s) \quad (\text{eqn. 6})$$

$$V_p = \frac{m_p}{\rho_p} \quad (\text{eqn. 7})$$

$$V_d = \frac{m_d}{\rho_d} \quad (\text{eqn. 8})$$

$$V_f = V_p + V_d \quad (\text{eqn. 9})$$

$$V_s = \pi r_s^2 d \quad (\text{eqn. 10})$$

$$Vol. fraction = \frac{V_p + V_d}{\pi r_s^2 d} \quad (\text{eqn. 11})$$

$$\epsilon_{rc} = C \cdot \frac{d}{\epsilon_0 A_f} = C \cdot \frac{d^2}{\epsilon_0 (V_p + V_d)} \quad (\text{eqn. 12})$$

The frequency dependent properties of pure PVDF and DIPAB doped PVDF nanofibres with varying DIPAB content ratio at room temperature were measured in the range of 40 Hz to 1 MHz. DIPAB doped PVDF nanofibres showed an enhanced dielectric constant in comparison to the previously reported dielectric constants for pure PVDF nanofibres which were in the range of 11 to 18 at low frequencies.⁷⁻⁹ The data showed a decrease in dielectric constant with increasing frequency in all of the nanofibre samples due to the decreasing effective number of dipoles^{10,11} (**Figure 68**). The dipoles' oscillations at lower frequencies are synchronised with the alternating field, while at higher frequencies they are not able to match the speed of the alternating (AC) field. This resulted in a reduction in the effective number of dipoles. The DIPAB nanocrystals dispersion inside the PVDF nanofibres resulted in a large interfacial area between the two materials. Due to the large difference in the electrical conductivities of PVDF and DIPAB, the charges can migrate and accumulate

at the interface of materials on the application of the electric field. This resulted in interfacial polarisation, and hence a relatively high dielectric constant.¹² With the increasing DIPAB content, the inter-particle distance decreased and the interfacial area per unit mass increased.¹³ This resulted in the improvement of the average polarisation associated with the coupling between neighbouring grains leading to a significantly higher dielectric enhancement of the composite nanofibres. The interfacial polarisation works smoothly at lower frequencies as the charges have enough time to move. At higher frequencies, the mismatch between frequency and charge carrier movements result in a decrease in dielectric constant.¹⁴ The dielectric constant was also affected positively when DIPAB was added to PVDF, because of the highly ionic nature of the DIPAB crystals, which contributed to the dielectric constant by ionic polarisation.

Figure 68: Frequency dependent dielectric constant of aligned DIPAB doped PVDF nanofibres along the length displaying an improvement in the dielectric constant.

The two-way relative dielectric constant measurements (parallel (**Figure 68**) as well as perpendicular (**Figure 70**) to the nanofibres) were undertaken to prove the alignment of dipoles along the direction of the nanofibres. During the electrospinning process, the PVDF nanofibres were spun under a very high applied voltage (ranging from 10 kV to 17.5 kV). This resulted in the poling in PVDF structure where the alignment of the dipoles is along the direction of spinning of nanofibres that cause an increase in the effective dipole moment in these structures. This phenomenon is known as orientation polarisation. It can be seen from **Figure 68** that the addition of DIPAB to the PVDF has resulted in very well aligned nanofibres, which increased effective dipole moments, and hence higher relative dielectric constants. **Figure 69** illustrates the aligned dipoles of PVDF and interfacial polarisation due to DIPAB nanoparticles interface with PVDF. With the dipoles aligned, enhancement in the piezoelectric response of the ferroelectric nanofibers is enhanced which directly depends on the degree of alignment.^{15,16} and hence, making them highly desirable for ME applications.

Figure 69: Illustration of orientation polarisation (right) and interfacial polarisation (left) taking place in the DIPAB doped PVDF nanofibres in an applied electric field.

The maximum dielectric constant recorded was ~102 in 5 wt% DIPAB doped PVDF (DIPAB 5%) nanofibre samples when the measurements were performed parallel to the

nanofibres (Figure 11). To the best of our knowledge, this was by far the highest value ever recorded for this type of composite material. As discussed previously, Yang et al.² achieved a maximum dielectric constant of 94 at 40 Hz with similar nanocomposites in the form of thin films. The interfacial polarisation is the result of the migrated charge carriers that accumulate at the interface of DIPAB and PVDF because of a large difference in the conductivities. It results in a large polarisation and in turn a relatively high dielectric constant. But the frequency mismatch at high AC electric fields limit the charge carrier moments. At low concentrations of DIPAB, its crystal particles are separated from each other. With the increasing DIPAB concentration, the interfacial area per unit mass increase that in turn positively affects the dielectric constant value. As mentioned earlier, the 5 wt% DIPAB doped PVDF sample showed the highest ϵ_r value above which interfacial area per unit mass might decrease because of the agglomeration of DIPAB nanocrystals,

Figure 70: Frequency dependent dielectric constant of aligned DIPAB doped PVDF nanofibres perpendicular to the length displaying a lower dielectric constant when compared with the measurements performed parallel to the nanofibres.

The dielectric values when measured perpendicular to the nanofibres were much lower (~19 at 40 Hz) for the 5 wt% DIPAB sample (**Figure 70**). This proved that most of the dipoles present in the nanofibres were contributing to the dielectric behaviour of nanofibres in the direction along the length of the nanofibres showing the effect of orientation

polarisation. The values are lower in all samples when measured perpendicular to nanofibres and they followed the trend like other nanofibres with increasing frequency. The dielectric constant of DIPAB 5 % sample was observed to be the highest at low frequencies as a result of the formation of DIPAB nanoparticles that are equally dispersed in the nanofibres.

Figure 70 showed that the dielectric constant of the higher DIPAB doped samples (e.g. DIPAB 24%) was lower than DIPAB 5% sample. This can be attributed to the formation of larger DIPAB particles at higher doping. The increased DIPAB particle size resulted in decreased surface area to volume ratio and hence decreased surface area between the two materials. The decreased surface area resulted in a lower interfacial polarisation as it was directly dependent on the interface area. The dielectric constant should increase with the increasing DIPAB concentration since DIPAB has relatively higher ϵ_r but the decreasing trend of ϵ_r proved that the ionic polarisation was dominated by the interfacial polarisation. This proved the domination of interfacial polarisation at low frequencies. The ionic polarisation exceeded the interfacial polarisation at high DIPAB concentration as the interfacial area decreased with the increasing size of DIPAB particles inside PVDF nanofibres. The dielectric measurements performed parallel to the nanofibres further proved the point that interfacial polarisation played a huge role in enhancing the dielectric properties. The ionic and interfacial polarisation can usually be attributed to the distinguishable dielectric loss factor peaks. However, the complex network of DIPAB-PVDF in this work cannot be represented by a simple model and the specific dielectric loss factor peaks associated with different polarisations could not be plotted. The individual fibres and the conjunction between the fibres corresponded to multiple peaks where individual peaks were indistinguishable from each other. Overall, the dielectric constant was most affected by the orientation of dipoles followed by the interfacial polarisation as a result of charge trapping followed by the ionic polarisation.

The loss tangent vs frequency values have been shown in **Figure 71**. The loss tangent value decreased with the increasing frequency as expected due to the Maxwell-Wagner-Sillars effect.² This effect describes apparent dielectric loss in an inhomogeneous media.¹⁷ The Maxwell-Wagner-Sillars effect takes place at the inner dielectric boundary layers of two materials which, in our case, are the interfaces of DIPAB and PVDF. This leads to the separation of charges, and usually, these charges are separated at a considerable distance that results in higher dielectric losses. The DIPAB 5% sample had a loss tangent of 0.3 at

40 Hz parallel to the nanofibres. The highest loss tangent of 0.55 was shown by the 10% DIPAB sample at low frequency. The loss tangent for all the samples measured perpendicular to the nanofibres' orientation was very low (< 0.1). The loss tangent tends to increase at higher frequencies, which was caused by conductance.

Figure 71: Frequency dependent loss tangent of aligned DIPAB doped PVDF nanofibres parallel to the length (**solid line**) and perpendicular to the length (**dashed line**). The loss tangent increases at higher frequencies.

The alternating current (AC) conductivity increased with increasing frequency as shown in **Figure 72**. It was found to be highest in the 10% DIPAB sample with a value of $1.1 \text{ e}^{-9} \text{ S/cm}$ at 40 Hz. The DIPAB 5% sample had a low AC conductivity of $0.43 \text{ e}^{-9} \text{ S/cm}$ at 40 Hz.

Figure 73 shows the comparison of relative dielectric constants of all the fibres parallel and perpendicular to the nanofibres for varying DIPAB doping in the nanofibres at 40 Hz. The DIPAB 5% sample had the highest relative dielectric constant. The value of ϵ_r decreased gradually with an increasing amount of DIPAB doping. The values of ϵ_r , when measured perpendicular to the nanofibres, were very low for the same fibres because of a very low number of effective dipoles. This proves that the orientation polarisation and presence of DIPAB play a significant role in the enhancement of the dielectric properties of the material.

Figure 72: Frequency dependent AC conductivity of DIPAB-PVDF nanofibres that increases with the increasing frequency of operation.

Figure 73: DIPAB content dependence of dielectric constant in DIPAB-PVDF nanofibres. The difference in the dielectric constant (high value) when measured parallel to the nanofibres in comparison to dielectric constant (lower value) when measured perpendicular

to the nanofibers indicated the domination of orientation polarisation from PVDF structure along the length.

The use of DIPAB-PVDF nanocomposites with low dielectric constants can be used as isolators for signal carrying conductors. They should also be suitable for use as interlayer material to decrease the resistance-capacitance time delays, crosstalk and power dissipation. The flexibility makes them an optimal material for packaging and encapsulation of multilayer integrated circuits where they provide isolated pathways for the electronic connections.¹⁸ With the optimisation of microprocessors, the materials with controlled dielectric constants reduce adverse effects of stray and coupling capacitances. Also, the above properties make them suitable to be used as capacitors, piezoelectric transducers and dielectric amplifiers. The electronics setup requirement of higher shelf life, high breakdown strength, inertness and low remanence properties from the dielectric materials are fulfilled by DIPAB-PVDF composites.

To conclude, DIPAB, which is a highly ferroelectric compound was successfully dispersed in PVDF nanofibres. The electrospinning and addition of DIPAB helped to obtain dominant β -phase, improved alignment and crystallinity in the fibres in comparison to the thin-film samples. The dielectric properties were significantly improved and by far the highest relative dielectric constant was observed in this composite material. Incorporating DIPAB in PVDF is an effective way to produce anisotropic and highly dielectric nanofibres that may be ideal candidates for 1-D magnetoelectric applications because of their uniaxial dielectric properties and ease of fabrication. The flexibility, semicrystalline nature and room temperature fabrication of DIPAB doped PVDF polymer are the optimal choice to be used alongside crystalline magnetic structures to form ME composites with high interfacial contact area resulting in high magnetoelectric coefficients.

4.2. MULTIFERROIC COMPOSITES FORMATION

During PhD, synthesis techniques were applied to synthesise monodispersed BaTiO₃-CoFe₂O₄ core-shell nanoparticles. BaTiO₃ was synthesised using hydrothermal method, thermal decomposition of organometallic precursors and calcination of barium & titanium precursors at high temperatures. They have been discussed briefly.

0.51g of titanium butoxide (precursor for Ti^{4+}), 7.5 mL of oleic acid and 0.3g of sodium oleate were added to 52.5 mL ethanol to form Solution A. Another solution (Solution B) was prepared by dissolving 0.383 g barium acetate in 15 mL water. Solution B acted as a precursor for barium. Further, a solution C was prepared which was a sodium hydroxide solution. Solution B and C were successively added to sol A and were further stirred for 15 minutes. It resulted in a white translucent solution which was loaded in a 50 mL Teflon lined hydrothermal bomb. The hydrothermal bomb was sealed and placed in a muffle furnace with a ramp rate of 2 °C/h till the temperature rose to 160 °C. The solution was then kept at this temperature further for 8 hours and then cooled down to room temperature at the same ramp rate. The obtained solution was washed twice with ethanol followed by centrifugation at 10k rpm. It resulted in a white precipitate which was dispersed in hexane. Following optimisation, we were able to synthesise cubic barium titanate nanoparticles as shown in **Figure 74**.

Figure 74: Synthesis of barium titanate nanocubes by hydrothermal synthesis. Improvement in dispersity was observed (right) by optimising the heating rates during the synthesis.

Before the nucleation and growth process, while synthesising cobalt ferrite nanoparticles by thermal decomposition of cobalt oleate and iron oleate, the obtained BaTiO_3 nanocubes were added to the solution to see whether the growth of nanocrystal can take place over BaTiO_3 nanocubes. However, the synthesis resulted in the growth of CoFe_2O_4 nanoparticles separately and not on BaTiO_3 nanocubes (**Figure 75**). This happened probably due to phase mismatch between BaTiO_3 and CoFe_2O_4 crystals. The lattice parameter of barium titanate was 0.39 nm in comparison to the observed lattice parameter of 0.84 for CoFe_2O_4 nanoparticles.

Figure 75: Small CoFe_2O_4 nanoparticles formation alongside pre-synthesised BaTiO_3 nanocubes.

New barium precursors for barium titanate formation by thermal decomposition were synthesised in collaboration with Martyn Coles group. The synthesis of the BaTiO_3 could allow for the one-step core-shell growth. Anhydrous Barium iodide (BaI_2), potassium bis(trimethylsilyl)amide, oleylamine, 1-octadecene, oleic acid and tetrahydrofuran were used to synthesise the suitable barium precursor $[\text{Ba}\{\text{N}(\text{SiMe}_3)_2\}_2(\text{THF})_{1.6}]$.¹⁹ This structure tends to decompose at lower temperatures ($\sim 100^\circ\text{C}$) and release Ba^{2+} ion which can react with the Ti^{4+} precursor to form barium titanium oxide. To summarise, the idea was to synthesise BaTiO_3 and CoFe_2O_4 nanoparticles in the same solution by thermal decomposition technique. This process should be beneficial in comparison to the hydrothermal method where the nanoparticles must be transferred from one setup to others. The whole procedure was performed in the N_2 filled glove box. Barium iodide (BaI_2 , 2.77 mmol) and potassium bis(trimethylsilyl)amide ($\text{KN}(\text{SiMe}_3)_2$, 5.53 mmol) were added to 30 mL solution of tetrahydrofuran. It was then stirred for 3.5 days at 20°C . A white precipitate was observed when the stirring was stopped. Then, THF was removed under vacuum. The leftover white solid was triturated two times with 20 mL of hexane. The white solid was then extracted with 30 mL of hexane two times followed by filtration through a self-made zeolite filter. The obtained filtrate was then concentrated under vacuum giving around 0.99 g of $[\text{BaN}(\text{SiMe}_3)_2\}_2(\text{THF})_{1.6}]$. 0.135 g of the formed $[\text{BaN}(\text{SiMe}_3)_2\}_2(\text{THF})_{1.6}]$ was taken out from the glove box and dissolved in 5 mL ODE under N_2 atm. An equimolar amount of titanium isopropoxide was added to the above solution. It was further stirred for 1 hour to form solution 'A'. Solution 'A' was hot injected to the mixture of 2 mL oleylamine and 12.5 mL octadecene (Solution B) at 250°C and then the reaction was maintained at 230°C for 1 h 10 min. Solution B was degassed at 100°C

for 1 h before the hot injection. The nanoparticles were obtained by washing with the mixture of ethanol and butanol two times followed by centrifugation at 10,000 rpm. The precipitate was dispersed in hexane.

Figure 76: TEM micrographs of Barium Titanium Oxide nanoparticles formed by thermal decomposition of $[\text{BaN}(\text{SiMe}_3)_2]_2(\text{THF})_{1.6}$ and titanium oxide.

Figure 76 shows the TEM micrograph of the formed barium titanium oxide nanocrystals. However, they were not easily reproducible and the high air-sensitivity of the precursors made it difficult to continue the following method to prepare magnetoelectric core-shell nanoparticles.

The use of ferroelectric polymers along with ferro/ferrimagnetic nanomaterials where the polymer encapsulates the nanomaterials fully would induce a ME effect.^{20,21} Care has to be taken that a contact is maintained between the magnetic filler and the ferroelectric matrix. To achieve this, the surface of magnetic metal oxide nanoparticles is usually functionalised to allow for better contact with the other material. This has been discussed in the following section where the combination of iron ferrite nanoparticles with DIPAB doped PVDF structures led to the formation of a multiferroic composite structure.

4.2.1. FABRICATION DIPAB-PVDF- Fe_3O_4 (DPM) THIN FILMS

MATERIALS

All chemicals that were used in the reaction were of analytical grade. Cobalt (II) chloride hexahydrate (ACS reagent, 98%), iron (III) chloride hexahydrate (ACS reagent, 97%), 1-octadecene (ODE, 80-90% technical grade), oleic acid (Technical Grade), N-N dimethylformamide (DMF), diisopropylamine and hydrobromic acid (HBr) were

purchased from Sigma Aldrich. Ethyl alcohol and NaOH (AR grade) were purchased from Chem. Supply. Poly-(vinylidene difluoride) (HSV 900) in powder form was purchased from MTI chemicals, USA.

SYNTHESIS OF Fe₃O₄ NANOPARTICLES

The Fe₃O₄ nanoparticles as synthesised in **Section: Side project (ii)** of the **APPENDIX** were used as the magnetic component for the fabrication of multiferroic thin films and nanofibres. The oleic acid coated Fe₃O₄ nanoparticles were ligand exchanged with NOBF₄ to increase the affinity of their surface towards PVDF. The ligand exchange was performed by the same method that was used in **Section: Side project (ii)** of the **APPENDIX** to obtain BF₄⁻ functionalised MNPs.

SYNTHESIS OF DIPAB-PVDF- Fe₃O₄ THIN FILMS

A 9.8 wt% homogenous solution of PVDF powder in DMF was obtained by the same way as that for DIPAB-PVDF nanofibres. 5 wt% DIPAB was added to the clear solution of PVDF once the solution was cooled down. This specific concentration was chosen based on previously obtained results from the dielectric measurements of DIPAB doped PVDF nanofibres. 5 wt% DIPAB in PVDF had the highest dielectric strength among other samples. The mixture was left to stir at room temperature overnight to ensure complete dissolution of DIPAB. Once a clear solution was achieved, 15 wt% BF₄⁻ functionalised Fe₃O₄ nanoparticles were added to it. The solution was left to stir further for overnight resulting in a proper dispersion of Fe₃O₄ nanoparticles in the solution. The solution was smooth with no visual agglomeration. DPM thin film was prepared using the method adopted by Sui et al.¹ to fabricate DIPAB doped PVDF thin films. The DPM solution was drop cast on the Si-wafer and left in the vacuum oven for 2 hours at 70 °C. The evaporation of the solvent from the polymer solution resulted in the formation of DPM thin film on the silicon wafer.

4.2.2. CHARACTERISATION AND ANALYSIS OF DIPAB-PVDF-Fe₃O₄ THIN FILMS

Figure 77 compares the X-Ray diffraction (XRD) patterns of PVDF, DIPAB, Fe₃O₄ nanoparticles and DPM thin films. The XRD for DPM film was performed by preparing the DPM film on glass rather than Si-wafer. Silicon has a strong diffraction peak which made the analysis of the nanoparticles in DPM's XRD spectra difficult as low concentration of the nanoparticles had a comparatively weaker peak. The diffraction peak observed in the DPM thin film at 20.3°, correspond to the β -phase of PVDF. The XRD of ferroelectric α -phase of DIPAB was compared with the previously fabricated DIPAB crystals.³ The α -phase or the 1-F (ferroelectric) phase of DIPAB was visible through the presence of characteristic 2 θ peaks in the XRD at 12.5°, 17.0°, 22.4°, 25.2° and 27.6°. These peaks correspond to the monoclinic system of DIPAB crystals. The obtained XRD pattern of the Fe₃O₄ nanoparticles was compared with the JCPDS reference file for Fe₃O₄ (reference code – 01-080-6402) belonging to the Fd-3m space group. The XRD of multiferroic film compliments the XRD diffraction patterns of all the three materials.

Figure 77: XRD patterns for PVDF nanofibres, DIPAB and Fe₃O₄ nanoparticles DIPAB-PVDF-Fe₃O₄ nanofibres. The dominating β -phase of PVDF and 1-F phase of DIPAB was observed in all the respective samples.

Figure 78 shows the SEM micrograph of DPM film. The micrograph shows the formation of *in-situ* grown DIPAB microcrystals. They were present inside the thin film which could

be observed as higher contrast (dot-like) structures in **Figure 78 (a)**. Agglomeration was also observed in some places. Top view (**Figure 78 (b)**) of the DPM film had cracks that might have been caused while the film was cooling down in the furnace during the thin film formation. Still, it proved the successful formation of DIPAB and Fe_3O_4 doped PVDF thin films. The elemental mapping in the figure confirmed the dispersion of DIPAB and Fe_3O_4 in the film (**Figure 79**). However, clustering of the nanoparticles was evident which can be improved by thin film fabrication physical parameters. Due to time constraints, no further magnetic, dielectric or ME measurements were performed on the samples. DPM films make them suitable for applications such as EM wave absorbers as the combination of magnetic and dielectric materials would result in enhanced electromagnetic wave absorption.^{22–25}

Figure 78: DIPAB-PVDF-iron ferrite (DPM) thin film **(a)** cross-section; **(b)** top view. The brighter contrast dotlike structures are the iron ferrite nanoparticles. The aggregation was observed indicated by the (red circle).

Figure 79: Elemental map obtained by SEM for DPM film indicating the presence of DIPAB (Nitrogen signal), PVDF (Fluorine signal) and iron ferrite (iron and oxygen signal).

To conclude, DPM films with 15 wt% Fe_3O_4 nanoparticles and 5 wt% DIPAB dispersed in PVDF were successfully fabricated. They were characterised to observe the even distribution of fillers in the PVDF matrix in the form of thin films. The ease of processibility, flexibility, inertness and high interfacial areas due to 2-D structure formation prove their worth to be used as a multiferroic composite material in the field of magnetic sensing and electromagnetic wave absorption.

SUMMARY OF THE CHAPTER

The chapter discussed the fabrication of DIPAB doped PVDF nanofibres which showed the unique flexibility of PVDF and improved dielectric strength by DIPAB nanoparticles incorporation. The improvement in dielectric constant is the important factor for the ferroelectric component as it directly corresponds to the higher piezoelectric coefficient which is a requisite for high magnetoelectric coefficient in a multiferroic composite. The improved in the relative dielectric constant by over 12 times and flexibility of this polymeric structure makes them an optimal choice for the formation of flexible magnetoelectric sensors and magnetoelectric energy harvesters. The ease of fabrication at room temperature and semicrystalline nature of DIPAB doped PVDF aids in the incorporation of multiple types of pre-synthesised suitable magnetic nanomaterials. It

results in the formation of magnetoelectric nanocomposites with magnetic nanomaterials incorporated inside the DIPAB-PVDF polymer matrix. The formation of DIPAB-PVDF-MNP thin film showed the concept of magnetoelectric thin films formation and can be used directly as magnetic sensors and electromagnetic wave absorbers.

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CHAPTER 5

CONCLUSION AND FUTURE WORK

The improvement in the synthesis/fabrication techniques for nanomaterials formation have allowed the scientists to synthesise new structures with interesting properties. It is possible to create composite structures with the desired magnetic and electric properties especially at the nanoscale. Thermal decomposition of metal-organic precursors allows for the formation of metal/metal oxide nanoparticles with desired crystal structure by the optimisation of the reaction conditions. It also leads to the formation of the nanoparticles with different sizes and shape. The fabrication techniques like electrospinning not only allow for the fabrication of polymeric nanofibres but also aid in the formation of 1-D metal/metal oxide structures when the high-temperature calcination processes are incorporated along. The setup can be modified based on atmospheric conditions such as the use of specific gas and temperature modifications. This makes electrospinning suitable for the formation hygroscopic materials with ease too. Electrospinning process has a potential to be upscaled for industrial applications based on low cost of this fabrication process. This can be done by increasing the size of collector and no. of extrusion needles. The relevant technological advances to date have been discovered to increase the volume of the production. It is based on the optimisation of the polymer injection system by introducing multi-spinneret components that allow for the parallel multi-processing and the development of free surface electrospinning methods.

CONCLUSION

Thermal decomposition technique proved to be a useful way to synthesise cobalt iron oxide and iron ferrite nanoparticles. The nanoparticles were monodispersed, and an appropriate size was obtained based on the time dependent growth by thermal decomposition technique. The magnetic studies on cobalt ferrite nanoparticles showed an increasing saturation magnetisation with the increase in the nanoparticles' size from 8 nm to 12 nm. It was because the magnitude of spin disorder increases with the increasing surface area to volume ratio. The 8 nm sized cobalt ferrite nanoparticles showed negligible coercivity at room temperature which indicates a low magnetic anisotropy. It makes them suitable for use in magnetoelectric material formation.

Electrospinning of the PVP polymer solution containing iron nitrate and nickel acetate precursors followed by the high temperature reduction at 600 °C in 95% Ar : 5% H₂ atmosphere resulted in Ni_{0.47}Fe_{0.53} nanofibres. These Ni_{0.47}Fe_{0.53} fibre fused together to form fibre mats varying from sizes ~600 nm to ~900 nm. The saturation magnetic moment per formula was less than the bulk value and matched with reported studies of nanostructured Ni_{1-x}Fe_x with similar *x* values. An effective and thin oxide coating on the surface of these fibre mats prevented further oxidation to maintain the dominant ferromagnetic phase in the structure. The presence of nickel in the structure results in improved permeability which makes them suitable for use in magnetoelectric material formation and wireless charging applications.

DIPAB, which is a highly ferroelectric compound was successfully dispersed in PVDF nanofibres. The electrospinning and addition of DIPAB helped to obtain very high β -phase, improved alignment and crystallinity in the fibres in comparison to the thin film samples. With the right concentration of DIPAB, a certain dielectric permittivity was obtained in the structure while maintaining the flexibility and inertness of PVDF. The dielectric properties were significantly improved and by far the highest relative dielectric constant (~102) was observed for 5 wt% DIPAB in PVDF sample when compared with similar composite structure. DIPAB's concentration based optimisable dielectric properties along with high electrical resistivity and low dielectric losses make them suitable for incorporation into devices. The flexibility and sharp shape dielectric anisotropy of the composite structure make it capable for use in flexible electronics. It also overcome the problems faced by

recent non-polymeric multiferroic composites materials which though show high ME coefficients but are fragile and limited by unwanted reactions at the interfaces.

The coupling of electric and magnetic orders through an elastic interaction (coupling) by the combination of iron ferrite / cobalt ferrite in the superparamagnetic range with high magnetostriction and DIPAB doped PVDF polymer structure with high ferroelectric coefficient will result in the formation of multiferroic composite. The cobalt ferrite nanoparticles were modified with BF_4^- to bind well with the polymer. These ligands also prevent aggregation during multiferroic composite formation. The induced flexibility alongside the ME response makes these structure suitable for small scale energy scavenging applications too. The embedding of the Fe_3O_4 nanoparticles separated in the DIPAB-PVDF composite have strong electronic interactions and multi-interfaces which make them suitable for EM wave absorption in GHz frequency. On the other hand, the nickel-iron fibres composite structure should display high magnetostriction and high permeability because of the ferromagnetic phase of iron and high nickel content in the structure, respectively. The high permeability also makes them suitable for zero power magnetic sensors formation. The nickel-iron fibres coated with DIPAB doped PVDF composite polymer will result in 1-D core-shell multiferroic composite.

Nickel-iron magnetic nanofibres showed the confined size and enhanced anisotropy resulting in improved magnetic induction perpendicular to the fibres. This makes them a primary choice to be studied as suitable magnetic materials for inductive power transfer applications as well. RPEVs can make use of the technology as 1-D structures can direct the magnetic flux towards vehicles' receiving pad. It decreases the inductive losses and increase the efficiency of wireless charging. The high nickel content results in the decreased coercivity which increases the switching speeds. This should increase the power transfer capacity speeds and low losses at operating frequencies, respectively.

Novel monodispersed $\text{Co}_{0.33}\text{Fe}_{0.67}\text{O}$ nanooctapods were synthesised by thermal decomposition technique and were found to be antiferromagnetic. The controlled oxidation of antiferromagnetic $\text{Co}_{0.33}\text{Fe}_{0.67}\text{O}$ nanooctapods would lead to the formation of antiferromagnetic-ferrimagnetic $\text{Co}_{0.33}\text{Fe}_{0.67}\text{O}-\text{CoFe}_2\text{O}_4$ core-shell nanoparticles. This structure should have a high magnetic anisotropy because of the spin blocking at the interface of the ferrimagnetic and antiferromagnetic phase. This synthesis procedure allows to synthesise the core-shell structures with varying core and shell components. The

exchange coupling between the AFM and FM would also result in high coercivities and loops shifts. These properties make them suitable in the field of spin valves, magnetic tunnel junctions and magnetoelectric-RAMs.

Overall, the ferrimagnetic CoFe_2O_4 nanoparticles and related nanostructures with high magnetostriction & low magnetic anisotropy were synthesised. Ferromagnetic nickel-iron fibres mats with high saturation magnetisation and nickel content dependent improved permeability were fabricated. These are effective magnetic components for magnetoelectric applications. DIPAB doped PVDF fibres with enhanced dielectric anisotropy and DIPAB content dependent optimisable dielectric properties were also fabricated as a promising candidate in the form of ferroelectric component for magnetoelectric applications.

FUTURE WORKS

1. Incorporation of cobalt ferrite nanoparticles inside DIPAB-PVDF polymer composite while avoiding the clustering of magnetic nanoparticles using appropriate ligands. This would lead to the formation of an array of nanoparticles embedded inside the composite polymer matrix. The use of magnetic nanoparticles of different sizes to form the above composite structure will result in different magnetoelectric coefficient. Hence, the magnetoelectric effect can be optimised and used for the formation of magnetoelectric sensors with optimised sensitivity.
2. The synthesis of antiferromagnetic-ferrimagnetic $\text{Co}_{0.33}\text{Fe}_{0.67}\text{O}$ - CoFe_2O_4 core-shell nanoparticles by the controlled oxidation of as formed $\text{Co}_{0.33}\text{Fe}_{0.67}\text{O}$ nanoparticles. The similar structures have previously shown electrically tuneable magnetism. With the change in the size of the core to the shell, desired exchange bias properties can be obtained such as the adjustable blocking and Neel temperatures. Hence these particles can be specifically designed for the above applications.
3. Fabrication of nickel iron nanofibres with varying ratio of nickel to iron using the established fabrication method to produce nickel-iron nanofibres. The magnetic properties of the composite structure can be optimised by changing the precursor ratios. An appropriate magnetostriction and magnetocrystalline anisotropy can be achieved by changing the nickel content. The lower iron content structure has a smaller magnetic saturation. Thus, the magnetocrystalline anisotropy will be low

which is favourable for the formation of magnetic sensors with high magnetic sensitivity. These structures also have higher permeability and hence better flux guiding for their use in wireless power transfer. Also, by changing the nickel content an appropriate magnetostriction can be obtained which allows for their use magnetoelectric applications.

4. The formation of DIPAB-PVDF polymer coated nickel-iron nanofibres for 1-D multiferroic composite structure formation. The DIPAB-PVDF polymer coating should improve the mechanical strength of the ferromagnetic fibres. The magnetoelectric properties can further be optimised by using the nickel-iron fibres with varying content ratios.

APPENDIX

I. $\text{Co}_{0.33}\text{Fe}_{0.67}\text{O}$ SPHERICAL NANOPARTICLES: SYNTHESIS AND CHARACTERISATION

Spherical nanoparticles of $\text{Co}_{0.33}\text{Fe}_{0.67}\text{O}$ were synthesised the same way as $\text{Co}_{0.33}\text{Fe}_{0.67}\text{O}$ nanooctapods were synthesised. The only difference was that the heating rate was kept at 4 °C/min. The spherical nature of the nanoparticles showed thermodynamically favourable growth. Hence, a heating rate dependent geometry was observed in the nanoparticles when metal oleate complexes were thermally decomposed. It also proved the heating rate dependence of the reaction on the shape of nanoparticles. **Figure 80** shows the TEM micrographs and respective SAED pattern obtained from the nanoparticles.

Figure 80: TEM Micrographs of spherical $\text{Co}_{0.33}\text{Fe}_{0.67}\text{O}$ nanoparticles. The inset of figure (a) shows the characteristic diffraction rings.

The XRD pattern of the nanoparticles (**Figure 81**) was compared to the JCPDS reference file of CoO (reference code- 00-048-1719) and FeO (reference code- 01-089-0687). The

reference JCPDS files related to FeO and CoO suggested cubic crystal system for the synthesised nanoparticles.

The elemental mapping at high magnification using TEM setup (Jeol 2100F) with energy dispersive X-Ray spectrometry (EDXS) was performed on $\text{Co}_{0.33}\text{Fe}_{0.67}\text{O}$ nanoparticles. **Figure 82** shows that the elemental signals of cobalt, iron and oxygen confirming the formation of cobalt iron oxide instead of cobalt oxide and iron oxide forming separately.

Figure 81: XRD pattern obtained for spherical $\text{Co}_{0.33}\text{Fe}_{0.67}\text{O}$ nanoparticles.

Figure 82: Elemental analysis of spherical $\text{Co}_{0.33}\text{Fe}_{0.67}\text{O}$ nanoparticles by STEM mapping showing the presence of cobalt iron oxide structure formation instead of iron oxide nanoparticles and cobalt oxide nanoparticles separately.

II. SIDE PROJECTS:

Two side projects were conducted alongside magnetoelectric materials developments. They have been discussed below:

i. WATER DISPERSIBLE Fe_3O_4 NANOPARTICLES

Ligands have been employed along with the formation of materials to control their geometry, physical properties and also to attain a self-assembly¹⁻⁷ The nanocrystal's synthesis procedure, purification technique and the affinity of the surface towards the head groups have a huge effect on the above-mentioned properties.⁸⁻¹⁰ One of the most important area for the use of nanomaterials with specific ligands lies in the field of biomedical applications.¹¹ However, the use of nanomaterials for biomedical applications is a big concern because of their toxicity.^{12,13} The primary cell defence barrier i.e., cell membrane majorly decides the uptake of nanoparticles (NPs)¹⁴⁻¹⁶ which depends on their surface morphology. For example, the NPs can stick to the amphiphilic lipid bilayer surface or they can enter the bilayer alkane chain region depending on hydrophilic/hydrophobic interactions. It can lead to disturbance in phospholipid bilayers and eventually cause blocking in membrane proteins.^{17,18} Some applications just require the nanoparticles flow in bloodstream rather than being taken up by the cells. Magnetic nanoparticles with size in the superparamagnetic range and narrow particle size distribution can be used magnetic resonance imaging¹⁹⁻²² and magnetic hyperthermia.²³⁻²⁵ A coating with some organic or an inorganic material is a requisite to confirm the biocompatibility, stability, and non-toxic nature of nanoparticles especially for *in-vivo* uses. The chemical routes such as sol-gel²⁶, co-precipitation²⁷, microemulsion²⁸ and thermal decomposition²⁹ have been applied to obtain the materials with the above-mentioned properties. Other physico-chemical techniques such as sonochemical³⁰ and electrosynthesis³¹ have also been applied. The polymers such as polyethylene glycol, polyvinylpyrrolidone, polyvinyl alcohol, chitosan and dextran have been used frequently as biocompatible polymers. Among them, dextran coated nanoparticles have been used extensively for *in-vivo* applications owing to their non-toxic nature. Low commercial availability of biocompatible superparamagnetic iron oxide nanoparticles (SPIONS) is a concern and a lot of research is going on to produce monodispersed SPIONS. They are available in the market by the names of Ferridex I.V. and Ferumxyltol which find their use as contrast agents for MRI and anaemia.³²⁻³⁵

Peng et al.³⁶ synthesised dextran coated SPIONs where the SPIONs were first fabricated by co-precipitation method at low temperatures. The dextran solution was prepared and SPIONs were added to it which after ultrasonication for 5 hrs at 45°C resulted in the coating of dextran around SPIONs. However, the particles obtained using co-precipitation method were not monodispersed. Though the use of nanoparticles synthesised using techniques such as co-precipitation technique can result to water-dispersible nanoparticles, the lack of control over the particles' size, shape and monodispersity at the nanoscale compromises the characteristic properties of the material. This review discusses the properties, applications, and synthesis of magnetic iron oxides that allow for the control over the size, morphology, surface treatment and magnetic properties of the nanoparticles. Some challenges to further development of these materials and methods are also presented. Since dextran is held to the nanoparticles by non-covalent bonding interactions, there are chances that the dextran coating may dissociate from their surface under certain biological conditions. To prevent this from happening, conventional functional groups can be added for multivalent conjugation on the iron ferrite nanoparticles surface. Ferumoxytol nanoparticles which are fabricated and sold by AMAG pharmaceuticals are designed to minimise immunologic sensitivity. These nanoparticles have a size around 6-7 nm.³⁷ These are the carboxymethyl dextran based magnetic nanoparticles.

The nanoparticles that we obtained by the thermal decomposition technique have shown a high monodispersity and size control and brilliant colloidal stability by steric stabilisation in non-polar solvents. However, they cannot be used directly in the biological applications because of bulky and long hydrocarbon molecules which limit their use in the field of bio-imaging, catalysis, hyperthermia, and other biological applications. The usual approach to synthesise non-agglomerated, monodispersed and water-dispersible nanoparticles is the ligand exchange after the synthesis of the nanoparticles, i.e. the exchange of the original hydrophobic ligands with hydrophilic ligands. The free energy difference between the interactions of ligand-solvent, solvent-solvent and ligand-ligand defines colloidal stability. Hence, a change of the ligand's end groups towards the solvent may affect the nanoparticles' solubility. The nanoparticles can be made water soluble using the ligands with hydroxyl end groups that interact at the nanoparticle-water interface. Herein, we synthesised monodispersed Fe_3O_4 nanoparticles with sizes lower than the superparamagnetic limit which are formed by the thermal decomposition method previously used to synthesise CoFe_2O_4 nanoparticles. Since this method results in the

formation of nanoparticles coated with oleic acid ligands that make them dispersible in non-polar solvents, a two-step ligand exchange strategy was applied to transfer the Fe_3O_4 nanoparticles in water with the help of carboxymethyl dextran (CMDx) ligands while ensure a complete ligand exchange on the surface of the nanoparticles.

ii. SYNTHESIS OF WATER DISPERSIBLE IRON FERRITE NANOPARTICLES

SYNTHESIS OF OLEIC ACID COATED IRON FERRITE NANOPARTICLES

2.4 g Fe-oleate paste in 60 mL 1-octadecene (ODE) was stirred at room temperature to mix them evenly. The reaction mixture was heated at 200 °C for 1 h. It was followed by heating the solution to the refluxing temperature of ODE (318 °C). A constant heating rate (5 °C/min) was maintained for the above step. The solution was kept at the refluxing temperature for 7 min. The reaction yielded a black–brownish solution that was cooled to room temperature. The nanoparticles were obtained by washing with a mixture of ethyl alcohol and butanol followed by centrifugation at 10,000 rpm for 10 min. The precipitate was collected and dispersed in a limited amount of hexane that resulted in the formation of a high concentration of Fe_3O_4 nanoparticles solution (**Figure 83 (a)**).

Another batch of Fe_3O_4 nanoparticles was synthesised during this PhD on which a different ligand exchange process was tried. The same synthesis procedure was followed. The solution was kept at 318 °C for 15 minutes that resulted in larger particles.

LIGAND EXCHANGE OF IRON FERRITE NANOPARTICLES

Ligand exchange processes to transfer the as synthesised Fe_3O_4 nanoparticles to water was performed in two ways. A two-step ligand exchange strategy was applied for both the processes which are described below:

1. The oleic acid ligands were replaced with nitrosonium tetrafluoroborate (NOBF_4) as an intermediate ligand. 20 mg NOBF_4 was collected in the septa vial inside the N_2 filled glove box along with a magnetic bead. The septa vial containing NOBF_4 was taken out of the glove box and 12 ml dichloromethane was injected into it. The solution was kept on stirring for 30 minutes. A 20 mg/ml solution of Fe_3O_4 nanoparticles in hexane was

injected to the NOBF_4 solution and stirred for 24 hours. It resulted in the ligand exchange of particles where the oleic acid was replaced owing to a highly acidic environment created by the presence of NOBF_4 . The nanoparticles were collected by centrifugation of the solution at 10,000 rpm. The obtained particles were dried in a vacuum desiccator to remove the leftover solvents. In a separate vial, a clear solution of 0.35g carboxymethyl dextran (CMDx) in 5 ml DI water was prepared. The dried nanoparticles after the first ligand exchange strategy were added to the CMDx-water solution and stirred for the whole day. The particles were collected by washing with ethanol, centrifugation at 10,000 rpm and drying in a vacuum desiccator to obtain CMDx coated Fe_3O_4 nanoparticles. (**Figure 83 (b)**).

2. The oleic acid ligands were replaced with meso-2,3-dimercaptosuccinic acid (DMSA) which acted as intermediate ligands. As synthesised nanoparticles were mixed with 0.25 mM solution of DMSA in dimethyl sulfoxide (DMSO). The solution was sonicated for 4 hours or till the precipitation occurred. The supernatant was removed, and the collected precipitate was added to the CMDx-water solution. It was further left for stirring overnight to ensure complete functionalisation with CMDx. The solution containing nanoparticles was washed with 1,4-dioxane. The nanoparticles were collected by centrifugation at 10,000 rpm and dispersed in deionised water (**Figure 83 (c)**).

Figure 83: Iron ferrite nanoparticles dispersed in (a) hexane; (b) DI water (intermediate ligand NoBF_4) and; (c) DI water (intermediate ligand DMSA).

RESULTS AND DISCUSSIONS

The precipitation of nanoparticles from hexane solution in the presence of NOBF₄ proved the success of the intermediate ligand exchange with BF₄⁻. The NOBF₄ molecule in water react according to the following equation:

Neither of the NO⁺ and BF₄⁻ ions formed during the addition of NOBF₄ solution in Fe₃O₄ dispersion have a strong affinity for the surface of the nanoparticles. However, NO⁺ ions act as a good leaving group which can be reduced to NO. The NO further oxidises during the ligand exchange process, gets converted to NO₂ and escapes the solution. Moreover, the NO⁺ ions result in the formation of nitrous acid (HNO₂) with water. The BF₄⁻ ions react with water to form fluoroboric acid (HBF₄). The highly acidic solution was formed because of acid formations (pK_a of HNO₂ = 3.4 and pK_a of HBF₄ = -0.4). The BF₄⁻ anions available after the release of NO⁺ cause the protonation of oleic acid ligands. Although the BF₄⁻ coated iron ferrite nanoparticles stabilise in polar solvents such as water, dimethylformamide and dimethylsulfoxide, the BF₄⁻ does not seem to be a suitable ligand for *in-vivo* applications because they are toxic (classification - 8.2 B; 8.3 A; H314, H318). The *in-vivo* applications require a mild ligand coating of iron ferrite nanoparticles that is non-toxic. The polyanionic carboxymethyl dextran (CM-dextran) salt used is the O-carboxymethyl groups attached to the dextran chain where the carboxyl content is ~5%. The non-toxicity and water solubility of CMDx makes it a suitable candidate for *in-vivo* biological applications and has been used readily as a starting material in many diagnostic and clinical products. The continuous stirring of BF₄⁻ modified Fe₃O₄ nanoparticles in the CMDx-water solution resulted in the final ligand exchange on the surface of nanoparticles.

The second ligand exchange strategy involving the use of DMSA in DMSO was performed and compared to the first ligand exchange strategy. The addition of DMSA/DMSO solution to the nanoparticle solution resulted in the lowering of pH (~2.3). The acidic nature of solution triggered the protonation of the oleic acid ligands and resulted in the precipitation of nanoparticles. It was followed by the introduction of CMDx-solution which resulted in the second ligand exchange where the particles were stabilised with CMDx ligands. The successful ligand exchange by both methods was confirmed by TEM and FTIR. No further

magnetic measurements were performed to prove the superparamagnetic nature of the nanoparticles. **Figure 84** shows the schematic representation for the preparation of water-dispersible Fe_3O_4 nanoparticles from as-synthesised Fe_3O_4 nanoparticles using two different ligand exchange methods.

Figure 84: Schematic representation for water-dispersible iron ferrite nanoparticles (MNPs) from as-synthesised MNPs using two different ligand exchange methods.

The XRD measurements were performed on as synthesised Fe_3O_4 nanoparticles. The formed nanoparticles were dispersed in hexane and drop cast on a microscopic glass slide. **Figure 85** shows the X-Ray diffraction pattern of the MNPs. The XRD pattern matched with available XRD pattern of Fe_3O_4 (JCPDS- 01-080-6402). The reference files suggested

the cubic crystal system of spinel ferrites. The average particle size as calculated Scherrer's formula was 8.28 nm. The lattice parameters ($a=b=c$) as calculated from characteristic 2θ peak at 35.5° was 0.83 nm which was comparable the lattice parameters 0.837 nm as mentioned in the reference file.

Figure 85: X-Ray diffraction pattern for Fe_3O_4 nanoparticles coated with oleic acid.

The HR-TEM micrographs of as synthesised oleic acid coated nanoparticles show that the particles were monodispersed (**Figure 86 (a,b)**). The dependence of the growth of Fe_3O_4 nanoparticles on refluxing time was reflected by the formation of small particles. They fall in the superparamagnetic range which is desirable for biomedical applications.^{38–40} The particles were dispersed and no visible agglomeration was observed on the TEM grid. The particle size of nanoparticles was ~ 7.62 nm. The interfringe distance was found to be 0.29 nm which correspond to (220) plane of Fe_3O_4 . **Figure 86 (c, d)** show the TEM micrograph of CMDx coated Fe_3O_4 nanoparticles which were made using NOBF_4 as intermediate ligands. TEM of CMDx- Fe_3O_4 nanoparticles were dispersed at few sections of the TEM GRID (**Figure 86 (c)**), while agglomeration was observed in some places (**Figure 7 (d)**). This is quite common when we have CMDx coating on the nanoparticles because of the crosslinking nature of CMDx.³⁵ The CMDx- Fe_3O_4 nanoparticles were stable in water and started settling down after a few hours. A clear solution was observed at low concentrations. The solution was not cloudy at high concentrations which indicated some aggregation in particles. This aggregation can be attributed to the crosslinking nature of CMDx.

Figure 86: TEM micrographs (a, b) Oleic acid coated iron ferrite nanoparticles; and (c, d) CMDx coated iron ferrite nanoparticles by NOBF_4 intermediate ligand exchange.

In the other ligand exchange performed on larger nanoparticles (particle size ~ 12 nm) as shown in **Figure 87**, the DMSA intermediate ligand resulted in a better ligand exchange strategy. A high stability of nanoparticles in water and transparency of the solution was clearly visible.

Figure 87: TEM micrographs (a) Oleic acid coated Fe_3O_4 nanoparticles (inset- HR-TEM image of MNPs); and (b) CMDx coated Fe_3O_4 nanoparticles by NOBF_4 intermediate ligand exchange.

FTIR studies were performed on the nanoparticles with different ligands as discussed above. FTIR spectra of oleic acid coated nanoparticles and DMSA coated nanoparticles have negative peaks as initially in these samples the background was not subtracted. This mistake was observed later when we did not have any material left for reanalysis. It was kept the same way to ensure that all the FTIR and TEM runs were performed on the same batch of the nanoparticles. The Fe_3O_4 nanoparticles showed noticeable peaks at 2849 cm^{-1} and 2930 cm^{-1} that can be assigned to the C-H stretching vibrations and a weak feature at 1460 cm^{-1} corresponding to the CH_2 bending vibrations (**Figure 88 (light green)**). These features are the characteristics of oleic acid ligands.

The NOBF_4 ligand exchange resulted in new features that appeared as bands at 1080 cm^{-1} and the 1648 cm^{-1} (**Figure 88 (magenta)**). The feature at 1080 cm^{-1} can be assigned to BF_4^- . The feature at 1460 cm^{-1} is the result of C-H stretching from residual oleic acid. The weak band at 1648 cm^{-1} corresponds to DMF (solvent). A nitrosonium peak should be observed at $2100\text{--}2200\text{ cm}^{-1}$ as the result of the formation of NO^+ during the ligand exchange. However, NO^+ gets converted to NO and leaves the reaction.

The adsorption band at 3410 cm^{-1} can be assigned to the left-over solvents in DMSA coated nanoparticles (**Figure 88 (green)**). The peaks at 1397 cm^{-1} and 1641 cm^{-1} can be attributed to the asymmetric and symmetric carboxylate radical stretches.

Figure 88 (bottom) shows the FTIR spectrum of CMDx coated nanoparticles from NOBF_4 (**Figure 88 (blue)**) and DMSA intermediate ligands (**Figure 88 (red)**). The characteristic vibrational modes of CMDx can be represented by the peaks at 3290 cm^{-1} , 2930 cm^{-1} , 1411 cm^{-1} and 1321 cm^{-1} which correspond to the $-\text{OH}$, $-\text{CH}_2$, and $-\text{CH}$ bonds present in the structure, respectively. The peak at 1002 cm^{-1} characteristic of a $-\text{COC}$ bond was observed. The band at 1590 cm^{-1} was attributed to the antisymmetric COO^- stretching of carboxylic acid. The 2849 cm^{-1} and 2930 cm^{-1} can be again assigned to the C-H stretching vibrations and the appearance of the peak at 1460 cm^{-1} corresponding to the CH_2 bending vibrations as the CM-dextran bonds to the surface of Fe_3O_4 nanoparticles by the carboxyl groups. The studies prove a successful ligand exchange on the surface of Fe_3O_4 nanoparticles by both methods.

Figure 88: FTIR spectrum of MNPs functionalised using oleic acid (**light green**); BF_4^- (**magenta**); DMSA (**green**); CMDx coated MNPs by two step ligand exchange using NOBF_4 (**blue**) and DMSA (**red**).

To conclude, Fe_3O_4 nanoparticles falling in the superparamagnetic limit were synthesised by thermal decomposition technique. Ligand exchange of the synthesised nanoparticles led to their phase transfer from non-polar to aqueous phase. The original non-polar ligands were replaced with CM-dextran by the two-step ligand exchange strategies. Nitrosyl tetrafluoroborate and dimercaptosuccinic acid were used as intermediate ligands, respectively. The nanoparticles displayed colloidal stability in water making them suitable for biomedical applications.

iii. MAGNETIC TOROIDS FOR INDUCTIVE POWER TRANSFER APPLICATIONS

The focus on the use of the electronic device at high operating frequency and use of energy-efficient devices is requisite in today's world. It has resulted in the replacement of conventional materials with nanocrystalline materials. The use of nanomaterials has shown improved magnetic properties at high working frequencies.⁴¹ Recent IPT system uses ferrites as ferromagnetic materials for coupling since they display good magnetic permeability at high frequencies and suitable electrical properties.⁴² However, these ferrites suffer from large mechanical and thermal stresses as a result of their extremely brittle nature. Soft Fe_3O_4 composite materials seem to be an alternate way to overcome the above problems. Polymer bonded soft magnetic composites consist of a polymer (dielectric binder) with embedded magnetic particles inside the dielectric matrix.

Role of the toroidal shape of coils:

- The toroidal-shaped coil result in increased transmission distance as the coupling coefficient is increased between the coils at the source and load using this kind of geometry. By making the coils larger in size, the coupling coefficient can further be increased. As the effective area increases, the volume of the coil system greatly increases.
- In toroids, when the windings are short and in a closed magnetic field, the impedance in the toroidal transformer is low. This increases overall efficiency and electric performance.

Figure 89: Illustration of toroid consisting of filler material with coil windings.

The AC magnetic properties of the toroidal shaped samples can be calculated firstly by weighing and calculating their density. The toroids are wound with an insulated copper wire and then it is connected to LCR meter. **Figure 89** shows an illustration of a toroidal shaped coil with wire windings. The toroid has an air core. The inductance of the air core (L_0) is calculated by:

$$L_0 = \frac{\mu_0 N^2 h}{2\pi} \ln \frac{b}{a} \quad (\text{eqn. 12})$$

where a, b and h are the inner radius, outer radius, and height of the toroid. N is the number of windings on the air core.

The inductance of the sample (L_{sample}) can be calculated as:

$$L_{\text{sample}} = \frac{\mu_0 \mu_r N^2 h}{2\pi} \ln \frac{b}{a} \quad (\text{eqn. 13})$$

Since the dimensions of the core are different with respect to the toroid encased by the coil and the inductance is measured with the core, the permeability of the toroid can be calculated as:

$$\mu_r = 1 + \left((L_{\text{sample}} - L_0) \frac{2\pi}{\mu_0 N^2 h_{\text{core}} \ln \frac{b_{\text{core}}}{a_{\text{core}}}} \right) \quad (\text{eqn. 14})$$

The project involving the use of soft magnetic composites was conducted along with the IPT team, Wellington at GNS Science and Robinson Research Institute (Victoria University of Wellington) both of which are based in Lower Hutt, New Zealand. The project deals with the formation of electromagnetic materials consisting of different magnetic powders in varying ratios that are embedded in a PVDF matrix and shaped in the form of toroids.

FORMATION OF MAGNETIC TOROIDS.

To shape the toroids, 3D printed moulds were used. These moulds were specifically made of Teflon so that they can be used at temperatures as high as 250 °C. The toroids were formed by the mixing a variety of magnetic materials with the weight ratios of each material

as mentioned in **Tables 3** to **Table 6**. PVDF was used as the binder materials owing to its good strength, unique dielectric properties and stability at high temperatures. These materials were mixed with PVDF in specific ratios. The idea behind using the specific ratios of magnetic material inside to study which specific toroid provides optimised structural performances, thermal properties and power transfer efficiency. The commercially obtained magnetic materials and formed toroids were characterised using XRD, TEM and SEM. As such, no physical analysis of the samples was performed since they are out of the scope of the thesis. Further studies of the toroids based on the above-mentioned properties were performed at GNS sciences by IPT Wellington team. The magnetic materials and PVDF powder were evenly mixed to create a blend with certain weight percentages. These blends were added to the toroid mould and transferred in a vacuum furnace. The temperature was then increased to 220 °C and maintained for 2 hours under vacuum. The high temperature resulted in the melting of PVDF powder. The samples were then cooled down room temperature which resulted in the hardening of PVDF in the shape of a toroid. The magnetic loadings higher than 80 wt% was not possible since the PVDF matrix losses strength and falls apart.

Table 3: Magnetic toroids formation by incorporation of Fe₃O₄ nanoparticles with increasing wt% in the PVDF matrix.

S. No.	Filler 2 Fe ₃ O ₄ np (wt%)	PVDF (wt%)
1	10	90
2	20	80
3	30	70
4	40	60
5	50	50
6	60	40
7	70	30
8	80	20

Table 4: Magnetic toroids formation by incorporation of Fe₃O₄ nanoparticles (50 wt%) and AU-Ferrite microparticles with increasing wt% in the PVDF matrix.

S. No.	Filler 1 Fe ₃ O ₄ n.p (wt%)	Filler 2 AU ferrite (wt%)	PVDF (wt%)
1	50	0	50
2	50	5	45
3	50	10	40
4	50	15	35
5	50	20	30
6	50	25	25
7	50	30	20

Table 5: Magnetic toroids formation by incorporation of AU-Ferrite microparticles (50 wt%) and Fe₃O₄ nanoparticles with increasing wt% in the PVDF matrix.

S. No.	Filler 1 Fe ₃ O ₄ n.p (wt%)	Filler 2 AU ferrite (wt%)	PVDF (wt%)
1	5	50	45
2	10	50	40
3	15	50	35
4	20	50	30
5	25	50	25
6	30	50	20

Table 6: Magnetic toroids formation by incorporation of Fe₃O₄ nanoparticles (50 wt%) and Iron powder with increasing wt% in the PVDF matrix.

S. No.	Filler 1 Fe ₃ O ₄ n.p (wt%)	Filler 2 iron powder (wt%)	PVDF (wt%)
1	50	5	45

2	50	10	40
3	50	15	35
4	50	20	30
5	50	25	25
6	50	30	20

CHARACTERISATION OF FILLER MATERIALS

Figure 90: TEM micrographs of filler materials in PVDF (a, b) MNPs; (c, d) AU-Ferrite microparticles.

Figure 90 shows the TEM micrographs of the magnetic filler materials. **Figure 90 (a, b)** correspond to the Fe_3O_4 nanoparticles. **Figure 90 (c, d)** correspond to the ferrite microparticles. The samples were in the form of dry powders.

SEM was performed on the chunks of ferrite microparticles/ Fe_3O_4 n.p/PVDF in the ratio 10/50/40 (**Figure 91 (a)**) and 50/10/40 (**Figure 91 (b)**). Platinum coating was performed on the SEM sample to prevent charging during imaging. **Figure 91a (bottom)** shows the strong iron signal coming from larger microparticles with 50/10/40 ratio of ferrite microparticles/ Fe_3O_4 n.p/PVDF mixture, respectively. **Figure 91b (bottom)** shows more uniform iron signal due to higher doping of Fe_3O_4 nanoparticles with 50/10/40 ratio for ferrite microparticles/ Fe_3O_4 n.p/PVDF mixture, respectively. It proved the successful doping of the mixture of two magnetic material with different size in the PVDF matrices in toroid form.

The samples were handed over to the IPT team for magnetic measurements.

Figure 91: SEM micrographs (**Top**) and elemental maps (**Bottom**) of **(a)** 50 : 10 : 40 ratio Fe_3O_4 n.p / AU ferrite / PVDF mixture; **(b)** 50 : 10 : 40 ratio of AU ferrite / Fe_3O_4 n.p / PVDF mixture.

To conclude, the magnetic toroids with varying doping ratios between the magnetic materials and PVDF polymer were fabricated with the help of 3D printed moulds. They were characterised to prove the even dispersion of magnetic materials in the polymer. These magnetic toroids will be studied for their use as magnetic coils in charging pads for wireless charging of electric cars based on their power transfer efficiencies.

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