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Synthesis, Fabrication and Characterization of Magnetic and Dielectric Nanoparticles and Nanocomposite Films

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SYNTHESIS, FABRICATION AND CHARACTERIZATION OF MAGNETIC AND DIELECTRIC NANOPARTICLES AND NANOCOMPOSITE FILMS

By

XIAOHUA LIU

A dissertation submitted to the Graduate Faculty in Chemistry in partial fulfillment of the requirements for the degree of Doctor of Philosophy, The City University of New York.

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THE CITY UNIVERSITY OF NEW YORK
Abstract

Synthesis, Fabrication and Characterization of Magnetic and Dielectric Nanoparticles and Nanocomposite Films

by

Xiaohua Liu

Adviser: Dr. Stephen O’Brien

Materials science is an interdisciplinary field investigating the structure-property relationship in solid-state materials scientifically and technologically. Nanoscience is concerned with the distinctive properties that matter exhibits when confined to physical dimensions on the order of $10^{-9}$ meters. At these length scales, behaviors of particles or elaborate structures are often governed by the rules of quantum mechanics in addition to the physical properties associated with the bulk material.

The work reported here seeks to employ nanocrystals, binary nanocomposites and thin films of materials, to build versatile, functional systems and devices. With a focus on dielectric, ferroelectric, and magnetoelectric performance, a series of materials has been synthesized and different types of nanocomposites have been built. Barium strontium titannate particles at various sizes was developed, aiming at high dielectric constant and low loss at high frequency range. Cobalt ferrite-polymer nanocomposite was fabricated with potential magnetoelectric coupling. Along with synthesis, advanced electron microscopies (TEM, SEM, STEM, EELS) at atomic resolution were employed to thoroughly investigate the crystallinity, morphology and
composition. By means of spin-coating and printing techniques, single and multiple layered capacitors featuring improved dielectric performance (high k, low loss, high breakdown voltage, etc.) were developed through a) electrode deposition, b) dielectric layer deposition, and c) parylene evaporation. Such capacitors are further incorporated into electric power converters for LED lighting. Hopefully in the future we can make electronic devices more efficient, sustainable, smaller and cheaper.

By advancing our knowledge of nanomaterials, especially those with potential of multifunction, energy efficiency and sustainability, we have strived to push the limits of synthesis, characterization, fabrication and property analysis of nanostructures towards new, reliable and low-cost multifunctional systems. Some of our efforts are described in the following chapters.
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To Min Hou and Qian Wang
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Chapter 1 Introduction

1.1 Ferroelectric Perovskite Materials

As one of the most important materials for both fundamental science and technical applications in electronic industry, ferroelectric perovskite materials have attracted tremendous attention. Industrial applications of these materials embrace embedded capacitors, MLCCs (multilayered ceramic capacitors), transducers, sensors, memory and power storage devices. With the ever-growing trend towards integration, miniaturization and versatility, ferroelectrics at nanoscale regime have been thoroughly studied through chemical synthesis, experimental physics, computer modeling, material property analysis, etc.

Possessing a spontaneous dipole moment, the orientation of the polarization of ferroelectric materials can be switched by the application of an electric field. The ferroelectricity of perovskite materials occurs in and only in the tetragonal phase, where the center atom moves off-center due to the change of the external field, leaving a 180° difference in polarization direction. Materials falling into this category include: BaZrO$_3$, PbTiO$_3$, PbZrO$_3$, (Ba,Sr)TiO$_3$, Pb(Zr,Ti)O$_3$, LiNbO$_3$, etc.$^{1-3}$

Barium titanate (BaTiO$_3$, BT), strontium titanate (SrTiO$_3$, ST), and barium strontium titanate ((Ba,Sr)TiO$_3$, BST), featuring high dielectric constant and low intrinsic dielectric loss, are among the most extensively studied perovskites. A typical barium titanate lattice is shown in Figure 1.1, representing both cubic and tetragonal phases. The transition temperature between the two phases is called Curie temperature ($T_c$), above which the oxide is cubic (paraelectric) and below which it is tetragonal (ferroelectric). Because of the small atom size and high charge of the
Ti\textsuperscript{4+} ion, a large amount of potential energy can be stored at the off-center position. Therefore a large dielectric constant (permittivity, k) is exhibited. A dielectric constant as high as 11000 was observed for a BaTiO\textsubscript{3}/ SrTiO\textsubscript{3} mixture\textsuperscript{4}. Further, it is reported that the dielectric constant is higher at the materials’ Curie temperature, and can be tuned by atomic ratio of barium and strontium. High k at room temperature can also be achieved by tuning the ratio between BT and ST\textsuperscript{3}.

![Figure 1.1 Schematic diagram of perovskite BaTiO\textsubscript{3} crystallographic structure and its phases.](image)

Because of the distinctive ferroelectric properties and dielectric properties, BaTiO\textsubscript{3}-based materials have been widely used in high k dielectric components for decades\textsuperscript{5}. Leading by a steady trend of investing in high capacitance designs, the global market for ceramic capacitors is projected to reach $11.4 billion by 2015\textsuperscript{6}. Exploration of different material systems is currently of great interest, mainly focusing on dielectric performance enhancement in terms of high
permittivity, high strength and low loss/leakage, at multiple frequency ranges to serve various applications.

Improvements in the development of ceramic capacitors require manufacturing techniques that allow reduced dielectric thickness lower than 1 mm. Such thin layers can only be achieved if monodisperse, nanosized dielectric nanocrystals without crystal grain are available and can be deposited by techniques more advanced than tape casting and screen printing. These processes require phase-pure, homogeneous, weakly agglomerated ultrafine nanoparticles as building blocks.

Owing to the rapid advances in nanoscience, materials at nanoscale with tunable size/morphology, high quality/low defects, and controlled microstructure can be prepared via various routes: top-down or bottom-up. Traditional preparation of perovskites require high temperature (>1100°C) solid-state reactions between titania and alkaline earth metal carbonates, which yield microsized crystal grains. Subsequent heat treatment is required to induce crystallization. Recently intensive efforts have been focused on solution-phase wet chemical routes to prepare BT/BST nanoparticles (e.g., sol–gel,\textsuperscript{7} hydrothermal,\textsuperscript{8} solvothermal,\textsuperscript{9} and micellar\textsuperscript{10}), in order to achieve moderate reaction condition, gain overall control of size and morphology. Kareiva \textit{et al.}\textsuperscript{7} reported a preparation of microsized, pure tetragonal-phase BT nanoparticle via sol-gel synthesis followed by calcination at 1300°C. Xu \textit{et al.}\textsuperscript{8} reported a hydrothermal method to prepare tetragonal BaTiO\textsubscript{3} with diameter around 70nm, and after sintering with dielectric constant up to 6900 (1 kHz). Piothan \textit{et al.}\textsuperscript{10} described preparation of BT nanoparticles (10nm) via microemulsion-mediated hydrolysis of mixed metal alkoxides. Nanocrystalline tetragonal barium titanate with particle size ranging from 30 to 100 nm was synthesized by Nyutu \textit{et al.}\textsuperscript{11} via microwave-assisted hydrothermal route at various microwave
frequencies and sweep times. Kolen’ko et al.\textsuperscript{9} reported a solvothermal procedure of preparing BT particles in the range of 5 – 37 nm, with precise control over size by varying the water content of the reaction mixture. A comprehensive review of various chemical techniques for the preparation of ultrafine BaTiO\textsubscript{3} powders has been given by Pithan.\textsuperscript{12}

For barium titanate nanoparticles, although the tetragonal phase is thermodynamically stable at room temperature ($T_c = 130^\circ$C), synthesis at low temperature does not generate the preferred tetragonal polymorph generally. Also, there is a size effect associated with the nanoparticles: barium titanate nanoparticles with size $\geq 30$ nm is requisite for generating tetragonal phase - below which the ferroelectricity is diminishing. An explanation for the latter is the depolarization field formed on the surface of the nanoparticles by the impurity ions, which prevent the formation of tetragonal phase below certain scale. Subsequent sintering followed by annealing step is required to generate pure tetragonal phase, which invariably results in particle growth, agglomeration, and broad size, or destruction of the morphology.

1.2 Nanocomposite Thin Films

Nanodielectrics is an emerging field studying the fabrication of structures, devices, and systems with novel dielectric properties due to their nanometric structure.\textsuperscript{13} Thin films featuring high dielectric constant have widespread electronic applications such as embedded capacitors,\textsuperscript{14,15} multilayer capacitors (MLCC),\textsuperscript{16} and gate insulators in organic field-effect transistors (OFETs).\textsuperscript{17} Rational design of hierarchical nanostructures such as thin films, superlattice, and core-shell structures depends on many factors, chief among which are the surface/interface, crystal size, shape, self-assembly, and defects.\textsuperscript{18} Investigation of size control,
surface chemistry, and self-assembly of metal oxide nanocrystals into closed-packed thin films has enabled rational design of a variety of high quality, functional nanodevices.

Polymer-ceramic nanocomposites provide a means of combining the high permittivities ($\varepsilon$) of metal oxide nanoparticles with the high dielectric strength (breakdown voltage) of polymeric matrix. Large amount of work has been done on mixing various polymers (e.g. PVDF,\textsuperscript{19,20} P(VDF-HFP)\textsuperscript{21}, polyimide\textsuperscript{22,23}) with different metal oxide fillers to achieve excellent dielectric behavior. A key factor towards high quality polymer-ceramic nanocomposite film and the aforementioned interesting properties is homogeneous disperse of the nanocrystals into bulk polymer matrices. Simple mixing fails to do so, due to the agglomeration and phase separation induced by the high surface energy, as well as incompatibility between the nanoparticles and the polymer matrix.

Modification of the interface in order to build stronger interaction between the metal oxides and the polymer is one strategy to improve the film quality and processibility, another is optimization of the arrangement and packing of the nanocrystal fillers suspended in polymer host. Jayasundere and Smith\textsuperscript{21} first proposed a modified Kerner model to correlate effective permittivity with volume fraction for dense packing (> 50 vol %) films, which is expressed as:

$$\varepsilon_{eff} = \frac{\varepsilon_h f_h + \varepsilon_f f_f (A)(B)}{f_h + f_f (A)(B)}$$

where $\varepsilon_h$, $f_h$, and $\varepsilon_f$, $f_f$ are the permittivity and volume fractions of the host and filler, respectively, and

$$A = \frac{3\varepsilon_h}{\varepsilon_f + 2\varepsilon_h}$$

$$B = 1 + \frac{3f_f (\varepsilon_f - \varepsilon_h)}{\varepsilon_f + 2\varepsilon_h}$$
Kim et al.\textsuperscript{24} incorporated porosity as another factor influencing the permittivity, breakdown voltage and leakage current. The modified Kerner model indicates that the effective permittivity of thin films depends not only on the permittivity of nanocrystals, but also the permittivity of polymers, as well as the volume ratio of filler and matrix. Therefore, a balance over compatibility, permittivity, volume fraction and porosity of both fillers and hosts has to be thoroughly considered. High performance thin films can be designed via the combination of high-k nanocrystals and reasonable-k polymer hosts, in a close-packing low-porosity way.

### 1.3 Magnetolectric Materials and Multiferroics

Ferroelectricity, the spontaneous ordering of electric dipole moments, is in analogy to the phenomena of ferromagnetism, in which a material exhibits spontaneous ordering of orbital and spin magnetic moments. Ferromagnetism was already known when ferroelectricity was discovered in 1920 in Rochelle salt by Valasek.\textsuperscript{25} And the two types of ordering - ferromagnetism and ferroelectricity, can coexist in one material in the absence of external electric and magnetic fields. Following Schmid\textsuperscript{26}, these materials are now called multiferroics (Fig. 1.2). With the two degrees of freedom coupling with each other, multiferroic materials show huge potential for practical applications in multiple-state memory elements, magnetolectric sensors, phase shifters, and microwave frequency transducers.
Figure 1.2 Multiferroics combine the properties of ferroelectrics and magnets (adapted from Ref\textsuperscript{27}). The magnetization of a ferromagnet (blue) in a magnetic field displays the usual hysteresis, and ferroelectrics (yellow) have a similar response to an electric field. For multiferroics (green) that are simultaneously ferromagnetic and ferroelectric, there is a magnetic response to an electric field, or, vice versa, a polarization response to a magnetic field.

Single-phase multiferroics, such as BiFeO\textsubscript{3}\textsuperscript{28}, YMnO\textsubscript{3}\textsuperscript{29}, and CdCr\textsubscript{2}S\textsubscript{4}\textsuperscript{30}, exhibit intrinsic magnetoelectric (ME) coupling between magnetic and electric orders. However, they are empirically rare\textsuperscript{31} and magnetoelectrically weak due to the contraindication between ferroelectricity and magnetism\textsuperscript{32}. The observed magnetoelectric effect occurs far below room temperature\textsuperscript{33}, which limits the practical use in device fabrication. An alternative approach is to introduce two-phase composites, in which the ferromagnetic and ferroelectric phases are combined from different sources. With various connectivity schemes: particulate 0–3 type, laminate 2–2 type, and fiber/rod 1–3 type, binary magnetoelectric materials offer tunability between ferroelectric and magnetic properties independently. And the ME coefficient of the composite is 3 orders of magnitude higher than their single-phase counterparts\textsuperscript{34}. 
The mechanism of magnetoelectric coupling in most multiferroic composites is strain-mediated, in which the ME effect is a concerted result of the piezoelectric and magnetostrictive effect from the two phases respectively. An external electric field induces a distortion of the piezoelectric phase, which further distorts the magnetostrictive phase, generating a magnetic field, and vice versa. Strong ME coupling requires: a) a ferroelectric phase possessing a high piezoelectric coefficient, b) a magnetic phase possessing large magnetostriction and resistivity, and c) an intimate mechanical contact between the two.\(^{35}\)

Polymer composites have the magnetic oxides embedded in ferroelectric polymer matrix, which offers mechanical flexibility and enables facile processing. With high strength and good stability\(^{36}\), poly-vinylidene difluoride (PVDF) and its copolymers such as poly(vinylidenefluoride-co-trifluoroethylene) (P(VDF-TrFE))\(^{37}\) and poly(vinylidene fluoride-hexafluoropropylene) (P(VDF-HFP))\(^{38,39}\) are well known for their ferroelectricity and piezoelectricity, which make them ideal candidates for multiferroic film fabrication and ME effect exploration. Transition metal ferrites such as cobalt iron oxide (CoFe\(_2\)O\(_4\), CFO) possessing a large magnetostriction coefficient (\(\lambda \approx 10^{-4}\)) and high Curie temperature (\(T_c > 600\) K)\(^{40}\), serve as excellent candidates for the magnetic phase.

Although the mechanism of the magnetoelectric coupling is straightforward, complications arise when quantifying the details of polymer-based nanocomposites. The presence of polymorphism (e.g., \(\alpha, \beta, \gamma, \delta\) phases in PVDF), domain walls, grain boundaries, residual stain/magnetization, surface charge, and voids can significantly hinder the ME effect. Andrew and Clarke\(^{41}\) found that the inclusion of well-dispersed Ni\(_{0.5}\)Zn\(_{0.5}\)Fe\(_2\)O\(_4\) nanoparticles in a PVDF matrix can enhance the ferroelectric phase content. Liu et al.\(^{42}\) reported epitaxial BaTiO\(_3\)-CoFe\(_2\)O\(_4\) nanocomposite thin films (thickness, 100 nm) with phase transition mediated
by tensile strain. Recently, a magnetoelectric coupling coefficient of 12 V/cm \cdot Oe was obtained for P(VDF-HFP)/Metglas laminates\textsuperscript{43}. Martins \textit{et al.}\textsuperscript{44} fabricated ferrites/PVDF nanocomposite films with thickness of 40 to 50 µm by solvent casting and melt processing. Guo and co-workers prepared particulate Ni\textsubscript{0.5}Zn\textsubscript{0.5}Fe\textsubscript{2}O\textsubscript{4}/P(VDF-TrFE) films (thickness, 50 to 60 µm) by wet chemistry routes, with observable magnetodielectric coefficients represented as a percentage change of dielectric constant with and without an external magnetic field\textsuperscript{45}.

1.4 Motivation

The work reported here has two major research activities. First, as part of the Metacapacitor project, we strive to understand the fundamental process of perovskite BaTiO\textsubscript{3} nanoparticle synthesis and nanocomposite assembly, fabricate and fully characterize the role of the nanocomposite films as high k dielectrics in capacitors. The processing techniques, size control and film preparation all contribute to the ability to produce new devices with low cost and high efficiency in power conversion and energy storage, and are therefore fully investigated.

The second part of the research aims to build particulate two-phase magnetoelectric nanomaterials, and to understand the physics and mechanism of the magnetoelectric coupling. Different combination of raw materials, processing techniques, and phototypes of devices based on the nanoparticle-polymer composite, enables potential applications in multifunctional devices, transducers actuators and sensors.

The investigation of both perovskite and spinel materials and their polymer-based composite will establish a systematic and controllable processing from multi-phase nanoparticle dielectric composites with optimized properties, and provide fundamental understanding of the
structure-property relationship of the nanomaterials, leading to technology innovation and advancement in multifunctional devices and systems.
Chapter 2 Nanocrystal Synthesis and Structural Characterization

2.1 Nanocrystal Synthesis

2.1.1 Raw Materials

*Synthesis of BaTiO$_3$ nanoparticles:* barium acetate, Ba(C$_2$H$_3$O$_2$)$_2$ or Ba(OAc)$_2$ (99.0-102.0%, Alfa Aesar), strontium acetate, Sr(C$_2$H$_3$O$_2$)$_2$ or Sr(OAc)$_2$ (97%, Aldrich), titanium isoproxydode Ti(OiPr)$_4$ (97+%, Alfa Aesar), sodium hydroxide, NaOH (Fisher Scientific), potassium hydroxide, and KOH (85+%, Fisher Scientific).

*Synthesis of transition metal ferrites:* manganese (II) acetylacetonate, Mn(acac)$_2$ (Sigma-Aldrich), nickel (II) acetylacetonate, Ni(acac)$_2$ (95%, Sigma-Aldrich), zinc (II) acetylacetonate hydrate, Zn(acac)$_2$ • xH$_2$O (Sigma-Aldrich), iron (III) acetylacetonate, Fe(acac)$_3$ (97+%, Sigma-Aldrich), cobalt (II) nitrate hexahydrate, Co(NO$_3$)$_2$ • 6H$_2$O (98+%, Sigma-Aldrich), iron (III) nitrate nonahydrate, Fe(NO$_3$)$_3$ • 9H$_2$O (98+%, Sigma-Aldrich), hexanol (98%, Sigma-Aldrich), 200-proof ethanol (100%, Decon Laboratories), ethanolamine (98+%, Sigma-Aldrich), and ammonium hydroxide (28.0 – 30.0 %, Sigma-Aldrich).

*Solvents and polymers for device fabrication:* N,N-dimethylformamide, DMF (99.8%, Sigma-Aldrich), Furfuryl alcohol, (FA, Aldrich), poly(vinylidene fluoride-co-hexafluoropropylene), P(VDF-HFP) (pellets, Sigma-Aldrich), polyvinylpyrrolidone, PVP (MW ~ 10,000, Sigma-Aldrich), parylene-C (poly-p-xylylene, Specialty Coating System), Micro-90 cleaning solution (Sigma-Aldrich), acetone (99.5+%, Fisher Scientific), and isopropyl alcohol (68-72%, Fisher Scientific).
2.1.2 Barium Strontium Titanate Nanocrystal Synthesis

Adapting proven solvothermal methods\textsuperscript{46,47}, the synthesis of (Ba,Sr)TiO\textsubscript{3} nanocrystals is based on a refluxing method using barium, strontium and titanium alkoxide or acetate salts as precursors and 95% ethanol as solvent. Sodium hydroxide is added to maintain a strong basic condition to assist alcoholysis of precursors (Equation 2.1, Figure 2.1).

\[
\text{Ba(OAc)}_2 + \text{Sr(OAc)}_2 + \text{Ti(OiPr)}_4 \xrightarrow{\text{OH}, \text{H}_2\text{O}, 79^\circ\text{C}, 4 - 10 \text{ h}} (\text{Ba,Sr})\text{TiO}_3
\]  

(2.1)

Figure 2.1: Synthesis of (Ba,Sr)TiO\textsubscript{3} nanoparticles via refluxing methods (a) with temperature control (b), and the resultant nanoparticles in dry format (c), low concentration suspension in ethanol (d), and high concentration suspension in ethanol (e).

In a typical reaction, 3.58 g Ba(OAc)\textsubscript{2} and 1.23 g Sr(OAc)\textsubscript{2} were dissolved in 10 ml deionized water (Mixture 1) and 16.00 g NaOH was dissolved in 20ml DI water (Mixture 2). In a
round-bottom flask, first 5.92 ml Ti(OiPr)$_4$, then Mixture 1 was added dropwise, followed by 70 ml of ethanol poured in and Mixture 2 dropwise. The reaction mixture was heated at 79°C under magnetic stir for 4 to 30 h. The resultant mixture after the reaction showed milky appearance. The white precipitate suspended in the mixture was collected by centrifugation and washed with ethanol and deionized water. This process reaches a yield of ~ 90% based on the recovery from metal Ba. For tests requiring solids of sample such as X-ray diffraction (XRD) and thermogravimetric analysis (TGA), the powders were dried at 90°C in oven overnight. For tests in solvent or suspension and thin film fabrication, the (Ba,Sr)TiO$_3$ powders were redispersed in ethanol or DMF solvent using 30min of ultrasonication. Some (Ba,Sr)TiO$_3$ nanocrystals were pre-treated with hydrochloric acid before suspended in ethanol, to test whether the H$^+$ treatment had an effect on the particle morphology and solvent dispersibility and suspension stability.

The solvothermal process involves alcoholysis between two sources: a metal-organic precursor, metal alkoxide or acetate, and ethanol. No high boiling point solvent or organic or halide ligand are involved. This method produces highly pure nanocrystals with minimal organic residuals, and is free from ligand contamination.

### 2.1.3 Transition Metal Ferrite Nanocrystal Synthesis

The MFe$_2$O$_4$ (M = Mn, Ni, Co, Zn) nanocrystals were synthesized by several solvothermal routes. Route 1$^{48}$ (Equation 2.2): 2 mmol Mn(acac)$_2$, Ni(acac)$_2$, or Zn(acac)$_2$ and 4 mmol Fe(acac)$_3$ was first dissolved in 30 ml hexanol via continuous magnetic stirring for 40 min. The mixture was then transferred into a Teflon-lined stainless steel autoclave and heated at 180 °C for 24 h in oven. Route 2 (Equation 2.3): 1 mmol Co(acac)$_2$, and 2 mmol Fe(acac)$_3$ were first dissolved in 40ml ethanol via magnetic stirring. The mixture was then transferred into a Teflon-lined stainless steel autoclave and heated at 180 °C for 20 h in oven. Route 3$^{49}$ (Equation
2.4): 2 mmol Co(NO$_3$)$_2$ · 6H$_2$O and 4 mmol Fe(NO$_3$)$_3$ · 9H$_2$O were first dissolved in deionized water. Ethanolamine was dropwise added in the solution until precipitation completed. The obtained solids were collected by centrifugation and washed thoroughly with deionized water. 35 ml NH$_3$ · H$_2$O was then added to redissolve the solids. The resultant ammonium hydroxide suspension was transferred into a Teflon-lined stainless steel autoclave, with 80% volume filled, and heated at 200°C for 10 to 40 h. The chemical reactions of the three routes are summarized in Equation 2.2 - 2.4.

\[
\text{M(acac)$_2$ + 2Fe(acac)$_3$} \xrightarrow{\text{Hexanol}} \text{MFe$_2$O$_4$} \quad (M = \text{Mn, Ni, Zn}) \quad (2.2)
\]

\[
\text{Co(acac)$_2$ + 2Fe(acac)$_3$} \xrightarrow{\text{Ethanol}} \text{CoFe$_2$O$_4$} \quad (2.3)
\]

\[
\text{Co(NO$_3$)$_2$ · 6H$_2$O + 2Fe(NO$_3$)$_3$ · 9H$_2$O} \xrightarrow{\text{NH$_3$ · H$_2$O}} \text{CoFe$_2$O$_4$} \quad (2.4)
\]

After the reaction, the autoclave was cooled down to room temperature. The resultant dark brown nanopowders were collected by centrifugation and thoroughly washed with ethanol and deionized water. For XRD and magnetic property tests, the powders were dried in oven at 90°C overnight. For TEM characterization and thin film fabrication, the nanoparticles were redispersed in ethanol or DMF by assistance of 30 min ultrasonication.

2.2 X-Ray Diffraction (XRD) Spectroscopy

2.2.1 X-Ray Diffraction and Bragg’s Law

X-rays are a class of electromagnetic radiation that possesses wavelengths on the order of atomic spacing of crystals. When a beam of X-rays impinges on a crystal, atoms within the
beam’s path scatter X-ray waves through elastic scattering. Although the scattered waves cancel each other out in most directions - the interference is nonconstructive or destructive so as to yield a very low-intensity diffracted wave, they add constructively in a few directions, determined by Bragg's law (Figure 2.2):

\[ n \lambda = 2 d \sin \theta \]  

where \( n \) is the order of reflection which can be any integer (1, 2, 3,…), \( \lambda \) is the wavelength of the incident x-rays, \( d \) is the spacing between diffraction planes, and \( \theta \) is the incident angle. Bragg’s law relates the x-ray wavelength and interplanar spacing to the angle of the incident/diffracted beam, which describes the necessary conditions for diffraction of x-rays by a periodic arrangement of atoms.

Figure 2.2: Schematic representation of Bragg diffraction of x-rays by plans of atoms (adapted from Ref\(^{50}\)).
In practice, a diffractometer is used to precisely control the angles between the x-ray source, powdered specimens, and detector. Its components are represented in Figure 2.3. An x-ray beam is generated at the tube, and the intensities of diffracted beams are detected with a detector. Utilization of slits provides a near-monochromatic beam. A $\theta$ rotation of the specimen is accompanied by a $2\theta$ rotation of the detector, ensuring that the incident and reflection angles equal each other. As the incident beam rotates at constant angular velocity, the diffracted beam intensity is monitored by the detector and plotted as a function of $2\theta$ (termed the diffraction angle). The lattice geometry was confirmed from the angular positions of the reflection peaks.

![Figure 2.3: Schematic diagram of typical components and angles of the goniometer for a $\theta$-$2\theta$ x-ray diffractometer (adapted from Ref\textsuperscript{51}).](image)

The x-ray diffraction was employed to determine the structure of various crystallographic systems, as well as to estimate the average particle size by Scherrer's equation.
2.2.2 Instrumental and Sample Preparation

The phase purity and crystal structure of the perovskite and spinel nanoparticles was analyzed by a PANalytical powder X-ray diffractometer (Almelo, The Netherlands) with Ni-filtered Cu Kα radiation ($\lambda = 1.54056$ Å). The dried nanoparticles were first ground into fine powder with a mortar and pestle and then evenly spread on glass sample holder. The powdered specimen consisted of many fine and randomly oriented particles, which assured that some particles were in such proper orientations that every possible set of crystallographic planes were diffracted. The reflections were recorded in step scanning mode of diffraction angle ($2\theta$) from 20° to 80° for both dielectric and magnetic nanoparticles.

2.2.3 Perovskite Structure of Barium Strontium Titanate

The solvothermal approach enables the production of aggregate free, high crystalline BaTiO$_3$ and (Ba,Sr)TiO$_3$ nanoparticles with controls over size ranging from 8 to 50 nm. Figure 2.4 presents typical X-ray diffraction (XRD) patterns of the BaTiO$_3$ or (Ba,Sr)TiO$_3$ specimens prepared using different barium, strontium, and titanium metal-organic sources. All reflections can be assigned to the perovskite phase (Joint Committee on Powder Diffraction Standards JCPDS No. 31–174) without the presence of any BaCO$_3$ peaks. With 30% substitution of Ba by Sr, the reflection peaks shift to higher diffraction angles, as is expected from the smaller unit cell resulted from the substitution by the small atomic radius Sr atoms.

Figure 2.4: XRD patterns of BaTiO$_3$ and Ba$_{0.7}$Sr$_{0.3}$TiO$_3$ nanocrystals prepared from solvothermal methods using barium, strontium alkoxide salts (a) and acetate salts (b).

The results obtained from XRD is analyzed by the Scherrer equation$^{52}$ (Equation 2.6) to estimate the average particle size.
\[ \tau = \frac{K \lambda}{\beta \cos \theta} \]  

Here \( \tau \) represents the diameter of crystallites, perpendicular to the plane which corresponds to the measured diffraction peak. \( K \) is the Scherrer constant, depending on the how the width is determined, the shape of the crystal, and the size distribution. \( \beta \) represents is the full width of the diffraction line at half the maximum intensity measured in radians. \( \lambda \) is the x-ray wavelength and \( \theta \) is the Bragg angle.

The calculated particle size is 13 and 21 nm for (Ba,Sr)TiO\(_3\) specimens prepared from the Ba(OAc)\(_2\)-Sr(OAc)\(_2\)-Ti(OiPr)\(_4\) and Ba(OiPr)\(_2\)-Sr(OiPr)\(_2\)-Ti(OiPr)\(_4\) sources, respectively, in a 4 h alcohol-thermal treatment with 2\% of water added. The sizes of the nanocrystals vary when different metal-organic sources were used, which is also indicated by the extent of the diffraction peak broadening. This effect is attribute to the speed of alcoholysis of different metal organic precursors in ethanol. Additionally, the amount of water (2\% - 5\% wt) plays a minor role on size tunability, which result from the combination and competition of precursors’ hydrolysis and alcoholysis. The measurements from x-ray diffraction confirm the exclusive presence of perovskite-phase BaTiO\(_3\) and (Ba,Sr)TiO\(_3\) in high crystallinity, and are consistent with the results based on the TEM analysis.

### 2.2.4 Spinel Structure of Metal Ferrites

Highly crystalline MFe\(_2\)O\(_4\) (\( M = \) Mn, Ni, Mn\(_{0.5}\)Zn\(_{0.5}\), Ni\(_{0.5}\)Zn\(_{0.5}\)) nanocrystals with a relatively narrow size distribution and reduced tendency toward aggregation were prepared. Typical XRD patterns of as-synthesized cubic spinel powders are given in Figure 2.5. The patterns show the reflection planes (220), (311), (400), (422), (511), (440) and (533), which confirm the presence of single-phase MnFe\(_2\)O\(_4\), NiFe\(_2\)O\(_4\) and their zinc substituted nanocrystals,
with a face-centered cubic structure. Except for the impure phases of Ni for the NiFe$_2$O$_4$ specimen shown in Figures 2b, which has a space group of Fm3m, the remaining peaks correspond to the standard pattern of MnFe$_2$O$_4$ (cubic, space group: Fd3m; JCPDS: 01-073-3820, and NiFe$_2$O$_4$ (cubic, space group: Fd3m; JCPDS: 00-044-1485)

Figure 2.5: XRD patterns of transition metal ferrites synthesized from solvothermal methods: MnFe$_2$O$_4$ (a), NiFe$_2$O$_4$ (b), Mn$_{0.5}$Zn$_{0.5}$Fe$_2$O$_4$ (c), and Ni$_{0.5}$Zn$_{0.5}$Fe$_2$O$_4$ (d).

The average diameter of the magnetic nanocrystals calculated by the Scherrer equation was summarized in Table 2.1. The slight change of particle diameter is attributed to the variation of atomic radius from manganese, nickel to zinc.
Table 2.1 The metal ferrite particle diameter perpendicular to (311) plane calculated by the Scherrer formula.

<table>
<thead>
<tr>
<th></th>
<th>MnFe₂O₄</th>
<th>NiFe₂O₄</th>
<th>Mn₀.₅Zn₀.₅Fe₂O₄</th>
<th>Ni₀.₅Zn₀.₅Fe₂O₄</th>
</tr>
</thead>
<tbody>
<tr>
<td>Diameter</td>
<td>6.1 nm</td>
<td>8.3 nm</td>
<td>8.4 nm</td>
<td>9.2 nm</td>
</tr>
</tbody>
</table>

Figure 2.6 demonstrates XRD reflections of the cobalt ferrite specimens that were prepared by Route 3 at various times. The position and relative intensity of all reflection peaks match well the cubic inverse spinel CoFe₂O₄ structure (JCPDS No. 04-006-4148), without indication of crystalline byproducts. The average diameter of the nanocrystals, calculated by the Scherrer formula was determined to be 9, 11 and 15 nm for 10, 20, and 30 h treatments, respectively, indicating a slight increase in the average diameter with longer thermal treatment. The increase in particle dimension is ascribed to the longer reaction time, which allows and promotes the crystal growth after nucleation in the solvent.

Figure 2.6: XRD patterns of CoFe₂O₄ nanoparticles synthesized via Route 3 with solvothermal process of 10 h (a), 20 h (b) and 30 h (c).
2.3 Transmission Electron Microscopy

2.3.1 Principle of TEM

A detailed introduction of the principle of transmission electron microscopy is written in Chapter 3. In this section basic TEM analysis and characterization is discussed. The advanced TEM analysis with atomic resolution is elaborated in Chapter 3.

2.3.2 Instrumental and Sample Preparation

The TEM images were recorded on a JEOL 3000 F (Akishima-shi, Japan) with accelerating voltage of 300 kV. The nanoparticles were first dissolved in ethanol with a low concentration (~2 mg/ml), followed by 30 min ultrasonication. One drop of the solution was transferred on a 300 mesh carbon film coated copper grid, and baked in air at 60°C for 30 min.

2.3.3 TEM Analysis of (Ba,Sr)TiO$_3$ Nanoparticles

Representative TEM images of the as-prepared (Ba,Sr)TiO$_3$ nanoparticles are displayed at various magnifications (Figure 2.7). An overview image at low magnification (Figure 2.7 a and b) illustrates that the specimen consists of nanosized crystals with a narrow size distribution. Following solvent evaporation during the TEM sample preparation, loose and localized aggregation occurs, possibly due to weak intermolecular interactions amongst and high surface energy associated with the nanoparticles. Images of isolated nanocrystals at higher magnification (Figure 2.7 e and f) show that the particles are mostly spherical in shape with diameter of 12 to 18 nm. Nanocrystals of this size range are predominantly single crystal, below a natural limit for domain formation. The average size determined by statistical analysis of the TEM images is consistent with that calculated by the Scherrer equation from corresponding XRD patterns.
Figure 2.7: Representative TEM micrographs of the $\text{Ba}_{0.7}\text{Sr}_{0.3}\text{TiO}_3$ nanoparticles at various magnifications.
2.3.4 TEM Analysis of CoFe$_2$O$_4$ Nanoparticles

Figure 2.8 shows TEM images of CoFe$_2$O$_4$. The discrete, nanosized cobalt ferrite sample exhibit diameter of 8 to 18 nm with a low distribution. The particle shape is spherical, cubic, or in between. The particle size and shape is less uniform than the case of Ba$_{0.7}$Sr$_{0.3}$TiO$_3$ sample. Loose and localized agglomeration is also observed, possibly due to weak intermolecular interactions and/or magnetic attraction amongst the nanoparticles. The chemical composition was obtained using energy-dispersive X-ray spectroscopy (EDX or EDS, Figure 2.8b). Neglecting the peaks of carbon film and copper grid generated by the TEM sample holder, the ratio of the elemental peaks is in good agreement with expected chemical composition. The average size determined by statistical analysis of the TEM images is consistent with that calculated by the Scherrer equation from the XRD patterns, giving additional evidence of phase purity and single crystallinity.
2.4 Scanning Electron Microscopy

2.4.1 Principle of Scanning Electron Microscopy

Scanning electron microscopy (SEM) is a type of electron microscopy that is used for investigating three-dimensional morphology, texture, chemical composition, and crystalline structure and orientation of materials with a magnification range from micro to nanoscale. SEM produces images by scanning a sample with a focused beam of high-energy electrons. When an
accelerated electron beam hits a sample, the energy carried by accelerated electrons is dissipated as a variety of signals, which include secondary electrons, backscattered electrons, diffracted backscattered electrons, characteristic X-rays, etc. Secondary electrons are primarily used for SEM imaging. Figure 2.9 shows the major components of an electron column.

Figure 2.9: Schematic Diagram of an electron column showing the electron gun, lenses, the deflection system, and the electron detector (adapted from Ref\(^53\)).
2.4.2 Instrumental and Sample Preparation

Ba$_{0.7}$Sr$_{0.3}$TiO$_3$ or CoFe$_2$O$_4$ nanoparticles suspended in ethanol or DMF were drop casted on silica wafer, followed by 80°C thermal treatment in air for 30 min to remove residual solvents. The BST nanoparticle films are optically transparent and the CoFe$_2$O$_4$ films are transparent with a dark brown tone in the visible light range.

Nanoparticle’s morphology and size distribution was evaluated by a Zeiss Supra 55VP SEM (Oberkochen, Germany). Correct instrumental calibration and review of the film over several regions were performed.

2.4.3 SEM Characterization of Ba$_{0.7}$Sr$_{0.3}$TiO$_3$ Nanoparticles

SEM images (Figure 2.10) demonstrate the morphology of pure ceramic nanoparticles spin-coated on silica wafers. The particles are uniform in size with a spherical or cubic shape, and touching one another. Pores and voids are presented between nanoparticle clusters due to solvent evaporation and high surface energy of the nanoparticles. Particles coated with ethanol as solvent (Figure 2.10 c, d, e and f) shows better spread across the silica wafer than those from DMF (Figure 2.10 a and b). This is because the particles synthesized by the alcoholysis of metal-organic source have hydroxyl group chemically or physically attached on the surface, which make them better suspended in ethanol than DMF. Some BST samples were treated with hydrochloric acid before suspended in ethanol (Figure 2.10 e and f), to further identify whether the surface modification / charge will affect the solvent stability and dry film quality. We found that the acid treated nanoparticles were more uniformly and evenly deposited on the substrate, with individual nanoparticles isolated from each other. This is because the H$^+$ ions increase the surface potential and electrostatic interaction amongst individual nanoparticles, which is consistent with the results from dynamic light scattering (DLS).
Figure 2.10: Representative SEM images of $\text{Ba}_{0.7}\text{Sr}_{0.3}\text{TiO}_3$ nanoparticles spin coated on silica wafer using DMF solvent (a and b), ethanol solvent (c, d, e, f), and pretreated with $\text{H}^+$ (e and f).
2.4.4 SEM Characterization of CoFe$_2$O$_4$ Nanoparticles

Cobalt ferrite nanoparticles by themselves show poor spreading and processibility on silica wafer, and spin-coating the pure nanoparticles in solvent generates low quality films, evidenced by the SEM images (Fig. 2.11) with great amount of aggregation, holes and voids between nanoparticle clusters. This is a combined result from solvent evaporation and magnetic interactions between individual particles.
2.5 Dynamic Light Scattering

XRD, TEM and SEM analysis gives information of the solid nanoparticles, which is critical to identify the crystal structure. Nanoparticles’ behavior in a wet form, such as in solution,
is also of great significance, for binary nanocomposite thin film preparation and device fabrication using spin-coating techniques.

2.5.1 Principle of Dynamic Light Scattering

Dynamic Light Scattering, also referred to as Photon Correlation Spectroscopy or Quasi Elastic Light Scattering, is a technique for measuring the size of molecules or particles in solution or suspension with diameter typically lower than 1 µm. The Brownian motion of nanoparticles in suspension causes laser light scatter at different intensities – smaller particles fluctuate more rapidly than larger ones. Analysis of these intensity fluctuations yields the diffusion coefficient and thus the particle size using the Stokes-Einstein relationship:

\[ d(H) = \frac{kT}{3\pi\eta D} \]  

(2.7)

where \( k \) is Boltzmann constant, \( T \) is the temperature, \( \eta \) is the viscosity and \( D \) is the diffusion coefficient. Figure 2.12 demonstrates the components of a typical dynamic light scattering instrument.

Figure 2.12: Schematic diagram of conventional 90° dynamic light scattering instrument
The measurements from DLS describe how a particle diffuses within a solvent. The size obtained is referred to as hydrodynamic diameter, which is the diameter of a sphere that exhibits the same translational diffusion coefficient as the particle. The hydrodynamic size depends not only on the particle core, but also on any surface structure and its kinetics with the medium.

2.5.2 Instrumental and Sample Preparation

The experiment was performed on a Zetasizer Nano ZS (Malvern Instrument). The solution was prepared by dissolving BST nanoparticles in various solvents with concentration of 4 mg/ml. The solution was ultrasonicated, centrifuged and filtered through syringe membrane filters with pore size lower than 0.4 um prior to the measurements, in order to eliminate dust and other large particles so that only the mobility of the single particles will be measured. 1 µl filtered solutions were then transferred into a clear disposable zeta cell. The hydrodynamic size and the zeta potential was measured at room temperature for all samples. 4-6 measurements were conducted for each sample to ensure accuracy.

2.5.3 DLS Analysis of Ba$_{0.7}$Sr$_{0.3}$TiO$_3$ nanoparticles

In general, nanoparticles prepared through wet chemistry routes have a tendency to aggregate and show poor dispersion capabilities. Striving to test and improve the suspension stability, various solvent - Ba$_{0.7}$Sr$_{0.3}$TiO$_3$ nanoparticle combinations were prepared and analyzed by DLS (Table 2.2).
Table 2.2 Comparison of particle sizes obtained from TEM and DLS and their stability tests of different size Ba$_{0.7}$Sr$_{0.3}$TiO$_3$ nanoparticles in various solvents (4 mg/ml at 25°C).

<table>
<thead>
<tr>
<th>Sample</th>
<th>Solvent</th>
<th>Size from TEM (nm)</th>
<th>Hydrodynamic Diameter</th>
<th>Stability</th>
</tr>
</thead>
<tbody>
<tr>
<td>BST-1</td>
<td>Ethanol</td>
<td>5-10</td>
<td>Number Mean (nm)</td>
<td>Intensity Mean (nm)</td>
</tr>
<tr>
<td>BST-2</td>
<td>Ethanol</td>
<td>20-25</td>
<td>10.0</td>
<td>46.2</td>
</tr>
<tr>
<td>BST-3</td>
<td>Ethanol</td>
<td>40-50</td>
<td>35.9</td>
<td>83.1</td>
</tr>
<tr>
<td>BST-4</td>
<td>DMF</td>
<td>5-10</td>
<td>62.7</td>
<td>144.1</td>
</tr>
<tr>
<td>BST-5</td>
<td>2-Methoxyethanol</td>
<td>5-10</td>
<td>3.32</td>
<td>56.4</td>
</tr>
<tr>
<td>BST-6</td>
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<td>5-10</td>
<td>40.5</td>
<td>66.6</td>
</tr>
<tr>
<td>BST-7</td>
<td>Toluene</td>
<td>5-10</td>
<td>N/A</td>
<td>N/A</td>
</tr>
<tr>
<td>BST-8</td>
<td>Ethanol</td>
<td>40-50</td>
<td>1463</td>
<td>1925</td>
</tr>
<tr>
<td>BST-9</td>
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<td>40-50</td>
<td>76.5</td>
<td>114.8</td>
</tr>
<tr>
<td>BST-10</td>
<td>Ethanol with 10% HCl</td>
<td>40-50</td>
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</tbody>
</table>

Ba$_{0.7}$Sr$_{0.3}$TiO$_3$ particles ranging from 5 to 50 nm are dispersible and stable in most polar and nonpolar solvents. For almost all samples the intensity mean of dynamic diameter is around 2-5 times larger than the size from electron microscopy; while the number mean of dynamic diameter is much closer to the TEM size. Since the large particles in solution contribute more to the intensity mean, the results indicate that, while the majority of particles fall into the size range consistent with TEM, there is small portion of nanoparticles aggregated to larger ones with size equivalent to 2-5 times of single particles. Further, although the samples are born with hydroxyl group attached chemically on the surface from the solvothermal process, different solvents have different functional groups that are also physically absorbed by electrostatic absorption or by van der Waals forces to the nanoparticles. Therefore samples with the same dry diameter from TEM (BST-1, 4, 5 and 6) exhibit distinct hydrodynamic diameters. Additionally, comparison of sample 8, 9 and 10 suggests how acid treatment affects suspension stability and particle size. By
increasing the concentration of $H^+$ ions in the system, the pH value decreases and gets away from the isoelectric point of the BST-ethanol solution$^{57}$, leaving the solution better stabilized and nanoparticles isolated from one another.
Chapter 3 Crystal Structural Analysis Using Advanced Transmission Electron Microscopy

Experimental methods for electron microscopy have been pushing the limits of nanoscience and materials science. Over the past two decades, a remarkable development of transmission electron microscopy is the spherical aberration of the objective lens. Image resolution below 1 Å can now be achieved regularly. Locating and identifying individual atoms inside crystal systems has become a very popular and widespread technique.51 Meanwhile, the number of publications making use of scanning transmission electron microscopy (STEM) techniques has increased dramatically recently although the principle of this technique for providing high-resolution structural and analytical information have been known for a long time. The key to the recent popularity is the availability of STEM modes available on major TEM instruments.58

3.1 Principle of Transmission Electron Microscopy

Transmission electron microscope has become a premier tool for nano/micro-structural characterization of materials. A modern TEM is capable of imaging the variations in diffraction (diffraction contrast imaging), imaging the phase contrast of the specimen (HRTEM), obtaining diffraction patterns from selected areas (SAED), and performing electron energy loss spectroscopy (EELS) and energy dispersive spectroscopy (EDS/EDX) measurements for elemental analysis.
3.1.1 TEM

A diagram of components of a typical TEM is shown in Figure 3.1. Transmission electron microscopy produces images from a specimen by illuminating the specimen with highly energetic electrons within a vacuum. A beam of electrons is transmitted through an ultra-thin specimen, interacting with the specimen, and was detected after it passes through. By analyzing the electrons transmitted through the specimen, an image is formed, magnified and focused onto a fluorescent screen, a layer of photographic film, or a CCD camera.
Figure 3.1: Typical components of a modern TEM (adapted from Ref\textsuperscript{51}).

3.1.2 STEM

Figure 3.2 shows a block diagram of a typical TEM with STEM capability. In scanning transmission electron microscope, a narrow, focused electron beam is moved in a raster pattern across the specimen. Transmitted electrons are acquired with a moveable detector in synchronization with the scan. Since STEM permits the acquisition of a “chemical map” by scanning across a sample, it is especially useful for spectroscopy work. Various data from the
specimen can be collected, such as emitted x-rays, secondary electrons, or backscattered electrons.

Annular dark field images are formed in STEM mode by collecting incoherent elastic scattered electrons with an annular dark-field detector. An annular dark field image formed only by very high angle, and is highly sensitive to variations in the atomic number (Z) of atoms in the specimen. Therefore this technique is also called high-angle annular dark-field imaging (HAADF), or Z-contrast images. The contrast of HAADF images strongly depends on the average atomic number in atom columns that is encountered by the incident probe, and is unaffected by dynamical diffraction effects, small changes in objective lens defocus, or specimen
thickness. A schematic diagram of HAADF, conventional ADF and bright field detectors are shown in Figure 3.3 with the range of electron scattering angles.

![Schematic diagram of HAADF, conventional ADF and bright field detectors](image)

Figure 3.3: Schematic of the HAADF detector setup for Z-contrast imaging in a STEM. The conventional ADF and BF detectors are also shown along with the range of electron scattering angles gathered by each detector (Adapted from Ref\textsuperscript{59}).

### 3.1.3 EDS and EELS

Besides diffraction imaging, the high-energy electron beam also generates electronic excitations, which is further used to obtain composition information of a specimen. Analytical TEM uses two types of spectrometries to acquire elemental information from electronic excitations: energy-dispersive x-ray spectrometry (EDS, EDX, or XEDS) and electron energy-loss spectrometry (EELS).

Energy-dispersive X-ray spectroscopy is a technique to perform elemental analysis or chemical characterization available on most TEMs or SEMs. EDS makes use of the X-ray
spectrum emitted by a solid sample illuminated with a focused electron beam to obtain a localized chemical analysis. Every element has a unique atomic structure exhibiting unique set of X-ray peaks. The incident beam excites an electron in an inner, lower-energy shell, ejecting it from the shell leaving an electron hole. The remaining core hole decays quickly, often by the emission of a characteristic x-ray. The number and energy of the X-rays emitted from a specimen are characteristic of the atomic structure of the element from where it was emitted, which enables the determination of the concentrations of different elements in the specimen. In principle, elements from beryllium (Z = 4) to uranium (Z = 92) can be detected. Qualitative analysis involving identification of the lines in the spectrum is fairly straightforward owing to the uniqueness of X-ray spectra.

In electron energy-loss spectrometry, energy losses of the electrons are measured after the electrons have passed through the specimen atoms. These electrons may have lost no energy or have suffered plasmon excitations and core electron excitations. Plasmons are brief oscillations of the free electrons, whose energies (~ 10 eV) increase with electron density. Therefore plasmon excitation spectra can be used to estimate free electron density. Core excitations generated by electrons that ionize atoms are used for microchemical analysis. Local information on chemistry and electronic structure obtained from features in EELS spectra also reveals details of bonding/valence state, the nearest-neighbor atomic structure, their dielectric response, and the specimen thickness. EELS offers higher spatial resolution and analytical sensitivity compared to EDS which include just elemental identification. Figure 3.4 shows a schematic diagram and ray path of an EELS interfaced below the viewing screen of a TEM.
Figure 3.4: Schematic diagram and ray path of an EELS interfaced below the viewing screen of a TEM (adapted from Ref\textsuperscript{69}).
3.1.4 Instrumental and Sample Preparation

The HRTEM, STEM and EELS characterization were performed at Department of Material Science and Condensed Matter Physics, Brookhaven National Laboratory, Upton, New York.

We used a JEOL 3000 F (Akishima-shi, Japan) for HRTEM, and a JEOL ARM 200CF equipped with cold field emission gun and double spherical-aberration correctors for STEM and EELS. The HRTEM was performed with accelerating voltage of 300 kV and the STEM and EELS were with 200 kV electrons. The collection angles for high-angle annular-dark-field (HAADF) detectors were from 68 to 280 mrad. The energy resolution for EELS was about 0.5 eV with 0.25 eV/ch dispersion.

MFe$_2$O$_4$ (M = Mn, Ni, Mn$_{0.5}$Zn$_{0.5}$, Co) nanocrystals were first dissolved in ethanol with a concentration of ~ 2 mg/ml, followed by 30 min ultrasonication. One drop of the as-prepared solution was transferred onto a 300 mesh, carbon film coated copper grid, and baked in air at 80°C for 30 min.

A series of barium manganese titanium oxide (Ba-Mn-Ti-O) crystal samples were synthesized by a gel-collection method$^{60}$ and characterized with STEM and EELS in order to identify the crystal structure and chemical composition. They were first dissolved in ethanol and then deposited on ultrathin carbon grids and air dried.
3.2 Structure Analysis of Transition Metal Ferrites Using HRTEM

3.2.1 MnFe$_2$O$_4$

Images of isolated nanocrystals at various magnifications (Figure 3.5 a and b) confirm the crystallinity and phase purity of the as-synthesized manganese ferrite nanoparticles. The well-defined two-dimensional lattice fringes of 8 nm nanocrystal indicate good crystallinity and lack of structural defects. The measured (022) interplane spacing is 3.094 Å, in good agreement with the plane distance of the reported MnFe$_2$O$_4$ lattice (JCPDS: 01-073-3820). The fast Fourier transformation (FFT; Figure 3.5 c) of the square area of the HRTEM image resembles well the one (Figure 3.5 e) generated by the crystal model in Figure 3.5d. In both images the spots are related to the Fd3m cubic spinel phase of manganese ferrites.
Figure 3.5: HRTEM images of isolated MnFe₂O₄ nanocrystal synthesized by solvothermal method (a and b) and its Fourier power spectrum (c); (d) projection of the spinel structure of MnFe₂O₄ nanoparticle along the <211> zone axis and its corresponding Fourier transformation (e).

3.2.2 Mn₀.₅Zn₀.₅FeO₄

The HRTEM micrograph of Mn₀.₅Zn₀.₅FeO₄ nanoparticles (Figure 3.6) is recorded in zone axis <111> with 50% substitution of manganese by zinc. The positions of the white spots in Figure 3.6 b are in good agreement with those of a cubic spinel structure (Fd₃m) demonstrated in Figure 3.6 d along the <111> direction. The measured (20̅2) interplane distance is 2.83 Å, smaller than pure MnFe₂O₄ crystals due to the introduction of zinc with a smaller ionic radius.
As shown by the FFT (Figure 3.6 c), HRTEM patterns are corresponding with strong satellite peaks in reciprocal space. The modeled structure of \( \text{Mn}_{0.5}\text{Zn}_{0.5}\text{Fe}_2\text{O}_4 \) depicted in Figure 3.6 d resembles well the experimental micrograph (Figure 3.6 b), with the corresponding FFT (Figure 3.6 e) exactly match the live FFT (Figure 3.6 c).

Figure 3.6: HRTEM micrographs of isolated \( \text{Mn}_{0.5}\text{Zn}_{0.5}\text{FeO}_4 \) nanocrystal at various magnifications (a and b) and its corresponding FFT (c); projection of the spinel structure of \( \text{Mn}_{0.5}\text{Zn}_{0.5}\text{Fe}_2\text{O}_4 \) nanoparticle along the <111> zone axis (d) and its corresponding FFT (d).
3.2.3 NiFe$_2$O$_4$

Similar results are also observed for NiFe$_2$O$_4$ nanoparticles (Figure 3.7). The lattice structure and fringe is well defined as observed in the high magnification images (Figure 3.7 b). The measured distance between (040) planes of 2.18 Å is in good agreement with reported data (JCPDS: 00-044-1485) with tiny variation. Consistency between live FFT (Figure 3.7 c) and modeled FFT (Figure 3.7 e) further confirms high crystallinity and lack of defects.

Figure 3.7: HRTEM images of isolated NiFe$_2$O$_4$ nanocrystal at various magnifications (a and b) and its corresponding FFT; modeled structure of NiFe$_2$O$_4$ nanoparticle (d) and its corresponding FFT (e).
3.2.4 CoFe$_2$O$_4$

HRTEM micrograph in Figure 3.8 gives evidence of crystallinity and phase purity of the solvothermal-synthesized cobalt ferrites nanoparticles. The well-defined two-dimensional lattice fringes of 10-nm nanocrystal indicate good crystallinity with no observable structural defects. The plane distance is measured as 2.99 Å, in good agreement with the (220) interplane spacing of the reported cubic CoFe$_2$O$_4$ lattice. The positions of the spots in the reciprocal space in live FFT corresponds well with inverse spinel structure (Fd-3m) of cobalt ferrite seen along the <111> direction.

Figure 3.8: High resolution transmission electron microscopy image of CoFe$_2$O$_4$ nanoparticle seen along <111> zone axis (a), stimulated diffraction patterns (b), and the corresponding live FFT (c).
3.3 Structure Analysis of CoFe$_2$O$_4$ Using STEM

Considering that the magnetic properties of the cobalt ferrite nanocrystals are to be compared with the known bulk material, unequivocal identification of the crystal phase, symmetry, and composition of an individual nanocrystal is highly desirable. To further verify the crystal structure and composition, the samples is studied by high angle annular dark field STEM and compared with a calculated model. Figure 3.9 a illustrates the projection of the atomic structure model of CoFe$_2$O$_4$ along the <011> zone axis, with oxygen atoms removed out. Figure 3.9 b shows the HAADF-STEM image of the as-prepared nanocrystals, where the bright spots represent cobalt or iron atoms. The calculated positions of the transition metal atoms are superposed on the HAADF-STEM image, indicating that the elements and positions suggested in the model precisely fit those observed in STEM mode. As the contrast of the high-angel electron scattering scales roughly with the atomic number ($Z^{1.7}$)\textsuperscript{61}, oxygen atoms are not visible while cobalt and iron atoms are present. Since the atomic numbers of cobalt ($Z = 27$) and iron ($Z = 26$) are close with each other, it is difficult to distinguish one another in the HAADF image. However, some columns exhibit stronger contrast/intensity than others in Figure 2b, suggesting a higher atom density than the dimmer ones, which is consistent with the inverse spinel structure of the cobalt ferret lattice projected along the <011> zone axis. In addition, the measured interplane distance of (111) planes (4.80 Å) is in good agreement with reported CoFe$_2$O$_4$ crystal information (JCPDS No. 04-006-4148).
Figure 3.9: Projection of the inverse spinel structure and the HAADF STEM image of CoFe$_2$O$_4$ nanoparticles. (a) Projection of the inverse spinel structure of CoFe$_2$O$_4$ along the <011> zone axis. Red balls represent iron atoms; green balls represent cobalt atoms; oxygen atoms have been removed for clarity. (b) Atomic resolution HAADF-STEM image of CoFe$_2$O$_4$ nanoparticles. Bright spots correspond to cobalt and ferrite atoms. Superimposed points are cobalt and ferrite atom positions calculated from the crystal model.

3.4 Structure and Composition Analysis of Ba-Mn-Ti-O Crystal

Complex oxides of main group and transition metals have been of longstanding interest due to the extensive range of properties derived from their electronic structure, and the library of metallic ions that can be intersubstituted in order to tune or transform the electronic behavior.
One recurring aspect is the presence of partially filled $d$- (or $f$-) orbitals that lead to strongly correlated behavior that differentiates complex oxides definitively from metals or semiconductors. Single phase oxides that contain three or more metals provoke excitement in structure and property discovery, especially where the properties are remarkable: CaCu$_3$Ti$_4$O$_{12}$ possesses a giant dielectric constant, YBa$_2$Cu$_3$O$_{x}$ and extended family, is famously a high temperature superconductor, La$_{0.7}$Ca$_{0.3}$Mn$_{1-y}$Ti$_y$O$_3$ is a giant magneto-resistive material, Sr$_3$Co$_2$Fe$_{24}$O$_{41}$ exhibits a low field room temperature magnetoelectric effect, and La$_{0.67}$Ca$_{0.33}$MnO and PbZr$_{0.95}$Ti$_{0.05}$O$_3$ have been reported to possess giant magnetocaloric and electrocaloric effects respectively. In the case of multiferroics research is driven by the technologically exciting prospect of controlling charges by applied magnetic fields and spins by applied voltages, for application in sensors, transducers, 4-state logic, and spintronics. Pursuing single phase multiferroics, which are uncommonly rare, especially when the magnetoelectric coupling is not strain-mediated, provides strong motivation to push further for synthetic exploration and rational design of complex oxides. Progress has been limited by physical restrictions on the co-existence of substantive magnetic or electrical polarization in a single compound. Composite materials can produce magnetoelectric effects through strain mediated coupling, but the prospect of intimate coupling in a single crystal phase remains of great interest, since it potentially relies on fundamental quantum mechanical effects. Recently, the field has grown to explore, both theoretically and experimentally, the means for placing lower constraints on the coexistence of ferroelectricity with ferromagnetism, such as “improper ferroelectrics.” This inspires further the potential for finding field tunable magnetoelectric behavior in novel compounds, in particular, complex oxides.
Our group developed a project, led by Dr. Shuangyi Liu,\(^6\) that targeted synthesis of complex manganese and titanium oxide frameworks since they present possibilities for achieving direct spin-polarization coupling due to the diversity in magnetism of the manganese cations (S=5/2, 2 and 3/2 for Mn\(^{2+}\), Mn\(^{3+}\) and Mn\(^{4+}\) respectively), combined with the “\(d^0\)-ness” of Ti\(^{4+}\) cations, which can facilitate long range ordering through LUMO hybridization with O 2p orbitals, and drive bulk electric polarization.\(^3\) In nature, and excluding silicates, there are fourteen oxides that contain Ba, Ti, and O ions, and fifteen that contain Ba, Mn and O ions (co-residing with a number of other metal cations such as Fe, Cr, V etc.). Synthetic Ba-Mn-Ti-O compounds, prepared under high temperature conditions, have been reported.\(^7\)\(^4\),\(^7\)\(^5\)

The barium manganese titanium oxide crystal was synthesized from a gel-collection method. Gel collection, developed in our group, is a low temperature precursor driven technique inspired from sol-gel,\(^7\)\(^6\) nucleation/growth mediated nanocrystal synthesis,\(^7\)\(^7\) and non-hydrolytic approaches.\(^7\)\(^8\) The notable features of the gel-collection pathway are: (i) the final product structure can, in part, be determined through selection of the type of metal alkoxide precursor. For example, structures containing edge-shared octahedra are favored by acetylacetonate coordination complexes, while corner-shared octahedra in structures are best replicated by alkoxides. Gel-collection was applied to the synthesis of Barium, Manganese, and Titanium compositions, with the goal of introducing multifunctionality into a lattice framework by using Mn and Ti ions to obtain complimentary magnetic and dielectric/ferroelectric properties. The synthetic approach allowed for a family of Ba-Mn-Ti-O compounds to be prepared with tunability in composition. Initially, the structure of these compounds was not known, and the structure needed to be solved. Our group had collaboration with Columbia University to perform X-ray analysis and solve the structure by powder X-ray diffraction and simulation. In parallel,
we investigated the structure by high resolution TEM at Brookhaven National Labs. To investigate the morphology, structure and composition of this new material system, STEM, together with EDS and EELS characterization was performed.

### 3.4.1 STEM Analysis of Ba-Mn-Ti-O Complex Oxide

Figure 3.10 presents the morphology of the complex oxide at various magnifications with bright field images and their corresponding HAADF images. The nanocrystal is manifested as laminate atomic arrangement with thick center and thin semi-spherical edges. They exhibit high crystallinity with no observable evidence of defects. The atomic resolution HAADF image from spherical abbreviated STEM (Figure 3.11) further confirms the crystallographic structure of hollandite group, A\textsuperscript{II}[M\textsuperscript{IV}, M\textsuperscript{III}]O\textsubscript{16}. The projection of modeled hollandite structure fits precisely the observed diffraction patterns, with the brighter and bigger spots corresponding to barium (Z = 56) and the dimmer and smaller spots corresponding to manganese (Z = 25) and titanium (Z = 22).
Figure 3.10: Bright field (BF) STEM images (a, c, e) and corresponding HAADF STEM images (b, d, f) of Ba-Mn-Ti-O complex oxide crystals collected at various magnifications.
3.4.2 EDS and EELS Analysis of Ba-Mn-Ti-O Complex Oxide

In order to investigate the atomic ratio of Ba, Mn, Ti and O elements in the crystal, energy-dispersive x-ray spectrometry (EDS) and electron energy-loss spectrometry (EELS) was performed.

Figure 3.12 shows the energy-dispersive x-ray spectrums from three different areas of a sample. Figure 3.13 and 3.14 show two Electron energy-loss spectrums of Ba-Mn-Ti-O complex oxide. The corresponding elemental composition is summarized in Table 3.1. The elemental ratio acquired from EDS is in good agreement with the one obtained from EELS, with standard
derivation below 3%. The final chemical formula is determined to be BaMn$_3$Ti$_4$O$_{14.25}$, solved by a combination of synchrotron X-ray diffraction, scanning transmission electron microscopy (STEM) and X-ray photoelectron spectroscopy (XPS).

Figure 3.12: Energy-dispersive x-ray spectrums (EDS) of Ba-Mn-Ti-O complex oxide obtained from three areas.
Figure 3.13: Electron energy-loss spectrums (EELS) of Ba-Mn-Ti-O complex oxide.
Figure 3.14: Electron energy-loss spectrums (EELS) of Ba-Mn-Ti-O complex oxide.

Table 3.1 Elemental ratio of Ba-Mn-Ti-O complex oxide according to EDS and EELS spectrums.

<table>
<thead>
<tr>
<th>Element</th>
<th>EDS 1</th>
<th>EDS 2</th>
<th>EDS 3</th>
<th>EELS 1</th>
<th>EELS 2</th>
<th>Average</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ba (%)</td>
<td>6.08</td>
<td>4.97</td>
<td>5.78</td>
<td>4.42</td>
<td>4.54</td>
<td>5.31 ± 0.76</td>
</tr>
<tr>
<td>Mn (%)</td>
<td>10.09</td>
<td>10.51</td>
<td>13.4</td>
<td>11.93</td>
<td>13.46</td>
<td>11.48 ± 1.50</td>
</tr>
<tr>
<td>Ti (%)</td>
<td>14.39</td>
<td>15.55</td>
<td>14.80</td>
<td>19.23</td>
<td>21.07</td>
<td>15.99 ± 2.21</td>
</tr>
<tr>
<td>O (%)</td>
<td>69.43</td>
<td>68.97</td>
<td>66.28</td>
<td>64.42</td>
<td>60.92</td>
<td>67.28 ± 2.36</td>
</tr>
</tbody>
</table>
3.4.3 Conclusion on Ba-Mn-Ti-O System

The structure of the oxide was solved by a combination of synchrotron X-ray diffraction, scanning transmission electron microscopy (STEM) and X-ray photoelectron spectroscopy (XPS), determining the structure to be $\text{BaMn}_3\text{Ti}_4\text{O}_{14.25}$. The crystal structure belongs to the hollandite supergroup, $\text{A}^{II}[\text{M}^{IV}, \text{M}^{III}]\text{O}_{16}$. X-ray powder diffraction data was collected at the National Synchrotron Light Source (NSLS, Brookhaven National Laboratory) and analyzed using atomic pair distribution function analysis\(^\text{60}\). The refinement results closely resemble the redledgeite structure ($I\bar{4}/m$). The Mn and Ti cations are located inside corner and edge-shared oxygen octahedra with Ba cations in the channels (as Figure 3.15 b). The Ba atoms have local displacements along the $z$-axis, with a fraction sitting off their equilibrium sites, identifiable at low-$r$ range (< 20Å). Imaging of the atomic arrangement by HRTEM is presented in Figure 3.15 c and 2d. The spherical-aberration corrected STEM image shows the hollandite type lattice, projecting down the channels (Figure 3.15 c and d). At lower magnification there is evidence of a small (< 6°) lattice rotation, attributed to possible local cation disorder but not twinning. XPS confirms the presence of stable Ti$^{4+}$ and mixed Mn$^{3+}$ and Mn$^{4+}$ cations. No Ti$^{3+}$ or Mn$^{2+}$ is detected. The PDF refinement, the EDX, EELS and XPS analysis, all corroborate the Ba:Mn:Ti stoichiometric ratio to be 1:3:4, identical to the initial reactant concentration.
Figure 3.15: Structural characterization of BMnT-134 (BaMn$_3$Ti$_4$O$_{14.25}$) a, Synchrotron X-ray powder diffraction and PDF refinement patterns of crystalline BaMn$_3$Ti$_4$O$_{12.5}$. b, crystal structure and model of the spin and charge distribution in the lattice. c and d, the atomic images obtained by spherical-aberration corrected STEM, with the zone axis is along [001] (adapted from Ref$^{60}$).
Chapter 4 Thin Film Capacitor Fabrication and Their Dielectric Properties

4.1 Thin Film Fabrication Using Spin-Coating Techniques

Pure nanoparticle films prepared by spin-coating show poor processibility since it generates holes and voids unfavorable for device fabrication. In order to fabricate high quality films, polymers were introduced as host or matrix, to build a smooth, compatible, and functional interface. Polymers such as parylene-C (PyC), Polyvinylidene fluoride (PVDF) or polyvinylpyrrolidone (PVP) allow facile processing at lower temperatures into a variety of forms, such as 0-3 particulate type or 2-2 laminate multilayers.

Nanoparticle thin films with variable thickness can be prepared on silica wafer, metal electrode coated glass substrates or flexible polyethylene naphthalate (PEN) substrates by multiple spin-coating followed by thermal treatment.

4.1.1 BST-Polymer Films

(Ba,Sr)TiO$_3$ nanocrystal thin films were prepared on Si wafer, glass, or Polyethylene naphthalate (PEN) substrates by cast-coating or spin-coating of an ethanol suspension of a concentration around 20 mg/ml. First the substrates were spin-casted with BST/ethanol solution at a speed of 1000 rpm for 45 sec for four times, and baked by a hot plate at 90 °C for 5 min. Then BST/FA solution (diluted 1:1 with ethanol) was coated at 1000 rpm for 45 sec for four times, followed by a hot plate thermal treatment at 60 °C for 5 min. The whole procedure from the begging was repeated three times to achieve a total of 12 BST/FA spin layers. A vacuum bake for 12 hr was performed starting at 60 °C and increased to 130 °C. Finally, a 100 nm thick
PyC layer was deposited by chemical vapor deposition. This process forms a BST/FA/PyC composite layer of around 100 nm thick, with optical transparency in the visible range.

### 4.1.2 CoFe$_2$O$_4$-polymer Films

The CoFe$_2$O$_4$-polymer nanostructured films were prepared by similar fashion, which is multiple spin coating or cast coating followed by thermal treatment (Figure 4.1). DMF was used to dissolve CoFe$_2$O$_4$ nanoparticles and P(VDF-HFP) pallets or polyvinylpyrrolidone (PVP) powder separately, with concentration of 20 mg/ml for both CFO/DMF and P(VDF-HFP)/DMF or PVP/DMF solutions. Then under ultrasonication the two suspensions were mixed, yielding a series of CFO+P(VDF-HFP) / DMF or CFO+PVP / DMF suspensions with various CFO versus polymer ratio. On top of silica wafer or glass (with or without bottom electrode) pure ethanol was spin-coated at 9000 rpm for 1 min to clean substrates. Then the as prepared CFO+P(VDF-HFP) / DMF or CFO+PVP / DMF suspension at a speed 300-1000 rpm for 30 sec, followed by hot plate thermal treatment at 60°C for 30 sec to remove the solvent residual and to make the films stabilized and evenly spread on the substrate surface. The “spin-coating + baking” step was repeated multiple time (6-14) times to achieve various film thickness. The as prepared thin films further underwent thermal treatment at 90°C under vacuum overnight. The thickness of the obtained thin films (200 nm to 1.6 μm) was controlled by the times and/or rotation speed of the spin coating. The CFO-polymer films are optically transparent with a dark brown tone.
4.2 Electrode Deposition and Fabrication of Capacitors

4.2.1 Substrate Cleaning and Instrumental

Bare glass substrates were cleaned by the following procedure. First, acetone, followed by IPA, followed by deionized water was used to rinse both sides of the glass. The substrates was then soaked in diluted Micro-90 cleaning solution under ultrasonication for 30 min. After three time cleaning with deionized water, the substrates were rinsed again with acetone, followed by IPA, followed by deionized water. The substrates were finally exposed under UV radiation for 5 minutes after air gun drying.
Flexible PEN substrates were rinsed by acetone, followed by IPA, followed by deionized water, and then dried by air gun to remove any dirt or stain before electrode deposition.

The thermal evaporator used for electrode deposition was an Angstrom engineering AMOD evaporation system, which was integrated with a glove box. This integration allows evaporation and PVD processes to be performed under nitrogen environment without exposure to air and water. The evaporation boats are from R.D. Mathis. The boat for copper evaporation is molly boats with alumina coating. All metal pallets are ordered from Kurt J. Lesker. The 50 mm × 50 mm and 20 mm × 20 mm bare glass substrates are from Luminescence Technology Corporation.

### 4.2.2 Electrode Deposition

There were two types of parallel plate capacitors fabricated: one with area of 20 mm × 40 mm, the other with square area of 1 mm². The patterns of electrodes were controlled by using different metal stencil shadow masks. Both large and small area capacitors were made by three steps: a) bottom electrode deposition, b) thin film spin-coating and c) top electrodes deposition.

In a typical top electrode deposition of a large area electrode (20 mm × 40 mm), chrome was first deposited directly on glass for better attachment between electrodes and substrates. It was evaporated at a rate of 0.3 A/s with the substrates at room temperature under a pressure of < 1.5 × 10⁻⁶ torr. Copper was deposited after Cr at a rate of 1.0 A/s under a pressure of < 2.0 × 10⁻⁶ torr. One more layer of gold was deposited after copper at a rate of 0.8 A/s under a pressure of < 1.5 × 10⁻⁶ torr. The thickness of the top electrodes is around 450 nm (7.5 nm chrome, 400 nm copper and 40 nm gold), controlled by the deposition time of each metal. After the thin film was spin coated and dried, 400 nm thick, top electrodes composed of copper were deposited under
the same condition. A schematic illustration of the procedure to fabricate a large area capacitor is shown in Figure 4.2, and finished devices are shown in Figure 4.3.

<table>
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<th>Substrate Cleaning</th>
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<tr>
<td>Glass:</td>
</tr>
<tr>
<td>• soap wash, sonication</td>
</tr>
<tr>
<td>• acetone, IPA, DI water</td>
</tr>
<tr>
<td>• UV treatment</td>
</tr>
<tr>
<td>PEN:</td>
</tr>
<tr>
<td>• acetone, IPA, and DI water</td>
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<table>
<thead>
<tr>
<th>Bottom Electrode Deposition</th>
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</thead>
<tbody>
<tr>
<td>Chrome (on glass only, 7.5 nm)</td>
</tr>
<tr>
<td>Copper (400 nm)</td>
</tr>
<tr>
<td>Gold (40 nm)</td>
</tr>
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</table>

<table>
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<tr>
<th>Dielectric Film Preparation – Spin Coating</th>
</tr>
</thead>
<tbody>
<tr>
<td>Step 1: BST/EtOH at 1k rpm × 45 s × 4; bake at 90°C × 5 min</td>
</tr>
<tr>
<td>Step 2: BST/TA at 1k rpm × 45 s × 4; bake at 90°C × 5 min</td>
</tr>
<tr>
<td>Repeat Step 2 for 3 times</td>
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<table>
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<tr>
<th>Parylene C Deposition</th>
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<tbody>
<tr>
<td>12-hour vacuum bake, starting at 60 °C, rising to 130 °C</td>
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<td>100 nm Parylene-C by CVD</td>
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</tbody>
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<tr>
<th>Top Electrode Deposition</th>
</tr>
</thead>
<tbody>
<tr>
<td>Copper (400 nm)</td>
</tr>
<tr>
<td>Gold (40 nm)</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Test &amp; Failure Analysis</th>
</tr>
</thead>
<tbody>
<tr>
<td>Impedance Analyzer</td>
</tr>
<tr>
<td>SEM</td>
</tr>
</tbody>
</table>

Figure 4.2: Schematic diagram of the procedure to fabricate 20 mm × 40 mm capacitors on both glass and PEN substrates.
Small area capacitors (1 mm$^2$) were deposited with 60 nm thick silver for both bottom and top electrodes. 1 mm × 5mm shadow masks were used, by depositing bottom electrodes at one direction and rotating the mask 90° for top electrodes, leaving the composite film sandwiched between two electrodes with square crossed area of 1 mm$^2$ (Figure 4.4).
Figure 4.4: Array of 1mm² capacitors prepared on glass substrates using Ba$_{0.7}$Sr$_{0.3}$TiO$_3$ (a) and CoFe$_2$O$_4$-P(VDF-HFP) (b) as dielectrics, and a schematic diagram of these devices (c).

### 4.3 Scanning Electron Microscopy Characterization

#### 4.3.1 Instrumental and Sample Preparation

Nanoparticle-polymer thin film’s morphology and texture were evaluated by a Zeiss Supra 55VP SEM (Oberkochen, Germany). Substrate was scored and fractured in order to observe film cross sections. Correct instrumental calibration and review of the film over several regions were performed, and the thicknesses could be determined to within ±7%.
4.3.2 BST-Polymer Films

Efforts were made in investigating advanced dielectric formulations to determine a recipe that is effective on both glass and PEN substrates, with high yield and reliable quality. The PyC layer was added to mitigate any pinholes in the composite dielectric layer. Figure 4.5 shows SEM images of BST film on a silica wafer with and without a top layer of PyC. Without the polymer the film shows holes and pores among nanoparticle clusters (Figure 4.5 a). By depositing ~ 100 nm PyC, continuous, crack-free BST/PFA/PyC films are prepared. The average film thickness is 300 – 500 nm with tunability. This recipe largely improved the yield, with 3 out of 4 working devices from the initial batch.

Following the fabrication of single-layer BST/PFA/PyC capacitors, a second dielectric layer and another top electrode was applied in an effort to bring higher device capacitance, by both spin-coating and spray coating. These two-layered devices were unsuccessful due to shortage. However, cross-section SEM images reveal the heterostructure of the devices, with PyC capping layer continuous cover the dielectric (Figure 4.6). BST/FA films prepared by spay (Figure 4.6 b) shows a fairly denser texture than those prepared by spin-coating (Figure 4.6 a).
Figure 4.5: SEM images of pure BST and BST-Parylene laminate films spin coated on silica wafer.
Figure 4.6: SEM cross-section of two-layer BST/PFA/PyC capacitors on glass substrate by spin-coating (a) and spray-coating (b) the dielectric film.
4.3.3 CoFe$_2$O$_4$-Polymer Films

In terms of transition metal ferrites – polymer films, interest is focused on fabricating 0-3, particulate type nanocomposite with an intimate physical interaction between nanoparticles and polymer. Emphasis is on preparing homogenously film with CoFe$_2$O$_4$ nanoparticles evenly embedded in polymer matrix so any concerted interactions between the two phases is observable.

Figure 4.7 demonstrates typical top and cross-sectional SEM images of the CFO-polymer films. The top view of as-prepared film indicates that monodisperse, ultrafine cobalt ferrite nanoparticles are well embedded in the polymer matrix, forming typical 0–3, particulate type nanocomposites. Loose and localized agglomeration occurs partially because of the magnetic attraction among the nanocrystals. Defects, pinholes, or phase separation are not observed. The cross-sectional image confirms the thickness of the freestanding film of approximately 1.5 µm, which can be mediated by spin coating. The observation of intimate physical contact between the CFO and polymer phase components is a good starting point for attempting to build mechanical, magnetic, or electrical coupling between two.
Figure 4.7: Top (a) and cross sectional (b) view SEM images of CoFe$_2$O$_4$/P(VDF-HFP) composite thin films deposited on silica water (CFO content: 25 wt %; film thickness: 1.1 µm).

4.4 Dielectric Property Characterization

Dielectric measurements including frequency dependence of capacitance or dielectric constant ($\varepsilon'$), and dielectric loss (tan $\delta$), were measured by a) an HP4284A LCR meter or HP4156C semiconductor parameter analyzer in the frequency range of 10Hz to 1MHz, for the BST/PFA/PyC devices, and b) an Agilent 4294A precision impedance analyzer in the frequency region of 100 to 1M Hz for CFO/polymer devices. The electric field – polarization hysteresis was measured in air with a Radiant Precision Workstation.

4.3.1 Barium Strontium Titanate – Parylene C

Figures 4.8 displays the impedance testing results of the (BST/PFA/PyC) devices. Capacitance of the 8 cm$^2$ device is above 75 nF and 70 nF up to 100 kHz for glass and PEN substrates, respectively. Similarly the loss tangent is very low (< 0.04 for both substrates) in the
same frequency range. Performance degraded above 100 kHz, the cause of which is related to the relatively high series resistance losses due to the thin 400 nm Cu electrodes and the contact resistance with the impedance probes.

Figure 4.8: Capacitance and loss tangent of single-layer BST/PFA/PyC devices (2 cm × 4 cm) prepared by spray coating on glass (a) and PEN (b) substrates.
4.3.2 CoFe$_2$O$_4$ – P(VDF-HFP) Nanocomposite$^{79}$

Continuous and crack-free CFO nanocrystal thin films of various CFO content were prepared on metal electrode-coated 1 mm$^2$ substrates. The effective permittivity ($\varepsilon_{\text{eff}}$) and loss/dissipation factor (tan $\delta$) of the ferrites/polymer thin films (thickness of approximately 1 µm) were measured over the frequency region from 100 Hz to 1 MHz (Figure 4.9). Both the dielectric constant and loss tangent of the films show a systemic increase as a function of the loading of the cobalt ferrite loadings. The measured dielectric constant of the pure P(VDF-HFP) films is 8 at 100 Hz, consistent with the data from other groups$^{80,81}$, and increases to 44 in the case of the 30 wt.% CFO samples, by including higher dielectric constant magnetic component ($k$(CoFe$_2$O$_4$) $\approx$ 400)$^{82}$ (Figure 4.9 a). Electric polarization in ferrites originates from the electronic exchange between Fe$^{2+}$ and Fe$^{3+}$ irons and hole transfer between Co$^{2+}$ and Co$^{3+}$ ions in the spinel structure, which fails to follow the alternating electric field beyond a certain frequency$^{83}$. When the space charge carriers cannot keep up and lag behind the alternation of the electric field and its direction, the composites' dielectric constant and loss drops monotonically with frequency. Once the frequency goes beyond 10 kHz, a relaxation mechanism with the P(VDF-HFP) phase dominates the overall behavior of the effective permittivity$^{49}$. The decrease in loss (Figure 4.9 b) with frequency at low frequencies (<1 kHz) is associated with the ionic DC conduction contribution from P(VDF-HFP), which generates spatial charge polarization$^{84}$. The sharp increase in loss above 100 kHz leads to degraded performance, the cause of which is suspected to be relatively high series resistance losses due to the thin 400 nm Cu electrodes and contact resistance with the impedance probe. Figure 4c further demonstrates the dielectric constant as a function of CFO content. The nanocomposites exhibit a low composition dependency with lower slope for 100 kHz, since the dielectric behavior is dominated by the copolymer phase. The PVP films generally
exhibit lower permittivity (Figure 4.8 d) because the PVP polymer possesses a lower intrinsic dielectric constant of 5.1 (at 100 Hz)\textsuperscript{85}.

Figure 4.8: Dielectric properties of the CFO/polymer thin films. Effective permittivity (a) and loss tangent (b) of CFO/P(VDF-HFP) nanocomposite with frequency; effective permittivity as function of CFO content (c); effective permittivity of CFO/PVP films.

In particulate nanocomposites with nanoscale fillers discretely embedded in a matrix, the effective permittivity of the films can be predicted by the modified Kerner model (or Kerner equation)\textsuperscript{24,86} as shown in Equation 4.1:
where

\[
A = \frac{3\varepsilon_h}{\varepsilon_f + 2\varepsilon_h}
\]  

(4.2)

and

\[
B = 1 + \frac{3f_f(\varepsilon_f - \varepsilon_h)}{\varepsilon_f + 2\varepsilon_h}
\]  

(4.3)

The effective permittivity of the composite can be estimated by the average of the host and the filler’s dielectric constant (\(\varepsilon_h\) and \(\varepsilon_f\)) in which the contributions are weighted by the content of each phase (\(f_f\) for filler and \(f_h\) for host, Equation 4.1-4.3). The measured and calculated effective permittivities for both P(VDF-HFP) and PVP films are summarized in Table 4.1.

Table 4.1 Comparison of effective permittivity of the CFO/polymer films at 100 kHz from experimental and modified Kerner model.

<table>
<thead>
<tr>
<th>Sample</th>
<th>(\varepsilon_{\text{eff}}) (measured)</th>
<th>(\varepsilon_{\text{eff}}) (calculated from Kerner equation)</th>
<th>(\Delta\varepsilon_{\text{eff}})</th>
</tr>
</thead>
<tbody>
<tr>
<td>P(VDF-HFP) films</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>10 wt.% CFO</td>
<td>9.1</td>
<td>7.3</td>
<td>+1.8</td>
</tr>
<tr>
<td>20 wt.% CFO</td>
<td>19.08</td>
<td>13.44</td>
<td>+5.64</td>
</tr>
<tr>
<td>30 wt.% CFO</td>
<td>28.56</td>
<td>19.71</td>
<td>+8.85</td>
</tr>
<tr>
<td>PVP films</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>10 wt.% CFO</td>
<td>9.17</td>
<td>8.82</td>
<td>+0.35</td>
</tr>
<tr>
<td>20 wt.% CFO</td>
<td>14.59</td>
<td>13.62</td>
<td>+0.97</td>
</tr>
<tr>
<td>30 wt.% CFO</td>
<td>18.05</td>
<td>19.90</td>
<td>−1.85</td>
</tr>
</tbody>
</table>

The effective permittivity of the P(VDF-HFP) films shows a distinctive and systematic increase relative to the theoretical values predicted by the Kerner equation, contrary to the expectations based solely on composited effective. This is contrasted with PVP films, which
follows expected behavior for a simple combination of two components, with $\varepsilon_{\text{eff}}$ shows dramatically less deviation between experiment and calculation. This observation, of the deviating behavior of CFO/P(VDF-HFP), is interesting and strongly suggests additional interactions between the polymer and nanoparticles, which we think is the elastic and interfacial effect between the magnetic filler and the piezoelectric matrix. Due to the piezoelectric effect, P(VDF-HFP) goes through lattice distortion under an applied electric field, which leads to local stresses and strain at the CFO-copolymer interface. P(VDF-HFP) is a thermal shrinking polymer, which makes a complete physical coverage over the nanoparticle surface. Both CFO and P(VDF-HFP) are mechanically hard, with Young's modulus of 141.6$^{87}$ and 237 GPa$^{88}$, respectively, therefore the interfacial stress will be inversely applied to the copolymer via strong elastic interactions. The spatial charges and electric dipoles amongst the copolymer matrix are redistributed, manifested as derivation of effective permittivity from the Kerner model. With higher nanoparticle content, the interfacial elastic effect is stronger, with a more pronounced derivation from the theoretical value.
Chapter 5 Magnetic Property and Magnetoelectricity in CoFe$_2$O$_4$ nanocrystal-P(VDF-HFP) Thin Films

5.1 Magnetic Properties of Pure CoFe$_2$O$_4$ Nanocrystals

Magnetic measurements of the CoFe$_2$O$_4$ nanocrystals were conducted in both ZFC/FC, and hysteresis modes were analyzed. Figure 5a shows the low field (100 Oe) magnetization dependence with temperature (1.84 to 400 K) in ZFC/FC modes. After a ZFC process, the magnetization of the ferrite nanoparticles increases with rising temperature. Unlike other transition metal ferrite nanoparticles (e.g., Fe$_3$O$_4$, NiFe$_2$O$_4$, and MnFe$_2$O$_4$), no maximum magnetization is detected in the ZFC process, indicating that the blocking temperature ($T_b$) of CoFe$_2$O$_4$ nanoparticles is above 400 K, which is consistent with reported data of $T_b$(CoFe$_2$O$_4$) = 525 K. Additionally, an irreversible magnetic behavior is indicated by the splitting between the ZFC and FC curves. The irreversibility arises from the competition between the energy required for magnetic moment reorientation against the energy barrier associated with magnetoelectricity and the crystalline anisotropy. The field-dependent magnetization at ambient temperature (Figure 5b) shows a hysteresis with coercivity of 400 Oe, suggesting typical ferrimagnetic behavior. The coercivity represents the strength of the field that is needed to surpass the anisotropy barrier. The saturation magnetization ($M_s$) and remnant magnetization ($M_r$) is 66 and 10 emu/g, respectively, comparable with CoFe$_2$O$_4$ nanocrystals obtained by other approaches with similar sizes. The $M_s$ value of 66 emu/g is equivalent to magnetic moment dipole of 21.6 $\mu_B$ per cubic cobalt ferrite unit cell, which is 2.7 $\mu_B$ from each Co$^{2+}$ ion. Generally Co$^{2+}$ ions can offer three net spin magnetic moments. The lower value of magnetic moment and subsequent saturation magnetization of these CFO nanoparticles results from the high surface area and concurrent
surface disorder. At room temperature, the magnetic anisotropy prevents the magnetization direction of the nanocrystals to completely follow the direction of the external magnetic field.

Figure 5.1: Zero field-cooled and field-cooled (ZFC/FC) and room temperature magnetization curves (a) and hysteresis loop (b). Measured for pure CoFe$_2$O$_4$ nanoparticles. Inset, central region on an expanded scale.
5.2 Magnetoelectricity in Cobalt Ferrite-Polymer Nanocomposites

M(H) hysteresis loops of the CoFe$_2$O$_4$/P(VDF-HFP) and CFO/PVP nanocomposite thin films were recorded under an applied magnetic field up to 50 kOe. Figure 6a shows hysteresis loops of the 30 wt.% CoFe$_2$O$_4$/PVDF-HFP thin films at various temperatures, indicating typical ferri/ferromagnetic behavior. At 1.9 K, the 30 wt.% CFO/PVDF-HFP sample is not completely saturated at an applied magnetic field up to 50 kOe, while at higher temperatures (100 to 300 K), it gives a saturation magnetization ($M_s$) of approximately 20 emu/g. The coercivity of the assembly is 400 Oe at 300 K and reaches 13 kOe at 1.9 K. Figure 7b shows the influence of the nanoparticle loading in the copolymer matrix to the saturation magnetization and remnant magnetization ($M_r$). The increase in CFO phase content (as volume fraction) gives rise to a systematic increase in the overall $M_s$ value; the non-magnetic P(VDF-HFP) polymer does not appear to inhibit the interactions of the magnetic polarization in individual nanocrystals. The composite films show the same coercivity, irrespective of the CFO content.
Figure 5.2: Field-dependent magnetization hysteresis of CoFe$_2$O$_4$/P(VDF-HFP) nanocomposites. (a) With 30 wt.% CFO loading at various temperatures and (b) at 300 K with various CFO weight fraction. Inset, central region on an expanded scale.
In order to verify the concerted interaction between the magnetic and ferroelectric phases, hysteresis loops of the CFO/PVP nanocomposites were recorded (Figure 5.3) and compared with those of the CFO/P(VDF-HFP), presented in Table 2. The saturation magnetization of PVP films...
is lower compared to PVDF-HFP films with the same composition over the entire magnetic field range. The differences are +1.36 and +2.97 emu/g for 10 and 50 wt.% CFO loading, respectively. The change of the \( M_s \) values of the nanocomposite films was normalized for weight fraction and analyzed by the following equation:

\[
\Delta M_s \% = \frac{M_s - M_{s0}}{M_{s0}} f
\]

(5.1)

where \( M_s \) is the saturation magnetization of a film with certain CFO weight fraction, \( f \) is the corresponding weight percentage, \( M_{s0} \) is the saturation magnetization of pure CFO, and \( \Delta M_s \% \) is the normalized percentage change of the \( M_s \) value of each polymer-based film relative to the comparative weighted, pure cobalt ferrite films. The \( \Delta M_s \% \) values for both P(VDF-HFP) and PVP films are summarized in Table 5.1. The \( \Delta M_s \% \) for the CFO/PVP films is close to zero for all three samples, indicating that the net magnetic moments of the thin films is equivalent to the sum of the contributions from each individual CFO grain inside the PVP matrix (volume fraction contribution only). In contrast, all CFO/P(VDF-HFP) films exhibit positive values of \( \Delta M_s \% \), with a gradual increase as the copolymer fraction increases. This observation was carefully calibrated against possible errors in the calculation of the volume fraction, most notably through measurement of the film thickness by SEM (see ‘Methods’ section). This observation strongly suggests a contribution to the \( \Delta M_s \) due to the presence of P(VDF-HFP) in the form of an enhancement of the saturation magnetization of the composite, with the enhancement stronger for samples with a lower CFO:P(VDF-HFP) ratio.
Table 5.1 Saturation magnetization ($M_s$) and normalized percentage change of saturation magnetization ($\Delta M_s\%$) values for CFO/P(VDF-HFP) and CFO/PVP films with various CFO contents.

<table>
<thead>
<tr>
<th>Sample</th>
<th>$M_s$ (emu/g)</th>
<th>$\Delta M_s%$</th>
</tr>
</thead>
<tbody>
<tr>
<td>P(VDF-HFP) films</td>
<td></td>
<td></td>
</tr>
<tr>
<td>10 wt.% CFO</td>
<td>8.0</td>
<td>+20.7%</td>
</tr>
<tr>
<td>30 wt.% CFO</td>
<td>21.8</td>
<td>+9.61%</td>
</tr>
<tr>
<td>50 wt.% CFO</td>
<td>36.0</td>
<td>+8.60%</td>
</tr>
<tr>
<td>PVP films</td>
<td></td>
<td></td>
</tr>
<tr>
<td>10 wt.% CFO</td>
<td>6.6</td>
<td>+0.09%</td>
</tr>
<tr>
<td>30 wt.% CFO</td>
<td>20.2</td>
<td>+0.96%</td>
</tr>
<tr>
<td>50 wt.% CFO</td>
<td>33.0</td>
<td>−0.36%</td>
</tr>
</tbody>
</table>

Pure CoFe$_2$O$_4$ nanocrystal powders show less than 1% variation in hysteresis loops, whereas CFO/P(VDF-HFP) films show enhancements up to 20.7% in $\Delta M_s$. The enhancement of the $M_s$ value from the P(VDF-HFP) phase, we believe, is a concerted effect and is evident of a ME effect, specifically, through inverse magnetostrictive coupling. First, the magnetostrictive effect induces a distortion of the crystal lattices of CoFe$_2$O$_4$ under an applied magnetic field, which in turn leads to local strains or stresses of between the piezoelectric and magnetic phases via intimate mechanical contact. The hypothesis of the influence of intimate mechanical contact between nanocrystals and P(VDF-HFP) is already supported by the observation of permittivity changes unexplained by volume fraction alone, described above. We postulate that the interfacial stress is inversely applied on the CFO phase, which further leads to the change of domain magnetization as a result of an inverse magnetostrictive effect. The effect is quantified by Equation 5.2:

$$E = \frac{3}{2} \lambda_s \sigma \sin^2 \theta$$  (5.2)
where $E$ is the magnetic strain energy density, $\lambda_s$ is the magnetostrictive expansion at saturation, $\theta$ is the angle between the saturation magnetization, and $\sigma$ is the stress applied on a single magnetic domain. With limited expansion allowed by intimate contact of two hard phases, when compression is applied to CFO phase, the energy is minimized when magnetization is parallel to $\sigma$ ($\theta = 0$). Consequently, $M_s$ is increased by tension. Moreover, in a sample of pure CFO nanoparticles ($M_s = 66$ emu/g) each Co$^{2+}$ ion exhibits a magnetic moment of 2.7 $\mu_B$, while in the 10 wt.% CFO/P(VDF-HFP)) films ($M_s = 8.0$ emu/g), the Co$^{2+}$ ion shows a net magnetic moment of 3 $\mu_B$, which equals the maximum magnetic moment a Co$^{2+}$ ion can offer in the inverse spinel structure. This observation indicates that by intimate mechanical coverage of the CFO particles, P(VDF-HFP) reduces the nanocrystals' degree of surface disorder and surface anisotropy via redistributing charges and dipoles within the copolymer matrix, which allows the magnetization of the cobalt ions to completely follow the external magnetic field. Additionally, as the content of cobalt ferrite nanoparticles increases, the particles' tendency towards agglomeration increases. The interfacial area is reduced due to the formation of small clusters of nanoparticles, and therefore, the interfacial interaction is weakened. This explains why the $M_s$ enhancement is strongest in the 10 wt.% sample (+20.7%), in which the nanoparticles are more completely dispersed, compared to 30 and 50 wt.% samples (+9.6% and +8.6%, respectively).

The magnetoelectric effect associated with the magnetostrictive/piezoelectric coupling typically can only be observed under high magnetic fields at a very low temperature. In this work, the nanocomposite thin films show substantial magnetoelectric coupling at room temperature. The piezoelectric properties of P(VDF-HFP) and ferrimagnetic properties of CoFe$_2$O$_4$ nanocrystals are ideal and complimentary in this respect, resulting an observable magnetoelectric coupling.
Conclusion

In summary, we prepared by solvothermal synthesis: a) individual, highly crystalline (Ba,Sr)TiO$_3$ nanocrystals with narrow size distribution and dispersibility that can be used as building blocks for high k dielectric thin films for capacitors, and b) nanosized transition metal ferrite crystals that can be fabricated in to polymer-based, particulate nanocomposite with observed indirect magnetoelectric coupling that enables potential application in sensors and multifunctional devices. We demonstrated the use of atomic resolution transmission electron microscopy (TEM), scanning transmission electron microscopy (STEM), electron energy loss spectroscopy (EELS) and energy dispersive spectroscopy (EDX) to fully characterize the crystal structure, morphology and composition. We developed dielectric thin films using solution-deposited high k (Ba,Sr)TiO$_3$ nanocrystals together with parylene-C to fabricate wide area (8 cm$^2$) on both glass and flexible substrates, which offers good capacitance, low loss, and high strength. Magnetic CoFe$_2$O$_4$ nanoparticles together with P(VDF-HFP) and PVP films were also prepared via spin-coating techniques, aiming to establish intimate contact binary nanocomposties. The comparison of effective permittivity and saturation magnetization of CoFe$_2$O$_4$/P(VDF-HFP) and CoFe$_2$O$_4$/PVP films gives indirect evidence of magnetoelectric coupling via strong elastic interactions between the magnetic fillers and the ferroelectric host.

The low-temperature solution process using soluble nanocrystals as building blocks opens multiple possibilities for incorporating metal oxide nanoparticles in integrated circuit technology, energy storage devices, multiferroics and future flexible electronics. The solution deposition route to superior oxide films can be adapted to suit a variety of techniques, such as spin-coating, ink-jet printing, and photolithographic. The evaporatively driven assembly, coupled
with the use of polymer or polymer precursors, can infiltrate the porous nanocrystal thin film network post-assembly, leading the intercrystal void space minimized, while simultaneously promoting connectivity between the polymer phase and the metal oxide phase. These benefits enable low cost processing and fabrication of nanodevices. Magnetoelectric composite thin films have becoming a popular topic in the past few years, however they are far from mature. The magnetoelectricity at room temperature observed in this work allows design of practical ME device, although the coupling interaction may still be weak. The ongoing research on different types of structures is likely to bring more exciting materials and a better understanding of the physics governing this phenomenon, along with novel device design concepts featuring multifunctional applications.
References


49. Guo, Y. *et al.* Giant Magnetodielectric Effect in 0-3 Ni0.5Zn0.5Fe2O4-Poly(vinylidene-fluoride) Nanocomposite Films. *J. Phys. Chem. C* 13861–13866 (2010).


56. Instruments, M. Dynamic Light Scattering Instrumentation for classical 90 degree scattering measurements.


60. Liu, S. *et al.* Synthetic Hollandite Supergroup Multiferroics Prepared by Gel Collection.


67. Zhang, X. X. *et al.* Magnetcocaloric effect in La0.67Ca0.33MnOδ and La0.60Y0.07Ca0.33MnOδ bulk materials. *Appl. Phys. Lett.* **69**, 3596 (1996).


