

Many material properties are mutually exclusive, and are therefore, unlikely to be found in a single material. An example of this is permittivity and permeability, a measure of the ability of a material to be polarized in an electric or magnetic field, respectively. If one plots existing materials with permittivity on one axis and permeability on the other, most materials would fall on one axis or the other. Although materials in a class known as magnetic ferroelectrics, or multi-ferroics, exhibit both ferromagnetism and ferroelectricity, they fall in the lower left corner, having both a low permittivity and low permeability. A material with both a high permittivity and a high permeability would be novel, however, such a material has yet to be developed.

The benefits of nanoparticles can be harnessed to solve this problem and to create the first material exhibiting both a high permittivity and permeability. One of the common problems plaguing ferroelectrics and ferromagnets are energy losses on field switching caused by the interaction between neighboring domains and domain wall movement. This is manifested by hysteresis loops in plots of Polarization vs. Applied Electric field and Magnetization vs. Applied Magnetic field, respectively. At high frequency these oscillations cause a significant loss of energy, in the form of heat. One way to minimize if not altogether eliminate these losses would be to create single domain ferroelectric and ferromagnetic oxide particles, of small enough size that they would become superparaelectric or superparamagnetic.

Louis Néel was probably the first to predict the properties of single domain ferromagnetic nanoparticles [1]. Néel showed that when ferromagnetic particles are below a critical size, the hysteresis behavior disappears and they become superparamagnetic. In other words, they become single domain particles, capable of rotating freely in an applied field, as in an ideal paramagnet, while maintaining the high magnetic moment characteristic of a ferromagnet. This is based on the idea that below some critical size it becomes energetically unfavorable for a particle to support a multi-domain structure. Superparamagnets, therefore, exhibit no hysteresis loss on switching, and maintain a high saturation magnetization. This phenomenon, however, depends on there being no coupling between neighboring particles. In my proposed composite material magnetic nanoparticle isolation will be accomplished by surrounding the particles with

an organic shell, or capping agent, which along with the neighboring ferroelectric particles, will control interparticle interactions.

Single domain ferroelectric particles, superparaelectrics, on the other hand, are a far less studied system and therefore provide a very exciting area of research. Current research in nanometer sized dielectric particles has focused on making multilayer capacitors from thin films with nanocrystalline grains for memory applications [2-4]. Analogous to ferromagnets there should exist some lower size limit at which it will become energetically unfavorable for a multi-domain structure to exist. At this point the ferroelectric should exhibit a superparaelectric behavior, where the energy losses on switching go to zero while maintaining a high polarization. However, in my own literature survey I have found no measurements on the dielectric behavior of unsintered nanoparticles. Ferroelectricity is directly related to crystal structure, and is only found in structures that are non-centrosymmetric. A common crystal structure found in ferroelectrics is the tetragonal perovskite. This direct link between crystal structure and ferroelectricity does lead to some problems. For small particles the tetragonal crystal structure can become energetically unfavorable, resulting in a transformation to a cubic structure and loss of ferroelectric behavior. There are many reports of just such a lower size limit in the literature but no single theory seems to be able to account for these size effects. Differing theories center on surface effects of small particles to large defect concentrations in small barium titanate particles [5]. In my research I hope to illuminate this area through the characterization of ferroelectric nanoparticles.

I propose to synthesize both magnetic and ferroelectric single domain nanoparticles using solution chemistry techniques. In order to control the size of the particles, I have used LaMer's theory of condensation from a supersaturated solution for producing monodispersed magnetic particles, and have done preliminary research in order to apply the same techniques to the synthesis of ferroelectric particles [6]. This theory outlines the growth of an insoluble precipitate from an initially supersaturated solution. Initially the concentration of the reactants increases to some critical value at which nucleation of the insoluble product spontaneously occurs. After this rapid nucleation step there is a regime of diffusion controlled growth until the solubility limit is reached. The nucleation rate can be controlled by the initial concentration of reactants and the pH of the solution. One of the many advantages of this method is that it is high yield, of considerable interest for commercial applications. In order to keep the particles from

aggregating I will use a capping agent, such as an end functionalized long chain hydrocarbon that will chemisorb with the surface creating a steric repulsion between the particles in solution. For magnetic nanoparticles it has been shown that oleic acid, a long chain hydrocarbon with a carboxylic acid group on one end, interacts with the positively charged ferrite surface and adsorbs to the particles [7]. A proposed capping agent for the ferroelectric particles would be a diblock copolymer that would promote self-assembly.

In order to assemble the two types of nanoparticles into three-dimensional nanocomposite arrays I plan to use various techniques, including polymer assisted and relative size ratio on the packing of the two types of particles. Polymer assisted self-assembly consists of capping the magnetic nanoparticles with a long chain hydrocarbon such as oleic acid, then capping the other particle with a diblock copolymer. This diblock copolymer would be chosen such that one block would adsorb to the ferroelectric particle and the other would interact with the long chain hydrocarbon adsorbed on the magnetic particle. Size selective self-assembly is based on research done by M. J. Murray and J.V. Sanders many years ago on the close packing of opal spheres of two different sizes [8, 9]. They have showed that by using spheres with specific size ratios the spheres will self assemble into close-packed structures on heating at low temperature. This technique has subsequently been used by Chris Murray and coworkers at IBM to create nanocrystal assemblies [10].

In my first year of graduate study the majority of my research has centered on the synthesis and size characterization of magnetic, dielectric, and ferroelectric nanoparticles. Based on this I feel qualified to extend this knowledge to answering some of the questions I have proposed, to synthesize new types of nanoparticles, and to create novel engineering devices. The beauty of this proposal is that it combines physics, chemistry, and many disciplines within the field of materials science including ceramics, polymers, and electronics into one project. I will be able to draw on my current knowledge of inorganic chemistry synthesis techniques while learning more about the intermolecular interactions taking place in the formation of self-assembled structures. I can then use this information to create innovative real-engineering devices.

Synthesized ferroelectric and magnetic nanoparticles may contain defects that have a deleterious effect on the material properties of interest. Therefore, a major part of this project will be the characterization of these nanopowders both individually and in their final products as

nanocomposites. Size characterization will be done by a number of techniques including powder x-ray diffraction (XRD) using Debye-Scherrer calculations for an average size, and transmission electron microscopy (TEM) and small angle x-ray scattering (SAXS) to get size distribution information. Fourier Transform Infrared Spectroscopy (FTIR) will be used to look for defects, including hydroxyl defects that prevent ferroelectric behavior by stabilizing a pseudo-cubic structure. Magnetic and ferroelectric measurements will then be made separately on the individual nanopowders and the nanocomposites. TEM and scanning electron microscopy (SEM) will also be used to determine the degree to which the nanocomposites self-assemble into three-dimensional arrays. Using this range of characterization techniques, I will be able to evaluate my nanoparticles, and refine the synthesis process to achieve material properties of technological merit.

The final step will be the realization of these three-dimensional nanocomposite arrays into practical engineering devices. By varying the sizes and percentage of the two particles in the final composite I will be able to tune the response of the material, and therefore its use in real engineering devices. The realization of a multifunctional nanocomposite device lends itself to the current trend of device miniaturization. As circuit boards become more and more populated, performance will be limited by electromagnetic interference (EMI) that results from component crowding and high frequency mixed signal circuitry. Currently, EMI filters consist of bulky networks of capacitors and inductors [11], however, a paradox exists here: as devices get smaller and smaller, larger and larger EMI filters are needed to minimize crosstalk, counteracting the drive towards miniaturization. I suggest instead using a nanocomposite device that would instead act as a tunable EMI screening device. The implementation of the final device will only come with patience and a complete understanding of the system as a whole, in this way exploiting the unique properties of nanoparticles.

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