Ferrites at Room Temperature: Materials Science, Chemistry, Physics, and Metrology on Tailored Compositions

Patrick Doherty\textsuperscript{1a}, James Masi\textsuperscript{1b}, and Deedra Zeeh\textsuperscript{1a}

Abstract – Iron oxide (Fe$_2$O$_3$) based nanoparticles have become a centerpiece for research in the scientific community over recent years. This work was conducted with the intent of developing a nano-particulate variable Fe, Ni, Zn, Mn oxide chemistry which was easy to implement at low temperatures in the lab/classroom, and which is not tied to high temperature fabrication methods and phase considerations (metastability).

The initial tests were made by fabricating inductor cores (both imbedded in epoxy and pressed into toroids with optimal magnetic properties, measurable in the laboratory for L, Q, and Z vs. frequency, from 100 Hz to 1.8 GHz. Using a ferric oxide (Fe$_2$O$_3$) base for the materials and varying levels of nickel, manganese, and zinc oxide, we have created several cores which reduce the loss tangent. The cores created have a much smaller loss tangent that is consistent over a wide range of frequencies (since they are super-paramagnetic). By using iron oxide (FeO·Fe$_2$O$_3$, with varying Ni, Zn, and Mn substitutions for the divalent Fe) nanoparticle cores, the behavior of the inductor can be altered, due to different magnetic properties of materials at the nanoscale versus micro/macro scale. The simplicity of the methods makes implementation and understanding possible in both secondary and post-secondary labs. The cross-disciplinary physics, biochemistry, and materials science enhances learning.

Keywords: ferrites, nano particles, magnetic properties, magnetic devices.

Overview/Background

Iron oxide (Fe$_2$O$_3$) based nanoparticles have always attracted the attention of scientists from many fields. The potential applications for these nanoparticles cover many fields including the energy, mechanical, biomedical, magnetic, catalysis, and electrical areas, to name a few. Magnetic particles have already been used in medical imaging/therapy and information storage, and nano-sized particles may offer unique or improved properties. For example, magnetic nanoparticle contrast agents may improve contrast between healthy and diseased tissue in magnetic resonance imaging (MRI). The prepared nanocrystals could have potential in environmental and biomedical applications (such as in targeted drug delivery).

There are a number of methods for producing nano-particulate iron oxide particles, among which are:

1. Ferric/ferrous chloride reaction with sodium hydroxide;
2. High temperature calcining of carbonates;
3. High temperature hydrothermal growth [1];
4. Nitrate/hydroxide reactions, thermal or microwave [2];
5. Glycerol and Sodium dodecyl sulfate assisted ferrite reactions; and
6. Ferrofluid methods using various carboxylic acids or poly acrylic acid formulations [2].

Many of the approaches for synthesizing superparamagnetic iron oxide nanocrystals require complex processes and the use of toxic materials. This study used a co-precipitation method that follows the green chemistry principle (environmentally friendly and economical) to prepare superparamagnetic iron and mixed oxide nanocrystals.
This work was conducted with the intent of developing a nano-particulate (variable composition) Fe, Ni, Zn, Mn oxide (e.g. Mn$_{0.67}$Zn$_{0.33}$Fe$_2$O$_4$, manganese-zinc ferrite) chemistry which was easy to implement at low temperatures in the lab/classroom, and which is not tied to high temperature fabrication methods and phase considerations (metastability).

**Methods /Materials**

**Ferrofluid Methods**

The evolution of ferrofluid methods for nanoparticle production is shown below in Figure 1.

**Role of magnetic nanoparticles**

In the early 20\textsuperscript{th} century → Solid state physics

<table>
<thead>
<tr>
<th>1960 ~</th>
<th>Condensed matter physics</th>
<th>Nanoscale science &amp; technology</th>
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<tr>
<td>including Soft Materials:</td>
<td>Fluids</td>
<td>Nanoparticles</td>
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<td>Liquid crystals</td>
<td>Polymers</td>
<td>Nanostructured materials</td>
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<td>Emulsions</td>
<td>Colloids</td>
<td>Nanodevices</td>
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Magnetic fluid methods

**Multi modal ferrite materials and devices**

**Figure 1. Ferrofluid evolution method**

Initially, to produce the ferrite, we followed a standard process [2]. In this process, 10 milliliters (mL) of both PCB etchant and distilled water are combined. Steel wool is added to the solution until a complete color change and reaction occurs. Grade one filter paper is used to filter the larger steel wool particles out of solution. The filtered solution should be green; this is ferrous chloride (FeCl$_2$). Then, 20mL of PCB etchant (which is ferric chloride, FeCl$_3$) are added to the green filtered solution. This sets up the ratio of FeCl$_2$ to FeCl$_3$ for the proper reactions (see below) to take place.

The next step involves adding 150mL of ammonia solution (10\% by weight NH$_4$OH) to the ferric chloride/ferrous chloride mixture, which causes FeO \cdot Fe$_2$O$_3$ to precipitate out. The chemical equations for this process/reaction (rxn) are as follows:

Rxn 1: FeCl$_3$(aq) + 6NH$_4$OH(aq) $\rightarrow$ Fe$_2$O$_3$(s) + 3H$_2$O(l) + 6NH$_4$Cl(aq), $\Delta H_{rxn} = -204.13$ KJ/mol-rxn

Rxn 2: FeCl$_2$(aq) + 2NH$_4$OH(aq) $\rightarrow$ FeO(s) + H$_2$O(l) + 2NH$_4$Cl(aq), $\Delta H_{rxn} = -8.55$ KJ/mol-rxn

Rxn 3: FeO(s) + Fe$_2$O$_3$(s) $\rightarrow$ FeO \cdot Fe$_2$O$_3$(s), $\Delta H_{rxn} = +79.5$ KJ/mol-rxn

Combined Rxn: FeCl$_3$(aq) + FeCl$_2$(aq) + 6NH$_4$OH(aq) $\rightarrow$ FeO \cdot Fe$_2$O$_3$(s) + 4H$_2$O(l) + 8NH$_4$Cl(aq), $\Delta H_{rxn} = -133.18$ KJ/mol-rxn

The combined reaction occurs readily and spontaneously in the ammonia solution. The solution is heated to just below boiling, and the surfactant is applied. In order to keep the nanoparticles from colliding and aggregating, oleic acid is used as a surfactant. Oleic acid is a long carbon chain with a carboxylic acid group (-COOH) at one end (Figure 2). The carboxylic acid group contains a highly polar oxygen-hydrogen (O-H) bond which causes a small partial charge to be induced on both the oxygen and hydrogen atoms. This polar head forms a weak bond to the nanoparticles before they can aggregate. When several of these oleic acid molecules surround a nanoparticle, it
forces any others away from it. The distance that the oleic acid pushes the nanoparticles away from each other causes some abnormal magnetic effects in the material.

**Figure 2. Oleic acid (or other surfactant) surrounding ferrite nano-particle**

When a magnetic field passed through a normal aggregate iron oxide mass, each cell in the crystal structure would induce a magnetic field on the adjacent cells and there would be a chain reaction in the structure. In the case of nanoparticles, a magnetic field causes each one to react independently instead of the particles around it influencing its induced field. In an ideal situation, the surfactant coated nanoparticles would each behave as an independent magnetic particle.

Solutions of ferric and ferrous chloride can also be reacted directly [3] in the presence of a base (sodium hydroxide) can also be used to form iron oxide nanocrystals. However, the resultant reaction products have a tendency to contaminate the nano-particles. Polyacrylic acid can also be used as a surfactant to stabilize the particles.

By using the chlorides of Fe, Ni, Zn, and Mn, iron oxide, FeO·Fe₂O₃, with varying Ni, Zn, and Mn substitutions for the divalent Fe, can be formed. Hence, the mixed ferrite can be formed. Other metal chlorides may be substituted in for the ferrous chloride (FeCl₂) as long as they are divalent metals

- i.e. ZnCl₂, NiCl₂, CuCl₂, MnCl₂, etc.
- Note: They may also be included in addition to the ferrous chloride

- 4FeCl₃ + FeCl₂ + NiCl₂ + 16NH₄OH → FeO·NiO·Fe₂O₃ + 8H₂O + 16NH₄Cl

The direct synthesis using FeCl₃ with Ni-, Zn-, MnCl₂ is easier and easier to control agglomeration of the nanoparticulates.

Some interesting air baked (80°C) samples and their dendritic patterns and directionality are shown in Figure 3.

**Figure 3. Air dried samples and interesting morphology.**
Testing/Metrology

Testing began with different samples of iron oxide nanoparticles processed in different ways, such as rapid heating, gradual heating, and suspension in epoxy, into a premade, air-core inductor and toroid (Supplied by Sandia National Laboratories) as shown in Figure 4.

![Inductor and Toroid](image)

(a) Sandia inductor  
(b) toroid  
50/50 nano/epoxy

Figure 4. Conformations of two types of inductors tested

Testing the inductor with these nanoparticle cores revealed in which direction we would go when creating toroids for experimental testing. Suspending the nanoparticle-surfactant complex into epoxy created a rigid structure that could be easily molded before drying and had strong normalizing effects on the Quality factor (Q) of the inductor. Measurements were mad on a 0-40 MHz HP Gain-Phase Impedance Bridge, an HP 5-1800 MHz High Frequency Materials analyzer, and a Walker High Frequency B-H tester (Figure 5). Loss tangent = \( \tan\delta = \frac{\mu''}{\mu'} \).

![Test/Analysis equipment](image)

0-40 MHz HP Gain-Phase Impedance Bridge  
High Frequency B-H tester  
HP 5-1800 MHz High Frequency Materials analyzer

Figure 5. Test/Analysis equipment
A B-H curve of one of the nano-ferrite/epoxy cores is shown below in Figure 6.

![B-H hysteresis loop for a material with μ~25](image1)

**Figure 6.** B-H hysteresis loop for a material with μ~25

The initial tests were made by fabricating inductor cores (both imbedded in epoxy and pressed into toroids with optimal magnetic properties, measurable in the laboratory for L, Q, and Z vs. frequency, from 100 Hz to 1.8 GHz. Using a ferric oxide (Fe₂O₃) base for the materials and varying levels of nickel, manganese, and zinc oxide, we have created several cores which reduce the loss tangent for the cores. For the sake of brevity, only the iron and nickel data will be shown. Relative to the factory-made ferrite cores, the cores created have a much smaller loss tangent, consistent over a wide range of frequencies (since they are super-paramagnetic) (Figure 7).

![Permeability Comparison For Various Cores](image2)

**Figure 7.** Permeability and loss for various cores

**Conclusions**

By using iron oxide (FeO - Fe₂O₃ with varying Ni, Zn, and Mn substitutions for the divalent Fe) nanoparticle cores, the behavior of the inductor can be altered, due to different magnetic properties of materials at the nanoscale versus micro/macro scale. In order to test the effect of nanoparticle cores on inductors, our process includes manufacturing...
the particles, designing a process for core production, testing the properties of the cores, and altering the chemical structure of the cores for optimal magnetic performance. By using a green, co-precipitate method, mixed ferrite, super-paramagnetic nano structured materials and low-loss devices can be formed at low temperatures.

The simplicity of the methods makes implementation and understanding possible in both secondary and post-secondary labs. The cross-disciplinary Physics, biochemistry, and materials science backgrounds of the co-investigators serve as a learning experience for all.

REFERENCES


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