Nanoparticle-Chiral Nematic Liquid Crystal Composites

by

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Abstract

The advancement of the fabrication of a one-dimensional photonic crystal without
time-reversal and space-inversion symmetries was pursued. Theoretical studies predict
that such a system would exhibit unusual optical properties, including indirect photonic
band gaps and backward wave propagating eigenmodes. Such a system can be created
experimentally by combing magnetooptical nanoparticles with a chiral nematic liquid
crystal. The fabrication of this material system was advanced through two distinct phases
of research.

The first phase seeks to produce magnetooptical yttrium iron garnet (YIG)
nanoparticles with an average diameter on the order of 15-50 nm. It was determined that
a commercially available yttrium iron oxide nanopowder (purchased from Sigma-Aldrich
Corporation) exhibited YIG and orthorhombic yttrium iron oxide (YFeO$_3$) phases after
being calcined at 800 °C for two hours. These nanoparticles were slightly smaller than
desired, having diameters on the order of 10-20 nm. Direct nanoparticle synthesis via
coprecipitation in microemulsions produced superior results, resulting in a pure YIG
material with diameters on the order of 30-50 nm.

The second phase examines the manner in which nanoparticles co-assemble with
a chiral nematic liquid crystal. It was determined that the addition of nanoparticles to a
5CB-COC system disrupts the system’s helical structure. This disruption lowers the
system’s phase transition temperatures and inhibits the system’s ability to form
reflectivity peaks.

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The process of scientific research is fraught with setbacks and frustration. While a research plan is often devised, it is seldom followed without significant deviation. However, research success is made possible by the support and assistance of others. Some offer a high level of scientific knowledge and guidance in the research process; others are kind enough to offer the use of their facilities; and some simply provide the love and compassion necessary to sustain the researcher through the most difficult of times. I would like to thank those who have helped make my research successful.

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Table 4-1: This table indicates the phase transition temperatures for various 5CB-COC systems as determined by DSC.
Chapter 1

Introduction

This thesis is the initial phase of a larger project that seeks to add magnetooptical nanoparticles to a chiral nematic liquid crystal in order to create a unique optical system with rather unusual properties.

Photonic crystals are defined as dielectric structures that are designed to influence electromagnetic wave propagation in the same manner that periodic potential affects electron wave motion in a semiconductor, by defining allowed and forbidden energy bands. In this thesis, I investigate a special type of photonic crystal, one that does not have the usual characteristics of space-inversion and time-reversal symmetry.

When a three dimensional structure is described by a locus $L(x, y, z)=C$ and an inversion of that structure through the origin leaves the structure unchanged, i.e. $L(-x, -y, -z)=C$, the structure is said to possess space-inversion symmetry. Many (indeed most) photonic crystals exhibit this characteristic. Photonic crystals without space-inversion symmetry can still exhibit time-reversal symmetry. An electromagnetic wave passing through a structure can be expressed as a function of time. When time-reversal symmetry is present, this expression will be unchanged when the sign associated with time is changed:

$$\psi(t)=\psi(-t)$$
where $\psi$ is the traveling wave and $t$ is time.\textsuperscript{4} The goal in this thesis is to advance the fabrication of a one-dimensional photonic crystal that breaks both space-inversion and time-reversal symmetries.

Theoretical work has previously been conducted investigating the properties of photonic crystals without time-reversal and space-inversion symmetries. This was accomplished by modeling a one-dimensional, lossless dielectric helical media with magnetooptic activity (the effect of rotating the polarization of light via a magnetic field).\textsuperscript{5} In such a system, the photonic band gap exhibits unusual properties. These include indirect photonic band gaps (edges not aligned in k-space) and backward wave propagating eigenmodes (which allow for negative refraction).\textsuperscript{6,7} These properties are illustrated in Figure 1-1.
Figure 1-1: This figure shows the band gap structures of a 1-D periodic medium with and without magnetooptical activity. The solid lines show the band structure when magnetooptical activity is present, while the dashed lines indicate the band gap as it would otherwise appear. The red and green lines indicate light with circular polarization of opposite handedness. The addition of magnetooptical activity leads to misaligned band structures. In addition, backward wave propagating eigenmodes are indicated by points on the band structure where the $\omega$ divided by $k$ has the opposite sign of the band structure’s slope ($\partial \omega / \partial k$).

These predictions can be tested by creating this system experimentally. For example, a one-dimensional photonic crystal without space-inversion and time-reversal symmetries can be fabricated by adding magnetic nanoparticles to a chiral nematic liquid crystal and then adding the presence of an external magnetic field. The addition of nanoparticles to a material system is an established means of modifying and enhancing that material’s properties; however, there are experimental challenges with creating this system.
The experimental approach is comprised of two phases: The first phase seeks to produce magnetooptical yttrium iron garnet (YIG) nanoparticles with an average diameter on the order of 15-50 nm. Nanoparticles of this size are candidates to enhance a material system’s optical properties because they are small enough not to cause significant light scattering or absorption, but still enhance the system’s magnetic properties. The second phase examines the manner in which nanoparticles co-assemble with a chiral nematic liquid crystal. This was accomplished by adding readily available silica nanoparticles (as a surrogate for the YIG nanoparticles) to a mixture of the nematic liquid crystal 5CB (4-pentyl-4'-cyanobiphenyl) and the chiral dopant COC (cholesteryl oleyl carbonate).

Initially, the challenge was to obtain magnetic YIG nanoparticles of the appropriate size. Appropriate sizes are those at which the particles have not yet become Rayleigh scatters and have diameters in the range of about 15-50 nm. Producing such nanoparticles is not a trivial matter, due to the tendency for particle aggregation.

Next the task was to uniformly disperse the nanoparticles in the chiral nematic liquid crystal. Achieving such a dispersion requires that the nanoparticles be coated with a material that is compatible with the liquid crystal matrix. Once this nanoparticle dispersion is achieved, its effect on the structure of the liquid crystal must be understood. Specifically, the manner in which nanoparticle-liquid crystal co-assembly affects the photonic band structure of the chiral nematic must be determined in the absence of any magnetic field. This information is indicative of the effect of nanoparticles on the liquid crystal system’s helical structure.
Chapter 2 provides an overview of the scientific principles necessary to understand the presented research. Chapter 3 discusses attempts and successes in obtaining appropriately sized magnetic nanoparticles from commercially available precursor nanopowders and from laboratory nanoparticle synthesis. X-ray diffraction (XRD) and transmission electron microscopy (TEM) were used to analyze the nanoparticles produced. In Chapter 4, the effects of adding (silica) nanoparticles to a 5CB-COC chiral nematic mixture are examined. Differential scanning calorimetry (DSC) was used to determine the phase transition temperatures for the chiral nematic liquid crystal-nanoparticle systems. An optical microscope with a spectrometer attachment was used to assess the manner in which the addition of nanoparticles affects the reflectivity of these systems. Chapter 5 seeks to tie all the presented finding together in order to determine the appropriate scientific conclusions.
Chapter 2

Background

2.1 Breaking Time-Reversal and Space-Inversion Symmetries

Symmetry is defined as the property of correspondence in size, shape, and relative position of parts on opposite sides of a dividing line or median plane or about a center or axis.\textsuperscript{8} When discussing a material system, there are different types of symmetry that can be observed. If a three dimensional structure is described by a locus \( L(x, y, z)=C \) and an inversion of that structure through the origin is described by the locus \( L(-x, -y, -z)=C \), the system is said to have space-inversion symmetry. After performing the inversion operation, such a structure will be indistinguishable from its inversion through the origin.\textsuperscript{9} Photonic crystals are defined as dielectric structures that are designed to influence electromagnetic wave propagation in the same manner that periodic potential affects electron motion in a semiconductor, by defining allowed and forbidden energy bands.\textsuperscript{10} Traditional one-dimensional periodic photonic crystal systems consist of material layers with alternating indexes of refraction. Such a structure possesses space-inversion symmetry and is shown in Figure 2-1.\textsuperscript{11}
Another periodic photonic crystal can also be created by a helical structure, in which the continuously rotating molecular orientation results in continuously changing index of refraction. Such a structure is shown in Figure 2-2.
This type of photonic crystal lacks space-inversion symmetry as a result of the
handedness imparted by the helical twist.\(^{12}\)

Time-reversal symmetry (in the context of photonic crystals) is the property that
the band gap structure possesses inversion symmetry (even though the system’s crystal
structure may not).\(^{13}\) An electromagnetic wave passing through such a structure can be
expressed as a function of time. When time-reversal symmetry is present, this expression
will be unchanged when the sign associated with time is changed:
\[
\psi(t) = \psi(-t) \quad \text{and} \quad \psi = \psi_0 e^{i(kx-\omega t)}
\]
where \(\psi\) is the traveling wave, \(t\) is time, and \(\psi_0\) is an arbitrary constant.\(^{14}\) The band gap
structure for a helical photonic crystal is shown in Figure 2-3.\(^{15}\)
Figure 2-3: This is a diagram of a band gap structure for a helical photonic crystal. A band gap only forms for the eigenmode whose circular polarization has the same handedness as the helical structure. This eigenmode is shown in green. The eigenmode with circular polarization of the opposite handedness is shown in red. The symmetry of the band gap structure indicates the structure has time-reversal symmetry.

The symmetry of this band structure indicates time-reversal symmetry.

However, time-reversal symmetry can be broken by the addition of magnetic components to a photonic crystal and application of an external magnetic field. Such a system will rotate the polarization of light propagating through the system, an effect known as magnetooptical activity. This effect alters the system’s band gap structure and breaks time-reversal symmetry as shown in Figure 2-4.\textsuperscript{16}
Figure 2-4: This figure shows the band gap structures of a photonic crystal with and without magnetooptical activity. The solid lines show the band structure when this effect is present, while the dashed lines indicate the band gap as it would otherwise appear. The red and green lines indicate light with circular polarization of opposite handedness. The lack of band gap symmetry indicates that the magnetooptical effect breaks time-reversal symmetry.

The effect of breaking both space-inversion and time-reversal symmetries in a photonic crystal was initially investigated by Figotin and more extensively studied in the PhD thesis of I. Bita. This later work predicts that such a system would exhibit unusual optical properties. These include indirect photonic band gaps (edges not aligned in k-space) and backward wave propagating eigenmodes (sign of phase velocity, \( v_p = \omega/k \), is opposite that of the group velocity, \( v_g = \partial \omega / \partial k \)). These properties are indicated by the band structure illustrated in Figure 2-5.\(^{17}\)
Figure 2-5: This figure shows the band gap structures of a photonic crystal with and without magneto-optical activity. The solid lines show the band structure when this effect is present, while the dashed lines indicate the band gap as it would otherwise appear. The red and green lines indicate light with circular polarization of opposite handedness. The addition of magneto-optical activity leads to misaligned band structures. In addition, backward wave propagating eigenmodes are indicated by points on the band structure where the $\omega$ divided by $k$ has the opposite sign of the band structure’s slope ($\partial \omega / \partial k$).

One way to create such a system experimentally is to combine a magneto-optical material with a helical photonic crystal. This can be accomplished by dispersing magneto-optical nanoparticles in a chiral nematic liquid crystal and applying an external magnetic field directed along the helical axis. The helical structure of the liquid crystal
would create a photonic crystal without space-inversion symmetry, while the interaction between the magnetic field and nanoparticles would break time-reversal symmetry.

2.2 Magnetooptical Materials

Magnetooptical materials are generally classified into one of two groups. The first group consists of metals and metal alloys. However, the fact that these materials lose all transparency for wavelengths in the visible and near infrared at thicknesses exceeding 100 nm limits their usefulness. The second group consists of dielectric and semimagnetic materials. These materials are generally much more useful for practical applications such as optical isolators. An optical isolator is a one-way light valve that prevents reflected light from returning to its source. Yttrium iron garnet, a form of yttrium iron oxide and the material examined in this work, is a member of this second group.

Yttrium iron oxide is a material widely used in microwave filters. This substance exists in a variety of crystal structures. These include orthorhombic and cubic structures.

One molecular formula of orthorhombic yttrium iron oxide is YFeO$_3$. Orthorhombic yttrium iron oxide can also refer to a material represented by the molecular formula Y$_3$Fe$_5$O$_{12}$. While Y$_3$Fe$_5$O$_{12}$ can pack into an orthorhombic cell, it can also crystallize into a cubic structure with space group Ia3d. Yttrium iron oxide exhibiting this cubic structure is often referred to as yttrium iron garnet (YIG). It is the cubic crystal structure that gives rise to the interesting magnetic and optical properties exhibited by YIG.
2.3 The Magnetooptical Properties of Yttrium Iron Garnet

The magnetooptical properties of magnetic garnet materials, such as YIG, were first studied in the late 1950s. These studies focused on the manner in which the polarization of light passing through the material was rotated by interaction with an applied magnetic field, an effect called the Faraday rotation. It was determined that the magnetic moments associated with the Fe$^{3+}$ ions on the octahedral and tetrahedral crystal sites contribute differently to the ultimate Faraday rotation exhibited by these materials. The octahedral ions provide a greater, positive rotation, while the tetrahedral ions provide a lesser, negative rotation and give rise to the magnetooptical activity exhibited by YIG. When this magnetooptical activity is added to a photonic crystal system, time-reversal symmetry is broken. YIG is an excellent choice for adding magnetooptical activity to a material system because of its relatively high Verdet constant (which indicates $\circ$ rotation per material length per magnetic field strength) of $5.33 \frac{\circ}{G \cdot cm}$.

2.4 Liquid Crystals

Most materials exhibit three well-known and understood phases of matter: the solid, liquid, and gas states. Water is one such substance, exhibiting at 1 atmosphere of pressure, a solid state below 0 °C, a liquid state between 0 °C and 100 °C, and a gaseous state above 100 °C. However, some materials exhibit other states of matter. For instance, 5CB (4-pentyl-4'-cyanobiphenyl) is a solid below 22.5 °C and an isotropic liquid above 34.2 °C. However, this material exists in a viscous, cloudy state between
these temperatures. This phase of matter is known as the liquid crystalline phase. The defining characteristics of this class of materials are fluidity and overall molecular orientation.

A crystalline solid material is one in which molecules occupy specific positions, a property known as positional order, and are constrained with regard to the manner in which they orient themselves to one another, a property known as orientational order. When a solid melts and becomes a liquid, these order parameters are broken and the molecules move freely and in a random fashion. However, when a crystalline solid melts to the liquid crystal state, while the three-dimensional positional order is lost, some degree of orientational order remains and can be accompanied by (at most) one or two dimensional positional order. Unlike in a solid, the orientational order in a liquid crystal is limited. In fact, the liquid crystal molecules only exhibit an average preferred orientation. These different phases are illustrated in Figure 2-6.25

![Solid, Liquid Crystal, Liquid](image)

**Figure 2-6:** This figure illustrates the differences in molecular orientation at different states of matter. Molecules in a crystalline solid exhibit positional and orientational order parameters. In the liquid crystal phase, molecules lose three dimensional positional order, but maintain some degree of orientational order. Molecules in a liquid arrange themselves randomly and show no order. Adapted from *Liquid Crystals: Nature's Delicate Phase of Matter* by P.J. Collings, Figure 1.3, page 9.
As fore mentioned, liquid crystal molecules exhibit an average preferred orientation. The direction of this preferred orientation can be represented by an arrow and is called the director of the system. A liquid crystal system and its associated director are shown in Figure 2-7.

**Figure 2-7:** The figure is an illustration of a liquid crystal system and its associated director. The director indicates the preferred orientation of the liquid crystal molecules. However, the fact the director is illustrated as pointing upward is arbitrary, as it would be equally correct to draw it pointing downwards.

In this figure, the director is shown as pointing upward. However, it would be equally correct to show the director as pointing downwards, as these two directions are equivalent in the liquid crystal.26
2.4.1 Nematic Liquid Crystals

Liquid crystal molecules that are rod or disc shaped and exhibit an average, parallel alignment, are known as nematic liquid crystals. This name was derived from the fact that this class of liquid crystals exhibits defects that reminded researchers of threads. As a result, the word nematic, which is derived from the Greek word for thread, was chosen to describe these materials. A nematic liquid crystal is illustrated in Figure 2-8.27

**Figure 2-8:** The figure is an illustration of a nematic liquid crystal system. Intermolecular forces cause the rod shaped molecules to align relatively parallel to one another, fixing the system’s director.

5CB (4-pentyl-4'-cyanobiphenyl), a component of the liquid crystal system examined in this work, is an example of a nematic liquid crystal.
2.4.2 Chiral Nematic Liquid Crystals

Unlike nematic liquid crystals, the intermolecular forces that govern some other liquid crystal systems can cause the molecules to align at a slight angle to one another. In such a system, the director is not fixed in a preferred direction, but rather rotates in a helical fashion about a particular axis. The distance over which the director makes one full turn is known as the system’s pitch. The most common systems to exhibit this liquid crystalline phase are associated with cholesterol. For this reason, these materials are commonly referred to as cholesteric liquid crystals. However, since there are many such materials that are not related to cholesterol, the name chiral nematic liquid crystal is more appropriate. Such a system is illustrated in Figure 2-9.

![Figure 2-9](image)

**Figure 2-9:** This figure illustrates a chiral nematic liquid crystal. Intermolecular forces cause the individual molecules to align at an angle to one another. This causes the director to rotate in a helical fashion throughout the system. The distance over which the director rotates in one full turn is known as the pitch of the liquid crystal and is indicated by P. The illustration indicates one half pitch, the distance over which the director rotates 180°, and is indicated by P/2. Taken from *The Structure of Materials* by S.M. Allen and E.L. Thomas, Figure 4.9, page 222.

A chiral nematic liquid crystal system can be created by doping a nematic liquid crystal with a chiral material. COC (cholesteryl oleyl carbonate), a component in the
liquid crystal system examined in this research, is one such chiral material. In this type of chiral nematic system, the ratio of nematic liquid crystal to chiral dopant determines the system’s pitch.29

2.4.3 Optical Properties of Chiral Nematic Liquid Crystals

Light which has its electric field oriented in one particular direction is said to be linearly polarized. Linearly polarized light is shown in Figure 2-10.

![Figure 2-10: This figure shows linearly polarized light. The light is propagating in the z-direction and the electric field is oriented in the x-direction.](image)

This illustration shows the electric field oriented in the x-direction for linearly polarized light propagating along the z-axis. When light’s electric field is not fixed in a particular
direction, but rather rotates at a uniform rate about the axis of propagation, that light is said to be circularly polarized.\textsuperscript{30}

When linearly polarized light interacts with a chiral nematic liquid crystal, it is useful to consider the linear polarization as consisting of two distinct circular polarizations with opposite handedness. When these two components are added together, they result in the simple linear polarization. The manner in which two components of circularly polarized light combine to give linearly polarized light is shown in Figure 2-11.\textsuperscript{31}

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{figure211.png}
\caption{The top two diagrams show right handed and left handed circularly polarized light at 8 different times. The bottom diagram shows how, when these circularly polarized components are combined, they result in a linear polarization along the y-axis. Adapted from \textit{Liquid Crystals: Nature's Delicate Phase of Matter} by P.J. Collings, Figure 5.2, page 78.}
\end{figure}

Interesting optical effects occur when linearly polarized light propagates along the helical axis of a chiral nematic liquid crystal. The circularly polarized component with
handedness opposite to that of the helical structure passes through the material for all wavelengths of light. The component of light with circular polarization of the same handedness as the material reacts differently. Light with this circular polarization and a wavelength that is equal to the product of the liquid crystal pitch length and index of refraction experiences a periodic variation of the optical path length and is selectively reflected, while other wavelengths of the same handedness pass through the material. This effect forms a reflective band structure and is referred to as selective reflection. This effect is shown in Figure 2-12.  

![Figure 2-12](image)

**Figure 2-12:** When linearly polarized light propagates along the helical axis of a chiral nematic liquid crystal, its circularly polarized components react differently. Wavelengths with circular polarization handedness opposite to that of the structure pass through the material. The wavelength (\(\lambda\)) equal to the product of the liquid crystal pitch length (P) and index of refraction (n) and of the same handedness as the material is reflected while other wavelengths of this handedness are transmitted, forming a reflection band structure. Adapted from *Liquid Crystals: Nature’s Delicate Phase of Matter* by P.J. Collings, Figure 5.5, page 82.
Chapter 3

Production of Magnetooptical Nanoparticles

Research was conducted in an effort to obtain magnetooptical nanoparticles with an average diameter on the order of 15-50 nm. Nanoparticles of this size are excellent candidates to add magnetooptical activity to a photonic crystal because they are too small to cause Rayleigh scattering for visible wavelengths, but can still enhance the system's magnetic properties. The nanoparticles produced in this study consist of the magnetooptical material yttrium iron garnet (YIG). This material is both commercially available and can be easily synthesized.

Two distinct experimental pathways were pursued to obtain nanometer sized YIG. The first approach was to obtain appropriately sized YIG nanoparticles from manipulation of commercially available YIG precursor nanopowder. The second approach was to obtain such nanoparticles via direct synthesis.

3.1 Commercially Available YIG Nanopowder

In order to investigate the possibility of obtaining YIG nanoparticles by manipulation of commercially available nanopowder, yttrium iron oxide was purchased from Sigma-Aldrich Corporation. Sigma-Aldrich lists yttrium iron garnet (YIG) as a
synonym for this material. This nanopowder was studied through X-ray diffraction (XRD) and transmission electron microscopy (TEM).\textsuperscript{34}

### 3.1.1 X-Ray Diffraction (XRD) Analysis

XRD was initially conducted on the yttrium iron oxide nanopowder to access the material’s crystal structure and is shown in Figure 3-1.

![XRD Data](image)

**Figure 3-1:** This figure shows XRD data for yttrium iron oxide as purchased from Sigma-Aldrich Corporation. This data shows unexpected amorphous features and a poor match to the expected peaks (indicated in red) of a YIG powder diffraction pattern.

This data shows an amorphous feature inconsistent with any crystal structure associated with yttrium iron oxide. Consequently, this data is a poor match to the powder diffraction peaks expected for YIG.

The literature indicates that the crystal structure for yttrium iron oxide is dependent on the heat treatment to which the material is exposed. However, while these heat treatments allow the material’s crystal structure to be altered, they may also lead to the undesirable effect of particle aggregation.\textsuperscript{35} Despite this potential drawback, the
amorphous nanopowder was calcined in a tube furnace at various temperatures in an attempt to induce the YIG crystal structure.

The raw nanopowder was initially calcined at 720 °C for two hours. The associated data is shown in Figure 3-2.

![Figure 3-2](image)

**Figure 3-2**: This figure shows the XRD data associated with commercially available yttrium iron oxide that was calcined at 720 °C for two hours. This heat treatment induced orthorhombic crystal structures of yttrium iron oxide. The expected peaks for YFeO$_3$ are indicated in blue and the expected peaks for Y$_3$Fe$_5$O$_{12}$ are indicated in green. Unaccounted for peaks are the result of contaminants.

This data indicates that calcination eliminates the material’s amorphous features.

Furthermore, calcination at 720 °C for two hours induces orthorhombic yttrium iron oxide, but not the desired cubic YIG.

The calcination temperature was then increased to 760 °C in an effort to create YIG. The data corresponding to this heat treatment is shown in Figure 3-3.
Figure 3-3: This figure shows the XRD data associated with commercially available yttrium iron oxide that was calcined at 760 °C for two hours. This heat treatment induced the orthorhombic crystal structures of yttrium iron oxide. The expected peaks for YFeO$_3$ are indicated in blue and the expected peaks for Y$_3$Fe$_5$O$_{12}$ are indicated in green. Unaccounted for peaks are the result of contaminants.

There is very little difference between this data and the data associated with calcination at 720 °C, both heat treatments induce orthorhombic yttrium iron oxide crystal structures.

The raw nanopowder was then calcined at 800 °C. This data is shown in Figure 3-4.

Figure 3-4: This figure shows the XRD data associated with commercially available yttrium iron oxide that was calcined at 800 °C for two hours. This heat treatment leads to excellent agreement with the desired YIG crystal structure. Some orthorhombic yttrium iron oxide is also present in this sample. The expected peaks for YFeO$_3$ are indicated in blue and the expected peaks for YIG (cubic Y$_3$Fe$_5$O$_{12}$) are indicated in red.
Calcination at this temperature causes YIG to become the primary crystal structure present in the material. Orthorhombic yttrium iron oxide (YFeO$_3$) is also present to a lesser extent. This result indicates that calcining yttrium iron oxide at 800°C for two hours creates a nanoparticle system that is primarily YIG.

It is interesting to juxtapose this set of XRD data in order to observe the nanopowder’s crystal structure change (from an amorphous material to a material dominated by YIG) as a function of calcination temperature. This transformation is made clear in Figure 3-5.
Figure 3-5: This figure contrasts XRD data of the raw nanopowder with that of the nanopowder calcined at various temperatures. The raw material data shows amorphous features. The material calcined at 720 °C and 760 °C indicates orthorhombic yttrium iron oxide crystal structures. Data taken from nanopowder calcined at 800 °C shows excellent agreement to the pattern expected for YIG.
3.1.2 Nanoparticle Dispersion

Having determined a heat treatment that induces the YIG crystal phase in the commercially available nanopowder, the nanoparticles were dispersed in solution and examined under transmission electron microscopy (TEM) to determine their size. The dispersion was achieved by diluting the YIG nanoparticles (to a concentration between 0.03 and 0.05 weight percent) in basic water conditions (with a pH between 11.3 and 11.8). Basic conditions were chosen in order to create a surface charge on each nanoparticle, causing the nanoparticles to repel one another. This helps stabilize the dispersion and combats particle aggregation. This solution was mechanically dispersed by a probe sonicator for 1.5 hours. Following this sonication, the dispersion was applied to a carbon coated TEM grid and the nanoparticle size accessed.

3.1.3 Transmission Electron Microscopy (TEM)

The raw commercially available nanopowder was examined using bright field (BF) TEM in order to determine the nanoparticle size as received from Sigma-Aldrich. This BF TEM image is shown in Figure 3-6.
**Figure 3-6:** This TEM image shows commercially available yttrium iron oxide nanopowder as received from Sigma-Aldrich Corporation. The particles are cylindrically shaped and aggregated. The particle size is on the order of 500 nm.

The dark, strongly scattering nanoparticles are cylindrically shaped with an average aspect ratio of approximately 2-3 and have a particle diameter on the order of 500 nm. This data also indicates significant particle aggregation.

Selected area electron diffraction (SAD) was also utilized to examine the nanopowder crystal structure. This data supplements the data obtained from X-ray Diffraction (XRD). In this analysis, the $d$ spacing associated with a particular reflection is calculated and then compared to the reflections predicted by the YIG powder diffraction file. A portion of the YIG powder diffraction file is shown in Table 3-1.\textsuperscript{36}
Table 3-1: This table shows a portion of the YIG powder diffraction file. This data connects a $d$ spacing to its corresponding reflection. The relative intensities of each reflection are indicated. The (4 0 0) and (4 2 0) reflections are the most intense and the clearest indicators of the presence or lack of YIG. Taken from the YIG Powder Diffraction File.

<table>
<thead>
<tr>
<th>$d$ (Å)</th>
<th>$(h\ k\ l)$</th>
<th>Relative Intensity</th>
</tr>
</thead>
<tbody>
<tr>
<td>5.0507</td>
<td>2 1 1</td>
<td>Very Weak</td>
</tr>
<tr>
<td>4.3742</td>
<td>2 2 0</td>
<td>Very Weak</td>
</tr>
<tr>
<td>3.3075</td>
<td>3 2 1</td>
<td>Very Weak</td>
</tr>
<tr>
<td>3.0942</td>
<td>4 0 0</td>
<td>Medium</td>
</tr>
<tr>
<td>2.7680</td>
<td>4 2 0</td>
<td>Very Strong</td>
</tr>
<tr>
<td>2.6410</td>
<td>3 3 2</td>
<td>Very Weak</td>
</tr>
<tr>
<td>2.5270</td>
<td>4 4 2</td>
<td>Medium</td>
</tr>
<tr>
<td>2.4279</td>
<td>4 3 1</td>
<td>Very Weak</td>
</tr>
<tr>
<td>2.2603</td>
<td>5 2 1</td>
<td>Weak</td>
</tr>
<tr>
<td>2.1888</td>
<td>4 4 0</td>
<td>Very Weak</td>
</tr>
<tr>
<td>2.0084</td>
<td>5 3 2</td>
<td>Weak</td>
</tr>
<tr>
<td>1.8259</td>
<td>6 3 1</td>
<td>Very Weak</td>
</tr>
<tr>
<td>1.7869</td>
<td>4 4 4</td>
<td>Weak</td>
</tr>
<tr>
<td>1.7170</td>
<td>6 4 0</td>
<td>Medium</td>
</tr>
<tr>
<td>1.6849</td>
<td>5 5 2</td>
<td>Very Weak</td>
</tr>
<tr>
<td>1.6545</td>
<td>6 4 2</td>
<td>Medium</td>
</tr>
<tr>
<td>1.5724</td>
<td>6 5 1</td>
<td>Very Weak</td>
</tr>
<tr>
<td>1.5476</td>
<td>8 0 0</td>
<td>Weak</td>
</tr>
<tr>
<td>1.5247</td>
<td>7 4 1</td>
<td>Very Weak</td>
</tr>
<tr>
<td>1.5016</td>
<td>8 2 0</td>
<td>Very Weak</td>
</tr>
</tbody>
</table>

The electron diffraction pattern associated with the raw yttrium iron oxide nanopowder is shown in Figure 3-7.
Figure 3-7: This diffraction pattern was taken from the raw yttrium iron oxide nanopowder. The reflections that correspond closely with those predicted by the YIG powder diffraction pattern are indicated. However, many expected YIG reflections are not observed, indicating a poor match to YIG.

The information corresponding with this image is shown in Table 3-2.

<table>
<thead>
<tr>
<th>Reflection Number (from center)</th>
<th>Calculated d</th>
<th>PDF d</th>
<th>Associated Reflection &lt;h k l&gt;</th>
<th>Error (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>3.04</td>
<td>3.0942</td>
<td>&lt;4 0 0&gt;</td>
<td>1.63</td>
</tr>
<tr>
<td>2</td>
<td>2.57</td>
<td>2.5270</td>
<td>&lt;4 4 2&gt;</td>
<td>-1.91</td>
</tr>
<tr>
<td>3</td>
<td>2.09</td>
<td>2.0084</td>
<td>&lt;5 3 2&gt;</td>
<td>-4.19</td>
</tr>
<tr>
<td>4</td>
<td>1.64</td>
<td>1.6545</td>
<td>&lt;6 4 2&gt;</td>
<td>0.32</td>
</tr>
<tr>
<td>5</td>
<td>1.52</td>
<td>1.5247</td>
<td>&lt;7 4 1&gt;</td>
<td>0.19</td>
</tr>
</tbody>
</table>

Table 3-2: This table shows the information that compares the electron diffraction reflections from the raw yttrium iron oxide nanopowder to those predicted by YIG’s powder diffraction file. Some reflections show good agreement; however, many predicted reflections are missing from the diffraction image, indicating that the material is a poor match to YIG.
This data indicates that, while several of the observed reflections show agreement to those predicted in the YIG powder diffraction file, many more are missing. This indicates that the material is a poor match to YIG.

The YIG nanopowder, which had been calcined at 800 °C in order to induce the correct crystal structure, was also investigated by TEM. An image of this calcined nanopowder is shown in Figure 3-8.

![Figure 3-8](image)

**Figure 3-8:** This BF TEM image shows commercially available yttrium iron oxide nanopowder after calcination at 800 °C. Although there is some aggregation, most nanoparticles are well dispersed. The particle size is on the order of 10-20 nm.

This image indicates that, while there is some degree of particle aggregation, the majority of nanoparticles are well dispersed. The average nanoparticle size is on the order of 10-20 nm. TEM lattice images taken at high magnification also provide evidence that the calcined material is crystalline. This is shown in Figure 3-9.
3.2 Synthesized Yttrium Iron Garnet (YIG)

An effort was also made to create YIG nanoparticles through direct nanoparticle synthesis. The procedure employed synthesized YIG by a known method called coprecipitation in microemulsions. In this process, two microemulsion systems were created. The first consisted of oil, surfactant, and an aqueous metal salt solution. The second microemulsion system consisted of oil, surfactant, and an aqueous basic solution. The first system was added to the second and the combined microemulsion system stirred. This process allowed the microemulsions containing the metal and basic solutions to collide and chemically interact with one another. This caused the
microemulsions to act as nanoreactors in which YIG precursor particles were formed.

This process is diagrammed in Figure 3-10.

Figure 3-10: The synthesis method required the creation of two microemulsion systems, one containing a metal salt solution and the other containing a basic solution. When mixed, the microemulsions in each system react with one another, creating YIG precursor particles.

These precursor particles were separated from the solution by ultracentrifugation at 5000 rpm for 10 minutes. The precursor particles were washed twice with ethanol and dried at 80 °C. The precursor particles were then calcined at 300 °C for one hour, then at 400 °C for a second hour, and finally at 760 °C for two more hours to rid the particles of surfactant and induce the YIG crystal state. Specific information regarding the materials used in this process is listed in Table 3-3.
Table 3-3: Materials and their respective ratios used to synthesize YIG nanoparticles. Adapted from *Synthesis of yttrium iron garnet nanoparticles via coprecipitation in microemulsion* by P. Vaqueiro, M.A. Lopez-Quintela, and J. Rivas, Journal of Materials Chemistry, 7(3), 501-504, 1997.

<table>
<thead>
<tr>
<th>Metal Salt Microemulsion System</th>
<th>Surfactant</th>
<th>Oil Phase</th>
<th>Aqueous Phase</th>
</tr>
</thead>
<tbody>
<tr>
<td>Igepal CA-520</td>
<td>Heptane</td>
<td>Fe(NO₃)₃·9H₂O (0.2 mol dm⁻³) and Y(NO₃)₃·6H₂O (0.12 mol dm⁻³)</td>
<td></td>
</tr>
<tr>
<td>Basic Microemulsion System</td>
<td>Igepal CA-520</td>
<td>Heptane</td>
<td>(NH₄)₂CO₃</td>
</tr>
<tr>
<td>Mass Fraction</td>
<td>38.13 %</td>
<td>53.87 %</td>
<td>8 %</td>
</tr>
</tbody>
</table>

3.2.1 X-Ray Diffraction (XRD) Analysis

The existence of the YIG crystal state was verified through X-ray Diffraction (XRD). This data is shown in Figure 3-11.

![Figure 3-11: X-ray Diffraction (XRD) verifies that the synthesized nanoparticles exhibit the YIG crystal structure.](image-url)
XRD indicates that the synthesized nanoparticles are an excellent match to YIG. Also, YIG is the only crystal structure present in this material. The fact that orthorhombic forms of yttrium iron oxide are not present indicates that the synthesis method is superior to the calcination of commercially available nanopowder in creating a pure cubic magnetooptical material.

### 3.2.2 Transmission Electron Microscopy (TEM)

This synthesized system was dispersed using the same procedure used to disperse the commercially available nanopowder. After this dispersion, TEM was used to analyzed the synthesized nanoparticles (see Figure 3-12).

![BF TEM image of synthesized YIG nanoparticles. This data indicates an average particle diameter on the order of 30-50 nm.](image)

**Figure 3-12:** This is a BF TEM image of the synthesized YIG nanoparticles. This data indicates an average particle diameter on the order of 30-50 nm.
Although some particle aggregation is evident, individual nanoparticles are visible. This data indicates that the average nanoparticle diameter is on the order of 30-50 nm, an ideal size to be added to an optical system.

Electron diffraction patterns taken from the microemulsion synthesized YIG samples were also analyzed. An electron diffraction pattern corresponding to the synthesized material is shown in Figure 3-13.

**Figure 3-3:** This is a TEM diffraction pattern taken from the synthesized YIG nanoparticles. This pattern indicates reflections that match those predicted for the YIG crystal structure.
This data indicates strong agreement with all the major reflections predicted for YIG.

The information corresponding to this diffraction pattern is provided in Table 3-4.

<table>
<thead>
<tr>
<th>Reflection Number (from center)</th>
<th>Calculated ( d )</th>
<th>PDF ( d )</th>
<th>Associated Reflection ( &lt;h k l&gt; )</th>
<th>Error (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>3.33</td>
<td>3.3075</td>
<td>(&lt;3 2 1&gt;)</td>
<td>-0.62</td>
</tr>
<tr>
<td>2</td>
<td>3.12</td>
<td>3.0942</td>
<td>(&lt;4 0 0&gt;)</td>
<td>-0.90</td>
</tr>
<tr>
<td>3</td>
<td>2.72</td>
<td>2.7680</td>
<td>(&lt;4 2 0&gt;)</td>
<td>1.78</td>
</tr>
<tr>
<td>4</td>
<td>2.64</td>
<td>2.6410</td>
<td>(&lt;3 3 2&gt;)</td>
<td>-0.11</td>
</tr>
<tr>
<td>5</td>
<td>2.58</td>
<td>2.5270</td>
<td>(&lt;4 2 2&gt;)</td>
<td>-1.96</td>
</tr>
</tbody>
</table>

**Table 3-4:** This table shows the information that compares the electron diffraction reflections from the synthesized YIG nanoparticles to those predicted by YIG's powder diffraction file. The observed reflections show strong agreement with consecutive reflections predicted for YIG.

This information corresponds to the XRD data in that it indicates that the synthesized nanoparticles are in fact YIG.
Chapter 4

Nanoparticle-Liquid Crystal Co-Assembly

4.1 Untreated 5CB-COC System

In order to examine the manner in which nanoparticles affect a chiral nematic liquid crystal, such a chiral nematic phase was created by combining the nematic liquid crystal 5CB (4-pentyl-4'-cyanobiphenyl) and the chiral dopant COC (cholesterol oleyl carbonate). This mixture contained 39.75 wt % 5CB and 60.25 wt % COC, which results in a helical pitch that reflects visible wavelengths.38

4.1.1 Differential Scanning Calorimetry (DSC)

Differential scanning calorimetry (DSC) was used to establish the phase transition temperatures of the 5CB-COC system. This data is shown in Figure 4-1.
Figure 4-1: This DSC data shows the phase transitions associated with the untreated 5CB-COC system. This material changes from solid to chiral nematic at approximately 20.5 °C and from chiral nematic to liquid at approximately 36 °C.

This data shows that the material transitions from solid to chiral nematic at approximately 20.5 °C and from chiral nematic to isotropic liquid at approximately 36 °C.

4.1.2 Test Cell Preparation

The 5CB-COC system was inserted into a liquid crystal test cell purchased from E.H.C. Corporation in Japan. These test cells consist of a 25 micron gap (with an error of +/- 5 microns) between rubbed polyimide layers. The liquid crystal molecules conform to the rubbed layers, inducing parallel alignment in the molecules in contact with the two surfaces. This alignment causes the system’s numerous helical axes to uniformly align in the test cell gap. Such a test cell is shown in Figure 4-2.
The test cell was filled by placing liquid crystal on the test cell ledge and heating the system beyond its clearing point. Once the liquid crystal is in its isotropic state, it flows into the test cell gap by capillary action.

4.1.3 Reflectivity Data

Reflectivity data from the 5CB-COC filled test cell was obtained using an optical microscope with a spectrometer attachment. A metal mirror (that reflects all visible wavelengths equally) was used as a reflective standard, defining what will be considered 100% reflectivity. Reflectivity data was taken at 5 distinct locations on the test cell at various temperatures throughout the chiral nematic range. From this data, average reflectivity and average peak reflected wavelength were determined.

The reflectivity spectrum resulting from this liquid crystal system differs with system temperature. A typical set of this reflectivity data is shown in Figure 4-3.
Clearly, the peak wavelength in the reflected band varies as a function of temperature.

This is shown in Figure 4-4.
Reflectivity Peak as a Function of Temperature

![Graph showing the relationship between temperature and reflected wavelength.

Figure 4-4: The peak wavelength in the band reflected by the chiral nematic liquid crystal varies with temperature. Specifically, peak reflected wavelength decreases as temperature increases. This effect is reversible with respect to temperature.

This data indicates that the peak reflected wavelength decreases with increasing temperature in a non-linear fashion. In addition, this effect is reversible when the system is cooled from the isotropic state through the chiral nematic region. The data point shown is an average value and the error bars indicate one standard deviation above and below that value.

The degree of reflectivity exhibited by a test cell system also varies with temperature. This data is shown in Figure 4-5 and indicates that reflectivity decreases with increasing temperature.
Reflectivity as a Function of Temperature

Figure 4-5: Reflectivity for the pure 5CB-COC system decreases with increasing temperature. This trend is reversible, though the sample generally exhibited greater reflectivity when heated through the chiral nematic temperature range than when cooled from the isotropic state.

In addition, while this trend is reversible, the system exhibits higher reflectivity when heated through the chiral nematic range than when cooled from the isotropic state. Again, the data points shown are average values. The error bars shown indicate one standard deviation above and below this average.

4.2 Toluene Treated 5CB-COC System

In order to dope 5CB-COC with nanoparticles, the liquid crystal system was dissolved in a dispersion of nanoparticles in toluene and the toluene was subsequently evaporated. This being the case, it was important to determine the effect this process had on the liquid crystal material. This matter was investigated by dissolving 7.66 g of 5CB-
COC in 1.3 mL of toluene. Vacuum was induced by attaching the system to a vacuum line and the toluene was allowed to evaporate over a period of 24 hours. This evaporation process was sufficient to eliminate the vast majority of toluene (though traces of toluene presumably remained) and allowed the liquid crystal to reconsolidate.

4.2.1 Differential Scanning Calorimetry (DSC)

Differential scanning calorimetry (DSC) indicated that the toluene treated 5CB-COC system exhibited slightly lower phase transition temperatures than the untreated liquid crystal system. This data is shown in Figure 4-6.

Figure 4-6: This DSC data shows the transition temperatures for toluene treated 5CB-COC. This material changes from solid to chiral nematic at 19.5 °C and from chiral nematic to liquid at 35 °C. These transition temperatures are lower than those of the pure 5CB-COC system by 1 degree.
This material changes from solid to chiral nematic at approximately 19.5 °C and from chiral nematic to isotropic liquid at approximately 35 °C. Both of these transitions are 1 degree lower than those exhibited by the untreated 5CB-COC system.

4.2.2 Reflectivity Data

After filling a test cell with toluene treated 5CB-COC chiral nematic liquid crystal, reflectivity data was taken. A typical set of this reflectivity data is shown in Figure 4-7.

**Figure 4-7:** Reflectivity spectra associated with the toluene treated 5CB-COC system at various temperatures.

The average peak wavelength in the reflected band was determined as a function of temperature. This data is shown in Figure 4-8.
The average peak reflected wavelength for the toluene treated system at a given temperature is indicated. The error bars indicate one standard deviation above and below this average value. The peak reflected wavelength decreases as temperature increases. This effect is reversible.

The data indicates that the peak reflected wavelength decreases with increasing temperature and that this effect is reversible.

It is interesting to note that the sample continued to create a reflectivity band when heated to 36 °C, a temperature at which, according to the DSC data, the material should be in its isotropic state. This slight discrepancy can be attributed to the calibration of the DSC and the fact that there is a temperature gradient between the heating stage and the liquid crystalline material, caused by the glass slide of the test cell that separates the two.
This material’s degree of reflectivity was also investigated. This data is shown in Figure 4-9 and indicates that reflectivity decreases with increasing temperature, a trend also observed in the untreated 5CB-COC sample.

**Figure 4-9:** This data indicates that reflectivity decreases with increasing temperature for the toluene treated 5CB-COC system. It is also evident that this material is less reflective than the pure 5CB-COC system.

However, while these samples showed similar reflectivity trends, the pure material showed significantly higher reflectivity.

### 4.3 5CB-COC System Doped with Nanoparticles

The 5CB-COC liquid crystal was doped with nanoparticles by dissolving the system in a dispersion of silica nanoparticles (with an average diameter of 40 nm) in toluene. This solution was attached to a vacuum line and allowed to evaporate for a
period of 24 hours, leaving a nanoparticle-chiral nematic liquid crystal composite containing 3.4 wt % silica nanoparticles.

4.3.1 Differential Scanning Calorimetry (DSC)

Differential scanning calorimetry (DSC) indicated that the nanoparticle-chiral nematic composite exhibited lower transition temperatures than those observed in the pure and toluene treated samples. This data is shown in Figure 4-10.

**Figure 4-10:** Differential scanning calorimetry (DSC) indicates that the nanoparticle-chiral nematic liquid crystal composite exhibits lower transition temperatures than those observed in the pure and toluene treated samples. This nanoparticle doped material changes from solid to chiral nematic at 17.25 °C and from chiral nematic to liquid at 32 °C.
DSC indicates that this nanoparticle doped material transitions from solid to chiral nematic at approximately 17.25 °C and from chiral nematic to isotropic liquid at 32 °C.

### 4.3.2 Reflectivity Data

After filling a test cell with the nanoparticle doped 5CB-COC system, the average peak wavelength in the reflected band was determined as a function of temperature. While five locations on the test cell were examined, only three of those locations produced distinguishable reflectivity peaks. The other two test cell locations showed “reflectivity shoulders” (a term used to describe data that takes a step-like shape). A typical set of reflectivity data (for a test cell location that did exhibit reflectivity peaks) is shown in Figure 4-11.

**Figure 4-11:** Reflectivity spectra associated with the 5CB-COC system doped with silica nanoparticles at various temperatures.
The data associated with the observed reflectivity peaks is shown in Figure 4-12.

![Graph showing Reflectivity Peak as a Function of Temperature](image)

**Figure 4-12:** This data shows average reflectivity peak as a function of temperature. This average value was determined from the three test cell locations that showed reflectivity peaks. The error bars indicate one standard deviation above and below this average value. The data indicates that the peak wavelength in the reflected band decreases as temperature increases and that this effect is not reversible with respect to temperature.

As in the pure and toluene treated systems, reflectivity peak decreases as temperature increases. However, unlike the pure and toluene treated samples, this reflectivity data is not reversible with respect to temperature. This means that, while reflectivity peaks are observed when heating the specimen through its chiral nematic temperature range, those peaks do not reform when the material is cooled from its isotropic state.

It should be noted that this system did not become isotropic until the heating stage exceeded 34 °C, while DSC data indicated that the material has a clearing point of 32 °C. As was the case for the toluene treated material, this discrepancy can be attributed to the
calibration of the DSC and the fact that there is a temperature gradient between the heating stage and the liquid crystalline material, caused by the glass slide of the test cell that separates the two.

Average reflectivity data was also collected for the three test cell locations that produced reflectivity peaks. This data is shown in Figure 4-13.

**Reflectivity as a Function of Temperature**

![Reflectivity as a Function of Temperature](image)

Figure 4-13: This data shows reflectivity as a function of temperature for 5CB-COC doped with silica nanoparticles. While this doped system shows low reflectivity, it is clear that reflectivity decreases with increasing temperature.

As in the untreated and toluene treated materials, reflectivity decreases a function of temperature. However, the addition of nanoparticles causes this sample to show significantly lower reflectivity than its untreated and toluene treated counterparts.
4.4 Comparison of 5CB-COC Systems

It is useful to combine the corresponding sets of data described in the previous sections of this chapter. This allows the various 5CB-COC systems to be more easily compared and facilitates the process of interpreting the data.

4.4.1 Differential Scanning Calorimetry (DSC)

Combining the DSC data for the untreated, toluene treated, and nanoparticle doped 5CB-COC systems provides an interesting contrast. This data is shown in Figure 4-14.

![Comparison of 5CB COC Systems](image)

**Figure 4-14:** This DSC data shows phase transition temperatures for various 5CB-COC systems.
The approximate phase transition temperatures deduced from this data are shown in Table 4-1.

<table>
<thead>
<tr>
<th>Transition Temperatures</th>
<th>Solid→Chiral Nematic (°C)</th>
<th>Chiral Nematic→Liquid (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pure</td>
<td>20.5</td>
<td>36.0</td>
</tr>
<tr>
<td>Toluene Treated</td>
<td>19.5</td>
<td>35.0</td>
</tr>
<tr>
<td>Silica NPs 3.4 wt %</td>
<td>17.25</td>
<td>32.0</td>
</tr>
</tbody>
</table>

This data suggests that impurities disrupt the systems’ chiral nematic order, resulting in phase transitions occurring at lower input energies. Furthermore, there appears to be a direct correlation between the degree of structural disruption and the amount by which the phase transition temperatures are lowered.

4.4.2 Reflectivity Data

Superposition of the reflectivity data is also useful. Figure 4-15 shows average peak reflected wavelength as a function of temperature.
Figure 4-15: This data shows average peak reflected wavelength as a function of temperature. The data suggests that the addition of nanoparticles inhibits the material’s ability to form reflectivity bands. This data shows that the addition of nanoparticles to a 5CB-COC system inhibits the material’s ability to form reflectivity bands. This is indicated by the fact that the doped system showed reflectivity bands for only three of the five test cell locations investigated, the fact that the doped system became isotropic beyond 34 °C (as opposed to the pure and toluene treated systems, which became isotropic beyond 36 °C), and the fact that (unlike the pure and toluene treated materials) the data associated with the doped system was not reversible with respect to temperature.

A superposition of reflectivity as a function of temperature is shown in Figure 4-16.
Comparison of 5CB COC Systems

Figure 4-16: This data shows reflectivity as a function of temperature for the untreated, toluene treated, and nanoparticle doped 5CB-COC systems. This data indicates that the addition of impurities lowers the system’s overall reflectivity.

This data indicates that the presence of impurities lowers the overall reflectivity of the system.
Chapter 5

Conclusions

This portion of the thesis provides a summary of the scientific conclusions derived from the research on the production of magnetooptical nanoparticles and nanoparticle-liquid crystal co-assembly.

5.1 Production of Magnetooptical Nanoparticles

X-ray diffraction (XRD) data indicates that yttrium iron oxide, purchased from Sigma-Aldrich is not actually YIG as received, but can be partially converted to a YIG phase after being calcined at 800 °C for 2 hours (see Figure 3-5). This YIG phase is accompanied by orthorhombic yttrium iron oxide (YFeO$_3$). Transmission electron microscopy (TEM) indicates that this calcined YIG material can be well dispersed and has an average nanoparticle diameter on the order of 10-20 nm (see Figure 3-8). This small nanoparticle size and the presence of orthorhombic yttrium iron oxide indicate that calcination of a commercially available nanopowder is not a viable means of obtaining YIG nanoparticles with diameters between 20-50 nm.

Nanoparticle synthesis via coprecipitation in microemulsions provides more promising results for obtaining approximately 100% YIG nanoparticles in the range of 30-50 nm diameter. The close match of the five most prominent peaks in XRD and the
absence of any noticeable non-YIG peaks indicates that this process produces YIG exclusively (see Figure 3-11). In addition, TEM shows that the synthesized YIG nanoparticles have diameters on the order of 30-50 nm (see Figure 3-12).

5.2 Nanoparticle-Liquid Crystal Co-Assembly

The reflectivity spectra associated with a chiral nematic liquid crystal system composed of 5CB (4-pentyl-4′-cyanobiphenyl) and the chiral dopant COC (cholesteryl oleyl carbonate) was investigated. The reflectivity and peak reflected wavelength associated with this system both decreased with increasing temperature (see Figures 4-15 and 4-16). The addition of impurities disrupted the system’s helical structure. This was evident from the lower energy required to thermally transform the chiral nematic order to the isotropic phase (phase transitions occur at lower temperatures). Furthermore, the degree of structural disruption determines how far the phase transition temperatures are lowered. Trace amounts of solvent (that were purposefully added) lowered the system’s phase transition temperatures by 1° and the addition of nanoparticles lowered the phase transition temperatures by approximately 3° (see Figure 4-14).

The addition of nanoparticles also inhibited the system’s ability to form reflectivity peaks. The nanoparticle doped 5CB-COC system showed reflectivity peaks for only three of the five test locations investigated. In addition, unlike was the case for the untreated and toluene treated systems; these reflectivity peaks did not reform when the system was cooled from its isotropic state (see Figure 4-11).
5.3 Future Work

The ultimate goal, advanced by this work, is to incorporate magnetooptical YIG nanoparticles (which can break time-reversal symmetry) into the chiral nematic periodic dielectric (which breaks space-inversion symmetry). This system could be created by coating YIG nanoparticles with a compound that is compatible with a solvent and a chiral nematic matrix. Once coated, the nanoparticles would have to be dispersed in a solvent capable of dissolving the chiral nematic liquid crystal. After achieving a dispersion of YIG nanoparticles in solvent, the dispersion could be used to dissolve the liquid crystal. The solvent could then be removed by evaporation, leaving a system consisting of a chiral nematic liquid crystal doped with magnetooptical nanoparticles. When such a system is achieved, optical studies could be conducted in the presence of an applied magnetic field.
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