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Photonic Band Gap Materials: Optical Properties of Hollow Spherical Shells

by

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A THESIS SUBMITTED IN PARTIAL FULFILLMENT OF THE REQUIREMENTS FOR THE DEGREE

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Abstract

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Optical transmission studies of three-dimensionally ordered photonic crystals of close-packed spherical shells are presented. These samples are fabricated using a double-template method, which allows for extensive control over shell thickness. The transmission spectra exhibit an optical stop band, whose spectral position and width depend on the thickness of the shell and on the overlap between adjacent spheres, in a manner consistent with numerical simulations. These parameters can be controlled over a wide range, thus permitting systematic studies of the optical properties, and providing a valuable method for engineering the characteristics of the optical stop band in colloidal photonic media.
ACKNOWLEDGEMENTS

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CHAPTER 1: INTRODUCTION

1.1 PHOTONIC BAND GAP MATERIALS

The past 50 years has seen semiconductor technology play a major role in almost every aspect of our lives. A technology that started with crude manipulation of millions of electrons in a periodic lattice, to spur the growth of the modern computer, has now reached such levels of precision that we can control the movement of a few tens of electrons in logic circuits. In order to do better we need to overcome fundamental physical limits in our drive towards miniaturization. For some time now researchers have been looking towards light rather than electrons as the information carrier. Already in many areas of telecommunication current-carrying copper wires have been replaced with their electromagnetic counter-part, the optical fiber. Until now this has been the easiest and most effective method to control the propagation of light, and has gone a long way to making optical instruments more compact. Now a new class of materials, analogous to semiconductors, is emerging that allows us to control the propagation of light in a completely new way; these are known as photonic band gap materials.

Electrons traveling in a periodic lattice experience a periodic potential. The geometry of the lattice and the strength of the potential cause Bragg-like diffraction effects to arrange the electrons into energy bands separated by gaps in which propagating states are
prohibited. The reason why semiconductors have proved to be such marvelous manipulators of electrons is because the propagation of electrons can be controlled by manipulating the electronic band gap. Similarly an electromagnetic wave that interacts with a medium having a periodic dielectric function also has certain frequencies which are prohibited from propagating within the material. These gaps in the allowed electromagnetic frequencies are referred to as photonic band gaps. Controlling these gaps is the key to developing photonic applications.

Figure 1.1 Examples of one, two and three-dimensional photonic crystals. The different colors represent different values of the dielectric constant.

1.2 APPLICATIONS

Photonic band gap (PBG) materials can have a profound impact on many areas of pure and applied physics. The absence of any optical modes in these gaps can suppress spontaneous emission for photons with frequencies within the gap.\(^1\) For example, by tuning the photonic gap to straddle the electronic band edge, electron-hole recombination
in semiconductors can be controlled increasing the efficiency and reducing the noise of semiconductor lasers and other such devices. The suppression of spontaneous emission can also be used to prolong the lifetime of certain chemical species in catalytic processes. PBG materials can also be used in frequency selective mirrors, band-pass filters and optical resonators. By introducing controlled defects in these materials one can observe localization of electromagnetic waves leading to the fabrication of waveguides for integrated optical circuits. Photonic band gap materials may revolutionize current technology in the same way that semiconductor technology sparked unprecedented growth 50 years ago.

1.3 Electromagnetic Propagation in an Inhomogeneous Dielectric

Electromagnetic propagation in a dielectric medium is described by Maxwell's equations

\[ \nabla \cdot B = 0 \]
\[ \nabla \cdot D = 4\pi \rho \]
\[ \nabla \times E + \frac{1}{c} \frac{\partial B}{\partial t} = 0 \]
\[ \nabla \times H - \frac{1}{c} \frac{\partial D}{\partial t} = \frac{4\pi}{c} J \]

(1)

For an inhomogeneous dielectric, like in the case of photonic crystals, the dielectric function \( \varepsilon(r,\omega) \) has spatial and perhaps even frequency dependence. To simplify the problem, we make a few valid assumptions.
First it is assumed that the medium has no free charges or currents. This enables us to set \( \rho = J = 0 \). D is related to E as follows,

\[
D_i = \sum_j \varepsilon_{ij} E_j + \sum_j 4\pi\chi_{ik} E_j E_k + O(E^3).
\]

where \( \chi \) is the susceptibility tensor. Here too we can make some reasonable approximations which are valid for many dielectrics. First we assume that the fields are small so that we are in the linear regime. This eliminates all the terms in the above equation except the first. Second we assume that the medium is isotropic leading to a scalar relation between \( D(r,\omega) \) and \( E(r,\omega) \). Third, we assume that there is no frequency dependence of the dielectric. In other words, the dielectric function is a constant over the range of frequencies we consider. Fourth, we assume the material to have negligible loss. This means that \( \varepsilon(r) \) is purely real. We also assume that the magnetic permeability is equal to unity. All these assumptions lead us to the following modified equations.

\[
\begin{align*}
\nabla \cdot H(r, t) &= 0 \\
\nabla \cdot \varepsilon(r) E(r, t) &= 0 \\
\n\nabla \times E(r, t) + \frac{1}{c} \frac{\partial H(r, t)}{\partial t} &= 0 \\
\n\nabla \times H - \frac{\varepsilon(r)}{c} \frac{\partial E(r, t)}{\partial t} &= 0
\end{align*}
\]

For mathematical convenience we can use a complex valued field to describe the electromagnetic radiation.

\[
\begin{align*}
H(r, t) &= H(r)e^{i\omega t} \\
E(r, t) &= E(r)e^{i\omega t}
\end{align*}
\]
The two divergence equations then become,

\[ \nabla \cdot \mathbf{H}(r) = \nabla \cdot \mathbf{D}(r) = 0 \quad (4) \]

This tells us that the medium has no point sources or sinks of displacement or magnetic fields and that the fields are electromagnetic transverse waves. The two curl equations become

\[ \nabla \times \mathbf{E}(r) + \frac{i\omega}{c} \mathbf{H}(r) = 0 \quad (5a) \]
\[ \nabla \times \mathbf{H}(r) - \frac{i\omega}{c} \varepsilon(r) \mathbf{E}(r) = 0 \quad (5b) \]

These two equations can be manipulated and combined to form the master equation that governs the electromagnetic behavior of the propagation. This can be done by dividing equation (5b) by \( \varepsilon(r) \) and taking the curl. Then we can use equation (5a) to eliminate \( \mathbf{E}(r) \) obtaining the master equation which is only a function of \( \mathbf{H}(r) \).

\[ \nabla \times \left( \frac{1}{\varepsilon(r)} \nabla \times \mathbf{H}(r) \right) = \left( \frac{\omega}{c} \right)^2 \mathbf{H}(r) \quad (6) \]

This equation completely determines \( \mathbf{H}(r) \) for a known dielectric function. Therefore the modes of the system \( \mathbf{H}(r) \) can be found for a particular frequency. Subsequently we can use equation (5b) to determine the electric field. The problem can be thought of as an eigenvalue problem when represented as follows.

\[ \Theta \mathbf{H}(r) = \left( \frac{\omega}{c} \right)^2 \mathbf{H}(r) \quad (7) \]
where $\Theta$ is the differential operator defined as

$$
\Theta H(r) = \nabla \times \left( \frac{1}{\varepsilon(r)} \nabla H(r) \right)
$$

(8)

The question of why we use the magnetic field and not the electric field for calculations is a valid one. We could very well have solved for the electric field directly by decoupling equations (5a) and (5b) and then obtained the magnetic field. However expressing the master equation in terms of the electric leads to an equation where the operator $\Theta$ is not hermitian resulting in a more complicated calculation. For this reason the above approach is the one that is most widely used.

This is the basis for all of the numerical calculations involving photonic band gap optical modes that are presented in this thesis.\textsuperscript{2} All subsequent calculations are a result of solving the master equation using a numerical technique. The numerical technique and the computer code employed in this thesis was developed by the Joannopoulos group at M.I.T. It is a fully vectoral three-dimensional calculation based on a plane wave expansion of the solutions. The entire calculation is in the frequency domain, allowing for simultaneous calculation of the optical modes and frequencies.

Some other commonly used methods for calculating band structure and transmission spectra involve transfer matrix calculations and plane wave expansion of Maxwell's equations.\textsuperscript{6, 7}
CHAPTER 2: FABRICATION OF PHOTONIC BAND GAP MATERIALS

2.1 WAVE PROPAGATION IN PHOTONIC CRYSTALS: THE BAND GAP

A photonic crystal is broadly classified as any material which has a periodic modulation of its refractive index. This periodicity allows us to use the terminology already developed for crystallography to describe this system. In other words, we can use the ideas of a reciprocal lattice, a Brillioun zone and a band structure to characterize photonic band gap materials.

As we know from crystallography electromagnetic radiation sees different lattice planes along different directions of propagation. This anisotropy causes the light propagating through a photonic crystal to see a direction-dependent periodic potential. This means that the band structure will also be dependent on the propagation vector. Unless the band gaps for all the propagation directions overlap at one frequency, the photonic crystal will not possess a complete band gap; i.e. frequencies for which light propagation is forbidden irrespective of the direction. In order to achieve a complete gap the lattice should have a high degree of symmetry with the Brillioun zone being spherical (for a three-dimensional crystal) \(^8\). However finding such a structure is challenging. Historically, the quest for a complete band gap structure followed a trial and error method with several different types of geometries being considered. Eventually it was discovered, by Yablonovitch, that a
material with a diamond structure and a refractive index contrast greater than 2 would form a complete photonic band gap. Figure 2.1 shows this structure, called Yablonovite, which consists of a dielectric block with a triangular array of holes; each being drilled three times at an angle of 35.26° away from the normal and spread 120° on the azimuth. As the periodicity in this case was of the order of centimeters, the band gap developed in the microwave wavelength range. The challenge now was to make these structures in the visible or infrared wavelengths, so important for numerous applications.

![Diagram of Yablonovite structure](image)

Figure 2.1 The Yablonovite structure consists of a dielectric slab in which a triangular array of holes is drilled. Each hole is drilled three times at an angle of 35.26° away from the normal and spread 120° about the azimuth. This results in a three-dimensional photonic crystal whose (1 -1 0) cross section is shown on the left.
The description of light propagation in photonic crystals involves the solution of Maxwell's equations with a periodic dielectric function. One of the appealing aspects of Maxwell's equations is that there is no fundamental length scale. Thus the solutions are scale invariant, which means that if the Yablonovite structure is scaled down to sufficiently small dimensions (comparable to the wavelength of visible light) a structure is obtained that has a complete band gap in the visible. However, material and fabrication difficulties have only recently allowed researchers to come close to manufacturing such a material. For example, Ozbay et al. have proposed a woodpile structure which is topologically equivalent to an FCC lattice structure. This type of structure was recently fabricated to have a band gap in infrared wavelengths. Another group recently demonstrated a technique capable of large scale fabrication of photonic crystal and has inferred a complete gap at 1.5 microns. Both groups however have yet to fully characterize their materials thereby successfully demonstrating a complete band gap.

2.2 Fabrication Approaches

To fabricate materials having a band gap in the visible or infra-red wavelengths, the periodicity of the refractive index has to be on the same length scales, i.e. sub-micron. Methods as simple as drilling holes in dielectrics will therefore not work easily at sub-micron lengths. It is clear that other methods, far more precise and creative, are required.
There have been two types of approaches to fabricating photonic crystals; a top-down and a bottom-up approach. The former involves lithographic techniques to etch out appropriate structures. The latter uses chemical self-assembly techniques to cause sub-micron spheres to spontaneously assemble into ordered arrays.

Lithographic techniques\textsuperscript{12-15} allow for precise control over the structure and give almost defect-free photonic materials. However, this process is expensive and painstaking so only a few repeated layers can be fabricated. Also samples made in this way are not suitable for applications requiring large areas of coverage. The self assembly technique on the other hand is ideally suited for growing large, three-dimensional planar samples with tens or hundreds of repeated layers. The technique involves simple chemistry and is inexpensive. The drawback is that, compared to the lithographically prepared samples, these have many defects which are difficult to control. However, this technique holds promise for making a variety of interesting structures, some of which could have a complete band gap. All the photonic materials in this study are fabricated using the self-assembly technique and the remainder of the text shall be devoted to discussions based on these types of photonic materials referred to as colloidal crystals.

\textbf{2.3 Fabrication of Colloidal Crystals}

Nature too makes its own photonic band gap material. Natural opal, used in the jewelry business is actually a photonic crystal. It consists of naturally self-assembled domains of
ordered nano-sized silica spheres. Figure 2.2 shows a photograph of an opal and an SEM image revealing the underlying ordering. The iridescence of an opal is due to the randomly oriented ordered domains, diffracting different wavelengths of light in several

![Image](http://aussie-opal.com/ir2mulbl.jpg)

Dr. R. K. Iler, The Chemistry of silica, Wiley, 1979

**Figure 2.2** Natural opal consists of domains of ordered self-assembled nano-sized silica spheres. The diffraction effects of each of these domains gives the opal its iridescence. A scanning electron microscopic image on the right reveals the order produced by natural self-assembly.

different directions. In the laboratory we try and mimic this process to produce single domain synthetic opals that are ordered on a much larger scale. All photonic colloidal crystals in the laboratory are made starting from a colloidal suspension of dielectric spheres. The chemistry to fabricate monodisperse silica nanospheres has been known for decades and was initially described by Stofer, Fink and Bohn. Nanospheres with diameters ranging from 200 to 700 nm and relative standard deviations of less than 7% are readily obtained. Figure 2.3 is a schematic illustration of this process. First ethanol is
The Colloid Chemistry of Silica, American Chemical Society, Washington, DC, 1994

**Figure 2.3** Schematic illustrating the Stober-Fink-Bohn process to make silica spheres. First filtered ethanol is mixed with a calculated quantity of ammonia and water; to this is added the TEOS. The TEOS is broken down in the presence of the catalyst ammonia to form hydrolyzed silica in the form of nano-particles. These are then aggregated to form silica colloids.
thoroughly filtered and a calculated amount of ammonia and water is added to it. Then
the vacuum-distilled tetraethyl orthosilicate is mixed with this mixture. The ammonia in
this mixture acts as a catalyst in the reaction, shown in figure 2.3. The end product is
hydrolyzed silica nanoparticles. These nano-particles are allowed to aggregate to form
larger spherical colloids. This colloidal suspension is then crystallized to form a three-
dimensional photonic crystal, which is essentially a synthetic opal. There are several
methods to initiate the crystallization. Almost all the methods result in a crystal that has
face-centered cubic (FCC) symmetry.

One of the more popular methods for forming crystals is to use a gravity sedimentation
technique.\textsuperscript{17-20} The silica spheres are allowed to sediment, under the influence of
gravitational or centrifugal forces, in a capillary and the solvent is evaporated. Films
prepared in this manner have many polycrystalline domains each approximately one
square millimeter in area. The crystal formation occurs only at specific volume fractions
of the colloidal solution, so it is difficult to control the crystal growth. As a result the film
thickness is not adjustable. This method provides very thick films but can take up to 10
days to grow a single sample. Another technique involves crystallization by shear
alignment.\textsuperscript{21}

Our group has found a new method to crystallize the colloids.\textsuperscript{22} This method relies on
strong capillary forces to self-organize the colloids into a regular FCC crystal. These
arrays are ordered over large areas (\(~1 \text{ cm}^2\)). Importantly, the thickness of the film can be
precisely controlled by varying the volume fraction of the colloidal solution. Moreover, the crystallization process only takes a few days. Figure 2.4 is a schematic explaining the process. The photonic crystal is formed on a glass slide immersed in a colloidal solution. The capillary force of the meniscus draws the spheres towards each other causing them to pack together. As the solution evaporates the lower regions of the glass surface are coated. The thickness of the film is controlled by adjusting the volume fraction of the colloidal solution. The higher the volume fraction the thicker the film. However, for volume fractions higher than 4% the film quality degrades rapidly. Therefore thicker samples are made by multiple coatings, whereby the film is dried and re-immersed in solution several times to obtain a thick mult-coated colloidal crystal.

![Diagram](image)

**Figure 2.4** Schematic illustrating the processes involved in the self assembly process. The surface tension of the meniscus forces the spheres to draw towards each other resulting in their being tightly packed. With evaporation the meniscus coats a lower region on the glass slide in the same manner.
2.4 Characterization of Colloidal Crystals

The colloidal crystal samples are characterized using a Scanning Electron Microscope (SEM), Atomic Force Microscope (AFM) and by optical transmission measurements. The SEM reveals information about the ordering of the crystal. As shown in figure

Figure 2.5 Top down SEM images of silica colloidal crystals. The insets are the Fourier transforms of the images which simulate diffraction spots. The uniformity and order of the crystal can be inferred from such images. The top image is taken from a very ordered sample giving rise to clear diffraction spots. The bottom image is obtained from a disordered sample and reveals a smearing of the diffraction spots
2.5, top-down images of different regions of the sample facilitate the measurement of the sphere sizes. The sphere diameter can then be statistically estimated giving quantitative information about the monodispersity of the colloids. A digital Fourier transform of the image, indicated in the insets of the images, gives an indication of the uniformity of the sample by simulating diffraction spots. A crystal with a high degree of disorder produces a smearing of the diffraction spots to resulting in ring patterns. To show long range order we analyze Fourier transforms from low magnification images.

Figure 2.6 Fourier transforms of four 11.75 x 11.75 μm regions of a 1 cm² silica colloidal single crystal. These were part of a series of images taken every 50 μm over a 4x4 mm square region; they represent the four corners of the square. The four parallel dashed lines in the right image indicate one reference direction demonstrating that the four images are roughly the same orientation, as were all intermediate images. The largest deviation is ~1.6° represented in image c. The crystallographic orientation is preserved over this entire region.
We compared micrographs of 40 μm² area images which were collected as the sample was translated. The presence of any grain boundaries would be indicated by a shift in the alignment of the diffraction spots. Figure 2.6 shows four representative images taken at the four corners of a square of side 4 mm. That the periodicity of the lattice is maintained is demonstrated by the alignment of the diffraction spots. These as well as the intermediate images show no evidence of grain boundaries, indicating of the high degree of crystalline order.

Cross-sectional images confirm the FCC symmetry and enable us to measure the number of repeated layers and hence the sample thickness. Figure 2.7 shows cross-sectional SEM images of different samples. The samples are highly uniform for several tens of layers as illustrated. Figures 2.7 (b) and (d) are especially worth noting as they are thick containing about 50 repeated layers with no stacking faults. The cracks in the samples are not inherent defects, but are artifacts of the charging in SEM measurements upon breaking the sample to expose the cross-section. Top down images taken using an atomic force microscope reveal substantially fewer cracks, clearly demonstrating that the colloidal crystals are practically free of grain boundaries.

Before we can understand the optical properties of this crystal, we need to understand how the FCC geometry influences the transmission spectra. The first Brillouin zone of an FCC crystal is illustrated in figure 2.8, with the different crystallographic directions
Figure 2.7 Cross-sectional scanning electron microscope images of colloidal crystals. (a) and (c) are thin samples with about 15 repeated layers. (b) and (d) are much thicker samples having about 50 repeated layers. The absence of stacking faults is especially clear in the thick samples. The cracks in the images are due to stress upon cutting the sample and also due to SEM charging. Top-down images on AFM show fewer cracks.

marked with capital letters. The figure is in reciprocal space and represents diffraction conditions in three-dimensions. To probe a complete gap we need to measure transmission spectra along all the crystallographic directions. Our crystals grow in the (111) direction, hence the (111) direction is perpendicular to the plane of the crystal surface. This is the L point in figure 2.8. The L point is the closest point to the center and
hence the diffraction gap formed along this direction will correspond to the longer wavelengths as compared to any gap formed along the other crystallographic directions. It is this gap that we probe in all our experiments. Higher order gaps may be observed upon extending this picture beyond the first Brillouin zone. However in all our experiments the relevant gap that falls in the visible spectrum is associated with the first Brillouin zone.

![Brillouin zone](image)

**Figure 2.8** First Brillouin zone of an FCC lattice crystal. The capital letters denote specific crystallographic directions. In particular, the L-direction corresponds to the (111) direction. It is along this direction that all the normal incidence transmission spectra are taken. (Figure adapted from reference\(^8\))

Optical transmission spectra enable measurement of the photonic band gap. The manner in which the crystal forms produces a planar film in which normal incidence transmission measurements probe the gap along the L direction. As these crystals are not expected to possess a complete band gap\(^7\), the partial gap along the L direction, between the 2\textsuperscript{nd} and 3\textsuperscript{rd} bands, is measured. Theoretically the mid-gap position and the gap-width can be predicted. The Fabry-Perot fringes, in the optical data, arising from reflections of the
front and back surface of the film, allow for an independent estimation of the film thickness. A typical background-subtracted transmission spectrum with these fringes is shown in figure 2.9.

![Graph](image)

**Figure 2.9** Typical normal incidence transmission spectra of a colloidal crystal. A background monotonically increasing with decreasing wavelength, observed in all such samples has been subtracted. The fringes enable determination of the sample thickness. The amplitude and width of the band gap give an indication of the uniformity of the crystal in the region.
2.5 Optical Properties of Colloidal Crystals

Previous studies on crystals grown using the sedimentation technique primarily dealt with reflection studies on account of non-uniformities in the sample thickness and the presence of a large number of defects. We have fine-tuned our method to produce optical quality films with relatively few point defects and practically no grain boundaries. Therefore the defects that have plagued previous optical studies are no longer the dominant factor in measurements making our crystals ideal candidates for conducting optical transmission studies.

One of the exciting aspects of this photonic crystal is that the same process of self-assembly can be applied to produce films having band gaps from the ultraviolet right up to infrared wavelengths. We can change the band structure of the material significantly by simply altering the geometry of the spheres. The precise control we have over the sphere growth enables us to engineer crystals with specific predetermined optical properties. Figure 2.10, shows normal incident optical spectra of the partial gap along the (111) direction for different sphere sizes. Films with larger spheres develop stop bands in regions of longer wavelengths. By growing spheres with a specific diameter we can position the band gap anywhere in this wavelength range. A simple scalar effective medium theory can be used to predict the position of the band gap. This theory assumes that the photonic crystal behaves like a homogeneous diffracting medium with
Figure 2.10 Normal incidence transmission spectra of colloidal crystals with different sphere diameters. For samples grown with larger spheres the mid-gap peak shifts to longer wavelengths. The peak can be positioned anywhere in the visible spectrum.

an effective weighted refractive index and that the scattering occurs mainly from one set of lattice planes ((111) plane in this case).
In other words,

\[ \lambda_{\text{PBG}} = 2 \cdot n_{\text{eff}} \cdot d_{111} \quad (1a) \]

\[ n_{\text{eff}} = \left( \varepsilon_{\text{sphere}} \cdot \phi + \varepsilon_{\text{interstitial}} \cdot (1 - \phi) \right)^{1/2} \quad (1b) \]

where \( \lambda_{\text{PBG}} \) is the central wavelength of the gap, \( n_{\text{eff}} \) the effective refractive index, \( \varepsilon \) the dielectric constant and \( \phi \) the volume fraction (for a FCC crystal of close packed spheres, \( \phi = \pi \sqrt{2} / 6 \approx 0.74 \)). This is the usual form for Bragg diffraction at normal incidence. Thus by selecting the refractive index of the material and the separation of the lattice plane (which is directly related to the sphere diameter and is adjustable), the band gap can be manipulated.

The band gap is also affected by the thickness of the film. Just like in x-ray diffraction theory, thin films with a few repeated layers, have broader peaks in transmission spectra than thicker films. As the thickness of the film increases the peak narrows. This is clearly seen in figure 2.11, which shows transmission spectra of colloidal films of varying thickness. The full width at half maximum (FWHM) narrows as the number of layers in the sample increases. The narrowing of the bandwidth saturates after about 15-20 layers. For crystals of high dielectric contrast (of the order of 1), the diffraction is very strong, in the vicinity of the gap, causing the amplitude of the propagating electromagnetic radiation to attenuate rapidly with distance into the crystal. Therefore most of the
interaction is with the first several layers and increasing the thickness beyond a critical value has only a minimal effect on the bandwidth.

![Graph showing optical density vs. wavelength for 7, 30, and 67 layers](image)

**Figure 2.11** Normal incidence transmission spectra of three samples with increasing film thickness (average sphere diameter = 279.2nm). The peak height has been normalized. The thin 7 layer sample has a broad mid-gap peak. As the thickness is increased the peak becomes narrower and saturates beyond 20 layers. The change in thickness can also be seen in the Fabry-Perot fringes becoming more closely spaced.
2.6 Templating Strategies: Inverted Opal

As mentioned earlier, such an FCC crystal of dielectric spheres in air does not possess a complete photonic band gap. This is indicated by the calculated band structure on the left in figure 2.12. However it has been shown that if the spheres are embedded in a material of higher dielectric constant a complete band gap can exist if the refractive index contrast is greater than 2.8. The band structure on the right in figure 2.12 is a simulation for an inverted structure, i.e. a dielectric matrix with air spheres. The material in this case has

![Band structure plots](image)

**Figure 2.12** The band diagrams plot the normalized frequency versus the propagation direction. The standard directions in the Brillouin zone are marked by the usual convention of alphabets as in figure 2.8. The diagram on the left has been calculated for colloidal crystals with a spheres having a dielectric of 11.9. There is no evidence of a complete photonic band gap for this type of structure. The band structure on the right has been calculated for a macroporous material of dielectric 11.9. This type of structure possesses a full gap between the 8\(^{th}\) and 9\(^{th}\) bands. The fractional band gap ($\Delta\omega/\omega$) is 4.25%
refractive index of 3.45 which is the same as silicon. A complete band gap develops between the 8th and 9th energy bands as indicated by the red band. The fractional bandwidth, defined as the ratio of the bandwidth and gap central frequency ($\Delta \omega / \omega$), is about 4.25%. This gap becomes larger for materials with higher refractive index contrasts. Using the colloidal crystal as a template we can make such an inverted structure with many different materials.

The colloidal crystal is first grown using the convective self-assembly technique as described above. Then the interstitial regions are filled with another material (e.g. a monomer) in liquid phase. The liquid is drawn up the spaces between the spheres through capillary action. Once the entire region between the spheres is filled, a chemical reaction solidifies the liquid (e.g. in the case of a polymer the monomer is polymerized). Subsequently the original silica scaffolding is etched or burned away leaving an FCC array of spherical voids in a dielectric matrix, or a macroporous photonic crystal. This technique, illustrated in figure 2.13 is applicable to a wide range of materials. Already we have made several different types of macroporous crystals from polymers, ceramics and metals. Subsequently other groupshave also used similar methods to form macroporous polymers, oxides and semiconductors.

It is important to note that the band structure for the inverted crystal shown in figure 2.12 assumes an ideal crystal of close-packed air spheres, so that the center-to-center distance
Figure 2.13 A schematic illustrating the principle behind the preparation of macroporous structures. First the interstitial region of the colloidal crystal is filled with a polymer (or other material). After polymerization the silica spheres are chemically etched away leaving a dielectric matrix with an FCC array of air spheres.
is precisely equal to the diameter. In this case, the connections or windows between adjacent air spheres are vanishingly small. It also assumes that the interstitial regions are completely filled with the high index material. Busch et al. have shown, by numerical simulations, that parameters such as the degree of incomplete filling of the interstitial regions and the linkage between the air spheres are important for controlling the band gap characteristics in such a crystal \(^{24}\). Importantly, careful manipulation of these parameters can significantly increase the band gap. In recent experimental work, Richel and co-workers have noted that the incomplete filling of the interstitial areas in a macroporous oxide film can influence its optical properties \(^{35}\). Any method to make photonic crystals that permits control of these parameters is a significant step towards engineering these materials for specific applications.

This thesis describes the first experimental report on the optical properties of colloidal films where these important morphological parameters are systematically controlled. We have recently developed a synthetic method which, for the first time, permits the formation of close-packed colloidal crystals of hollow spheres, with controllable shell thickness. These materials are topologically very similar to the macroporous structures imagined by Busch et al. \(^{24}\), and they exhibit similar enhancements in the width of the optical stop band. We demonstrate the systematic control of the band gap characteristics through engineering of the structural parameters of the hollow spherical shells, particularly the shell thickness.
CHAPTER 3: FABRICATION OF HOLLOW SPHERICAL SHELLS

3.1 DOUBLE TEMPLATE

The fabrication of crystals of hollow spherical shells relies on a double-template method. This approach is so termed because the colloids are formed by templating inside the cavities of a macroporous polymer which is itself a template of a silica colloidal crystal. Because this is a physical rather than a chemical strategy, a large number of different materials can be used to create these films. The method relies on the high perfection of the silica colloidal crystals. The hollow spheres formed from these crystals effectively replicate the uniformity and size distribution of the original silica template.

The colloidal crystal is used as a first template to form a macroporous polymer as described earlier. An important feature of these macroporous polymers is that the air spheres are interconnected. In an FCC geometry each sphere is surrounded by 12 nearest neighbors. In forming the macroporous structure the polymer cannot penetrate the region between two touching spheres leaving a tube-like connection between the air spheres once the colloid has been removed. Each air void is therefore connected to 12 other voids. This is clearly visible in SEM images as indicated in figure 3.1. Moreover the diameter of these tubes can be controlled through the viscosity of the starting monomer as illustrated in figures 3.1(a) through (c). This networked structure allows the macroporous
Figure 3.1 SEM images of macroporous polymers. These images clearly show that the spheres are interconnected. The polymer cannot penetrate the region between two touching silica spheres. When the spheres are etched away this region is not filled with polymer and acts like a window between the air voids. A sphere embedded within the crystal would have 12 connecting windows (FCC structure has 12 nearest neighbors). However as these images are of the surface of the macroporous polymer only some of these windows are visible. The window size can be manipulated by controlling the viscosity of the starting monomer as illustrated in (a) through (c)
polymers to be filled with different liquid precursor solutions in a second templating process. To fabricate hollow spheres the inner surface of the macroporous polymer is coated with another material that forms a film on the polymer surface. The film thickness can be controlled by adding multiple coatings. Subsequently the polymer is removed leaving an FCC array of hollow spherical shells. This is shown as a schematic in figure 3.2.

Table 3.1 illustrates that this method can be applied to a wide range of materials including semiconductors, polymers and ceramics. The numbers in parenthesis indicate the standard deviation of the sphere diameter. It also demonstrates how effectively the technique preserves the original properties of the colloidal crystal with only a slight shrinkage of the sphere diameter and a small increase in the polydispersity.

3.2 Titania hollow spherical films

For the purposes of this study hollow spheres of titania were prepared using the double template technique via the hydrolysis of titanium alkoxides. Figure 3.3(a) shows a transmission electron micrograph of the edge of a film of titania hollow spheres. Figure 3.3(b) shows a close-up image of a single hollow sphere. The shell is uniform, with controllable thickness over a wide range. Figures 3.3(c) shows an electron micrograph of a large area on the sample surface, indicating the uniformity and surface quality. The
Figure 3.2 Schematic illustrating the fabrication process for creating hollow spheres. First the inner surface of a macroporous polymer is coated with a material. Subsequent coats of the same or different material can be applied at this stage. The polymer is then chemically etched leaving only the shell structure.
Table 3.1 Statistics of the fabrication process of hollow spherical shells

<table>
<thead>
<tr>
<th>Materials</th>
<th>Silica Template (nm)</th>
<th>Macroporous Polystyrene Template (nm)</th>
<th>Double-Templated Materials (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>TiO₂</td>
<td>335.9 (3.7%)</td>
<td>332.7 (4.3%)</td>
<td>325.0 (5.2%)</td>
</tr>
<tr>
<td>ZrO₂</td>
<td>341.9 (3.9%)</td>
<td>337.4 (4.2%)</td>
<td>333.5 (4.4%)</td>
</tr>
<tr>
<td>Al₂O₃</td>
<td>391.6 (4.0%)</td>
<td>387.3 (4.4%)</td>
<td>381.6 (4.8%)</td>
</tr>
<tr>
<td>Polypyrrole</td>
<td>335.9 (3.7%)</td>
<td>332.7 (4.3%)</td>
<td>322.0 (4.8%)</td>
</tr>
<tr>
<td>CdS</td>
<td>335.9 (3.7%)</td>
<td>332.7 (4.3%)</td>
<td>323.7 (6.3%)</td>
</tr>
</tbody>
</table>

Few compressed spheres in the image reveal that the spheres are indeed hollow. Figure 3.3(d) is a photograph of one of the samples used to perform the optical measurements. The lettering on the paper underneath the sample is clearly visible and undistorted indicating the excellent optical transmission properties of the photonic crystal. Analysis of images such as these supports the assertion that the hollow shells replicate both the size and crystallinity of the spheres in the first template, with only slightly larger size dispersion.
Figure 3.3 Images of titania hollow spheres formed using the double template technique. (a) TEM image of a section of a sample. The average shell thickness is 13 nm. (b) A close-up TEM image of a single titania hollow sphere with an average shell thickness of 26 nm. (c) A scanning electron micrograph showing a top-down view of a crystal of hollow spheres, demonstrating the excellent uniformity in the plane parallel to the substrate. The sphere diameter is 280 nm, with a size dispersion of ~7%. (d) An optical transmission image of a crystal of hollow spheres, showing the high optical quality.
CHAPTER 4: OPTICAL PROPERTIES OF HOLLOW SPHERES

4.1 NUMERICAL DESCRIPTION OF HOLLOW SPHERES

Like the macroporous polymer the hollow spheres are also connected by air tubes. These internal windows serve as the controlling feature for the overlap between the air spheres, since, because of these windows, the air spheres can be closer to each other than one sphere diameter. The schematic in figure 4.1 illustrates this point. The three cartoons show a simplified picture of the connection between two adjacent hollow spheres for different degrees of overlap. As illustrated, for a particular shell thickness, the window between the spheres becomes larger for greater overlap permitting the control of sphere overlap by modulating the window size. Here $R=0.5a$ represents two spheres just touching; i.e. their radii are half the distance between their centers (also defined as the lattice parameter 'a'). Larger values of $R$ represent spheres that are closer than one sphere diameter. The proximity of the centers of adjacent spheres therefore directly determines the size of the connecting window. Thus, this methodology not only allows for accurate control over the shell thickness (analogous to the degree of infiltration) but also the overlap between spheres (analogous to the sphere connectivity). These are the two parameters identified by Busch et al. $^{24}$ as key factors in controlling the width of the stop band.
In order to motivate the significance of these two morphological parameters, we have performed band structure calculations in which the shell thickness or the sphere overlap is systematically varied. We find that the maximum fractional gap is more than twice as

![Diagram showing the degree of overlap between hollow spheres](image)

**Figure 4.1** Schematic illustrating the degree of overlap between hollow spheres quantified in terms of the normalized outer radius. The shell thickness for each of these spheres is 0.1R. R=0.5a indicates that the radius is equal to half the center to center separation between spheres (lattice parameter), that is, the spheres are just touching. As the value of R increases the centers of the spheres are closer than a diameter causing them to overlap to a greater extent; clearly indicated for R values of 0.55a and 0.63a.
broad as that found in a fully infiltrated macroporous face-centered cubic lattice. This optimum structure is achieved with a shell thickness of $T = 0.18$, in units of the outer radius of the hollow sphere. The optimal sphere overlap parameter $Z$, defined as the outer radius of the sphere in units of the primitive lattice parameter, is found to be 0.622. Figure 4.2 shows the variation of the full gap (between the 8th and 9th bands) with each of these parameters, keeping the other one fixed. This shows that both these parameters permit sensitive tuning of the optical properties of the band gap. To demonstrate that these parameters do indeed describe the system accurately we have performed the

![Graph](image)

**Figure 4.2** The results of band structure calculations for an FCC lattice of hollow spheres, with $\varepsilon = 11.9$. (a) Variation in the fractional band gap $\Delta\omega/\omega$ between the 8th and 9th bands with shell thickness (in units of the outer radius) at the optimal sphere overlap of $Z = 0.662A$ (where $A$ is the lattice parameter). (b) Variation in the fractional band gap versus sphere overlap (in units of the lattice parameter) at the optimal shell thickness of $T = 0.18$. 

calculation with \( T = 0.207a \) and \( Z = 0.707a \). For these particular values of shell thickness and sphere overlap the structure is fully infiltrated with the air spheres just touching; that is a conventional macroporous material of the type simulated in figure 2.11 above. Therefore the band structure of the hollow spheres with these parameters should be identical to the band structure for a macroporous material, as is indeed the case.

4.2 Optical Measurements and Discussion

To demonstrate that the double-template method provides the ability to tune the band gap using these new parameters, we have studied optical transmission spectra of a series of films. These films were formed using silica colloids of 280 nm diameter, and the number of repeating layers was held constant at \( \sim 15 \). We have recently shown that this is sufficient for the bandwidth to have reached its limiting value, so that \( \Delta \omega \) is not a sensitive function of film thickness.\(^{36}\) The titania hollow spheres were formed with progressively increasing shell thickness, from \( \sim 13 (\pm 4) \) nm to \( \sim 50 (\pm 6) \) nm. Even if we can approach the critical refractive index contrast of 2.8, with spheres of this diameter (280 nm), the complete band gap lies in the ultraviolet, where the materials absorb strongly. We therefore probe the partial gap, between the second and third bands, that falls in the visible spectrum, using normal incidence transmission measurements. As with most previous reports on the optics of colloidal crystal-based materials, a small background, monotonically increasing with decreasing wavelength, has been subtracted.
in order to facilitate analysis of the Bragg peak. Figure 4.3 shows transmission spectra for several samples. There is an evident red-shift of the stop band as the shell thickness is increased. This is phenomenologically consistent with Bragg's law at normal incidence,

![Graph showing transmission spectra with varying shell thicknesses.](image)

**Figure 4.3** Transmission spectra of titania hollow spheres for increasing shell thickness. The band gap develops along the (111) direction between the 2<sup>nd</sup> and 3<sup>rd</sup> bands. The average sphere diameter (280 nm) and the number of layers (~15) were fixed. The stop band is red shifted as the shell thickness increases.

$\lambda_{\text{peak}} = 2 \cdot n_{\text{eff}} \cdot d$. As the shell thickness is increased, the material volume fraction is also increased resulting in a higher average refractive index of the film. Since the index is directly proportional to the position of the band gap, this index increase leads to a red-shift of the peak in the transmission spectra. This simple scalar theory, using an effective
medium approximation, has been shown to be reasonably accurate for propagation along high symmetry axes 23.

The dashed line in figure 4a shows the prediction of Bragg's law, assuming that the titania matrix has a refractive index of 2. In order to explain the bandwidths, we must resort to a more sophisticated theoretical approach. We calculate the photonic band structure for the hollow sphere system using a full vector numerical technique from which both the spectral position and width of the stop band can be extracted. This method uses a frequency-domain iterative approach to perform a direct computation of the eigenstates and eigenvalues of Maxwell's equations using a plane wave basis 37. The solid lines in figure 4 show the results of these calculations. We note that, because both the shell thickness and the sphere overlap can be determined from electron microscopy, these are not adjustable parameters in the simulations. The only unknown parameter is the refractive index of the titania shells; it is known that the hydrolysis reactions used to form these samples produce oxides with lower indices than those of the bulk materials 33, 38, 39. As with the Bragg's law calculation mentioned above, the simulations shown in figure 4.4 assume a refractive index of 2 for the shell material, consistent with previous reports 39. The agreement between the data and these simulations is excellent, particularly for the fractional band widths.
Figure 4.4 Transmission spectra analysis of the partial gap along the (111) direction. (a) Central frequency $\omega_0$ of the stop band as a function of the shell thickness. The black squares are the experimental data points, the dashed line is the prediction using a simple Bragg's law analysis and the solid line is the prediction from a full vector calculation (b) Relative gap as a function of the shell thickness. There is an optimal shell thickness to maximize the gap width.
CHAPTER 5: CONCLUSION

5.1 SUMMARY

We have demonstrated that the newly developed double template method affords additional degrees of control over sample morphology, and that these can be used to tune the characteristics of the optical stop band. Because these materials are formed via templating of high quality colloidal crystals, they are planar with controlled thickness, and contain few defects and few grain boundaries. This makes them excellent candidates for optical transmission studies.

Titania hollow spheres in particular are of great interest as its bulk refractive index approaches the critical value to observe a complete photonic band gap. Although the titania prepared in this study is of the anatase phase having a bulk index of 2.6, it is known that the rutile phase of titania has a refractive index of 2.9 which is above the predicted critical value of 2.8. Efforts are being made to grow thin films of rutile-titania. Achieving a full photonic band gap with this system allows for considerable flexibility in tuning the band gap. Figure 5.1 is a simulated gap map, illustrating the effect of the geometrical parameters on complete gap, for the system we described. This gap develops between the $8^{th}$ and $9^{th}$ bands for a material with a refractive index of about 3.5. The $x$-axis is the normalized shell thickness and the $y$-axis represents the overlap between the
hollow spheres in units of the lattice parameter (as described earlier). Again for an outer radius of $R=0.5a$ the hollow spheres are just touching. The bar on the right is the color code for the fractional band width ($\Delta \omega / \omega$). Notice that below a critical sphere overlap there is no gap for any value of shell thickness. This means that the connectivity of the spheres plays a very important role in the development of the band gap. Beyond the

![Graph](image)

**Figure 5.1** Predicted gap map of hollow silicon spheres. The horizontal axis is the shell thickness in units of the sphere outer radius and the vertical axis is the overlap in units of radii. The color bar indicates the value of the fractional band gap. This intensity plot represents the simulated complete gap for hollow silicon spheres. The gap is sensitive to both the sphere overlap and the shell thickness and exists only for a narrow range of these values. An optimum gap of 9.7% appears at $Z=0.622$ and $T=0.18$. There is also a critical value of overlap below which the gap is closed for all values of shell thickness.
critical overlap, there is a range of shell thickness for which the gap develops and this can be used as an adjusting knob to set the parameters of the gap to desired values. At the optimum shell thickness (T=0.18) and sphere overlap (R=0.622), the fractional gap is more than twice that predicted for a normal macroporous material of the same refractive index.

As we are able to engineer the dimensions of the samples precisely, with high enough refractive index contrast, we are able to place the gap of the samples virtually anywhere on the gap map. With the versatility afforded by such chemical templating methods, these colloidal crystal films should find increasing applications as diffractive optical materials.

5.2 Future Directions

The role of photonic band gap materials in manipulating the propagation of light is an important one. A greater understanding of the working of these materials is essential for their ultimate use in various applications.

Recently the tunability of the crystals under discussion has been a focus of research.\textsuperscript{40-42}. The interest has been primarily with the incorporation of a liquid crystal into the colloidal crystal to control the effective refractive index. However the application of a deformation to these materials can also change the band structure, thereby changing the optical
properties of these crystals. This type of deformation has already been mapped out by theorists. However a systematic experimental demonstration of this type of tuning is still lacking. Currently we are conducting experiments with deformable photonic crystals. Our fabrication methods (described earlier in the thesis) permit us to make crystals which can be temporarily or permanently deformed. We can then measure the optical response of such a deformation and understand the mechanism behind it.

Another very interesting property of these photonic crystals is that they have very large group velocity dispersion near the band edges. Thus they behave similarly to fiber Bragg gratings, except the refractive index contrast for these crystals is several orders of magnitude higher, making them far more dispersive. There have been some pulse propagation experiments conducted on these colloidal crystals, however most of these are in the linear optical regime or dealing with second order nonlinearities. A host of interesting nonlinear phenomena involving third order effects such as Kerr nonlinearity and solitons can also be observed. Our group is currently in collaboration with the Physics department at the University of Toronto with the goal of observing and modelling the nonlinear effects in our crystals.

Other significant experiments can be done with larger crystals that would have gaps in the terahertz frequencies. This would enable us to use our terahertz spectrometer setup to measure the complete electric field of the transmitted radiation. One experiment that can be done is on two-dimensional PBG materials. These types of crystals are being studied
with the purpose of engineering an efficient optical waveguide. The primary loss mechanism for such waveguides is the inefficient coupling of the electromagnetic radiation into and out of the photonic crystal. We can study the effect of surface termination on the transmission properties of the crystal. We propose to perform these experiments in the terahertz frequencies because the crystals are relatively easy to manufacture and the surface termination easy to control compared to crystals fabricated in submicron length scales.

Another important issue that persists in the area of opal photonic crystals is the role of defects on the optical properties. There have been a few theoretical papers on the subject\textsuperscript{48, 49}, but no conclusive experimental studies that systematically pinpoint the effect of certain defects on the optical properties of these synthetic opals. It is feasible to build a near perfect crystal in millimeter length scales (which would bring the photonic band gaps into terahertz frequencies) and create controlled point and stacking defects to observe the evolution of the transmission spectra in the terahertz as the type and the number of defects are systematically varied. Such a study, along with quantitative measurements on our silica colloidal crystals, would provide a better understanding of the role of defects in these crystals.
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