Temperature Dependent Photoluminescence of Erbium Doped YAG, Zinc Nitride and Manganese-doped Cadmium Selenide Optical Materials

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PREFACE

This dissertation is submitted for the degree of Doctor of Philosophy at the University of Surrey, UK. The research described in this thesis was carried out by me in the period of January 2013 to January 2017, under supervision of Professor Richard Curry, and Professor Kevin Homewood of Advanced Technology Institute, University of Surrey.

To the best of my knowledge, the work described in this thesis is original, except were due references has been made to the work of to others. This thesis is the result of my own work. Unless stated the experiments were performed by myself using the facilities provided by the University of Surrey.

No part of this thesis, or any similar to it, has been or is currently being submitted for any degree at this, or any other university.

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January 2017
ABSTRACT

Temperature dependent studies of a selection of materials including erbium-doped yttrium aluminum garnet (Er:YAG), zinc nitride nanocrystals (NCS) and manganese-doped cadmium selenide (CdMnSe) NCS have been undertaken in order to determine their fundamental optical properties. The study is based upon the measurement of their photoluminescence (PL) and PL transient decay transient over the temperature range of 300K to 5K.

For the Er:YAG samples, two different sample types are studied as a function of erbium concentration that are a fast-cooled (mono-phase) and a slow-cooled (bi-phasic) polycrystalline material. Due to the presence of emission upconversion in these materials the emission dependence on excitation power is also studied. It is found that for high Er concentrations (40-50%) energy transfer upconversion (ETU) occurs that may be of use for assisting population inversion at the $^4I_{11/2}$ level for the laser 3µm emission. Generally it is confirmed that the single phase and bi-phasic materials possess slightly different optical properties and that the material production must therefore be carefully controlled in order to realize optimized materials for optical applications.

Zinc nitride NC materials are studied for the first time with four samples representing a range of NC diameters characterized. These materials were highly susceptible to oxidation which presented a significant challenge in their handling and study. Strong emission was observed across the visible spectral region though the origin of this it was found probably included trap state emission and for the smallest NC samples organic ligand emission. The PL was found to shifting to higher energies as the size of the NC is decreased as expected due to increased quantum confinement and in line with the Brus equation. Two of the samples (8.9nm and 2.7nm diameter NCs) display a temperature dependence of the optical properties in line that seen in other semiconductor NCs such as PbS. The other samples displayed anomalous behavior that could be due to ligand emission (2.5nm NC sample) or higher energy trap states caused by localized oxidation (3.8nm NCs).
A study of temperature dependent optical properties of CdMnSe NCs was focused around the role of NC shape and type. Core only, core/shell and dot-in-rod samples were studied and all found to display a blue shift as temperature is reduced from 300K to ~5K of between ~24meV to 58meV. The core only NCs display a different luminescent behavior to that of the core-shell and dot-in-a-rod samples. The PL is related to the recombination of confined excitons within the NC, together with a contribution from what are most probably trap states located at the surface of the NC. In these samples no contribution from the Mn$^{2+}$ ion is found suggesting that the dopant ions are not fully incorporated into the NC but may reside on the surface.
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CHAPTER 1

INTRODUCTION

1.1 The optical properties of emitting material

There is a need for the constant development and improvement of emitting materials to enable the realization of future technologies (e.g., laser and LED) and as markers for biological applications. The emitting materials in these technologies are known as fluorescent materials which luminesce when excited either optically by the absorption of a photon or electrically by the injection of opposite charge carriers. In this thesis, the focus will be on optically excited materials that exhibit photoluminescence. Normally, the most important optical property is high luminescence intensity when the material is excited which implies high quantum efficiency. Other key properties include good colour tunability and purity, particularly when the desired application is display technologies. Finally, the luminescent lifetime of the material is important with a long lifetime desirable for population inversion to occur (for example of the Er$^{3+}$ $^{4}I_{11/2}$ energy level) which is a prerequisite for lasing applications, whilst a short lifetime is desirable for fast switching devices such as metal oxide semiconductor field effect transistor (MOSFET). Based on these desired properties, there has been a long-established interest in the development of new rare-earth phosphor materials and more recently in size tuneable semiconductor nanocrystals (NC). It is these classes of materials that are studied in this thesis with the aim of developing an improved understanding of their optical properties to guide future development.
1.2 Rare earth materials

The rare earths are fascinating elements to investigate due to their high potential for use in a variety of applications, and in particular due to their unique optical properties which make them attractive for use in optoelectronics devices. Their unique optical properties relate to the 4f-4f intra-atomic electronic transitions that take place within the trivalent rare earth elements. These are shielded from external ligand fields by the 5s and 5p electronic shells making the energies of the 4f-4f transitions only weakly dependent on the host material. A variety of rare earth doped Yttrium Aluminium Garnet (YAG) ceramics have been reported for example including: Nd:YAG [1][2], Er:YAG [3][4], Tm:YAG [5] and Yb:YAG [6].

In this thesis, the rare earth element of focus is erbium (Er³⁺) which can provide lasing in the near-infrared region at \( \sim 1550\text{nm} \) enabling optical amplification, and also supports near infrared upconversion to visible emission for use in photovoltaic systems [7][8]. Historically significant research has been conducted for erbium ions (Er³⁺) due to its well-known \( ^{4}I_{13/2} \) to \( ^{4}I_{15/2} \) emission band centred around 1.53\( \mu \text{m} \) which matches the low-loss of silica optical fibres that is suitable for telecommunication applications [9][10]. Er³⁺ is also utilised, in high doping concentrations (~50%-70%), as a dopant in YAG crystals providing a lasing emission at 3\( \mu \text{m} \) which can be used in medical applications due to strong absorption by water (OH) at this wavelength [11][10]. Furthermore, this energy does not penetrate human retina is considered safe for use. The rare-earth-doped YAG materials are also widely used in cathode-ray tubes and displays [12][13]. Common applications of the various optical transitions found within the erbium ion are listed in Table 1.1. The energy of emission due to 4f-4f- transitions clearly depends on the energy difference between the emitting (I) and final (F) 4f levels. Er³⁺ has 11 electrons in the 4f orbital and the ground state is labeled \( ^{4}I_{15/2} \) the nomenclature of which is described within [14].

The interest of researchers towards Er:YAG continues today for new optical and electronic applications. As seen in Table 1.1 this material has wide range of emissions spanning various wavelengths in the visible to near-infrared red [15]. YAG has become one of the
most promising hosts for providing an upconversion system \cite{7}\cite{12}\cite{16} and is a well-known lasing system. This is due to the combination of the long radiative lifetimes of \textit{Er}^{3+} emitting levels and low phonon energy of the host which enables population inversion to occur which is a requirement for the laser to operate successfully \cite{10}. Laser emission that exploits the $^{4}I_{13/2}$ (excited state) to $^{4}I_{15/2}$ (ground state) transition ($\sim 1.53$ $\mu$m) at room temperature is utilized as a three level system with the upper state being $^{4}I_{9/2}$.

\begin{table}[h]
\centering
\begin{tabular}{|c|c|c|c|c|}
\hline
\textbf{Lanthanide} & \textbf{G} & \textbf{I} & \textbf{F} & \textbf{Emission wavelength} & \textbf{Applications} \\
\hline
\textit{Er}^{3+} & $^{4}I_{15/2}$ & $^{2}H_{11/2}$ & $^{4}I_{15/2}$ & 520-560 nm & Green laser \cite{7}\cite{8} \\
\textit{Er}^{3+} & $^{4}F_{9/2}$ & $^{4}I_{15/2}$ & 650-670 nm & Red laser \cite{7}\cite{8} \\
\hline
$^{4}I_{11/2}$ & $^{4}I_{15/2}$ & 980 nm & NIR laser & \\
\hline
$^{4}I_{11/2}$ & $^{4}I_{13/2}$ & 3 $\mu$m & Medical surgery, dentistry\cite{17} & \\
\hline
$^{4}I_{13/2}$ & $^{4}I_{15/2}$ & 1.54 $\mu$m & Telecommunication applications \cite{9} & \\
\hline
\end{tabular}
\caption{The applications of the rare earth material (\textit{Er}^{3+}) in accordance of the emission wavelength.}
\end{table}

The other main advantages of YAG as a host system is its high chemical stability and low phonon energy. In addition, YAG forms a stable lattice (with high symmetry) and retains a high-temperature mechanical strength.

\textbf{1.3 Semiconductor nanocrystals}

Semiconductor nanocrystals (NCs) are a unique class of materials that may have a high impact in the miniaturisation of future electronic devices, for example by providing improvements in device efficiency. NCs are typically defined by the fact that their size and shape gives effect to their properties. As a result the study of nano-structures has become a new challenge, where different experimental and theoretical approaches have been applied to understand the variation of their electronic structure as a function of size and shape. In
particular, the study of quantum confinement in NCs has become interesting as this determines their electronic behavior. Due to their discrete energy level structure light emission can be tuned from ultraviolet through to the infrared simply by changing the size of the NC. NCs bridge the gap between small molecules and bulk crystals by displaying discrete electronic transitions. Efforts continue to explore the new physical properties of these materials and to engineer them for variety of technological applications[18].

Due to their small size NCs (typically 10nm) display different physical properties than their parent bulk material. As particle sizes become smaller, the ratio of surface to non-surface atoms increases leading to the surface properties playing an important role in the properties of the material. Researchers can take advantage of this to further control their electronic and chemical properties by surface treatment (e.g. attaching organic ligands). This has to date enabled a large variety of devices to be fabricated [19] and most recently their use in commercial emitting devices (e.g. televisions)[20].

NCs have a crystalline structure with confinement of charge carriers in 1D, 2D or 3D. Small quantum dots for example, provide 3D confinement and have a NC diameter between of 2-10 nanometers (~10-50 atoms). The NC electrical properties are changed when quantum confinement of charge carriers occur which increases their spatial overlap and thereby modifying the strength of optical transitions. As a consequence, the size and the shape of the structures can be used to change the optical response by controlling the desired transition energies.

Confinement in 2D and 3D concentrates the density of states (DOS) into narrower energy bands which in the 3D case resemble atomic-like states (hence the use of the term ‘artificial atoms’ that is sometimes used to describe NCs). This situation is ideal for optical performance as it concentrates transitions to narrow bands of similar energy. The advantage of using confined structure for optics is therefore summarized as: a) control of energy level separation and thereby emission wavelengths and b) increased binding between excited electron-hole pairs leading to efficient light emission.
Chapter 1: Introduction

One of the main areas of research focus is towards realizing lasing devices, where the NCs properties can be controlled by tuning the emission wavelength by varying the NC size. For example, the emission of cadmium selenide (CdSe) can be tuned from deep red to blue by reduction in the dot radius from 5 nm to 0.7 nm. The effect of temperature has become an important issue for laser device operation as it directly influences the laser threshold current and emission wavelength. In NCs the spacing between energy levels is typically far greater than the available thermal energy, so thermal depopulation of the lowest electronic states is inhibited. As a result the lasing threshold should become insensitive to temperature. Also, due to a higher density of states at the CB and VB edge, compared to bulk, band-edge emission is more probable because of the higher carrier concentration. This in turn leads to a lower ‘pumping’ energy in order to obtain lasing (i.e. a lower threshold)[21]. The current generations of lasers have a high power output and low lasing threshold, are stable over a wide range of temperatures and are cheap and easy to produce. Due to the ability to control the bandgap of the NC, this allows their potential application in a range of devices.

1.4 Thesis motivation and objectives

The motivation of doing this research is to provide the foundations of a longer-term route towards demonstrating an efficient laser or light emitting diode (LED) through different system such as Er:YAG, zinc nitride NCs and doped cadmium selenide NCs. The study of these three different systems enables their comparison; Er:YAG may have significant potential in up- and down-conversion applications (e.g. for solar) and is known to display long radiative lifetimes thus is of interest for lasing. The NC materials studied focus on the visible wavelength regime and offer higher radiative efficiencies along with tunability.

The experimental work undertaken on Er:YAG focuses on investigating the effect of Er concentration on energy transfer between the ions and the effects of temperature on these processes. Recently Er:YAG was shown to exist in two distinct crystal phases. The work undertaken therefore also seeks to understand if the existence of these phases accounts for the variable optical properties reported in terms of emission and energy transfer efficiency.
Chapter 1: Introduction

The work reported within NC materials is focused on the study of new material systems (Zn$_3$N$_2$ and Mn-doped CdSe). In addition to studying the size dependent optical properties the temperature dependence of the emission is studied in detail. The emission is also studied to identify if direct band-to-band recombination or trap state emission dominates.

1.5 Organisation of the research

The first year of the PhD was devoted to the study of the Er:YAG materials that displayed phase segregation within the prepared crystals. This work was undertaken in collaboration with the Prof. Cheetham group at the University of Cambridge who prepared all samples for study. Following this study focus was given to the study of semiconductor NCs including doped cadmium selenide and zinc nitride. As the cadmium selenide material is considered toxic to consumers, our collaborators at Sharp Europe prepared the zinc nitride materials as a non-toxic alternative. Significant effort was expended on these later materials as they had not been previously studied.

1.6 Thesis outline

The thesis consists of 7 main chapters with each of them related to achieving the objective of this research:

**Chapter 2** reviews the fundamentals of rare earth materials and their optical properties. Some of the fundamentals relating to absorption, photoluminescence and ion-ion interactions are reviewed. In addition, energy transfer processes that are probable within these materials such as upconversion is also explained.

**Chapter 3** reviews on the fundamentals of semiconductor NCs, comparing the properties of NCs with bulk systems. The known properties of zinc nitride are reviewed such as the crystal structure and reported optical properties including the bandgap. Following this the optical properties of cadmium selenide is reviewed along with the reported temperature dependence.
Chapter 4 describes the experimental methods used in the thesis and the preparation of the samples. The techniques are focused on the photoluminescence spectroscopy and transient studies of the PL lifetime. The preparation of each sample type, such as Er:YAG, zinc nitride and cadmium selenide, are described and the material structures described. All of the samples studied where provided by our collaborators which are for Er:YAG (the Cheetham group, University of Cambridge), zinc nitride (Sharp Laboratories Company) and cadmium selenide (the green group, King's College, London).

Chapter 5 presents a detailed study of the temperature dependence, and pump power dependence of the optical properties of Er:YAG from the 300K to 5K. The optical studies include the PL and PL lifetime as a function of temperature and excitation power for Er doping concentration from 2% to 50%. The temperature dependence studies show that energy transfer processes take place and are modified leading to upconversion emission when exciting at 980nm excitation. The power dependence studies show no variation with the temperature.

Chapter 6 describes the detailed study of the temperature dependence (300K to 5K) of the optical properties of zinc nitride for three different sizes of nanocrystal. The different size NC samples provide different emission wavelengths spanning the visible spectrum. The variation of the PL with temperature (e.g. peak position, FWHM etc.) is fitted using different models from the literature including, the Varshni and Einstein models, and compared to other better understood NC systems.

Chapter 7 describes similar studies as undertaken in chapter 6 but focused on CdMnSe core only, core-shell and dot-in-rod samples. These samples are doped with Mn$^{2+}$ impurities in an attempt to observe quantum enhanced magnetic interactions. Analysis of their temperature dependence again follows the models used in the literature (Varshni, Einstein and O'Donnell) with the results compared to systems not doped by Mn$^{2+}$.

Chapter 8 provides suggestions of further work and draws together the conclusions of the experimental results presented within the thesis.
References


Chapter 1: Introduction


CHAPTER 2

FUNDAMENTALS OF RARE-EARTH DOPED PHOSPHORS

2.1 Introduction

The rare-earth elements typically form luminescent materials when intentionally doped inside the host materials and in particular crystals (such as YAG). The rare-earth dopants usually from trivalent lanthanide ions and the energy transfer and optical transitions involved originate from 4f-4f transitions of the ions and between these states and the host material. In order to understand the energy transfer processes in more detail we need to better understand the accompanying optical processes that give rise to the absorption and emission they display and it is this that forms the focus of the work presented. Following this second (and higher) order processes are considered that lead to upconversion in erbium-doped yttrium aluminum garnet (Er:YAG) materials.
Chapter 2: Fundamentals of Rare-Earth Doped Phosphors

2.2 Energy levels rare earth elements

2.2.1 Electronics structure of lanthanide elements

The rare-earth series, often referred to as the lanthanide series, contains 15 elements starting from lanthanum through to lutetium in the periodic table with atomic numbers from 57 to 71 (Table 2.1). The electronic configuration of the rare earth elements consists of filled 5s, 5p and 6s shell with electrons being added to the 4f shell as the series progresses. Upon bonding the rare earths tend to form trivalent ions by losing the two 6s electrons and an electron from the 4f shell [1]. As a result the electronic configuration of the trivalent rare earth ions is given by \(5s^2\ 5p^6\ 6s^2\ 4f^n\) where \(n\) varies from \(n=1\) (Cerium, \(\text{Ce}^{3+}\)) to \(n=13\) (Ytterbium, \(\text{Yb}^{3+}\)).

Table 2.1: The list of lanthanide series from the lanthanum to lutetium and its 4f electron

<table>
<thead>
<tr>
<th>Lanthanide</th>
<th>Ions</th>
<th>(4f) Electrons</th>
<th>Ground state</th>
</tr>
</thead>
<tbody>
<tr>
<td>Lanthanum</td>
<td>(\text{La}^{3+})</td>
<td>0</td>
<td>(^1S_0)</td>
</tr>
<tr>
<td>Cerium</td>
<td>(\text{Ce}^{3+})</td>
<td>1</td>
<td>(^2F_{5/2})</td>
</tr>
<tr>
<td>Praseodymium</td>
<td>(\text{Pr}^{3+})</td>
<td>2</td>
<td>(^3H_4)</td>
</tr>
<tr>
<td>Neodymium</td>
<td>(\text{Nd}^{3+})</td>
<td>3</td>
<td>(^4I_{9/2})</td>
</tr>
<tr>
<td>Promethium</td>
<td>(\text{Pm}^{3+})</td>
<td>4</td>
<td>(^5I_4)</td>
</tr>
<tr>
<td>Samarium</td>
<td>(\text{Sm}^{3+})</td>
<td>5</td>
<td>(^6H_{5/2})</td>
</tr>
<tr>
<td>Europium</td>
<td>(\text{Eu}^{3+})</td>
<td>6</td>
<td>(^7F_0)</td>
</tr>
<tr>
<td>Gadolinium</td>
<td>(\text{Gd}^{3+})</td>
<td>7</td>
<td>(^8S_{7/2})</td>
</tr>
<tr>
<td>Terbium</td>
<td>(\text{Tb}^{3+})</td>
<td>8</td>
<td>(^7F_6)</td>
</tr>
<tr>
<td>Dysprosium</td>
<td>(\text{Dy}^{3+})</td>
<td>9</td>
<td>(^6H_{15/2})</td>
</tr>
<tr>
<td>Holmium</td>
<td>(\text{Ho}^{3+})</td>
<td>10</td>
<td>(^5I_{8})</td>
</tr>
<tr>
<td>Erbium</td>
<td>(\text{Er}^{3+})</td>
<td>11</td>
<td>(^4I_{15/2})</td>
</tr>
<tr>
<td>Thulium</td>
<td>(\text{Tm}^{3+})</td>
<td>12</td>
<td>(^3H_6)</td>
</tr>
<tr>
<td>Ytterbium</td>
<td>(\text{Yb}^{3+})</td>
<td>13</td>
<td>(^2F_{7/2})</td>
</tr>
<tr>
<td>Lutetium</td>
<td>(\text{Lu}^{3+})</td>
<td>14</td>
<td>(^1S_0)</td>
</tr>
</tbody>
</table>
Optical transitions therefore occur within the 4f shell of the trivalent ions. As the 4f shell is shielded by the 5s² and 5p⁶ outer shells the energy levels of the 4f valence electrons is not strongly affected by the host crystal field as seen in Figure 2.1 [2]. As a result the lanthanides have sharp and well defined spectral features originating from relatively stable 4f energy levels who’s energy is not strongly dependent on the host material [3][4][5].

2.2.2 4f energy level

The 4f energy levels of the lanthanide ions are labelled using term symbol \( ^{2S+1}L_J \) introduced by Russell-Saunders[4]. The superscripts refer to the number of possible orientations of the total spin of the ion by \( 2S+1 \) where the \( S \) is the total spin of electrons in the 4f shell. The subscript \( J \) refers to the total angular momentum. The total orbital momentum \( L \) is denoted using the spectroscopic notation S, P, D, (= 1, 2, 3...). Total angular momentum, \( J \) is defined by adding both, \( L \) and \( S \) components.

Figure 2.1: Rare earth atomic structure with different orbitals. The 4f shell lies inside the 5s²5p⁶ orbital and therefore is shielded from the crystal field. As a result 4f-4f intra-atomic transitions are generally spectrally sharp in nature[4].
2.2.3 4f energy level splitting

A free atom has spherical symmetry but when a rare earth ion are doped into a solid (host), the degeneracy of free ion energy level is removed by coulombic, spin-orbit and crystal field interaction as seen in **Figure 2.2**.

![Figure 2.2: The 4f energy level splitting of a rare earth ion in a host lattice. The 4f-4f transition is based on the spin-orbit coupling that involves the S+L=J, S=spin, L=orbital angular momentum and J=total angular momentum [4]. The emission is an atomic emission.](image)

The first interaction which is Coulombic (electrostatic) interaction is due to the repulsive interaction of lanthanide 4f electrons. As a result, the free ion energy level is split into $^{2S+1}L$ energy level. The electrostatic energy is around $10^4$ cm$^{-1}$.

Secondly, for the spin-orbit interaction, it involves interaction between electron spin magnetic momentum and orbital angular momentum due to electron movement in the 4f orbital. The energy level is split into $^{2S+1}L_J$ and the energy of splitting is $10^3$ cm$^{-1}$[4].

The last interaction involving 4f electron with the crystal field which give Stark splitting. The Stark splitting is occur when the electric field in the 4f levels split up by the local
atomic configuration around the Er\(^{3+}\) ion. The Stark splitting is dependent on the strength of the crystal field. The energy is in order \(10^2\) cm\(^{-1}\). The number of Stark levels is given by \((2J+1)\) for number of electrons. For example, erbium has 11 electrons and the value of \(J\) is therefore 15/2. Using \((2J+1)\) to calculate the number of Stark levels gives a total of 16.

The spin-orbit interaction is larger than the crystal field interaction due to the shielding effect in the 4f shell. As such there is only a slight difference in the energy of 4f states as the host materials is varied [6]. As such the fine structure of 4f-4f transition may be used to investigate host symmetry (as opposed to composition), via the study of photoluminescence (PL) or absorption spectroscopy, as well as contributing to the broadening of the intra-atomic optical transitions.

2.2.4 The Dieke diagram

The Dieke diagram is produced based on the \(^{2S+1}L_J\) energy level of lanthanide ion doped in lanthanum chloride (LaCl\(_3\)) by Dieke and the co-workers [7]. The 4f energy levels are found to incur small shifting, in the range of 100 to 200 cm\(^{-1}\), in Er\(^{3+}\) (free ion), Er\(^{3+}\) in lanthanum fluoride (LaF\(_3\)) and Er\(^{3+}\) in LaCl\(_3\). As a result the PL peak position does not vary significantly between hosts, e.g. the YAG materials, however the PL intensity of intra-atomic transition does.

The energies of the 4f ground and excited states shown in Figure 2.3 have been calculated and confirmed experimentally by detailed studies of their salts by Carnall et al. (1960). The energy level diagrams produced from this work are still of significant use due to the comparative invariance of the \(J\) multiplet energies on the different host crystal. As such, the 4f energy level diagram of the lanthanide ions has become valuable in designing suitable host materials for phosphors and lasers. Based on this diagram the absorption and emission spectra obtained from each ion is assigned to a particular 4f-4f intra-atomic transition.
Figure 2.3: Energy levels of the trivalent rare-earth ion as popularized by Dieke [8]. The erbium transition used for telecommunications is the $^4I_{13/2}$ to $^4I_{15/2}$ emitting at 1532 nm.

2.2 Lanthanide excitation process

There are 3 types of the excitation process which may occur consisting of 4f-4f transitions, 4f-5d transitions and charge-transfer state (CTS) transitions. In this thesis, the 4f-4f transition is the main focus for spectroscopy measurement. The restricts excited electrons to remaining within the 4f orbital on the same lanthanide ion. The 4f-4f transitions are however forbidden in theory (due to parity) and the selection rules describing them will be discussed in Section 2.3.1.1.
2.2.1 Absorption process

When the energy of light incident on a sample is resonant with an electronic transition within the sample absorption may occur, where an electron from a ground state (E1) is excited to an excited state (E2) as shown schematically in Figure 2.4. Therefore it is possible to determine the energy separation of optically active electronic levels by measuring the absorption of light as a function of wavelength where the energy difference, ΔE, is obtained using Equation 2.1

$$h\nu = \frac{hc}{\lambda} = \Delta E = E_2 - E_1$$  \hspace{1cm} (Equation 2.1)

Figure 2.4: Absorption process takes place when electron moves from the ground state, E1 to the excited state, E2.

The amount of energy transferred to the material can be determined as it is directly proportional to the number of incident photons and described via the Beer-Lambert law in Equation 2.2:

$$I(x) = I_o e^{-\alpha x}$$  \hspace{1cm} (Equation 2.2)

Where $I(x)$ is the intensity inside the material at distance $x$, $I_o$ is the incident intensity at the surface of the material and $\alpha$ is absorption coefficient (cm$^{-1}$).
2.3 Lanthanide de-excitation process

The emission process is the inverse of absorption. The atom is unstable in the excited state so it will attempt to return to its ground state. In this process it may emit a photon via radiative emission or lose energy via non-radiative processes.

2.3.1 Radiative emission transition

Radiative emission typically takes place when the electron relaxes directly from the E2 energy level to E1 ground state as seen in Figure 2.5. The radiative emission spectrum emitted during relaxation of the electron to the ground state can be measured. The movement of electron from the excited state to the ground state can be followed by measuring the PL intensity as a function of time after the initial excitation.

![Figure 2.5: The radiative emission takes place between E₂ and E₁ energy level.](image)

2.3.1.1 Selection rules

The relative intensity of individual optical transitions varies as transitions between different energy levels occur with different probabilities. The probability of electronic transitions from the ground state to the excited state is determined by ‘selection rules’ (Table 2.3) which determine whether such a transition is ‘allowed’ (i.e. highly probable) or ‘forbidden’ (highly improbable) transition. However, these terms need to be used with caution as for example experimentally it is observed that the 4f-4f transitions in rare-
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earths can result in photon emission yet they are labelled as being forbidden. This luminescence stems from a transition within the 4f orbitals of the same lanthanide ions and is mostly due to electric dipole (ED) and weaker magnetic dipole (MD) interactions. There are some conditions that need to fulfill in order to have allowed transition:

**Electric dipole**

The electric dipole (ED) operator is odd. Thus, the transitions can only occur if, wavefunction initial ($\Psi_i$) and wavefunction final ($\Psi_f$) is odd. This shows that ($\Psi_i$) and ($\Psi_f$) must have different parities.

**Magnetic dipole**

The magnetic dipole (MD) operator is even. Thus, transition takes place when the both wavefunction ($\Psi_i$) and ($\Psi_f$) has same parities.

**Table 2.3:** The allowed selection rules for the intra-atomic 4f-4f transition. For the electric dipole (ED) transition, the parity must be changed whilst for the magnetic dipole (MD), the parity must remain unchanged in order for both transition to be allowed.

<table>
<thead>
<tr>
<th>Transition</th>
<th>$\Delta S$</th>
<th>$\Delta L$</th>
<th>$\Delta J$</th>
<th>Parity Allowed</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>ED</strong></td>
<td>$\Delta S = 0$</td>
<td>$\Delta L = 0, \pm 1$</td>
<td>$\Delta J = 0, \pm 1$</td>
<td>opposite</td>
</tr>
<tr>
<td><strong>MD</strong></td>
<td>$\Delta S = 0$</td>
<td>$\Delta L = 0$</td>
<td>$\Delta J = 0, \pm 1$</td>
<td>same</td>
</tr>
</tbody>
</table>

**Forced electric dipole**

In theory the 4f-4f transition is parity forbidden. By introducing the lanthanide into crystal it can become partially allowed by mixing 4f wavefunction with a small amount of different parity wavefunctions such as 5d states or charge transfer states. As a result, the forced electric dipole transition is observed [9]. The 4f shell is shielded from the influence of external field results in the spin-orbit interaction dominating. Thus, it gives rise to their spectrally sharp transitions, discussed above, and hence their desirability for use in a wide variety of optoelectronic applications.
2.3.2 Nonradiative emission

Typically, nonradiative relaxation takes place when the energy difference between energy levels is small and comparable to the phonon energy of the host material. For example in the schematic in Figure 2.6 the electron relaxes nonradiatively from the E2 to E3 energy level via phonon emission. Other non-radiative transfer processes may also take place, for example multiphonon relaxation and concentration quenching.

![Figure 2.6: The nonradiative relaxation happens between E2 and E3 energy](image)

2.3.2.1 Multiphonon relaxation

Multiphonon relaxation takes place when the ions in the excited state transfer energy to the lattice without photon emission. A useful 'rule of thumb' is that radiative emission can compete with nonradiative emission when the energy gap is 5 times higher than host phonon energy. Therefore to minimise nonradiative relaxation a low phonon energy host must be used. Table 2.4 below shows list of variance of inorganic host with its phonon energy.
Table 2.4: List of different inorganic host material for phonon energy that related to the multiphonon relaxation.

<table>
<thead>
<tr>
<th>Host</th>
<th>Phonon energy (cm(^{-1}))</th>
</tr>
</thead>
<tbody>
<tr>
<td>Chloride</td>
<td>180-250</td>
</tr>
<tr>
<td>Oxide</td>
<td>400-600</td>
</tr>
<tr>
<td>Fluoride</td>
<td>400-600</td>
</tr>
<tr>
<td>Germinate</td>
<td>800-975</td>
</tr>
<tr>
<td>Silicate</td>
<td>1000-1100</td>
</tr>
</tbody>
</table>

2.3.2.2 Concentration quenching

Concentration quenching takes place when the rare-earth dopant concentration is high and therefore the average distance between the dopant ions is small. If the distance between ions is small, the probability of energy transfer between the ions is increased which reduces the efficiency of optical processes. This will increase the probability of having the cross relaxation (an energy loss process), where one fraction of the excitation energy is absorbed by the luminescent ion and transfer to another ion, further discussion is in Section 2.4.1

2.4 Energy transfer

The probability of energy transfer between the donor(D) and acceptor(A) was examined by Foster (1948) and Dexter (1953) who independently derived governing expressions [10]. The energy transfer can be written as D\(^*\) + A → D + A\(^*\) where D is the donor and A the acceptor with ‘\(^*\)’ indicating the excited state. An energy transfer process is schematically shown in Figure 2.7 with the distance between the D and A given as ‘R’. The excitation energy \(hν_D\) is absorbed by the donor exciting and electron from the ground to the excited state (D\(^*\)). The absorbed energy is then transferred to the acceptor resulting in non-radiative relaxation of this excited state. As a consequence, within the acceptor an electron is promoted from the ground state A to an excited state A\(^*\). A photon may then be emitted by the radiative relaxation of the acceptor to its ground state with the energy \(hν_A\). This
generally produces a red shift in the observed emission as $h\nu_A < h\nu_D$ and also a delay in the emission process due to the time taken for energy transfer to occur.

![Figure 2.7: A schematic of energy transfer between donor (D) and acceptor (A) states. The distance between the donor and acceptor is typically 1-10nm.](image)

The rate of the energy transfer is dependent on the overlap between the donor emission spectrum and the acceptor absorption spectrum. When the energy differences between the excited and ground states of the donor and acceptor are equal, the strongest overlap happens. If the energy between donor and acceptor is mismatched, a phonon with appropriate energy is required to allow for the energy transfer (phonon-assisted). The energy transfer probability $P_{DA}$ is given by

$$P_{DA} = \frac{2\pi}{\hbar} |\langle D^* A | H_{DA} | DA^* \rangle|^2 \int g_D(\nu)g_A(\nu) d\nu$$

(Equation 2.3)

Where $\hbar$ is the reduced Plank constant, $H_{DA}$ is Hamiltonian interaction between donor and acceptor and $\int g_D(\nu)g_A(\nu) d\nu$ is the spectral overlap between emission spectrum of donor $g_D(\nu)$ and absorption spectrum of acceptor $g_A(\nu)$. 

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2.4.1 Energy transfer by cross-relaxation (CR)

Cross-relaxation (CR) occurs when an excited ion transfers part of its energy to another ion as seen in Figure 2.8. The probability of cross relaxation occurring at low dopant concentrations is small. In highly doped material, energy may be transferred between the ions (as the distance between ions is decreased), this often leads to non-radiative cross relaxation and ultimately reduces emission efficiency. Whilst the transfer of energy to a neighboring ion does not necessarily quench the luminescence by itself, the probability of quenching is enhanced by permitting transfer of energy onto a site where more rapid nonradiative decay takes place.

![Figure 2.8: An example of non radiative cross-relaxation (CR).](image)

2.5. Upconversion (UC)

The phenomenon of upconversion (UC) was been discovered by Auzel in 1960 [11] and lead to research focused on the upconversion of infra-red light to visible involving laser diode (LD) excitation at 980nm. The focus of much of this work was on lanthanide doped fluoride and oxide host materials. Fluoride materials have generally exhibit poor chemical stabilities thus oxide materials started to attract increasing interest for upconversion. Present research is focused on the potential of new upconversion materials for applications that include lasing, photovoltaics (PV), bio-imaging and telecommunications.
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UC occurs when low energy photons are used to excite a material which then emits photons of a higher energy. The process shown below in Figure 2.9 is a non-linear process where 2-photons are involved in the conversion of two incident photons into one emitted photon of higher energy. The processes involved in UC can include two photon absorption (TPA), excited state absorption (ESA) and energy transfer upconversion (ETU) depending on the excitation conditions and the specific pump wavelengths used [12][11]. Qin et al. first studied the upconversion luminescent properties of transparent Er:YAG ceramics in 2004. In 2007, the high concentration Er-doped YAG transparent ceramics which emit at 2940 nm were reported by Yagi et al. In 2010, Kupp et al. first reported the an Er:YAG ceramic laser for 1645 nm wavelength with Ter-Gabrielyan et al. subsequently demonstrating a higher laser efficiency from a composite Er:YAG ceramic[13].

![Figure 2.9: The different between the TPA, ESA and ETU that takes place for upconversion process.](image)

UC can therefore occur through a number of different processes involving only a single lanthanide ion or via the interaction of two (or more) ions. TPA involves a virtual intermediate level that means two excitation photons must coincide. This makes TPA inefficient and requires the need for high excitation powers. There are a number of literature reviews available focusing on a variety of systems including Er\(^{3+}\):VO\(_4\)[14], Er\(^{3+}\),Yb\(^{3+}\):NaYF\(_4\)[15], Er\(^{3+}\):YAG[16] and Er\(^{3+}\),Yb\(^{3+}\):YAG[17]. All system listed above are doped
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with the lanthanide ion in order to give optical emission. Undoped systems of these host materials, such as YAG, do not typically display emission except from defects centers which is weak [18].

2.5.1. Main Upconversion Mechanism

2.5.1.1. Excited State Absorption (ESA)

ESA involves the sequential absorption of two photons as illustrated in Figure 2.10. It is the simplest upconversion mechanism and involves one dopant, typically a trivalent lanthanide such as Er$^{3+}$. The first excitation via photon absorption excites an electron from the ground state to an intermediate energy level, $E_1$. The lifetime of this initially excited state, $E_1$, should in principle be long to improve the probability of a second incident photon being absorbed. This then further excites the electron from its intermediate state $E_1$ to a higher excited state $E_2$, from which upconversion luminescence originates.

Figure 2.10: Excited state absorption (ESA) which excite two photon in the red line and has one photon emission in a green line.

The dependence of the emission intensity varies quadratically with incident light intensity due to the two photon absorption process that takes place. The two photon process can be experimentally determined by fitting the upconversion luminescence intensity as a function of the laser power [12] and this type of UC by ESA has been previously observed in Er$^{3+}$:YAG samples [19].
2.5.1.2 Energy Transfer Upconversion (ETU)

The ETU process was introduced by Auzel who named it APTE (Addition de Photons par Transferts d’Energie) [20]. This turns out to be a very efficient UC mechanism compared to other UC processes. It is a nonradiative energy transfer between two dopants, a donor (e.g. Er\(^{3+}\)) and acceptor (e.g. Er\(^{3+}\)). In the case of two ions [21] it is possible to obtain the same outcome by each ion being initially excited followed by the energy gained from one ion relaxing being transfered to excite the second ion, Figure 2.11. This process is known as energy transfer upconversion (ETU). This is the most efficient process for upconversion.

![Energy transfer upconversion (ETU)](image)

**Figure 2.11**: Energy transfer upconversion (ETU) which excite 2 photon in red solid line and one of the photon transfer the energy(red dashed line) to the another ion. Higher photon emission can relax directly from the E2 level to G level. The solid red lines represent photon excitation, the red dashed line represents energy transfer and the green solid arrow represents the photon emission.

ETU is similar to ESA in terms of the necessity to absorb two photons to populate the metastable level. The difference between ETU and ESA is that ETU is excited by two neighbouring ions for the energy transfer. The two neighbouring ions can absorb photons at the same energy populating the metastable level of E1. Following this nonradiative energy transfer (i.e. not emission and re-absorption) may occur in which one ion is promoted to the excited state E2 and the other is relaxed in the ground state G. Emission may then occur from this higher energy level. The distance between the neighbouring ions is determined by the dopant concentration and related to the UC efficiency of ETU process.
[22]. The ETU mechanism has been reported in a number of systems including Er\(^{3+}\):GGG[23], Er\(^{3+}\),Cr\(^{3+}\):YAG[24], Yb\(^{3+}\),Er\(^{3+}\),Tm\(^{3+}\):Y\(_2\)BaZnO\(_5\) [25] and Yb\(^{3+}\),Er\(^{3+}\),Tm\(^{3+}\):Y\(_2\)O\(_3\)[26]

2.5.1.3 Lifetime of upconversion process

The decay lifetime of the upconversion emission depends on the nature of the upconversion process involved. Generally either ESA or ETU dominates the upconversion process. As discussed GSA consists equal 2 photon absorption by single dopant whilst ETU involve two dopants. If the ESA dominates the mechanism, the upconversion emitting state is populated during the excitation pulse, and the upconversion emission intensity presents an exponential decrease once the excitation is turned off. In contrast, in the case where ETU dominates, the upconversion luminescence transient exhibits a clear rise (after the end of excitation pulse) followed by a decay. In many cases this enables the type of transfer process to be determined experimentally as schematically shown in **Figure 2.12**

![Figure 2.12](image)

**Figure 2.12:** The different between ESA and ETU lifetime. None ET takes place that has sharp decay. The ETU has wide decay that shows ET.
The luminescence decay is used to measure the total lifetime ($\tau_{\text{total}}$) that consists of radiative transition ($\tau_R$) and non radiative transition $\tau_{NR}$.

$$\frac{1}{\tau_{\text{total}}} = \frac{1}{\tau_R} + \frac{1}{\tau_{NR}} \quad \text{(Equation 2.4)}$$

The radiative component may itself made up of a number of different processes and in the case of ETU emission and standard emission being present at least two should be present. It is however not always easy to determine which of these two of more processes dominates.

### 2.5.1.4 Power dependence

If the UC process (ETU or ESA) is competitive with the spontaneous relaxation rate, then the population of the ETU emitting state, $N_2$ (E2 in Figure 2.13) is proportional to the incident pump power, $P$. If the spontaneous relaxation dominates, then $N_2$ directly proportional to $P^2$ which means that the population density of the UC emitting energy state is quadratic with excitation pump power.

![Figure 2.13](image)

**Figure 2.13:** The different between ESA and ETU process and comparing both with the UC emission as a function of power dependence.
2.6 Upconversion system

In this section, the upconversion system studied in this thesis, Er:YAG, is reviewed and the energy transfer processes may occur are discussed.

2.6.1 Erbium

Erbium is the 11th ion in the rare earth series as seen in Table 2.1, and was discovered in the Swedish town Ytterby in 1842. The electronic structure of erbium is [Xe] 4f\(^{12}\) 6s\(^2\). However, when added as impurity in host, it becomes trivalent charge state with electronic configuration of [Xe] 4f\(^{11}\). This configuration is shielded from the surrounding by the 5s and 5p shells as mentioned in Section 2.2.1. The 4f electron can has spin-orbit interaction.

The energy of the Er ion \(4{I}_{13/2}\) to \(4{I}_{15/2}\) transition happens to coincide with the low-loss window of silica optical fibres used in optical telecommunication technology and as a result Er has become the most technologically important rare-earth ion. Due to its unique electronic properties, erbium is an interesting probe for a large variety of physical effects and Er-Er interactions can be identified by studying Forster energy transfer between excited ions [6].

2.6.2 Host material (YAG) properties

The need for materials for application in solid-state lasers, medical devices, and optoelectronic devices has made the investigation of ceramic materials of increasing importance. The \(\text{Y}_3\text{Al}_5\text{O}_{12}\) (YAG) crystalline host has superior thermal conductivity, excellent chemical stability as well as mechanical properties [27] [28] than many other materials including glasses. Crystalline YAG exists in the cubic form [29]. With the bulk crystal displaying insulator like properties due to its wide (>5 eV) bandgap, which also makes it transparent in the visible and near-IR spectral region [4].
YAG, in a single crystal form, is widely used in solid state lasers as a gain host due to its high fracture strength, good chemical stability, excellent thermal and optical properties [30]. However, single crystals are difficult to prepare in large sizes which take a long time and significant effort to grow [31]. This problem can be solved by fabricating ceramic (polycrystalline) YAG which is relatively easy to fashion into different shapes and low-cost [16][32]. As a result presently most researchers are turning to the used of ceramics for future laser development.

**2.6.2.1 Low phonon energy**

The host-material mainly influences the emission efficiency of Er$^{3+}$ intra-atomic transitions through the host material phonon energy (i.e. the lattice vibration energy). The phonon energy for the YAG material is 0.08eV (close to 700cm$^{-1}$) [30][33][34]. For most optical applications it is important for the host material to have low phonon energy to prevent multiphonon relaxation, which allows the ion’s excited states to relax through nonradiative phonon emission and indirectly leads to lower emission efficiency [35]. Although YAG (an oxide) has a higher phonon energy than fluoride crystals, its superiority in terms of mechanical hardness, thermal conductivity and optical properties make it a material of choice [36][30].

**2.6.3 Er:YAG system**

Er:YAG is useful for 1.5$\mu$m emission for telecommunication applications as stated above. The transmitted signal can be amplified using the erbium doped fibre amplifier (EDFA) that exploits the Er$^{3+}$ $^4I_{13/2}$ to $^4I_{15/2}$ transition without the need of optical to electrical conversion of the signal. The EDFA is used to overcome losses in long-haul silica fibre transmission systems. Other than that, Er doped YAG is used in the NIR region for solid state lasers.

When excited at 488nm, the Er$^{3+}$ ion is excited to the $^4S_{3/2}$ energy level. Subsequent emission is then possible a visible wavelengths centred at 555nm and in the near infrared at 965nm and 1532nm. The green emission occurs due to relaxation between the $^4S_{3/2}$ to
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$^4I_{15/2}$ levels whilst the 965nm emission is due to the $^4I_{9/2}$ to $^4I_{15/2}$ transition as seen in Figure 2.14.

For the high Er$^{3+}$ concentrations of ~50%, $^4I_{11/2}$ to $^4I_{13/2}$ transition can be observed. The population density $N_1$ at $^4I_{11/2}$ energy level is greater than the population density $N_2$ $^4I_{13/2}$ which means $N_1 > N_2$, and thus a population inversion occurs. This enables amplification of photons (gain) occurring which can be used to obtain lasing. The lifetime of the upper laser level $^4I_{11/2}$ is shorter than the lower laser travel at the $^4I_{13/2}$ energy level.

Figure 2.14: The energy level refers to 488nm excitation for the radiative transition and nonradiative transition. The solid blue line refers to the excitation wavelength whilst solid line (green, red and black) refer to emission wavelength. The solid lines refer to the radiative transition whilst the non-radiative transition is referring to dashed arrow. The other nonradiative transition which is multiphonon relaxation is referring by the dotted line of 488nm excitation and the probability of radiative emission or nonradiative relaxation 1532nm.
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In the upconversion processes that occur when exciting at 980nm it is expected that green and/or red emission will result. The red emission is due to $^4I_{11/2}$ to $^4I_{15/2}$ transitions whilst the green the above mention $^2H_{11/2}/^4S_{3/2}$ to $^4I_{15/2}$ transitions, Figure 2.14.

The upconversion mechanism for the green emission process is GSA ($^4I_{15/2}$ to $^4I_{11/2}$) followed by ESA ($^4I_{11/2}$ to $^4F_{7/2}$) and via ET ($^4I_{11/2}$ to $^4I_{15/2}$, $^4I_{11/2}$ to $^4F_{7/2}$) followed by non-radiative relaxation from $^4F_{7/2}$ to the $^2H_{11/2}/^4S_{3/2}$ states. This route is referred to as ‘A’ in Figure 2.14. The upconversion mechanism for red light emission is GSA ($^4I_{15/2}$ to $^4I_{11/2}$) followed by multi-phonon relaxation to $^4I_{13/2}$ and then ET ($^4I_{11/2}$ to $^4I_{15/2}$, $^4I_{13/2}$ to $^4F_{9/2}$) and finally $^4F_{9/2}$ to $^4I_{15/2}$ relaxation which is referred to as route B [12] [38].

For the 1532nm emission a possible mechanism involves cross relaxation. Route C takes place following which the ion relaxes nonradiatively to level $^2H_{11/2}/^4S_{3/2}$. The cross-relaxation involves one ion being de-excited from $^2H_{11/2}/^4S_{3/2}$ and the other ion is excited from the ground state to $^4I_{11/2}$.

Upconversion can take place where most Er$^{3+}$ ions are in the first excited state. The condition consists of two excited ions in the $^4I_{13/2}$ energy level, one electron is then excited to the upper energy level $^4I_{9/2}$ and the other electron moves to the ground state, resulting in the loss of one excited ion. Upconversion can also occur through absorption of a photon by an already excited Er$^{3+}$ ion (ESA). Since upconversion can effectively limit the maximum degree of population inversion attainable in the material, it is a crucial to understand it in the design of optical devices such as amplifiers [39].
References


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Chapter 2: Fundamentals of Rare-Earth Doped Phosphors


In this chapter, the fundamentals of bulk and nanocrystalline semiconductors are reviewed focusing on their optical and electronic properties. The semiconductor materials studied in the thesis are zinc nitride and cadmium selenide systems.

3.1 Introduction to Semiconductor Nanocrystals

A semiconductor is defined as a material that is neither a good conductor nor a good insulator. The conductivity of the semiconductor material can change due to temperature variation or by the presence of impurity atoms. Semiconductors display an energy bandgap within which no electronic states exist, and the size of the bandgap is generally less than 4eV. Semiconductors may exist in crystalline or an amorphous state though here we only consider the former.

The bandgap of the semiconductor is determined by the regular arrangement of the constituent atoms. The periodicity of these is mirrored in the electronic potential seen by charge carriers and may be modeled using a Bloch wave approach. The periodicity results in the definition of a unit of cell which is repeated to create the bulk material. The primitive cell is defined in reciprocal space (momentum) and is known as the (first) Brillouin zone.
The importance of this concept is that once the energy of electrons is found within the Brillouin zone is it known for the entire crystal. The minimum energy difference between the valence band (VB) (bonding) and conduction band (CB) (anti-bonding) states is known as the electronic bandgap. It is referred to as being a ‘direct’ bandgap is when the maximum VB and minimum CB occur at the same point in reciprocal space enabling excitation/emission via photon absorption/emission. In the opposite case, i.e. the VB maximum and CB minimum occur at different points in reciprocal space the capture/release of the phonon is required in addition to a photon in order to conserve momentum.

Semiconductor nanocrystals (NCs) are a unique class of materials that have the potential to have a high impact on the miniaturization of electronic devices. Through control of the size (Figure 3.1) and shape of the nanocrystal (NC) it is possible to control their electronic properties and thereby those of devices incorporating them. The size dependent optical and electronic properties of semiconductor NCs have been studied extensively due to the quantum confinement effects that cause electron and hole wavefunctions to be localized in confined space being evident at room temperature. As a result, the electronic energy levels become quantized, and the bandgap size increases as the NC size decreases to become comparable with the electron (and hole) de Broglie wavelength. The ability to tune the bandgap of the material is restricted at the low energy end of the spectrum by their bulk bandgap. However, by changing material it is possible to obtain NCs displaying absorption/emission ranging from the ultraviolet through to the near-infrared (NIR). A direct result of the quantum confinement in NCs is to restrict the available charge carrier energy levels to discrete values. This results in an atomic-like discrete density of states leading to semiconductor NCs often being referred to as artificial atom. The above properties have led to the use of NCs in a variety of applications such as solar energy conversion[1], molecular and cellular imaging[2], optoelectronic devices[3][4] and ultrasensitive detection[5].
Chapter 3: Fundamentals of Semiconductor Nanocrystal

The NCs studied within this thesis are zero-dimensional (0D) thus presenting spatial confinement in all directions. Typical NC diameters are in the 2-10 nanometers range (10-50 atoms). Converting this to a volume measurement gives an approximate 100 to 100,000 atoms per NC. NC size and shape is normally confirmed using high-resolution transmission electron microscopy (HRTEM)[6].

![Diagram of Band Gap and Quantum Dots Size]

**Figure 3.1:** As the size of the nanocrystal decreases, the size of the band gap increases.

The small diameters presented by NCs leads to a large surface to volume ratio and as a result the surface can play an important role in modifying their properties. Furthermore, the small diameters lead to the generation of defect-free internal structures as defects are driven to the surface by energy minimization. The crystal arrangement of atoms within NCs can be changed with the application of high pressure, transforming structure between two
distinct phases [7]. Another advantage of using semiconductor NCs, compared to the bulk material, is that the excited charge carrier for tightly bound excitons whose emission can be easily seen at room temperature and exploited in devices [8].

3.1.1 Background history

Research into semiconductors continues to increase rapidly as they are widely used in the majority of electronic and optical commercial devices and as a result more scientists are interested in contributing to their further development. The first reduction of semiconductor dimensionality was demonstrated in 1974 with the creation of quantum well structures. These are two dimensional (2D) structures (films) that confine charges in the third dimension. The structure is formed by sandwiching one semiconductor between another semiconducting material with a wider bandgap, for example GaAs-AlGaAs. Further effort was then expended to reduce the structural confinement further to one dimensional (1D) yielding so called ‘quantum wires’ [9]. Finally, confinement in all three spatial directions was realized (0D systems) providing what are commonly called quantum dots.

The first 0D quantum dots were reported by Reed et al [9] from Texas Instrumental Incorporated in which complete quantization of the electron was observed. The quantum dots were formed via etching to give cubic structures with a length of ~250nm. Following this work, AT&T Bell Laboratories and Bell Communications Research Incorporated successfully discovered quantum dots in smaller size in dimensions around 30-45 nm [10].

3.2 The properties of nanocrystal semiconductor

Nanocrystal (NC) optical and electrical properties can be controlled by modifying the size of the nanocrystal (bandgap) as described above. NCs have unique electronic properties that are between a bulk semiconductor and a discrete molecule due to high surface-to-volume ratio.
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The electronic states of the nanocrystal are similar to those of atoms due to the quantum confinement as illustrated in Figure 3.2(b). In a bulk semiconductor charge carrier confinement may be provided by a variety of sources such as external electrode, doping and strain. The other source of confinement is the semiconductor surface, for example in semiconductor nanocrystals and also at the interface between different semiconductor materials (e.g. in core-shell nanocrystal systems). The atomic-like nature of the electronic states is manifested in experimentally observable properties such as absorption and photoluminescence and can provide useful information about the nanocrystal size [7].

Figure 3.2: (a) The direct band gap where the electrons are excited from the VB to the CB and (b) The energy level is discrete due to size reduction of the nanocrystal.
3.2.1 Quantum confinement in semiconductor nanocrystals

When electron is excited to the conduction band (CB), a positive hole is created in the valence band (VB). As the charges are opposite, they are attracted to each other by the Coulomb force and may become bound as an electron-hole pair known as exciton as seen in Figure 3.3. The excited electron eventually relaxes to the valence band either via radiative recombination (emission of photon) or non-radiative recombination. In bulk semiconductors the Coulomb attraction between an electron and hole is weak due to the large dielectric constant of the materials.

![Figure 3.3: The formation of exciton by Coulombic attraction of an electron-hole pair](image)

As stated above, when the size of the nanocrystal becomes similar to the de Broglie wavelength of the electron and hole, quantum confinement occurs. Bohr radius is the distance between electron and hole in the bulk and can be defined as

$$a_B = \frac{4\pi\varepsilon_r h^2}{m_0 e^2}$$  \hspace{1cm} (Equation 3.1)

where $\varepsilon_r$ are the dielectric constant of the material, $h$ is a Plank constant, $m_0$ is the rest mass of the electron, $e$ is fundamental of electronic charge. The electron and hole effective mass are dependent upon the semiconductor material. For example in CdSe, the hole mass(0.45) is heavier than the electron mass(0.13)[11] thus the distance between hole energy levels is smaller than the electron energy levels.
The undergraduate ‘particle in a box’ system can be used to illustrate the effect of confinement. As the size of the box is reduced it is found that the wavefunctions that give the solution to the Schrodinger equation move apart in energy as seen in Figure 3.4. Therefore, the band gap energy increases as the crystal size decreases.

![Figure 3.4: The particle in the box system used to illustrate quantum confinement](image)

To calculate each of the energy level equation 3.2 is used which is related to the particle in the box as mentioned above. If the L value is increase, the energy level become small and vice versa.

\[
E_n = \frac{n^2 h^2}{8mL^2}
\]  

(Equation 3.2)

The n value is refer to the energy level n=1, 2, 3, h is the Plank constant, m is the mass of the particle and the L is the length.
Confinement also explains the observed atomic-like electronic density of states (DOS) found in NC systems (Figure 3.5). Confinement modifies the optical response of the bulk semiconductor, for example in a quantum well a thin layer is sandwiched between two higher bandgap semiconductor materials, which provide a barrier to excited charge carriers. In such quantum well structures, electron and holes are confined in 1D but remain free to move in the plane of the layer. As a result of quantum well confinement, the band edge of each sub-band is shifted to a higher energy due to confinement energy. When a semiconductor is confined in 2 dimensions (2D), a 1 dimensional (1D) quantum wires is produced with carrier free to move along wire axis. If the structure is confined in 3 directions, a ‘0D’ NC is produced with no free motion. As the dimensional confinement is increase to 2D to form a wire or 3D to form dot, the kinetic energy becomes quantised. This quantization causes the DOS at the sub-band edge to pile up, leading to a DOS that is singular at the sub band edges for quantum wire. The sub band is shifted to higher energy due to additional confinement but remains a continuous band.

Figure 3.5: The density of state (DOS) versus the energy. In quantum dot, the electron is easier to move around the quantum dot compared to quantum well. Due to this factor, the energy level in quantum dot is much easy to confine.
A further measure of confinement is provided by the ratio of NC surface area over volume, which is related in understanding the optical and electronics properties[7]:

\[
\text{Ratio} = \frac{\text{surface (cm}^2\text{)}}{\text{volume (cm}^3\text{)}}
\]  

(Equation 3.2)

If the surface energy states are within the semiconductor bandgap, they can trap charge carriers at the surface, thereby reducing the overlap between the electron and hole, thus increase the probability of nonradiative decay. An emission in the NC can involve with shallow traps and deep traps followed by radiative recombination[2].

The confinement present in NCs enables tuning of optical properties not by compositional variation but purely by control of NC size. Figure 3.6 illustrates this well with CdSe NCs demonstrating emission spanning the visible spectrum. As a result of this, coupled to their high PL quantum efficiencies, these systems are of interest for use in biological imaging and for optoelectronic devices.

![Figure 3.6: The absorption and fluorescence spectra with different sizes by having different colours and has different photon energy][2].
Measurement of the optical absorption enables estimation of the NC bandgap energy \((E_g)\) and the corresponding PL measure of the exciton binding energy. In NC ensembles with narrow size distribution it is possible to identify the individual transitions (e.g. \(1s_h - 1s_e\) ground state transition) as peaks/features in the spectrum. This enables direct observation of quantum effects at room temperature. Typically, if the energy of the absorbed photon is larger than \(E_g\), the excited electron will initially relax via non-radiative (e.g. Auger or phonon scattering) processes before any radiative recombination occurs [12].

### 3.2.2 Bandgap engineering

In additional to the use of NC size bandgap engineering may be done through impurity doping and/or through the development of core-shell NC systems exhibiting heterostructure band-offset. An impurity doping such as CdMnSe where the manganese (Mn\(^{2+}\)) is added can create an intraband electronic energy level that allows lower energy light emission from the defects state to the ground state. Doped NCs can have interesting properties for biolabeling and device applications.

The manipulation of NC heterostructure can have control over charge carrier wavefunction, resulting in new optical properties. Bawendi and co-workers developed core-shell semiconductor which the CB and VB of the core and shell material are staggered, resulting in segregation of the electron and hole between the core and shell materials (Figure 3.7) [2]. Normally the core is coated with a wider bandgap shell material that stabilizes the NC and maximizes the fluorescence. This makes the charge carrier concentrate in the core instead of surface and a good advantage for the LED application. In addition, surface defect and trap states, that present deleterious affects on optical properties, are minimized through the use of such core-shell systems.
3.3 Zinc nitride properties

Zn$_3$N$_2$ is an inorganic compound whose properties have received little attention [13]. The material was first synthesized by Juza and Hahn in 1940 [14] but remained under-studied for many years with interest re-emerging in 1993 [15]. It is considered a promising material for electronic and optoelectronic applications due to its high electron mobility ($100 \text{ cm}^2\text{V}^{-1}\text{s}^{-1}$ [16]), high carrier concentration ($10^{20} \text{ cm}^{-3}$ [17]) and resulting conductivity.

An advantage of this material is that it is earth-abundant which makes the synthesis process low cost thus mass production for electronic systems is viable [17]. There are various techniques that can be used as fabrication methods for zinc nitride including direct chemical synthesis, chemical vapour deposition (CVD) and reactive sputtering [14]. The zinc nitride is less toxic than the CdX (X=S,Se) materials thus researchers are interested in it as an alternative nanocrystal system.

Recently there has been interest in Zn$_3$N$_2$ due to its promising application in realizing p-type zinc oxide thin films [14][18][15]. The p type dopant uses the N which has a similar ionic size to O [19][20]. Due to the donor defects such as oxygen vacancies or zinc interstitials, the effort to make p-type ZnO has been unsuccessful. However, Zn$_3$N$_2$ has a serious disadvantage which is its easy oxidation in ambient conditions. Due to this factor,
the study of Zn$_3$N$_2$ properties is difficult and thus the value of the Zn$_3$N$_2$ bandgap remains controversial.

Zn$_3$N$_2$ is a group II–V compound that has a cubic structure with a body-centered cubic lattice [21] and it lattice constant $a = 0.978$nm [22]. It has high melting point and it is not soluable in water. The bandgap of bulk zinc nitride is 1.0eV [18]. Zinc nitride has high mobility that can improve the efficiency of electronic devices such as thin film transistors (TFT)[23].

![Figure 3.8: The crystal structure of Zn$_3$N$_2$ where the silver sphere is the zinc atom whilst the yellow and the blue spheres are the nitrogen atom[17].](image)

### 3.3.1 Bandgap

The true bandgap of the Zn$_3$N$_2$ is becoming an issue as different values have been reported [24]. The values reported are between 1.0eV and 3.4eV and are given as either direct or indirect depending on the deposition and characterisation method used, as well as the microstructure (thin films) [14][25][26][23][27]. In 1993, Kuriyama et al. prepared the first zinc nitride films through direct reaction between ammonia and metal zinc [14]. In 2005, Toyoura et al. [11] reported the band gap found to be around 1.01–1.23eV when studying zinc nitride films made using a molten salt electrochemical process. In 2006, Zong et al. [16] deposited zinc nitride films on quartz substrates through a reactive rf magnetron sputtering technique and stated an indirect band gap of 2.12eV. The band gap reported by
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Kuriyama et al. [14] is 3.2eV and 1.23 eV by Futsuhara et al.[21]. Table 3.1 shows summary of the optical properties for various structure of Zn$_3$N$_2$.

Table 3.1: The summary of the optical properties various structure of Zn$_3$N$_2$

<table>
<thead>
<tr>
<th>Structure of Zn$_3$N$_2$</th>
<th>Optical bandgap(eV)</th>
<th>Bandgap character</th>
<th>Type of conduction</th>
<th>Ref</th>
</tr>
</thead>
<tbody>
<tr>
<td>Polycrystalline Zn$_3$N$_2$ film</td>
<td>1.23</td>
<td>Direct</td>
<td>N type</td>
<td>[16]</td>
</tr>
<tr>
<td>Polycrystalline Zn$_3$N$_2$ thin film - (Prep in N$_2$ plasma)</td>
<td>3.40</td>
<td>-</td>
<td>N type</td>
<td>[19]</td>
</tr>
<tr>
<td>Polycrystalline Zn$_3$N$_2$ thin film (300°C)</td>
<td>3.20</td>
<td>Direct</td>
<td>N type</td>
<td>[28]</td>
</tr>
<tr>
<td>Polycrystalline Zn$_3$N$_2$ thin film (500°C)</td>
<td>2.25</td>
<td>Direct</td>
<td>P type</td>
<td>[28]</td>
</tr>
<tr>
<td>Polycrystalline Zn$_3$N$_2$ film</td>
<td>2.11</td>
<td>Indirect</td>
<td>-</td>
<td>[29]</td>
</tr>
<tr>
<td>Zn$_3$N$_2$ hollow structure</td>
<td>2.81</td>
<td>Indirect</td>
<td>-</td>
<td>[30]</td>
</tr>
</tbody>
</table>

The variation in the value of the optical bandgap is believed to be due to the experimental conditions with three possible transitions identified. The first transition is from the valence band (VB) to Fermi level (FL) and the second transition is from Fermi level to conduction band (CB). The third transition is from the VB to CB which is the largest optical gap. The 1.23eV bandgap is corresponding to first transition done by Futsuhara et al. The larger optical band gap (2.12 to ~3.2 eV) might be due to the band-to-band transition[27]. The other reason that may give different values of the band gap is the presence of structural defects formed during growth and the inclusion of impurities within the Zn$_3$N$_2$ structure that relate to the growth technique or by the post-growth storage conditions [31]. Table 3.2 shows the different in bandgap and Bohr radius (discussed above in relation to NCs) for different samples.

Table 3.2: Different material exhibits different bandgap with various Bohr radius

<table>
<thead>
<tr>
<th>Sample</th>
<th>Bandgap(eV)</th>
<th>Bohr radius(nm)</th>
<th>Ref</th>
</tr>
</thead>
<tbody>
<tr>
<td>Zn$_3$P$_2$</td>
<td>1.51</td>
<td>3-7</td>
<td>[16][32][33]</td>
</tr>
<tr>
<td>Zn$_3$N$_2$</td>
<td>1.20, 2.30, 3.40</td>
<td>Not reported</td>
<td>[17][33]</td>
</tr>
<tr>
<td>Zn$_3$As$_2$</td>
<td>0.93, 1.0</td>
<td>Not reported</td>
<td>[34][33]</td>
</tr>
</tbody>
</table>
Chapter 3: Fundamentals of Semiconductor Nanocrystal

The groups II−VI NCs (CdSe) are easy to synthesised with precise morphological control that has led to an excellent general understanding of these materials. In contrast the use of II−V(Zn$_3$N$_2$) to realize NCs remains understudies but their much larger excitonic radius indicates that they should be able to demonstrate strong size quantization [32].

3.3.2 Zinc nitride optical properties

This section presents the previous experiments on zinc nitride NCs focusing on the photoluminescence (PL) measurement. Taylor et. al prepared three nanocrystal solutions with different NC sizes (2nm, 4nm and 6nm) each displaying different emission wavelengths peaking at 585nm, 752nm and 1073nm. The full width half-maximum of the emission peaks of these three samples (117nm, 163nm and 282nm) indicates that there is a large size distribution of nanocrystals within each sample [18].

Wei et al. have reported an emission peak at ~1.34eV (925nm) from zinc nitride Figure 3.9 a and b. The group showed that exposure to oxygen quenched this emission (sample S3 was exposed to air for 3 days). A second emission centered at ~0.9eV (1460nm) was also observed that was not present in the as synthesized sample S1) which displays the signature of water absorption within it. Temperature dependent measurements (15K to 300K)(Figure 3.9b) were undertaken by the group which showed that the ~1.34eV (925nm) PL intensity decreases as the temperature decreases indicating that the emission is not a pure radiative transition but requires thermal excitation[35].
Figure 3.9: The PL of zinc nitride samples before (S1) and after (S2,3) exposure to air a) and the temperature dependence of zinc nitride as reported by Wei et al. b) [35]

3.4 Cadmium selenide properties

CdSe is a group II–VI compound which consists of an element in column II and column VI in the periodic table. The cadmium atom has two valence electrons in orbital s [Kr]4d\(^{10}\)5s\(^2\) whilst selenium atom has six valence electrons in the s and p orbitals: [Ar]3d\(^{10}\)4s\(^2\)4p\(^4\). The CdSe crystal consist of selenium p orbital in VB and cadmium orbital of s in the CB.

There are two types of crystalline forms that exist for the CdSe which is zinc blende(cubic) and wurtize (hexagonal) (Figure 3.10). The unit cell is of the cubic structure is face-centered cubic [36]. The hexagonal structure has lattice parameters a=b=4.299 Å and c=7.010 Å on the other hand, the cubic a=b=c 6.05 Å [36]. In this experiment there are three different structures of CdSe used which is spherical core, core-shell and rod. The band gap energy of CdSe with the zinc blende structure is 1.8 eV, but the PL peak energy of the CdSe QDs is above 2.3 eV in both structures [37].
Figure 3.10: The crystal structure of CdSe in cubic (a) wurtzite (b)

3.5 Optical properties of temperature dependence

Temperature dependence gives effect to the size of the band gap as well as the peak widths. As the temperature is increased from low temperature to higher temperature, the peak becomes broadened. The broadening of the emission peak can be separated into inhomogeneous and homogeneous parts. The effects of temperature on the homogeneous and inhomogeneous linewidths are listed below:

a) **Homogeneous broadening** - Homogeneous broadening is temperature dependent, and is related to exciton scattering by acoustic and optical phonons[38]. The main contribution to the homogeneous linewidth for semiconductor NC is exciton–acoustic phonon coupling. At high temperature, the exciton–phonon coupling is stronger thus the single molecule absorption linewidth become broad [39].

b) **Inhomogeneous broadening** - Inhomogeneous broadening is due to the variation in size, shape and composition of the NC [40] and is independent with variation of temperature [41].
The other factor that gives effect to the energy gap (E_g) in NCs as a function of temperature is modeled using [40]:

\[
\frac{dE_g}{dT} = \frac{dE_g^0}{dT} + \frac{dE_{\text{conf}}}{dT} + \frac{dE_{\text{e-ph}}}{dT} \tag{Equation 3.3}
\]

The first term, \( \frac{dE_g^0}{dT} \), is the temperature dependence of the band gap (\( E_g^0 \)) depends on the thermal expansion of the lattice constant, \( a \)

\[
\frac{dE_g^0}{dT} = \frac{dE_g^0}{da} \frac{da}{dT} \tag{Equation 3.4}
\]

The second term, \( \frac{dE_{\text{conf}}}{dT} \) is the temperature dependence related to quantum-confined energy (\( E_{\text{conf}} \)) depends on the thermal expansion of nanocrystal size (\( R \), nanocrystal radius) which is \( E_{\text{conf}} \propto 1/R^2 \)

\[
\frac{dE_{\text{conf}}}{dT} = \frac{dE_{\text{conf}}}{dR} \frac{dR}{dT} = -\frac{2E_{\text{conf}}}{R} \frac{dR}{dT} \tag{Equation 3.5}
\]

If the thermal expansion coefficient of the nanocrystals material, \( \alpha \) is used, \( \frac{dR}{dT} = \alpha R \), above equation can be expressed as

\[
\frac{dE_{\text{conf}}}{dT} = -2 \alpha E_{\text{conf}} \tag{Equation 3.6}
\]

Generally, the confinement energy increases with the decrease of nanocrystals size.

The third term, \( \frac{dE_{\text{e-ph}}}{dT} \), is the temperature dependence of the electron-phonon coupling energy (\( J_{\text{e-ph}} \)) depends on the phonon energy. According to Wise et al.’s work,

\[
\frac{dE_{\text{e-ph}}}{dT} = -S(R) < \hbar \omega > \frac{dn}{dT_{\rightarrow \infty}} - S(R) k_B \tag{Equation 3.7}
\]

where \( S(R) \) refer to the dimensionless electron-phonon coupling strength which depends on the size of the NCs; \( \hbar \omega \) is an average phonon energy; and \( k_B \) is Boltzmann constant. All the components depend on both temperature and NC size. At high temperature, the average phonon energy will increase. Thus, the absolute value of electron-phonon coupling energy increases and induces larger temperature coefficients[40]. The strength of the electron-phonon coupling is found to increase as the quantum dot size decreases [8].
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The temperature dependence of photoluminescence (PL) intensity can be influenced by a number of different mechanisms of carrier relaxation, including radiative recombination, Auger nonradiative scattering, thermal escape from the dot as well as trapping in surface states and/or defect states. At high temperature, the defect and surface states are thermally activated, which increases the trapping probability and as a result the intensity is decreased[38].

The integrated PL intensity is expected to decrease exponentially as the temperature increase due to the thermal quenching. The thermal quenching in the core and core-shell NC is due to the carrier trapping which involve the surface defects states or traps or thermal escape assisted by the scattering with multiple LO phonons[41]. Jing et al. reported that as the temperature is increases the PL intensity of core-only NCs decreases quickly due to the large amount of nonradiative traps on the surface of the core NC that cause strong thermal quenching [41]. At high temperature, a decreased in intensity is observed due to the thermal/phonon assisted escape from the CdSe dot [38].

3.5.1 Temperature dependence of bandgap

There are three types of model that used to fit the PL graph which is

a) Varshni Fitting

The Varshni fitting that has been reported for the CdSe NC has the same value for bulk which is around 23–27meV for LO phonon [38]. The Varshni equation is

\[ E_g(T) = E_g(0) - \frac{\alpha T^2}{(T+\beta)} \]

(Equation 3.8)

The \( E_g(T) \) is representing the energy gap (direct or indirect), the \( E_g(0) \) is the energy gap at 0K, \( \alpha \) is the temperature coefficient \( dE_{PL}/dT \) whilst parameter \( \beta \) is related to the Debye temperature. The \( \alpha \) and \( \beta \) are related to the thermal expansion that give effect to the lattice[42]. The temperature coefficient value (\( \alpha \)) is compared with the literature and found same with the bulk CdSe value. This means that the temperature dependence is due to the intrinsic properties of CdSe-lattice [43]. For the group II–VI semiconductor NCs, the
temperature coefficient of the bandgap $\frac{dE_g}{dT}$ value that has been reported is -0.28 meV/K [39].

b) **Bose Einstein fitting**
Einstein temperature fitting is used as an alternative due to the graph provide more accurate results as the error returned by the fitting is smaller than the Varshni fitting [8]. The equation that used is

$$E_g(T) = E_g(0) - \kappa / (e^{\Theta_e/T} - 1)$$  \hspace{1cm} (Equation 3.9)

The $E_g(0)$ represent band gap peak at zero temperature (K), $\kappa$ represent the strength electron-average phonon interaction and the $\Theta_e$ is the Einstein temperature which means $\Theta_e$ is a T corresponding to average phonon energy. The $\Theta_e$ value is related to the acoustic phonons that contribute to the bandgap redshift. If the $\Theta_e$ value is low compared to LO-phonon energy, it means that the acoustic phonon contribution to the bandgap shrinkage is high due to electron-phonon interaction.

c) **O’Donnell**
An improved expression proposed by O’Donnell and Chen[44] used to describe temperature dependence of the band gap in core/shell NCs based on the analysis of the electron–phonon coupling that responsible for the shifting of bandgap, The equation is

$$E_{PL}(T) = E_{PL}(0) + S \langle E_{ph} \rangle \left[ \coth(\langle E_{ph} \rangle/2k_B T) - 1 \right]$$  \hspace{1cm} (Equation 3.10)

The expression $E_{PL}(0)$ represent the peak energy at '0 K', $S$ is a dimensionless coupling constant and $E_{ph}$ is the average phonon energy. The parameter $S$ refer to Huang-Rhys parameter and it represent the strength of exciton-phonon coupling where the higher the Huang-Rhys factor, the stronger the coupling. The $k_B$ is representing Boltzman constant.
3.5.2 Temperature dependence of full width half-maximum (FWHM)

The full width at half-maximum (FWHM) increases with increasing temperature, indicating a broadening of the emission peak as temperature increases [38]. The factor that causes band broadening in semiconductor NC is acoustic and optical phonon [43]. The FWHM increase as temperature increase is due to lifetime broadening that correspond to the increasing of electron-phonon scattering rate [45]. The increase of the exciton-acoustic phonon coupling is due to the quantum confinement and exciton-longitudinal optical (LO) phonon coupling constant is reduced to 21meV respect to bulk CdSe[46]. The broadening of the PL emission peak can be fitting using below

\[ \Gamma(T) = \Gamma_{inh} + \sigma T + \Gamma_{LO} / \left( \exp \left( \frac{E_{LO}}{k_B T} \right) - 1 \right) \]  \hspace{1cm} (Equation 3.11)

where \( \Gamma_{inh} \) is the inhomogeneous broadening and the last two terms represent homogeneous broadening due to acoustic and optical phonon scattering; \( \sigma \) is the excitonic-acoustic phonon coupling coefficient, \( \Gamma_{LO} \) represents the strength of exciton–LO phonon coupling and \( E_{LO} \) is the LO phonon energy. Due to the different dependence of the terms on temperature, acoustic phonons play a dominant role at low temperatures, while the optical phonons contribute at the higher temperatures[38].

3.5.3 Temperature dependence of integrated PL intensity

The nonradiative process in the relaxation of NC can be analysed using the integrated PL intensity as a function of temperature and its relation dynamics. If the resulting fitting parameters are different to bulk semiconductor, the PL peak observed in this study is not purely intrinsic to semiconductor NCs as it involves electron and holes near bandgap edge of CdSe material. This can be supported by the activation energy value that refer to transition between intrinsic and defect states [47]. If the activation energy value is small, it means the structure has small trap depth [48]. By plotting the graph of PL integrated
intensity versus 1/temperature, the activation energy value can extracted from the Arrhenius equation below:

\[
I(T) = \frac{I_o}{1 + C \exp^{-Ea/kT}} 
\]

(Equation 3.12)

Where the \( I_o \) is the integrated emission intensity at 0 K, \( C \) is a constant related to the ratio of the radiative to nonradiative lifetime, \( Ea \) is the activation energy and \( K \) is the Boltzmann constant.

### 3.5.4 Temperature dependence of Lifetime

The PL lifetime of the QD structure decreases as the temperature increases. This is due to the nonradiative recombination process [37]. C. de Mello Donegá et.al reported that as the size of the CdSe become smaller from 6.3nm to 1.7nm, the lifetime become longer. The CdSe lifetime has bi-exponential decay that consists of fast and slow component. The fast component in the biexponential decay curves is ascribed to bright exciton decay prior thermalisation between the lower (dark exciton) and the upper (bright exciton) emitting states [49].
References


Chapter 3: Fundamentals of Semiconductor Nanocrystal


Chapter 3: Fundamentals of Semiconductor Nanocrystal


This chapter provides a review of all experimental methods that are involved in the work reported within this thesis. Principally this involves the study of photoluminescence (PL) and PL lifetime decay. Both were undertaken as a function of temperature and excitation power. Three different classes of sample were studied that are generally referred to as erbium-doped yttrium aluminum garnet (Er:YAG) and zinc nitride nanocrystals (NCs) and manganese-doped cadmium selenide NCs. Each of these systems is described below.

For the Er:YAG sample, the synthesis and the structural characterization has been done by the Dr. Shakiba Kaveh with the Prof Cheetham group at University of Cambridge[1]. The zinc nitride sample were synthesised by the Dr. Peter Taylor as well as the structural characterization[2]. Lastly, the cadmium selenide were synthesised and the structural characterization undertaken by Dr. Simon Fairclough at King’s College, London.
4.1 Er: YAG sample

YAG:Er$^{3+}$ samples are found in two forms: (i) as a single crystal and (ii) as a polycrystalline ceramic. Single crystals are prepared using conventional melt growth such as using the Czochralski method described elsewhere[3]. This study uses polycrystalline YAG:Er$^{3+}$ ceramics synthesized using a solid state reaction as outlined below. Previous work has been reported showing that the spectroscopic properties and laser performance of single crystal YAG:Er$^{3+}$ and polycrystalline YAG:Er$^{3+}$ ceramics are similar [4][5][6][7]. However, the ceramic form is much cheaper for applications such as use as a phosphor or a laser medium, it is easier to handle and can be formed into different shapes, and therefore preferred in this experiment.

In these studies two sets of ErX:YAG samples with 5 different erbium concentrations (X=2%, 10%, 20%, 30% and 50%) are examined. The two sets of samples are labelled as fast-cooled ErX and slow-cooled ErX sample where X is the erbium doping concentration. The difference between the both samples is the rate of cooling during their synthesis. One set of samples is fast-cooled ErX from 1650°C while the other set of samples are slow-cooled ErX from 1650°C at 10°C min$^{-1}$.

4.1.1 Sample preparation

The synthesis of all samples and their structural characterization was performed by collaborators in the Prof Cheetham group at the University of Cambridge. (Y$_{1-x}$Er$_x$)$_3$Al$_5$O$_{12}$ phosphors (0.02 ≤ x ≤ 0.7) were prepared by using conventional solid state synthesis via grinding stoichiometric amounts of Y$_2$O$_3$, Er$_2$O$_3$, and Al$_2$O$_3$ as desired. The aluminum garnet underwent multiple sintering stages at 1350°C (10 hours), 1400°C (10 hours) and finally 1650°C for 24 hours with intermediate grinding stages. The list of synthesis protocol and structural characterization are listed below[1]:

---

---
<table>
<thead>
<tr>
<th>Samples</th>
<th>Sintering condition</th>
<th>Structural composition</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fast-cooled</td>
<td>The ((Y_{1-x}Er_x))(3Al_5O_{12}) samples ((0.02 \leq x \leq 0.7)) were achieved by fast cooling from the reaction temperature of 1650°C.</td>
<td></td>
</tr>
</tbody>
</table>

The structural condition for the fast-cooled sample is taken using the powder X-ray diffraction pattern. By using synchrotron radiation the fast-cooled Er:YAG (20%) sample, no impurities were found in the pure garnet phases as seen by the good quality of the Rietveld refinements below in **Figure 4.1a**

**Figure 4.1**: The structural Rietveld refinement using the synchrotron powder diffraction of fast-cooled sample Er:YAG (Er20%) a) magnified section of XRD pattern b) lattice parameter as a function of the erbium concentration in fast-cooled sample which follow the Vegard’s law [1].

**Figure 4.1b** shows the compositional dependence of the lattice parameters in the garnet structure with different erbium concentrations which follow Vegard’s law. As the erbium concentration increase
the lattice parameter decrease linearly due to the smaller ionic radii of Er$^{3+}$ compared to Y$^{3+}$[1].

<table>
<thead>
<tr>
<th>Slow cooled sample</th>
<th>The(Y$<em>{(13)}$,Er$</em>{x}$)$<em>{3}$Al$</em>{5}$O$_{12}$ samples (0.02 ≤ x ≤ 0.7) were achieved by slow cooling from the reaction temperature at 1650°C with a cooling rate of 10°C min$^{-1}$.</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>The synchrotron powder diffraction of slow-cooled Er:YAG(20%) shows no impurities but two garnet phases were found with different erbium concentration as seen in Figure 4.2a and b. The phase segregation can be found by the peak splitting using the XRD pattern by referring figure 4.2b. The peak splitting at high angles due to the difference between the ionic radii of Er$^{3+}$ and Y$^{3+}$</td>
</tr>
</tbody>
</table>

**Figure 4.2a** Rietveld refinement based upon the synchrotron powder diffraction of slow-cooled Er:YAG (20%) **b** lattice parameter as a function of the erbium concentration in slow-cooled sample [1].
Table 4.1 below summarizes the samples prepared which in slow-cooled sample shows two phase separation in Er10%, Er20% and Er30%.

**Table 4.1: Types of the sample used in the experiment include 2%, 10%, 20%, 30% and 50% of the erbium concentration. In fast-cooled samples, only one phase is found but in the slow-cooled sample, Er10%, Er20% and Er30% has 2 crystal phases.**

<table>
<thead>
<tr>
<th>Erbium Concentration (X %)</th>
<th>Fast-cooled sample</th>
<th>Slow-cooled sample</th>
</tr>
</thead>
<tbody>
<tr>
<td>2</td>
<td>No phase separation</td>
<td>No phase separation</td>
</tr>
<tr>
<td>10</td>
<td>No phase separation</td>
<td>Phase separation</td>
</tr>
<tr>
<td>20</td>
<td>No phase separation</td>
<td>Phase separation</td>
</tr>
<tr>
<td>30</td>
<td>No phase separation</td>
<td>Phase separation</td>
</tr>
<tr>
<td>50</td>
<td>No phase separation</td>
<td>No phase separation</td>
</tr>
</tbody>
</table>
4.1.2 Percentage of erbium concentration in slow-cooled and fast-cooled sample

For the slow cooled sample which is bi-phasic, two crystal phases are found. These have been determined to have 8% to 50% erbium concentrations using the synchrotron radiation source to obtain the powder X-ray diffraction XRD patterns[1]. The atomic percentage of the erbium ions in each sample determined by these studies are summarized below in Table 4.2.

Table 4.2: The atomic percentage of erbium concentration for slow-cooled samples that have two crystal phases which is between 8% and 50% of erbium concentration

<table>
<thead>
<tr>
<th>Er concentration (fast-cooled ErX)</th>
<th>Er concentration (slow-cooled ErX)</th>
<th>Relative ratio of phases in slow-cooled ErX samples (8% and 50%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>2 %</td>
<td>2%</td>
<td>-</td>
</tr>
<tr>
<td>10 %</td>
<td>12.2%</td>
<td>0.9 (8%) + 0.1(50%)</td>
</tr>
<tr>
<td>20 %</td>
<td>20.6%</td>
<td>0.7 (8%) + 0.3 (50%)</td>
</tr>
<tr>
<td>30 %</td>
<td>29%</td>
<td>0.5 (8%) + 0.5(50%)</td>
</tr>
<tr>
<td>50 %</td>
<td>50%</td>
<td>-</td>
</tr>
</tbody>
</table>

The phase segregation of the slow-cooled sample is can be clearly seen using the SEM-EDX equipment. In Figure 4.4a shows Er:YAG 20% fast-cooled sample has homogeneous erbium distribution. This figure is produced by Dr. Shakiba Kaveh from University of Cambridge and it is a collaboration work with them.
Figure 4.4a: The difference of the Er:YAG Er20% for fast-cooled and slow-cooled sample. a) fast-cooled which there is no phase separation and the erbium distribution is homogeneous and b) slow-cooled obviously show phase separation where there is a high concentration of erbium in one part of the sample (shown green) which is known as erbium rich region and another part known as erbium deficient region (less erbium concentration) [1].

4.2 Zinc nitride sample

A variety of zinc nitride (Zn$_3$N$_2$) NC samples were studied with their emission varying as shown in Table 4.3 and Figure 4.5

Table 4.3: Zinc nitride sample with different emission of wavelength that have been conducted in this experiment

<table>
<thead>
<tr>
<th>Colour of samples</th>
<th>Emission of sample</th>
<th>Peak emission wavelength of sample</th>
</tr>
</thead>
<tbody>
<tr>
<td>Dark brown</td>
<td>NIR</td>
<td>831nm</td>
</tr>
<tr>
<td>Orange</td>
<td>Red</td>
<td>570nm</td>
</tr>
<tr>
<td>Yellow</td>
<td>Green</td>
<td>515nm</td>
</tr>
<tr>
<td>Colourless</td>
<td>Blue</td>
<td>454nm</td>
</tr>
</tbody>
</table>


**Chapter 4: Methodology**

Figure 4.5: The PL measurement for all samples at 300K with different NCs sizes

### 4.2.1 Nitride sample preparation

<table>
<thead>
<tr>
<th>Synthesis</th>
<th>Structural</th>
</tr>
</thead>
</table>
| • The synthesis is based on the reaction between diethylzinc and ammonia gas at 225°C in the presence of a capping agent (oleylamine).  
  • Typical steps involved are the mixing of 1-octadecene (30 ml) and oleylamine (1 ml) and heating to 225°C. At the same time, ammonia gas is flowed through the solvent at a rate of 5 ml min⁻¹.  
  • Diethylzinc (102 ml) was then injected into the reaction mixture. | • The powder x-ray diffraction (XRD) θ–2θ measurements were performed on thin films and protected using the Kapton (prevent oxidation) which is deposited on the amorphous silicon wafer. The samples were purified by precipitation with alkyl nitriles.  
  • The diffraction pattern of the sample is measured using the Bruker D2 Phaser diffractometer. Scherrer broadening is apparent in the diffraction peaks due to the |
at 5 minutes intervals and NC growth observed via monitoring of the bathochromic shift in the absorption.

- The subsequent addition of diethylzinc resulted in signs of further NC growth, but no signs of nucleation of additional NCs were observed. This enabled control of NC size through limiting the availability of precursor. It was found that if the diethylzinc, is added in a large initial quantity control was lost over NC size and the smallest and largest NCs cannot be produced effectively [2].

### Effect of ammonia gas on NCs

- The reaction parameter is changing (flow rate of the ammonia gas) to see the effect on the synthesis and the other parameter is left unchanged.

- The amount of ammonia changes the size of nanocrystals seen in Figure 4.6. As the flow rate decrease, the NC size become larger and vice versa. When the flow rates of ammonia decrease, fewer nanocrystals nucleate so definite domain size of the nanocrystals.

- The expected reactions for $\text{Zn}_3\text{N}_2$ (anti-bixbyite structure) can be seen from the (004) and (440) lattice planes, the reaction can be very weak and missing altogether ((321) and (332)) as seen in Figure 4.7. This could be related to preferential alignment of the (100) and (110) planes of the nanocrystals parallel to the plane of the film[2].

![Figure 4.7: Powder X-ray diffraction patterns shows emission peaking at at 585 nm (solid line), 752 nm (dotted line) and 1073 nm (dashed line) for](image)
these grow larger after the addition of a given quantity of diethylzinc. This enable control the sizes of NC by controlling the degree of nucleation.

- The amount of diethylzinc also give effect to the size of NCs. High injection diethylzinc (2.0 mmol) produced bigger size NCs whereas smaller injections (0.5 mmol) decrease the NCs size. This provides an alternative method to control the amount of nucleation[2].

Figure 4.6: The rate of ammonia flow give effect to the Zn$_3$N$_2$ NCs sizes with the addition of diethylzinc[2]

- The ratio of the diethylzinc to ammonia controls the point which nanocrystal growth commences.

- Transmission electron microscopy (TEM) is used to further study the structure of the nanocrystals. The toluene solutions of the purified samples were drop cast onto ultra-smooth carbon or lacy carbon grids.

- The TEM images support the size tuning observed in the XRD patterns and expected from the optical spectra. The histograms clearly show a plurality of similarly sized nanoparticles in each sample.

- Due to the poor stability under the electron beam, analysis using energy dispersive X-ray spectroscopy (EDX) is permitted but elemental analysis gave a Zn–N atomic ratio of 3.0:2.1 which is expected for zinc nitride material[2].
Figure 4.8: The a) b) and c) shows the histograms of the size distribution of three samples from the largest to smallest size[2]

Based on the value calculated from Scherrer analysis of the (440) peak in the corresponding XRD patterns is in agreement with the mean sizes.

Figure 4.8d and f shows images of two representative crystals by using HRTEM. The FFT patterns is shown in Figure 4.8e and g which indicate plane spacings of {004}2.52Å, {440}1.72Å, {444}1.42Å, and {408}1.09Å, which are in good agreement with the expected spacings for Zn$_3$N$_2$ (2.44 Å, 1.73 Å, 1.41 Å and 1.09Å) [2].

The Zn$_3$N$_2$ samples were prepared by the project partners (P. Taylor at Sharp Laboratories of Europe) company with various sizes as previously reported[2]. All samples were provided in sealed quartz ampules that preserved their inert atmosphere. Significant problems were encountered when attempting to form thin films for study as they rapidly oxidised. Additionally, the solutions are very oily in nature due to the use of octadecene and oleylamine as a solvent thus evaporation of solvent during this process was very slow and required a flow of nitrogen. It was quickly established that exposure to air during this process led to a rapid loss in film colour as oxidation took place.

To prevent the sample from oxidising, the drop casting of films within a glove box was attempted. However, upon transfer to the cryostat for measurement the films again
oxidised. Attempts to encapsulate the Zn$_3$N$_2$ NCs within a polymer matrix of methyl methacrylate did not work presumably due to the presence of oxygen (or OH) within the polymer.

Attempts by Sharp to provide samples in a lower boiling point solvent (toluene) to speed up film formation were trialled. This enabled the successful preparation of films from the largest diameter NC samples and transfer to the cryostat without obvious oxidation (i.e. the film retained its colour and emission). The same approach did not allow successful film formation and transfer however as the rate of oxidation was much faster resulting in the films losing colour during transfer and loading into the cryostat. As a result the remaining samples were measured using NC solutions in sealed cuvettes directly loaded into the cryostat.

### 4.3 Manganese-Doped Cadmium Selenide Nanocrystals (CdMnSe NCs)

A series of cadmium selenide NCs doped with manganese (CdMnSe NCs) were prepared for study by our collaborators (the Green group, King’s College London (KCL)). Samples were provided as toluene solutions in order to enable films formation by drop casting. Three different forms of NCs were synthesized as described in Table 4.4 which is classified as core only, core/shell and dot-in-rod NCs. The position of the doped Mn ions within the NC is the focus of current high-resolution transmission electron microscopy studies by the group and the schematic shown in Table 4.4 is a ‘cartoon’ of the intended doping profile.
Table 4.4: Cadmium selenide (CdSe) doped with manganese sample with different emission of wavelength that have been conducted in this experiment.

<table>
<thead>
<tr>
<th>Sample name</th>
<th>Sample type</th>
<th>NC size</th>
<th>Schematic representation</th>
</tr>
</thead>
<tbody>
<tr>
<td>CdMnSe</td>
<td>Core</td>
<td>3.8nm (SD = 4.4%)</td>
<td><img src="image" alt="CdSe" /></td>
</tr>
<tr>
<td>CdMnSe/Cds</td>
<td>Core-Shell (spherical)</td>
<td>8.1nm SD = 8% 6.8 monolayers</td>
<td><img src="image" alt="CdSe" /></td>
</tr>
<tr>
<td>CdMnSe/CdS</td>
<td>Dot-in-rod</td>
<td>12nm SD = 15% 8 monolayers</td>
<td><img src="image" alt="CdS" /></td>
</tr>
</tbody>
</table>
### 4.3.1 Sample preparation

<table>
<thead>
<tr>
<th>Sample</th>
<th>Sample synthesis</th>
</tr>
</thead>
<tbody>
<tr>
<td>CdMnSe precursor preparation</td>
<td>Se TBP 2.316M 0.457g Se in 2.5ml TBP Degassing ODA 0.8g 1-octadecane (ODA) heat to 100°C under nitrogen Making Cd Stearate 0.249M The material that needed consist of cadmium oxide (CdO) for 0.5536 g, stearic acid 1.4122g and 1-octadecene (ODE) for 8ml. Degassed at 100°C for 1 hour and the temperature was raised to 250°C until clear. The Mn Stearate was made previously from [8].</td>
</tr>
<tr>
<td>CdMnSe manufacture</td>
<td>The 0.05g Mn Stearate and 8g (10.13ml) 1-octadecene (ODE) placed in a 50ml. Then degassed by bubbling nitrogen at 100°C for 15 minutes. After that, the temperature was raised to 290°C and injected a warm 0.5ml Se-TBP+ 0.8g ODA using a warm syringe (heat to ~80°C). After that, the temperature was reduced to 250°C for 45 minutes. The 2ml of the Cd-Stearate was injected at 250°C and grow for 5 minutes. If necessary cool it to 250°C and 2ml of Cd-Stearate was injected further. The sample was cleaned by using the methanol 10ml and toluene 10ml extraction for 4 times thus followed by the acetone centrifugation and re-dispersion in hexane.</td>
</tr>
<tr>
<td>CdS Shelling</td>
<td>A 250 ml round bottom (r.b) flask was charged with~2×10⁻⁷mol of washed CdSe cores with 5ml of oleylamine and 5ml of</td>
</tr>
</tbody>
</table>
octadecane. The stock solutions (0.2M elemental sulphur) dissolved in 1-octadecane (OD) and 0.2M Cd–oleate in OD were used as precursors for shell growth.

Before started using the Successive Ionic Layer Adsorption and Reaction (SILAR), the Se-rich surfaces of the CdSe cores were passivated by addition of Cd–oleate that is equivalent to one Cd monolayer. Each growing monolayer of the precursor was calculated based on the increment volume of each monolayer shell, determine by the different of NQD size with the grown successive monolayer. The monolayer deposition cycles for the first 5–8 shell, the ratio of Cd/oleic acid or the 0.2 M Cd–oleate stock solution that using was 1:4, while that for the stock solution was 1:10 used for each succeeding layer. The reaction temperature was 240°C and the growth times were 1 hour for the sulfur addition whilst 2.5 hour for the cadmium addition. Reactions were continued until the preferred shell thickness was achieved. Core-shell NQDs were washed by precipitating 2–3 times with ethanol and redispersing in hexane[9].

<table>
<thead>
<tr>
<th>Cds Shelling</th>
<th>Cds Shelling</th>
</tr>
</thead>
<tbody>
<tr>
<td>CdSe/Cds dot-in-rod</td>
<td>NCs were synthesized using different procedure used for spherical CdSe/Cds NCs. 2ml of CdSe NCs in hexane (~80μM) were mixed with 1ml of hexadecylamine (HDA) and 5 ml of ODE and degassed at 70°C for 30 minutes. After that, the solution was heated at 230°C. The Cd(OA)₂ for the first Cd volume, 0.5M prepared at 300°C and diluted in ODE(0.1M), was dropwise injected. The S(ODE) 0.1M was injected dropwise after 15 minutes of reaction, and the temperature was increased to 240°C. The Cd and S precursor solutions were injected for every 5 minutes and the temperature remained at 240°C. The last</td>
</tr>
</tbody>
</table>
deposition of S monolayer, NQDs were washed by precipitating 2–3 times with ethanol and redispersing in hexane[10].

4.3.2 Characterisation

Photoluminescence measurements were taken using a Fluoromax-4 fluorometer whilst the absorption spectroscopy was conducted using a Hitachi 4100 absorption spectrometer. For transmission electron microscopy (TEM), cleaned samples were drop cast Agar Scientific ultra-thin holey carbon supported on a Cu 400 mesh grid and was conducted on JEOL 2100 running at 200 kV with ensemble EDX taken on Oxford Instrument EDX. Scanning transmission electron microscopy-HAADF and EDS was conducted using FEI Titan ChemiSTEM running at 200kV. Powder XRD was conducted on a Cu-κα PANalytical X’Pert Powder diffractometer. Mn concentration was verified via ICP-MS, the NC were digested with aquaregia and analysed using PerkinElmer NexION 350D. EPR was conducted on a Bruker EMX Micro X-band with 1.0 T electromagnet. The figure of the SEM-EDX measurement is shown in Figure 4.9 below.
Figure 4.9: The picture shows the Mn position (green colour) which is situated outside of the sample.

Figure 4.9 above shows the STEM-EDX measurement that is the final proof which there was no any Mn inside the sample.
The average size of the NCs in each sample is obtained from TEM images which were undertaken by Dr. Simon Fairclough at KCL and are shown in Figure 4.10, Figure 4.11 and Figure 4.12 below.

**Figure 4.10**: The TEM image of CdMnSe NC core only sample. Analysis of the NC diameters gives an average size of 3.8nm with a standard deviation of 4.4%. The scale bar shown represents 10nm.

**Figure 4.11**: The TEM image of CdMnSe NC core-shell sample. Analysis of the NC diameters gives an average size of 8.1nm with a standard deviation of 8% and 6.8 monolayers. The scale bars shown represent 50nm (left) and 10nm (right).
Figure 4.1: The TEM image of CdMnSe NC dot-in-rod sample. Analysis of the NC diameters gives an average size of 12nm with a standard deviation of 15% and 8 monolayers. The scale bars shown represent 20nm (left) and 10nm (right).

4.4 Photoluminescence Experimental Arrangement

4.4.1 PL measurement

For photoluminescence experiments a laser source was used to excite the samples. A pulsed Nd:YAG pumped OPO laser (Spectra Physics Quanta-Ray and versaScan) source with repetition rate of 21Hz, pulse width of ~8ns and average power of 0.2mW was used operating at an excitation wavelength of 488nm. Alternatively a 405nm laser diode operating at ~30mW and chopped using an optical chopper was employed. The excitation laser was guided using mirrors from the source to the sample using appropriate filters to remove lower energy idler emission in the case of the OPO. The sample was held using a recessed metal plate that was covered with a quartz slide. The size of the sample is 5 mm in diameter and 2 mm thickness. This was then mounted inside a cryostat with fused silica windows providing optical access (Oxford Instruments Optostat DN-V).
Figure 4.3: The set-up of photoluminescence experiment that consist of a tuneable Nd:YAG pumped OPO laser system or 405 nm laser diode, shortpass (FES) filter, a pair of lenses (L₁ and L₂) and long pass filter (LPF) as well as monochromator with Newport 818-SL or 818-IG detector, photomultiplier tube detector and oscilloscope.

Following excitation, emission was collected, collimated and focused using a pair of lenses (L₁ and L₂) as indicated in Figure 4.3. The laser spot size on the sample is focused to ~2 mm in diameter. Before the collected light was passed into a monochromator (Bentham TMc300) long pass filters (LPF) were used to prevent scattered laser light entering. In order to completely suppress any laser scattering from the samples we put a suitable filter in front of the input slit of the monochromator [8]. These interference filters were also used to prevent the detection of any second order grating reflections during measurement. The monochromator was equipped with two gratings (1200 mm⁻¹ and 600 mm⁻¹) and two exit slits allowing both visible and near-IR detection using two detectors. A variety of detectors could be attached to these exit slits as are summarised in Table 4.5. Typically for transient
measurements the visible and near-IR photomultiplier tubes were used whilst for PL measurements standard Si or InGaAs detectors were used. For PL measurements the signal from the detector was sent to a lock-in amplifier (Signal Recovery DSP7265) referenced at the source repetition rate. Monochromator movement and data collection was carried out using bespoke software written in LabView. All the PL spectra collected have been corrected for the spectral response of the system such as filters, gratings and detectors which were used as appropriate to the experiments.

Table 4.5: Different types of the detector used and their spectral range.

<table>
<thead>
<tr>
<th>Detector</th>
<th>Range (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Bentham PMT</td>
<td>400-800nm</td>
</tr>
<tr>
<td>818-SL</td>
<td>500-1100nm</td>
</tr>
<tr>
<td>818-IG</td>
<td>800-1700nm</td>
</tr>
<tr>
<td>818-IR</td>
<td>800-1700nm</td>
</tr>
<tr>
<td>Hamamatsu PMT</td>
<td>800nm-2000nm</td>
</tr>
</tbody>
</table>

For the PL power dependent measurements the excitation source power/energy was fixed and neutral density (ND) filters used to vary the energy impinging on the sample. Table 4.6 shows the typical excitation powers and transmission factors afforded by this method.

Table 4.6: The various power of neutral density (ND) filter used in the experiment. By using the Cary 5000, the value for transmission are achieved.

<table>
<thead>
<tr>
<th>Neutral Density (ND) filter</th>
<th>Transmission (%)</th>
<th>Transmitted power (mW)</th>
</tr>
</thead>
<tbody>
<tr>
<td>No filter</td>
<td>100</td>
<td>0.200</td>
</tr>
<tr>
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<td>4A</td>
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</tr>
<tr>
<td>1E</td>
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</tbody>
</table>
The mounting of the samples within a cryostat enabled PL measurements to be undertaken at temperatures between 300K and 4K. Measurements were typically performed as the temperature was reduced from ambient in 25K steps ensuring sufficient time at each temperature for thermal equilibrium to be reached.

4.4.2 Lifetime measurement

Photoluminescence lifetime measurements were performed using the same photoluminescence (PL) setup described for PL studies in Section 4.4.1. Excitation of the sample was undertaken using the pulsed OPO source and detection using the photomultiplier tubes. The output of the detectors was connected to an oscilloscope (LeCroy Waverunner LT372) taking care to ensure impedance matching (50 ohm) of the detector output and oscilloscope input. The system response was carefully measured using the OPO source and found to be in Figure 4.14.

![Figure 4.14](image)

**Figure 4.14:** The transient response of the detection system and a single exponential fit yielding a response time of 12ns.

The PL decay lifetime is a measure of the time taken for the excited state to radiatively recombine. The lifetime decay is fitted using an exponential decay function (equation 4.1) to obtain the lifetime of the PL emission as a given wavelength (Figure 4.15).
Chapter 4: Methodology

\[ I = I_0 e^{-\frac{t}{\tau}} \]  \hspace{1cm} (Equation 4.1)

\( I_0 \) = Initial intensity when \( t = 0 \)
\( t \) = time
\( \tau \) = time taken for the population to decrease by 1/e

There are two types of the decay mechanism which are radiative or nonradiative relaxation. The radiative lifetime for Er:YAG sample is found to be microsec and nano second for NC’s zinc nitride respectively as it is depends on the crystal structure and electronic properties. The radiative and nonradiative process are competing each other and therefore the measured decay lifetime involves both of these processes. Cooling the sample down reduces to the non-radiative relaxation so that at very low temperatures (e.g. 4K) the measured lifetime is a good approximation of the true radiative lifetime.

Figure 4.1: The example of the radiative decay of emission at 1532nm. The red curve is the fit to the decay from which the lifetime is obtained. The black colour shows the original decay transient.
4.5 Spectra Correction Factors

As mentioned above the photoluminescence spectra obtained must be corrected for the transmission of filters and the detector response.

4.5.1 Filter corrections

The transmission of the various long pass interference filters (FEL) was measured using a Varian Cary 5000 spectrophotometer and plotted in Figure 4.16. Additionally, the transmission of the neutral density filters used for power dependent measurements was measured and plotted in Figure 4.17. Using these spectra correction factors were obtained and used to take filter transmission into account.

![Figure 4.16: Transmission spectra of the various long pass filters used in the experiments to measure the emission.](image-url)
Figure 4.17: Transmission spectra of the various neutral density (ND) filters used in the experiment to measure the photoluminescence for power dependence.

4.5.2 Grating and detector corrections

For the photoluminescence and radiative lifetime experiments, the measurement can be taken using one of two gratings within the Bentham TMc300 monochromator which have either 1200g/mm or 600g/mm. The choice of the grating depends on the wavelength range that is used and each grating has different spectral diffraction efficiency. Additionally, one of two types of detector may be used with these gratings, which themselves have different detectivities, which are a Newport 818-SL (silicon) and 818-IG (InGaAs) detector. Normally the Newport 818-IG is used for near infrared wavelengths while Newport 818-SL is used for the visible wavelength. The need to correct spectra for the grating and detector efficiency can be seen in Figure 4.18(a) and (b). System correction curves have been previously obtained using a calibrated white light blackbody source.

**Corrected magnitude = (PL magnitude) x (Filter correction) x (Detector correction)**
Figure 4.18: Correction factors for the detector used for (a) 818-SL (500-1100nm) and (b) 818-IG (800-1700nm).

4.5.3 Spectra obtained from two different detectors

To combine spectra taken using two different detectors, ensuring that the relative intensity of PL emission peaks are correct, the two PL spectra obtained were compared in the spectral region where they overlap (900-1000nm). Both sets of data were then normalized to the PL peak intensity in this region by dividing spectra by the intensity at the 963nm as seen in Figure 4.19 below.
Figure 4.1: Normalised the graph to value one with two different detector which are Newport 818-SL detector and 818-IG detectors for the photoluminescence experiment.

In order to measure PL transient decays that is faster than the ~13ns system response, a commercial ‘LifeSpec’ instrument (Edinburgh Instruments) was used. It is based on the use of time correlated single photon counting and only allowed measurement at room temperature. This apparatus also enables the cross checking of PL transient decay measurements performed using the OPO laser.

This instrument consists of pulsed laser diode (LD), sample chamber, adjustable lens and the monochoramator and detector as seen in Figure 4.20. The LifeSpec spectrometer is controlled by commercial F900 software that communicates with both the LifeSpec controller and the TCC900 data acquisition card. To obtain a measurement the sample is placed in the provided holder with the internal monochromator set to the emission wavelength of interest. The signal strength may then be manually adjusted using a variable iris and monochromator slits. Data collection is automated by the software and may be saved and exported for further analysis.
Figure 4.20: The LifeSpec spectrometer that use to measure the lifetime of the material at the room temperature.
References


CHAPTER 5

OPTICAL CHARACTERISATION OF 
ERBIUM-DOPED YTTRIUM 
ALUMINUM GARNET PHOSPHOR MATERIALS

5.1 Introduction

In chapter 5, the photoluminescence (PL) of erbium doped $\text{Y}_3\text{Al}_5\text{O}_{12}$ (YAG) is studied as a function of temperature and excitation power dependence. PL spectra are obtained using two different excitation wavelengths which are 488nm and 980nm. The samples studied are prepared as described in Chapter 4, with two different quenching conditions representing fast and slow cooling from the elevated temperatures used during preparation. The fast-cooled samples are homogenous (single phase) in nature whereas those slowly cooled are found to have a phase separation. Comparison of both samples reveals similar optical properties, with PL upconversion observed mostly in monophasic sample when excited at 980nm wavelength. The upconversion may find interesting applications in solid state lasers though this is beyond the scope of the work presented. Historically significant research has been investigated in the use of erbium ions ($\text{Er}^{3+}$) due to its well-known $^4I_{13/2}$ to $^4I_{15/2}$ emission band centred at 1.53µm which matches the low-
loss window of silica optical fibres. Emission of the erbium ion can be observed in both visible and NIR spectrum with upconversion under intense optical pumping due to the favourable intra-atomic 4f energy level structure [1][2][3]. Erbium doped YAG normally exhibits emission at around 550nm[4][5][6], 665nm[7], 965nm[8] and 1013nm[9], 1532nm[10][11] and 1620nm[12].

Previous work by our collaborators has shown that the use of different cooling rates of erbium doped YAG during synthesis (solid state reaction) can result in crystal phase separation[13]. The finding of biphasic erbium doped YAG resulting from slow cooling occurs for erbium concentrations between 8%-50%. In the present work, we focus on the investigation of erbium doped YAG for NIR emission and in particular the study of the optical properties to provide information on ion-ion interactions. Studies as a function of erbium dopant concentration are performed and the results of both temperature and power dependence studies, and of emission lifetime measurements are presented in this chapter. Upconversion processes are observed from the Er³⁺:YAG samples with red upconversion emission found in both single phase and biphasic samples when excited at 980nm. Under 488nm or 980 nm excitation the characteristic erbium emission band centred at ~1532 nm (⁴I₁₃/₂ to ⁴I₁₅/₂) is observed and studied as a function of temperature.

The flow of this chapter is such that we first focus on the 488nm excited PL followed by the 980nm excitation. Then, the temperature dependence of the PL and the PL lifetime is presented again with the 488nm excitation preceding that of the 980nm excitation. Attention is then turned to focus on the upconversion obtained under 980nm excitation. Finally, the excitation power dependence of the PL and PL lifetime under 488nm and 980nm excitation are discussed.
5.2 Concentration Dependence of Er:YAG Photoluminescence

5.2.1 488nm excitation of fast-cooled and slow-cooled Er:YAG

The PL of both fast and slow-cooled samples were measured using 488nm excitation. For each type of sample (fast and slow-cooled) the erbium doping concentration is varied (2, 10, 20, 30 and 50%) and characterised as a function of temperature. PL measurements were undertaken at various temperatures between 300K and 4K. Full PL spectra however are only presented (Figure 5.1) for two temperatures: (i) room temperature (300K) and (ii) 77K. To obtain full PL spectra, measurements are taken over two overlapping ranges, from 500nm-1100nm and 800nm-1700nm, as described in Chapter 4 using an excitation wavelength of 488nm. Within the NIR there are two main emission bands; one is centred at around 965nm and is due to the \( ^{4}I_{11/2} \) to \( ^{4}I_{15/2} \) transition (used to normalise the two spectra) whilst the second is centred at 1532 nm and is due to the \( ^{4}I_{13/2} \) to \( ^{4}I_{15/2} \) transition. This later emission is suited for the telecommunications due to overlapping with the ‘low-loss’ window of silica optical fibres, thus 1532nm emission is our main focus in this chapter.

The effect of doping at high concentration does not give effect to the structural changes for the fast-cooled and slow-cooled samples. It only gives changes to the Er10%, Er20% and Er30% for the slow-cooled sample which can be referred Figure 4.2a (page 68). If the structure of the material changes, phase separation can be seen clearly. Below Er10% concentration, the sample maintains the same structure.

The mono-phase and bi-phase “term” is referring to the phase separation of the material. Mono-phase means that only a single phase is present whilst the bi-phase refer to the phase separation found in the material which contain Er rich and Er deficient regions[13].
5.2.1.1 PL of fast-cooled (mono-phase) Er:YAG

Figure 5.1: The 488nm excited PL of fast-cooled Er:YAG samples as a function of Er concentration (2, 10, 20, 30 and 50%) at 300K (a) and 77K (b). All spectra are normalised at 965nm.
The PL spectrum of the fast-cooled samples, at 300K, is shown in Figure 5.1(a) with each spectrum normalized at 965nm as a result of the need to use two detectors and gratings to collect the full spectra. This also enables the comparison of relative PL intensities between the various Er transitions within each sample and subsequently between samples. In the visible region at low concentrations there is a broad emission band centred at ~570nm. The origins of this emission is not clear, however the spectrally sharp intra-atomic erbium ion emission may rule out indicating that it could be host (YAG) related. Supporting this is the present of a sharp peak at ~550nm originating from the \( {^4S_{3/2}} \) to \( {^4I_{15/2}} \) Er\(^{3+}\) transition superimposed onto this broad emission. It is also noticeable that as the erbium concentration increased, the intensity of the broad peak reduces and eventually disappears, reducing the overall PL intensity in this region. This also enables the sharp erbium related emission to be clearly seen as the erbium concentration is increased.

In the near infrared (NIR) region weaker emission is observed compared to visible emission at low erbium concentrations. The observed emission bands originate from the Er\(^{3+}\) \( {^4I_{9/2}} \) (~860nm), \( {^4I_{11/2}} \) (~965nm) and \( {^4I_{13/2}} \) (~1532nm) to ground state \( {^4I_{15/2}} \) transitions. As the erbium concentration is increased, the PL intensity is generally seen to decrease and is commonly associated with ion-ion quenching. For doping concentrations above 2% the NIR emission dominates over the visible emission. Ion-ion quenching occurs as the distance between neighbouring erbium ions is reduced as a result of the erbium concentration increasing, which increases the probability of non-radiative processes (energy transfer) occurring. High erbium concentrations can also lead to the clustering of erbium ions resulting in a non-homogeneous ion distribution.

The full PL spectrum of the fast-cooled samples obtained at 77K, also normalized at ~965nm, is shown in Figure 5.1(b). Again a broad emission is observed around 500nm to 750nm for the Er2% sample, though reduced in relative intensity to the intra-atomic erbium emission in this region. It therefore appears that the origin of this broad emission is more temperature sensitive than the erbium emission supporting it being host related. The broad emission might be related to the host due to defects easily incorporated into the powder material during the grain growth process. The defects could potentially be
removed by a post-synthesis anneal if performed at temperatures well below the synthesis temperature [14]. As the erbium concentration is increased the broad emission reduces, as also observed at 300K, thus the sharp emission peaks from the erbium ion can be observed.

In the near infrared (NIR) region weaker erbium emission is observed compared to the visible region with the PL originating from the $^4I_{9/2}$ (860nm), $^4I_{11/2}$(965nm) and $^4I_{13/2}$(1532nm) to ground state transitions.
Figure 5.2: The 488nm excited PL of fast-cooled Er:YAG samples as a function of Er concentration (2, 10, 20, 30 and 50%) at 300K (a) and 77K (b). All spectra are normalised at 965nm.
Figure 5.2a and b show the detailed PL spectra originating from the $^4I_{11/2}$ to $^4I_{15/2}$ transition, normalized at ~965nm, in which clear Stark splitting can be observed. Similar Stark splitting is seen for all the erbium concentrations studied except for the Er50% sample. This is an experimental artefact due to the use of a wider slit width in order to measure the weak emission from this sample. As the slit width is increased the spectral resolution is reduced. Normally the slit width on the monochromator is set to 1 mm but for the Er50% sample the slit width used was 2 mm. As the intensity scales at the square of the slit width (i.e. area) the scaling factor is 1:4 between the Er50% spectrum and that of the others.

In Figure 5.2a and b the Stark splitting of the $^4I_{11/2}$ to $^4I_{15/2}$ transition can be seen and is divided by a ~15nm gap at ~990nm into low and high energy emission bands. There is little variation between the relative intensities of these two bands for the majority of the fast-cooled ErX samples. However, an additional component at ~1045nm is seen in the Er2% sample (reproducible and also present in the 300K PL) which for the Er50% sample the PL of the low energy band dominates over the higher energy emission. The peak at ~1045nm in the Er2% sample indicates that this emission originates from a transition at the bottom of the $^4I_{11/2}$ manifold to the top of the $^4I_{15/2}$ manifold and becomes stronger due to the reduced thermal energy of excited electrons.

This measurement has been made twice for each sample and the slit width difference is due to a variance in the measurement conditions. For an idealised experimental setup it would be possible to correct the intensities for variance in the slit width used as this scales with the square of the slit width. However, the spectral resolution cannot be improved. No correction was attempted as the precise measurement geometry in practice would vary between the measurement of each sample.
Figure 5.3: The 488nm excited PL of fast-cooled Er:YAG samples as a function of Er concentration (2, 10, 20, 30 and 50%) at 300K (a) and 77K (b). All spectra are normalised at 965nm.
Upon excitation at 488nm the characteristic ~1532nm PL, and its Stark splitting, can be clearly observed (Figure 5.3a). As the erbium concentration is increased the emission intensity reduces due to the well-known ion-ion quenching effect as the distance between neighbouring ions is reduced with increasing Er$^{3+}$ concentration[15]. The reduction in distance between ions increases the probability of energy transfer between neighbouring ions. This often leads to non-radiative cross relaxation (CR) and ultimately reduces emission efficiency.

The results of performing the same measurement on the fast-cooled Er:YAG samples at 77K are shown in Figure 5.3b. In this case emission from lower energy Stark levels within the $^4I_{13/2}$ manifold appear to be enhanced compared to the higher energy (~1450nm to 1500nm) emission. This might be expected as the thermal population of the manifold’s higher levels is reduced at these temperatures. The energy difference between high energy (0.80eV = 1550nm) and lower energy (0.75eV = 1650nm) is 50meV. The thermal energy (kT) at 300K is 25meV and reduced to 6meV at 77K, thus electrons are unlikely to occupy the upper Stark levels.
5.2.1.2 PL of slow-cooled (bi-phase) Er:YAG

Figure 5.4: The 488nm excited PL of slow-cooled Er:YAG samples as a function of Er concentration (2, 10, 20, 30 and 50%) at 300K (a) and 77K (b). All spectra are normalised at 965nm.
The PL spectra of the slow-cooled ErX samples at 300K have been normalised at ~965nm and are shown in Figure 5.4a. Comparison with the PL spectra of the fast-cooled ErX samples (Figure 5.1a) shows that the emission in the visible region is significantly weaker in the slow-cooled ErX samples. The broad emission in the visible range is still observed for the slow-cooled Er2 and Er20 samples that could be related to the host (YAG) as discussed above. However, the sharp emission peaks resulting from erbium ion emission in this region are clearly observable. The emission in the NIR region also displays sharp peaks originating from the Er\textsuperscript{3+} \( ^4I_{9/2}\) (860nm), \( ^4I_{11/2}\)(965nm) and \( ^4I_{13/2}\)(1532nm) levels. The \( ^4I_{13/2}\)(1532nm) emission can be seen to be stronger than the visible emission for all slow-cooled samples at 300K. This is in contrast to the behaviour observed in the fast-cooled ErX samples where the visible emission dominated. In the NIR region, as the erbium concentration is increased from the lowest Er2% to the highest Er50% the NIR PL intensity is decreased due to ion-ion interactions as discussed above.

Reducing the temperature of the slow-cooled ErX samples to 77K is seen to lead to a general shift in the balance of emission to the visible region, Figure 5.4b. The same broad emission is observed in the visible range for both the slow-cooled Er2 and Er10 samples at room temperature as seen in Figure 5.4a. The PL intensity is increased by a factor of ~3 if compared with slow-cooled Er10 sample at room temperature. This increase in visible emission may be expected as the temperature is reduced as radiative relaxation is more probable as competing non-radiative relaxation pathways are reduced. As a result electrons relax directly from the higher excited states to the ground state emitting a high energy (visible) photon. The result of this is that fewer electrons relax down to the lower excited state and so the infrared emission is reduced.
Figure 5.5: The 488nm excited PL of slow-cooled Er:YAG samples as a function of Er concentration (2, 10, 20, 30 and 50%) at 300K (a) and 77K (b). All spectra are normalised at 965nm.

The normalized PL spectra (at 965nm) of the Er\(^{3+}\) \(4I_{11/2}\) energy level emission and Stark splitting can be seen clearly in Figure 5.5a and b. The same monochromator slit width (1mm) was used for all measurements (c.f. Figure 5.2a). The PL intensity is seen to increase, particularly in the low energy range (1000nm to 1050nm), as the erbium concentration increases. This is due to more efficient non-radiative relaxation of higher excited 4f states in these samples as the erbium concentration increase. Unlike for the fast-cooled Er2% sample (Figure 5.2b), the slow-cooled sample Er2% displays no emission in the 1040-1050nm range.
Figure 5.6: The 488nm excited PL of slow-cooled Er:YAG samples as a function of Er concentration (2, 10, 20, 30 and 50%) at 300K (a) and 77K (b). All spectra are normalised at 965nm.
Similar inspection of the \( \text{Er}^{3+} \, ^4I_{13/2} \) emission from slow-cooled Er:YAG (Figure 5.6a) also reveals the characteristic of Stark splitting. As for the fast-cooled samples it is seen that the PL intensity reduces with increasing erbium concentration. This is expected due to the increase in ion-ion quenching as discussed above.

The Stark splitting of the \( ^4I_{13/2} \) emission at 77K can be seen clearly in Figure 5.6b. The variation of the PL intensity with concentration is somewhat unexpected. It is not the lowest erbium concentration (2%) sample that displays the strongest emission, but the sample with an erbium concentration of 30%. This indicates that the population mechanisms that lead to an electron residing in the \(^4I_{13/2}\) erbium level have been modified significantly resulting in a higher population of electrons in the \(^4I_{13/2}\) energy level, thus the PL intensity increasing. Another possible reason that must be considered is that as the sample is bi-phasic it is possible that each phase has a significantly different erbium concentration. For example one phase could be 1/3 erbium rich and the other 2/3 erbium depleted. Furthermore, it is noted that the 20% and 50% doped sample display the weakest emission, with the 2% sample displaying PL emission intensity just below the 30% sample. This will be discussed further after considering further results in this chapter.
5.2.2 980nm excitation of fast-cooled and slow-cooled Er:YAG

The PL of all of the fast and slow-cooled samples described above were measured using 980nm excitation. PL measurements were undertaken at various temperatures between 300K and 5K. The PL spectra obtained taken for this excitation are restricted to wavelengths longer than, or much shorter than, the excitation wavelength, thus the spectra are not normalised at 965nm and cannot be directly compared with those obtained using 488nm excitation. Specifically, all the PL spectra were obtained at (i) room temperature (300K) and (ii) 77K for spectral ranges spanning 500nm-950nm and 1000-1700nm. For wavelengths shorter than the excitation, upconversion emission bands centred at 545nm, 677nm and 864nm are observed and discussed in section 5.4. Within the NIR there is one main emission band centred at 1532 nm and due to the $^4I_{13/2}$ to $^4I_{15/2}$ transition.
5.2.2.1 PL of fast-cooled (mono-phase) Er:YAG

**Figure 5.7**: The 980nm excited PL of fast-cooled Er:YAG samples as a function of Er concentration (2, 10, 20, 30 and 50%) at 300K (a) and 77K (b).

*Figure 5.7a* shows the 980nm excited PL which displays the same trend in PL intensity found when exciting at 488nm (c.f. *Figure 5.5a*) for the reasons discussed above (ion-ion quenching). Reducing the temperature to 77K does not change this trend as is seen in *Figure 5.7b*. Once again there does appear to be a relative increase in the lower energy PL observed from the $^4I_{13/2}$ manifold upon reduction in temperature again supporting a reduction in electron population of the higher energy Stark levels.

Based on the structural analysis that had been undertaken by the University of Cambridge, we confirmed that the slow-cooled sample has one phase only (refer *Figure 4.1a page 67*).
5.2.2.2 PL of slow-cooled (bi-phase) Er:YAG

Figure 5.8: The 980nm excited PL of slow-cooled Er:YAG samples as a function of Er concentration (2, 10, 20, 30 and 50%) at 300K (a) and 77K (b).

Excitation of the slow-cooled sample at 980nm (Figure 5.8a and b) also reveals similar behaviour as for when excited at 488nm (c.f. Figure 5.6a and b). At 300K the PL intensity is the highest for the Er2% sample and steadily reduces as the Er3+ concentration is increased to 50%. As the temperature is reduced to 77K, the PL intensity again is found not to follow the expected trend with increasing Er3+ concentration. As previously found the PL obtained from the sample doped with 20% Er3+ is enhanced though the difference in this case (i.e. when exciting at 980nm compared to 488nm) is not as great. Nonetheless it confirms that this behaviour is reproducible under different excitation conditions and is not an experimental artefact.
5.3 Temperature dependence of Er:YAG Photoluminescence

5.3.1 488nm excitation

5.3.1.1 Integrated PL intensity for fast-cooled sample and slow-cooled sample

Figure 5.9: The integrated ~1532nm PL intensity of 488nm excited fast-cooled (a) and slow-cooled (b) samples ErX (X = 2, 10, 20, 30 and 50) from 300K to 4K.
The integrated PL intensity originating from the $^4I_{13/2}$ energy level (1532nm) is shown in Figure 5.9, normalised for each sample to the integrated emission intensity at 300K. Considering the intensity of the emission centred at 1532nm it is seen that the fast-cooled and slow-cooled ErX samples display different behaviour. For the fast-cooled sample, Er10 and Er30% have similar initial temperature dependence displaying a fast reduction in intensity as the temperature is reduced from 300K to 250K. The PL intensity then remains stable for these samples until 150K below, which the Er2% sample then continues to gradually decrease. This initial behaviour indicates a common underlying population mechanism of the lower erbium energy levels that is quickly modified as the temperature is reduced. The remaining samples reduce in intensity gradually as the temperature is reduced with the Er20% sample behaving similarly to the Er30% at temperatures below 150K and not reducing in intensity further and perhaps increasing slightly. This makes the Er20% sample the strongest emitter of ~1532nm PL at temperatures below 150K.

For the slow-cooled samples, it is observed that cooling reduces the PL intensity significantly as seen in Figure 5.9b for all samples down to 150K. Below this temperature the Er30% sample is the strongest emitter, in contrast to that seen in the fast-cooled sample, and is seen to increase in intensity with reducing temperature to ~75K before reducing again slightly. In general the higher erbium concentration samples emit the strongest PL at low temperatures. This indicates that either ion-ion non-radiative relaxation processes of the emitting $^4I_{13/2}$ level have been reduced, or those ion-ion interactions of higher levels are increasing the population of the $^4I_{13/2}$ level (e.g. down conversion). Such processes are typically two-photon related and may be studied via excitation power dependence studies.

For slow-cooled sample (bi-phase) it is worth recalling that there exists a high concentration region (erbium rich) phases in which ion-ion interactions are likely to be enhanced. The percentage of the erbium in each of the sample can be referred in the discussion section which is 5.6
The result is anomalous from that expected and may be an artefact of the measurement condition. However, the measurements were repeated yielding the same result indicating that it is probably a real effect and is related to the sample properties.

5.3.1.2 Lifetime of PL intensity for fast-cooled sample

Figure 5.10: The long (a) and short (b) 1532nm lifetimes obtained from bi-exponential fits of the 488nm excited fast-cooled samples ErX (X = 2, 10, 20, 30 and 50) from 300K to 4K.

The decay transient of the 1532nm emission excited at 488nm was recorded for all samples and found to have two lifetimes, ($\tau_1$ and $\tau_2$) as seen in Figure 5.10 and Figure 5.11. As the erbium concentration increases from Er2% to Er50% the PL lifetime reduces as expected due to increase in ion-ion quenching interaction as discussed above and indicates more non-radiative transition takes place between the energy levels. As the temperature decreases from 300K to 4K in 25K steps, the PL lifetime of Er2% and Er10% is decreased whilst the Er20%, Er30% and Er50% samples display little temperature dependence of their 1532nm PL lifetime. The bi-exponential decay observed clearly points to the presence of either two population pathways of the $^4I_{13/2}$ level or two distinct sites in
which the Er ion reside. As these samples are single-phase (fast-cooled) it is likely that the former is correct.

5.3.1.3 Lifetime of PL intensity for slow-cooled sample

Figure 5.11: The long (a) and short (b) 1532nm lifetimes obtained from bi-exponential fits of the 488nm excited slow-cooled samples ErX (X = 2, 10, 20, 30 and 50) from 300K. Note that for Er2% $\tau_1 = \tau_2$

For the slow-cooled samples Er2% has single lifetime $\tau_1$ at all temperatures whilst the remaining samples exhibit bi-exponential behaviour ($\tau_1$ and $\tau_2$) in Figure 5.11. The exception to this is the Er20% sample which also displays single exponential behaviour below 150K. Upon reducing the temperature all lifetimes are typically reduced. The Er10% sample deviates from this trend slightly with $\tau_1$ increasing slightly as temperatures below 100K. This behaviour, and that of the Er20% sample, may be related to the percentage of erbium concentration in each phase of the sample and will be discussed further below. It is interesting to note that the emission lifetime of the Er50% sample appears to be a thermal, displaying no change over the 300K to 4K temperature range.
Comparison of the lifetimes obtained from fitting the PL decay for each sample is provided in Table 5.1. At both 300K and 4K there is no clear trend when comparing fast and slow-cooled samples of the same concentration as to which is generally longer. This could be due to the numerous competing relaxation pathways present in each sample when exciting at higher energy (488nm).

**Table 5.1: The summary of the lifetime different between the fast-cooled and slow-cooled sample for τ₁ and τ₂ for 488nm excitation**

<table>
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<th>4K Tau 1 (µs)</th>
<th>4K Tau 2 (µs)</th>
<th>300K Tau 1 (µs)</th>
<th>300K Tau 2 (µs)</th>
</tr>
</thead>
<tbody>
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<td>Er2% (FC)</td>
<td>4740</td>
<td>1530</td>
<td>7000</td>
<td>3660</td>
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<td>2960</td>
<td>-</td>
<td>3940</td>
<td>-</td>
</tr>
<tr>
<td>Er10% (FC)</td>
<td>1830</td>
<td>744</td>
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<td>-</td>
<td>1250</td>
<td>450</td>
</tr>
<tr>
<td>Er30% (FC)</td>
<td>1030</td>
<td>281</td>
<td>1110</td>
<td>344</td>
</tr>
<tr>
<td>Er30% (SC)</td>
<td>1150</td>
<td>361</td>
<td>1850</td>
<td>463</td>
</tr>
<tr>
<td>Er50% (FC)</td>
<td>394</td>
<td>142</td>
<td>603</td>
<td>172</td>
</tr>
<tr>
<td>Er50% (SC)</td>
<td>940</td>
<td>264</td>
<td>1100</td>
<td>322</td>
</tr>
</tbody>
</table>
5.3.2 980nm excitation

5.3.2.1 Integrated PL intensity for fast-cooled sample and slow-cooled sample

![Graph showing Integrated PL intensity versus Temperature for fast-cooled and slow-cooled samples.](image)

**Figure 5.12:** The integrated ~1532nm PL intensity of 980nm excited fast-cooled (a) and slow-cooled (b) samples ErX (X = 2, 10, 20, 30 and 50) from 300K to 4K.

Upon 980nm excitation all samples display a reduction in the 1532nm PL integrated intensity as the temperature is decreased from 300K to 4K (**Figure 5.12**). The temperature dependence of the PL for all fast-cooled samples except the Er2% are similar and display an initial rapid reduction in intensity as the temperature is reduced to ~275K before continuing to steadily reduce. The Er2% sample shows similar behaviour but of much reduced magnitude. This trend (rapid initial then steady reduction in intensity) is mirrored in the slow-cooled samples with the most obvious difference being the increasing magnitude of the trend as Er concentration is increased. This clearly points to the population mechanisms of the $^4I_{13/2}$ energy level being affected by both ion-ion and electron-phonon interactions with a degree of interdependency also are being present.
5.3.2.2 Lifetime of PL intensity for fast-cooled (mono-phase) sample

![Figure 5.13](image_url)

Figure 5.13: The long (a) and short (b) 1532nm lifetimes obtained from bi-exponential fits of the 980nm excited fast-cooled samples ErX (X = 2, 10, 20, 30 and 50) from 300K to 4K.

Considering the 1532nm emission lifetime, all of the fast-cooled samples display bi-exponential decay with a general reduction in both ($\tau_1$ and $\tau_2$) with decreasing temperature, Figure 5.13. The only anomaly is for Er2% that shows a small increase in the shorter of the two lifetimes $\tau_2$ as temperature is reduced. This is indicative of the associated process being phonon related. It is interesting to note that the value of $\tau_2$ reduces with increasing Er concentration and therefore this process must be affected by ion-ion quenching. $\tau_1$ on the other hand does not reduce in the same way with increasing Er concentration but is similar for the Er10% and 20% samples and also for the Er30% and 50% samples. This again suggests that the process related to $\tau_1$ is very similar in these sets of samples.
5.3.2.3 Lifetime of PL intensity for slow-cooled (bi-phase) sample

Figure 5.14: The long (a) and short (b) 1532nm lifetimes obtained from bi-exponential fits of the 980nm excited slow-cooled samples ErX (X = 2, 10, 20, 30 and 50) from 300K to 4K.

As has been seen for the fast-cooled samples above the 1532nm emission lifetime is found to be bi-exponential and to generally reduce with both temperature and increasing erbium concentration, Figure 5.14. The Er30% and 50% samples display only a small temperature dependence which indicates that ion-ion interactions dominate the quenching processes in these samples and not intra-atomic phonon interactions. Comparing the fast-cooled and slow-cooled samples at 300K it is found that the slow-cooled Er2% sample has a longer lifetime at 300K than the fast-cooled. This trend is reversed for the Er50% samples with the fast-cooled sample displaying the longer lifetime, Table 5.2. At intermediate Er concentrations no clear pattern is found at 300K which may, for the slow-cooled samples, be related to the percentage of the erbium ion in each phase and will be discussed later in this chapter. At 4K the slow-cooled samples typically have a shorter lifetime than the fast-cooled samples of the same Er concentration with the exception of the Er30% sample.
Table 5.2: The summary of the lifetime different between the fast-cooled and slow-cooled sample for $\tau_1$ and $\tau_2$ at 980nm excitation

<table>
<thead>
<tr>
<th>Sample</th>
<th>4K</th>
<th>300K</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Tau 1(µs)</td>
<td>Tau 2(µs)</td>
</tr>
<tr>
<td>Er2% (FC)</td>
<td>4910</td>
<td>1940</td>
</tr>
<tr>
<td>Er2% (SC)</td>
<td>4510</td>
<td>1780</td>
</tr>
<tr>
<td>Er10% (FC)</td>
<td>2690</td>
<td>1070</td>
</tr>
<tr>
<td>Er10% (SC)</td>
<td>2450</td>
<td>880</td>
</tr>
<tr>
<td>Er20% (FC)</td>
<td>2840</td>
<td>577</td>
</tr>
<tr>
<td>Er20% (SC)</td>
<td>2660</td>
<td>678</td>
</tr>
<tr>
<td>Er30% (FC)</td>
<td>1920</td>
<td>482</td>
</tr>
<tr>
<td>Er30% (SC)</td>
<td>2210</td>
<td>517</td>
</tr>
<tr>
<td>Er50% (FC)</td>
<td>1980</td>
<td>354</td>
</tr>
<tr>
<td>Er50% (SC)</td>
<td>859</td>
<td>223</td>
</tr>
</tbody>
</table>

At room temperature, Er2% fast-cooled sample shows a small variation in $\tau_2$ compared to the Er2% slow-cooled sample. The small difference between the two values may be due to the experimental artefact during the measurement. Likewise, other variations can be found (e.g. for the Er30% samples) that are related to the percentage of Er rich and Er deficient regions. It is also observed that the lifetime decreases in the Er30% samples if compared to Er20% which is an indication of other processes (e.g. ETU) starting to impact. For the Er50% fast-cooled sample and slow-cooled sample two different lifetimes are found which may indicate that for the Er50% slow-cooled sample 3um emission is more probable, as so explaining the 1532nm lifetime reduction.
5.4 Upconversion 980nm excitation

5.4.1 PL intensity of fast-cooled sample

Figure 5.15: Upconversion photoluminescence of 980nm excited fast-cooled samples at 300K (a) and 77K (b).

**Figure 5.15** shows the upconversion PL for fast-cooled ErX (X = 10, 20, 30 and 50%) samples under 980nm excitation obtained at 300K and 77K. Three main emission bands are found centred at 545nm ($^4S_{3/2}$-$^4I_{15/2}$), 677nm ($^4I_{9/2}$-$^4I_{15/2}$) and 864nm ($^4I_{9/2}$-$^4I_{15/2}$). At 300K, as the erbium concentration increases the upconversion PL intensity increases with Er30% showing the highest intensity. As the temperature is reduced to 77K, the Er50% shows the highest intensity especially at 677nm and 864nm where little difference in intensity of found for the other samples. The Er2% sample was found not to display upconversion.
5.4.2 PL intensity of slow-cooled sample

Figure 5.16: Upconversion photoluminescence of 980nm excited slow-cooled samples at 300K (a) and 77K (b).

**Figure 5.16** shows the upconversion PL obtained from the slow-cooled samples again at 300K and 77K. As for the fast-cooled samples the same three emission bands centred at 545nm ($^4S_{3/2}$-$^4I_{15/2}$), 677nm ($^4I_{9/2}$-$^4I_{15/2}$) and 864nm ($^4I_{9/2}$-$^4I_{15/2}$) are found. At 300K, the upconversion increases in intensity in line with the erbium concentration. This contrasts the 1532nm emission which displays the highest intensity for the lowest Er concentration samples. This provides support for the above observations of quenching being linked to ion-ion interactions of which upconversion is one outcome.

As the temperature is reduced to 77K, Er30% shows the strongest upconversion unlike what was found for the fast-cooled samples. This deviation between the behaviour of the fast and slow-cooled samples is indicative of the phase separation seen in these samples. As for the fast-cooled samples the slow-cooled Er2% sample does not display any upconversion PL.
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5.5 Power dependence of Er:YAG

5.5.1 488nm excitation

5.5.1.1 PL integrated intensity for fast-cooled and slow-cooled sample

Figure 5.17: The 1532nm integrated PL intensity versus laser excitation power for 488nm excitation of fast-cooled samples ErX (X = 2, 10, 20, 30 and 50) at 300K (a) and 77K (b).

Figure 5.18: The 1532nm integrated PL intensity versus laser excitation power for 488nm excitation of slow-cooled samples ErX (X = 2, 10, 20, 30 and 50) at 300K (a) and 77K (b).
Study of the excitation power dependence of PL can be used to provide evidence of upconversion and downconversion was therefore taken. For example if upconversion due to a 2-photon process is present then the intensity emission would vary quadratically \( (n^2) \) with the excitation power.

For the emission centred 1532nm, at 300K all fast-cooled ErX samples display a linear dependence of the PL intensity with respect to the excitation power as seen in Figure 5.17a. The PL intensities of each ErX% sample are normalised to that measured at 300K. Upon reducing the temperature to 77K, no change in the linear dependence of PL intensity with respect to excitation power was found, Figure 5.17b.

The same behaviour is observed with the slow-cooled samples where at 300K a linear dependence of the 1532nm PL intensity with respect to the excitation power as seen in Figure 5.18a. Upon reduction of temperature to 77K the Er2% and Er50% samples continue to display a linear dependence on excitation power, Figure 5.18b. However, the remaining sample display marked deviations from this behaviour with the Er20% sample appearing to show saturation of PL intensity and the Er30% sample displaying a peak in PL intensity. This behaviour for these samples point to the presence of a depopulation pathway ‘turning on’ at high excitation intensities of the \( ^4I_{13/2} \) energy level.
5.5.1.2 PL lifetime for fast-cooled sample

Figure 5.19: The results of bi-exponential fits, $\tau_1$ (a) and $\tau_2$ (b), to the 1532nm PL lifetime as a function of 488nm excitation power for the fast-cooled ErX (X = 2, 10, 20, 30 and 50) samples at 300K.

Figure 5.20: The results of bi-exponential fits, $\tau_1$ (a) and $\tau_2$ (b), to the 1532nm PL lifetime as a function of 488nm excitation power for the fast-cooled ErX (X = 2, 10, 20, 30 and 50) samples at 77K.
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The 1532nm PL lifetime was measured and fitted using a bi-exponential decay for all samples as a function of 488nm excitation power. It was found that at 300K all fast-cooled samples show no dependence of the PL lifetime on excitation, Figure 5.19a and b. For some samples as the excitation power was reduced the signal strength was too weak to measure the lifetime (PL spectra were able to be recorded as lock-in detection was used to improve the signal to noise ratio). Reducing the temperature to 77K, Figure 5.20a and b, does not change this behaviour which is as would be expected from the linear PL intensity dependence on excitation power.

5.5.1.3 PL lifetime for slow-cooled sample

Figure 5.21: The results of bi-exponential fits, $\tau_1$ (a) and $\tau_2$ (b), to the 1532nm PL lifetime as a function of 488nm excitation power for the slow-cooled ErX (X = 2, 10, 20, 30 and 50) samples at 300K.
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Figure 5.22: The results of bi-exponential fits, $\tau_1$ (a) and $\tau_2$ (b), to the 1532nm PL lifetime as a function of 488nm excitation power for the slow-cooled ErX ($X = 2, 10, 20, 30$ and $50$) samples at 77K.

Continuing the study with the slow-cooled samples as above for the temperature dependence studies we find that the Er10%, Er20%, Er30% and Er50% exhibit bi-exponential decay with the Er2% sample PL decay being single exponential. At 300K only the Er10% sample shows any dependence on excitation power with the slow component of the decay getting fast with decreasing temperature, Figure 5.21a and b. As the temperature is reduced to 77K the only sample showing slight dependence on excitation power is the Er2% sample who’s PL lifetime (both components) are reduced, Figure 5.22a and b.
5.5.2 980nm excitation

5.5.2.1 PL integrated intensity for fast-cooled and slow-cooled sample

Figure 5.23: The 1532nm integrated PL intensity versus laser excitation power for 980nm excitation of Fast-cooled samples ErX (X = 2, 10, 20, 30 and 50) at 300K (a) and 77K (b).

Figure 5.24: The 1532nm integrated PL intensity versus laser excitation power for 980nm excitation of slow-cooled samples ErX (X = 2, 10, 20, 30 and 50) at 300K (a) and 77K (b).
We now examine the 980nm excitation dependence of the 1532nm PL obtained from the various samples. At 300K the intensity of fast-cooled sample PL displays a linear dependence with respect to the excitation power as seen in Figure 5.23a. As the temperature is reduced to 77K, Figure 5.23b, a small deviation from linear dependence is observed that is most obvious at lower temperatures. Considering the slow-cooled samples, Figure 5.24a and b, similar behaviour is found but with the non-linearity now also becoming evident at 300K in addition to 77K.

As mentioned above, power dependence studies give evidence for competing depopulation mechanisms taking places including upconversion. Previous studies have reported upconversion in the Er:YAG samples [15][16][17]. In order to understand the contribution of such two-photon process we studied the pump power dependence of the green and red upconversion emission intensity[18] under 980nm excitation.

![Graph](https://via.placeholder.com/150)

Figure 5.25: The 677nm integrated PL intensity versus laser excitation power for upconversion of fast-cooled samples ErX (X = 10, 20, 30 and 50) at 300K (a) and 77K (b).

Figure 5.25a and b presents a log-lin plot of the 677nm (red) integrated intensity versus laser power. For each sample the data is fitted (\( \log(I) = nI + I_0 \)) in order to extract the value
of $n$ which gives the average number of the photons absorbed per upconverted photon emitted.

The values of $n$ obtained for the fast-cooled sample at 300K and 77K are presented in Table 5.3 below. From the recorded PL spectra it is known that at room temperature upconversion occurs which is shown in the values obtained for $n$ which increase from $\sim 1.8$ to 2.3 as the Er concentration increases. It can be seen that additional upconversion pathways become available as the concentration is increased to 20%. Above this Er concentration there then must exist competing pathways as $n$ is reduced again. This is not surprising as higher concentrations are typically used to obtain 3$\mu$m emission which would reduce the upconversion emission. As the temperature is reduced to 77K it is seen that the average number of photons involved in the upconversion process reduces. It means that, at low temperature, due to a reduced phonon population, phonon assisted processes would be reduced in probability. This therefore provides evidence that the energy transfer that occurs in the upconversion process is between states with a slight mismatch of energy hence requiring phonon involvement. The energy transfer that involved is energy transfer upconversion (ETU) which can be referred in B in page 147.

Table 5.3: The $n$ value for the fast-cooled sample (677nm excitation) at 300K and 77K

<table>
<thead>
<tr>
<th>Fast-cooled sample</th>
<th>n value at 300K</th>
<th>n value at 77K</th>
</tr>
</thead>
<tbody>
<tr>
<td>Er10%</td>
<td>1.83 ±0.07</td>
<td>1.32±0.10</td>
</tr>
<tr>
<td>Er20%</td>
<td>2.65±0.25</td>
<td>1.62±0.07</td>
</tr>
<tr>
<td>Er30%</td>
<td>2.49±0.22</td>
<td>1.38±0.16</td>
</tr>
<tr>
<td>Er50%</td>
<td>2.28±0.10</td>
<td>1.65±0.08</td>
</tr>
</tbody>
</table>
Figure 5.26: The 677nm integrated PL intensity versus laser excitation power for upconversion of slow-cooled samples ErX (X = 10, 20, 30 and 50) at 300K (a) and 77K (b).

The values of n obtained from fitting the data of the slow-cooled sample, Figure 5.26, are given in Table 5.4. It can be seen that at 300K all samples have $n \geq 2$ thus confirming the 2-photon nature of the upconversion process. As for the fast-cooled samples at low temperature (77K) competing pathways and the energy mismatch between the Er energy levels leads to a reduction in n.

Table 5.4: The n value for the slow-cooled sample (677nm excitation) at 300K and 77K

<table>
<thead>
<tr>
<th>Slow-cooled sample</th>
<th>n value at 300K</th>
<th>n value at 77K</th>
</tr>
</thead>
<tbody>
<tr>
<td>Er10%</td>
<td>2.38±0.29</td>
<td>1.57±0.07</td>
</tr>
<tr>
<td>Er20%</td>
<td>2.35±0.24</td>
<td>1.28±0.19</td>
</tr>
<tr>
<td>Er30%</td>
<td>2.07±0.25</td>
<td>1.53±0.07</td>
</tr>
<tr>
<td>Er50%</td>
<td>2.02±0.06</td>
<td>1.29±0.13</td>
</tr>
</tbody>
</table>
Figure 5.27: The 565nm integrated PL intensity versus laser excitation power for upconversion of slow-cooled samples ErX (X=10, 20, 30 and 50) at 300K (a) 77K (b).

Figure 5.27 plots the 565nm upconversion intensity against pump power using a log-lin plot. It can be seen that the data deviates significantly from the expected linearity as seen for the red emission. As such when fitting the data to obtain a value of n the error is much higher. Table 5.5 provides the obtained value which for all samples and temperatures studied show n<1. This indicates that the primary source of ‘upconversion’ for this emission is the sequential absorption of individual photons by the same Er ion as opposed to an ion-ion energy transfer process. This is much less efficient but is possible due to the long lifetimes of the Er$^{3+}$ energy levels (evidence by the microsecond PL lifetimes).

Table 5.5: The n value for the fast-cooled sample (565nm excitation) at 300K and 77K

<table>
<thead>
<tr>
<th>Fast-cooled sample(green)</th>
<th>n value at 300K</th>
<th>n value at 77K</th>
</tr>
</thead>
<tbody>
<tr>
<td>Er10%</td>
<td>0.53±0.09</td>
<td>0.49±0.06</td>
</tr>
<tr>
<td>Er20%</td>
<td>0.53±0.12</td>
<td>0.61±0.10</td>
</tr>
<tr>
<td>Er30%</td>
<td>0.90±0.17</td>
<td>0.79±0.11</td>
</tr>
<tr>
<td>Er50%</td>
<td>-0.06±0.11</td>
<td>0.36±0.13</td>
</tr>
</tbody>
</table>
Figure 5.28: The 565nm integrated PL intensity versus laser excitation power for upconversion of slow-cooled samples ErX (X = 10, 20, 30 and 50) at 300K (a) and 77K (b).

*Figure 5.28* shows the 565nm upconversion intensity against pump power and again results in values of $n < 1$ from the fitting for the reasons discussed above. The values of $n$ can be referred in *Table 5.6*

Table 5.6: The $n$ value for the slow-cooled sample (545nm excitation) at 300K and 77K

<table>
<thead>
<tr>
<th>Slow-cooled sample(green)</th>
<th>n value at 300K</th>
<th>n value at 77K</th>
</tr>
</thead>
<tbody>
<tr>
<td>Er10%</td>
<td>0.41±0.19</td>
<td>0.80±0.04</td>
</tr>
<tr>
<td>Er20%</td>
<td>0.62±0.18</td>
<td>0.44±0.04</td>
</tr>
<tr>
<td>Er30%</td>
<td>-0.01±0.07</td>
<td>0.17±0.10</td>
</tr>
<tr>
<td>Er50%</td>
<td>0.25±0.09</td>
<td>0.39±0.15</td>
</tr>
</tbody>
</table>
5.5.2.2 PL lifetime of fast-cooled sample (mono-phase)

The 1532nm PL lifetime of fast-cooled and slow-cooled samples were measured under 980nm excitation as a function of excitation power, Figure 5.29a and b, and Figure 5.30a and b. Only the 1532nm PL lifetime of the Er2% sample could be measured at the lowest excitation powers used. As for 488nm excitation at 300K little excitation power dependence is found for the fast-cooled samples. At 77K at low pump powers the two fitted decay lifetimes appear to reduce though this trend could not be followed due to the weak PL signal.

Figure 5.29: The results of bi-exponential fits, $\tau_1$ (a) and $\tau_2$ (b), to the 1532nm PL lifetime as a function of 980nm excitation power for the fast-cooled ErX ($X = 2, 10, 20, 30$ and $50$) samples at 300K.
Figure 5.30: The results of bi-exponential fits, $\tau_1$ (a) and $\tau_2$ (b), to the 1532nm PL lifetime as a function of 980nm excitation power for the fast-cooled ErX (X = 2, 10, 20, 30 and 50) samples at 77K.
5.5.2.3 PL lifetime of slow-cooled sample

Figure 5.31: The results of bi-exponential fits, $\tau_1$ (a) and $\tau_2$ (b), to the 1532nm PL lifetime as a function of 980nm excitation power for the slow-cooled ErX ($X = 2, 10, 20, 30$ and $50$) samples at 300K.

Figure 5.32: The results of bi-exponential fits, $\tau_1$ (a) and $\tau_2$ (b), to the 1532nm PL lifetime as a function of 980nm excitation power for the slow-cooled ErX ($X = 2, 10, 20, 30$ and $50$) samples at 77K.
Study of the slow-cooled samples at 300K (Figure 5.31) indicates little dependence of the PL decay lifetimes on the excitation power. For these samples the PL emission intensity was generally stronger than the fast-cooled samples hence PL decays could be recorded down to lower pump powers. Reducing the temperature to 77K it appears has little affect on the PL lifetimes (Figure 5.32) with no sign of the reduction found at the lowest recordable excitation intensities hinted at in the fast-cooled samples.
5.6 Discussion

Using the results presented in sections 5.2 to 5.6 it is possible to obtain a more detailed understanding of the emission properties of these samples and the effect of phase separation on them. This section is focused on comparing the emission bands in the visible and near infrared, including the upconversion that is observed under 980nm excitation.

5.6.1 488nm excitation

A variety of radiative and non-radiative (multiphonon) competing relaxation pathways are present following 488nm excitation and are summarised in Figure 5.33. The Er ion is initially excited to \( ^4F_{7/2} \) energy level following which rapid non-radiative relaxation occurs to lower energy levels including the \( ^2H_{11/2}, ^4S_{3/2}, ^4F_{9/2}, ^4I_{11/2} \) and lastly \( ^4I_{13/2} \) energy levels from which 1532nm emission originates (\( ^4I_{13/2} \rightarrow ^4I_{15/2} \) transition).

The emission bands observed in the above PL spectra under 488nm excitation are due to relaxation to the Er \( ^4I_{15/2} \) ground state as follows:

- **a)** Visible range (~565nm) \( ^4S_{3/2} / ^2H_{11/2} \rightarrow ^4I_{15/2} \) transition
- **b)** Visible range (~677nm) \( ^4F_{9/2} \rightarrow ^4I_{15/2} \) transition
- **c)** Near infrared (~965nm) \( ^4I_{11/2} \rightarrow ^4I_{15/2} \) transition
- **d)** Near infrared (~1532nm) \( ^4I_{13/2} \rightarrow ^4I_{15/2} \) transition

As each of these transitions occurs to the Er ground state it is clear if any of (a) to (c) occur then this precludes that ion emitting 1532nm emission. Radiative relaxation between excited Er energy levels is also possible as occurs for the following transitions:

- **e)** Near infrared (~850nm) \( ^4S_{3/2} \rightarrow ^4I_{13/2} \) transition

In the case of transitions (e) it is clear that subsequent emission may then also occur from the \( ^4I_{13/2} \) level at ~1532nm.
Figure 5.33: Schematic energy level diagram of the Er\(^{3+}\) ion displaying the various transitions involved in the results reported. Solid lines refer radiative transitions and dashed lines to non-radiative transitions. The solid blue line refers to the 488nm excitation wavelength whilst solid line (green, red and black) refer to the emission of photons at the given wavelengths. Cross-relations (CR) and energy transfer upconversion (ETU) are shown as long dashed lines.

As can be seen there are therefore a large number of possible relaxation pathways that influence the probability of obtaining 1532nm emission that involve relaxation within a single ion. As the concentration of Er ions in the sample increases the possibility of ion-ion (often phonon assisted) energy transfer taking place also adds to this picture. One such process is cross relaxation where an excited electron may relax from a higher excited state via the promotion of an electron from the ground state in a neighbouring ion:
In the above example an electron is initially excited to the \( ^4F_{7/2} \) energy level and then relaxes non-radiatively to the \( ^2H_{11/2} \) energy level. From here energy transfer (cross-relaxation) takes place \( ^2H_{11/2} \rightarrow ^4I_{9/2}, ^4I_{15/2} \rightarrow ^4I_{13/2} \), leading to the sensitization of a second Er ion which may then relax emitting 1532nm emission. Likewise the electron in the first Er ion may continue to relax non-radiatively from the \( ^4I_{9/2} \) to \( ^4I_{13/2} \) level and also emit a 1532nm photon. This type of behaviour which results in the emission of two low energy photons following the absorption of a single high energy photon is often referred to as ‘quantum cutting’ and may be used to improve the efficiency of devices such as solar cells through the reduction of thermal losses.

The presence of energy transfer is typically exhibited in the measurement of the PL lifetime. As the erbium concentration increases, thus increasing the probability of energy transfer, the decay of the 1532nm emission is modified. However, this effect also competes with non-radiative relaxation of the \( ^4I_{13/2} \) energy level thus it is difficult to obtain independent rates for each process. Figure 5.34 plots the 1532nm emission lifetime as a function of Er concentration for the fast and slow-cooled samples. It is clear that for the fast cooled samples a similar reduction in both of the PL lifetimes, \( \tau_1 \) and \( \tau_2 \), occurs that is correlated to the increasing Er concentration. In the slow-cooled samples however only the shorter of the two fitted lifetimes has this similar correlation. The second fitted lifetime, though reducing with Er concentration, does not do so as the same rate. This point to the modification of the processes associated with this rate being modified.
Figure 5.34: The fitted lifetimes of the 1532nm emission as a function of erbium concentration for the fast-cooled (a) and slow-cooled (b) samples.

The CR process depends on the Er-Er inter-ion distance, and it is therefore related to the erbium concentration. Additionally, this two-ion CR process requires the absorption of a phonon of energy $\sim 400\text{cm}^{-1}$ due to the small mismatch in energy between the transitions involved. The host YAG crystal is known to have a phonon energy of around $850\text{cm}^{-1}$ [19] at 300K, thus can facilitate CR.

The picture of ion-ion interactions is further complicated in the slow-cooled biphasic samples. These samples, as discussed in below section 5.6.2, contain regions of Er-rich and Er-deficient concentration for the Er10%, Er20% and Er30% samples. Both of these regions will contribute to the observed PL each with a different emission intensity and radiative lifetime. As a result the results for these samples presented are in fact an average for the two regions. In the Er-deficient region processes such as CR will be reduced for example and thus may dominate the observed behaviour at low temperatures.
b) ETU: $^4{I_{13/2}} \rightarrow ^4{I_{15/2}}, ^4{I_{13/2}} \rightarrow ^4{I_{9/2}}$

Energy transfer upconversion (ETU) competes with CR in that it results in the reduction of overall 1532nm luminescence. This process takes place by transferring the energy associated with non-radiative $^4{I_{13/2}}$ to $^4{I_{15/2}}$ transition to further excite an electron in a neighbouring ion from the $^4{I_{13/2}}$ to $^4{I_{9/2}}$ level, route B in Figure 5.33. The electron promoted to the $^4{I_{9/2}}$ level can then of course emit a higher energy photon or relax back to the $^4{I_{13/2}}$ level and emit at 1532nm. In this way the lifetime of the 965nm emission may be modified (e.g. for samples Er20% and Er30%) with the effect expecting to reduce with Er concentration. Relaxation from the $^4{I_{9/2}}$ level to the $^4{I_{11/2}}$ level is non-radiative and occurs so fast that the two levels may be considered as one energy level. This can therefore be useful for achieving 3µm emission which originates from the $^4{I_{11/2}}$ to $^4{I_{13/2}}$ transition. As a result ETU, requiring high erbium concentrations, is beneficial in realising population inversion for 3µm lasing.

Figure 5.35: The bi-exponential fitted lifetimes of the 965nm emission as a function of erbium concentration for the fast-cooled and slow-cooled samples for 488nm excitation

Figure 5.35 shows the result of fitting the 985nm emission decay as Er concentration is increased for both the fast and slow cooled samples. It can be seen that the lifetime is
similar at each Er concentration for both types of sample until high concentrations are present. For the Er30% fast-cooled samples the 965nm lifetime is increased as ETU starts to impact. In the Er30% slow-cooled sample this effect is not seen as the bi-phasic nature means that overall within the sample only a half of the sample has a 'high' Er concentration (see Table 5.7 below). At 50% Er concentration both samples are single phase and thus in this case it appears that the process of slow-cooling has an additional strong effect which is lost in the fast-cooled samples. As such, though beyond the scope of this work, this processing method may be beneficial in the area of improving Er-based 3µm laser sources. Clearly, 985nm emission needs to be minimised if 3µm emission is to be achieved as they originate from the same energy level. Therefore variations in processing are likely to have a large effect on the laser performance (e.g. lasing threshold).

### 5.6.2 Comparison of direct and upconverted emission

The spectra in Figure 5.36a, b, c and d compare the difference in visible and near-IR PL intensity for 488nm and 980nm (due to upconversion) excitation. The 488nm excited samples have a stronger green, red and ~865nm emission intensity as compared to when using 980nm excitation as expected. However, the relative strength of the (normalised) green emission and red is quite different. Furthermore, it can be seen that the broad emission in the visible is only present when exciting at 488nm and is therefore host related. This point to an increased multiphonon relaxation of the $^4F_{7/2}$ level to levels below (e.g. $^4F_{9/2}$ for red emission) in comparison to when excitation occurs via upconversion. The same behaviour can be observed by slow-cooled sample.
Figure 5.36: The PL intensity for 488nm and 980 nm excited fast-cooled samples with an erbium concentration of 10% (a), 20% (b), 30% (c) and 50% (d). Spectra are shown obtained at 300K and 77K.

As implied above when exciting at 980nm upconversion emission in the green dominates over the red and near-IR emission. This is true for both the fast-cooled and slow-cooled samples under 980nm excitation. As the Er concentration is increased the relative strength of the green upconversion emission is reduced. The transitions associated with the upconversion emission are listed below:
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a) Visible (545nm) - ($^4S_{3/2} \rightarrow ^4I_{15/2}$) transition (green emission)

b) Visible (677nm) - ($^4F_{7/2} \rightarrow ^4I_{15/2}$) transition (red emission)

c) Near infrared (1532nm) - $^4I_{13/2} \rightarrow ^4I_{15/2}$ transition

The two principle mechanisms involved for achieving upconversion emission under 980nm excitation both rely on high excited state populations of the $^4I_{11/2}$ or $^4I_{13/2}$ energy levels:

(a) ESA: $^4I_{11/2} \rightarrow ^4F_{7/2}$  
(b) ETU: $^4I_{15/2} \rightarrow ^4I_{11/2}, ^4I_{13/2} \rightarrow ^4F_{9/2}$

ESA is able to directly populate the $^4F_{7/2}$ energy level from which green emission may result. ETU is not able to produce green emission but may lead to red upconversion emission from the $^4F_{9/2}$ level. Both of these processes are in effect 2-photon (nonlinear) mechanisms. These are shown in Figure 5.37 with route A (ESA) found to be more efficient at leading to green emission than red. Route B of course may only lead to red emission [16]. All fast-cooled and slow-cooled ErX (X=10, 20, 30 and 50) samples display upconversion with the exception of Er2% due to the reduced ion-ion interaction in this sample.
Figure 5.37: Schematic energy level diagram for Er$^{3+}$ ions under 980 nm excitation for visible and NIR emission. The blue arrow (solid line) show the excitation wavelength whilst the other colours (solid lines) are the emission wavelength. The dashed arrow shows the nonradiative energy transfer whilst the dotted arrow show the multiphonon relaxation.

Comparing the relative intensities of the upconverted green and red emission it is found that the green has ~5 times greater intensity than the red. As such this indicates that route A dominates over route B as the principle mechanism for obtaining upconversion.

Figure 5.25 plots the intensity of the red upconversion emission as a function of excitation power which fitting clearly demonstrates the non-linear nature of the excitation mechanism. The value of $n = 2.65$ obtained indicates more than one process which is expected as both routes A and B may contribute to red emission\[18\].
Figure 5.38: The intensity of red upconversion emission as a function of erbium concentration at 300 and 77K.

Figure 5.38 plots the red upconversion emission intensity as a function of Er concentration. As expected the intensity increases with concentration as ion-ion interactions become more probable. The fast-cooled samples indicate that there is a temperature dependence which is most prominent at an Er concentration of 30%. The slow cooled samples show no such dependence. It is typically found that optimum ETU occurs when the erbium concentration is between 20-30% as above these concentrations other non-radiative ion-ion interactions start to dominate. This is indeed the trend observed within the fast-cooled samples at room temperature with the Er50% having reduced red upconversion emission. That this is not seen in the slow-cooled samples is related to the bi-phasic nature of the Er concentrations.

Table 5.7 shows the measured Er concentration in each sample for the slow-cooled samples in each phase. This work was performed by our collaborators at Cambridge and reported elsewhere[13]. It can be seen that each of the bi-phasic samples consists of an 8% and 50% Er-rich phase. As a result neither phase is optimal for obtaining upconversion even though the overall Er concentration may be ‘ideal’. This therefore accounts for the
variations observed in behaviour between the samples and re-iterates the importance of understanding and controlling sample preparation when synthesising the phosphors.

Table 5.7: Total amount of erbium concentration in the fast-cooled sample and slow-cooled sample.

<table>
<thead>
<tr>
<th>Er concentration (Fast-cooled ErX)</th>
<th>Er concentration (Slow-cooled ErX)</th>
<th>Relative ratio of phases in slow-cooled samples (8% and 50%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>2 %</td>
<td>2%</td>
<td>-</td>
</tr>
<tr>
<td>10 %</td>
<td>12.2%</td>
<td>0.9 (8%) + 0.1(50%)</td>
</tr>
<tr>
<td>20 %</td>
<td>20.6%</td>
<td>0.7 (8%) + 0.3 (50%)</td>
</tr>
<tr>
<td>30 %</td>
<td>29%</td>
<td>0.5 (8%) + 0.5(50%)</td>
</tr>
<tr>
<td>50 %</td>
<td>50%</td>
<td>-</td>
</tr>
</tbody>
</table>

Table 5.8: The value of n for green and red emission fast-cooled and slow-cooled sample for 980nm excitation

<table>
<thead>
<tr>
<th>Erbium concentration (ErX)</th>
<th>Red n value (300K)</th>
<th>Green n value(300K)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fast-cooled Er2</td>
<td>None</td>
<td>None</td>
</tr>
<tr>
<td>Slow-cooled Er2</td>
<td>None</td>
<td>None</td>
</tr>
<tr>
<td>Fast-cooled Er10</td>
<td>1.83 (UC)</td>
<td>0.53</td>
</tr>
<tr>
<td>Slow-cooled Er10</td>
<td>2.38 (UC)</td>
<td>0.41</td>
</tr>
<tr>
<td>Fast-cooled Er20</td>
<td>2.65 (UC)</td>
<td>0.53</td>
</tr>
<tr>
<td>Slow-cooled Er20</td>
<td>2.35 (UC)</td>
<td>0.62</td>
</tr>
<tr>
<td>Fast-cooled Er30</td>
<td>2.49 (UC)</td>
<td>0.90</td>
</tr>
<tr>
<td>Slow-cooled Er30</td>
<td>2.07 (UC)</td>
<td>-0.01</td>
</tr>
<tr>
<td>Fast-cooled Er50</td>
<td>2.28 (UC)</td>
<td>-0.06</td>
</tr>
<tr>
<td>Slow-cooled Er50</td>
<td>2.02 (UC)</td>
<td>0.25</td>
</tr>
</tbody>
</table>
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The upconversion emission when exciting at 980nm directly competes with 1532nm emission as an effective alternative relation mechanism and is therefore deleterious. Figure 5.39 shows the integrated 1532nm PL intensity as a function of Er concentration under 980nm excitation.

Figure 5.39: The integrated intensity of 1532nm emission as a function of erbium concentration at 300 and 77K for a) fast-cooled sample b) slow-cooled sample.

For 980nm excitation, emission ~1532nm, the PL intensity decreases linearly as the temperature is reduced. This is may be due to the 980nm excited $^4I_{11/2}$ level relaxing non-radiatively to the $^4I_{13/2}$ level followed by a second photon upconverting the excited state to $^4F_{9/2}$. From this state non-radiative relaxation through the $^4F_{9/2} \rightarrow ^4I_{11/2} \rightarrow ^4I_{13/2} \rightarrow ^4I_{15/2}$ levels may occur, eventually giving 1532nm emission. In the process excitation energy required and the second photon energy are slightly mismatched however and therefore in order for ET to occur a phonon is required. As the temperature is decreased so is the phonon population and the ET becomes less probable resulting in the PL intensity also being reduced.

Inspection of the 980nm excited 1532nm emission lifetime measurements (Figure 5.40) shows that as the erbium concentration increases the PL lifetime reduces for both fast and
slow-cooled samples. This is due to the energy transfer that takes place[18] including the ETU discussed above. Other studies have found similar results with PL quenching and a reduction in the lifetime being observed [20] [21].

Figure 5.40: The 980nm excited 1532nm PL lifetime as a function of erbium concentration for the fast-cooled (a) and slow-cooled (b) samples.

5.7 Conclusion

In these studies two sets of Er:YAG samples with 5 different erbium concentrations (2%, 10%, 20%, 30% and 50%) are examined. There are two sets of samples that differ as a result of the rate of quenching used during their synthesis. The fast-cooled sample has been shown to be monophase whilst the slow-cooled to consist of two-Er phases.

The optical properties of Er:YAG were investigated as a function of Er concentration, temperature and excitation power dependence. It is generally observed that the two types of sample have slightly different optical properties resulting from the bi-phasic nature of the Er concentration in the slow-cooled samples. This presents difficulties in clearly resolving the dominant mechanisms that govern the emission obtained from the samples
but clearly indicate that sample preparation is critical if consistent performance is to be achieved.

Under 980nm excitation upconversion emission at 545nm and 677nm was observed which in the bi-phasic samples is reduced and therefore may assist in improving the yield of 1532nm emission and also 3\(\mu\)m emission. This later emission may be strongly affected by the ETU process and therefore has important implications on the performance of Er:YAG 3\(\mu\)m lasers. In these devices an erbium concentration of 40-50\% is required to obtain strong ETU from the \(^{4}I_{13/2}\) level which then reduce the lifetime of the 1532nm emission. This is required in order to achieve a population inversion of the \(^{4}I_{11/2}\) from which the 3\(\mu\)m emission occurs.

For 1532nm emission the Er2\% monophasic sample displays the strongest emission and longest lifetime.

As a conclusion, mono-phasic and bi-phasic Er:YAG samples can be used as a potential material for obtaining emission. Careful choice of material, based on synthesis, may enable improved performance by either promoting or reducing ion-ion interactions. Equally, lack of control over the synthesis may lead to unforeseen deleterious effects due to phase separation.
References


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Chapter 5: Optical Characterisation of Erbium-doped Yttrium Aluminum Garnet Phosphor Materials


In this chapter, the temperature dependence of zinc nitride (Zn₃N₂) nanocrystal (NC) optical properties is investigated. The experimental studies undertaken include PL and PL lifetime measurements from 300K to ~9K. The zinc nitride material used in these experiments is considered a new class of semiconductor NC and as such little existing work has been reported. We present results from four samples of zinc nitride NC representing a range of NC diameters (8.9nm to 2.5nm). The samples were provided Sharp Laboratories of Europe and synthesized by Dr P.N. Taylor.

6.1 Introduction

The first Zn₃N₂ powder was synthesized by Juza and Hahn in 1940 [1]. Due to its optical and electrical properties Zinc nitride is a promising material for electronic, optoelectronic, photovoltaic and sensor application. These properties include n-type semiconductor
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behavior with a high electron mobility of \( \sim 100 \text{ cm}^2\text{V}^{-1}\text{s}^{-1} \) at room temperature, and a direct band gap of 1.23 eV for the thin films reported by Futsuhara et.al[2]

Even though excellent device performances have already been demonstrated using other semiconductor NCs, such as CdSe and PbS, there is a desire for alternative materials that extend existing or provide additional functionality and that do not contain toxic elements[3]. Zinc nitride materials have additional advantages such as their composition based on earth-abundant elements and a potentially low fabrication cost. During the past few years zinc nitride (Zn\(_3\)N\(_2\)) has attracted growing research interest due to the ability to modify it into p-type ZnO:N after oxidation at temperatures higher than 400 °C. This may lead to the development of cheap and reliable transparent optoelectronic devices[1].

Zn\(_3\)N\(_2\) is a group II nitride semiconductor and as a new material its physical properties are less understood. Within the limited existing literature there is variation in the reported electronic band gap, \( E_g \), between \( \sim 1 \text{ eV} \) and 3.2 eV and hence further research is needed[4] [5]. Furthermore its bandgap has been reported as being both direct or indirect nature, with the material deposition method and the underlying microstructure (i.e. thin films and hollow nano-balls) seeming to determine this[1]. Several methods for the fabrication of zinc nitride films have been used including direct chemical synthesis, reactive sputtering and chemical vapour deposition. The major challenge in producing a semiconducting zinc nitride material is the prevention of undesired oxidation of thin films. Variation of the synthesis has been used to change the optical properties of the NCs for example giving a wide range of emission wavelengths that extend from below 500nm to above 1100nm.[3]

Temperature dependence studies of Zn\(_3\)N\(_2\) from 300K to 15K have been reported by the Pai-Chun Wei group on cubic anti-bixbyite ‘microtips’, focusing on the effect of oxygen. PL measurements were performed to compare the different emission obtained from the optical bandgap with that of defect-related emission. Three samples were prepared, two as-grown samples and one sample exposed to the air for three days, they found that the PL emission for two as grown samples displayed a sharp infrared band-to-band emission peak at 1.34eV (925nm) with a full width at half maximum (FWHM) of \( \sim 100\text{meV} \). The PL at
~1.34eV was found to not follow the conventional trend of lowering in intensity at elevated temperature. The sample that was exposed to air only displayed ~0.85 eV (~1460nm) emission assigned to an oxygen-related defect[6].

Our collaborators as Sharp found out that the PL emission peak maximum is strongly dependent on NC size indicating that the emission in their samples is from the recombination of charge carriers within NC in the strong quantum confinement regime [3]. Due to the lack of previous work in zinc nitride NC systems we base our analysis of their optical properties on that previously undertaken for other NC materials such as Zn$_3$As$_2$, Zn$_3$P$_2$ or CdSe.

The quantum dot size dependence of the optical properties occurs when the thickness of the electronic layer (i.e. NC diameter) approaches the de Broglie wavelength of the electron in the quantum well structure. This is often related to the excitonic Bohr radius of excited electron-hole pairs within the NCs. When the radius of the quantum dot is smaller than the Bohr radius, it is known as the strong confinement regime. The broadness of the measured PL peak depends on the size distribution of the NCs within a given sample and gives rise to inhomogeneous broadening of the spectrum. Single NCs display a much narrower emission peak that (after repeated measurement) is governed by the homogeneous broadening resulting from electron-phonon interactions. Typically, the temperature dependence of the NC bandgap is closely related to the electron-phonon coupling and the emissive state. However, analysis is often complicated by the need to take into account traps that may be present due to NC ligands and defects as these often also display radiative recombination. To overcome such issues capped NCs have been developed in which a wider bandgap material encapsulates the core thus preventing surface defects from being important. This however is a major challenge for the zinc nitride system due to its large (0.978nm ± 0.01) lattice constant [7][8]. This has to date prevented a compatible capping material to be developed.
6.2 Temperature dependent optical studies of Zn$_3$N$_2$ Nanocrystals

Temperature dependence of Zn$_3$N$_2$ NC PL and PL lifetime is studied in the temperature range of 300K to 5K. Four different Zn$_3$N$_2$ NC samples are characterized representing a range of NC diameters ranging from 2.5nm to 8.9nm. The results are presented in order of reducing NC size to allow the discussion of stable NC thin films first as discussed below.

6.2.1 Optical properties of 8.9nm Zn$_3$N$_2$ NCs (Thin film)

6.2.1.1 Photoluminescence temperature dependence

The 300K PL spectrum is shown in Figure 6.1 and can be fitted using a sum of two Gaussians, Table 6.1. Doing so gives low and high energy peak positions of 1.462 eV (~850nm) and 1.642 eV (~755nm) both of which are situated in the NIR. The PL spectrum shows the typical inhomogeneous broadening due to the variable size of the NCs within the sample.

![Figure 6.1: The PL of 405nm excited 8.9nm diameter Zn$_3$N$_2$ NC film obtained at 300K. Also shown is the result of fitting the PL with a double-Gaussian.](image)
Table 6.1: Gaussian fitting parameters for the 8.9nm Zn$_3$N$_2$ NC PL at 300K.

<table>
<thead>
<tr>
<th>Gaussian fitting</th>
<th>Peak 1</th>
<th>Standard error (±)</th>
<th>Peak 2</th>
<th>Standard error (±)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Peak position (eV)</td>
<td>1.462 (848nm)</td>
<td>0.002</td>
<td>1.642 (755nm)</td>
<td>0.055</td>
</tr>
<tr>
<td>FWHM (meV)</td>
<td>227</td>
<td>6.61</td>
<td>345</td>
<td>51.7</td>
</tr>
</tbody>
</table>

Figure 6.2 shows the PL lifetime decay transient obtained from the Zn$_3$N$_2$ film at 300K. The decay displays periodic features on the ~0.3 µs timescale which are an artifact of the measurement system and do not originate from the sample. The measured system response is 12ns (see chapter 4). The PL decay can be fitted with the double exponential decay function giving the fit shown in the figure. This gives a slower lifetime ($\tau_1$) of 184ns ±2 and a shorter lifetime ($\tau_2$) of 55ns ±0.4.

Figure 6.2: The PL decay of 8.9nm diameter Zn$_3$N$_2$ NC at 300K.
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Figure 6.3: The PL spectra of the 8.9nm Zn$_3$N$_2$ NC for temperature dependence from the 300K to 5K

The PL spectra of the 8.9nm Zn$_3$N$_2$ NC film as a function of temperature are shown Figure 6.3. It can be observed that the PL intensity increases with reducing temperature and this is accompanied by a blue shift in the PL peak position. The PL peak’s movement to higher energy is due to a reduced electron-phonon interaction and also lattice contraction at low temperature. The PL spectrum at each temperature is fitted using a double Gaussian and the resulting peak positions plotted in Figure 6.4. This clearly shows that only the higher energy Gaussian peak position is temperature dependent with the peak undergoing a redshift of ~62meV from 1.642eV at 300K to 1.580eV at 5K. The lower energy peak remains insensitive to temperature at ~1.46eV.
Figure 6.4: The temperature dependence of the 8.9nm diameter Zn$_3$N$_2$ NCs peak position as obtained using double Gaussian fits. Also shown is the use of the Varshni and Einstein expressions fitted to the high energy peak position.

The Varshni equation is often used in describing the temperature dependence of semiconductor bandgaps [9]. The Varshni expression is given as:

$$E_g(T) = E_g(0) - \alpha \frac{T^2}{(T+\beta)}$$  \hspace{1cm} (Equation 6.1)

The term $E_g(T)$ represents the measured the bandgap (direct or indirect) and $E_g(0)$ is the bandgap when the temperature is ‘0K’ (often approximated by the value obtained at ~4K). The value of $\alpha$ is the temperature coefficient $dE_{PL}/dT$ whilst the parameter $\beta$ is related to the Debye temperature. The Debye temperature is used to predict the phonon contribution to the specific heat (heat capacity) in solid based on treating atomic lattice vibrations (heat) as phonons in a box. At high temperatures it is expected to have a linear dependence on the temperature whilst as the temperature is reduced the thermal expansion coefficient becomes nonlinear. The above graph shows a red shift, instead of blue shift, which is seen
in other nanocrystal systems such as PbS. The red shift indicates that the bandgap has become smaller at lower temperature and has previously been attributed to an acoustic phonon interaction dominance over optical phonons at low temperatures.

Also shown in Figure 6.4 is the use of the Varshni expression (Equation 6.1) to fit the temperature dependence of the high energy peak position. This produces a poor fit with an $R^2$ value of 0.89. The obtained values of $\alpha$ and $\beta$ have significant error due as their exists a mutual dependency between these parameters. Furthermore, the fitting parameters obtained using this expression, shown in Table 6.2, are not tightly defined.

Table 6.2: Fitting parameters use to fit the temperature dependence of the 8.9nm Zn$_3$N$_2$ NC PL peak position using the Varshni and Einstein temperature models.

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value</th>
<th>Expression</th>
</tr>
</thead>
<tbody>
<tr>
<td>$E_g(0)$</td>
<td>1.579 ± 0.0013</td>
<td>Varshni</td>
</tr>
<tr>
<td>$\alpha$(eV/K)</td>
<td>-124.4 ± 4.18X10$^7$</td>
<td>Varshni</td>
</tr>
<tr>
<td>$\beta$(K)</td>
<td>1.97X10$^8$ ± 6.65X10$^{13}$</td>
<td>Varshni</td>
</tr>
<tr>
<td>$R^2$</td>
<td>0.89</td>
<td>Varshni</td>
</tr>
<tr>
<td>$E_g(0)$</td>
<td>1.581± 6.71x10$^{-4}$</td>
<td>Einstein</td>
</tr>
<tr>
<td>$\kappa$</td>
<td>-0.72 ± 0.26</td>
<td>Einstein</td>
</tr>
<tr>
<td>$\Theta_e$</td>
<td>725.8± 86.1</td>
<td>Einstein</td>
</tr>
<tr>
<td>$R^2$</td>
<td>0.96</td>
<td>Einstein</td>
</tr>
</tbody>
</table>

Due to the poor fit obtained using the Varshni equation we also fitted the data with an empirical expression that incorporates the Einstein temperature [10]. The Einstein temperature model treats the atoms in the crystal as simple harmonic oscillators all having the same frequency and the expression is given as:
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\[ E_g(T) = E_g(0) - \kappa / (e^{\Theta_e/T} - 1) \]  
(Equation 6.2)

Again \( E_g(0) \) represents the material band gap at ‘0K’, whilst \( \kappa \) is an amplitude constant and the \( \Theta_e \) is the Einstein temperature. Using this expression yields an improved fit, also shown in Figure 6.4, with an \( R^2 \) value of \( \sim 0.96 \).

The values of the fitted parameters are given in Table 6.2 with \( \kappa \) being negative as required in order to produce a redshift in peak position with reducing temperature. The obtained value for \( \Theta_e \) is \( \sim 730K \) which is significantly higher than previously reported values for CdSe/ZnS sample which is 150K [10].

Study of the PL temperature dependence is continued by analysis of the PL FWHM parameters extracted from the double Gaussian fit. Upon cooling of the \( \text{Zn}_3\text{N}_2 \) film from 300K to 5K the FWHM reduces for both fitted peaks, narrowing from \( \sim 350\text{meV} \) to \( \sim 260\text{meV} \) for the high energy peak and from \( \sim 220\text{meV} \) to \( \sim 190\text{meV} \) for the lower energy peak, Figure 6.5. Such behavior is indicative of a reduction in exciton-photon interaction if emission occurs from a single state, or from the reduction in the Boltzmann distribution of electrons in closely separated states (with an accompanying redshift in the emission).
Figure 6.5: The FWHM of the double Gaussian fit to the 8.9nm Zn$_3$N$_2$ NC film PL temperature dependence.

The FWHM may be fitted using the following expression:

\[
FWHM = \Gamma_{inh} + \alpha T + \beta e^{-\frac{E_{1Q}}{k_B T}}
\]  

(Equation 6.3)

The right hand side of equation 6.3 is divided into three terms with the first term representing the inhomogeneous broadening at 0K. The second term accounts for the interaction of the exciton with acoustic phonons and the final term represents exciton LO-phonon interaction.

Using this expression reasonable fits could be obtained for both the high energy ($R^2 = 0.986$) and low energy ($R^2 = 0.975$) peaks FWHM. The values of all fitting parameters are listed in Table 6.3
Table 6.3: Fitting parameters obtained for the temperature dependence of the Zn$_3$N$_2$ NC PL FWHM.

<table>
<thead>
<tr>
<th></th>
<th>High energy</th>
<th>Low energy</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\Gamma_{inh}$ (meV)</td>
<td>256 ± 0.64</td>
<td>188.7 ± 0.68</td>
</tr>
<tr>
<td>$\alpha$ (meV/K)</td>
<td>0.06 ± 0.01</td>
<td>0.017 ± 0.012</td>
</tr>
<tr>
<td>$\beta$ (meV)</td>
<td>1322 ± 404</td>
<td>766.7 ± 342.6</td>
</tr>
<tr>
<td>$E_{LO}$ (meV)</td>
<td>68.1 ± 7.08</td>
<td>75.2 ± 11.71</td>
</tr>
</tbody>
</table>

The value obtained for $\alpha$ is 0.06 ± 0.01 meV and is related to the acoustic phonon interaction that is considered minimal in comparison to the optical-phonon interactions which present a $\beta$ value of 1322 ± 404 meV. From using this expression the energy of the optical phonons is obtained as 68 ± 7 meV. Comparing these values for those of CdSe NCs ($\Gamma_{inh} = 79 \pm 0.4$ meV, $\alpha = 20\pm3$ $\mu$eV/K, $\beta = 30\pm5$ meV and $E_{LO} = 24.5$ meV) indicates that the NCs have a higher optical phonon energy that dominates the temperature dependence [11]. A similar conclusion is obtained by comparison with alternative core/shell CdSe/ZnS studies (reporting $\Gamma_{inh} = 85.5 \pm 0.7$ meV, $\alpha = 71.9 \pm 9$ $\mu$eV/K, $\beta = 21\pm7$ meV and $E_{LO} = 24.5$ meV) [12].
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Figure 6.6: The integrated PL intensity graph for the low energy and high energy fitted peak as a function of temperature from 300K to 5K.

To further understand the nature of temperature dependent electron-phonon coupling in Zn$_3$N$_2$ NCs, the PL integrated intensity is studied. The PL integrated intensity, $I_{PL}(T)$ is obtained by integration of the PL spectrum at each temperature and plotted in Figure 6.6. The PL integrated intensity increases for both the low and high energy peak as the temperature is reduced from the 300K to $\sim$25K before remaining constant. This implies that at temperatures below 25K non-radiative relaxation is minimized thus the PL intensity is increased. The activation energy value can be calculated using the Arrhenius equation below by plotting the graph of PL integrated intensity versus $1/T$:

$$I(T) = \frac{I_o}{1+C \exp^{-Ea/kT}} \quad (Equation \ 6.4)$$

Where the $I_o$ is the integrated emission intensity at 0 K, C is a constant related to the ratio of the radiative to nonradiative lifetime, $Ea$ is the activation energy and K is the Boltzmann
constant. The value of the activation energy is \(~37\) meV which is roughly half the value of \(E_{LO}\).

Figure 6.7: The relative PL peak energy shift with respect to the 300K peak position.

Figure 6.7 re-plots the data in Figure 6.4 as the relative change in PL peak position for the two Gaussian fits from that obtained at 300K, using the expression given in Equation 6.5. The low energy peak position is approximately temperature independent over the entire temperature range which indicates that this emission could be related to optically active surface trap states. The high energy peak initially increases linearly (over the 300K – 150K range) before significantly reducing in gradient as the temperature is reduced further.

\[
\Delta E_{PL}(T) = \Delta E_{PL}(300K) - \Delta E_{PL}(T) \tag{Equation 6.5}
\]
6.2.1.2 Photoluminescence lifetime temperature dependence

Figure 6.8: The PL decay of the 8.9nm Zn$_3$N$_2$ thin film as a function of temperature from 300K to 5K.

The PL lifetime of the 8.9nm Zn$_3$N$_2$ sample is shown in Figure 6.8. Generally, as the temperature decreases from 300K the PL lifetime increases as non-radiative competing pathways are reduced. As the temperature is reduced below 75K there is a noticeable increase in the PL lifetime which then does not then undergo any further sizeable increase as the temperature is reduced to 5K. The radiative decay curves are fitted using a bi-exponential function that gives two lifetimes, $\tau_1$ and $\tau_2$, for each temperature given by

$$y = y_0 + A_1 e^{-t/\tau_1} + A_2 e^{-t/\tau_2}$$  \hspace{1cm} \text{(Equation 6.6)}$$

where $y_0$ is a non-zero offset and $A_1$ and $A_2$ are the amplitudes of each component. Occasionally (not for this sample and typically at low temperatures) when fitting using this expression the values obtained for $\tau_1$ and $\tau_2$ are found to be identical indicating single exponential decay behavior.
Figure 6.9: The extracted PL lifetimes of 8.9nm Zn$_3$N$_2$ NC thin film obtained as a function of temperature.

The values of $\tau_1$ and $\tau_2$ are plotted in Figure 6.9 and (tabulated in Table 6.4) indicating that the longer of the two lifetimes, $\tau_1$, displays a strong temperature dependence whilst the shorter, $\tau_2$, only changes slightly over the 300K to 5K range. This is characteristic of two level emission only one of which is due to direct band-to-band recombination and the other from a trap state (unaffected by changes in the NC quantum confinement). As seen in the analysis of the PL spectra we also observe dual-state emission with the low energy emission peak not displaying any strong temperature dependence. Due to the spectral overlap of these emitting states it was not possible to obtain further information from wavelength dependent PL lifetime studies. As such, though the low energy emission appears to be correlated with the temperature dependence of the faster lifetime, $\tau_2$, this cannot be positively confirmed and as discussed below may not be the case.

Assigning these lifetimes to processes is therefore complex but the faster component would be expected to be due to band-to-band emission, whereas the slow PL decay attributed to the recombination of the localized (trapped) carriers at the surface. Such traps would require energy in order to release the charge carrier thus this would become less probable as temperature is reduced hence the emission be delayed further. This does not however explain the reduction in lifetime observed for $\tau_1$ at very low temperatures (<25K).
Table 6.4: Values of $\tau_1$ and $\tau_2$ obtained from bi-exponential fitting of the temperature dependent PL transient decay.

<table>
<thead>
<tr>
<th>Temperature (K)</th>
<th>Lifetime $\tau_1$ (ns)</th>
<th>Lifetime error $\tau_1$ (ns)</th>
<th>Lifetime $\tau_2$ (ns)</th>
<th>Lifetime error $\tau_2$ (ns)</th>
</tr>
</thead>
<tbody>
<tr>
<td>300</td>
<td>184</td>
<td>2.0</td>
<td>55</td>
<td>0.4</td>
</tr>
<tr>
<td>275</td>
<td>198</td>
<td>2.2</td>
<td>62</td>
<td>0.5</td>
</tr>
<tr>
<td>250</td>
<td>220</td>
<td>2.4</td>
<td>70</td>
<td>0.6</td>
</tr>
<tr>
<td>225</td>
<td>222</td>
<td>2.6</td>
<td>71</td>
<td>0.6</td>
</tr>
<tr>
<td>200</td>
<td>222</td>
<td>2.5</td>
<td>70</td>
<td>0.7</td>
</tr>
<tr>
<td>175</td>
<td>230</td>
<td>2.3</td>
<td>71</td>
<td>0.8</td>
</tr>
<tr>
<td>150</td>
<td>250</td>
<td>2.2</td>
<td>76</td>
<td>0.7</td>
</tr>
<tr>
<td>125</td>
<td>263</td>
<td>2.4</td>
<td>76</td>
<td>0.7</td>
</tr>
<tr>
<td>100</td>
<td>301</td>
<td>2.5</td>
<td>82</td>
<td>0.8</td>
</tr>
<tr>
<td>75</td>
<td>338</td>
<td>3.0</td>
<td>78</td>
<td>0.8</td>
</tr>
<tr>
<td>50</td>
<td>405</td>
<td>4.3</td>
<td>88</td>
<td>1.0</td>
</tr>
<tr>
<td>25</td>
<td>426</td>
<td>4.1</td>
<td>80</td>
<td>0.8</td>
</tr>
<tr>
<td>15</td>
<td>430</td>
<td>4.2</td>
<td>82</td>
<td>1.0</td>
</tr>
<tr>
<td>10</td>
<td>410</td>
<td>3.8</td>
<td>78</td>
<td>0.8</td>
</tr>
<tr>
<td>7.5</td>
<td>399</td>
<td>3.6</td>
<td>74</td>
<td>0.7</td>
</tr>
<tr>
<td>5</td>
<td>392</td>
<td>4.5</td>
<td>77</td>
<td>0.9</td>
</tr>
</tbody>
</table>
Figure 6.10 plots the intensity of the fast and slow components of the normalized bi-exponential decay. It is seen that the slow component ($A_1$) dominates over the entire temperature range (300K-5K) indicating the efficient transfer of excited charge carriers into the emitting state responsible for this emission. Interestingly at very low temperatures (<25K) the faster process increases in relative intensity. This is indicative of the charge transfer process between these two levels (or into these levels from the initially excited state) being phonon assisted. This would typically be found if the faster process was from a state lower in energy ($k_B T = 2$ meV at 25K) than the slower emitting state. Considering this, along with the reduction in the slow lifetime in the low-temperature regime, suggests that it is the slower process that originates from band-to-band emission. A simple schematic of an energy level system that would provide the observed results is provided in Figure 6.11.
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Figure 6.11: A schematic energy level system that would display temperature dependent behavior similar to that observed experimentally from 8.9nm Zn$_3$N$_2$ NC films.

In this picture a band of closely spaced states is able to emit PL with temperature dependent charge transfer between them. It might be assumed that these represent the variation in NC diameter within the sample. Alternatively this set of levels may be replaced by single state whose energy decreases as temperature reduces. It is difficult to establish a mechanism that would give such behavior, for example quantum confinement typically increases with reducing temperature, though not impossible. A second deeper energy level is also able to emit but is sufficiently below the higher level to prevent significant electron transfer into the high state.

6.2.2 Optical properties of 3.8nm Zn$_3$N$_2$ NCs (Solution)

The optical properties of 3.8nm Zn$_3$N$_2$ NCs are described below. These samples are expected to display a higher degree of quantum confinement than those described above. Attempts to fabricate thin films for study proved unsuccessful due to the NC tendency to undergo oxidation within seconds if exposed to air. As a result sealed solutions were prepared within a N$_2$ glovebox and mounted into the cryostat. The solvent used
(octadecane) has a melting point of ~16 degC thus is expected to rapidly solidify upon cooling creating a frozen suspension of NCs.

**6.2.2.1 Photoluminescence temperature dependence**

The 300K PL spectrum is shown in Figure 6.12 and as for the 3.8nm NC samples can be fitted using double Gaussian expression. From this fit therefore, two peaks are obtained centered at 2.229 eV (~556nm) and 2.225 eV (~557nm) (Table 6.5). The sample displays the typical homogeneous broadening due to the NC size distribution within the sample. Comparison of the PL obtained from the smaller and larger NC samples clearly shows a strong blueshift occurs as the diameter is reduced in line with expectation.

![Figure 6.12: The PL of 405nm excited 3.8nm diameter Zn₃N₂ NC solution obtained at 300K. Also shown is the result of fitting the PL with a double-Gaussian.](image-url)
Table 6.5: Gaussian fitting parameters for the 3.8nm Zn$_3$N$_2$ NC PL at 300K.

<table>
<thead>
<tr>
<th>Gaussian fitting</th>
<th>Peak 1</th>
<th>Standard error (±)</th>
<th>Peak 2</th>
<th>Standard error (±)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Peak position (eV)</td>
<td>2.229</td>
<td>0.001</td>
<td>2.225</td>
<td>0.001</td>
</tr>
<tr>
<td>FWHM (meV)</td>
<td>467</td>
<td>6.7</td>
<td>287</td>
<td>4.3</td>
</tr>
</tbody>
</table>

Figure 6.13 shows the PL lifetime decay transient obtained from the Zn$_3$N$_2$ at 300K. The PL decay is fitted using a double exponential decay function giving the fit shown in the figure below. This gives a slower lifetime ($\tau_1$) of 156ns ± 1.1 and faster lifetime ($\tau_2$) of 50ns ±0.8 both of which are slightly faster than the equivalent lifetimes obtained from the larger NC sample at 300K. It should be noted however that the effective dielectric constant of the host medium will vary between the samples with the 3.8nm NC being capped with oleic acid ligands and in octadecene solvent. The 8.9nm NC thin film samples do not contain (significant) solvent and thus will have a slightly lower dielectric constant.

Figure 6.13: The PL decay of 3.8nm diameter Zn$_3$N$_2$ NC at 300K.
The PL spectra of the 3.8nm Zn$_3$N$_2$ NC solution as a function of temperature are shown in Figure 6.14. Each spectrum is fitted using a double Gaussian function from which the peak positions, FWHM and integrated intensity are obtained. Both fitted peaks display a blueshift in their peak position as the temperature is reduced and which is of a similar magnitude (~28 meV), Figure 6.14. Closer inspection of the data shows that the PL blueshift with reducing temperature occurs either side of the 25K and 150K temperature range. The observed blueshift is in contrast to that found for the 8.9nm NC sample and was found to be reproducible.
Figure 6.15: The temperature dependence of the 3.8nm diameter Zn$_3$N$_2$ NCs peak position as obtained using double Gaussian fits. Also shown is the use of the Varshni and Einstein expressions fitted to the high and low energy peak position.

Figure 6.15 also shows the attempts to fit the PL temperature dependence using the Varshni and Einstein model expressions described above. It can be seen that in general the Einstein model is able to better represent the observed behavior except for at very low temperature (<25K) where there is a significant increase in the rate of blue shift. The fitting parameters obtained for each model are presented in Table 6.6.
Table 6.6: Fitting parameters use to fit the temperature dependence of the 3.8nm Zn$_3$N$_2$ NC PL peak position using the Varshni and Einstein temperature models.

<table>
<thead>
<tr>
<th></th>
<th>Value for high energy</th>
<th>Value for low energy</th>
<th>Expression</th>
</tr>
</thead>
<tbody>
<tr>
<td>$E_g (0)$ (eV)</td>
<td>2.256 ± 0.001</td>
<td>2.252 ± 0.001</td>
<td>Varshni</td>
</tr>
<tr>
<td>$\alpha$ (eV/K)</td>
<td>816520</td>
<td>2.25 X10$^9$</td>
<td>Varshni</td>
</tr>
<tr>
<td>$\beta$</td>
<td>3.137 X 10$^{12}$</td>
<td>8.465 X 10$^{15}$</td>
<td>Varshni</td>
</tr>
<tr>
<td>$R^2$</td>
<td>0.91</td>
<td>0.91</td>
<td>Varshni</td>
</tr>
<tr>
<td>$E_g (0)$ (eV)</td>
<td>2.254 ± 0.001</td>
<td>2.250±0.0004</td>
<td>Einstein</td>
</tr>
<tr>
<td>$\kappa$ (eV)</td>
<td>0.244 ± 0.98</td>
<td>0.279 ± 0.074</td>
<td>Einstein</td>
</tr>
<tr>
<td>$\Theta_\varepsilon$ (K)</td>
<td>723.3 ± 104.9</td>
<td>746.9 ± 68.6</td>
<td>Einstein</td>
</tr>
<tr>
<td>$R^2$</td>
<td>0.95</td>
<td>0.98</td>
<td>Einstein</td>
</tr>
</tbody>
</table>

It is immediately clear from inspection of the obtained parameters that the Varshni model is not meaningful in this case, with their existing a significant dependency between the $\alpha$ and $\beta$ parameters yielding significant uncertainty in their values.

The Einstein model yield more realistic parameter values and better qualities of fit with $R^2$ being 0.952 and 0.979 for the high and lower energy peaks respectively. The value obtained for $\kappa$ is positive in this case (~0.24) due to the blueshift with reducing temperature (c.f. -0.72 for the 8.9nm NC samples). The validity of the model is supported by the value obtained for $\Theta_\varepsilon$ (~723 K) which is similar to that found for the 8.9nm samples (~726 K). Similar parameter values are found for the low energy peak temperature dependence (e.g $\Theta_\varepsilon$ ~747 K).

Further analysis of the PL temperature dependence is performed by considering the PL FWHM, shown in Figure 6.16, and fitting using equation 6.3. Inspection shows a reduction in the FWHM of both fitted peaks as temperature is reduced though the effect is not a
pronounced as seen for the 8.9nm NC sample. It is noted that in this case the absolute value of the FWHM is typically <100 meV than the equivalent observed in the case of the 8.9nm samples indicating a larger NC size distribution and inhomogeneous broadening.

Figure 6.16: The FWHM of the double Gaussian fit to the 3.8nm Zn$_3$N$_2$ NC solution PL temperature dependence.

The lack of a strong temperature dependence of the FWHM indicated that in this NC sample electron-phonon interactions are in general reduced compared to the 8.9nm NC sample. Inspection of the parameters obtained from the fits of the FWHM (Table 6.7) indicate that if anything the weaker acoustic phonon interaction (given by the $\alpha$ term) are increased slightly but the dominating optical phonon interactions are significantly reduced. Furthermore, the value of the optical phonon in these samples is approximately half that of the value found for the large 8.9nm NCs. This would then directly lead to a reduced temperature dependence of the FWHM.
Table 6.7: Fitting parameters obtained for the temperature dependence of the 3.8nm Zn$_3$N$_2$ NC PL FWHM.

<table>
<thead>
<tr>
<th></th>
<th>High energy</th>
<th>Low energy</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\Gamma_{inh}$ (meV)</td>
<td>275.04 ±0.006</td>
<td>460.94 ±5.59</td>
</tr>
<tr>
<td>$\alpha$ (meV/K)</td>
<td>0.168 ± 0.146</td>
<td>0.138 ±0.114</td>
</tr>
<tr>
<td>$\beta$ (meV)</td>
<td>-102.02 ±79.7</td>
<td>-152.62 ±108.94</td>
</tr>
<tr>
<td>$E_{LO}$ (meV)</td>
<td>23.76 ±9.82</td>
<td>37.76 ± 2.603</td>
</tr>
</tbody>
</table>

Figure 6.17: The integrated PL intensity graph for the low energy and high energy peak as a function of temperature between 300K to 8.8K.

To further examine the importance of any temperature dependent electron-phonon coupling in this Zn$_3$N$_2$ NC sample the integrated PL intensity is plotted in Figure 6.17. The first data point (300 K) is for the sample in solution form whereas at all lower temperatures the sample should be a frozen solution which would scatter the emitted PL. As a result the first data point should be excluded when looking for trends and hence the
initial reduction in intensity is an experimental artifact. It can be clearly seen that initially as temperature is reduced the intensity increases (typically expected as non-radiative pathways are ‘turned off’) until at ~200K the trend reverses. This again contrasts the behavior of the 8.9nm NC sample which displays a continuing increase in PL intensity as temperature is reduced. The behavior seen here is consistent with a reduced electron-photon interaction in these samples thus below 200 K other factors are dominating the PL temperature dependence. This is further confirmed by the shape of the intensity vs. 1/T plot in Figure 6.17 that does not follow the typical Arrhenius behavior.

6.2.2.2 Photoluminescence lifetime temperature dependence

![Image](image.png)

Figure 6.18: The decay curve of the 3.8nm Zn$_3$N$_2$ NC as a function of temperature from 300K to 8.8K

The PL transient decays of the 3.8nm Zn$_3$N$_2$ NCs are shown in Figure 6.18. As the temperature is reduced from 300K to 8.8K it is seen that the PL lifetime increases gradually. The transient decay curves are again fitted using a bi-exponential function that gives two lifetimes, $\tau_1$ and $\tau_2$, Figure 6.19.
Figure 6.19: The lifetime of 3.8nm Zn$_3$N$_2$ NC from the 300K to 8.8K as a function of temperature dependence.

As might be expected from the above results, the temperature dependence of the PL lifetime is not as strong for the 3.8nm NC sample compared to the 8.9nm sample. The faster lifetime increases slightly from ~50 ns to 70ns upon cooling from 300 K ~5K with only a slightly large increase seen in the low lifetime over this range (~30ns from 156 ns to 196ns). Again due to the spectral overlap of the two fitted peak to the PL no spectrally resolved PL lifetime measurements could be made. The values obtain for each of the bi-exponential fits at each temperature are given in Table 6.8.
Table 6.8: The lifetime and lifetime error for ($\tau_1$ and $\tau_2$) as the temperature decreases from 300K to 8.8K by 25K steps

<table>
<thead>
<tr>
<th>Temperature (K)</th>
<th>Lifetime $\tau_1$ (ns)</th>
<th>Lifetime error $\tau_1$ (ns)</th>
<th>Lifetime $\tau_2$ (ns)</th>
<th>Lifetime error $\tau_2$ (ns)</th>
</tr>
</thead>
<tbody>
<tr>
<td>300</td>
<td>156</td>
<td>1.1</td>
<td>50</td>
<td>0.80</td>
</tr>
<tr>
<td>275</td>
<td>162</td>
<td>1.2</td>
<td>53</td>
<td>0.71</td>
</tr>
<tr>
<td>250</td>
<td>164</td>
<td>1.1</td>
<td>51</td>
<td>1.00</td>
</tr>
<tr>
<td>225</td>
<td>167</td>
<td>1.2</td>
<td>48</td>
<td>0.82</td>
</tr>
<tr>
<td>200</td>
<td>174</td>
<td>1.4</td>
<td>53</td>
<td>0.97</td>
</tr>
<tr>
<td>175</td>
<td>176</td>
<td>1.2</td>
<td>51</td>
<td>0.91</td>
</tr>
<tr>
<td>150</td>
<td>178</td>
<td>1.2</td>
<td>55</td>
<td>1.24</td>
</tr>
<tr>
<td>125</td>
<td>184</td>
<td>1.5</td>
<td>59</td>
<td>1.20</td>
</tr>
<tr>
<td>100</td>
<td>188</td>
<td>1.7</td>
<td>63</td>
<td>1.33</td>
</tr>
<tr>
<td>75</td>
<td>190</td>
<td>1.9</td>
<td>67</td>
<td>1.52</td>
</tr>
<tr>
<td>50</td>
<td>193</td>
<td>1.8</td>
<td>63</td>
<td>1.25</td>
</tr>
<tr>
<td>25</td>
<td>196</td>
<td>1.7</td>
<td>69</td>
<td>1.83</td>
</tr>
<tr>
<td>15</td>
<td>195</td>
<td>2.0</td>
<td>68</td>
<td>1.72</td>
</tr>
<tr>
<td>10</td>
<td>200</td>
<td>2.5</td>
<td>75</td>
<td>1.94</td>
</tr>
<tr>
<td>8.8</td>
<td>196</td>
<td>2.2</td>
<td>70</td>
<td>1.98</td>
</tr>
</tbody>
</table>
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Figure 6.20: The temperature dependent normalised amplitude of the fast(A2) and slow(A1) component of the PL lifetime decay between 300K to 8.8K.

Study of the relative contributions of the two processes, (Figure 6.20) indicates that there is no strong competition between them and that they are not thermally linked. In practice this implies that if the higher energy level ‘feeds’ the lower then the process is not reversible through the capture of thermal energy. Figure 6.21 provides a schematic two-state system that reproduces the observed behavior of the 3.8nm NC samples.

Figure 6.21: A schematic energy level system that would display temperature dependent behavior similar to that observed experimentally from 3.8nm Zn3N2 NC solutions.
In this type of system to obtain a blue shift in the PL energy as temperature is reduced their cannot be a band of closely spaced levels (e.g. due to the inhomogeneous NC diameter population) with thermally enabled energy transfer between them. Instead each level must remain ‘isolated’ which for a solution is feasible as NC to NC charge transfer is likely to be improbable. The isolated level may then feed a lower energy level associated with a trap state on the same NC but the reverse process does not appear to occur as discussed above.

**6.2.3 Optical properties of 2.7nm Zn$_3$N$_2$ NCs (Solution)**

Measurement of the optical properties of 2.7nm Zn$_3$N$_2$ NCs were also undertaken and are described below. As for the 3.8nm NC sample the measurements were undertaken using frozen solutions due to the oxidation of thin film samples.

**6.2.3.1 Photoluminescence temperature dependence**

The 300K PL spectrum is shown in Figure 6.22 and can be fitted using the double Gaussian expression ($R^2 = 0.998$) in contrast to a single Gaussian expression that does not provide the best fit ($R^2 = 0.956$). The peak energy of the two fitted Gaussians are 2.316 eV and 2.516 eV (Table 6.9) thus presenting a further blueshift of the PL in comparison to the 3.8nm NC sample. The PL spectrum shows significant inhomogenous broadening with a long low-energy tail indicating a dispersion of NC diameters within the sample. It should be noted however that for such small NC diameters as small variation in size (e.g. 5%) leads to a much greater PL emission width than would be the case for the larger diameter NCs due to the non-linear nature of quantum confinement on NC diameter.
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Figure 6.22: The PL of 405nm excited 2.7nm diameter Zn$_3$N$_2$ NC solution obtained at 300K. Also shown is the result of fitting the PL with a double-Gaussian.

Table 6.9: Gaussian fitting parameters for the 2.7nm Zn$_3$N$_2$ NC PL at 300K.

<table>
<thead>
<tr>
<th>Gaussian fitting</th>
<th>Peak 1</th>
<th>Standard error (±)</th>
<th>Peak 2</th>
<th>Standard error (±)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Peak position</td>
<td>2.516</td>
<td>0.002</td>
<td>2.316</td>
<td>0.023</td>
</tr>
<tr>
<td>FWHM (meV)</td>
<td>239</td>
<td>6</td>
<td>379</td>
<td>18</td>
</tr>
</tbody>
</table>

Figure 6.23 shows the PL transient decay obtained from the Zn$_3$N$_2$ solution at 300K. The PL decay is fitted with the double exponential decay function giving the fit shown in the figure below. The value of the fast lifetime ($\tau_1$) is 364ns ±13.5 whilst the slow lifetime ($\tau_2$) is 192ns ±5.8 and the system response measured is 12ns. In comparison with the 3.8nm and 8.9nm NC samples these lifetimes are much longer.
Figure 6.23: The PL decay of 2.7nm diameter Zn$_3$N$_2$ NC at 300K.
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Figure 6.24: The PL spectra of the 2.7nm Zn$_3$N$_2$ sample for temperature dependence from the 300K to 8.8K

The temperature dependent PL spectra of the 2.7nm Zn$_3$N$_2$ NC sample are shown in Figure 6.24. Each spectrum is fitted using the same double Gaussian expression as previously used yielding peaks at 2.316 eV (~535 nm) and 2.516 eV (~493 nm) at 300K. Upon cooling down to 8.8K both of these peaks display a small redshifts of ~14meV for the low energy peak and of ~10meV for the higher energy. This behavior is more akin to that seen for the larger 8.9nm NC sample which also displayed a small redshift with reducing temperature.
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Optical Properties

Figure 6.25: The temperature dependence of the 2.7nm diameter Zn$_3$N$_2$ NCs peak position as obtained using double Gaussian fits. Also shown is the use of the Varshni and Einstein expressions fitted to the high energy peak position.

The analysis of the 2.7nm Zn$_3$N$_2$ NC PL temperature dependence is continued by fitting the peak position temperature dependence using the Varshni and Einstein expressions, Figure 6.25 and Table 6.10. Fitting using the first of these is not possible due to the weak temperature dependence observed and its near linear behavior. This results in the fitting parameters ($\alpha$ and $\beta$) displaying uncertainties of greater than 100%. Turning to the Einstein model yields parameter values of $\kappa$ (-55 meV and -17 meV) and $\Theta$ (263 K and 144 K) which are significantly smaller than obtained for the other samples studied but nonetheless do provide a fit to the experimentally derived data.
Table 6.10: Fitting parameters use to fit the temperature dependence of the 2.7nm 
Zn$_3$N$_2$ NC PL peak position using the Varshni and Einstein temperature models.

<table>
<thead>
<tr>
<th></th>
<th>Value for high energy</th>
<th>Value for low energy</th>
<th>Expression</th>
</tr>
</thead>
<tbody>
<tr>
<td>$E_g(0)$ (eV)</td>
<td>2.505 ± 0.005</td>
<td>2.302 ± 0.003</td>
<td>Varshni</td>
</tr>
<tr>
<td>$\alpha$ (meV/K)</td>
<td>-0.236 ± 0.331</td>
<td>-0.12 ± 0.062</td>
<td>Varshni</td>
</tr>
<tr>
<td>$\beta$ (K)</td>
<td>239 ± 720</td>
<td>85 ± 183</td>
<td>Varshni</td>
</tr>
<tr>
<td>$R^2$</td>
<td>0.59</td>
<td>0.76</td>
<td>Varshni</td>
</tr>
<tr>
<td>$E_g(0)$ (eV)</td>
<td>2.505 ± 0.005</td>
<td>2.302 ± 0.003</td>
<td>Einstein</td>
</tr>
<tr>
<td>$\kappa$ (eV)</td>
<td>-0.055 ± 0.078</td>
<td>-0.017 ± 0.021</td>
<td>Einstein</td>
</tr>
<tr>
<td>$\Theta_e$ (K)</td>
<td>263.07 ± 242.71</td>
<td>144.48 ± 142.52</td>
<td>Einstein</td>
</tr>
<tr>
<td>$R^2$</td>
<td>0.60</td>
<td>0.76</td>
<td>Einstein</td>
</tr>
</tbody>
</table>

Figure 6.26: The FWHM of the double Gaussian fit to the 2.7nm Zn$_3$N$_2$ NC solution PL 
temperature dependence.
Analysis of the PL FWHM temperature dependence can be undertaken as before using the data obtained from the Gaussian fits and plotted in Figure 6.26. At 300K it is noted that the FWHM for both the high and low energy peaks is at a minimum (≈38 meV and ≈24 meV respectively). Upon cooling to 275 K these values increase sharply which may be due to the sample freezing as discussed further below. The FWHM then reduces as the temperature is lowered with a ‘step’ being observed at ≈200K. The presence of this step-like feature is also found independently in the PL peak position behavior shown in Figure 6.25. Fitting the FWHM of the Gaussian peak’s temperature dependence yields the parameters provided in Table 6.11. This shows the large intrinsic inhomogeneous broadening present in the sample at low temperature in addition to providing a value for the optical phonon energy (≈28 meV) for this sample. This value is again reduced with respect to the other samples studied (c.f. ≈68 and 75 meV for the 8.9nm NCs and ≈24 and 38 meV for the 3.8nm samples). Assigning this reduction to an increase quantum confinement is however not consistent with the bulk definition of the optical phonon and perhaps points to another origin of the observed emission than NC PL.

Table 6.11: Fitting parameters obtained for the temperature dependence of the Zn$_3$N$_2$ NC PL FWHM.

<table>
<thead>
<tr>
<th></th>
<th>High energy(eV)</th>
<th>Low energy(eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>$I_{inh}$(meV)</td>
<td>396.53± 5.49</td>
<td>251.2 ±7.41</td>
</tr>
<tr>
<td>$\alpha$(meV/K)</td>
<td>-0.142 ± 0.015</td>
<td>-1.45 ±0.02</td>
</tr>
<tr>
<td>$\beta$(meV)</td>
<td>347 ±0.08</td>
<td>415± 0.12</td>
</tr>
<tr>
<td>$E_{LO}$(meV)</td>
<td>27.9± 6.14</td>
<td>29.8± 8.21</td>
</tr>
</tbody>
</table>
Figure 6.27: The integrated PL intensity graph for the low energy and high energy peak as a function of 1/Temperature between 300K to 8.8K.

Studying the PL intensity as a function of temperature shows a small increase in intensity as the temperature is reduced, Figure 6.27. Again the 300 K data point should be treated as anomalous as it is from the liquid sample. This then leads to typical Arrhenius type behavior for the PL intensity which can be fitted yielding an activation energy of 4.8meV for high energy and 13.2meV for low energy peak.
6.2.3.2 Photoluminescence lifetime temperature dependence

Figure 6.28: The decay curve of the Zn$_3$N$_2$ 2.7nm sample as a function of temperature from 300K to 8.8K

The PL transient decay of the 2.7 nm Zn$_3$N$_2$ NCs are shown in the Figure 6.28 and fitted as previously described using a bi-exponential function yield two characteristic lifetimes (Table 6.12). As the temperature is reduced from 300K to 250K an initial decrease in both lifetimes is observed, Figure 6.29. With further cooling this behavior is reversed leading to lifetimes that are approaching the microsecond regime (0.25 $\mu$s and 0.55 $\mu$s).
Figure 6.29: The lifetime of 2.7nm Zn$_3$N$_2$ NC solution from the 300K to 8.8K as a function of temperature dependence
Table 6.12: The lifetime and lifetime error for ($\tau_1$ and $\tau_2$) as the temperature decreases from 300K to 5K by 25K steps

<table>
<thead>
<tr>
<th>Temperature (K)</th>
<th>Lifetime $\tau_1$ (ns)</th>
<th>Lifetime error $\tau_1$ (ns)</th>
<th>Lifetime $\tau_2$ (ns)</th>
<th>Lifetime error $\tau_2$ (ns)</th>
</tr>
</thead>
<tbody>
<tr>
<td>300</td>
<td>364</td>
<td>13.5</td>
<td>192</td>
<td>5.8</td>
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<tr>
<td>275</td>
<td>353</td>
<td>8.4</td>
<td>164</td>
<td>3.2</td>
</tr>
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<td>335</td>
<td>6.1</td>
<td>150</td>
<td>4.1</td>
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<td>225</td>
<td>343</td>
<td>6.6</td>
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<td>378</td>
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<td>380</td>
<td>9.9</td>
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<td>413</td>
<td>14.8</td>
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<td>208</td>
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<td>500</td>
<td>29.2</td>
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<td>5.2</td>
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<td>50</td>
<td>527</td>
<td>37.2</td>
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<td>532</td>
<td>36.2</td>
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<td>5.5</td>
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<td>15</td>
<td>547</td>
<td>41.4</td>
<td>255</td>
<td>5.5</td>
</tr>
<tr>
<td>10</td>
<td>557</td>
<td>40.3</td>
<td>254</td>
<td>5.4</td>
</tr>
<tr>
<td>8.8</td>
<td>545</td>
<td>36</td>
<td>252</td>
<td>5.4</td>
</tr>
</tbody>
</table>
Figure 6.30: The temperature dependent normalized amplitude of the fast ($A_1$) and slow ($A_2$) component of the PL lifetime decay between 300K to 8.8K.

Figure 6.30 shows the relative contribution of the fast and slow recombination processes to the PL transient decay. It can be seen that for temperature between ~175 K and 300 K there is strong competition between the processes as they contribute approximately equally to the observed emission. As the temperature is reduced below ~175 K the fast process starts to dominate indicating a phonon assisted coupling of the two emitting states. This is similar in nature to the behavior of the 8.9nm NC sample. As such, and taking the experimental data discussed above into account the equivalent energy level model for this sample shown in Figure 6.31 can be proposed.
Figure 6.31: A schematic energy level system that would display temperature dependent behavior similar to that observed experimentally from 2.7nm Zn$_3$N$_2$ NC films.

6.2.4 Optical properties of 2.5nm Zn$_3$N$_2$ NCs (Solution)

The measurement of a final set of Zn$_3$N$_2$ NCs with a smaller average diameter (2.5nm) was also undertaken and is described below. As for the 3.8nm and 2.7nm NC samples the measurements were undertaken using frozen solutions due to the oxidation of thin film samples.

6.2.4.1 Photoluminescence temperature dependence

The 300K PL spectrum is shown in Figure 6.32 with the high energy tail curtailed due to the proximity of the excitation wavelength (405 nm, ~3 eV) and the need to protect the detector from it. Again the use of a double Gaussian fit (R$^2$ = 0.999) is required in order to ensure a reasonable fit to the recorded spectrum. The peak position of the PL spectrum is further shifted from that of the 2.5nm NC sample with the two fitted Gaussians having their maxima at 2.558 eV (~484.75nm) and 2.729 eV (~454.38m) (Table 6.13).
Figure 6.32: The PL of 454nm excited 2.5nm diameter Zn$_3$N$_2$ NC solution obtained at 300K. Also shown is the result of fitting the PL with a double-Gaussian.

Table 6.13: Gaussian fitting parameters for the 2.5nm Zn$_3$N$_2$ NC PL at 300K.

<table>
<thead>
<tr>
<th>Gaussian fitting</th>
<th>Peak 1</th>
<th>Standard error (±)</th>
<th>Peak 2</th>
<th>Standard error (±)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Peak position (eV)</td>
<td>2.729</td>
<td>0.001</td>
<td>2.558</td>
<td>0.031</td>
</tr>
<tr>
<td>FWHM (meV)</td>
<td>349</td>
<td>4.56</td>
<td>496</td>
<td>15.23</td>
</tr>
</tbody>
</table>

Figure 6.33 shows the PL decay transient obtained from the Zn$_3$N$_2$ solution at 300K. The PL decay can be fitted with the single exponential decay function giving the fit shown in the figure. The value of the lifetime is 14.95 ns±0.1 which is similar to the system response (12ns).
Figure 6.33: The PL decay of 2.5nm diameter Zn$_3$N$_2$ NC at 300K.
Figure 6.34: The PL spectra of the 2.5nm Zn$_3$N$_2$ NC solution for temperature dependence from the 300K to 8.8K

The PL spectra of the 2.5nm Zn$_3$N$_2$ NC as a function of temperature are shown in Figure 6.34. Inspection shows that there is no shift in the position of the PL maximum with temperature. The feature at \(\sim2.05\) eV (\(\sim605\) nm) could not be identified but becomes prominent as temperature is reduced. The width of the PL spectra is similar to that expected from inhomogeneous broadening and again the use of two Gaussian functions is required in order to fit them. However, due to the incomplete nature of the spectra resulting from the excitation wavelength used a detailed analysis as performed above is not justified. For completeness attempts to do this resulted in the extraction of parameters with high uncertainty in most cases.
Figure 6.35: The integrated PL intensity graph as a function of temperature between 300K to 5K.

Figure 6.35 shows the integrated PL integrated intensity as a function of temperature. The behavior exhibited is complex and not what would be expected if the PL origin was simply due to exciton recombination within the NC. It does however display some of the characteristics found in the 3.8nm NC diameter sample with an initial increase in intensity as the temperature is lowered to ~200K. The intensity then reduces again as the temperature is reduced to ~4K. No attempt to fit this behavior with an Arrhenius type express have been made as it is clear that no simple activation energy can result.
6.2.4.2 Photoluminescence lifetime temperature dependence

Figure 6.36: The decay curve of the 2.5nm Zn$_3$N$_2$ NC solution sample as a function of temperature from 300K to 8.8K

The PL transient decays of the 2.5nm Zn$_3$N$_2$ NC sample are shown in Figure 6.36 as temperature is reduced from 300K to 8K. It can be seen that the decay rate increased (lifetime reduces) as the temperature is reduced which is not typical behavior. A single exponential function was fitted to each decay transient (Table 6.14) and the resulting PL lifetime plotted in Figure 6.37. It can be seen that the lifetime eventually appears to saturate at ~13ns at low temperatures though in practice it is likely to be faster as the measurements are limited by the system response.
Figure 6.37: The lifetime of 2.5nm Zn$_3$N$_2$ NC at the 300K to 8.8K as a function of temperature dependence.
Table 6.14: The lifetime and lifetime error for ($\tau_1$ and $\tau_2$) as the temperature decreases from 300K to 8.8K by 25K steps

<table>
<thead>
<tr>
<th>Temperature (K)</th>
<th>Lifetime $\tau_1$ (ns)</th>
<th>Lifetime error $\tau_1$ (ns)</th>
</tr>
</thead>
<tbody>
<tr>
<td>300</td>
<td>14.95</td>
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</tr>
<tr>
<td>275</td>
<td>14.83</td>
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</tr>
<tr>
<td>250</td>
<td>14.25</td>
<td>0.09</td>
</tr>
<tr>
<td>225</td>
<td>14.17</td>
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</tr>
<tr>
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</tr>
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</tr>
<tr>
<td>8.8</td>
<td>13.00</td>
<td>0.09</td>
</tr>
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</table>
Based on the above data it is highly probable that the observed emission obtained from the 2.5nm NC sample originates from the organic ligands rather than the NCs themselves. This is in line with the fast radiative decay (limited by the system response) observed which is characteristic of \( \pi-\pi^* \) transitions in organic materials and is orders of magnitude faster than the PL observed from the other NC samples.

**Comparison of lifetimes for three different samples**

![Graphs showing PL lifetimes vs. Temperature for different sizes of Zn\(_3\)N\(_2\) NC samples](image)

**Figure 6.38a and b**: The PL lifetimes of 8.9nm, 3.8nm and 2.7nm Zn\(_3\)N\(_2\) NC samples obtained from bi-exponential decay fitting.

**Figure 6.38a and b** provides a comparison of the PL lifetimes obtained from fitting the PL decay transients of the NC samples. The 2.5nm sample is not included as this displays emission characteristic of the organic ligands. It can be observed that there is no general trend of increasing PL lifetime with NC diameter as might be expected (due to reduced charge confinement). Some similarities between the lifetime temperature dependence can be observed, for example the longer lifetime of the 8.9nm and 2.7 nm samples and the shorter lifetime of the 8.9nm and 3.8nm samples. However, there is no general temperature dependent trend that all samples follow.
6.3 Discussion

The results presented above represent the first detailed characterization of Zn$_3$N$_2$ NCs. It is clear that their optical properties and temperature dependence are complex and can vary significantly from sample to sample. Setting aside the 2.5nm NC sample (for the reasons outlined above) it is observed that there exists a blueshift in the PL as the NC diameter is reduced, Figure 6.39. The effect of NC diameter on the electronic bandgap is typically expressed using the Brus equation[13]

\[ E = E_g + \frac{\hbar^2 n^2}{2R^2} \left[ \frac{1}{m_e} + \frac{1}{m_h} \right] \]  

(Equation 6.7)

Where, the $E_g$ is the bandgap energy, $\hbar$ is Planck's constant, $R$ is the NC radius, $m_e$ is the electron effective mass and the $m_h$ is the hole effective mass. As can be seen the three data points available from this study show approximately nonlinear dependence on NC diameter (radius) as expected $1/R^2$ dependence from equation 6.7

![Figure 6.39: 300K PL peak position as a function of average Zn$_3$N$_2$ NC radius.](image-url)
Comparison of the studied parameters (PL peak position, PL FWHM and PL lifetime) as a function of temperature indicates that the 8.9nm and 2.7nm samples display very similar dependence on temperature. For example they both show a redshift and narrowing of their PL with reducing temperature and increasing PL lifetimes for each component of similar magnitude. This suggests that the emission in each of these cases originates from a similar process. The 3.8nm NC sample displays quite different behavior including a blueshift in PL and limited reduction in width as the temperature is reduced. This sample also displays a much smaller increase in PL lifetime as the temperature is reduced with both lifetimes being significantly shorter than for the other samples. Possible explanations for this deviation include that the sample has partially oxidized leading to the modification of the bandgap (broadening) and quenching of NC emission. Recalling that the excitation energy of the 405nm laser is ~3.06eV initially excited electrons are well above the lowest excited state and thus may become trapped in oxidized sites above the lowest exciton energy level during relaxation. These traps could act as higher energy emitting centers themselves and therefore as the temperature is reduced thermalisation out of these traps would be reduced yielding a blue shift in the PL spectrum. This would also have the effect of increasing the peak energy of the PL at 300K providing the apparent linear dependence of NC PL with diameter in Figure 6.39. Additionally, emission these traps would have to compete against thermalisation resulting in the faster PL lifetimes observed.

It is worth noting that the reported temperature dependence of Zn$_{3}$N$_{2}$ PL does not always follow the typical behavior of common semiconductors and shows wide variation. For example, PL studies of Zn$_{3}$N$_{2}$ thin film samples have been reported showing a decrease in PL intensity as the temperature is reduced from 300K to 150 K before increasing again as the temperature is further reduced to 15K[6]. In these samples the PL intensity at 300K is higher than that at 15 K. Such anomalous PL behavior was found in all as-grown Zn$_{3}$N$_{2}$ samples, although the intensity evolution with temperature is not always the same. Power dependent PL measurements, found a linear behavior between excitation power and PL intensity which was used as evidence to assign the PL (peaking at ~1.34eV) to direct band-to-band radiative recombination.
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In contrast to the above the 8.9nm Zn$_3$N$_2$ NC thin film and 2.7nm NC frozen solution displayed typical semiconductor behavior with the PL intensity is increasing as the temperature is reduced from 300K to 8K. The behavior of the 3.8nm sample deviated from this behavior with the PL intensity increasing to a maximum at 200K as temperature is reduced before starting to quench. This again indicates a variation of the emission process in the 3.8nm NC sample and is in line with trap-state emission.

Comparison of the fitting parameters obtained for each NC sample (e.g. from the Bose-Einstein and FWHM fitting) shows no clear trend or agreement. For example the longitudinal optical phonon energies, $E_{LO}$, obtained from fitting the FWHM (~70 meV, 23 meV and 28 meV for the 8.9nm, 3.8nm and 2.7 nm NC respectively) should in principle be the same as they are not found to vary with NC diameter (i.e. they show no confinement effect as they relate to local atomic bonding). However, a clear reduction in $E_{LO}$ is found as the NC diameter is reduced which is difficult to explain in any conventional model. This along with the variation in behavior found between samples indicates that in the samples studied the presence of impurities and varying degrees of oxidation are providing alternative radiative and non-radiative excitonic recombination pathways thus detracting from the current usefulness of these materials.

6.4 Conclusion

In this work, we have studied the temperature dependence of zinc nitride NC optical properties based on samples with different average NC diameters (8.9nm to 2.5nm) We have explored the temperature range from 300K to 8.8K presenting the first studies that measured the PL and PL lifetimes. As a result there is little pre-existing literature to compare our results with and no specific theoretical model of Zn$_3$N$_2$ NC electronic properties. The most important results from the studies undertaken can be summarized as:

- The PL displays a shifting to higher energies as the size of the NC is increased as expected due to increased quantum confinement. Setting aside the smallest average
diameter samples the dependence of the PL emission energy on NC diameter is approximated by the Brus equation.

- The Zn$_3$N$_2$ NCs are highly sensitive to oxidation sealed frozen solutions were used to the majority of measurements.

- Two of the samples (8.9nm and 2.7nm diameter NCs) display a temperature dependence of the optical properties in line that seen in other specific semiconductor NCs such as PbS. The other samples displayed anomalous behavior that could be due to ligand emission (2.5nm NC sample) or higher energy trap states caused by localized oxidation (3.8nm NCs).

- Phenomenological models (e.g. Varshni, Bose-Einstein etc) have a limited success in describing the observed behavior though there is a lack of consistency in the resulting parameters obtains (e.g. the value of $E_{LO}$).

Further work on these systems is required in order to fully understand their properties but the issue of NC stability is difficult to address. The synthesis of core/shell structures (to protect against oxidation) has not been possible due to the very large lattice constant of Zn$_3$N$_2$ meaning there are few materials that can be successfully used as a shell.
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References


In this chapter, the temperature dependence of manganese-doped cadmium selenide (CdMnSe) nanocrystals (NCs) optical properties are investigated. The experimental studies undertaken include PL and PL lifetime measurements from 300K to ~5K. We present results from three samples of CdMnSe NC representing a range of NC types (core only, core-shell and ‘dot-in-rod’). The results reported are based on our understanding of the temperature dependence of this system and have compared with the reports of other researchers on similar systems.
7.1 Introduction

Semiconductor NC materials have attracted attention in recent years generally for possible applications in optoelectronic devices that utilize their fascinating optical and electronic properties. These NCs are of particular interest as their optical emission can be tuned to cover the whole visible range by changing the particle size [1]. CdSe is in a group II–VI which consists of an element in column II and column VI in the periodic table. There are two types of crystalline forms that exist for the CdSe: wurtzite (hexagonal) and rock salt (cubic). The cubic structure can convert to the hexagonal structure via heating to 350-400°C [2]. The group II-VI semiconductor quantum dots have been applied to devices that include solar cells, tunable LEDs and lasers [3][4][5]. Other applications include biological labelling[6] and within photodetectors[7]. Despite their apparent advantages versus organic dyes (e.g. improved stability and efficiency) the presence of cadmium is a concern due to the element’s toxicity[5].

We use similar characterization methods as described in chapter 6 to investigate the effect of Mn-doping and NC type (core, core-shell etc) on the optical properties. The temperature dependence of CdSe bandgap has been reported by the Dai group[1]. With cooling from 300K the bandgap increases affected by the typical lattice contraction and electron–phonon coupling that are observed in bulk semiconductors [3].

Varshni fitting of the CdSe NC bandgap has been reported yielding a similar value of $E_{LO}$ for the bulk crystal of $\sim$23–27meV [8]. Debye and Einstein temperatures have also been obtained 195K ± 70K and 184K ±30K respectively [3] by fitting the bandgap temperature dependence based on the PL peak position.

The CdSe NCs may be capped with another wider bandgap materials (such as CdS) to remove the surface defects. Successful passivation is generally evidenced by an improvement in PL quantum yield. Furthermore, due to the advances in synthetic NC chemistry control over size, shape and composition is now possible. It is also possible to perform surface ligand exchange to strengthen the interaction of the NCs with surfaces and
also to perform doping of the NC with impurity atoms to control the carrier type and concentration. These improvements are integrated into the design of new NC electronic materials with improved properties [9].

### 7.2 Temperature dependence optical studies of CdMnSe/CdS

Temperature dependence of CdMnSe/CdS (core/shell) NC PL and PL lifetime is studied in the temperature range of 300K to 5K. Three different CdMnSe NC samples are characterized representing of NC diameters ranging from 3.8nm to 12nm measurement for this experiment and the sample preparation are described in chapter 4. The results are discussed by following sample 1(core only), sample 2(core-shell) and sample 3(dot-in-rod). Samples were prepared by our collaborators, the Green group, at the King's College London with synthesis performed by Dr Simon Fairclough.
7.2.1 Sample 1 CdMnSe (Core only)

7.2.1.1 PL measurement

The 300K PL spectrum is shown in Figure 7.1 and can be approximated using a single Gaussian ($R^2 = 0.984$, Table 7.1) peaking at $\sim 2.113$ eV ($\sim 587$ nm). The spectrum shows the inhomogeneous broadening due to the variable size of the NCs within the sample.

Figure 7.1: The PL of for CdMnSe NC sample (core only) obtained at 300K. Also shown is the result of fitting the spectrum with single Gaussian curve.

Table 7.1: Gaussian fitting parameters for the CdMnSe NC (core only) at (300K).

<table>
<thead>
<tr>
<th>Gaussian fitting</th>
<th>Peak (core only)</th>
<th>Standard error ($)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Peak position (eV)</td>
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</tr>
<tr>
<td>FWHM (meV)</td>
<td>61.1</td>
<td>0.67</td>
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</tbody>
</table>
Figure 7.2 shows the PL lifetime decay transient for CdMnSe NC (core only) at 300K. The decay is fitted with the double exponential decay (as in equation 6.6). There are two lifetimes, one ‘fast’ ($\tau_1$) and one ‘slow’ ($\tau_2$), suggesting that radiative recombination may originate from two processes that could be from the band-to-band emission or related to trap. The value of the slower lifetime ($\tau_2$) is 23.6 ns ± 2.3 whilst the faster lifetime ($\tau_1$) is 13.4ns ± 3.3. The system response was measured to be ~12ns as described in chapter 4. The features seen in the PL decay between 100ns and 400nm are experimental artifacts that could not be removed.

![Figure 7.2: The PL decay of CdMnSe NC sample (core only) at 300K](image-url)
Figure 7.3: The PL spectra of the CdMnSe NC sample (core only) obtained as a function of temperature between 300K to 5K

The PL spectra of the CdMnSe NC (core only) obtained as a function of temperature between 300K and 5K are shown in Figure 7.3. The PL intensity is seen to increase as temperature is reduced from 300K to 150K before it starts to reduce as temperature is further decreased to 5K. The increase in intensity is indicative of an initial reduction in competing non-radiative recombination pathways. The subsequent reduction in intensity below 150K infers that the emission may be phonon assisted which is eventually frozen out at very low temperatures. All the spectra continue to show inhomogenous broadening due to variation of NCs sizes though the spectra do narrow as temperature is reduced. This again indicates a strong exciton–phonon coupling that reduces a the temperature is reduced[1].

Fitting each spectrum using a single Gaussian curve enables the temperature dependence of the PL peak to be obtained, Figure 7.4. This shows a blueshift in energy between 300K
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and 5K of 23.65meV with the presence of the characteristic ‘hook’ at very low temperatures as emission moves from singlet to triplet state exciton emission[10].

Figure 7.4: The PL peak of CdMnSe NC sample (core only) from 300K to 5K of temperature dependence for Varshni, Einstein temperature and O'Donell models.

Three different models have been used in the literature to fit the PL peak position as a function of temperature as previously discussed: the Varshni, Einstein and O'Donell expressions (see chapter 3). Each of these was used to fit the data in Figure 7.4 with the obtained fitting parameters presented in Table 7.2.
Table 7.2: Fitting parameters obtained from fitting the temperature dependence of the core CdMnSe PL peak position using the Varshni, Einstein temperature and O'Donell models.

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value</th>
<th>Expression</th>
</tr>
</thead>
<tbody>
<tr>
<td>$E_g (0)$</td>
<td>2.137 ± 0.001</td>
<td>Varshni (Eqn. 6.1)</td>
</tr>
<tr>
<td>$\alpha$ (eV/K)</td>
<td>9.583x10^{-5} ± 8.44x10^{-6}</td>
<td>Varshni</td>
</tr>
<tr>
<td>$\beta$ (K)</td>
<td>16.624 ± 28.71</td>
<td>Varshni</td>
</tr>
<tr>
<td>$R^2$</td>
<td>0.97015</td>
<td>Varshni</td>
</tr>
<tr>
<td>$E_g (0)$</td>
<td>2.137 ± 0.001</td>
<td>Einstein(Eqn. 6.2)</td>
</tr>
<tr>
<td>$\kappa$</td>
<td>0.00436 ± 0.00415</td>
<td>Einstein</td>
</tr>
<tr>
<td>$\Theta_e$</td>
<td>45.008 ± 40.569</td>
<td>Einstein</td>
</tr>
<tr>
<td>$R^2$</td>
<td>0.97117</td>
<td>Einstein</td>
</tr>
<tr>
<td>$E_{PL} (0)$ eV</td>
<td>2.137 ± 0.001</td>
<td>O'Donell(Eqn. 7.1)</td>
</tr>
<tr>
<td>$S$</td>
<td>-0.562 ± 0.041</td>
<td>O'Donell</td>
</tr>
<tr>
<td>$E_{ph}$ (meV)</td>
<td>3.88 ± 3.48</td>
<td>O'Donell</td>
</tr>
<tr>
<td>$R^2$</td>
<td>0.97117</td>
<td>O'Donell</td>
</tr>
</tbody>
</table>

The Varshni equation (equation 6.1 in Chapter 6) is used in fitting temperature dependence for the semiconductor bandgaps [11]. Using this expression a poor fit is obtained ($R^2=0.97$) with significant uncertainty in the value of $\beta = 16.24 \pm 28.71$. Furthermore reported bulk CdSe values for $\alpha=3.7X10^{-4}$ eV/K and $\beta=150K$ do not agree with the parameters obtained which are both significantly lower [8][12]. Others have reported bulk CdSe values for $\alpha$ of $2.8 - 4.1 X10^{-4}$ eV/K and $\beta$ 181-315K, again both much higher than the values obtained here.
The use of the Einstein model to fit the data only marginally improves the fit quality ($R^2 = 0.97$). Again the parameter values obtained (Table 7.2) are below those reported by others for CdSe for example $\kappa = 6.7 \times 10^{-2}$ eV and $\Theta_\epsilon = 184$K [3].

The other model used is that proposed by O’Donnell et al [13] and subsequently modified by Collin et al [14] to give:

$$E_{PL}(T) = E_{PL}(0) + S < E_{ph} > [\coth(< E_{ph} >/2k_B T) - 1] \quad (Equation\ 7.1)$$

In this expression $E_{PL}(0)$ represent the peak energy at ‘0 K’, $S$ is a dimensionless coupling constant and $E_{ph}$ is the average phonon energy. The parameter $S$ is interpreted as the Huang-Rhys parameter. It can be seen, Figure 7.4 and Table 7.2, that use of this expression does not improve the quality of fitting obtained ($R^2 = 0.97$). Again the parameter values obtained are below those of previous reports for example $S = 1.7$ and $E_{ph} = 26$ meV in reference [8].

Further analysis of the PL temperature dependence is continued by considering the PL FWHM. The expression that is used for the FWHM fitting is given in Equation 6.3. The FWHM is plotted in Figure 7.5 and shows that at low temperatures (<175K) a reduction indicating that the phonon coupling is decreasing. At higher temperatures the FWHM displays an increases as the temperature is reduced from 300K. It is unclear what type of mechanism would lead to such an effect except for perhaps a two-emitting state system where the emission gradually shifts from one state to the other as temperature is reduced. This would initially increase the FWHM up until the point where emission from each state is balanced.
Figure 7.5: The FWHM graph for CdMnSe sample (core only) that shows the energy peak as a function of temperature from 300K to 5K.

Table 7.3: Fitting parameters obtained for the temperature dependence of the CdMnSe core NC PL FWHM.

<table>
<thead>
<tr>
<th>Fitting Parameter</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>( \Gamma_{inh} ) (meV)</td>
<td>60.7 ± 0.4</td>
</tr>
<tr>
<td>( \alpha ) (µeV/K)</td>
<td>-58 ± 11.7</td>
</tr>
<tr>
<td>( \beta ) (meV)</td>
<td>27.6 ± 5.3</td>
</tr>
<tr>
<td>( E_{LO} ) (meV)</td>
<td>9.3 ± 0.92</td>
</tr>
</tbody>
</table>

The value of the \( E_{LO} \) obtained from the fitting is 9.3 ±0.92meV which is significantly smaller than obtained from studies of CdSe NCs of 24-27meV [8] and 25meV [15][16]. However, given the poor quality of the fit, especially in the low temperature regime where \( E_{LO} \) is a key fitting parameter, the significance of this finding cannot be established.
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To further explore the effect of temperature on CdMnSe NCs, the integrated PL intensity as a function of temperature is plotted in Figure 7.6(inset). Figure 7.6 shows a clear initial increase in intensity is obtained as the temperature is decreased from 300K to 150K below which however the PL intensity is rapidly reduced again. The observed trend closely matches that see in Figure 7.5 for the FWHM. The initial increase in intensity is the expected behavior for a system with competing phonon-assisted non-radiative relaxation. The reduction in intensity at low temperatures is however in line with the emission itself being phonon assisted which would be the case for triplet exciton emission for example. A plot of the integrated PL intensity against 1/temperature is provided in Figure 7.6. It is clearly seen that a simple thermally activated emission process cannot be used to describe the behavior.
7.2.1.2 Lifetime measurement

![Figure 7.7: The PL decay of the CdMnSe NC sample thin film as a function of temperature from 300K to 5K.](image)

The PL transient decay of the CdMnSe NC sample as a function of temperature is shown in the Figure 7.7. As the temperature decreases from the 300K to 5K, the PL lifetime increases again and indicates of a reduction in competing non-radiative processes. Each transient decay curve is fitted with a bi-exponential function that gives two lifetimes $\tau_1$ and $\tau_2$ using Equation 6.6 in Chapter 6. It was found that at low temperature ($<50K$) the fitting resulted in $\tau_1 = \tau_2$ and thus a single exponential decay gives the best fit.
Figure 7.8: The lifetime of CdMnSe NC sample (core only) from the 300K to 5K as a function of temperature dependence.

Figure 7.8 plots the lifetimes $\tau_1$ and $\tau_2$ as a function of temperature. It is seen that the faster lifetime ($\tau_2$) displays little temperature dependence within the resolution of the system (the system response was measured to be $\sim$12ns). The longer lifetime is strongly temperature dependent, initially increasing as temperature is reduced from 300 K to 200 K before reducing until the process driving it vanishes (i.e. single exponential behavior is observed). Remaining is increased from the 300K to 225K.
Table 7.4: The lifetime and lifetime error for (τ_1 and τ_2) for CdMnSe (core only) as the temperature decreases from 300K to 5K by 25K steps

<table>
<thead>
<tr>
<th>Temperature (K)</th>
<th>Lifetime τ_1 (ns)</th>
<th>Lifetime error τ_1 (ns)</th>
<th>Lifetime τ_2 (ns)</th>
<th>Lifetime error τ_2 (ns)</th>
</tr>
</thead>
<tbody>
<tr>
<td>300</td>
<td>23.6</td>
<td>2.3</td>
<td>13.4</td>
<td>3.3</td>
</tr>
<tr>
<td>275</td>
<td>27.1</td>
<td>2.9</td>
<td>14.0</td>
<td>1.9</td>
</tr>
<tr>
<td>250</td>
<td>63.7</td>
<td>3.2</td>
<td>16.0</td>
<td>0.3</td>
</tr>
<tr>
<td>225</td>
<td>69.4</td>
<td>3.4</td>
<td>16.8</td>
<td>0.3</td>
</tr>
<tr>
<td>200</td>
<td>68.2</td>
<td>2.9</td>
<td>15.8</td>
<td>0.3</td>
</tr>
<tr>
<td>175</td>
<td>63.0</td>
<td>2.7</td>
<td>15.6</td>
<td>0.3</td>
</tr>
<tr>
<td>150</td>
<td>54.6</td>
<td>2.5</td>
<td>15.5</td>
<td>0.4</td>
</tr>
<tr>
<td>125</td>
<td>53.0</td>
<td>2.4</td>
<td>14.5</td>
<td>0.3</td>
</tr>
<tr>
<td>100</td>
<td>46.9</td>
<td>2.3</td>
<td>13.7</td>
<td>0.4</td>
</tr>
<tr>
<td>75</td>
<td>30.9</td>
<td>2.7</td>
<td>13.3</td>
<td>0.8</td>
</tr>
<tr>
<td>50</td>
<td>-</td>
<td>-</td>
<td>16.9</td>
<td>0.08</td>
</tr>
<tr>
<td>25</td>
<td>-</td>
<td>-</td>
<td>16.1</td>
<td>0.2</td>
</tr>
<tr>
<td>15</td>
<td>-</td>
<td>-</td>
<td>13.6</td>
<td>0.2</td>
</tr>
<tr>
<td>10</td>
<td>-</td>
<td>-</td>
<td>15.2</td>
<td>0.2</td>
</tr>
<tr>
<td>8.8</td>
<td>-</td>
<td>-</td>
<td>16.5</td>
<td>0.14</td>
</tr>
</tbody>
</table>
7.2.2 Sample 2 CdMnSe/CdS (Core-Shell)

Having studied core only CdMnSe systems where the surface of the NC is likely to contain trap states core/shell NC structures were studied. These were prepared with a CdS wider bandgap shell (2.42eV) by our collaborators.

7.2.2.1 PL measurement

Figure 7.9 shows the 300K PL spectrum obtained when exciting at 405nm, displaying a single broad emission that peaks at 2.018 eV (~614nm). The PL spectrum is fitted using a single Gaussian expression ($R^2=0.99142$) with the fitting parameters given in Table 7.5. The PL displays the typical inhomogeneous broadening of NC samples with a size distribution.

![Graph showing PL intensity vs energy for CdMnSe core shell NCs with Gaussian fitting.]

Figure 7.9: The PL of for CdMnSe NC sample (core-shell) obtained at 300K. Also shown is the result of fitting the spectrum with single Gaussian curve.
Table 7.5: Gaussian fitting parameters for the CdMnSe/CdS (core-shell) at 300K.

<table>
<thead>
<tr>
<th>Gaussian fitting</th>
<th>Peak 1 (core only)</th>
<th>Standard error (±)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Peak position (eV)</td>
<td>2.0183</td>
<td>0.0004</td>
</tr>
<tr>
<td>FWHM (meV)</td>
<td>48.9</td>
<td>0.43</td>
</tr>
</tbody>
</table>

Figure 7.10 shows the PL decay transient obtained from the CdMnSe core-shell NCs at 300K. The PL decay can be fitted with a double exponential decay function giving the fit shown in the figure. The value of the fast lifetime ($\tau_1$) is 15.3ns whilst the slow lifetime ($\tau_2$) is 106ns and the system response measured is 12ns. In comparison with the core only NCs the longer lifetime has increased by a factor of 4 with the shorter lifetime remaining the same within the system resolution.

Figure 7.10: The PL decay of CdMnSe/CdS sample (core-shell) at 300K.
Figure 7.11: The PL spectra of the CdMnSe/CdS NC sample (core-shell) as a function of temperature between 300K to 5K

The PL spectra of the CdMnSe/CdS (core-shell) NCs as a function of temperature are shown in Figure 7.11. The PL spectra are fitted using the single Gaussian expression which displays a 56meV blueshift in PL from 2.0183eV (~614.4nm) to 2.0744 eV (~597.8nm) at 5K. The PL intensity temperature dependence is more complex than previously observed. Upon initial cooling from 300K to 250K there is an initial decrease in intensity. Further cooling to 175K then produces a recovery of the intensity before below 150K a decrease is then observed. This complex behavior is difficult to interpret clearly but the overall reduction in intensity indicate the presence of trap states and phonon-assisted radiative recombination pathways. Supporting this it a reduction in the full width at half maximum (FWHM) as the temperature is reduced from ~49meV at 300K to ~40meV 5K in line with a reduction in electron-phonon interactions.
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Figure 7.12: The PL peak of CdMnSe/CdS (core-shell) from 300K to 5K of temperature dependence for Varshni, Einstein temperature and O’Donnell models.

The analysis of the CdMnSe NC (core-shell) temperature dependence is continued by plotting the PL peak, $E_{PL}$, as a function of temperature, Figure 7.12. Fitting this data with Varshni, Einstein temperature and O’Donell equation discussed in Chapter 6 yields similar results and fit qualities. In part this is due to the similar phenomenological nature of each of these models. The fitting parameters obtained in each case are provided in Table 7.6
Table 7.6: Fitting parameters obtained from fitting the temperature dependence of the core-shell CdMnSe PL peak position using the Varshni, Einstein temperature and O’Donell models.

<table>
<thead>
<tr>
<th></th>
<th>Value</th>
<th>Expression</th>
</tr>
</thead>
<tbody>
<tr>
<td>(E_g(0)) eV</td>
<td>2.077 ±0.0004</td>
<td>Varshni</td>
</tr>
<tr>
<td>(\alpha) eV/K</td>
<td>2.288x10^{-4} ± 7.60x10^{-6}</td>
<td>Varshni</td>
</tr>
<tr>
<td>(\beta) K</td>
<td>67.04 ± 10.93</td>
<td>Varshni</td>
</tr>
<tr>
<td>(R^2)</td>
<td>0.998</td>
<td>Varshni</td>
</tr>
<tr>
<td>(E_g(0)) eV</td>
<td>2.076 ± 0.0004</td>
<td>Einstein</td>
</tr>
<tr>
<td>(\kappa)</td>
<td>0.019 ± 0.003</td>
<td>Einstein</td>
</tr>
<tr>
<td>(\Theta_e)</td>
<td>88.893 ± 10.175</td>
<td>Einstein</td>
</tr>
<tr>
<td>(R^2)</td>
<td>0.998</td>
<td>Einstein</td>
</tr>
<tr>
<td>(E_{PL}(0)) eV</td>
<td>2.076± 0.431</td>
<td>O’Donell</td>
</tr>
<tr>
<td>(S)</td>
<td>-1.243 ± 0.027</td>
<td>O’Donell</td>
</tr>
<tr>
<td>(E_{ph}) meV</td>
<td>7.66 ± 0.87</td>
<td>O’Donell</td>
</tr>
<tr>
<td>(R^2)</td>
<td>0.998</td>
<td>O’Donell</td>
</tr>
</tbody>
</table>

For the Varshni fitting \((R^2 = 0.99831)\) the value of \(E_g(0)\) 2.077 eV is realistic as can see from the graph in Figure 7.12. The value of \(\alpha = 2.29x10^{-4} ± 7.60x10^{-6}\) which is similar to the reported bulk CdSe value of 3.7X10^{-4} eV/K [17][12] with other reported finding (for bulk CdSe) \(\alpha= 2.8\) to \(4.1 \times 10^{-4}\) eV/K [15]. The value of \(\beta\) obtained (67 K) is also in the range of that reported by others (61-70K [18]).

The Einstein expression has not been extensively used for these materials before (in particular the bulk material) but the value of \(\kappa\) \((1.9 \times 10^{-2}\) eV\) is of the same order of magnitude to a previously reported value \((6.7x10^{-2}\) eV [4]). The Einstein temperature
(~89K) is however below that reported (184K [3]) though as these systems are compositionally different variation would be expected.

The O’Donell fitting model is of more general interest at it provides a value for the average phonon energy $E_{ph} = 7.66 \pm 0.87$ meV. The is smaller than the reported value for CdSe of 26 meV [8] indicating a reduction in the probability of electron-phonon interactions (as more phonons are required).

![Figure 7.13: The FWHM graph for CdMnSe/CdS (core-shell) that shows the energy peak as a function of temperature from 300K to 5K](image)

**Figure 7.13** shows the fit obtained, using the expression in equation 6.3, of the FWHM a function of temperature. During the fitting the parameter $\alpha$ was initially set to 0 based on the assumption that the acoustic phonon interactions are minimal in these NCs in line with previous studies. This is supported by the shape of the temperature dependence as this contribution is a linear term that only dominates at very low temperatures (typically<25K). Having obtained a fit using only the remaining part of the expression $\alpha$ was then allowed to also vary in order to improve the fit quality.
Table 7.7: Fitting parameters obtained for the temperature dependence of the CdMnSe/CdS core-shell NC PL FWHM

<table>
<thead>
<tr>
<th></th>
<th>High energy</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\Gamma_{inh}$ (meV)</td>
<td>40.27 ± 0.14</td>
</tr>
<tr>
<td>$\alpha$ (µeV/K)</td>
<td>-12.43 ± 4.8</td>
</tr>
<tr>
<td>$\beta$ (meV)</td>
<td>22.37 ± 2.42</td>
</tr>
<tr>
<td>$E_{LO}$ (meV)</td>
<td>14.5 ± 0.46</td>
</tr>
</tbody>
</table>

The main focus of the FWHM fitting is the value of the $E_{LO}$ which is 14.5 meV which compares to the value reported for similar CdSe NCs of $E_{LO}$ = 24.5 meV[15]. Variation in these values is common in the literature due to the amplified nature of minor variations in size and shape in NC systems on measured properties. The remaining values are generally treated as fitting parameters and their direct correlation to physical properties is not fully understood.
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Figure 7.14: The integrated PL intensity graph for CdMnSe/CdS sample (core-shell) as a function of $1/\text{temperature}$ between 300K to 5K.

The integrated PL intensity is plotted in Figure 7.14 against $1/T$ and shown inset versus temperature. The intensity decreases as the temperature is reduced except for a small increase in the 150K to 250K regime as discussed earlier. The value of the activation energy obtained from the Arrhenius plot is 4.5meV.
7.2.2.2 Lifetime measurement

Figure 7.15: The PL decay of the CdMnSe/CdS (core-shell)NC thin film as a function of temperature from 300K to 5K

The PL transient decay of the CdMnSe/CdS sample (core-shell) is shown in Figure 7.15 as a function of temperature. It is seen that there exists little temperature dependence which is surprising. However, fitting with a double exponential decay expression yields a fast lifetime of ~15ns which is similar to the system resolution. As such if this lifetime decreases with temperature we would not be able to measure it. The fitting does reveal that at most temperatures (i.e. below 225K) single exponential behavior is found whilst above this temperature the slower lifetime does increase from ~100ns to 168ns as the temperature is lowered from 300K to 225K.
Figure 7.16: The lifetime of CdMnSe/CdS sample (core-shell) from the 300K to 5K as a function of temperature dependence

By referring Figure 7.16, the lifetime 1, $\tau_1$ is longer than the lifetime 2, $\tau_2$. These lifetimes could be the radiative recombination takes place at different energy level band-band emission or trap emission. There is a different for $\tau_1$ between 300K and 225K which is between 110ns to 170ns whilst the $\tau_2$ does change with temperature in a small step which is between 14ns to 16ns. For the $\tau_1$, roughly as the temperature decreases, the lifetime is increases from 300K to 225K. As the temperature <225K, the lifetime become single up to 5K. The value for each of the lifetime at each 25 step temperature can be referred in Table 7.8
Table 7.8: The lifetime and lifetime error for ($\tau_1$ and $\tau_2$) CdMnSe/CdS (core-shell sample) as the temperature decreases from 300K to 5K by 25K steps

<table>
<thead>
<tr>
<th>Temperature (K)</th>
<th>Lifetime $\tau_1$ (ns)</th>
<th>Lifetime error $\tau_1$ (ns)</th>
<th>Lifetime $\tau_2$ (ns)</th>
<th>Lifetime error $\tau_2$ (ns)</th>
</tr>
</thead>
<tbody>
<tr>
<td>300</td>
<td>106</td>
<td>8.4</td>
<td>15.3</td>
<td>0.13</td>
</tr>
<tr>
<td>275</td>
<td>130</td>
<td>12.5</td>
<td>15.1</td>
<td>0.1</td>
</tr>
<tr>
<td>250</td>
<td>150</td>
<td>19.7</td>
<td>15.7</td>
<td>0.09</td>
</tr>
<tr>
<td>225</td>
<td>168</td>
<td>24.0</td>
<td>14.7</td>
<td>0.09</td>
</tr>
<tr>
<td>200</td>
<td>-</td>
<td>-</td>
<td>15.6</td>
<td>0.07</td>
</tr>
<tr>
<td>175</td>
<td>-</td>
<td>-</td>
<td>15.3</td>
<td>0.07</td>
</tr>
<tr>
<td>150</td>
<td>-</td>
<td>-</td>
<td>15.2</td>
<td>0.07</td>
</tr>
<tr>
<td>125</td>
<td>-</td>
<td>-</td>
<td>15.1</td>
<td>0.07</td>
</tr>
<tr>
<td>100</td>
<td>-</td>
<td>-</td>
<td>14.9</td>
<td>0.07</td>
</tr>
<tr>
<td>75</td>
<td>-</td>
<td>-</td>
<td>15</td>
<td>0.07</td>
</tr>
<tr>
<td>50</td>
<td>-</td>
<td>-</td>
<td>14.8</td>
<td>0.06</td>
</tr>
<tr>
<td>25</td>
<td>-</td>
<td>-</td>
<td>14.6</td>
<td>0.06</td>
</tr>
<tr>
<td>10</td>
<td>-</td>
<td>-</td>
<td>14.7</td>
<td>0.06</td>
</tr>
<tr>
<td>7.5</td>
<td>-</td>
<td>-</td>
<td>14.6</td>
<td>0.06</td>
</tr>
<tr>
<td>5</td>
<td>-</td>
<td>-</td>
<td>14.8</td>
<td>0.07</td>
</tr>
</tbody>
</table>
### 7.2.3 Sample 3 CdMnSe/CdS (Dot-in-rod)

The final CdMnSe/CdS NC sample studied was found to be elongated rod-like structures. The core size is 3.8 nm and the shell has 8 monolayers (8.1 nm standard deviation 15%).

#### 7.2.3.1 PL measurement

The 300K PL spectrum of the CdMnSe/CdS NC rods is shown in Figure 7.17 displaying a single peak at 1.976 eV (~628 nm, Table 7.8). The PL spectrum is fitted using a single Gaussian expression ($R^2 = 0.99453$) and displays the typical inhomogeneous broadening expected.

![Figure 7.17: The PL of the CdMnSe/CdS NC sample (rod) obtained at 300K. Also shown is the result of fitting spectrum with single Gaussian curve.](image-url)
Table 7.9: Gaussian fitting parameters for the CdMnSe/CdS NC sample (rod) at (300K).

<table>
<thead>
<tr>
<th>Gaussian fitting</th>
<th>Peak 1 (rod)</th>
<th>Standard error (±)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Peak position (eV)</td>
<td>1.976</td>
<td>2.65x10^-4</td>
</tr>
<tr>
<td>FWHM (meV)</td>
<td>53.9</td>
<td>0.3</td>
</tr>
</tbody>
</table>

**Figure 7.18** shows the PL transient decay obtained from the CdMnSe/CdS NCs (rod) at 300K. The PL decay can be fitted using a double exponential decay function giving the fit shown in the figure. The value obtained for the slow lifetime ($\tau_1$) is 44ns ±3.2 whilst the fast lifetime ($\tau_2$) is 15ns ±0.3 which is again limited by the system response time (~12ns).
Figure 7.19: The PL spectra of the CdMnSe/CdS NC sample (rod) obtained as function of temperature between 300K to 5K.

The PL spectra of the CdMnSe/CdS NCs (rods) as a function of temperature are shown in Figure 7.19. The PL spectra are fitted using a single Gaussian expression yielding peaks at 1.976eV (~629.4nm) at 300K and 2.021 (~613.6nm) at 5K providing a ~51 meV blueshift. The PL intensity is found to decrease with cooling from 300K to 5K. This is evidence that phonons play an important role in the emission process in these materials either directly through electron-phonon coupling or indirectly via thermally activated trap emission.
Figure 7.20: The PL peak of CdMnSe/CdS NC sample (rod) from 300K to 5K of temperature dependence for the Varshni, Einstein temperature and O'Donnell models.

The analysis of the CdMnSe/CdS NC sample (rod) temperature dependence is continued by plotting the PL peak, $E_{PL}$ as a function of temperature as seen in Figure 7.20. It can be seen that the PL peak position blueshifts linearly with reducing temperature until low temperatures (<50K) where it saturates. The data in Figure 7.20 can be fitted with the Varshni, Einstein temperature and O'Donnell expressions each of which yield good quality fits ($R^2 > 0.99$). The parameter values obtained from the use of each expression are listed in Table 7.9.
Table 7.10: Fitting parameters obtained from fitting the temperature dependence of the rod CdMnSe/Cds PL peak position using the Varshni, Einstein temperature and O’Donell models.

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value</th>
<th>Expression</th>
</tr>
</thead>
<tbody>
<tr>
<td>$E_g (0)$</td>
<td>2.021 ± 0.001</td>
<td>Varshni</td>
</tr>
<tr>
<td>$\alpha$ (eV/K)</td>
<td>1.73x$10^{-4}$ ± 0.1x$10^{-4}$</td>
<td>Varshni</td>
</tr>
<tr>
<td>$\beta$ (K)</td>
<td>61.55 ± 21.36</td>
<td>Varshni</td>
</tr>
<tr>
<td>$R^2$</td>
<td>0.99454</td>
<td>Varshni</td>
</tr>
<tr>
<td>$E_g (0)$</td>
<td>2.021 ± 0.001</td>
<td>Einstein</td>
</tr>
<tr>
<td>$\kappa$</td>
<td>0.014 ± 0.004</td>
<td>Einstein</td>
</tr>
<tr>
<td>$\Theta_e$</td>
<td>87.408 ± 18.988</td>
<td>Einstein</td>
</tr>
<tr>
<td>$R^2$</td>
<td>0.99488</td>
<td>Einstein</td>
</tr>
<tr>
<td>$E_{PL} (0)$ eV</td>
<td>2.021 ± 0.001</td>
<td>O’Donell</td>
</tr>
<tr>
<td>$S$</td>
<td>-0.956 ± 0.034</td>
<td>O’Donell</td>
</tr>
<tr>
<td>$E_{ph}$ (meV)</td>
<td>7.53 ± 1.63</td>
<td>O’Donell</td>
</tr>
<tr>
<td>$R^2$</td>
<td>0.99488</td>
<td>O’Donell</td>
</tr>
</tbody>
</table>

As the peak position saturates at low temperature each expression yields the same value for the $E_g (0) = E_{PL} (0) = 2.021$eV. The Varshni fitting gives values of $\alpha$ and $\beta$ values that are approximately half of the reported bulk CdSe values ($\alpha = 3.7x10^{-4}$ eV/K and $\beta = 150$K [17][12]). A similar trend is found when comparing the parameters obtained from fitting with the Einstein expression (bulk values are $\kappa = 6.7x10^{-2}$ eV and $\Theta_e =184$K [3]). Finally, when using the O’Donnell expression the value of $S$ and $E_{ph}$ are again lower than the bulk ($S = 1.7$[8] and $E_{ph} = 26$meV[8]) though the value obtained for $E_{ph}$ is in line with that found for other NCs.
Figure 7.21: The FWHM graph for CdMnSe/CdS NC sample (rod) that shows the energy peak as a function of temperature from 300K to 5K

The PL FWHM is plotted in Figure 7.21 as a function of temperature and fitted using the expression given in equation 6.3. It can be seen that the FWHM decreases as the temperature is reduced from 300K to 5K. The fitted expression thought fitting well yields a value for the longitudinal optical phonon ($E_{LO}$) of 94meV. This is much higher than the value reported for the dotCdSe ($E_{LO} = 25\text{meV}$ [16]) and significantly higher than the value of $E_{ph}$ (~8meV) found from fitting the PL peak temperature dependence.

Table 7.11: Fitting parameters obtained for the temperature dependence of the CdMnSe/CdS rod NC PL FWHM

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\Gamma_{inh}$ (meV)</td>
<td>40.58 ± 0.1</td>
</tr>
<tr>
<td>$\alpha$ (µeV/K)</td>
<td>20.0 ± 1.29</td>
</tr>
<tr>
<td>$\beta$ (meV)</td>
<td>341.6 ± 0.1</td>
</tr>
<tr>
<td>$E_{LO}$ (meV)</td>
<td>94.47 ± 0.01</td>
</tr>
</tbody>
</table>
Figure 7.22: The integrated PL intensity graph for CdMnSe/CdS NC sample (rod) peak as a function of 1/temperature between 300K to 5K. The inset shows the integrated PL intensity as a function of temperature from 300K to 5K.

To further explore the relationship of temperature dependent electron-phonon coupling in CdMnSe/CdS rod NCs, the PL integrated intensity is plotted in Figure 7.22. The inset graph clearly shows the reduction in intensity as temperature is reduced from 300K to 5K, with a small plateau (~250K and 200K) where the intensity does not change. Plotting the data against 1/temperature enable fitting using the Arrhenius expression to determine an activation energy of $E_a = 5.7\text{meV}$.
7.2.3.2 Lifetime measurement

Figure 7.23: The PL decay of the CdMnSe/CdS NC sample (rod) thin film as a function of temperature from 300K to 5K

The transient PL decay of the CdMnSe/CdS NC sample (rod) are shown in the Figure 7.23. As the temperature is reduced from 300K to 5K the lifetime is found to decrease. This is unexpected in respect of the usual increase in PL lifetime as competing non-radiative pathways are reduced. When fitting the PL lifetime decay with a double exponential function however it is seen that it is only the slower component that in fact is reduced from ~44ns to ~20ns at 300K and 125K respectively, Figure 7.24 and Table 7.12. Below 125K the decay was found to be single exponential in nature. Furthermore, the shorter of the lifetimes (~15ns) does indeed increase very slightly as temperature is reduced.
Figure 7.24: The lifetime of CdMnSe/CdS NC sample (rod) from the 300K to 5K as a function of temperature dependence
Table 7.12: The lifetime and lifetime error for ($\tau_1$ and $\tau_2$) of CdMnSe/CdS NC sample (rod) as the temperature decreases from 300K to 5K by 25K steps

<table>
<thead>
<tr>
<th>Temperature (K)</th>
<th>Lifetime $\tau_1$ (ns)</th>
<th>Lifetime error $\tau_1$ (ns)</th>
<th>Lifetime $\tau_2$ (ns)</th>
<th>Lifetime error $\tau_2$ (ns)</th>
</tr>
</thead>
<tbody>
<tr>
<td>300</td>
<td>44.0</td>
<td>3.3</td>
<td>15.0</td>
<td>0.3</td>
</tr>
<tr>
<td>275</td>
<td>42.1</td>
<td>2.8</td>
<td>14.5</td>
<td>0.4</td>
</tr>
<tr>
<td>250</td>
<td>40.3</td>
<td>4</td>
<td>15.8</td>
<td>0.5</td>
</tr>
<tr>
<td>225</td>
<td>37.4</td>
<td>1.9</td>
<td>13.1</td>
<td>0.3</td>
</tr>
<tr>
<td>200</td>
<td>34.6</td>
<td>3.4</td>
<td>14.4</td>
<td>0.4</td>
</tr>
<tr>
<td>175</td>
<td>27.0</td>
<td>3.9</td>
<td>14</td>
<td>0.8</td>
</tr>
<tr>
<td>150</td>
<td>20.5</td>
<td>6.3</td>
<td>14.1</td>
<td>0.3</td>
</tr>
<tr>
<td>125</td>
<td>20.8</td>
<td>5.0</td>
<td>13.5</td>
<td>2.0</td>
</tr>
<tr>
<td>100</td>
<td>-</td>
<td>-</td>
<td>15.5</td>
<td>0.06</td>
</tr>
<tr>
<td>75</td>
<td>-</td>
<td>-</td>
<td>15.6</td>
<td>0.07</td>
</tr>
<tr>
<td>50</td>
<td>-</td>
<td>-</td>
<td>15.4</td>
<td>0.06</td>
</tr>
<tr>
<td>25</td>
<td>-</td>
<td>-</td>
<td>15.3</td>
<td>0.06</td>
</tr>
<tr>
<td>10</td>
<td>-</td>
<td>-</td>
<td>15.4</td>
<td>0.07</td>
</tr>
<tr>
<td>7.5</td>
<td>-</td>
<td>-</td>
<td>15.4</td>
<td>0.07</td>
</tr>
<tr>
<td>5</td>
<td>-</td>
<td>-</td>
<td>15.4</td>
<td>0.07</td>
</tr>
</tbody>
</table>
Figure 7.25: The normalised amplitude for the rod sample which A1 show fast component and A2 show slow component

The relative amplitudes of the fast and slower decay process obtained from the fitting are plotted in Figure 7.25. It can be seen that where the emission is described by a bi-exponential process the faster of these processes dominates ($A_2$). It is not clear if when single exponential decay takes over which of these processes remains as they are converging as temperature is reduced.
7.4 Discussion

PL Peak position

All samples studied display a blueshift with reducing temperature until as very low temperature a characteristic hook is observed that corresponds with a switch from singlet state to triplet state emission [10]. The core-only CdMnSe NCs display the smallest shift over the 300K to 5K temperature range studied of ~24meV, compared to core-shell and dot-in-rod NCs which display shifts of ~56meV and ~51 meV respectively. The core-shell sample has shell thickness of 6.8 monolayers (8.1nm standard deviation 8%) and the rod sample a shell thickness of 8 monolayers (12nm Standard deviation 15%) based on HRTEM studies of our collaborator. It is worth emphasizing that the core-shell sample has thin capping layer, in contrast rod sample, which could result in the CdS layer adopting the lattice parameters of CdSe and thereby reducing the strain at the interface. As such the effect of strain on the samples as the temperature is varied may be different making definitive comparisons difficult. It is known that the capping layer can accumulate a large strain at the interface and thus generate an additional band gap shift [8]. The effect of strain and it presence may be inferred however as the core only CdMnSe NCs display the smallest shift and have no capping layer.

The effect of the lattice deformation potential on the exciton-phonon coupling is important in these systems [19]. The electron is moving and at some point it need to couple with the lattice vibration (phonon) and after the coupling happened, the additional layer is created and the bandgap become larger at low temperature, thus the electron-phonon coupling gives effect to the size of bandgap.

When fitting the PL peak position temperature dependence little difference was found in the quality of fit between each of the three expressions that were used (the Varshni, Einstein and O'Donnell expressions). Of these three expressions the O'Donnell expression is the most commonly used one when studying NC systems as it includes the average phonon
energy $E_{ph}$ in it which can be directly related to a measurable parameter. The values obtained for the core, core-shell and rod samples (~3.9 meV, ~7.7 meV and ~7.5 meV) indicate that the addition of a shell increases the value of this parameter. At this time no Raman studies of these samples are available to compare these values to. The lower value found in the core only samples is in line with the presence of the ‘hook’ in the peak position at very low temperatures (due to the switch between single to triplet excitation recombination) which is less pronounced in the samples with shell capping layers. The values obtained are however lower than those found in the literature (~23-27 meV) which may result from the Mn doping of the NCs. Considering the value obtained for ‘S’, the Huang-Rhys factor, using the O’Donnell expression this should increase with increasing NC size as the coupling is proportional to $a_0^3/V$, where $a_0$ is the exciton bohr radius for the material. This is indeed what is generally found with the core, core/shell and rod NC having values of -0.562, -1.243 and -0.956 respectively.

Unsurprisingly the parameters obtained using the other two fitting expressions yield similar results for the capped samples with the parameters obtained being higher than those for the core only (Table 7.13)

**Table 7.13: The different of Varshni and Einstein temperature fitting for all the samples**

<table>
<thead>
<tr>
<th>Sample</th>
<th>Varshni fitting</th>
<th>Einstein temperature fitting</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Core</strong></td>
<td>$\alpha = 0.95 \times 10^{-4} \pm 8.44 \times 10^{-6}$</td>
<td>$\kappa = 0.44 \times 10^{-2} \pm 0.42 \times 10^{-2}$</td>
</tr>
<tr>
<td></td>
<td>$B = 16.6 \text{K}\pm28$</td>
<td>$\Theta_e = 45 \text{K}\pm40$</td>
</tr>
<tr>
<td><strong>Core-shell</strong></td>
<td>$\alpha = 2.29 \times 10^{-4} \pm 7.6 \times 10^{-6}$</td>
<td>$\kappa = 1.9 \times 10^{-2} \pm 0.3 \times 10^{-2}$</td>
</tr>
<tr>
<td></td>
<td>$B = 67 \text{K}\pm10.9$</td>
<td>$\Theta_e = 88.9 \text{K}\pm10$</td>
</tr>
<tr>
<td><strong>Dot-in-a-rod</strong></td>
<td>$\alpha = 1.73 \times 10^{-4} \pm 1.06 \times 10^{-5}$</td>
<td>$\kappa = 1.44 \times 10^{-2} \pm 0.36 \times 10^{-2}$</td>
</tr>
<tr>
<td></td>
<td>$B = 61.6 \text{K}\pm21.4$</td>
<td>$\Theta_e = 87 \text{K}\pm18.9$</td>
</tr>
</tbody>
</table>
PL intensity

The temperature dependence of the PL intensity can display complex behaviour due to the several available mechanisms of carrier relaxation including radiative recombination, Auger nonradiative scattering, thermal escape from traps as well as trapping in surface states and/or defect states.

Typically a semiconductor displays a lower PL intensity at high temperatures and as the temperature decreases, the PL intensity increases due to a reduction in non-radiative phonon interactions. Cadmium selenium (CdSe) does not follow this conventional trend however as the intensity, though initially increasing with reducing temperature, decreases at low temperatures. This low temperature reduction of the PL intensity is due to carrier trapping in defect states from which at low temperatures thermalization cannot occur. These trap states are often noticeable as a low-energy shoulder in the PL spectrum. [20][8].

In the doped CdMnSe NC samples studied above the core only NCs display this type of behavior with the PL intensity increasing before reducing as the temperature is reduced. In contrast the core/shell and rod NC samples do not display any initial increase in PL intensity but simply reduce in intensity as the temperature is lowered. Interestingly they do both display a small plateau over which the intensity remains constant over the 200K to 250K region.

Plotting the data against 1/temperature further emphasizes the difference between the core only and the other samples with the later displaying very similar behavior that can be fitted using an Arrhenius expression yielding activation energies of 4.5 meV and 5.7meV for the core/shell and rod samples respectively. It is clear that the core only sample contains a significant number of traps, as discussed above that are extended in energy as the Arrhenius plot displays a long tail.

The intensity is decrease as the carrier is trapped by the surface/defects in the dot and recombines nonradiatively as the results the PL intensity is reduces. Both core-shell and dot-in-rod has the VB edge is higher in CdSe than in rod thus, the hole localized in the core
whilst electron localized in the core or delocalized around the rod depending on the band alignment. Therefore, the mechanism that lead to the decreases in intensity is electron escaping out the core[8].

**FWHM**

Comparing of the FWHM temperature dependence of the three samples again indicates that the core only sample behaves somewhat differently. The expression used to fit the data has difficulty in fitting this data particularly at low temperatures thus caution must be used when comparing parameter values. The initial increase in FWHM before reduction as the temperature is lowered implies the involvement of at least two emitting states. This might be expected with the Mn doping as Mn$^{2+}$ has an intra-atomic transition in this spectral region. It may be possible that the NC energy gap is resonant with this and hence highly sensitive to variation in temperature. Ultimately this possibility is however unlikely as we will discuss further below.

The remaining samples behave similarly, both reducing with temperature, with the core/shell rods initial rate of FWHM reduction being higher hence the difference in 'line-shape' of the fits. This difference does however manifest itself in the parameters obtained from the fits and in particular the value of $E_{LO}$. In the three samples the value of $E_{LO}$ obtained is 9.3 meV, 14.5 meV and 94meV for the core only, core/shell and core/shell rod samples respectively. The high value obtained for the core shell sample is at odds with found for the other samples, the value of $E_{ph}$ from the PL peak fitting and other reports, and is a consequence of the fast initial decay. It is clear however that such a high value should be considered an artifact of the sample rather than a true value for $E_{LO}$ and further investigation is required to understand its full origin.
Figure 7.26 a) and b) : The lifetimes of core, core-shell and rod emission for slow lifetime 1 and fast lifetime 2.

Figure 7.26 shows together the values of the PL lifetime obtained from each sample with (a) being the longer of the two lifetimes obtained when a bi-exponential fit was required. It is immediately clear that the faster of the lifetimes all appear similar (~15ns) with little temperature dependence though they could in fact be faster than this as the measurement system resolution was ~13ns. The longer of the lifetimes are all sub microsecond and for the core only and rod samples sub 100ns. This for the core only samples is too faster a recombination for it to be related to the Mn$^{2+}$ intra-atomic emission mentioned above, which occurs on a microsecond timescale[21], hence our ruling it out as being the origin of the peculiar temperature dependence.

In order to further study the lifetime of these processes the samples were measured at room temperature using a system with ns resolution and compared to the measurements obtained using the OPO system available for temperature dependent studies. The results are tabulated in Table 7.14 where it is seen that the core only samples have a shorter lifetime than found using the OPO. The ~5ns fast decay is in line with expectations and
previous studies and indicative of the the electron and hole being spatially confined with strong wavefunction overlap. The lifetimes obtained using the OPO system for the core/shell and rod samples were very similar to that found using the fast system giving confidence to these values. Furthermore, in core/shell samples separation of the charge carriers can occur with the heavier hole residing in the core and electron in the shell. This reduces the overlap of their wavefunctions and thereby slows down the exciton recombination.

Table 7.14: The lifetime measurement using the OPO laser and the LifeSpec spectrometer

<table>
<thead>
<tr>
<th>Samples</th>
<th>OPO laser (300K)(ns)</th>
<th>LifeSpec (300K)(ns)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Core</td>
<td>13.4</td>
<td>4.7</td>
</tr>
<tr>
<td></td>
<td>23.6</td>
<td>23.3</td>
</tr>
<tr>
<td>Core-shell</td>
<td>15.3</td>
<td>15.2</td>
</tr>
<tr>
<td></td>
<td>106</td>
<td>90.3</td>
</tr>
<tr>
<td>Dot-in-rod</td>
<td>15.0</td>
<td>15.9</td>
</tr>
<tr>
<td></td>
<td>44.0</td>
<td>48.4</td>
</tr>
</tbody>
</table>

Advantage of having CdSe/CdS dot-in-rod

The advantage for optoelectronics of having dot-in-rod type samples is the ability to obtain a narrow distribution of length and diameters, high quantum yields, and importantly linearly polarized fluorescence and tunable emission wavelength that is controlled by the rod size and to a larger extent by the diameter of the core[8]. It has the advantage of increasing PL intensity as the lattice mismatch between CdSe and CdS can be relaxed due to the additional shell material within the rod shape. It is also worth noting that these samples have the maximum PL intensity at room temperature when compared to core and core-shell samples suggesting that these structures are more suited for room temperature applications such as fluorescence labeling [8].
7.5 Conclusion

In this work, we have studied the temperature dependence of the bandgap energy of CdMnSe NCs over the temperature range of 300K to 5K. The most important insights from the study may be summarized as follows:

- The core only NCs display a different luminescent behaviour to that of the core-shell and dot-in-a-rod samples. From the analysis of the temperature dependence, it is concluded that the observed PL is related to free excitons recombination together with emission from what are most probably trap states located at the surface. In these samples no contribution from the Mn$^{2+}$ ion is found (as previously observed [21]) suggesting that they are not fully incorporated into the NC but may reside on the surface.

It is possible to fit the temperature dependence of the optical properties using phenomenological expressions that provide values of the phonon energies in these samples. In most cases the value of $E_{ph}$ is found to be lower than previously reported. Likewise the values obtained for $E_{LO}$ vary widely between the samples ranging from ~9 meV to ~94meV.

- At room temperature the emission consists of at least two mechanisms based upon the bi-exponential decay obtained from fitting the PL decay transients. All of the measured lifetimes are too fast for Mn$^{2+}$ emission to be inferred further indicating that trap states play a critical role in the optical properties of these samples.
Chapter 7: Temperature Dependence of Manganese-doped Cadmium Selenide Nanocrystals Optical Properties

References:


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In this chapter the main conclusions from the experimental work are presented. In addition, a section is provided that suggests future work that would be of benefit for improving the understanding of the Er:YAG, zinc nitride and manganese-doped cadmium selenide samples.

8.1 Thesis conclusion

In chapter 5, the optical properties of Er:YAG were investigated as a function of Er concentration, temperature and excitation power dependence. The slow-cooled samples with bi-phase nature show a slight difference in their optical properties compared to fast-cooled single phase samples. Under 980nm excitation, upconversion emission at 565nm and 677nm was observed which in the bi-phasic samples is reduced and therefore may assist in improving the yield of 1532nm emission and also 3µm emission. This later emission may be strongly affected by the ETU process and therefore has important implications on the performance of Er:YAG 3µm lasers. In these devices an erbium
concentration of 40-50% is required to obtain strong ETU from the \( ^4I_{13/2} \) level which then reduces the lifetime of the 1532nm emission. This is required in order to achieve a population inversion of the \( ^4I_{11/2} \) from which the 3\( \mu \)m emission occurs. On the other hand, careful choice of material, based on synthesis, may enable improved performance by either promoting or reducing ion-ion interactions. Equally, lack of control over the synthesis may lead to unforeseen deleterious effects due to phase separation.

Chapter 6 reported the temperature dependence of the zinc nitride samples (in thin film and solution) with different average NC sizes. The measured PL peak shows shifting to a higher energy as the average size of the NC is decreased due to quantum confinement and follows the Brus equation. A number of phenomenological models (e.g. Varshni, Bose-Einstein etc) were found to have a limited success in describing the observed temperature dependent behavior of the PL with a lack of consistency in the resulting parameters obtained (e.g. the value of \( E_{LO} \)). Two of the samples (8.9nm and 2.7nm diameter NCs) display a temperature dependence of the optical properties in line that seen in other specific semiconductor NCs such as PbS. The other samples displayed anomalous behavior that could be due to ligand emission (2.5nm NC sample) or higher energy trap states caused by localized oxidation (3.8nm NCs).

In chapter 7, the temperature dependence of \( \text{Mn}^{2+} \) doped cadmium selenide NCs with different average NC sizes and shape are studied. The core only NCs display a different luminescent behavior to that of the core-shell and dot-in-a-rod samples. From the analysis of the temperature dependence, it is concluded that the observed PL is related to quantum confined exciton recombination together with emission from what are most probably trap states located at the surface. In these samples no contribution from the \( \text{Mn}^{2+} \) ion is found (as previously observed[1]) suggesting that they are not fully incorporated into the NC but may reside on the surface. It is possible to fit the temperature dependence of the optical properties using phenomenological expressions that provide values of the phonon energies in these samples. In most cases the value of \( E_{ph} \) is found to be lower than previously reported. Likewise the values obtained for \( E_{LO} \) vary widely between the samples ranging from \(~9\) meV to \(~94\)meV. At room temperature the emission consists of at least two mechanisms.
based upon the bi-exponential decay obtained from fitting the PL decay transients. All of the measured lifetimes are too fast for Mn\(^{2+}\) emission to be inferred further indicating that trap states play a critical role in the optical properties of these samples.

As a whole the thesis has provided a comprehensive study of the temperature dependence of three different material which is Er:YAG, zinc nitride and cadmium selenium. The reporting of zinc nitride NC temperature dependent optical properties was previously lacking in the literature upon commencement of the study and are being prepared for submission. Some part of the results in chapter 5 (Er:YAG) has been published in the academic literature [2].

### 8.2 Future work

Further improvement on the understanding of temperature-optical properties of Er:YAG can be achieved by collecting more data at 3\(\mu\)m as our detector is not sensitive enough to detect this emission. Since the reporting of our work on this system others have also taken interest in this area and performed some of these studies, though there is still plenty of scope for this further work. The interest would be study other variables including dopant species with different concentration such as terbium (Tm\(^{3+}\)) or europium (Eu\(^{3+}\)) that can be used in laser applications. In term of the synthesis further control over the bi-phase or only single phase material production should be developed.

For the zinc nitride NC materials, the most urgent need is for a capping shell to be developed to prevent oxidation. However, due to the large lattice spacing this may prove to be too difficult to realize. If achieved however detailed measurements of thin film samples will become possible and also their incorporation into the devices may be realized. This would provide a non-toxic alternative to current Cd-based NC systems that are used for visible emission. A natural extension would then be to attempt to dope these systems with ions such as Mn\(^{2+}\) to achieve giant magnetic effects.

Finally, with regards to the Mn\(^{2+}\) doped cadmium selenide NC materials it is important to fully understand the nature of the doping in these systems. This work is actively being
pursued by collaboration at Oxford and Manchester and will be reported along with the result presented within in the near future. These systems will also benefit from the measurement of their ultrafast dynamics once control of the Mn$^{2+}$ doping is improved in order to study their magneto-optical properties in details. Since the commencement of this work others have also taken interest in this area and started to undertaken some of these studies. There is however still plenty of scope for this further work and for their application in advanced photonic devices.
Chapter 8: Conclusions and Future work

References
