Efficient energy transfer from zinc oxide nanocrystals to europium (3+) and terbium (3+) ions embedded in an oxide matrix

Mangalam, Vivek

2019

Mangalam, V. (2019). Efficient energy transfer from zinc oxide nanocrystals to europium (3+) and terbium (3+) ions embedded in an oxide matrix. Doctoral thesis, Nanyang Technological University, Singapore.

<https://hdl.handle.net/10356/84124>

<https://doi.org/10.32657/10356/84124>

**NANYANG
TECHNOLOGICAL
UNIVERSITY**

SINGAPORE

**EFFICIENT ENERGY TRANSFER FROM ZINC OXIDE
NANOCRYSTALS TO EUROPIUM (3+) AND TERBIUM (3+)
IONS EMBEDDED IN AN OXIDE MATRIX**

VIVEK MANGALAM

SCHOOL OF ELECTRICAL & ELECTRONIC ENGINEERING

2018

**EFFICIENT ENERGY TRANSFER FROM ZINC OXIDE
NANOCRYSTALS TO EUROPIUM (3+) AND TERBIUM (3+)
IONS EMBEDDED IN AN OXIDE MATRIX**

VIVEK MANGALAM

School of Electrical & Electronic Engineering

A thesis submitted to the Nanyang Technological University
in partial fulfilment of the requirement for the degree of
Doctor of Philosophy

2018

Statement of Originality

I hereby certify that the work embodied in this thesis is the result of original research, is free of plagiarised materials, and has not been submitted for a higher degree to any other University or Institution.

19/07/2019

.....
Date

.....
Vivek Mangalam

Supervisor Declaration Statement

I have reviewed the content and presentation style of this thesis and declare it is free of plagiarism and of sufficient grammatical clarity to be examined. To the best of my knowledge, the research and writing are those of the candidate except as acknowledged in the Author Attribution Statement. I confirm that the investigations were conducted in accord with the ethics policies and integrity standards of Nanyang Technological University and that the research data are presented honestly and without prejudice.

19 July 2019
Date

Kantisara Pita

Authorship Attribution Statement

This thesis contains material from 4 paper(s) published in the following peer-reviewed journal(s) and from 1 paper accepted at conferences in which I am listed as an author.

Parts of Chapter 4 is published as V. Mangalam, K. Pita, and C. Couteau, "Study of energy transfer mechanism from ZnO nanocrystals to Eu^{3+} ions," Nanoscale Research Letters, journal article vol. 11, no. 1, pp. 1-9, 2016.

The contributions of the co-authors are as follows:

- I performed the experimental work, analysed the data and started the write-up.
- Prof. Kantisara Pita initiated and supervised the research work and improved the manuscript for submission and publication.
- Prof. Christophe Couteau participated in the studies and improved the manuscript for submission and publication.

Parts of Chapter 4 is also published as V. Mangalam and K. Pita, "Energy transfer from ZnO nanocrystals to Terbium (3+) ions: A spectral overlap study," presented at the 2016 IEEE Photonics Conference (IPC), Hawaii USA, 2-6 Oct. 2016, 2016.

The contributions of the co-authors are as follows:

- I performed the experimental work, analysed the data and started the write-up.
- Prof. Kantisara Pita initiated and supervised the research work and improved the manuscript for submission and publication.

Chapter 5 is also published as V. Mangalam and K. Pita, "Energy Transfer Efficiency from ZnO-Nanocrystals to Eu^{3+} Ions Embedded in SiO_2 Film for Emission at 614 nm," Materials, vol. 10, no. 8, p. 930, 2017.

The contributions of the co-authors are as follows:

- I performed the experimental work, analysed the data and started the write-up.
- Prof. Kantisara Pita initiated and supervised the research work and improved the manuscript for submission and publication.
- Prof. Sun Handong and Dr. Wang Yue from School of Physical and Mathematical Sciences, Nanyang Technological University helped to measure the time-resolved photoluminescence spectra of the samples used in this study. (Mentioned in the acknowledgement section of the publication)

Chapter 6 is also published as V. Mangalam and K. Pita, "Effect of the interaction distance on 614 nm red emission from Eu^{3+} ions due to the energy transfer from ZnO-nc to Eu^{3+} ions," *Optical Materials Express*, vol. 8, no. 10, pp. 3115-3132, 2018/10/01 2018.

The contributions of the co-authors are as follows:

- I performed the experimental work, analysed the data and started the write-up.
- Prof. Kantisara Pita initiated and supervised the research work and improved the manuscript for submission and publication.

Parts of Chapter 7 is also published as V. Mangalam and K. Pita, "Effect of the interaction distance on 614 nm red emission from Eu^{3+} ions due to the energy transfer from ZnO-nc to Eu^{3+} ions," *Optical Materials Express*, vol. 8, no. 10, pp. 3115-3132, 2018/10/01 2018.

The contributions of the co-authors are as follows:

- I performed the experimental work, analysed the data and started the write-up.
- Prof. Kantisara Pita initiated and supervised the research work and improved the manuscript for submission and publication.

19/07/2019

.....
Date

.....
Vivek Mangalam

Acknowledgement

Firstly, I would like to express my sincere gratitude to my supervisor, Prof. Kantisara Pita for giving me the opportunity to pursue my PhD with him. His guidance, patience and efforts in keeping me focused have helped me immensely in my research journey and in writing this thesis. His insightful comments and hard questions allowed me to learn, grow and understand my topic from various perspectives and I am grateful to have had the opportunity to work with such a dedicated professor.

Besides my supervisor, I would like to thank Prof. Christophe Couteau who was part of my PhD journey in the early days, and advised me on analysing my initial results improving my journal paper manuscript. I would also like to thank the rest of my thesis advisory committee: Prof. Yoo Seong Woo and Prof. Sun Handong for their insightful advice and motivation.

Next, my sincere thanks goes to Mr. Desmond Lim, Ms. Low Poh Chee, Ms. Yvonne, Mr. Yong Kim Lam, Mr. Tsay Chi Huang and Mr. Yeoh Tiow Koon, the lab technicians at Nanyang Technological University's Photonics Lab 1 and 2. Without their support, I would not have been able to run the experiments and complete my research.

I truly appreciate my family's support through this journey and would like to express gratitude for my parents and brother for their unfailing support and motivation throughout my years of study. Also a sincere thank you to my in-laws for their continuous encouragement through the process of PhD research and writing this thesis.

Most importantly, I would like to thank my wife, Radhika Vyas for being a part of this entire journey with me. I appreciate the encouragement, motivation and support she gave me, especially during the challenging times and also for making this journey memorable by celebrating the small successes and happy moments along the way. This accomplishment would not have been possible without her.

Table of Contents

Statement of Originality	i
Authorship Attribution Statement	iii
Acknowledgement	vi
Table of Contents	vii
Summary	xii
Table of Figures.....	xv
Table of Tables.....	xxi
Chapter 1: Introduction	1
1.1. Motivation.....	1
1.2. Objective	5
1.3. Major Contribution.....	7
1.4. Organisation of Thesis	11
Chapter 2: Literature Review	14
2.1. Introduction.....	14
2.2. Lanthanide Rare Earth Element	14
2.2.1. Electronic Configuration	15
2.2.2. Electronic States of Trivalent Lanthanide Ions	16
2.2.3. Luminescence.....	19
2.2.3.1. Radiative Relaxation vs. Non-Radiative Relaxation	20
2.2.3.2. Multi-Phonon Emission	21
2.2.3.3. Concentration Quenching	23
2.2.4. The Choice of Eu^{3+} and Tb^{3+} ions	25
2.3. Semiconductor Nanocrystals	27
2.3.1. Energy Transfer	28
2.3.1.1. Radiative Energy Transfer	29
2.3.1.2. Non-Radiative Energy Transfer	31
2.3.1.3. Energy Transfer Efficiency	33

2.3.2. Current Research on Semiconductor Nanocrystals as Sensitizers ..	34
2.3.2.1. Silicon nanocrystals	34
2.3.2.2. Cadmium Sulphide nanocrystals & Zinc Sulphide	37
2.4. Zinc Oxide Nanocrystals.....	38
2.4.1. ZnO-nc Emission Centres	39
2.4.2. Energy Transfer from ZnO-nc to Lanthanide ions	42
2.5. CIE Chromaticity	45
Chapter 3: Sample Preparation & Characterization Techniques.....	47
3.1. Introduction.....	47
3.2. Fundamentals of Thin Film Preparation	47
3.3.1. Choice of Sol-Gel Method.....	48
3.3.2. Thin film deposition by the sol-gel process.....	50
3.3.3. Radio-Frequency (RF) Magnetron Sputtering	59
3.3. Characterization Techniques	62
3.3.1. Spectrofluorometer System (SPEX Fluorolog-3).....	62
3.3.2. Surface Profiler (Sloan Dektak 3)	64
3.3.3. Streak Camera (OptoScope SC-10).....	65
3.4. Chapter Summary	67
Chapter 4: Energy Transfer Contribution from ZnO-Nanocrystals to Eu^{3+} Ions and ZnO-Nanocrystals to Tb^{3+} Ions.....	69
4.1. Introduction.....	69
4.2. Samples	70
4.3. Characterisation	71
4.4. Results and Discussion.....	71
4.4.1. Energy Transfer from ZnO-nc to Eu^{3+} ions.....	71
4.4.2. Energy Transfer from ZnO-nc to Tb^{3+} ions.....	85
4.4.3. Stability of PL emission from ZnO-nc, Eu^{3+} and Tb^{3+} ions.....	95
4.5. Chapter Summary	97
Chapter 5: Energy Transfer Efficiency from ZnO-Nanocrystals to Eu^{3+} Ions and ZnO-Nanocrystals to Tb^{3+} Ions.....	100

5.1. Introduction.....	100
5.2. Samples	101
5.3. Characterisation	102
5.4. Results and Discussion.....	102
5.4.1. Transfer Efficiency from Time-Resolved Photoluminescence Emission	102
5.4.2. Transfer Efficiency from Steady-State Photoluminescence Emission 109	
5.4.3. Discussion on Transfer Efficiency Values of Eu^{3+} ions.....	112
5.4.4. Discussion on Transfer Efficiency from ZnO-nc to Tb^{3+} ions	113
5.5. Chapter Summary	116
Chapter 6: Effect of Interaction Distance Among ZnO-nanocrystals and Eu^{3+} Ions	118
6.1. Introduction.....	118
6.2. Samples	119
6.3. Characterisation	122
6.4. Theoretical Calculation	122
6.5. Results and Discussion.....	134
6.6. Chapter Summary	142
Chapter 7: White light Emission from ZnO Nanocrystals co-doped with Eu^{3+} and Tb^{3+} ions in SiO_2 matrix.....	144
7.1. Introduction.....	144
7.2. Sample.....	145
7.3. Characterisation	146
7.4. Results and Discussion.....	147
7.5. Chapter Summary	157
Chapter 8: Conclusions and Recommendations	159
8.1. Conclusion	159
8.2. Recommendations for future research	165
Author's Publication	167

Bibliography.....	168
-------------------	-----

Summary

This thesis presents the study of energy transfer from Zinc Oxide Nanocrystals (ZnO-nc) to two different types of rare-earth (RE) ions, namely Europium (III) (Eu^{3+}) and Terbium (III) (Tb^{3+}) ions. RE ions, such as Eu^{3+} and Tb^{3+} , are important materials which have been extensively studied for their applications in lighting and display technologies. Eu^{3+} and Tb^{3+} ions have been used for red and green light emitting devices due to sharp red emission at 614 nm and sharp green emission at 545 nm, respectively.

However, the RE ions have their limitations. For instance, a specific excitation wavelength is required to excite a specific type of RE ion (e.g. 392 nm excitation wavelength is preferred to excite the Eu^{3+} ions while 348 nm is preferred to excite the Tb^{3+} ions). This makes excitation difficult in samples with more than one type of RE ions (e.g. to produce white light emitting sample with Eu^{3+} and Tb^{3+} ions) as different wavelengths are required to excite different types of RE ions. Furthermore, the RE ions have low absorption cross-section.

These difficulties can be overcome by using ZnO-nc nanocrystals as sensitizers to excite the RE ions. ZnO is a wide band gap semiconductor which emits light in blue and ultraviolet (UV) region of the electromagnetic spectrum. ZnO-nc have two main advantages, i) they have much higher absorption cross-section compared to the RE ions and ii) they can be excited using any wavelength above the optical band gap of ZnO-nc, hence specific excitation wavelength is not required. Thus, the ZnO-nc can be easily excited compared to the RE ions, which can then efficiently transfer the energy to RE ions, which in turn emit light through radiative de-excitation. ZnO-nc is also an attractive sensitizer as

can excite a wide variety of RE ions like Eu^{3+} , Tb^{3+} , Ce^{3+} , Er^{3+} , Yb^{3+} , Ho^{3+} and Dy^{3+} .

Although, various studies show energy transfer from ZnO-nc to Eu^{3+} ions and ZnO-nc to Tb^{3+} ions, a complete understanding of the energy transfer mechanism is still lacking to further develop energy efficient light emitting devices using these materials. For instance, studies on energy transfer contribution from ZnO-nc to RE ions, energy transfer efficiency from ZnO-nc to RE ions and effect of interaction distance between ZnO-nc and RE ions on energy transfer needs to be investigated. Furthermore, a white light emitting device using emission from ZnO-nc together with Eu^{3+} ions and Tb^{3+} ions has also not been reported.

In this work, the low cost sol-gel technique was used to develop thin film samples of ZnO-nc embedded in SiO_2 matrix co-doped with RE ions like Eu^{3+} and Tb^{3+} to address and study the above mentioned points which are currently lacking. The material characterisation was done by studying the photoluminescence (PL) emission, photoluminescence excitation (PLE) and time-resolved photoluminescence (TRPL) emission from the thin film samples.

In this work, the author clearly shows energy transfer from ZnO-nc to Eu^{3+} ions and Tb^{3+} ions. The excitation of Eu^{3+} ions through energy transfer from ZnO-nc is shown to be almost 7 times higher than the direct excitation of Eu^{3+} ions. The author also identified that the excitonic emission of ZnO-nc at 378 nm and Zn defect emission at 396 nm have the highest energy transfers contribution in exciting the Eu^{3+} ions and that the energy transfer efficiency of these emission centers were calculated to be more than 60%. Similarly, the band edge emission from ZnO-nc at 360 nm and excitonic emission at 378 nm have the highest energy transfer contribution to Tb^{3+} ions with transfer efficiency of 35%

for both the emission centers. In another study on the effect of interaction distance on the energy transfer process, it was shown that the distance of 5.11 nm between ZnO-nc and Eu^{3+} ions is the optimum distance for energy transfer. Finally, the author also fabricated a white light emitting sample in this work by combining the emission of Eu^{3+} , Tb^{3+} and ZnO-nc emissions. The concentration of Eu^{3+} and Tb^{3+} ions for the white light emitting sample was found to be 1.2 mol% and 2.4 mol%, respectively, though simulation which was confirmed by fabricating the sample.

The results from these works are important and can help in the development of future proficient red, green and white luminescent solid state devices based on a low-cost sol-gel technique. Extending these key analyses to systems with other rare earth elements will also help in making efficient light sources for wide ranging photonics applications like lasers, optical amplifiers, lighting and display technologies.

Table of Figures

Figure 2-1: Energy level diagram of Eu^{3+} ions [45].	20
Figure 2-2: Energy level diagram showing the multi-phonon emission process.	22
Figure 2-3: Illustration of concentration quenching process. The energy from an excited dopant migrates from one dopant (open circles) to another before it is non-radiatively dissipated through a quenching site (close pentagon) [47].	24
Figure 2-4: Energy level diagram representation of concentration quenching process [51].	24
Figure 2-5: A schematic representation of the radiative energy transfer process [69].	29
Figure 2-6: A graphical representation of spectral overlap of emission from a donor D and the absorption of an acceptor A.	30
Figure 2-7: An illustrative representation of the Förster resonance energy transfer process [69].	31
Figure 2-8: An illustrative representation of the Dexter energy transfer process [69].	32
Figure 3-1: A schematic diagram of the preparation steps in sol-gel process...	51
Figure 3-2: Illustration of the three steps in the spin coating technique, showing the deposition, spin and evaporation. [2]	55
Figure 3-3: Schematic representation of sol-gel fabrication steps used in this work.....	57
Figure 3-4: TEM images of ZnO-nc in SiO_2 [129].	58

Figure 3-5: The thickness of deposition of the SiO ₂ film as a function of deposition time in this work.	60
Figure 3-6: Schematic diagram of Spectrofluorometer (SPEX Fluorolog-3 Model FL3-11) [148].	63
Figure 3-7: Block diagram of a Sloan Dektak 3 surface profiler [1].	65
Figure 3-8: Schematic diagram of the TRPL system.	66
Figure 3-9: Schematic diagram showing the operating principal of Streak Camera (OptoScope SC-10) (Adopted from Hamamatsu streak camera guide)[151].	66
Figure 4-1: PL spectra of Eu ³⁺ :SiO ₂ , ZnO-nc:SiO ₂ and Eu ³⁺ _{0.12} :ZnO-nc:SiO ₂ samples. <i>Inset</i> a) and b) show, respectively, the photograph of Eu ³⁺ :SiO ₂ and Eu ³⁺ _{0.12} :ZnO-nc:SiO ₂ samples excited using a mercury vapour UV lamp.	73
Figure 4-2: (a) PLE spectra of Eu ³⁺ :SiO ₂ , ZnO-nc:SiO ₂ and Eu ³⁺ _{0.12} :ZnO-nc:SiO ₂ samples. (b) Schematic Dieke energy level diagram of the Eu ³⁺ ions in SiO ₂	75
Figure 4-3: PL spectra and 614 nm red emission intensity from the Eu ³⁺ _m :ZnO-nc:SiO ₂ samples. (a) 614 nm red emission intensity from the Eu ³⁺ _m :ZnO-nc:SiO ₂ samples as a function of Eu ³⁺ ion concentration at various annealing temperatures. (b) The PL spectra of the Eu ³⁺ _m :ZnO-nc:SiO ₂ samples RTP annealed at 450°C for various Eu ³⁺ ion concentrations. (c) The PL spectra of the Eu ³⁺ _{0.12} :ZnO-nc:SiO ₂ samples annealed by RTP at various temperatures.	78
Figure 4-4: The emission centers of ZnO-nc in (a) ZnO-nc:SiO ₂ and (b) Eu ³⁺ _{0.12} :ZnO-nc:SiO ₂ samples annealed at 450°C. See the main text for the various ZnO-nc emission centers. (c)The schematic energy level diagram of the emission centers of ZnO-nc in SiO ₂	79

Figure 4-5: An example of the spectral overlap. The spectral overlap of Zn_i to V_{Zn} defect state emission of ZnO-nc:SiO ₂ sample annealed at 450°C along with the Eu ³⁺ excitation spectrum.....	82
Figure 4-6: The intensity difference from ZnO-nc emission centers. The intensity difference between ZnO-nc:SiO ₂ and Eu ³⁺ _{0.12} :ZnO-nc:SiO ₂ samples annealed at 450°C which is due to the incorporation of Eu ³⁺ ions.....	83
Figure 4-7: A comparison of the spectral overlap integral and ZnO-nc emission intensity difference integral. The comparison for each of the seven ZnO-nc emission center for the samples annealed at 450°C.	85
Figure 4-8: PL spectra of Tb ³⁺ :SiO ₂ , ZnO-nc:SiO ₂ and Tb ³⁺ _{0.12} :ZnO-nc:SiO ₂ samples. Inset a) and b) show, respectively, the photograph of Tb ³⁺ :SiO ₂ and Tb ³⁺ _{0.12} :ZnO-nc:SiO ₂ samples excited using a mercury vapour UV lamp [153] © 2016 IEEE.	86
Figure 4-9: The PL spectra of the Tb ³⁺ _n :ZnO-nc:SiO ₂ samples RTP annealed at 450°C for various Tb ³⁺ ion concentrations [153] © 2016 IEEE.....	88
Figure 4-10: The PL spectra of the Tb ³⁺ _{0.12} :ZnO-nc:SiO ₂ samples annealed by RTP at 450°C and 500°C temperatures.....	90
Figure 4-11: The emission centers of ZnO-nc in (a) ZnO-nc:SiO ₂ and (b) Tb ³⁺ _{0.12} :ZnO-nc:SiO ₂ samples annealed at 450°C.	91
Figure 4-12: An example of the spectral overlap. The spectral overlap of Excitonic Emission center of ZnO-nc:SiO ₂ sample annealed at 450°C along with the Tb ³⁺ excitation spectrum.....	92
Figure 4-13: The intensity difference from ZnO-nc emission centers. The intensity difference between ZnO-nc:SiO ₂ and Tb ³⁺ _{0.12} :ZnO-nc:SiO ₂ samples annealed at 450°C which is due to the incorporation of Tb ³⁺ ions.....	93

Figure 4-14: A comparison of the spectral overlap integral and ZnO-nc emission intensity difference integral. The comparison for each of the seven ZnO-nc emission center for the samples annealed at 450°C.	94
Figure 4-15: The PL spectra of the $\text{Eu}^{3+}_{0.12}\text{:ZnO-nc:SiO}_2$ sample measured 5 months apart.	96
Figure 4-16: The PL spectra of the $\text{Tb}^{3+}_{0.12}\text{:ZnO-nc:SiO}_2$ sample measured 6 months apart.	97
Figure 5-1: Energy band diagram showing the energy transfer from ZnO-nc to Eu^{3+} ions in SiO_2 together with the various transitions corresponding to the emissions from ZnO-nc and Eu^{3+} ions.....	104
Figure 5-2: The time-resolved photoluminescence (TRPL) spectra of the ZnO-nc:SiO ₂ and $\text{Eu}^{3+}_{0.12}\text{:ZnO-nc:SiO}_2$ samples measured at (a) 360 nm; (b) 378 nm; (c) 396 nm; and (d) 417 nm, along with their respective stretched exponential fitting curves.	105
Figure 5-3: Transfer efficiency of ZnO nanocrystals emission centers due to the incorporation of the Eu^{3+} ions, calculated from the time-resolved photoluminescence (TRPL) spectra and steady-state photoluminescence (PL) emission data, along with their respective error bars.	112
Figure 5-4: Transfer efficiency of ZnO nanocrystals emission centers due to the incorporation of the Tb^{3+} ions, calculated from the steady-state photoluminescence (PL) emission data.....	114
Figure 6-1: Schematic diagram of the two types of samples presented in this chapter. a) A type Sample which is a single layer of SiO_2 matrix co-doped with ZnO-nc and Eu^{3+} ions b) B type Sample which is a three-layer thin film sample in	

which the ZnO-nc and Eu^{3+} ions are doped in separate layers of SiO_2 with a buffer layer of plane SiO_2 between them.....	120
Figure 6-2: Schematic diagram of ZnO-nc uniformly distributed in SiO_2 matrix.	126
Figure 6-3: Schematic diagram of Eu^{3+} ions uniformly distributed in SiO_2 matrix.	132
Figure 6-4: 614 nm PL emission intensity from the four different A_x samples along with the interaction distance between ZnO-nc and Eu^{3+} ions in these samples.....	135
Figure 6-5: 614 nm PL emission intensity from the four different A_x samples along with the interaction distance between two Eu^{3+} ions in these samples.	137
Figure 6-6: PL emission spectra of five different B_d samples with a spacer distance of 0, 2, 4, 6 and 8 nm.	138
Figure 6-7: 614 nm PL emission intensity from the five different B_d samples along with the interaction distance between ZnO-nc and Eu^{3+} ions and the interaction distance between two Eu^{3+} ions in these samples. The graph also shows the 614 nm PL emission intensity from the $A_{0.04}$ and $A_{0.12}$ samples for comparison.....	141
Figure 7-1: The PL spectra of $\text{Eu}^{3+}_0\text{Tb}^{3+}_0\text{:ZnO-nc:SiO}_2$, $\text{Eu}^{3+}_{0.03}\text{Tb}^{3+}_0\text{:ZnO-nc:SiO}_2$, $\text{Eu}^{3+}_{0.06}\text{Tb}^{3+}_0\text{:ZnO-nc:SiO}_2$ and $\text{Eu}^{3+}_{0.09}\text{Tb}^{3+}_0\text{:ZnO-nc:SiO}_2$ samples upon excitation using 325 nm excitation source.	148
Figure 7-2: The PL spectra of $\text{Eu}^{3+}_0\text{Tb}^{3+}_0\text{:ZnO-nc:SiO}_2$, $\text{Eu}^{3+}_0\text{Tb}^{3+}_{0.03}\text{:ZnO-nc:SiO}_2$, $\text{Eu}^{3+}_0\text{Tb}^{3+}_{0.06}\text{:ZnO-nc:SiO}_2$ and $\text{Eu}^{3+}_0\text{Tb}^{3+}_{0.09}\text{:ZnO-nc:SiO}_2$ samples upon excitation using 325 nm excitation source.	149

Figure 7-3: The PL spectra of $\text{Eu}^{3+}_0\text{:Tb}^{3+}_0\text{:ZnO-nc:SiO}_2$, $\text{Eu}^{3+}_{0.03}\text{:Tb}^{3+}_{0.03}\text{:ZnO-nc:SiO}_2$, $\text{Eu}^{3+}_{0.06}\text{:Tb}^{3+}_{0.06}\text{:ZnO-nc:SiO}_2$ and $\text{Eu}^{3+}_{0.09}\text{:Tb}^{3+}_{0.09}\text{:ZnO-nc:SiO}_2$ samples upon excitation using 325 nm excitation source.	150
Figure 7-4: CIE 1964 colour space plot with x and y points of $\text{Eu}^{3+}_0\text{:Tb}^{3+}_0\text{:ZnO-nc:SiO}_2$, $\text{Eu}^{3+}_m\text{:Tb}^{3+}_0\text{:ZnO-nc:SiO}_2$, $\text{Eu}^{3+}_0\text{:Tb}^{3+}_n\text{:ZnO-nc:SiO}_2$ and $\text{Eu}^{3+}_m\text{:Tb}^{3+}_n\text{:ZnO-nc:SiO}_2$ samples along with the white light point.	153
Figure 7-5: The simulated and experimental emission intensity spectra of four $\text{Eu}^{3+}_m\text{:Tb}^{3+}_n\text{:ZnO-nc:SiO}_2$ samples, namely a) $\text{Eu}^{3+}_0\text{:Tb}^{3+}_0\text{:ZnO-nc:SiO}_2$, b) $\text{Eu}^{3+}_{0.09}\text{:Tb}^{3+}_0\text{:ZnO-nc:SiO}_2$, c) $\text{Eu}^{3+}_0\text{:Tb}^{3+}_{0.09}\text{:ZnO-nc:SiO}_2$ and d) $\text{Eu}^{3+}_{0.03}\text{:Tb}^{3+}_{0.03}\text{:ZnO-nc:SiO}_2$	155
Figure 7-6: The simulated and experimental emission intensity spectra of $\text{Eu}^{3+}_{0.012}\text{:Tb}^{3+}_{0.024}\text{:ZnO-nc:SiO}_2$ sample. The inset shows the image of the sample emitting white light upon exciting the sample using 300 nm UV led light.	156
Figure 7-7: The simulated and experimental emission intensity spectra of $\text{Eu}^{3+}_{0.014}\text{:Tb}^{3+}_{0.084}\text{:ZnO-nc:SiO}_2$ sample.	157

Table of Tables

Table 4-1: Comparison of Tb^{3+} ions emission wavelength, for Tb^{3+} ions embedded in SiO_2 and Tb^{3+} ion in Dieke Diagram.	88
Table 5-1: The decay time (τ) and stretching exponential coefficient (β) values for the various ZnO-nc emission centers obtained from the time-resolved photoluminescence (TRPL) spectra of the samples with and without Eu^{3+} ions ($Eu^{3+}_{0.12}$:ZnO-nc: SiO_2 and ZnO-nc: SiO_2 samples, respectively).	107
Table 6-1: . A summary showing the names of the four different A_x samples and the five different B_d samples.	121
Table 7-1: List of 26 samples fabricated using the sol-gel process.	145
Table 7-2: CIE x, y and z chromaticity values of the twenty-four different samples used to establish the empirical equation of the PL intensity as a function of Eu^{3+} and Tb^{3+} ion concentrations.	151

Chapter 1: Introduction

1.1. Motivation

The periodic table is made up of 118 different elements, each with its own set of unique properties. Elements that share common properties are grouped together into categories such as metals, non-metals, transition elements and so on. One such group of elements titled Lanthanides or rare-earths (RE) are the focus in this research work and are discussed in depth in this Thesis.

Lanthanides are very important materials used in a wide range of industries such as defence, petroleum, bio-medical, communication, optoelectronics and so on [3]. Amongst all the applications of lanthanides, they are most extensively used in optoelectronics. The common characteristic of the 15 Lanthanides which have atomic numbers ranging from 56 to 71 is that they are a group of elements in which the 4f-orbital, that has 7 sub-orbitals, is filled with electrons. Within each sub orbital of 4f-orbital, only a maximum of two electrons can be filled. Electrons in the 4f-orbital of the lanthanides form a complex multi-electron system which is shielded by the electrons of the outer 5s and 5p orbitals. This gives the lanthanides unique optical properties such as sharp emission lines and metastable electronics states [3]. Owing to these unique properties, wide range of lanthanides are used in optical devices such as displays, lasers, LEDs, optical fiber amplifiers and fluorescent lamps [4].

For instance, Europium(3+) and Terbium (3+) ions are two such lanthanides that are commonly used in lighting and display technologies due to their sharp emission in red at 614 nm and green at 545 nm, respectively [5].

Neodymium ions, another type of lanthanides are the main constituents of the Nd:YAG laser which has an emission at 1064 nm. This laser is used for diverse applications ranging from medicine [6] to defence.

The most popular of the RE ions, is Erbium (3+) which emits at 1.54 μm [4], and it is the main component of the optical fiber amplifiers which amplifies the light signals for long-haul fibre communications. In all the optical devices that contain lanthanide ions, these ions need to be excited to emit photons. The excitation is most commonly achieved through optical excitation, usually using an external light source. When using the optical excitation, these lanthanide ions need to be excited at specific excitation wavelengths, which vary from one lanthanide ion to the other. For example the Eu^{3+} ions are preferably excited at 392 nm while the Tb^{3+} ions are preferably excited at 360nm. Moreover, these ions are not easily excited by the excitation light source. This is due to the poor absorption cross-section of the lanthanide ions. The absorption cross-section of lanthanide is in the range of 10^{-20} to 10^{-22} cm^2 [7], which is quite low.

To overcome this limitation, sensitizers [5] are used to excite the lanthanides. The sensitizers are usually species which can easily absorb the optical energy from the excitation light source and then transfer this energy to the lanthanide ions. This specific topic is the focus for this research work.

In recent years, semiconductor nanocrystals have been used as sensitizers to excite lanthanide ions. This is due to a few specific properties they exhibit, which make them the preferred choice as sensitizers. Firstly, the semiconductor nanocrystals have high absorption cross section which is in range of 10^{-15} to 10^{-18} cm^2 [8], and this is 100 to 100000 times larger than that of lanthanide ions. Secondly, the semiconductor nanocrystals have a broad excitation spectrum and hence can be easily excited at any wavelength above the optical gap of the semiconductor [9]. Thirdly, a single type of sensitizer can be used to excite multiple types of lanthanide ions. For example using zinc oxide nanocrystals, lanthanide ions like Eu^{3+} and Tb^{3+} ion can be excited

simultaneously. Moreover, the semiconductor nanocrystals also have the added advantage that they can be electrically excited, after which the semiconductor nanocrystals can then transfer the energy to excite the lanthanide ions.

Hence, due to the reasons mentioned, semiconductor nanocrystals sensitizers are preferred to excite the lanthanide ions. Semiconductor nanocrystals sensitizers of different types such as silicon, zinc oxide (ZnO), cadmium sulphide (CdS) and zinc sulphide (ZnS) have been shown to excite the lanthanide ions through energy transfer [10-12].

Amongst these different semiconductor nanocrystals, ZnO-nc have been intensively studied by various groups to understand their optical properties [13-15]. In this study, the author too has chosen zinc oxide nanocrystals (ZnO-nc). ZnO is an important semiconductor with a wide band gap of 3.37 eV. It also has a large exciton binding energy of 60 meV [16]. Moreover, ZnO-nc give a broadband emission in the blue and ultraviolet (UV) region of the electromagnetic spectrum with the emission ranging from 350 to 600 nm. Thus ZnO-nc can be used to excite a wide range of lanthanide ions like Ce^{3+} [17], Er^{3+} [18], Tb^{3+} [19, 20], Pr^{3+} [21, 22] and Eu^{3+} [9, 23-30]. Amongst these different lanthanide ions, Eu^{3+} ions and Tb^{3+} ions have been widely used for red and green emissions because of the sharp red emission at 614 nm and sharp green emission at 545 nm respectively. The Eu^{3+} ions and Tb^{3+} ions are usually either co-doped with ZnO-nc in a dielectric host matrix like SiO_2 [9, 28] or embedded inside the ZnO-nc [23-27]. Co-doping of ZnO-nc and Eu^{3+} or Tb^{3+} ions in a dielectric matrix is preferable due to the physical and chemical protection it provides to the dopants [13].

While there have been some studies reporting the energy transfer between ZnO-nc and lanthanide ions [9, 17, 18, 23-35], a comprehensive and detailed study of this energy transfer mechanism and the contribution of energy transfer especially between ZnO-nc and lanthanide ions like Eu^{3+} and Tb^{3+} ions has not been reported yet.

The areas that lack in extensive study and understanding are discussed here. Firstly, the study of the contribution of energy transfer from the various ZnO-nc emission centers like band edge emission and defect state emission to lanthanide ions like Eu^{3+} ions and Tb^{3+} ions, has not been investigated.

Secondly, the energy transfer efficiency from the various ZnO-nc emission centers to lanthanide ions like Eu^{3+} ion and Tb^{3+} ions has not been reported. The energy transfer efficiency values, similar to contribution of energy transfer, help in understanding the energy transfer mechanism from the various ZnO-nc emission centers to the lanthanide ions.

Thirdly, an important factor in the energy transfer process from ZnO-nc to lanthanide ions, is the distance of interaction among the nanocrystals and lanthanide ions. This interaction distance between the ZnO-nc and the lanthanide ions greatly affects the energy transfer from ZnO-nc to lanthanide ions and this in turn affects the emission from the lanthanide ions. A quantitative study detailing the optimum distance among the ZnO-nc and lanthanide ions has not been investigated.

Analysing these above mentioned important parameters such as interaction distance, energy transfer efficiency and contribution of energy transfer will help in better understating the energy transfer process especially between ZnO-nc and lanthanide ions such as Eu^{3+} and Tb^{3+} ions.

Furthermore, an additional area of research that has not been investigated in detail is using energy transfer from ZnO-nc to different lanthanide ions simultaneously such as Eu^{3+} and Tb^{3+} ions to create a light emitting device of any desired colour. These can be used to fabricate energy efficient white light emitting devices or light emitting devices of any desired colour, using a single excitation wavelength to excite ZnO-nc only. The desired colour can be achieved by calculating and controlling the concentration of ZnO-nc, Eu^{3+} and Tb^{3+} ions, in a single light emitting device, and hence controlling the blue emissions from ZnO-nc, red emissions from the Eu^{3+} ions and green emissions from the Tb^{3+} ions respectively. This research will help in making future energy proficient light emitting devices, which will have far reaching benefits in a wide range of industries like displays technologies, lighting applications, optoelectronics, telecommunication, defence and so on..

Hence, in this work, the author has focused on the study and investigation of the energy transfer processes from ZnO-nc to Eu^{3+} and Tb^{3+} ions to understand and obtain efficient emissions from the lanthanide ions. With these considerations the thesis work entitled 'Efficient Energy Transfer From Zinc Oxide Nanocrystals To Europium (3+) and Terbium (3+) Ions Embedded In An Oxide Matrix' is presented.

1.2. Objective

This work has six main objectives and the detailed objectives are listed as follows

1. To develop low cost sol-gel processes to fabricate thin film samples of ZnO-nc embedded in SiO_2 matrix co-doped with Eu^{3+} and thin film samples of ZnO-nc embedded in SiO_2 matrix co-doped with Tb^{3+} ions.

2. To show the energy transfer from ZnO-nc to Eu^{3+} and Tb^{3+} ions and to further maximize the emission from the lanthanide ions by optimising the fabrication parameters, such as Eu^{3+} and Tb^{3+} ion concentrations and annealing temperatures.
3. To understand the energy transfer mechanism and the contribution of energy transfer from various ZnO-nc emission centers to the Eu^{3+} ions and Tb^{3+} ions by measuring and analysing the steady state photoluminescence (PL) emission and photoluminescence excitation (PLE) spectra of the thin samples.
4. To study the energy transfer efficiency from the various ZnO-nc emission centers to Eu^{3+} and Tb^{3+} ions by measuring the time-resolved photoluminescence emission and the steady state photoluminescence emission of the samples.
5. To investigate the effect of the interaction distance among ZnO-nc and Eu^{3+} ions in the energy transfer process from ZnO-nc to Eu^{3+} ions, by creating a detailed model of the positions of the ZnO-nc and Eu^{3+} ions in the thin film samples. This model is used to derive and calculate the average shortest interaction distance between ZnO-nc and Eu^{3+} ions and average shortest interaction distance between two Eu^{3+} ions. These interactions distances are very important factors in the energy transfer from the ZnO-nc to Eu^{3+} ions and the subsequent red emission from these ions.
6. To establish a mathematical model to determine the optimum Eu^{3+} ion and Tb^{3+} ion concentrations to give white light emission or light emission of any desired colour and to develop a white light emitting thin film sample of ZnO-nc embedded in SiO_2 matrix co-doped with both Eu^{3+} and Tb^{3+} ions.

1.3. Major Contribution

The major contributions of this thesis are summarised as follows

1. In this work, firstly, the author developed thin film samples of ZnO-nc embedded in SiO₂ matrix co-doped with Eu³⁺ ions using the low-cost sol-gel process. It has been observed that, exciting the ZnO-nc at 325 nm has resulted in strong red emission at 614 nm from the Eu³⁺ ions due to energy transfer from ZnO-nc to Eu³⁺ ions. The photoluminescence excitation measurements of the samples also reveal that the excitation of Eu³⁺ ions by the energy transfer from ZnO-nc is around seven times higher than the highest direct excitation of Eu³⁺ ions at 392 nm. Furthermore, the fabrication parameters of the thin film samples were optimised in this work and it was found that the thin film sample with 12 mol% Eu³⁺ ions concentration which was annealed at 450°C annealing temperature gave the maximum red emission at 614 nm. The author has also developed thin film samples of Tb³⁺ ions and ZnO-nc embedded in SiO₂ matrix, which gives strong green emission from the Tb³⁺ ions at 545 nm due to energy transfer from ZnO-nc to Tb³⁺ ions. Similar to the study of Eu³⁺ ions samples, the green emission from the Tb³⁺ ions in the sample was also maximised by optimising the Tb³⁺ ion concentration and the sample annealing temperature. The Tb³⁺ ions samples with 12 mol% Tb³⁺ concentration annealed at 450°C gave the maximum green emission at 545 nm. The detailed discussion of these results has been presented in chapter 4 of this thesis and published in Paper-I and Paper -II listed below in page 11.
2. The author has studied the nature of the energy transfer mechanism from the ZnO-nc to the Eu³⁺ ions and ZnO-nc to the Tb³⁺ ions by analysing the photoluminescence emission and photoluminescence

excitation spectra of the sample with maximum red and green emission, respectively. For this purpose, the spectral overlap integral and the ZnO-nc emission intensity difference integral of the seven ZnO-nc emission centers were calculated and compared. It was clearly shown that excitonic emission at 378 nm and Zn defect emission center at 396 nm of the ZnO-nc contribute the highest in the energy transfer process from the ZnO-nc to Eu^{3+} ions. The oxygen defect emission centers has low energy transfer contribution to Eu^{3+} ions and experiences high energy loss to the defects induced by the incorporation of Eu^{3+} ions. However, for the energy transfer from ZnO-nc to Tb^{3+} ions, the band edge emission at 360 nm from the smallest ZnO-nc, which probably experience quantum confinement and the ZnO excitonic emission at 378 nm, have been shown to have the highest contribution to the energy transfer. The zinc defect and oxygen defect emission centers have low energy transfer contribution to Tb^{3+} ions and experience high energy loss to the defects induced by the incorporation of Tb^{3+} ions. The detailed discussion of these results has been presented in chapter 4 of this thesis and published in Paper-I and Paper -II listed below in page 11.

3. The time-resolved photoluminescence (TRPL) measurements were also analysed to calculate the energy transfer efficiencies from the various ZnO-nc emission centers to Eu^{3+} ions. The energy transfer efficiencies obtained from the decay time of the TRPL measurements were compared with the energy transfer efficiencies calculated from steady-state photoluminescence emission results for the various ZnO-nc emission centers. The results in this work show that the transfer efficiencies of the excitonic emission at 378 nm and Zn defect emission centers at 396 nm are more than 60%. The energy transfer from these

emission centers is mostly to Eu^{3+} ions which results in the radiative emission from the Eu^{3+} ions at 614 nm. The results also show that the oxygen defect emission centers have high energy transfer efficiency values. This is attributed to the energy transfer from these emission centers to the new defects created by the incorporation of the Eu^{3+} ions. The energy transfer efficiency from ZnO-nc emission centers to Tb^{3+} ions calculated from the steady-state photoluminescence emission were also studied. The results show that the ZnO band edge emission at 360 nm and excitonic emission at 378 nm transfer energy to Tb^{3+} ions with efficiency values of around 35% and this energy transfer results in radiative emission from the Tb^{3+} ions at 545 nm. On the other hand the energy transfer efficiencies of zinc defect and oxygen defect emission centers are higher in these samples, however this is due to the energy transfer from the emission center to the defects induced by the incorporation of Tb^{3+} ions. These results are consisted with the results from the energy transfer contribution study mentioned above. The details of the energy transfer efficiency analyses have been presented in chapter 5 of this thesis and published in Paper-III listed below in page 11.

4. The author also studied the effect of the average shortest interaction distance between the ZnO-nc and the Eu^{3+} ions and between two Eu^{3+} ions in the energy transfer process between ZnO-nc and Eu^{3+} ions embedded in SiO_2 matrix. A detailed model to calculate the interaction distances is developed in this work. It is clearly shown that the energy transfer from ZnO-nc to Eu^{3+} ions is higher with shorter average distance between ZnO-nc and Eu^{3+} ions. For the samples in this work, the average distance of 5.11 nm between the ZnO-nc and Eu^{3+} ions has been found to give maximum red emission at 614 nm due to the energy transfer

from ZnO-nc to Eu^{3+} ions. A competing process known as Eu^{3+} ion concentration quenching dominates as the average distance between two Eu^{3+} ions reduces below 0.57 nm which results in reduction of 614 nm emission from the Eu^{3+} ions. It is also shown that the radiative energy transfer from ZnO-nc to Eu^{3+} ions mostly occur when the average shortest interaction distance between the ZnO-nc and Eu^{3+} ions is 6.53 nm or greater. The details of this model and the discussion based on the calculation have been presented in chapter 6 of this thesis and published in Paper-IV listed below in page 11.

5. Finally, the author developed thin film samples of ZnO-nc in SiO_2 co-doped with both the RE ions of Eu^{3+} and Tb^{3+} , to produce white light emitting samples. The blue emission from ZnO-nc is combined with the red and green emissions from Eu^{3+} ions and Tb^{3+} ions, respectively to create a white light emitting sample. This was achieved by developing a polynomial equation to model and simulate the emission spectra of the thin film samples as a function of Eu^{3+} and Tb^{3+} ion concentrations. The polynomial equation together with the CIE xyz chromaticity values was then used to find the optimum concentration of Eu^{3+} and Tb^{3+} ions which gives a white light (or any other desired colour) emitting thin film sample. A sample with 1.2 mol% of Eu^{3+} ions and 2.4 mol% of Tb^{3+} ions was found to give white light emission and this was confirmed by fabricating the sample which indeed gave white light emission. The details of this analysis and the results of this work have been presented in chapter 8 of this thesis and published in Paper-V listed below in page 11.

The publications consisting all the major contributions and results mentioned above, are listed as follows:

[Paper-I] V. Mangalam, K. Pita, and C. Couteau, "Study of energy transfer mechanism from ZnO nanocrystals to Eu^{3+} ions," *Nanoscale Research Letters*, journal article vol. 11, no. 1, pp. 1-9, 2016.

[Paper-II] V. Mangalam and K. Pita, "Energy transfer from ZnO nanocrystals to Terbium ($3+$) ions: A spectral overlap study," presented at the 2016 IEEE Photonics Conference (IPC), Hawaii USA, 2-6 Oct. 2016, 2016.

[Paper-III] V. Mangalam and K. Pita, "Energy Transfer Efficiency from ZnO-Nanocrystals to Eu^{3+} Ions Embedded in SiO_2 Film for Emission at 614 nm," *Materials*, vol. 10, no. 8, p. 930, 2017.

[Paper-IV] V. Mangalam and K. Pita, "Effect of the interaction distance on 614 nm red emission from Eu^{3+} ions due to the energy transfer from ZnO-nc to Eu^{3+} ions," *Optical Materials Express*, vol. 8, no. 10, pp. 3115-3132, 2018/10/01 2018.

[Paper-V] Mangalam, V.; Pita, K. White light emission from thin-film samples of zno nanocrystals, Eu^{3+} and Tb^{3+} ions embedded in an SiO_2 matrix. *Materials* 2019, 12, 1997.

1.4. Organisation of Thesis

This thesis consists of eight chapters and its organisation is as follows:

Chapter 1 is the 'Introduction' for this work. It begins with the 'Motivation' followed by the 'Objective' of this work. This chapter also includes the 'Main Contribution' of this work. The chapter ends with the 'Organisation of Thesis' section.

Chapter 2 is 'Literature Review'. In this chapter, the basic principles of lanthanide ion emissions, energy transfer process, energy transfer efficiency and CIE chromaticity are discussed. The author also reviews the current works

on semiconductor nanocrystals, especially ZnO-nc, used as sensitizers to excite the lanthanide ions. The author also briefly reviews the studies on lanthanide ions used as phosphor, especially Eu^{3+} ions and Tb^{3+} ions and also the studies which present the origin of emission centres in ZnO-nc.

Chapter 3 is the 'Sample Preparation and Characterization Techniques'. In this chapter, the author provides details about the sol-gel and RF magnetron sputtering fabrication techniques and also includes the theory of the various characterisation techniques used in this work.

Chapter 4 is titled, 'Study of Energy Transfer Contribution from ZnO-nanocrystals to Eu^{3+} ions and ZnO-nanocrystals to Tb^{3+} ions'. In this chapter, the author studies the contribution of energy transfer from the various ZnO-nc emission centers to the Eu^{3+} ions and Tb^{3+} ions by calculating the spectral overlap integral and PL emission intensity difference integral of the ZnO-nc emission centers. The author also discusses the results of fabrication parameters like the lanthanide ion concentration and sample annealing temperature in this chapter. These results have been published in *Nanoscale Research Letters* (V. Mangalam, K. Pita, and C. Couteau, "Study of energy transfer mechanism from ZnO nanocrystals to Eu^{3+} ions," *Nanoscale Research Letters*, journal article vol. 11, no. 1, pp. 1-9, 2016) and 2016 IEEE Photonics Conference (IPC) (V. Mangalam and K. Pita, "Energy transfer from ZnO nanocrystals to Terbium ($3+$) ions: A spectral overlap study," in *2016 IEEE Photonics* © 2016 IEEE).

In Chapter 5, titled 'Energy Transfer Efficiency from ZnO-nanocrystals to Eu^{3+} ions and ZnO-nanocrystals to Tb^{3+} ions', the author discusses the results of energy transfer efficiency of the various ZnO-nc emission centers to Eu^{3+} ions and Tb^{3+} ions calculated from the time-resolved photoluminescence emission

and the steady state photoluminescence emission of the samples. The results have been published in Materials (V. Mangalam and K. Pita, "Energy Transfer Efficiency from ZnO-Nanocrystals to Eu³⁺ Ions Embedded in SiO₂ Film for Emission at 614 nm," *Materials*, vol. 10, no. 8, p. 930, 2017.)

Chapter 6 is the 'Study of Interaction Distance among ZnO-nanocrystals and Eu³⁺ ions'. In this chapter, the author presents a quantitative measure and the effect of interaction distance among ZnO-nc and Eu³⁺ ions in the energy transfer process from ZnO-nc to Eu³⁺ ions. The results have been published in Optical Materials Express (V. Mangalam and K. Pita, "Effect of the interaction distance on 614 nm red emission from Eu³⁺ ions due to the energy transfer from ZnO-nc to Eu³⁺ ions," *Optical Materials Express*, vol. 8, no. 10, pp. 3115-3132, 2018/10/01 2018.)

Chapter 7 is titled, 'White light Emission from ZnO Nanocrystals co-doped with Eu³⁺ and Tb³⁺ ions in SiO₂'. In this chapter, a white light emitting thin film sample of ZnO-nc in SiO₂ co-doped with Eu³⁺ and Tb³⁺ ions is developed based on an equation to predict the emission from the sample. The results are being submitted for publication in a reputable international journal.

Finally, in chapter 8, 'Conclusion and Recommendations', the author presents the conclusion of this work based on the results of this study and provides recommendations for future work in this topic.

Chapter 2: Literature Review

2.1. Introduction

In this chapter, the author presents some of the basic principles of the concepts used in this work along with the literature review of the current studies. The chapter begins with a section on lanthanide rare earth elements in which the electronic configuration, electronic state and luminescence of lanthanide rare earth ions is presented. The author also presents the choice of Eu^{3+} and Tb^{3+} ions used in this work. This is followed by a section on semiconductor nanocrystals as sensitizers and zinc oxide nanocrystals as sensitizers and the current research on these topics are presented. These sections focus on the review of the current literature which use semiconductor nanocrystals such as silicon, cadmium sulphide, zinc sulphide and zinc oxide to excite the lanthanide rare earth ions. The author focuses on the literature review of the energy transfer from Zinc oxide nanocrystals to lanthanide ions especially Europium (3+) and Terbium (3+) ions. The chapter ends with a section on the theory of CIE chromaticity, which is used in the study of fabrication of white light emitting thin film samples.

2.2. Lanthanide Rare Earth Element

Lanthanide rare earth elements are a group of elements that have atomic numbers ranging from 57 to 71. These elements, namely Lanthanum (La) to Lutetium (Lu), along with Scandium (Sc; atomic number 21) and Yttrium (Y; atomic number 39) make up the 17 lanthanide rare earth elements. The ions of these elements are also used in optical materials such as phosphors, where they form the optically active centers. The lanthanide rare earth ions in the phosphors emit light or photons when they are excited by light. The luminescence of lanthanide ions is unique compared to other elements of the

periodic table. This luminescence is better understood by first understanding the electronic configuration and the electronic state of the lanthanide rare earth ions.

The author gives a detailed description of the electronic configuration and the electronic state of the lanthanide rare earth ions in section 2.2.1 and section 2.2.2, respectively. This is followed by section 2.2.3, where the author discusses the basic principles of luminescence from the lanthanide rare earth ions which include reviews on radiative and non-radiative relaxation in lanthanide rare earth ions. The author also presents the choice of Eu^{3+} and Tb^{3+} ions used in this work and details the current research on rare-earth ion as luminescent materials or phosphors, in section 2.2.4. The author will refer to the lanthanide rare earth ions as lanthanide ions for convenience in the sections 2.2.1, 2.2.2, 2.2.3 and 2.2.4.

2.2.1. Electronic Configuration

The lanthanide atoms are the first set of elements in which the $4f$ orbitals are progressively filled with electrons starting from Cerium (Ce) all the way to Lutetium (Lu).

The trivalent ions of lanthanide atoms are formed when a neutral atom oxidizes by losing three electrons from the valence orbital, namely the two electrons from $6s$ and one electron from either $5d$ or $4f$ orbitals. The general electronic configuration of the trivalent lanthanide ion is written as [36]:

$$1s^2 2s^2 2p^6 3s^2 3p^6 3d^{10} 4s^2 4p^6 4d^{10} 4f^{n-1} 5s^2 5p^6 \quad (2.1)$$

The electrons in the incompletely filled $4f$ orbitals of the trivalent ions are the optically active electrons in these ions. These electrons in the $4f$ orbital absorb the energy upon excitation and transition to a higher state. The $4f$ electrons in the excited state then radiatively relax back to the ground state which results

in the photon emission from the lanthanide ions. The radiative relaxation of the $4f$ electrons results in sharp emission peaks with narrow bandwidth from the lanthanide ions. This is because the $4f$ orbital electrons are shielded by the outer $5s$ and $5p$ orbitals which result in discrete energy levels of $4f$ orbital electrons that are less affected by the field of the surrounding host material in which the lanthanide ions are embedded. These result in the sharp emission peaks from the $4f$ electrons of the lanthanide ions. Since the $4f$ electrons give rise to the interesting luminescence properties of these ions [37] and are solely responsible for the emission from the lanthanide ions, they are referred to as the $f-f$ transition.

2.2.2. Electronic States of Trivalent Lanthanide Ions

The electrons in the $4f$ orbital of the trivalent lanthanide ions transition from one electronic state to another during $f-f$ transition. The electronic states of the lanthanide ion are nothing but the energy levels of the ion. A figure showing this energy level of all the trivalent lanthanide ions was created by Dieke and his associates [38] and it has been named the 'Dieke Diagram' in his honor. The Dieke Diagram is essentially the energy level diagram of Lanthanide ($3+$) ions in Lanthanum trichloride (LaCl_3) [39]. Dieke Diagram clearly shows that each and every trivalent lanthanide ions have multiple electronic state and in this section the author explains the origin and the construction of these electronic states.

The electronic state of the atom or ions, including lanthanide ion, is described using quantum theory. In this theory, the electronic states are calculated based on the interactions of the electrons in the system. The electronic states of the trivalent lanthanide ions are commonly attributed to four different types of interactions [40], namely

- Potential energy between electron and nucleus and electron kinetics motion
- Coulomb and exchange interaction between electrons
- Spin orbit interaction
- Crystal field

To mathematically calculate the electronic state of a system, the Schrödinger equation is used in quantum theory and the Hamiltonian in the Schrödinger equation, which is a mathematical operator, corresponds to the total energy of a given system. For a lanthanide ion in a host material which has four interactions mentioned above, the Hamiltonian can be written as [41]:

$$H_L = H_0 + H_{ee} + H_{SL} + H_{CF} \quad (2.2)$$

where H_L is the total Hamiltonian of the system of lanthanide ions in a host material, H_0 is the Hamiltonian of the potential energy between electron and nucleus and electron kinetics motion, H_{ee} is the Hamiltonian of the coulomb and exchange interaction between electrons, H_{SL} is the Hamiltonian of the spin orbit interaction and H_{CF} is the Hamiltonian of the crystal field interaction. The first three interactions in equation (2.2), namely H_0 , H_{ee} and H_{SL} , correspond to the Hamiltonian of the free lanthanide ion while H_{CF} accounts for the effect of host material on the electronic state of lanthanide ion. The effect of these interactions is briefly described as follows [40, 42, 43]:

- H_0 results in the (ns, np, nd, nf) electron configuration of the atom
- H_{ee} leads to LS terms which is a result of the splitting of the $4f^n$ configuration
- H_{SL} leads to the splitting of LS terms into multiple levels
- H_{CF} splits the levels of free lanthanide ions, where ions with total angular momentum (J) is split into $(2J + 1)$ distinct sublevels

The electronic states of the lanthanide atoms and ions are represented using the notation

$$^{2S+1}L_J$$

where L is the total orbital angular momentum quantum number and S is the total spin quantum number. In a multi-electron atom, the orbital angular momentum quantum number and the spin quantum number of individual electrons, respectively, couples to form the total orbital angular momentum quantum number and total spin quantum number.

In this notation, L is comparable or equivalent to the possible values of orbital quantum number for a multi-electron atom, denoted by l' . The possible values of l' can be mathematically written as:

$$l' = |l_1 \pm l_2 \pm \dots \pm l_N|_{min}, |l_1 \pm l_2 \pm \dots \pm l_N|_{min} + 1, \\ \dots \dots \dots, |l_1 \pm l_2 \pm \dots \pm l_N|_{max} \quad (2.3)$$

where l is the orbital quantum number of individual electrons, N represent the optically active electrons in the atom and the modulus implies that only positive values of l' are allowed.

Similar to total orbital angular momentum quantum number (L), the total spin quantum number (S) is comparable or equivalent to the possible values of spin quantum number for a multi-electron atom, denoted by s' . The possible values of s' can be mathematically written as:

$$s' = |s_1 \pm s_2 \pm \dots \pm s_N|_{min}, |s_1 \pm s_2 \pm \dots \pm s_N|_{min} + 1, \\ \dots \dots \dots, |s_1 \pm s_2 \pm \dots \pm s_N|_{max} \quad (2.4)$$

where s is the spin quantum number of individual electrons and again the modulus implies that only positive values of s' are allowed.

In this notation, J is the total angular momentum quantum number which is comparable or equivalent to the possible values j' . The possible values of j' is derived from l' and s' as shown in the equation below

$$j' = |s' - l'|, |s' - l'| + 1, \dots, |s' + l'| \quad (2.5)$$

The electronic states of the lanthanide atoms and ions are represented using the notation, $^{2S+1}L_J$ [42, 44]. as they have numerous electrons which are optically active in the $4f$ orbital. The Dieke diagram shows the electronic states of all the trivalent lanthanide ions represented using this notation which is unique to multi-electron atoms or ions.

2.2.3. Luminescence

Luminescence is a general phenomenon of a material in which light is emitted from the material when it is excited using an external source. The electrons in the material are excited from the ground state to higher energy states when an external source is used for excitation. The excited electrons subsequently relax from the higher energy state to the ground state, radiatively by emitting photons. This process is called luminescence and it is specifically called photoluminescence when the external excitation source is a light source.

Photoluminescence is observed in most of the lanthanide ions. The optically active electrons in the trivalent lanthanide ions are excited from the ground state to the higher energy states upon excitation. In lanthanide ions, the excitation energy should be precisely equal to the energy difference between the ground state and excited state. For example, to excite the Eu^{3+} ions from its ground state of 7F_0 to higher energy state of 5L_6 , the ions should be excited at exactly 392 nm. This excitation process is illustrated in Figure 2-1 which shows the energy level diagram of Eu^{3+} ions. The excited lanthanide ions relax back to

ground state through a series of radiative and non-radiative relaxation processes.

Figure 2-1: Energy level diagram of Eu³⁺ ions [45].

The radiative relaxation processes results in the emission of photons from the excited lanthanide ion as it transitions from a higher energy state to lower energy state. The wavelength of the photon is precisely equal to the energy difference of the two levels. In the example of excited Eu³⁺ ions, the luminescence is predominantly due to the radiative relaxation from the ⁵D₀ state to ⁷F₂ state which results in the emission at 614 nm from the Eu³⁺ ions. This common process of photoluminescence is same in the other lanthanide ions including Tb³⁺ ions.

2.2.3.1. Radiative Relaxation vs. Non-Radiative Relaxation

Radiative and non-radiative relaxations are processes through which an excited atom or ion losses its energy [37]. The excited atom or ion transitions from a higher energy state to a lower energy state through these relaxation processes. Even though both these processes help in the relaxation of an excited atom or ion, radiative and non-radiative relaxation processes are

different. The radiative relaxation is a process in which energy is released from an excited material through emission of photons or light. On the other hand, during non-radiative relaxation process no photon is released. The energy from an excited material is released through the defects or through the generation of phonons in the material. The radiative and non-radiative relaxation processes are competing processes. Thus, to maximise luminescence from an excited atom or ion, the radiative relaxation process should be maximised and the non-radiative relaxation process should be minimised. In the lanthanide ions the non-radiative relaxation is mostly due to two types of processes, namely multi-phonon emission or emission through the defects due to concentration quenching. The author describes these two processes in detail in the following sections.

2.2.3.2. Multi-Phonon Emission

The atoms in any crystal vibrate about their mean position. The phonons are the quantised lattice vibrations or the quantised lattice wave in a crystal [46]. During the non-radiative relaxation process, phonons or lattice vibrations are generated which results in the production of heat [37]. The number of phonons involved in the non-radiative relaxation process depends on the energy separation between the higher energy state and lower energy state in an excited atom or ion and also on the energy of the phonon. In certain cases the dissipation of energy occurs through a single phonon relaxation and in other cases it occurs through multiple phonon relaxations. A single phonon emission is sufficient to relax an excited atom when the separation of energy between the excited state and the lower state is small and the energy of phonon is large. On the contrary, when the separation of energy between the excited state and the lower state is large and the energy of a single phonon is not large enough, then multi-phonon relaxation takes place. During multi-

phonon emission, the separation of energy between the excited state and the lower state is bridged through the emission of several numbers of phonons simultaneously [47]. An illustration of multi-phonon emission is shown in Figure 2-2.

Figure 2-2: Energy level diagram showing the multi-phonon emission process.

The probability of multi-phonon emission can be mathematically written using the following equation [37, 38, 48, 49]

$$W = Be^{-\alpha\Delta E} \quad (2.6)$$

where W is the multi-phonon transition probability, B and α are constants which depend on the host material. ΔE is the separation of energy which can be written as

$$\Delta E = \sum p_i \hbar\omega \quad (2.7)$$

where p_i is the number of effective phonons and $\hbar\omega$ is the energy of the phonon. The equation clearly shows the dependence of multi-phonon emission on the separation of energy between the excited state and lower state and the energy of a single phonon.

In an excited atom or ion, the non-radiative relaxation through phonon emission dominates in host materials with higher phonon energy. The high

phonon energy of the host material can absorb the excited energy of the dopant atoms or ions like lanthanide ions, which results in reduced luminescence from the excited atoms or ions. Multiple phonons are required to de-excite an atom or ion when the energy difference between the excited state and the lower state of an atom or ion is higher than the energy of a single phonon. The critical number of phonons for multi-phonon emission is generally limited to five phonons and above this number, the relaxation process is dominated by radiative emission [38].

The non-radiative relaxation through phonon emissions involving defects is also observed in host materials with defects. The defects can be in form of impurities, crystal defects or surface defects. These defects provide intermediate state between the excited state and the lower state for electrons to occupy. This results in the non-radiative relaxation of an excited atom by phonon emission through the intermediate defect states. This is an important reason to eliminate defects from the host material to improve the radiative emission.

2.2.3.3. Concentration Quenching

Concentration quenching is another relaxation process in which the energy from an atom (or ion) is dissipated non-radiatively, because of high concentration of the atom or ion, which results in the reduction of luminescence from the excited atom or ion. Concentration quenching is a process which affects the luminescence of dopant materials, like lanthanide ions, depending on the concentration of the dopant. As the concentration of the dopant material increases, the luminescence from the dopant also increases initially. However, beyond a critical concentration the luminescence from the dopant material decreases with increasing concentration [36, 37].

This phenomenon is called concentration quenching. In the concentration quenching process the energy of an excited dopant atom (or ion) is non-radiatively transferred to the adjacent dopant atom (or ion) of the same species. This energy transfer process is continuous from one dopant atom (or ion) to another until the energy is dissipated through the quenching sites in the host material. The quenching sites are usually the impurities or the defect centers in the host material, where the excitation energy is non-radiatively dissipated [37, 41, 50]. The concentration quenching process is illustrated in Figure 2-3 and 2-4.

Figure 2-3: Illustration of concentration quenching process. The energy from an excited dopant migrates from one dopant (open circles) to another before it is non-radiatively dissipated through a quenching site (close pentagon) [47].

Figure 2-4: Energy level diagram representation of concentration quenching process [51].

The probability of migration of energy between dopants is inversely proportional to d^6 , where d is the distance between adjacent dopants [36]. It

is clear from this simple relation that the migration of energy between dopant atoms (or ions) increases with decreasing distance between adjacent dopant atoms (or ions). The distance between adjacent dopant atoms (or ions) decreases with increasing concentration of the dopants. Thus, the concentration quenching process increases with increasing concentration of the dopant atoms (or ions) which results in the reduction of luminescence from the excited dopant atom (or ion).

In this work, the concentration quenching phenomenon is observed in lanthanide ions like Eu^{3+} and Tb^{3+} , which show reduction in photoluminescence with increasing concentration of the lanthanide ions. The results of concentration quenching are presented in detail in section 4.4.1 and section 4.4.2 of chapter 4. The author also determines the distance between the Eu^{3+} ions at which concentration quenching of Eu^{3+} emission occurs. These results have been presented in chapter 6.

2.2.4. The Choice of Eu^{3+} and Tb^{3+} ions

In this section, the author justifies the choice of lanthanides ions used in this work. The author chose Eu^{3+} ions and Tb^{3+} ions as the lanthanide ions for the study of energy transfer from ZnO-nc. The Eu^{3+} ion is one of the most widely used lanthanide ions because of its use as a red phosphor, which has a variety of commercial applications such as in florescent lamps, LCD backlighting, white light sources , plasma television and so on [52-54]. The Eu^{3+} ion is the most commonly used red emitter, due to its sharp red emission at 614 nm [53]. The other lanthanide ion chosen in this study is Tb^{3+} ion because it is the most commonly used green emitter due to its sharp green emission at 545 nm [53]. Similar to Eu^{3+} ion, Tb^{3+} ion is also used in commercial applications such as in florescent lamps, LCD backlighting, white light sources, plasma televisions and

so on [52-54], as a green phosphor. Moreover, the red emission from the Eu^{3+} ions and the green emission from the Tb^{3+} ions can be combined with blue emission from other materials like ZnO nanocrystals to create a white light emitting device. This is one of the reasons that Eu^{3+} ions and Tb^{3+} ions were chosen in this study.

Interestingly, even though these phosphors are being widely used in a variety of commercial devices, there are a number of studies on Eu^{3+} ion based red phosphors and Tb^{3+} ion based green phosphors to improve their efficiencies, even today. Studies to improve the red emission efficiency from the Eu^{3+} ions have been reported by Ko *et al.* [55], Ran *et al.* [56], Li *et al.* [57], Park *et al.* [58] and Kalidasan *et al.* [59]. While studies to improve the green emission efficiency from the Tb^{3+} ions have been reported by Zeng *et al.* [60], Wani *et al.* [61], Bharat *et al.* [62], Reddy *et al.* [63] and Singh *et al.* [64]. In most of these studies, the host material in which the lanthanide ions are doped is varied to help improve the efficiency of emission from the lanthanide ions. To explain further, lanthanide ions are doped in host materials with low phonon energy to reduce the non-radiative emission, thus improving the radiative emission from the lanthanide ions. Different host materials such as Y_2SiO_5 [55], MgMoO_4 [56], $\text{Ca}_3\text{Al}_2\text{O}_6$ [58], $\text{Li}_2\text{BaP}_2\text{O}_7$ [61] and Y_6WO_{12} [62] were used in these studies to improve the radiative emission from the lanthanide ions, namely Eu^{3+} and Tb^{3+} . In some of these studies, co-dopants like Li^+ [57] and Bi^{3+} [56] were used to transfer energy to the lanthanide ions to improve the efficiency of emission from the lanthanide ions.

Another way to improve the efficiency of emission from lanthanide ions is by using semiconductor nanocrystals to excite the lanthanide ions [65]. In fact, since the late 1990's there has been a lot of research to study the energy

transfer from semiconductor nanocrystals to lanthanide ions to improve the efficiency of emission from the lanthanide ions. The author presents energy transfer from semiconductor nanocrystals to lanthanide ions in detail, in section 2.3 and 2.4.

2.3. Semiconductor Nanocrystals

Semiconductors are an important class of materials which are widely used today. Their electrical and optical properties enable us to create and fabricate many important electronic and photonic devices. In the last couple of decades, a new class of materials called semiconductor nanocrystals have been fabricated and extensively studied because of their unique intrinsic properties. These nanometer sized crystals of semiconductors have properties that are different from those of bulk semiconductor crystals. They display, size dependent electronic and optical properties, which help in tuning the emission from the nanocrystal based on its size [66, 67]. These unique properties of semiconductor nanocrystals have resulted in them being used in a broad range of applications such as in solar cells, optoelectronic devices, imaging and ultrasensitive detection [66]. These tiny particles have also been used as sensitizers to excite the lanthanide ions through the energy transfer process.

In this section, the author presents a review of the work on semiconductor nanocrystals used as sensitizers to excite the lanthanide ions. This section does not include the review of work which uses ZnO-nc as sensitizers, as this is presented in detail in section 2.4. The author first presents the basic principles of the energy transfer process in section 2.3.1, where the different type of energy transfer processes are presented in detail. This is followed by the literature review of semiconductor nanocrystals used as sensitizers to excite the lanthanide ions in section 2.3.2.

2.3.1. Energy Transfer

A particle or species (which could be an atom or ion or nanocrystal), can make transitions from its ground state to the excited state when it is excited by light, at a specific excitation wavelength. The particle absorbs the energy of the photon during this process and then relaxes back to its lowest energy state or the ground state, in numerous different ways. Two different ways in which an excited particle relaxes from the excited state to the ground state is through radiative and non-radiative relaxation processes, which have been explained by the author in section 2.2.3.1 earlier.

Energy transfer is another process in which an excited particle relaxes from the excited state to the ground/lower state. In the energy transfer process, the excited particle relaxes back to the ground state by transferring its energy to an adjacent particle. In general, the energy transfer process can be divided into two different types, namely radiative energy transfer process and non-radiative energy transfer process. The two different energy transfer processes are presented in detail in section 2.3.1.1 and 2.3.1.2, respectively.

In section 2.3.1.1 and section 2.3.1.2, the author presents the energy transfer process by considering the energy transfer between two different types of species of dopants. The dopants can be in the form of an atom or ion or nanocrystal. The two different dopants are referred to as dopant D and dopant A. Dopant D is called a donor (hence, represented using the letter D) because this is the dopant which receives the excitation energy and transfers the energy to dopant A. Dopant A is called an acceptor (hence, represented using the letter A) because this is the dopant which receives the energy transferred from the donor and finally emits this energy as photons [68]. The dopant D and dopant A are separated from each other by a certain distance, which is an important factor that affects the energy transfer process. The excited state of

the dopants is represented by an (*). Thus, the excited state of dopant D is represented as D^* and the excited state of dopant A is represented as A^* .

2.3.1.1. Radiative Energy Transfer

Radiative energy transfer is a process in which the energy is transferred from the donor to acceptor through photons. The excited donors species (D^*) relaxes by emitting photons which are absorbed by the acceptor species (A). This results in the transition of the donor species from the excited state (D^*) to the ground state (D) and also the transition of the acceptor species from the ground state (A) to the excited state (A^*). A general schematic representation of the radiative energy transfer process between two species is shown in Figure 2-5 [68]. In this figure, the red and grey circles represent a particle or species (which is either an atom, ion or nanocrystals) in the excited and lower states, respectively.

Figure 2-5: A schematic representation of the radiative energy transfer process [69].

Unlike the non-radiative energy transfer process, the radiative energy transfer process does not require the interaction between the donor and acceptor species. Thus, radiative energy transfer does not depend on the distance between the donor and acceptor and can occur even when the distance between the two species is relatively large. The radiative energy transfer primarily depends on the spectral overlap of the emission spectra of excited dopant D^* and absorption spectra of ground state dopant A. In the region of

spectral overlap, the emission intensity of the excited donor D^* decreases and this energy is transferred to acceptor A. The acceptor A in turn emits this energy as its own characteristics emission [68, 70, 71]. A graphical representation of spectral overlap of emission from a donor D and the absorption of an acceptor A is shown in Figure 2-6.

Figure 2-6: A graphical representation of spectral overlap of emission from a donor D and the absorption of an acceptor A.

The integral of the region of spectral overlap gives a measure of the radiative energy transfer process. The spectral overlap integral is mathematically written as

$$J = \int_0^{\infty} I_D(\lambda)A_A(\lambda)d\lambda \quad (2.8)$$

where J is the spectral overlap integral value, I_D is the intensity of emission of the excited donor D^* and A_A is the absorbance of the acceptor dopant A [72].

The author uses this analysis of spectral overlap integral to study the energy transfer contribution from ZnO-nc to Eu^{3+} ions and ZnO-nc to Tb^{3+} ions. These results have been presented in chapter 4.

2.3.1.2. Non-Radiative Energy Transfer

In the non-radiative energy transfer process, the energy is transferred from the excited dopant (D^*) to the acceptor (A) without emission of photons from the dopant D. The energy is transferred as result of an interaction between the two dopants (D and A). The interactions between the dopants could be in the form of electrostatic interaction (Coulombic interaction) or exchange interaction [69].

The electrostatic interaction based non-radiative energy transfer is also called Förster resonance energy transfer (FRET) [73], named after Theodor Förster who first proposed this energy transfer process. In FRET, the excited electron in dopant D^* de-excites to the ground state and simultaneously transfers the energy to the acceptor dopant A through Coulombic interaction. The electron in the ground state of dopant A absorbs the transferred energy and is promoted to the excited state. Figure 2-7 shows an illustrative representation of the FRET process. Similar to Figure 2-5, in this figure the red and grey circles also represent a particle or species (which is either an atom, ion or nanocrystals) in the excited and lower state, respectively.

Figure 2-7: An illustrative representation of the Förster resonance energy transfer process [69].

The non-radiative energy transfer process could also occur through the exchange interaction between dopant D and A. In this process, exchange of two electrons between dopant D^* and dopant A result in the energy transfer

between the two species. Specifically, an excited electron from the donor D^* is transferred to the excited state of the dopant A, while another electron from the ground state of dopant A is transferred back to the ground state of dopant D. Figure 2-8 shows an illustrative representation of this energy transfer process. Again similar to the above figures, in this figure the red and grey circles also represent a particle or species (which is either an atom, ion or nanocrystals) in the excited and lower states, respectively. Energy transfer through exchange interaction was first proposed by D. L. Dexter and hence this energy transfer process is also called Dexter energy transfer process [74].

Figure 2-8: An illustrative representation of the Dexter energy transfer process [69].

In both the above mentioned non-radiative energy transfer processes, the distance between the donor D and acceptor A is a critical factor which greatly affects the energy transfer. The probability of non-radiative energy transfer process is inversely proportional to the distance between dopant D and dopant A [68]. The distance between dopant D and A should be small for the electrostatic interaction or exchange interaction to occur between the two dopants. Thus, the non-radiative energy transfer increases as the distance between the two dopant decreases. The dopant A excited through the energy transfer process emits photons as its own characteristics emission [68], similar to the dopant A excited through the radiative energy transfer process.

In this work, the energy transfer between ZnO-nc (donor dopant) and Eu^{3+} (acceptor dopant) and the energy transfer between ZnO-nc and Tb^{3+} (acceptor dopant), occurs through both radiative and non-radiative energy transfer processes. The author presents the study on the radiative and non-radiative energy transfer process between ZnO-nc and Eu^{3+} ions and between ZnO-nc and Tb^{3+} ions in chapter 4, 5 and 6.

2.3.1.3. Energy Transfer Efficiency

In this section, the author presents the discussion on a quantitative measure of the energy transfer process, namely energy transfer efficiency.

In the energy transfer process, the energy of the excited dopant D^* is transferred to dopant A. The excited dopant D^* could also relax back to the ground state through radiative and non-radiative relaxation processes, together with the energy transfer process. Thus, the energy transfer efficiency can be defined as the rate of the energy transfer to the rate of all the relaxation processes. Hence, mathematically, the energy transfer efficiency, denoted by the symbol E_T , can be written as

$$\text{Transfer efficiency } (E_T) = \frac{\Gamma^{tr}}{\Gamma^r + \Gamma^{nr} + \Gamma^{tr}} \quad (2.9)$$

where Γ^{tr} is the rate of energy transfer from an excited donor to acceptor, Γ^r is the rate of radiative emission of the excited donor and Γ^{nr} is the rate of non-radiative emission of the excited donor.

The energy transfer efficiency of a donor and acceptor pair can be calculated either from the steady-state photoluminescence emission or from the time-resolved photoluminescence emission of the donor. The author presents detailed discussions on the method to calculate the energy transfer efficiency from both the steady-state photoluminescence emission and the time-resolved

photoluminescence emission in chapter 5. In chapter 5, the author also presents the efficiency of energy transfer from ZnO-nc (donor in this work) to lanthanide ions like Eu^{3+} and Tb^{3+} (acceptor in this work) calculated using the two different methods.

2.3.2. Current Research on Semiconductor Nanocrystals as Sensitizers

The semiconductor nanocrystals use the energy transfer process presented above to excite the lanthanide ions. A wide variety of semiconductor nanocrystals have been shown to excite a variety of lanthanide ions. Semiconductor nanocrystals like Silicon (Si), Cadmium Selenide (CdSe), Cadmium sulphide (CdS), Zinc Sulphide (ZnS), Zinc Oxide (ZnO) have been shown to excite lanthanide ions such as Eu^{3+} , Tb^{3+} , Er^{3+} , Hm^{3+} , Ce^{3+} , Nd^{3+} , etc. In this section, the author reviews the studies on energy transfer from some of the semiconductor nanocrystals like Si-nc, CdS-nc and ZnS-nc.

This is followed by a detailed review of the semiconductor nanocrystal used in this work, which is ZnO-nc, in section 2.4.

2.3.2.1. Silicon nanocrystals

Silicon nanocrystals (Si-nc) were one of the first semiconductor nanocrystals to be used sensitizers to excite the lanthanide ions. Excitation of Er^{3+} ion through energy transfer from Si-nc has been reported as early as 1997 Fujii *et. al.* [65]. In this work by Fujii *et. al.*, it was reported that the emission from the silicon nanocrystal at 810 nm excites the Er^{3+} , which in turn gives its characteristic emission at 1540 nm. Since then, there has been many reports on the study of energy transfer from Si-nc to Er^{3+} ions [75-81] and other lanthanide ions like Nd^{3+} , Tm^{3+} and Yb^{3+} [82]. The main aim of these studies initially was to create an efficient silicon based light emitting device [82]. However, the later studies focused on achieving optical gain in a system of Si-nc and Er^{3+} ions which could

be used as efficient optical amplifiers in telecommunication devices [77, 83]. In these reports, various aspects of the energy transfer process like the mechanism of energy transfer, efficiency of energy transfer, the interaction distance between Si-nc (donor) and Er^{3+} (acceptor) were studied in detail to improve the energy transfer from Si-nc to the Er^{3+} ions.

There are two different reported methods of energy transfer from Si-nc to Er^{3+} ions. For instance, reports by [76-79] mention that the energy transfer from Si-nc to Er^{3+} ions is due to the excitonic emission from the Si-nc. In these reports, the 810 nm exciton emission from the Si-nc overlaps with the $^4\text{I}_{9/2}$ absorption peak of the Er^{3+} ions which result in the energy transfer from the nanocrystals. However in contrast, reports by Savchyn et al. [80, 83], mention that the energy transfer from the Si-nc to Er^{3+} was dominated by the defect state emission centers. The 650 nm and 857 nm defect emissions in a system of Si-nc in SiO_2 mostly excites the Er^{3+} ions as compared to the excitons of Si-nc. Interestingly, the nature of these defect emission centers was not reported by Savchyn et al. [80, 83]. This ambiguity where the energy transfer from the Si-nc to Er^{3+} could be due either to the excitonic emissions or the defect emissions, has been further studied to some extent by studies in reference [81]. The study shows that the exciton recombination in Si-nc show higher energy transfer as compared to the defect mediated energy transfer.

This multiple mechanism of energy transfer is not exclusive to the system of Si-nc and Er^{3+} ions. In general, a similar multiple mechanism of energy transfer is also reported in other systems of semiconductor nanocrystals and lanthanide ions. For example, the system of ZnO-nc and Eu^{3+} , ZnO-nc and Tb^{3+} presented in this work also show energy transfer due to band-edge emission from the nanocrystals and defect mediated energy transfer. The detailed review of the

reports on energy transfer from ZnO-nc systems is presented in section 2.4. Nonetheless, it is important to determine the dominated mechanism of energy transfer in any system of semiconductor nanocrystals and lanthanide ions to improve the energy transfer efficiency from the semiconductor nanocrystals and lanthanide ions.

The energy transfer efficiency is another important parameter that is often studied for any system of semiconductor nanocrystals and lanthanide ions. Even for Si-nc and Er^{3+} ions system, various reports on the energy transfer efficiency have been published. While it is important to have high energy transfer efficiency for efficient energy transfer from Si-nc to Er^{3+} ions, most of the studies report transfer efficiency of around 60%. For instance, Savchyn et al. reported a transfer efficiency of 60% [83], while Kik et al. reported a transfer efficiency of 55% [75] initially and then around 60% in later reports [76]. However, there has been one study by Heitmann et al. [77], which reports that energy transfer efficiency between Si-nc and Er^{3+} ions is as high as 90%. In these studies the energy transfer efficiency is mostly calculated from the time resolved photoluminescence emission of the Si-nc [75-77], except for the study by Savchyn et al. in which the transfer efficiency is calculated from both steady-state and time resolved photoluminescence emissions.

Another important parameter in the energy transfer mechanism is the distance of interaction between the donor and acceptor species as discussed in section 2.3.1. In the system of Si-nc and Er^{3+} ions, studies by Kik et al report that the distance between the Si-nc (donor) and Er^{3+} ion (acceptor) is ~ 1 nm [76]. However, there have been no reported studies on the effect of this distance of interaction between Si-nc and Er^{3+} on the energy transfer between the two species. This study on the effect of interaction distance between donor and

acceptor species is generally lacking in any system of semiconductor nanocrystals and lanthanide ions.

Overall, even though there have been numerous studies on energy transfer from Si-nc to Er^{3+} there have been difficulties in improving the efficiency of the energy transfer from the Si-nc to Er^{3+} ions due to the ambiguity in the nature of energy transfer from the Si-nc to Er^{3+} ions. Moreover, the energy transfer from Si-nc can only be used to excite the lanthanide ions with absorption peak in the Red-IR region of the electromagnetic spectrum because the emission from the Si-nc is in the Red-IR region. Lanthanide ions like Eu^{3+} and Tb^{3+} cannot be excited using Si-nc because the absorption peak of Eu^{3+} and Tb^{3+} ions are in the UV-blue region of the electromagnetic spectrum. Thus, due to these reasons Si-nc based devices have not been widely developed and commercially used. Furthermore, research on Si-nc has slowed down in recent years and the focus has shifted to studies on wide band-gap semiconductor nanocrystals such as Cadmium Sulphide (CdS), Zinc Sulphide (ZnS) and Zinc Oxide (ZnO). The author presents a detailed review of the energy transfer from wide band-gap semiconductor nanocrystals in the section below.

2.3.2.2. Cadmium Sulphide nanocrystals & Zinc Sulphide

In recent years, the research on semiconductor nanocrystals sensitizers has been focused on wide band-gap semiconductors such as Cadmium Sulphide (CdS), Zinc Sulphide (ZnS) and Zinc Oxide (ZnO). Amongst these wide band-gap semiconductors, most of the studies have used ZnO nanocrystals (ZnO-nc) to excite the lanthanide ions through the energy transfer process. Nonetheless, some works have reported energy transfer from nanocrystals of ZnS (ZnS-nc) and CdS (CdS-nc) to lanthanide ions like Nd^{3+} , Eu^{3+} and Tb^{3+} . In this section the author reviews the articles that have used ZnS-nc and CdS-nc as sensitizers.

Energy transfer from ZnS-nc to Eu^{3+} ions have been reported as early as 1998 by Sun *et al.* [84]. In the study by Sun *et al.*, the energy transfer process from ZnS-nc to Eu^{3+} ions was investigated by doping the Eu^{3+} ions in the ZnS nanocrystals, unlike the system of Si-nc and Er^{3+} where the Si-nc and Er^{3+} ions were doped in SiO_2 . Similar to ZnS-nc, the study of energy transfer from CdS-nc to Eu^{3+} ions was first reported by Hayakawa *et al.* in 2000 [85]. Since then, there have been more studies showing energy transfer from CdS-nc and ZnS-nc to lanthanide ions like Eu^{3+} , Tb^{3+} and Nd^{3+} [10-12]. While all these studies show energy transfer from the nanocrystals to the lanthanide ions, there is not much discussion on the mechanism and contribution of energy transfer from the nanocrystals to the lanthanide ions. Furthermore, to the best of the author's knowledge, there are no studies reporting the energy transfer efficiency and the effect of interaction distance between the ZnS and CdS nanocrystals and Eu^{3+} , Tb^{3+} and Nd^{3+} lanthanide ions.

More studies on energy transfer from ZnO-nc to the lanthanide ions have been reported because of the ability of ZnO-nc to excite a wide variety of lanthanide ions, which is presented in the section 2.4 below.

2.4. Zinc Oxide Nanocrystals

Zinc Oxide (ZnO) is a wide band gap semiconductor with a large exciton binding energy of 60 meV. The band gap of ZnO is 3.37 eV at room temperature. As a result, ZnO is an important material used in optoelectronic devices which operate in the blue and ultraviolet (UV) region of the electromagnetic spectrum. The nanoscale ZnO, namely Zinc Oxide Nanocrystals (ZnO-nc), have attracted much attention recently due to their inherent and intrinsic properties like size dependent luminescent properties, large absorption cross-sections and broad excitation spectra.

The myriad of unique properties of ZnO-nc has resulted in ZnO-nc being used as sensitizers to excite the lanthanide ions. ZnO-nc have been shown to excite a wide variety of lanthanide ions which include Ce^{3+} , Er^{3+} , Ho^{3+} , Nd^{3+} , Tm^{3+} , Dy^{3+} , Eu^{3+} and Tb^{3+} [17, 18, 25, 31-35]. The ZnO-nc easily absorb the photon energy upon optical excitation using a UV light source. This results in the excitation of electrons from the valance band to the conduction band of ZnO-nc. The excited electrons of ZnO-nc relax back to the ground state either through radiative or non-radiative relaxation or through energy transfer to the lanthanide ions. The lanthanide ions excited by energy transfer relax by emitting light in the visible or infrared wavelengths. Europium (Eu^{3+}) ions excited using ZnO-nc sensitizers emit red light at 614 nm and Terbium (Tb^{3+}) ions excited using ZnO-nc emit green light at 545 nm.

In this section, the author first reviews the origin of the broadband emission from ZnO-nc in SiO_2 matrix. This is followed by a detailed review of the literature of energy transfer from ZnO-nc to lanthanide ions, especially Eu^{3+} and Tb^{3+} .

2.4.1. ZnO-nc Emission Centres

As mentioned previously, ZnO is a wide band-gap semiconductor and the nanocrystals of ZnO-nc emit light through radiative relaxation when they are optically excited using a UV light source. In this section, the author reviews and presents the origin of the photoluminescence emission from the ZnO-nc mentioned in the literature. Overall, this knowledge is important to understand the energy transfer process and contribution of energy transfer from the ZnO-nc to the lanthanide ions.

The emission from the ZnO-nc is broadband in nature and there have been a lot of studies to understand this broadband emission from ZnO nanocrystals

[13, 15, 86-88]. In general, the broadband emission from ZnO nanocrystals can be roughly divided into two different categories, namely band-edge related emissions and defect related emissions.

Within the first category, the observed band-edge emission is due to the excitonic emission in most of the studies on ZnO. This is an emission which is related to the free or bound excitons in ZnO. Extensive studies done by Hamby et.al. [87], Zhang et.al. [88] and Teke et. al. [89] show that the excitons in ZnO result in an emission with a wavelength of 378 – 381 nm.

In the second category, namely defect related emissions, the emissions are due to the Zinc defects and Oxygen defects in ZnO [90, 91]. There are mainly four types of ZnO defects. These are Zinc interstitial, Zinc vacancy, Oxygen interstitial and Oxygen vacancy defects. There have been numerous studies to understand the nature of these ZnO defect emissions by various groups. For instance, Panigrahi et.al. [13] report emissions from ZnO-nc at 396 nm and 625 nm which are related to the Zn interstitial and Zn vacancy defects while the emission at 477 nm was reported to be due to the Oxygen vacancy defects. However, studies reported by Zhang et.al. [92] and He et.al [14], the Oxygen vacancy defect center was shown to emit at 446 nm and 506 nm wavelengths, respectively. In other studies, by Mahamuni et.al. [93] and Janotti et.al. [94], a 420nm defect emission was observed. This was attributed to the Oxygen Interstitial defect. Thus, these studies show the wide range of emission centres reported in ZnO-nc which contribute to their broadband emission spectrum.

It is important to note that, in general, the ZnO-nc in the above mentioned studies are either in the form of a powder, or in a colloidal solution, or embedded in some host material. There was also a study of emission from ZnO-nc embedded in SiO₂ [95]. The SiO₂ is intended to provide the physical and

chemical protection to ZnO-nc. The photoluminescence emission from the ZnO-nc embedded in SiO₂ matrix is broadband in nature with the emission ranging from 350 nm to 600 nm. In the above mentioned work [95], the broadband emission was shown to consist of seven different emission centres which was obtained by the deconvolution of the ZnO-nc photoluminescence emission spectra. The seven emissions from the ZnO-nc in SiO₂ are divided into two main emission regions. The first one is in the ultraviolet-blue range and the other is in the visible range of the electromagnetic spectrum. The ultraviolet-blue emission consists of three different emission centers with the emission peak centered at 360, 378 and 396 nm. While the visible emission consists of four different emission centers with the emission peak centered at 417, 450, 500 and 575 nm. The nature of these seven emission centers were studied and identified in the reference [95]. The 360 and 378 nm peaks were attributed to band-edge emission from the smallest ZnO-nc which possibly experiences quantum confinement effect and ZnO-nc excitonic emission, respectively. The 396 nm peak is attributed to the defect state electronic transition from Zn interstitial to Zn vacancy and the remaining emission peaks are due to the electronic transition from, or, to the oxygen-related defects, namely oxygen interstitial defect emission at 417 nm, oxygen vacancy emission at 450 nm, singly ionized oxygen vacancy emission at 500 nm and doubly charged oxygen vacancy emission at 575 nm. Thus, these seven different emission centres of ZnO-nc result in the broadband emission of the ZnO-nc embedded in SiO₂, which help in exciting a wide variety of lanthanide ions including the Eu³⁺ and Tb³⁺ ions used in this work.

The nature of the ZnO-nc emission centers presented in this section are important to understand the energy transfer process and contribution of energy transfer from the ZnO-nc to the lanthanide ions.

2.4.2. Energy Transfer from ZnO-nc to Lanthanide ions

ZnO-nc is one of the most widely used semiconductor nanocrystals that have been used to excite lanthanide ions through energy transfer. ZnO-nc have been used as sensitizers to excite lanthanide ions such as Ce^{3+} , Er^{3+} , Ho^{3+} , Nd^{3+} , Tm^{3+} , Dy^{3+} , Eu^{3+} and Tb^{3+} [17, 18, 25, 31-35]. The main purpose of these studies was to enhance the emission from the lanthanide ions for various applications such as visible-light-emitting devices, phosphors, biological fluorescence labelling, optical communication and so on. For instance, Shi *et al.* reports the enhancement of blue emission from the Ce^{3+} ions through energy transfer from ZnO-nc [17]. While studies by Xiao *et al.* and Liu *et al.* report the enhancement of infrared emission from Er^{3+} [18], Nd^{3+} and Tm^{3+} ions [32], respectively. Amongst the various lanthanide ions, the energy transfer from ZnO-nc to Eu^{3+} ion [9, 23-28, 96, 97] and ZnO-nc to Tb^{3+} ion [19, 34, 98-100] have been most widely studied by various groups because of the usefulness of the enhanced sharp red and green emissions from Eu^{3+} ions at 614 nm and Tb^{3+} ions at 545 nm, respectively. Interestingly, in most of the studies on energy transfer from ZnO-nc to lanthanide ions, the focus has been to understand the structural and optical properties of such a system and the nature of the energy transfer process. For example in some of the recent studies, Ntwaeaborwa *et al.* [96] and Pessoni *et al.* [97] report on the structural, optical and dielectric properties of ZnO-nc and Eu^{3+} system. While Najafi *et al.* [101] report about the effects of fabrication conditions and the nature of the intrinsic defects on the energy transfer process.

Even though there are many studies on the energy transfer from ZnO-nc to Eu^{3+} and Tb^{3+} ions, an understanding of the energy transfer mechanism from the ZnO-nc to the lanthanide ions is still lacking. While studies by Luo *et al.* and Zhang *et al.* report that this energy transfer is predominantly due to the free or

bound excitonic state emissions of ZnO-nc [26, 27], other studies report that the energy transfer takes place with the involvement of the defect states in ZnO-nc [9, 19, 24, 25, 28]. Report by Luo *et al.* [33] shows that the energy transfer from the ZnO-nc could be due to a combination of the band edge emission from the ZnO-nc and the defects in the ZnO-nc. Moreover, the nature of these defects involved in the energy transfer process is unclear or varies from one study to another. Lin *et al.* reports that the energy transfer to Eu^{3+} take place through oxygen vacancy defect in ZnO-nc [28] while Kabongo *et al.* reports that the energy transfer to Tb^{3+} ions takes place due to the oxygen vacancy defects and the defects introduced by the incorporation of Tb^{3+} ions [19]. Furthermore, none of these studies report the contribution of energy transfer from the various ZnO-nc emission centers to the lanthanide ions. A clear understanding of the energy transfer mechanism and contribution of energy transfer from the ZnO-nc to the lanthanide ions is essential in enhancing the emission from the lanthanide ions.

Another important parameter that is necessary in the energy transfer process for any system of semiconductor nanocrystals and lanthanide ions is the energy transfer efficiency. The energy transfer efficiency is most often calculated by measuring the time resolved photoluminescence (TRPL) emission from the energy donor which in this case, is ZnO-nc. However, most of the research on energy transfer from ZnO-nc to lanthanide ions is based on the steady state photoluminescence (PL) emission from the nanocrystals and there are only few studies, based on the time resolved photoluminescence (TRPL) measurements from the ZnO-nc, which are mainly by Xiao *et al.* [18, 102]. Moreover in these studies, the energy transfer efficiency from the ZnO-nc have not been reported. Thus, in general there are almost no studies to understand

the decay dynamics of the various ZnO-nc emission centers and their effect on the efficiency of energy transfer mechanism from ZnO-nc to lanthanide ions.

Furthermore, the interaction distance between the donor and acceptor is another important factor that affects the energy transfer processes and efficiency from the ZnO-nc to lanthanide ions. Surprisingly, there has been no report on the nature of energy transfer from ZnO-nc to lanthanide ions based on the interaction distance between ZnO-nc and lanthanide ions. This is an important parameter that needs to be investigated to better understand the energy transfer from ZnO-nc to lanthanide ions.

In most of the studies mentioned above, the energy transfers from ZnO-nc to a single type of lanthanide ion have been investigated. For example, the energy transfers specifically from ZnO-nc to Eu^{3+} ions [24, 26-28, 45, 96, 97, 101, 103-107] or from ZnO-nc to Tb^{3+} ions [35, 100, 108-110]. Remarkably however, there has been little work on co-doping both Eu^{3+} ions and Tb^{3+} ions together with ZnO-nc in the same SiO_2 matrix. This is particularly important as the blue emission from ZnO-nc can be combined with the red and green emissions from Eu^{3+} ions and Tb^{3+} ions, respectively, to create a white light emitting device or a light emitting device of any desired colour which can be excited using a single excitation wavelength. One such work on co-doping both Eu^{3+} ions and Tb^{3+} ions with ZnO-nc by Luo *et. al.* was on the energy transfer process and the energy transfer mechanism from ZnO-nc to the two lanthanide ions [34]. In this study, the energy transfer between the two lanthanide ions themselves is also investigated but it does not report on a pure white light emitting sample.

In conclusion, while there have been many studies showing energy transfer from ZnO-nc to different lanthanide ions, there is still scope for further studies in this energy transfer process. As mentioned above, the energy transfer

contribution, energy transfer efficiency and the effect of interaction distance on energy transfer between ZnO-nc and lanthanide ions needs to be further investigated. The author studies these in detail and the results are presented in Chapter 4, 5, and 6, respectively. In addition, the author also presents an additional new study in Chapter 7, where two lanthanide ions, namely Eu^{3+} and Tb^{3+} ions, were combined with ZnO-nc to produce a white light emitting sample using a single excitation wavelength.

2.5. CIE Chromaticity

In chapter 7 of this work, the author studies the colour of the emission from the ZnO-nc and the lanthanide ions like Eu^{3+} and Tb^{3+} . The intensity of emission from the ZnO-nc, Eu^{3+} ions and Tb^{3+} ions is controlled to create samples of desired colour. An important aspect in this regard is the numerical quantification of colour, which is defined by the CIE x , y and z chromaticity values of a spectrum. CIE stand for Commission Internationale de l'éclairage, which is an organisation that defines the international standard for measurements related to light and colour [111]. In this section, the author briefly describes the method to calculate the CIE x , y and z chromaticity values.

The CIE x , y and z chromaticity values are essentially normalised fractions which give a quantitative relation between the spectrum of emission from the sample and the colour perceived by the human eyes [112]. The x , y and z values represent the degree of red, green and blue colour, respectively, perceived by the human eye. The x , y and z values are calculated using the spectrum of emission from the sample or a light source and the CIE colour-matching functions. The CIE colour-matching functions, denoted by the symbols $\bar{x}(\lambda)$, $\bar{y}(\lambda)$ and $\bar{z}(\lambda)$, are a measure of the spectral response of the three different colour sensors of the human eye [112]. To obtain the CIE x , y

and z chromaticity values, the overlap integral of the intensity of emission from the sample a light source and each of the CIE colour-matching functions is first calculated. Mathematically it written as

$$X = \int_0^{\infty} I(\lambda)\bar{x}(\lambda)d\lambda \quad (2.10)$$

$$Y = \int_0^{\infty} I(\lambda)\bar{y}(\lambda)d\lambda \quad (2.11)$$

$$Z = \int_0^{\infty} I(\lambda)\bar{z}(\lambda)d\lambda \quad (2.12)$$

where $I(\lambda)$ is the intensity of emission from the sample a light source as a function of wavelength. The x , y and z values are then calculated from X , Y and Z by normalisation, which is shown in the following equation

$$x = \frac{X}{X + Y + Z} \quad (2.13)$$

$$y = \frac{Y}{X + Y + Z} \quad (2.14)$$

$$z = \frac{Z}{X + Y + Z} = 1 - x - y \quad (2.15)$$

As mentioned above, the x , y and z values represent the degree of red, green and blue colour. Thus, for instance, greater the value of x or y or z the more red or more green or more blue the sample looks, respectively.

Chapter 3: Sample Preparation & Characterization Techniques

3.1. Introduction

This chapter describes the basic principles, method of the sample fabrication techniques and the sample characterisation techniques. This chapter has been divided into two main sections. In the first section, the author describes the theory of the sample fabrication techniques, namely the sol-gel process and the RF magnetron sputtering, used to fabricate thin film samples of ZnO-nc embedded in SiO₂; Eu³⁺ and ZnO-nc embedded in SiO₂; Tb³⁺ and ZnO-nc embedded in SiO₂; and also Eu³⁺, Tb³⁺ and ZnO-nc embedded in SiO₂. The author also clarifies the reason for the choice of these fabrication techniques in this section. In the second main section, the author details the working principles of the characterisation equipment used to characterise the samples prepared in this work. The author describes the working of the spectrofluorometer used to measure the photoluminescence emission and photoluminescence excitation from the sample, streak camera used to measure the time-resolved photoluminescence measurement from the samples and also the surface profiler used to measure the thickness of the samples.

3.2. Fundamentals of Thin Film Preparation

Thin films are widely used for many applications like optical coating, electronic components, data storage, nanoscale optoelectronics (such as light source), interconnects and also as phosphors for lighting and display technology [113]. Preparation of thin films, especially for nanoscale optoelectronics is carried out in many ways such as pulsed laser deposition [114], ion implantation [115],

sputtering [116], chemical vapour deposition (CVD) [117], electron beam evaporation [118], electro deposition [119] and sol-gel process. Amongst all the different thin film deposition techniques, the sol-gel process and sputtering technique have been used to fabricate the thin film samples used in this work. In this section, the author presents an outline of the thin film preparation methods used in this work and also elucidates the reason for using these techniques.

3.3.1. Choice of Sol-Gel Method

Thin films of ZnO-nc in SiO₂ or Eu³⁺/Tb³⁺ and ZnO-nc in SiO₂ can be prepared using most of the thin film deposition techniques mentioned above. For instance, sputtering [120-123], ion implantation [124], plasma enhanced chemical vapour deposition (PECVD) [125] and sol-gel process [9, 25, 28, 126-129] have been used by various groups to deposit thin film samples of semiconductor nanocrystals and rare-earth ions. Most of these thin film deposition techniques are complex processes which require sophisticated fabrications systems. For instance, deposition method like sputtering and PECVD are plasma based methods and require complicated plasma generating systems. In addition to plasma generation, sputtering deposition is carried out in a vacuum environment which makes this technique even more complicated [130]. Moreover, deposition methods like sputtering and ion implantation generally produce non-stoichiometric materials. Among the above mentioned deposition techniques, sol-gel method is the favoured thin film preparation method due to its various advantages which are listed as follows

1. Low cost: The sol gel process does not require expensive equipment that need complex setups, such as the vacuum-based, plasma-based or high-temperature based instruments. The cost required to buy the chemicals and equipment for the sol-gel process are comparatively low as the mixing

of the precursors in the sol-gel process is mostly carried out in room temperature with atmospheric pressure [130-133]. The densification of the sample from a gel to a solid film does require annealing at relatively high temperatures, using for example, a thermal furnace or Rapid Thermal Annealing equipment.

2. Ability to control material composition: In the sol-gel process the sample fabrication occurs at a molecular level as the sol is prepared by mixing the chemical precursors, catalyst and the solvent. This allows for greater flexibility and easy control of material concentration as well as co-dopants during sample fabrication. Specifically, the type and the concentration of dopants and co-dopants can be easily controlled during the chemical mixing in sol-gel. This is a distinctive feature of the sol-gel process which is harder to control in other thin film preparation methods [132-134].
3. Superior stoichiometry of the material: As mentioned above, sol gel process is a molecular level process as the sol is prepared by mixing the chemical precursors, catalyst and the solvent. The chemicals react to form the desired material by forming bonds through the hydrolysis and condensation reactions. Thus, the sol gel process ensures extremely homogenous and stoichiometric films as it is a molecular sample fabrication process [130, 132, 135, 136].
4. Large area and Uniformity: The sol-gel process is essentially a densification process of liquid chemicals through chemical reaction and annealing. Thus, with appropriate precursor quantities, a large area of sample with uniform thickness can be easily deposited in a single fabrication cycle using the sol-gel process. This is particularly useful in scaling of the sample during mass production of devices [132, 133, 135].

Hence, due to these positive qualities and salient features of this process, the samples of ZnO-nc in SiO₂; Eu³⁺ and ZnO-nc in SiO₂; Tb³⁺ and ZnO-nc in SiO₂; and Eu³⁺, Tb³⁺ and ZnO-nc in SiO₂ prepared in this work have been through the sol-gel process.

3.3.2. Thin film deposition by the sol-gel process

In this section the author will describe the general chemistry of the sol-gel process used in this work, to fabricate thin film sample of ZnO-nc in SiO₂ co-doped with lanthanide ions like Eu³⁺ and Tb³⁺. The author presents the various steps of the process along with the chemical reactions involved in the process. In the subsequent section the author presents the exact recipe involved in the fabrication of the six different types of samples developed in this work.

The sol-gel process begins with the preparation of a sol, which is a colloidal suspension of solid particles in a liquid medium. The size of the solid particle is usually in the range of 1 nm to 100 nm [137, 138]. Whereas, the gel is essentially a transitional state between liquid and solid. It is a network of interconnected and rigid polymer which have submicron pores. These pores are usually filled with water or the liquid solvent used in the sol-gel process [2, 137-141]. The sol-gel process derives its name from the fact that during the chemical process the 'sol' transitions, through a series of hydrolysis, condensation and polymerisation reactions, to a 'gel' [137, 138, 142]. The sol-gel process can be divided into 4 major steps. These steps are chemical mixing, ageing and gelation, deposition, and densification and crystallisation. A general schematic diagram of these preparation steps are shown in Figure 3-1.

Figure 3-1: A schematic diagram of the preparation steps in sol-gel process

Step 1 – Chemical mixing: The chemical mixing is the first step of the sol-gel process where the starting reagents of precursors, solvent, catalyst and water are mixed together to create a sol. Separate sols are made for the two main components in the thin film like the host material which in this work is SiO_2 and the donor dopants which is ZnO-nc. The Eu^{3+} and Tb^{3+} lanthanide ions which are the acceptor dopants in this work are added during the ageing and gelation process which is explained in the next section.

For the formation of a SiO_2 matrix, a sol containing Tetraethyl Orthosilicate (TEOS) ($\text{Si}(\text{OC}_2\text{H}_5)_4$) precursor is mixed with ethanol ($\text{C}_2\text{H}_5\text{OH}$) along with a suitable amount of water (H_2O). Few drops of concentrated nitric acid (HNO_3) is added to this sol to initiate or catalyse the hydrolysis process for TEOS with water, which results in the replacement of alkoxide group ($-\text{OC}_2\text{H}_5$) with the hydroxyl group ($-\text{OH}$). The chemical equation 3.1 shows the hydrolysis process of TEOS which leads to the formation of a Si-OH bond [143].

The hydrolysis of TEOS is followed by the condensation process, in which the Si-O-Si network is formed. The condensation process occurs in two forms, namely alcohol condensation and water condensation as shown in equation 3.2 and 3.3, respectively.

For the formation of ZnO-nc, a sol with zinc acetate dihydrate ($\text{Zn}(\text{CH}_3\text{COO})_2 \cdot 2\text{H}_2\text{O}$) as the precursor and ethanol as the solvent is mixed with diethanolamine (DEA) which acts as the catalyst. Similar to the formation of SiO_2 , the first step in the formation of ZnO-nc is the hydrolysis reaction. The zinc acetate in the sol reacts with the water to replace the Zn-OCOCH_3 bond to form the Zn-OH bond through the hydrolysis reaction as shown in equation 3.4 [132].

The Zn-OH bond then leads to the formation of the Zn-O-Zn network by the condensation reaction. Again similar to the SiO₂ formation, the ZnO formation takes places through two types of condensation reactions as shown in equation 3.5 and 3.6.

The DEA in the ZnO sol acts as a stabilising agent which retards the condensation of Zn²⁺ and promotes the uniform formation of ZnO [132, 144]. This reaction of DEA in the sol is shown in the equation 3.7.

Step 2 – Aging and Gelation: Aging and Gelation is the second step in the sol-gel process. Aging time is the time before the deposition where the two different sols are continuously stirred, allowing time for the hydrolysis and condensation reactions of the precursor chemicals. The Si-O-Si and Zn-O-Zn bonds are very weak after the first step of chemical mixing and it is in the aging step of the sol-gel process, that the formation of the Si-O-Si and Zn-O-Zn linkage continues, leading to the formation of the three-dimensional SiO₂ matrix and ZnO-nc [2, 139, 140, 142]. The Si-O-Si and Zn-O-Zn polymeric linkage becomes stronger and stronger with increasing aging time.

This is also the step in the fabrication process where the rare-earth (RE) ion dopants like Eu³⁺ and/or Tb³⁺ can be easily added. The RE ions are doped in the SiO₂ matrix, by dissolving the precursor salt of RE ions, namely europium (III) nitrate pentahydrate (Eu(NO₃)₃.5H₂O) for Eu³⁺ ions and terbium (III) nitrate

pentahydrate ($\text{Tb}(\text{NO}_3)_3 \cdot 5\text{H}_2\text{O}$) for Tb^{3+} ions in the SiO_2 sol. The RE ion salt ionises into RE (3+) ions and nitrate ions upon dissolving in the SiO_2 sol and then the RE ions substitute into the weak Si-O-Si network which is shown in equation 3.8.

Step 3 – Deposition: The third step in the sol-gel process is the deposition. This step begins by mixing ZnO-nc sol into the SiO_2 sol which is then deposited onto a Si substrate. The deposition of the thin film is done by spin coating of the mixed sol. The spin coating consists of three stages, namely deposition, spin and evaporation, and this is illustrated in Figure 3-2. In the first stage of deposition, the sol is introduced onto the substrate using a syringe. Excess amount of sol is deposited on the Si substrate and it is ensured that the sol is fully distributed onto the substrate. In the second stage of spin coating the substrate is spun at an appropriate rotation speed for a suitable amount of time. The sol on the Si substrate flows radially outward towards the edge of the substrate due to the centrifugal force during the spinning process. A gelatinous thin film of uniform thickness of a few hundred nanometres is formed during this step. Furthermore, during this process, the evaporation of solvent and water molecules takes place from the pores of the thin film sample. After the deposition of the thin film sample, certain amounts of solvent and water

molecules would still be trapped in the pores of the thin film, which is removed during the final step of sol-gel process, densification.

Figure 3-2: Illustration of the three steps in the spin coating technique, showing the deposition, spin and evaporation. [2]

Step 4 – Densification and Crystallisation: Thin film samples deposited using the spin coating technique have excess, unwanted organic molecules and chemically bound water molecules. These excess chemicals are trapped in the pores of the thin film sample. In order to remove these excess chemicals, the sample is baked and annealed in the final step of the sol-gel process which leads to the densification of the thin film sample. The samples are baked using a simple hot plate, while the annealing is carried out using rapid thermal processor (RTP) or a normal furnace. RTP is an annealing process, in which the samples are heated to high temperatures in a timescale of several seconds to few minutes. During baking and annealing the excess molecules are eliminated in the form of gaseous waste like carbon dioxide (CO_2) or water vapour. Thin film samples of ZnO-nc in SiO_2 ; Eu^{3+} and ZnO-nc in SiO_2 ; Tb^{3+} and ZnO-nc in SiO_2 and Eu^{3+} , Tb^{3+} and ZnO-nc in SiO_2 are finally obtained after this step.

3.2.2.1. Sample fabrication

Having described the thin film deposition by the sol-gel process above, the author will now describe the detailed fabrication recipe for the samples fabricated in this work.

There are 6 different types of samples fabricated in this work and they are listed as follow:

1. ZnO-nanocrystals embedded in SiO₂ matrix (ZnO-nc:SiO₂)
2. Eu³⁺ ions incorporated in SiO₂ matrix (Eu³⁺:SiO₂)
3. Tb³⁺ ions incorporated in SiO₂ matrix (Tb³⁺:SiO₂)
4. Eu³⁺ ions and ZnO-nc incorporated in SiO₂ matrix (Eu³⁺_{*m*}:ZnO-nc:SiO₂ where *m* is the concentration of Eu³⁺ ions in molar fraction, and calculated using

$$m = \frac{\text{moles of } (Eu^{3+})}{\text{moles of } (Eu^{3+} + Zn + Si)}$$

5. Tb³⁺ ions and ZnO-nc incorporated in SiO₂ matrix (Tb³⁺_{*n*}:ZnO-nc:SiO₂ where *n* is the concentration of Tb³⁺ ions in molar fraction, and calculated using

$$n = \frac{\text{moles of } (Tb^{3+})}{\text{moles of } (Tb^{3+} + Zn + Si)}$$

6. Eu³⁺ ions and Tb³⁺ ions incorporated in SiO₂ matrix together with ZnO-nc (Eu³⁺_{*m*}:Tb³⁺_{*n*}:ZnO-nc:SiO₂ where *m* is the concentration of Eu³⁺ ions in molar

fraction, and calculated using $m = \frac{\text{moles of } (Eu^{3+})}{\text{moles of } (Eu^{3+} + Tb^{3+} + Zn + Si)}$ and *n* is the concentration of Tb³⁺ ions in molar fraction, and calculated using

$$n = \frac{\text{moles of } (Tb^{3+})}{\text{moles of } (Eu^{3+} + Tb^{3+} + Zn + Si)}$$

The samples were fabricated by first mixing the precursor, the solvent and the catalyst to create a sol. Two different sols for SiO₂ matrix and ZnO-nc were developed from Tetraethyl Orthosilicate (TEOS) and zinc acetate as precursors, respectively. The TEOS precursor was mixed with 69% nitric acid as a catalyst in ethanol as a solvent to create the SiO₂ sol, while the zinc acetate precursor was

mixed with diethanolamine (DEA) as a catalyst in ethanol as a solvent to create the ZnO-nc sol. For the samples with Eu^{3+} and Tb^{3+} ions (namely sample 4, 5 and 6), Europium (III) nitrate penthydrate and Terbium (III) nitrate penthydrate, respectively, were added into the SiO_2 sol after aging the SiO_2 sol for 24 hours. For the samples with ZnO-nc (namely sample 1, 4, 5 and 6), the SiO_2 and ZnO-nc sols were then mixed together and spin coated on a (100) Si wafer substrate. For the sample without ZnO-nc (namely sample 2 and 3), the SiO_2 sol was spin coated directly on a (100) Si wafer substrate. These samples were soft baked and were then annealed using rapid thermal processing (RTP) at various annealing temperatures ranging from 450°C to 600°C for 1 minute in an O_2 environment. The preparation method used for the above samples is similar to that described in our group's publication [129]. A schematic diagram of the preparation steps, is shown in Figure 3-3.

Figure 3-3: Schematic representation of sol-gel fabrication steps used in this work.

Different $\text{Eu}^{3+}_m\text{:ZnO-nc:SiO}_2$, $\text{Tb}^{3+}_n\text{:ZnO-nc:SiO}_2$ and $\text{Eu}^{3+}_m\text{:Tb}^{3+}_n\text{:ZnO-nc:SiO}_2$ samples were prepared in the work with m and n ranging from 0 to 0.16. The molar ratio of Zn:Si in all the sample with ZnO-nc was maintained at 1:2.

The formation of ZnO-nc in SiO_2 using the above mentioned fabrication recipe, was previously studied and verified using TEM images. The TEM images have been published in our group's work [129] and have also been presented below in Figure 3-4.

Figure 3-4: TEM images of ZnO-nc in SiO_2 [129].

In these TEM images the ZnO-nc can be identified by the presence of crystal planes which are indicated by white circles. The atomic spacing in these crystals planes is found to be indeed that of ZnO crystals [129]. The samples in this thesis use the exact same sample preparation recipe that was used to fabricate ZnO-nc in SiO₂ as reported by Pita *et al.* and furthermore the emission observed from ZnO-nc is similar to the PL emission observed from Pita *et al.*'s work. These PL emission results have been discussed in detail in chapter 4 of the thesis.

3.3.3. Radio-Frequency (RF) Magnetron Sputtering

The author used the radio-frequency magnetron sputtering to deposit a nanometre sized layer of SiO₂ film to study the effect of distance between the ZnO-nc and Eu³⁺ ions in the energy transfer process. The result of this study will be presented in chapter 6 and has been published in Optical Materials Express (V. Mangalam and K. Pita, "Effect of the interaction distance on 614 nm red emission from Eu³⁺ ions due to the energy transfer from ZnO-nc to Eu³⁺ ions," *Optical Materials Express*, vol. 8, no. 10, pp. 3115-3132, 2018/10/01 2018.). In this section the principle of RF magnetron sputtering is discussed.

Sputtering is a form of physical vapour deposition (PVD) method. It is one of the oldest and most mature forms of thin film deposition technique [145]. There are studies of thin film deposition using sputtering being reported as early as 1852 [146]. While there are numerous different types of sputtering techniques like ion beam sputtering, magnetron sputtering, high-target-utilisation sputtering, high-power impulse magnetron sputtering and reactive sputtering, the fundamentals of all the sputtering techniques are the same irrespective of the type of sputtering [147]. It essentially works on the principle of sputter-erosion of a target material by ionised particles [145], which is then deposited on the substrate where it condenses and forms a thin film. The

ionized particles are usually argon ions (Ar^+) which bombards the target material and in this work, the target material was SiO_2 .

The RF magnetron sputtering normally helps in fabricating thin film samples with excellent adhesion, accurate thickness control down to 1 nm, great smoothness and uniformity in deposition over a larger area. Hence, in this work the author uses RF magnetron sputtering to deposit SiO_2 layers to study the effect of distance between the ZnO-nc and Eu^{3+} ions in the energy transfer process.

Figure 3-5: The thickness of deposition of the SiO_2 film as a function of deposition time in this work.

The thickness of the SiO_2 film deposited on the substrate by RF magnetron sputtering can be controlled by either varying the sputtering voltage or the sputtering deposition time. In this work, the sputtering voltage was kept fixed at 150 V and the sputtering deposition time was varied to deposit SiO_2 film of varying thickness. Figure 3-5 shows the thickness of deposition of the SiO_2 film as a function of deposition time in this work. This was obtained by sputtering three different SiO_2 films with deposition time of 1200, 2400 and 3600 seconds

and measuring the thickness of these samples using a surface profiler. These values were then used to estimate the thickness of the SiO₂ films for various deposition times.

SiO₂ thin films with thickness varying from 2 nm to 8 nm were fabricated in this work. The deposition times for these samples were obtained from the graph above. The thickness of some of these SiO₂ thin films were measured using a surface profiler to confirm the thickness of the layer.

The sputtering deposition process was used in the fabrication of a three-layer thin film sample to study the effect of distance between the ZnO-nc and Eu³⁺ ions in the energy transfer process. The first layer of this sample was a thin film of SiO₂ matrix embedded with Eu³⁺ ions (Eu³⁺:SiO₂), which was prepared using the sol-gel process mentioned above in section 3.2.2 and deposited on the Si substrate by spin-coating. The second layer of the three-layer thin film sample was a layer of SiO₂ matrix, which was deposited on the first layer using radio-frequency (RF) magnetron sputtering of SiO₂ target. The RF magnetron sputtering was used for the second layer because it had a better control to deposit SiO₂ thin film of few nanometer thickness, as compared to the sol-gel process. The second layer which was a buffer layer of SiO₂, provided the space separation between the Eu³⁺ ions from the first layer, and ZnO-nc from the third layer. Finally, a third layer of ZnO-nc embedded in SiO₂ matrix (ZnO-nc:SiO₂) prepared again using the sol-gel process was deposited on the second layer by spin-coating a mixed sol of ZnO-nc and SiO₂. This layer was fabricated in exactly the same way samples of ZnO-nc in SiO₂ were prepared.

3.3. Characterization Techniques

In this section the author presents the basic principles of the various characterisation systems used to analyse the thin film samples fabricated in this work.

3.3.1. Spectrofluorometer System (SPEX Fluorolog-3)

The photoluminescence measurement of the samples were performed using the Spectrofluorometer (SPEX Fluorolog-3 Model FL3-11). The SPEX Fluorolog-3 was used to measure both the Photoluminescence (PL) Emission and Photoluminescence Excitation (PLE) spectra of the thin film samples. The SPEX Fluorolog-3 Model FL3-11 consists of a 450 W Xenon short arc lamp which is the light radiation source. The Xenon lamp has a broadband emission from 250nm to 2000nm and therefore to select light of a desired wavelength, the Spectrofluorometer has a diffraction grating monochromator. The Spectrofluorometer also comes with a sample compartment module which can hold either a thin film or a liquid sample. The emission intensity from the sample is detected at room-temperature using a photomultiplier tube (PMT) detector and similar to excitation, an emission monochromator with diffraction grating is used and positioned before the PMT to detect emissions of specific wavelengths. The diffraction gratings in both the monochromators can select wavelengths of light with 1 nm resolution ranging from 200 nm to 950 nm. However, the limiting factor is the PMT detector which works in the wavelength range of 250 nm to 900 nm. The schematic diagram of SPEX Fluorolog-3 Model FL3-11 is shown in Figure 3-6.

In this work, the samples were excited at 325 nm using the Xenon lamp to obtain the PL emission spectra. The diffraction grating in the excitation monochromator selects the 325 nm wavelength from the broadband emission of the Xenon lamp which is then guided to the sample compartment, to excite

the sample. A 325 nm line filter (Newport 10LF10-325) was placed after the excitation monochromator and before the sample to eliminate stray light of wavelengths close to 325 nm and as well as its harmonics. The emission monochromator was then used to scan the emission signals resulting from the sample from 345 nm to 640 nm and its intensity was then detected by the PMT detector. A 345 nm long pass filter (CVI LP-345-1) was placed before the emission monochromator to eliminate stray lights of wavelengths less than 345 nm from reaching the PMT detector.

Figure 3-6: Schematic diagram of Spectrofluorometer (SPEX Fluorolog-3 Model FL3-11) [148]

Similarly, the PL excitation spectra of the samples were obtained by exciting the sample using the Xenon lamp from 350 nm to 500 nm. The excitation

monochromator was used to select each wavelength from 350 nm to 500 nm. The resulting emission signals from the sample at 614 nm (for Eu^{3+} doped sample) or 545 nm (for Tb^{3+} doped sample) were obtained using the emission monochromator and were detected using the PMT detector.

To ensure consistency and accuracy of all measurements, certain precautionary steps were taken before different measurements in this work. For instance, to ensure that the radiation intensity from the Xenon lamp remained stable, the lamp was turned on for 10 minutes before measurements. In addition, to check the calibrations of the excitation monochromator, emission monochromator and the spectrofluorometer system, the Xenon lamp scan which has peak excitation intensity at 467 nm and water Ramen scan which has peak emission intensity at 398 nm wavelength, were conducted during every measurement. Also, when taking the measurement of the different samples in this work, the slit size of the monochromators was kept the same for all measurements.

3.3.2. Surface Profiler (Sloan Dektak 3)

Surface profiler was used to measure the thickness of the various samples prepared in this work. The surface profiler that was used in this work was a Sloan Dektak 3, which consists of a diamond tipped stylus connected to a linear variable differential transformer (LVDT) along with an amplifier, phase detection demodulator and an oscillator. A schematic block diagram which shows all the components of the surface profiler and its connections is shown in Figure 3-7.

The surface profiler measures the thickness of a thin film sample by moving the diamond tipped stylus along a step on the sample. The stylus moves electromechanically over the step profile in the sample which results in a

change in the position of the LVDT. This is because the stylus is coupled mechanically to the LVDT's core. The change in the core position of the LVDT generates electrical signal/current which relates to the movement of the stylus. Thus in summary, any variation in the surface thickness of the sample causes the stylus of the surface profiler to translate vertically which results in a proportional amount of electrical signal being generated from the LVDT. This electrical signal corresponds to the thickness of the sample. It is important to note that the surface profiler is sensitive to any form of environmental vibration which can affect the accuracy of the thickness measurement.

Figure 3-7: Block diagram of a Sloan Dektak 3 surface profiler [1]

Furthermore, the surface profiler was calibrated before the thickness measurement of the sample. A calibration standard with a thickness of $9450\text{\AA}$ was used to perform the thickness calibration scan of the system [1].

3.3.3. Streak Camera (OptoScope SC-10)

The time resolved photoluminescence (TRPL) spectra of the samples in this work was measured using a streak camera (OptoScope SC-10). Streak camera is

a sophisticated detector which measures ultra-fast variation of light intensity at different wavelengths with respect to time [149]. To measure the TRPL spectra, the samples were first excited using a femtosecond amplified-pulsed laser. The excitation wavelength was set at 325 nm using an optical parametric amplifier [150]. The excited samples emit light, whose emission intensity decay with respect to time and this is measured using a streak camera. Figure 3-8 shows the schematic diagram of the TRPL system.

Figure 3-8: Schematic diagram of the TRPL system

In this work, the TRPL spectra were obtained by exciting the sample using a pulsed laser with a pulse-width and repetition rate of 100 fs and 1 KHz, respectively. The TRPL emission was measured at various wavelengths ranging from 350 nm to 600 nm using the streak camera (OptoScope SC-10).

Figure 3-9 shows the schematic diagram of Optoscope SC-10 (adopted from Hamamatsu streak camera guide) and along with a graphic representation of its working principal [151].

Figure 3-9: Schematic diagram showing the operating principal of Streak Camera (OptoScope SC-10) (Adopted from Hamamatsu streak camera guide) [151]

Essentially, the photons emitted from the sample at different wavelengths are spatially separated using a diffraction grating. These photons enter the slit in

the streak camera at different horizontal position (corresponding to the wavelength) and strike the photocathode. This result in the generation of electrons from the photocathode, proportional to the number of photons or the intensity of light generated from the sample and received by the photocathode. The photons emitted at different time enter the slit in the streak camera at different time and strike the photocathode. The electrons from the photocathode pass through a pair of high voltage sweep electrodes, whose voltage varies with time. The electrons passing the electrodes at different times are deflected at different angle. The deflected electrons strike the micro-channel plate detector at different vertical positions where the electrons are multiplied thousands of times. Essentially, the number of these electrons is measured at different vertical positions which give a measure of the number of photons emitted from the sample at different time. Thus, in this manner the number of photons emitted from the sample at different wavelengths is spatially separated in horizontal axis and the number of photons emitted from the sample at different time is spatially separated in vertical axis. Thus, this camera is suitable to measure the time decay of processes, which is in the order of picosecond to nanosecond at different wavelengths.

3.4. Chapter Summary

In this chapter, the author describes the principle and the method of the fabrication techniques and also the characterisation techniques of the samples presented in the thesis. In the first section, the author has presented basic principles of the sample fabrication using the sol-gel process and the RF magnetron sputtering process. The understanding of thin film preparation is important as it helps in the studying the nature of the samples presented in this work. In the second section, the author has discussed the working

principle of the characterisation equipment used to characterise the samples in this thesis. This understanding helps in analysing the results in detail and thus in turn helps in studying the characteristics of the sample.

Chapter 4: Energy Transfer Contribution from ZnO-Nanocrystals to Eu^{3+} Ions and ZnO-Nanocrystals to Tb^{3+} Ions

4.1. Introduction

In this chapter, the author presents the results of the study of energy transfer contribution from ZnO-nc, to two different types of lanthanides ions, namely Eu^{3+} ions Tb^{3+} ions. While the energy transfer from ZnO-nc to Eu^{3+} ions [9, 23-28] and ZnO-nc to Tb^{3+} ions [34, 35, 152] have been reported by various groups, a comprehensive understanding of this energy transfer mechanism and the contribution of energy transfer from the various ZnO-nc emissions has not been reported. Some studies [9, 24, 25, 28] report that the energy transfer takes place with the involvement of the defect states in ZnO-nc, while others [26, 27] report that this energy transfer is predominantly due to the free or bound excitonic state emissions of ZnO-nc. In this chapter, the author presents a detailed study of the contribution of energy transfer from the seven emission centers of ZnO-nc embedded in SiO_2 matrix, to the two lanthanide ions (Eu^{3+} and Tb^{3+}). The author also suggests a suitable mechanism for the energy transfer process. In this study, the fabrication parameters like the annealing temperature and lanthanide ion concentration were also optimised to maximise the emission from the lanthanide ions, which has also been presented in this chapter. The results presented in this chapter are important to develop efficient red and green solid state light emitting devices, and also make an important contribution to have a better understanding of the energy transfer processes from nanocrystals to RE ions, in general.

The author first presents the study of energy transfer from ZnO-nc to Eu^{3+} ions and then the study of energy transfer from ZnO-nc to Tb^{3+} ions. Most of the

results presented in this chapter have been published in: *Nanoscale Research Letters* (V. Mangalam, K. Pita, and C. Couteau, "Study of energy transfer mechanism from ZnO nanocrystals to Eu³⁺ ions," *Nanoscale Research Letters*, journal article vol. 11, no. 1, pp. 1-9, 2016) [45] and 2016 IEEE Photonics Conference (IPC) (V. Mangalam and K. Pita, "Energy transfer from ZnO nanocrystals to Terbium (3+) ions: A spectral overlap study," in *2016 IEEE Photonics* © 2016 IEEE) [153]. This chapter also includes some additional results on the energy transfer contribution from ZnO-nc to Tb³⁺ ions which have not been presented in the 2016 IEEE Photonics Conference (IPC).

4.2. Samples

In this chapter, the author presents the study of energy transfer from ZnO-nc to two different lanthanide ions, namely Eu³⁺ and Tb³⁺. To study the energy transfer contribution from ZnO-nc to Eu³⁺ ions 3 different types of samples were prepared using the low-cost sol-gel technique. The three types samples were Eu³⁺ ions incorporated in SiO₂ matrix (Eu³⁺:SiO₂); ZnO-nanocrystals embedded in SiO₂ matrix (ZnO-nc:SiO₂) and Eu³⁺ ions and ZnO-nc incorporated in SiO₂ matrix (Eu³⁺_{*m*}:ZnO-nc:SiO₂ where *m* is the concentration of Eu³⁺ ions in molar fraction, and calculated using $m = \frac{\text{moles of (Eu}^{3+})}{\text{moles of (Eu}^{3+} + \text{Zn} + \text{Si})}$). Four Different Eu³⁺_{*m*}:ZnO-nc:SiO₂ samples were prepared with *m* ranging from 0.04 to 0.16. Similarly, to study the energy transfer contribution from ZnO-nc to Tb³⁺ ions another two more types of samples were prepared using the sol-gel technique. These samples were Tb³⁺ ions incorporated in SiO₂ matrix (Tb³⁺:SiO₂) and Tb³⁺ ions and ZnO-nc incorporated in SiO₂ matrix (Tb³⁺_{*n*}:ZnO-nc:SiO₂ where *n* is the concentration of Tb³⁺ ions in molar fraction, and calculated using $n = \frac{\text{moles of (Tb}^{3+})}{\text{moles of (Tb}^{3+} + \text{Zn} + \text{Si})}$). Four diffrenet Tb³⁺_{*n*}:ZnO-nc:SiO₂ samples were prepared with *n* ranging from 0.04 to 0.16. The detailed fabrication steps along with the

reason for choosing the sol-gel process have been discussed in detail in section 3.2.3 and 3.2.1, respectively.

4.3. Characterisation

The samples presented in this chapter were analysed by measuring the room-temperature photoluminescence (PL) emission spectra (PL) and photoluminescence excitation (PLE) spectra. A spectrofluorometer (SPEX Fluorolog-3 Model FL3-11) was used to excite the sample at 325 nm and the PL emission from the sample was measured at wavelengths ranging from 340 nm to 635 nm. While the PLE spectra were obtained by measuring the 614 nm emission intensity of the samples while varying the excitation wavelength from 325 to 550 nm. The schematic of the SPEX Fluorolog-3 Model FL3-11 along with its working principle has been discussed in detail section 3.3.1.

4.4. Results and Discussion

In this section the author presents the results and analysis of energy transfer from ZnO-nc to two different lanthanide ions, namely Eu^{3+} and Tb^{3+} . The study of energy transfer mechanism from ZnO-nc to Eu^{3+} ions is detailed in section 4.4.1. In section 4.4.2, a similar study of the energy transfer mechanism from ZnO-nc to Tb^{3+} ions is presented.

4.4.1. Energy Transfer from ZnO-nc to Eu^{3+} ions

The PL spectra of $\text{Eu}^{3+}:\text{SiO}_2$, $\text{ZnO-nc}:\text{SiO}_2$ and $\text{Eu}^{3+}_{0.12}:\text{ZnO-nc}:\text{SiO}_2$ samples annealed at 450°C using RTP is shown in Figure 4-1. The PL emission of the SiO_2 film alone (not shown) prepared using the sol-gel method showed negligible emission, which indicates that the spectra of the samples shown in Figure 4-1 are not affected by the presence of the host SiO_2 matrix. Firstly, the author observes that the $\text{ZnO-nc}:\text{SiO}_2$ sample shows a broadband emission from the ZnO-nc. The ZnO-nc broadband emission follows a trend similar to the sample

prepared in the earlier study by our research group [129]. The author also observes that the $\text{Eu}^{3+}:\text{SiO}_2$ sample shows negligible emission at all wavelengths including at 614 nm. This is a strong evidence that the optical excitation at 325 nm does not directly excite the Eu^{3+} ions in the sample [154]. The $\text{Eu}^{3+}_{0.12}:\text{ZnO-nc}:\text{SiO}_2$ sample, however, shows a broadband emission along with two high intensity sharp peaks at 590 and 614 nm. The 590 and 614 nm emissions are known as the $^5\text{D}_0 \rightarrow ^7\text{F}_1$ and $^5\text{D}_0 \rightarrow ^7\text{F}_2$ transitions from the Eu^{3+} ions [154] (see the energy level diagram in Figure 4-2(b)). These transitions together with the notation of the electronics states of the lanthanides ions like Eu^{3+} ions has been discussed in detail in section 2.2.2 and section 2.2.1, respectively. These results clearly demonstrate that the 325 nm light source excites the ZnO-nc which can then transfer the energy to the Eu^{3+} ions which in turn gives a strong emission in the red. In addition it can be seen that the intensity of the broadband emission from the $\text{Eu}^{3+}_{0.12}:\text{ZnO-nc}:\text{SiO}_2$ sample between 350 to 575 nm is lower than that from the $\text{ZnO-nc}:\text{SiO}_2$ sample, indicating that the reduction of the emission intensity is due to the energy transfer from ZnO-nc to the Eu^{3+} ions. The inset a) and b) in Figure 4-1 show, respectively, the photograph of $\text{Eu}^{3+}:\text{SiO}_2$ and $\text{Eu}^{3+}_{0.12}:\text{ZnO-nc}:\text{SiO}_2$ samples optically excited using a mercury vapour UV lamp. The bright red emission, due to the ZnO-nc mediated excitation of the Eu^{3+} ions, is clearly visible from the $\text{Eu}^{3+}_{0.12}:\text{ZnO-nc}:\text{SiO}_2$ sample.

Figure 4-1: PL spectra of $\text{Eu}^{3+}:\text{SiO}_2$, $\text{ZnO-nc}:\text{SiO}_2$ and $\text{Eu}^{3+}_{0.12}:\text{ZnO-nc}:\text{SiO}_2$ samples. *Inset a)* and *b)* show, respectively, the photograph of $\text{Eu}^{3+}:\text{SiO}_2$ and $\text{Eu}^{3+}_{0.12}:\text{ZnO-nc}:\text{SiO}_2$ samples excited using a mercury vapour UV lamp.

Further evidence of energy transfer from ZnO-nc to the Eu^{3+} ions is seen from the PLE spectra of $\text{Eu}^{3+}:\text{SiO}_2$, $\text{ZnO-nc}:\text{SiO}_2$ and $\text{Eu}^{3+}_{0.12}:\text{ZnO-nc}:\text{SiO}_2$ samples annealed at 450°C using RTP shown in Figure 4-2(a). As mentioned above in the characterisation section, the PLE spectra gives the measure of 614 nm red emission intensity of the samples as function of varying excitation wavelength. Firstly, it can be seen that the PLE spectrum of the $\text{ZnO-nc}:\text{SiO}_2$ sample show very low 614 nm emission at all excitation wavelengths. This very low 614 nm emission of the $\text{ZnO-nc}:\text{SiO}_2$ sample is due to the oxygen defect emission from ZnO-nc (Explained in Figure 4-4), upon excitation of ZnO-nc. Figure 4-2(a) also shows the PLE spectrum of $\text{Eu}^{3+}:\text{SiO}_2$ sample, in which the five major characteristic excitation peaks of the Eu^{3+} ions centered at 360, 380, 392, 412

and 463 nm which are due to ${}^7F_0 \rightarrow {}^5D_4$, ${}^7F_0 \rightarrow {}^5G_{J(J=2-5)}$, ${}^7F_0 \rightarrow {}^5L_6$, ${}^7F_0 \rightarrow {}^5D_3$ and ${}^7F_0 \rightarrow {}^5D_2$ transitions [154] of Eu^{3+} ions, respectively, is observed. The PLE spectrum of $\text{Eu}^{3+}:\text{SiO}_2$ sample also shows various other minor excitation peaks of Eu^{3+} ions. For example, it can be observed that there is a small excitation peak at 530 nm. This absorption peak is attributed to the ${}^7F_0 \rightarrow {}^5D_1$ transitions of Eu^{3+} ion [155]. Thus, similarly other transitions of Eu^{3+} ions from one energy level to another level result in other minor excitation peaks. The various excitation peaks of the Eu^{3+} ions in SiO_2 is represented schematically in the Dieke energy level diagram [156] in Figure 4-2(b). The Eu^{3+} ions in this sample upon excitation at the peak wavelengths, especially the five major excitation peaks, directly get excited and subsequently relax to the ground state through the radiative emission at 614 nm.

Interestingly, the PLE spectra of the $\text{Eu}^{3+}_{0.12}:\text{ZnO-nc}:\text{SiO}_2$ sample shows strong and broad 614 nm emission profile for excitation wavelengths between 325 to 370 nm, which then reduces till 450 nm. In this broad range, the 614 nm emission of the $\text{Eu}^{3+}_{0.12}:\text{ZnO-nc}:\text{SiO}_2$ sample is much greater than that of both $\text{Eu}^{3+}:\text{SiO}_2$ and $\text{ZnO-nc}:\text{SiO}_2$ sample. This is due to the fact that upon excitation at wavelength less than 450 nm, the ZnO-nc in the $\text{Eu}^{3+}_{0.12}:\text{ZnO-nc}:\text{SiO}_2$ sample were excited which then transferred the energy to the Eu^{3+} ions in the sample through the various excitation peaks of the Eu^{3+} ions at 360, 380, 392, 412 and 463 nm. The excited Eu^{3+} ions subsequently relaxed to the ground states giving the red emission at 614 nm. Two other striking features for the PLE of $\text{Eu}^{3+}_{0.12}:\text{ZnO-nc}:\text{SiO}_2$ sample is also observed. First of all, there is a bit of a plateau between 325 to 375 nm for the PLE and this is because in this range, the ZnO-nc are excited above its band gap where all of the ZnO-nc emission centers [129] (Explained in Figure 4-4) are excited, thus resulting in large energy transfer to the Eu^{3+} ions. Between 375 and 450 nm, as the excitation

wavelength goes below the band gap of ZnO, lesser and lesser ZnO-nc emission centers are excited which results in lesser energy transfer to the Eu^{3+} ion. The second feature is that there is a slight bump at 392 nm for the PLE of $\text{Eu}^{3+}_{0.12}:\text{ZnO-nc}:\text{SiO}_2$ due to the direct strong absorption line of the Eu^{3+} ions noticeable in the PLE of $\text{Eu}^{3+}:\text{SiO}_2$, this is in addition to the contribution of ZnO emission centers at this wavelength. Thus, these results from the PLE study undoubtedly confirms the energy transfer from ZnO-nc to the Eu^{3+} ions which was also observed from the PL spectra of the samples.

Figure 4-2: (a) PLE spectra of $\text{Eu}^{3+}:\text{SiO}_2$, $\text{ZnO-nc}:\text{SiO}_2$ and $\text{Eu}^{3+}_{0.12}:\text{ZnO-nc}:\text{SiO}_2$ samples. (b) Schematic Dieke energy level diagram of the Eu^{3+} ions in SiO_2 .

The PLE spectra presented in Figure 4-2(a) also reveal that the excitation of Eu^{3+} ions by the energy transfer from ZnO-nc is much higher than that by the

direct excitation of Eu^{3+} ions. At the 392 nm excitation (the excitation wavelength which can directly excite the Eu^{3+} ions), the 614 nm emission from the $\text{Eu}^{3+}_{0.12}:\text{ZnO-nc}:\text{SiO}_2$ sample (the sample with ZnO-nc) is much higher, about 7 time higher, than the 614 nm emission from the $\text{Eu}^{3+}:\text{SiO}_2$ sample. For the $\text{Eu}^{3+}_{0.12}:\text{ZnO-nc}:\text{SiO}_2$ sample, the Eu^{3+} ions are excited by the energy transfer from the ZnO-nc and also by the direct excitation of Eu^{3+} ions. While for the $\text{Eu}^{3+}:\text{SiO}_2$ sample (sample without ZnO-nc), the Eu^{3+} ions are excited by the direct excitation only. Since the emission from the the $\text{Eu}^{3+}_{0.12}:\text{ZnO-nc}:\text{SiO}_2$ sample is about 7 times higher than that from the $\text{Eu}^{3+}:\text{SiO}_2$ sample, this data implies that the energy transfer from ZnO-nc to Eu^{3+} ions dominate the excitation of Eu^{3+} ions.

Also at excitation at 340 nm, there is no direct excitation to Eu^{3+} ions. So, for the $\text{Eu}^{3+}_{0.12}:\text{ZnO-nc}:\text{SiO}_2$ sample, the excitation of Eu^{3+} are purely due to the energy transfer from ZnO-nc, and it is observed that the emission at 614 nm from this samples is 13 times higher than that from the $\text{Eu}^{3+}:\text{SiO}_2$ sample (sample without ZnO-nc), in which the Eu^{3+} ions are directly excited by the 392 nm excitation. These results clearly show that the excitation of Eu^{3+} ions by the energy transfer from ZnO-nc is much higher than that by the direct excitation.

To obtain the optimum red emission intensity from the $\text{Eu}^{3+}_m:\text{ZnO-nc}:\text{SiO}_2$ configuration, different samples with various annealing temperatures and different Eu^{3+} ion concentrations were fabricated and studied. Figure 4-3(a) presents the intensity of emission at 614 nm from the $\text{Eu}^{3+}_m:\text{ZnO-nc}:\text{SiO}_2$ samples as a function of Eu^{3+} ion concentration (m ranging from 0 to 0.16) at various annealing temperatures from 450°C to 600°C. The corresponding PL spectra of the $\text{Eu}^{3+}_m:\text{ZnO-nc}:\text{SiO}_2$ samples, with m ranging from 0 to 0.16, annealed at 450°C is shown in Figure 4-3(b). Here the author observes that the

red emission intensity shows a non-linear increase with increasing the Eu^{3+} ion concentration from 0 to 12 mol%. This is expected as increasing the Eu^{3+} ions decreases the distance between the ZnO-nc and the Eu^{3+} ions which results in enhanced energy transfer [9, 28]. Thus greater fraction of Eu^{3+} ions are excited with increasing concentration resulting in enhanced red emission. A further increase in Eu^{3+} ion concentration to 16 mol% shows a decrease in the 614 nm emission intensity. This is attributed to Eu^{3+} ion concentration quenching [157], i.e. migration of energy among the Eu^{3+} ions which is non-radiatively dissipated through the quenching sites. The close proximity of the Eu^{3+} ions due to increasing concentration results in concentration quenching. This trend is observed in all the $\text{Eu}^{3+}_m\text{:ZnO-nc:SiO}_2$ samples which were annealed at 450°C, 500°C, 550°C and 600°C. It is clearly shown here that the optimum Eu^{3+} ion concentration for maximum red emission is 12 mol%. This was also observed in $\text{Y}_2\text{O}_3\text{:Eu}^{3+}$ thin film phosphors [158]. In Figure 4-3(a), the author notes there is a small emission at 614 nm from the 0 mol% Eu^{3+} sample (i.e. ZnO-nc:SiO₂ sample) annealed at 450°C, this is due to the broadband nature of the ZnO-nc emission at this annealing temperature.

Figure 4-3: PL spectra and 614 nm red emission intensity from the $\text{Eu}^{3+}_m\text{:ZnO-nc:SiO}_2$ samples. (a) 614 nm red emission intensity from the $\text{Eu}^{3+}_m\text{:ZnO-nc:SiO}_2$ samples as a function of Eu^{3+} ion concentration at various annealing temperatures. (b) The PL spectra of the $\text{Eu}^{3+}_m\text{:ZnO-nc:SiO}_2$ samples RTP annealed at 450°C for various Eu^{3+} ion concentrations. (c) The PL spectra of the $\text{Eu}^{3+}_{0.12}\text{:ZnO-nc:SiO}_2$ samples annealed by RTP at various temperatures.

Figure 4-4: The emission centers of ZnO-nc in (a) ZnO-nc:SiO₂ and (b) Eu³⁺_{0.12}:ZnO-nc:SiO₂ samples annealed at 450°C. See the main text for the various ZnO-nc emission centers. (c) The schematic energy level diagram of the emission centers of ZnO-nc in SiO₂.

In Figure 4-3(c), the corresponding PL spectra of the $\text{Eu}^{3+}_{0.12}\text{:ZnO-nc:SiO}_2$ samples RTP annealed at temperatures ranging from 450°C to 600°C is also shown. Here the author observes that increasing the annealing temperature leads to a reduction in the red emission intensity from the samples. This is due to the change in the nature of the emissions from the ZnO-nc embedded in the samples with increasing annealing temperature. Energy is transferred from the ZnO-nc to the Eu^{3+} ions due to the overlap of the broadband ZnO-nc emission spectra [129] and Eu^{3+} ion excitation spectra (see Figure 4-2(a)). Within the emission range of ZnO-nc from 350 to 575 nm, there is a strong overlap with Eu^{3+} ion absorption which is responsible for the resonant energy transfer from the ZnO-nc to the Eu^{3+} ions in the samples. The energy transfer from ZnO-nc results in the excitation of the Eu^{3+} ions from their ground state ($^7\text{F}_0$) to any of the higher states ($^5\text{D}_2$, $^5\text{D}_3$, $^5\text{D}_4$, $^5\text{G}_{\text{J}(J=2-5)}$, $^5\text{L}_6$) which subsequently relax back to their ground state by the radiative emissions in the red at 614 and 590 nm (See the energy level diagram in Figure 4-2(b)). Since the broadband emission from the ZnO-nc is the largest at 450°C annealing, the energy transfer will also be the strongest at this annealing temperature. By the same token, when the annealing temperature increases, the bandwidth of the broad emission from ZnO-nc decreases thus resulting in decreasing the spectral overlap between the ZnO-nc broadband emission and the Eu^{3+} ion excitation, and therefore a reduction in energy transfer from the ZnO-nc to the Eu^{3+} ions leading to a reduction in the red emission intensity from the Eu^{3+} ions. In addition, the energy transfer from ZnO-nc to the Eu^{3+} ions is inhibited in the samples annealed at 550°C and 600°C due to the possible formation of Zn_2SiO_4 at the surface of the ZnO-nc [159]. Formation of Zn_2SiO_4 reduces the size of ZnO-nc causing reduction of PL emission [159] from the ZnO-nc and also results in increase in distance between ZnO-nc and Eu^{3+} ion which results in reduces

energy transfer from the ZnO-nc to the Eu^{3+} ions. In this work, the optimum RTP annealing temperature has been found to be 450°C.

In section 2.4.1 [129], the author presented details of the broad emission spectra of ZnO-nc embedded in SiO_2 which consists of seven Gaussian peaks centered at 360, 378, 396, 417, 450, 500 and 575 nm. The origins of these emissions have been studied and published in the author's group's work on ZnO-nc in SiO_2 [129]. The 360 and 378 nm peaks were attributed respectively to band edge emission from the smallest ZnO-nc which possibly experiences quantum confinement effect (labelled as QC) [160] and ZnO-nc excitonic emission (labelled as EE) [87, 89]. The 396 nm peak was attributed to the defect state electronic transition from Zn interstitial (labelled as Zn_i) to Zn vacancy (labelled as V_{Zn}) [13] and the remaining emission peaks were due to the electronic transition from, or, to the oxygen-related defects, namely oxygen interstitial (labelled as O_i) defect emission at 417 nm [93, 161], oxygen vacancy (labelled as V_{O}) emission at 450 nm, singly ionized oxygen vacancy (labelled as $\text{V}_{\text{O}}^{\bullet}$) emission at 500 nm and doubly charged oxygen vacancy (labelled as $\text{V}_{\text{O}}^{\bullet\bullet}$) emission at 575 nm [13-15]. The schematic energy level diagram of the seven ZnO-nc emission centers is shown in Figure 4-4(c). The energies of ZnO-nc emission centers are shown as broad vertical energy bands shown with a colour gradient to indicate the broad emission bandwidth of the various ZnO-nc emission centers. In this chapter, the author analyses the contribution of each of these emissions or de-excitation centers in exciting the Eu^{3+} ions. In order to do so, the PL emission spectra of the ZnO-nc: SiO_2 and $\text{Eu}^{3+}_{0.12}$:ZnO-nc: SiO_2 samples annealed at 450°C were deconvoluted using the seven de-excitation centers of ZnO-nc as shown in Figure 4-4(a) and Figure 4-4(b), respectively. The fitting parameters, such as peak wavelength and full

width at half maxima of the Gaussian peaks were kept the same as those in the author's groups' work on ZnO-nc in SiO₂ [129].

To study the contribution of energy transfer from the ZnO-nc emission centers to the Eu³⁺ ions the spectral overlap integral value of emission from each of the seven ZnO-nc emission centers in ZnO-nc:SiO₂ sample with the Eu³⁺ excitation spectrum was firstly determined. The spectral overlap integral value gives a measure of the radiative energy transfer from the ZnO-nc emission centers to the Eu³⁺ ions. An example of the spectral overlap between Zn_i to V_{zn} defect state emission of ZnO-nc:SiO₂ sample annealed at 450°C and the Eu³⁺ excitation is show in Figure 4-5. The spectral overlap integral from each of the seven ZnO-nc emission centers are shown in Figure 4-7 on the left axis (solid line).

Figure 4-5: An example of the spectral overlap. The spectral overlap of Zn_i to V_{zn} defect state emission of ZnO-nc:SiO₂ sample annealed at 450°C along with the Eu³⁺ excitation spectrum.

Furthermore, in Figure 4-4(a) and Figure 4-4(b), it is clearly observed that the emission intensities from various ZnO-nc emission centers in the $\text{Eu}^{3+}_{0.12}:\text{ZnO-nc}:\text{SiO}_2$ sample are lower than those in the $\text{ZnO-nc}:\text{SiO}_2$ sample. This intensity difference is due to the energy loss from the various ZnO-nc emission centers because of the incorporation of the Eu^{3+} ions. Figure 4-6 shows the intensity differences of each of the seven ZnO-nc emission centers between $\text{ZnO-nc}:\text{SiO}_2$ and $\text{Eu}^{3+}_{0.12}:\text{ZnO-nc}:\text{SiO}_2$ samples annealed at 450°C . Thus, calculating the integral value of the difference in the emission intensities of each of the seven ZnO-nc emission centers in Figure 4-6 gives a measure of energy loss from each of the ZnO-nc de-excitation centers in exciting the Eu^{3+} ions. The seven ZnO-nc emission centers intensity difference integral are also shown in Figure 4-7 on the right axis (dotted line).

Figure 4-6: The intensity difference from ZnO-nc emission centers. The intensity difference between $\text{ZnO-nc}:\text{SiO}_2$ and $\text{Eu}^{3+}_{0.12}:\text{ZnO-nc}:\text{SiO}_2$ samples annealed at 450°C which is due to the incorporation of Eu^{3+} ions.

In Figure 4-7 the measure of the energy transfer, which is the spectral overlap integral value, and the measure of energy losses, which is ZnO-nc emission center's intensity difference integral value, from each of the seven ZnO-nc emission centers is shown. Here, an identical trend between the spectral overlap integral and ZnO-nc emission intensity difference integral values from the QC, EE and Zn_i to V_{Zn} ZnO-nc emission centers which are centered at 360, 378 and 396 nm, respectively, is observed. Amongst these, the EE and Zn_i to V_{Zn} have the highest spectral overlap integral and ZnO-nc emission intensity difference integral values of energy transfer. This implies that the EE and Zn_i to V_{Zn} ZnO-nc emission centers contribute the most to energy transfer from ZnO-nc to the Eu^{3+} ions. In contrast, it is observed that the ZnO-nc emission intensity difference integral values from ZnO-nc emission centers like O_i , V_o and $V\dot{O}$ centered at 417, 450 and 500 nm, are higher than the spectral overlap integral values. The author proposes that this is due to defect centers induced by the incorporation of the Eu^{3+} ions in the $Eu^{3+}_{0.12}:ZnO-nc:SiO_2$ sample, providing non-radiative de-excitation paths for O_i , V_o and $V\dot{O}$ emissions. This means that only some portion of the O_i , V_o and $V\dot{O}$ ZnO-nc emissions transfer the energy to the Eu^{3+} ions. Large portion of the energy from the O_i , V_o and $V\dot{O}$ ZnO-nc emissions decay non-radiatively through the Eu^{3+} ion induced defect centers. In this way, even though the spectral overlap integral values of O_i , V_o and $V\dot{O}$ ZnO-nc emissions are low, their ZnO-nc emission intensity difference integral values can be relatively high since these de-excitations occur via the Eu^{3+} ion induced defect states.

Figure 4-7: A comparison of the spectral overlap integral and ZnO-nc emission intensity difference integral. The comparison for each of the seven ZnO-nc emission center for the samples annealed at 450°C.

4.4.2. Energy Transfer from ZnO-nc to Tb³⁺ ions

The study of the energy transfer from ZnO-nc to Tb³⁺ ions is presented in this section. Similar to the previous section, first the PL spectra of Tb³⁺:SiO₂, ZnO-nc:SiO₂ and Tb³⁺_{0.12}:ZnO-nc:SiO₂ samples annealed at 450°C using RTP is shown in Figure 4-8. The author observes that the ZnO-nc:SiO₂ sample shows a broadband emission from the ZnO-nc, which follows a trend similar to the sample prepared in the earlier study by our research group [129]. The author also observes that the Tb³⁺:SiO₂ sample shows negligible emission at all wavelengths including at 545 nm. This is strong evidence that the optical excitation at 325 nm does not directly excite the Tb³⁺ ions in the sample. The Tb³⁺_{0.12}:ZnO-nc:SiO₂ sample, however, shows a broadband emission along with

four high intensity sharp peaks at 489 nm, 545 nm, 586 nm and 621 nm. These emissions are known as the $^5D_4 \rightarrow ^7F_6$, $^5D_4 \rightarrow ^7F_5$, $^5D_4 \rightarrow ^7F_4$ and $^5D_0 \rightarrow ^7F_3$ transitions from the Tb^{3+} ions, respectively. These results clearly demonstrate that the 325 nm light source excites the ZnO-nc which can then transfer the energy to the Tb^{3+} ions which in turn gives a strong emission in the green.

Figure 4-8: PL spectra of Tb^{3+} : SiO_2 , $ZnO\text{-}nc:SiO_2$ and $Tb^{3+}_{0.12}:ZnO\text{-}nc:SiO_2$ samples. Inset i) and ii) show, respectively, the photograph of Tb^{3+} : SiO_2 and $Tb^{3+}_{0.12}:ZnO\text{-}nc:SiO_2$ samples excited using a mercury vapour UV lamp [153] © 2016 IEEE.

In addition it can be seen that the intensity of the broadband emission from the $Tb^{3+}_{0.12}:ZnO\text{-}nc:SiO_2$ sample between 350 to 575 nm is lower than that from the $ZnO\text{-}nc:SiO_2$ sample, indicating that the reduction of the emission intensity is due to the energy transfer from ZnO-nc to the Tb^{3+} ions. The inset a) and b) in Figure 4-8 show, respectively, the photograph of Tb^{3+} : SiO_2 and $Tb^{3+}_{0.12}:ZnO\text{-}nc:SiO_2$ samples optically excited using a mercury vapour UV lamp. The bright green emission, due to the ZnO-nc mediated excitation of the Tb^{3+} ions, is clearly visible from the $Tb^{3+}_{0.12}:ZnO\text{-}nc:SiO_2$ sample. The author would like to highlight again that the PL emission of the SiO_2 film alone (not shown)

prepared using the sol-gel method showed negligible emission, which indicates that the spectra of the samples shown in Figure 4-8 are not affected by the presence of the host SiO₂.

It is important to note here that the emission curves of Tb³⁺ ions are maintained after being incorporated in the host SiO₂ matrix. The ⁵D₄→⁷F₆, ⁵D₄→⁷F₅, ⁵D₄→⁷F₄ and ⁵D₀→⁷F₃ transitions of Tb³⁺ ions are the standard emissions which are attributed to the 4f electrons of the Tb³⁺ ions. Electrons in the 4f-orbital of the lanthanide ions form a complex multi-electron system which is shielded by the electrons of the outer 5s and 5p orbitals. This gives the lanthanide ions unique optical properties such as sharp emission lines and metastable electronics states which are not affected by the crystal field of the host matrix. The standard emission curves of Tb³⁺ ions can also be seen from the Dieke Diagram. The Dieke Diagram is essentially the energy level diagram of Lanthanide (3+) ions and this diagram gives an indication of standard emissions of the lanthanide (3+) ions [39]. In Dieke Diagram, the energy levels of the lanthanide (3+) ions were studied based on the chloride form of the lanthanide ions. For example, Tb³⁺ ions in TbCl₃ were studied to determine the standard emissions of Tb³⁺ ions. The comparison of Tb³⁺ ions emission wavelength, for Tb³⁺ ions embedded in SiO₂ and Tb³⁺ ion from Dieke Diagram, is shown in the table below. Table 4-1 shows the peak wavelength and the full width half maximum (FWHM) wavelength range of the four major emissions curves of Tb³⁺ ions embedded in SiO₂ and Tb³⁺ ion in Dieke Diagram. The FWHM wavelength range is indicated in the bracket next to the peak wavelength in the table. The table shows that the peak wavelength of the four major emissions curves of Tb³⁺ ions embedded in SiO₂ and Tb³⁺ ion in Dieke Diagram are very close. The FWHM wavelength range gives the bandwidth of the emission curve and it can be clearly seen FWHM wavelength range of Tb³⁺

ions embedded in SiO₂ overlaps with the FWHM wavelength range of Tb³⁺ ion in Dieke Diagram. Thus, this indicates that the emission curves of Tb³⁺ ions embedded in SiO₂ and Tb³⁺ ion in Dieke Diagram are the same. In conclusion, this shows that the emission curves of Tb³⁺ are maintained even after being incorporated into a host like SiO₂.

Table 4-1: Comparison of Tb³⁺ ions emission wavelength, for Tb³⁺ ions embedded in SiO₂ and Tb³⁺ ion in Dieke Diagram.

Tb ³⁺ Transition	Emission Wavelength of Tb ³⁺ ions embedded in SiO ₂	Emission Wavelength of Tb ³⁺ ion in Dieke Diagram
⁵ D ₄ → ⁷ F ₆	489 nm (483-498 nm)	495 nm (489-501 nm)
⁵ D ₄ → ⁷ F ₅	545 nm (540-552 nm)	549 nm (542-557 nm)
⁵ D ₄ → ⁷ F ₄	586 nm (580-595 nm)	588 nm (583-593 nm)
⁵ D ₀ → ⁷ F ₃	621 nm (614-627 nm)	621 nm (617-625 nm)

Figure 4-9: The PL spectra of the Tb³⁺_n:ZnO-nc:SiO₂ samples RTP annealed at 450°C for various Tb³⁺ ion concentrations [153] © 2016 IEEE.

To obtain the optimum green emission intensity from the $\text{Tb}^{3+}_n\text{:ZnO-nc:SiO}_2$ configuration, different samples with various Tb^{3+} ion concentrations annealed at 450°C and 500°C were fabricated and studied. The PL spectra of the $\text{Tb}^{3+}_n\text{:ZnO-nc:SiO}_2$ samples, with n (Concentration of Tb^{3+} ions in mole fraction) ranging from 0 to 0.16, annealed at 450°C is shown in Figure 4-9. The author observes that the green emission intensity shows a increase with increasing the Tb^{3+} ion concentration from 0 to 12 mol%. This is expected as increasing the Tb^{3+} ions decreases the distance between the ZnO-nc and the Tb^{3+} ions which results in enhanced energy transfer [9, 28]. Thus greater fraction of Tb^{3+} ions are excited with increasing concentration resulting in enhanced green emission. A further increase in Tb^{3+} ion concentration to 16 mol% shows a decrease in the 545 nm emission intensity. This is attributed to Tb^{3+} ion concentration quenching, which is similar to Eu^{3+} ion concentration quenching mentioned in section 4.2.1. Concentration quenching is the migration of energy among the lanthanide ions which is non-radiatively dissipated through the quenching sites. A detailed description of concentration quenching is presented in section 2.2.3.3. The close proximity of the Tb^{3+} ions due to increasing concentration results in concentration quenching.

In Figure 4-10, the PL spectra of the $\text{Tb}^{3+}_{0.12}\text{:ZnO-nc:SiO}_2$ samples RTP annealed at temperatures, 450°C and 500°C is shown. Here, the author observes that increasing the annealing temperature leads to a reduction in the green emission intensity from the samples. This is due to the change in the nature of the emissions from the ZnO-nc embedded in the samples with increasing annealing temperature. Energy is transferred from the ZnO-nc to the Tb^{3+} ions due to the overlap of the broadband ZnO-nc emission spectra and Tb^{3+} ion excitation spectra (see Figure 4-12). There is a strong overlap of ZnO-nc emission with Tb^{3+} ion absorption for the samples annealed at 450°C compared

to the samples annealed at 500°C. Thus in this work, the optimum RTP annealing temperature has been found to be 450°C.

Figure 4-10: The PL spectra of the $\text{Tb}^{3+}_{0.12}\text{:ZnO-nc:SiO}_2$ samples annealed by RTP at 450°C and 500°C temperatures.

Similar to energy transfer from ZnO-nc to Eu^{3+} ion, the author has analysed the contribution of each of the seven ZnO-nc emissions in exciting the Tb^{3+} ions. In order to do so, as before, the PL emission spectra of the ZnO-nc:SiO_2 and $\text{Tb}^{3+}_{0.12}\text{:ZnO-nc:SiO}_2$ samples annealed at 450°C were deconvoluted using the seven de-excitation centers of ZnO-nc as shown in Figure 4-11(a) and Figure 4-11(b), respectively. The fitting parameters, such as peak wavelength and full width at half maxima of the Gaussian peaks were kept the same as those in the author's group's work on ZnO-nc in SiO_2 [129].

Figure 4-11: The emission centers of ZnO-nc in (a) ZnO-nc:SiO₂ and (b) Tb³⁺_{0.12}:ZnO-nc:SiO₂ samples annealed at 450°C.

Figure 4-12: An example of the spectral overlap. The spectral overlap of Excitonic Emission center of ZnO-nc:SiO₂ sample annealed at 450°C along with the Tb³⁺ excitation spectrum.

To study the contribution of energy transfer from the ZnO-nc emission centers to the Tb³⁺ ions the spectral overlap integral value of emission from each of the seven ZnO-nc emission centers in ZnO-nc:SiO₂ sample with the Tb³⁺ excitation spectrum was firstly determined. The spectral overlap integral value gives a measure of the radiative energy transfer from the ZnO-nc emission centers to the Tb³⁺ ions. An example of the spectral overlap between excitonic emission of ZnO-nc:SiO₂ sample annealed at 450°C and the Tb³⁺ excitation is show in Figure 4-12. The spectral overlap integral from each of the seven ZnO-nc emission centers are shown in Figure 4-14 on the left axis (solid line).

Furthermore, in Figure 4-11(a) and Figure 4-11(b), it is clearly observed that the emission intensities from various ZnO-nc emission centers in the Tb³⁺_{0.12}:ZnO-nc:SiO₂ sample are lower than those in the ZnO-nc:SiO₂ sample.

This intensity difference is due to the energy loss from the various ZnO-nc emission centers because of the incorporation of the Tb^{3+} ions. Figure 4-13 shows the intensity differences of each of the seven ZnO-nc emission centers between ZnO-nc:SiO_2 and $\text{Tb}^{3+}_{0.12}\text{:ZnO-nc:SiO}_2$ samples annealed at 450°C . Thus, calculating the integral value of the difference in the emission intensities of each of the seven ZnO-nc emission centers in Figure 4-11 gives a measure of energy loss from each of the ZnO-nc de-excitation centers in exciting the Tb^{3+} ions. The seven ZnO-nc emission centers intensity difference integral are also shown in Figure 4-14 on the right axis (dotted line).

Figure 4-13: The intensity difference from ZnO-nc emission centers. The intensity difference between ZnO-nc:SiO_2 and $\text{Tb}^{3+}_{0.12}\text{:ZnO-nc:SiO}_2$ samples annealed at 450°C which is due to the incorporation of Tb^{3+} ions.

Figure 4- 14: A comparison of the spectral overlap integral and ZnO-nc emission intensity difference integral. The comparison for each of the seven ZnO-nc emission center for the samples annealed at 450°C.

In Figure 4-14 the measure of the energy transfer to Tb^{3+} ions, which is the spectral overlap integral value, and the measure of energy losses, which is ZnO-nc emission center's intensity difference integral value, from each of the seven ZnO-nc emission centers is shown. It can be seen that the QC and EE emission centers have the highest spectral overlap integral value while low intensity difference integral value. This implies that the QC and EE emission centers contribute the most to energy transfer from ZnO-nc to the Tb^{3+} ions. In contrast, it is observed that the ZnO-nc emission intensity difference integral values from ZnO-nc emission centers like Zn_i to V_{Zn} , O_i , V_o , V_O and V_O centered at 396, 417, 450, 500 and 505 nm, are high while their spectral overlap integral values are negligible. The author proposes that this is due to defect centers induced by the incorporation of the Tb^{3+} ions in the $\text{Tb}^{3+}_{0.12}\text{ZnO-nc:SiO}_2$.

sample, providing non-radiative de-excitation paths for Zn_i to V_{Zn} , O_i , V_o , $\dot{V}O$ and $\ddot{V}O$ emissions. This is similar to the defect created in $Eu^{3+}_{0.12}:ZnO\text{-}nc:SiO_2$ sample due the incorporation of Eu^{3+} ions. Most of the energy from the Zn_i to V_{Zn} , O_i , V_o , $\dot{V}O$ and $\ddot{V}O$ ZnO-nc emissions decay non-radiatively through the Tb^{3+} ion induced defect centers.

From the results presented above on the study of the energy transfer from ZnO-nc to Eu^{3+} and Tb^{3+} ions, it is clearly seen that the excitonic emission of ZnO-nc have high energy transfer contribution to both Eu^{3+} and Tb^{3+} ions. Moreover, both Eu^{3+} and Tb^{3+} ions create defects when co-doped with ZnO-nc in SiO_2 . The lanthanide ion induced defects result in the oxygen defect emission centers of ZnO-nc transferring energy to the lanthanide ion induced defects in both sample of Eu^{3+} ions and Tb^{3+} ions. The formation of lanthanide ion induced defect centers is a very important result that needs to be considered when fabricating light-emitting devices which use the energy transfer process from ZnO-nc to excite RE ions.

4.4.3. Stability of PL emission from ZnO-nc, Eu^{3+} and Tb^{3+} ions

The stability of PL emission of samples of ZnO-nc embedded in SiO_2 matrix co-doped with Eu^{3+} ions and samples of ZnO-nc in SiO_2 co-doped with Tb^{3+} ions is a very important factor that needs to be considered for the energy transfer from ZnO-nc to Eu^{3+} and ZnO-nc to Tb^{3+} ions. In this work, the ZnO-nc, Eu^{3+} and Tb^{3+} ions (the dopants) are embedded in the SiO_2 matrix which provides physical and chemical protection to the dopants. The SiO_2 ensures the stability of the dopants and thus ensuring that the PL emission from the ZnO-nc, Eu^{3+} and Tb^{3+} ions in the samples is stable over time. The stability of PL emission from the ZnO-nc, Eu^{3+} and Tb^{3+} ions is confirmed by Figure 4-15 and Figure 4-

16, which shows the PL spectra of the $\text{Eu}^{3+}_{0.12}:\text{ZnO-nc}:\text{SiO}_2$ sample measured 5 months apart and the PL spectra of the $\text{Tb}^{3+}_{0.12}:\text{ZnO-nc}:\text{SiO}_2$ sample measured 6 months apart, respectively.

Figure 4-15: The PL spectra of the $\text{Eu}^{3+}_{0.12}:\text{ZnO-nc}:\text{SiO}_2$ sample measured 5 months apart.

The figure clearly shows that the PL emission does not change over time. Thus, confirming that the ZnO-nc , Eu^{3+} and Tb^{3+} ions in the sample have long term stability. This is different from ZnO-nc in powdered form, where the PL emission from the ZnO-nc could change over time as they are directly exposed to surrounding environment.

Figure 4-16: The PL spectra of the $\text{Tb}^{3+}_{0.12}:\text{ZnO-nc}:\text{SiO}_2$ samples measured 6 months apart.

4.5. Chapter Summary

In summary, in this chapter the author presents the result of energy transfer from ZnO-nc to Eu^{3+} ions and ZnO-nc to Tb^{3+} ions. First, the author convincingly show that efficient energy transfer takes place from excited ZnO-nc to Eu^{3+} ions embedded in a SiO_2 matrix. This energy transfer gives strong red emission at 614 nm from the Eu^{3+} ions due to the $^5\text{D}_0 \rightarrow ^7\text{F}_2$ transition. This was observed using the PL emission spectra of the above mentioned samples which were optically excited using a continuous excitation at 325 nm. The energy transfer from the ZnO-nc to the Eu^{3+} ion was further confirmed by studying the photoluminescence excitation spectra of the samples. The photoluminescence excitation measurements of the samples also reveal that the excitation of Eu^{3+}

ions by the energy transfer from ZnO-nc is around seven times higher than the highest direct excitation of Eu^{3+} ions at 392 nm. The dependence of the Eu^{3+} red emission on the annealing temperature and also on the Eu^{3+} concentration in the sample were studied and optimised for an annealing temperature of 450°C and for a Eu^{3+} concentration of 12 mol%. The author also presents a detailed study of the energy transfer by identifying the contribution of the seven different emission centers of ZnO-nc in exciting the Eu^{3+} ions. It is clearly show that the EE and Zn_i to V_{Zn} ZnO-nc emission centers have the highest contribution to the energy transfer from ZnO-nc to the Eu^{3+} ions. While the O_i , V_o and $\text{V}\dot{\text{O}}$ ZnO-nc emission centers have low energy transfer contributions but high energy loss due to the presence of Eu^{3+} ions induced defect centers in the $\text{Eu}^{3+}_{0.12}:(\text{ZnO-nc}:\text{SiO}_2)$ sample.

Similarly, the author also shows that efficient energy transfer takes place from excited ZnO-nc to Tb^{3+} ions embedded in a SiO_2 matrix. This energy transfer gives strong green emission at 545 nm from the Tb^{3+} ions. Furthermore, the dependence of the Tb^{3+} green emission on the annealing temperature and also on the Tb^{3+} concentration in the sample were studied and optimised for an annealing temperature of 450°C and for a Tb^{3+} concentration of 12 mol%. The author also presents a detailed study of the energy transfer by identifying the contribution of the seven different emission centers of ZnO-nc in exciting the Tb^{3+} ions. It is clearly show that the QC and EE ZnO-nc emission centers have the highest contribution to the energy transfer from ZnO-nc to the Tb^{3+} ions. While the Zn_i to V_{Zn} , O_i , V_o , $\text{V}\dot{\text{O}}$ and $\text{V}\ddot{\text{O}}$ ZnO-nc emission centers have high energy loss due to the presence of Tb^{3+} ions induced defect centers in the $\text{Tb}^{3+}_{0.12}:(\text{ZnO-nc}:\text{SiO}_2)$ sample.

Finally, the long term stability of the ZnO-nc, Eu^{3+} and Tb^{3+} ions in the samples were analyzed and it was shown that the PL emission from ZnO-nc, Eu^{3+} and Tb^{3+} ions is stable over long time as it is embedded in SiO_2 matrix.

Chapter 5: Energy Transfer Efficiency from ZnO-Nanocrystals to Eu^{3+} Ions and ZnO-Nanocrystals to Tb^{3+} Ions

5.1. Introduction

In the previous chapter, the author had presented evidences for the energy transfer from ZnO-nc to Eu^{3+} ions and also showed the contribution of energy transfer from the seven different ZnO-nc emission centers to Eu^{3+} ions. In this chapter, the author will further present the study of the energy transfer from the seven different ZnO-nc emission centers to the Eu^{3+} ions by calculating the energy transfer efficiency.

The energy transfer efficiency is primarily calculated by measuring the time-resolved photoluminescence (TRPL) measurements from the sample. The steady state PL measurement can also be used to calculate the energy transfer efficiency and will be presented later in this chapter. While there have been few studies of energy transfer from ZnO-nc to lanthanide ions like Yb^{3+} and Er^{3+} based on time-resolved photoluminescence (TRPL) measurements [18, 102] a detailed understanding of the energy transfer efficiency from the seven different ZnO-nc emission centers to RE ions, especially Eu^{3+} ions and Tb^{3+} ions, has not been studied and reported previously. In this chapter, the author will first present and discusses the efficiency of energy transfer from the various ZnO-nc emission centres to Eu^{3+} ions calculated based on the decay time of TRPL measurements. Then, for comparison, the author presents the transfer efficiency calculated from the steady-state PL emission data. The author also presents the transfer efficiency from ZnO-nc to Tb^{3+} ions calculated from the steady-state PL emission data. The results in this chapter help to identify that the ZnO-nc emission centers which have high transfer efficiencies from ZnO-nc

to Eu^{3+} ions resulting in the radiative emission at 614 nm and the transfer efficiencies from ZnO-nc to Tb^{3+} ions resulting in the radiative emission at 545 nm. This knowledge is vital in understanding the process of energy transfer and in maximising the energy transfer from ZnO-nc to RE ions, especially Eu^{3+} ions and Tb^{3+} ions. Most of the results of the study presented in this chapter has been published in: Materials (V. Mangalam and K. Pita, "Energy Transfer Efficiency from ZnO-Nanocrystals to Eu^{3+} Ions Embedded in SiO_2 Film for Emission at 614 nm," *Materials*, vol. 10, no. 8, p. 930, 2017.) [107].

5.2. Samples

In this chapter, the author presents the study of three types of thin-film samples. The first type of sample is ZnO-nc in SiO_2 (referred to as ZnO-nc: SiO_2 sample, as stated in section 4.2) and the second type of sample is ZnO-nc in SiO_2 co-doped with 12 mol% Eu^{3+} ions (referred to as $\text{Eu}^{3+}_{0.12}$:ZnO-nc: SiO_2 sample, as stated in section 4.2). The type of sample is ZnO-nc in SiO_2 co-doped with 12 mol% Tb^{3+} ions (referred to as $\text{Tb}^{3+}_{0.12}$:ZnO-nc: SiO_2 sample, as stated in section 4.2).

The $\text{Eu}^{3+}_{0.12}$:ZnO-nc: SiO_2 sample and $\text{Tb}^{3+}_{0.12}$:ZnO-nc: SiO_2 sample were used in this study because the 12 mol% sample was found to have the highest PL emission from the Eu^{3+} ions at 614 nm and the highest PL emission from Tb^{3+} ions at 545 nm due to energy transfer from ZnO-nc, as explained in section 4.4.1 and 4.4.2. The samples analysed in this chapter are the same samples as those presented in the previous chapter. The detailed fabrication steps along with the reason for choosing the sol-gel process have been discussed in detail in section 3.2.2 and 3.2.1, respectively.

5.3. Characterisation

The two samples in this chapter were characterised by measuring the TRPL spectra and the steady-state PL spectra. The TRPL spectra was obtained by exciting the sample using a femtosecond amplified-pulsed laser, which was tuned to 325 nm using an optical parameter amplifier and detected using a streak camera (OptoScope SC-10, Optronis, Kehl, Baden-Württemberg, Germany). The pulse-width and the repetition rate of the excitation pulse were 100 fs and 1 KHz, respectively. The schematic of this measuring technique has been discussed in detail in section 3.3.3 . The steady-state PL measurements were obtained by exciting the samples at 325 nm using a spectrofluorometer (SPEX Fluorolog-3 Model FL3-11, Horiba, Edison, New Jersey, USA), just like in the previous chapter. The schematic of the SPEX Fluorolog-3 Model FL3-11 along with its working principle has been discussed in detail section 3.3.1 .

5.4. Results and Discussion

The author will first presents the TRPL results followed by the steady-state PL results and then present the analysis and discussion of the transfer efficiency obtained from the two measurements above.

5.4.1. Transfer Efficiency from Time-Resolved Photoluminescence Emission

As mention in section 2.4.1, the ZnO-nc have seven different emission centers and the peak wavelengths of these seven ZnO-nc emission centers are 360, 378, 396, 417, 450, 500, and 575 nm. These emission centers have been identified as band-edge emissions from the smallest ZnO-nc, which possibly experiences some quantum confinement effect (QC) [160], excitonic emission (EE) [87, 89], and five different defect state emissions, namely Zn defect (Zn_i to V_{Zn}) [13], oxygen interstitial defect (O_i) [93, 161], and oxygen vacancy defects

(V_o , $V\dot{O}$, $V\ddot{O}$) [13-15], respectively, in the increasing order of peak wavelengths. The TRPL spectra were measured at each of the peak wavelengths of the seven ZnO-nc emission centers for the two samples (ZnO-nc:SiO₂ and Eu³⁺_{0.12}:ZnO-nc:SiO₂). The TRPL signals from the last three longest wavelengths of the seven signals, namely at 450, 500, and 575 nm, were weak compared to the other four emissions at 360, 378, 396, and 417 nm. Even in the steady-state PL spectra presented in the previous chapter section 4.4.1, the 450, 500, and 575 nm emissions have the lowest emission intensity. These weak emissions are possibly due to the larger number of phonons required as compared to the emissions at 360, 378, 396, and 417 nm, shown schematically in Figure 5-1 (the energy band diagram of ZnO-nc in SiO₂ showing various transitions). The number of phonon emissions required by the 450, 500, and 575 nm emissions is estimated to be around three to nine times more than those required by the 417 nm emission process. The probability of multi-phonon emissions decreases with increasing the number of phonons required for the de-excitation process, leading to a lower number of excited state ZnO-nc electrons being involved in the emissions at 450, 500, and 575 nm, causing weak emissions at these wavelengths.

The number three to nine times was obtained based on the energy band diagram of ZnO-nc in SiO₂ which is shown in Figure 5-1. In the energy band diagram, it can be seen that the 417 nm emission is a result of transition of electron from conduction band to oxygen interstitial (O_i) defect state. The electrons in the O_i state, then relax back to the valance band of ZnO-nc through multi-phonon emission. The energy difference between O_i state and valance band is around 0.08 eV as shown in the energy band diagram. Now, for the 450 nm emission process, the electrons in the conduction band first transition to the oxygen vacancy (V_o) defect state through multi-phonon

emission. Subsequently, the electrons in the V_o state transition to the valance band resulting in 450 nm. The energy difference between conduction band and V_o state is around 0.23 eV as shown in the energy band diagram. This is around three times the energy difference between O_i state and valance band. Thus, the number of phonon emissions required by the 450 nm emission would be around three times the number of phonon emissions required by the 417 nm emission. Similarly, the 575 nm emission is a result of transition of electron from conduction band to the doubly charged oxygen vacancy ($V\ddot{O}$) defect state. The electrons in the $V\ddot{O}$ state, then relax back to the valance band through multi-phonon emission. The energy difference between $V\ddot{O}$ state and valance band is around 0.72 eV as shown in the energy band diagram. This is around nine times the energy difference between O_i state and valance band. Thus, the number of phonon emissions required by the 575 nm emission would be around nine times the number of phonon emissions required by the 417 nm emission.

Figure 5-1: Energy band diagram showing the energy transfer from ZnO-nc to Eu^{3+} ions in SiO_2 together with the various transitions corresponding to the emissions from ZnO-nc and Eu^{3+} ions.

The energy band diagram in Figure 5-1 also illustrates the energy transfer from various ZnO-nc emission centers to Eu^{3+} ions in the SiO_2 matrix, together with the various transitions corresponding to the emissions from ZnO nanocrystals and Eu^{3+} ions. This figure is a modified version of the band diagram presented in the previous chapter, where the bandwidth of the various ZnO-nc emission centers is represented using the colour gradients in the broad vertical energy bands. Here, the author notes that there is a possibility of back energy transfer from the excited Eu^{3+} ions to the ZnO-nc, especially from the $^5\text{D}_0$ state of Eu^{3+} to the VÖ defect center in the ZnO-nc with the cooperation of phonons. However, the author do not consider the effect of the energy back transfer process on the PL and TRPL emissions of the ZnO-nc for the study in this chapter.

Figure 5-2: The time-resolved photoluminescence (TRPL) spectra of the ZnO-nc:SiO₂ and $\text{Eu}^{3+}_{0.12}$:ZnO-nc:SiO₂ samples measured at (a) 360 nm; (b) 378 nm; (c) 396 nm; and (d) 417 nm, along with their respective stretched exponential fitting curves.

The normalized TRPL spectra (the decay of the normalized PL emission intensity with respect to time) of the ZnO-nc:SiO₂ and Eu³⁺_{0.12}:ZnO-nc:SiO₂ samples 360, 378, 396, and 417 nm are shown in Figure 5-2. It can be clearly seen that the PL intensity of the sample with the Eu³⁺ ions decays faster than the sample without Eu³⁺ ions at all emission wavelengths. The decay of the PL emission in the ZnO-nc:SiO₂ sample is due to the radiative and non-radiative de-excitation processes in the ZnO-nc. However, the decay of the PL emission in the Eu³⁺_{0.12}:ZnO-nc:SiO₂ sample has additional components that contribute to the decay rate, namely (i) the energy transfer from ZnO-nc to Eu³⁺ ions which results in the radiative emission from Eu³⁺ ions at 614 nm, and (ii) the energy transfer from ZnO-nc to the additional new defects created due to the incorporation of the Eu³⁺ ions (as introduced in section 4.4.1). To study the contribution of the energy transfers from the ZnO-nc to the Eu³⁺ ions and the defects created by the Eu³⁺ ions, the intensities of the different TRPL spectra of the two samples are expressed using the stretched exponential decay fitting function [162] as follows:

$$I(t) = I_0 e^{-\left(\frac{t}{\tau}\right)^\beta} \quad (5.1)$$

where $I(t)$ is the intensity of the TRPL measurement at time t , I_0 is the intensity of the TRPL measurement at $t = 0$, τ is the decay time of the TRPL intensity, and β is the stretching exponential coefficient, which is a wavelength-dependent constant. The stretched exponential decay fitting function is the most widely used fitting function to represent the TRPL decay curves of ZnO-nc [162], and semiconductor nanocrystals in general [163-166], as they account for the complex nature of the decay curves which cannot be expressed using simple exponential decay functions. Using the stretch exponential decay fitting function, the author obtained very good fitting curves

for the TRPL spectra of the ZnO-nc. In the stretched exponential decay equation, β ranges from 0 to 1 and is a measure of interaction between identical ZnO-nc emission centers. This interaction, for instance, could be in the form of the migration of excitons between ZnO-nc or the migration of carriers between identical ZnO-nc defect centers [165, 166]. The value of β approaches 0 when the effect of interaction between two or more identical ZnO-nc emission centers is large, and β approaches 1 when the effect of interaction between the identical emission centers is negligible [165, 166]. For the 360 nm band edge emission (QC) of the ZnO-nc, the value of β is 0.65 for the sample without Eu^{3+} ions and 0.69 for the sample with Eu^{3+} ions, as shown in Table 5-1. However, for the 378 nm excitonic emission (EE), 396 nm Zn defect (Zn_i to V_{Zn}) emission, and 417 nm oxygen interstitial defect (O_i) emission, the β values are around 0.61–0.62 for the samples with and without Eu^{3+} ions. These results indicate that the 360 nm band edge emission (QC) experiences lesser interactions compared to the EE, Zn_i to V_{Zn} , and O_i emissions. The weaker interaction of the 360 nm band edge emission (QC) center could be due to the smaller size of the ZnO-nc, as this emission is attributed to the possible quantum confinement effect.

Table 5-1: The decay time (τ) and stretching exponential coefficient (β) values for the various ZnO-nc emission centers obtained from the time-resolved photoluminescence (TRPL) spectra of the samples with and without Eu^{3+} ions ($\text{Eu}^{3+}_{0.12}\text{:ZnO-nc:SiO}_2$ and ZnO-nc:SiO_2 samples, respectively).

Sample	Emission Wavelength	$\tau(\text{ps})$	β
ZnO-nc:SiO ₂	360 nm	215 ± 8	0.65 ± 0.02
$\text{Eu}^{3+}_{0.12}\text{:ZnO-nc:SiO}_2$	(QC)	102 ± 7	0.69 ± 0.02
ZnO-nc:SiO ₂	378 nm	213 ± 4	0.62 ± 0.01
$\text{Eu}^{3+}_{0.12}\text{:ZnO-nc:SiO}_2$	(EE)	84 ± 4	0.62 ± 0.01
ZnO-nc:SiO ₂	396 nm	264 ± 6	0.61 ± 0.01
$\text{Eu}^{3+}_{0.12}\text{:ZnO-nc:SiO}_2$	(Zn_i to V_{Zn})	95 ± 5	0.61 ± 0.01
ZnO-nc:SiO ₂	417 nm	356 ± 15	0.62 ± 0.02
$\text{Eu}^{3+}_{0.12}\text{:ZnO-nc:SiO}_2$	(O_i)	125 ± 10	0.62 ± 0.02

Table 5-1 also show the decay time τ for different ZnO-nc emission centers of the ZnO-nc:SiO₂ and Eu³⁺_{0.12}:ZnO-nc:SiO₂ samples. The decay time τ is primarily the lifetime of the electrons in the excited state of the ZnO-nc emission center, and its values depend on the rates of the different de-excitation processes from the ZnO-nc emission centers. For instance, the decay time of any ZnO-nc emission center in the ZnO-nc:SiO₂ sample ($\tau^{ZnO-nc:SiO_2}$) is given by:

$$\tau^{ZnO-nc:SiO_2} = \frac{1}{\Gamma^r + \Gamma^{nr}} \quad 5.2$$

where, Γ^r is the rate of radiative emission and Γ^{nr} is the rate of non-radiative emission from the ZnO-nc emission center. Similarly, the decay time of any ZnO-nc emission center in the Eu³⁺_{0.12}:ZnO-nc:SiO₂ sample ($\tau^{Eu^{3+}_{0.12}:ZnO-nc:SiO_2}$) is given by:

$$\tau^{Eu^{3+}_{0.12}:ZnO-nc:SiO_2} = \frac{1}{\Gamma^r + \Gamma^{nr} + \Gamma^{tr}} \quad (5.3)$$

where, Γ^{tr} is the combined rate of energy transfer from ZnO-nc to Eu³⁺ ions which results in the radiative emission from the Eu³⁺ ions at 614 nm and energy transfer from ZnO-nc to the additional new defects created due to the incorporation of the Eu³⁺ ions. As expected, the decay time for the sample with Eu³⁺ ions ($\tau^{Eu^{3+}_{0.12}:ZnO-nc:SiO_2}$) is lower than the decay time for the sample without Eu³⁺ ions ($\tau^{ZnO-nc:SiO_2}$) for all wavelengths, due to the additional energy transfer decay mechanisms in the Eu³⁺_{0.12}:ZnO-nc:SiO₂ sample.

From the decay time results obtained from the TRPL measurements in Table 5-1, the energy transfer efficiency, denoted by E_T^{TRPL} , was then calculated according to the following equation:

$$\text{Transfer efficiency } (E_T^{TRPL}) = \frac{\Gamma^{tr}}{\Gamma^r + \Gamma^{nr} + \Gamma^{tr}} = 1 - \frac{\tau^{Eu^{3+}_{0.12}:ZnO-nc:SiO_2}}{\tau^{ZnO-nc:SiO_2}} \quad (5.4)$$

The E_T^{TRPL} transfer efficiency calculated for each of the four ZnO-nc emission centers is shown in Figure 5-3 in section 5.4.3 below. The results will be discussed together with the transfer efficiency calculated from the steady-state PL emission.

5.4.2. Transfer Efficiency from Steady-State

Photoluminescence Emission

In the previous section the author discussed the TRPL emission spectra of the two types of samples in this study and calculated the transfer efficiency of the ZnO-nc emission centers in the energy transfer process to the Eu^{3+} ions. In this section, for comparison, the transfer efficiency of each of the seven ZnO-nc emission centers was also calculated from the steady-state PL intensity measurements of the two samples used in this study, namely, ZnO-nc:SiO_2 and $\text{Eu}^{3+}_{0.12}\text{:ZnO-nc:SiO}_2$. Savchyn et al. [83] report a similar analysis calculating the transfer efficiency from the steady-state PL emission intensity for a silicon nanocrystals and Er^{3+} ions system. The steady-state PL intensity for the samples without and with Eu^{3+} ions have been presented in section 4.4.1 of this thesis and in this section the author uses the same results to calculate the energy transfer efficiency, denoted by E_T^{PL} . The intensity of steady-state PL emission from the ZnO-nc:SiO_2 ($I^{\text{ZnO-nc:SiO}_2}$) and $\text{Eu}^{3+}_{0.12}\text{:ZnO-nc:SiO}_2$ ($I^{\text{Eu}^{3+}_{0.12}\text{:ZnO-nc:SiO}_2}$) samples can be mathematically represented by Equations (5-5) and (5-6) [83], respectively:

$$I^{\text{ZnO-nc:SiO}_2} \propto N^{\text{ZnO-nc:SiO}_2} \times \Gamma^r \quad (5.5)$$

$$I^{\text{Eu}^{3+}_{0.12}\text{:ZnO-nc:SiO}_2} \propto N^{\text{Eu}^{3+}_{0.12}\text{:ZnO-nc:SiO}_2} \times \Gamma^r \quad (5.6)$$

where $N^{\text{ZnO-nc:SiO}_2}$ is the number of ZnO-nc per unit volume in the excited state of any emission center for the ZnO-nc:SiO_2 sample, and

$N^{Eu^{3+}_{0.12}:ZnO-nc:SiO_2}$ is the number of ZnO-nc per unit volume in the excited state of any emission center for the $Eu^{3+}_{0.12}:ZnO-nc:SiO_2$ sample. Under the steady-state condition of PL measurement, the rate equation of $N^{ZnO-nc:SiO_2}$ [167] can be written as follows:

$$\frac{\partial N^{ZnO-nc:SiO_2}}{\partial t} = +G - N^{ZnO-nc:SiO_2}(\Gamma^r + \Gamma^{nr}) = 0 \quad (5.7)$$

where, G is the total number of ZnO-nc generated to the excited state of an emission center per unit volume per unit time. The value of G depends on the intensity of the steady-state PL excitation source and the absorption cross-section of the ZnO-nc. Similarly, the rate equation of $N^{Eu^{3+}_{0.12}:ZnO-nc:SiO_2}$ [167] can be written as follows:

$$\frac{\partial N^{Eu^{3+}_{0.12}:ZnO-nc:SiO_2}}{\partial t} = +G - N^{Eu^{3+}_{0.12}:ZnO-nc:SiO_2}(\Gamma^r + \Gamma^{nr} + \Gamma^{tr}) = 0 \quad (5.8)$$

Thus, from Equations (5.7) and (5.8), it can be seen that during the PL measurement, i.e., under a steady-state condition $\left(\frac{\partial N}{\partial t} = 0\right)$, $N^{ZnO-nc:SiO_2}$ depends only on Γ^r and Γ^{nr} for the ZnO-nc:SiO₂ sample and $N^{Eu^{3+}_{0.12}:ZnO-nc:SiO_2}$ depends on Γ^r , Γ^{nr} , and Γ^{tr} for the $Eu^{3+}_{0.12}:ZnO-nc:SiO_2$ sample. Here, the author has assumed that the addition of Eu^{3+} ions into the SiO₂ matrix does not affect the generation process of ZnO-nc in the excited state of any given emission center, because the intensity of the steady-state PL excitation source and the absorption cross-section of ZnO-nc are constant values in the steady-state PL measurement of the two samples. This implies that the values of G are the same for the samples without and with Eu^{3+} ions. Since the intensity of the PL emission is directly proportional to the number of ZnO-nc per unit volume in the excited state of an emission center, as shown in

Equations (5.5) and (5.6), then using Equations (5.7) and (5.8), the following equation is obtained:

$$\frac{I^{Eu_{0.12}^{3+}:ZnO-nc:SiO_2}}{I^{ZnO-nc:SiO_2}} = \frac{\frac{G}{\Gamma^r + \Gamma^{nr} + \Gamma^{tr}} \times \Gamma^r}{\frac{G}{\Gamma^r + \Gamma^{nr}} \times \Gamma^r} \quad (5.9)$$

The energy transfer efficiency from the PL steady-state measurements (E_T^{PL}) can then be written as follows:

$$\text{Transfer efficiency } (E_T^{PL}) = \frac{\Gamma^{tr}}{\Gamma^r + \Gamma^{nr} + \Gamma^{tr}} = 1 - \frac{I^{Eu_{0.12}^{3+}:ZnO-nc:SiO_2}}{I^{ZnO-nc:SiO_2}} \quad (5.10)$$

The values of E_T^{PL} are shown in Figure 5-3, together with those of E_T^{TRPL} , for the energy transfer to Eu^{3+} ions from the various ZnO-nc emission centers. The figure also shows the error bar for each of the transfer efficiency values calculated using the two different methods. Figure 5-4 shows the values of E_T^{PL} for the energy transfer to Tb^{3+} ions from the various ZnO-nc emission centers. The results of energy transfer efficiency is discussed in detail the below section 5.4.3 and 5.4.4.

5.4.3. Discussion on Transfer Efficiency Values of Eu^{3+} ions

Figure 5-3: Transfer efficiency of ZnO nanocrystals emission centers due to the incorporation of the Eu^{3+} ions, calculated from the time-resolved photoluminescence (TRPL) spectra and steady-state photoluminescence (PL) emission data, along with their respective error bars.

Figure 5-3 shows the energy transfer efficiency values of the ZnO-nc emission centers calculated from the TRPL spectra and steady-state PL emission data. It can be seen that the E_T^{PL} and E_T^{TRPL} transfer efficiencies have similar values and are well within the error bars of the two measurements methods. The E_T^{PL} and E_T^{TRPL} transfer efficiencies are between 0.5 and 0.7 for most of the ZnO-nc emissions, except for VÖ defect emission at 575 nm. The transfer efficiencies obtained in this work are quite similar to the energy transfer efficiencies from silicon nanocrystals to Er^{3+} ions reported by Savchyn et al. [83], calculated using similar methods. In our previous chapter (section 4.4.1), the author calculated the spectral overlap integral of each of the seven ZnO-nc emissions with the Eu^{3+} excitation spectrum to obtain a measure of the energy transfer from ZnO-nc to the Eu^{3+} ions resulting in the emission at 614 nm. It has been found and presented in section 4.4.1 that the EE and Zn_i to V_{zn} emission centers emitting at 378 and 396 nm have the highest contribution to the

energy transfer from ZnO-nc to Eu^{3+} ions, while the oxygen defect emissions of ZnO-nc such as O_i , V_o , $\text{V}\dot{\text{O}}$, and $\text{V}\ddot{\text{O}}$, which are centered at 417, 450, 500, and 575 nm, respectively, have low energy transfer contributions to the Eu^{3+} ions. Thus, combining the results of spectral overlap integrals from the previous chapter with the transfer efficiencies results of this chapter, the author infers that the high transfer efficiencies E_T^{PL} and E_T^{TRPL} of EE and Zn_i to V_{Zn} emission centers are mostly the energy transfer from ZnO-nc to Eu^{3+} ions, which results in the radiative emission from the Eu^{3+} ions at 614 nm. It is also observed that for the oxygen defect emissions of ZnO-nc such as O_i , V_o , and $\text{V}\dot{\text{O}}$, the values of the transfer efficiencies E_T^{PL} and E_T^{TRPL} are similar to those of EE and Zn_i to V_{Zn} emission centers, even though the spectral overlap integral values of oxygen defect emissions are low. This implies that the energy transfer from these oxygen defect emission centers are the energy transfers from ZnO-nc to the additional new defects created due to the incorporation of the Eu^{3+} ions, which was proposed in the previous chapter.

5.4.4. Discussion on Transfer Efficiency from ZnO-nc to Tb^{3+} ions

In this section, the transfer efficiency of each of the seven ZnO-nc emission centers to Tb^{3+} ions is presented. The transfer efficiency is calculated from the steady-state PL intensity measurements of two samples used in this study, namely, ZnO-nc:SiO_2 and $\text{Tb}^{3+}_{0.12}\text{:ZnO-nc:SiO}_2$. Similar to the calculation of energy transfer efficiency from ZnO-nc to Eu^{3+} ions from the steady-state PL emission data using equation 5.10, the energy transfer efficiency from ZnO-nc to Tb^{3+} ions is also calculated using the equation:

$$\text{Transfer efficiency } (E_T^{PL}) = 1 - \frac{I^{\text{Tb}^{3+}_{0.12}\text{:ZnO-nc:SiO}_2}}{I^{\text{ZnO-nc:SiO}_2}} \quad (5.11)$$

where $I^{Tb^{3+}:ZnO-nc:SiO_2}$ is the intensity of steady-state PL emission from $Tb^{3+}:ZnO-nc:SiO_2$. The derivation of equation 5.11 is similar to the derivation of equation 5.10. The values of E_T^{PL} for energy transfer from each of the seven ZnO-nc emission centers to Tb^{3+} ions is shown in Figure 5-4.

Figure 5-4: Transfer efficiency of ZnO nanocrystals emission centers due to the incorporation of the Tb^{3+} ions, calculated from the steady-state photoluminescence (PL) emission data.

The E_T^{PL} transfer efficiencies for ZnO-nc emission centers to Tb^{3+} ions vary from wide range of 0.2 to 0.7, unlike the energy transfer efficiencies from ZnO-nc to Eu^{3+} ions which are mostly in the range of 0.5 to 0.6, except for V_O emission center. The band edge emission centers of ZnO-nc centered at 360 nm (QC) and 378 nm (EE) have a transfer efficiency of 0.33 each while the defect emission have a higher transfer efficiency, except for V_O defect emission at 575 nm. This trend is in contrast to the results of spectral overlap integral for

ZnO-nc emission centers and Tb^{3+} excitation presented in chapter 4. In the previous chapter (section 4.4.2), the author calculated the spectral overlap integral of each of the seven ZnO-nc emissions with the Tb^{3+} excitation spectrum to obtain a measure of the energy transfer from ZnO-nc to the Tb^{3+} ions resulting in the emission at 545 nm. It has been found and presented in section 4.4.2 that the QC and EE emission centers emitting at 360 and 378 nm have the highest contribution to the energy transfer from ZnO-nc to Tb^{3+} ions, while the zinc and oxygen defect emissions of ZnO-nc such as Zn_i to V_{Zn} , O_i , V_o , $\text{V}\dot{\text{O}}$, and $\text{V}\ddot{\text{O}}$, which are centered at 396, 417, 450, 500, and 575 nm, respectively, have low energy transfer contributions to the Tb^{3+} ions. Combining the results of spectral overlap integrals from the previous chapter with the transfer efficiencies results of this chapter, the author infers that the transfer efficiencies E_T^{PL} of QC and EE emission centers are the result of energy transfer from ZnO-nc to Tb^{3+} ions, which results in the radiative emission from the Tb^{3+} ions at 545 nm. While the high transfer efficiencies E_T^{PL} of Zn_i to V_{Zn} , O_i , V_o , $\text{V}\dot{\text{O}}$, and $\text{V}\ddot{\text{O}}$ emission centers of ZnO-nc are the result of energy transfer from ZnO-nc to the additional new defects created due to the incorporation of the Tb^{3+} ions, which was also proposed in the previous chapter.

These results are similar to the energy transfer efficiency results of ZnO-nc to Eu^{3+} ions discussed above. Particularly, EE emission center of ZnO-nc shows high energy transfer efficiency to both the lanthanide ions, while the oxygen defect emission centers like O_i , V_o , $\text{V}\dot{\text{O}}$, and $\text{V}\ddot{\text{O}}$ mostly transfer their energy to the defects created by the lanthanide ions. The formation of lanthanide ion-induced defect centers is a very important result that needs to be considered when fabricating light-emitting devices which use the energy transfer process from ZnO-nc to excite RE ions.

It is also important to note here that the energy transfer from ZnO-nc to Eu^{3+} ions which result in radiative emission from Eu^{3+} ions is higher than the energy transfer from ZnO-nc to Tb^{3+} ions which result in radiative emission from Tb^{3+} ions. This leads to higher energy transfer efficiency of EE and Zn_i to V_{Zn} emission centers of ZnO-nc to Eu^{3+} ions (around 0.6 to 0.7), which is higher than the energy transfer efficiency of QC and EE emission centers of ZnO-nc to Tb^{3+} ions (around 0.33). Thus as a result the emission from Eu^{3+} ions at 614 nm is higher than the emission from the Tb^{3+} ions at 545 nm due to energy transfer from ZnO-nc. This result is particularly important and also observed in thin film samples of ZnO-nc co-doped with both Eu^{3+} and Tb^{3+} ions doped in SiO_2 matrix, which is presented in chapter 7.

5.5. Chapter Summary

In summary, in this chapter the author presents the result of the TRPL spectra of ZnO-nc: SiO_2 and $\text{Eu}^{3+}_{0.12}$:ZnO-nc: SiO_2 samples to study the contribution of energy transfer to the Eu^{3+} ions from the various emission centers of ZnO-nc. The TRPL spectra of the two samples were analyzed by calculating the decay time and the stretching exponential coefficient values of the different ZnO-nc emissions centers at 360, 378, 396, and 417 nm using the stretched exponential decay function. The stretching exponential coefficient values, which are a measure of interaction between two or more identical ZnO-nc emission centers, show that the 360-nm band edge emission (QC) experiences lesser interactions compared to the EE, Zn_i to V_{Zn} , and O_i emissions centered at 378, 396, and 417 nm, respectively. The decay time showed that samples with Eu^{3+} ions experience faster decay because of the additional components, namely the energy transfer from ZnO-nc to the Eu^{3+} ions, which results in the radiative emission from the Eu^{3+} ions at 614 nm, and the energy transfer to the additional new defects created due to the incorporation of the Eu^{3+} ions,

contributing to the decay rate. Furthermore, the transfer efficiencies of the ZnO-nc emissions calculated from the decay time are consistent with the transfer efficiencies calculated using the PL emission intensity data. These results show that the high transfer efficiencies of EE and Zn_i to V_{Zn} emission centers emitting at 378 and 396 nm are mostly the energy transfer from ZnO-nc to Eu^{3+} ions, resulting in an emission at 614 nm, while the energy transfers from the oxygen defect emissions at 417, 450, 500, and 575 nm are most probably the energy transfer from ZnO-nc to the defects created due to the incorporation of the Eu^{3+} ions in the $Eu^{3+}_{0.12}:ZnO-nc:SiO_2$ samples, as proposed in the previous chapter (section 4.4.1).

In this chapter, the author also presented the energy transfer efficiencies of the ZnO-nc emissions to Tb^{3+} ions calculated using the steady-state PL emission intensity data. The energy transfer efficiency results show that the QC and EE emission centers emitting at 360 and 378 nm are mostly the energy transfers from ZnO-nc to Tb^{3+} ions, resulting in an emission at 545 nm, while the energy transfers from the defect emissions at 396, 417, 450, 500, and 575 nm are most probably the energy transfer from ZnO-nc to the defects created due to the incorporation of the Tb^{3+} ions in the $Tb^{3+}_{0.12}:ZnO-nc:SiO_2$ samples, as proposed in the previous chapter (section 4.4.2).

These results show that EE emission center is important for energy transfer from ZnO-nc to both Eu^{3+} and Tb^{3+} ions, while the oxygen defect emission results in energy loss through the defects created due to the incorporation of the lanthanide ions.

Chapter 6: Effect of Interaction Distance Among ZnO-nanocrystals and Eu^{3+} Ions

6.1. Introduction

In the energy transfer process, the interaction distance between a donor (ZnO-nc in this work) and an acceptor is an important parameter which greatly affects the energy transfer contribution. However, there has been no report on the nature of energy transfer from ZnO-nc to Eu^{3+} ions based on the interaction distance between ZnO-nc and Eu^{3+} ions.

In this chapter, the author reports the effect of varying average shortest interaction distance between the ZnO-nc and the Eu^{3+} ions on the energy transfer from ZnO-nc to the Eu^{3+} ions. The effect of the average shortest interaction distance between two Eu^{3+} ions is also presented, which helps in understanding the nature of 614 nm emission from the Eu^{3+} ions. The average shortest interaction distance between the ZnO-nc and the Eu^{3+} ions and the average shortest interaction distance between two Eu^{3+} ions is calculated by creating a theoretical model of the sample and deriving the equation based on the ratio of Zn, Si and Eu^{3+} ions in the sample together with the density and molecular mass of ZnO and SiO_2 . It is important to note that, the interaction distance between the ZnO-nc and the Eu^{3+} ions and the interaction distance between two Eu^{3+} ions are the average shortest distances between the two interaction species. However for convenience, in this chapter the author simply refers to them as the interaction distance between the ZnO-nc and the Eu^{3+} ions and the interaction distance between two Eu^{3+} ions.

The knowledge gained from this work on the energy transfer process from ZnO-nc to Eu^{3+} ions based on the interaction distance between the ZnO-nc and the Eu^{3+} ions, will definitely help in the advancement of energy efficient light

sources based on the energy transfer process from semiconductor nanocrystals to rare-earth ions. These could be used to make lasers, phosphors, amplifiers, etc. which can be used for varied applications in numerous industries. The study presented in this Chapter has been published in: optical materials express (V. Mangalam and K. Pita, "Effect of the interaction distance on 614 nm red emission from Eu^{3+} ions due to the energy transfer from ZnO-nc to Eu^{3+} ions," *Optical Materials Express*, vol. 8, no. 10, pp. 3115-3132, 2018/10/01 2018.) [168]

6.2. Samples

In this chapter, the author presents the study of two types of thin-film samples. In the first type, the ZnO-nc and Eu^{3+} ion are co-doped in the same SiO_2 matrix and in the second type, three layer thin film samples are fabricated with the ZnO-nc and Eu^{3+} ions doped in separate layers of SiO_2 which are separated by a buffer layer of SiO_2 matrix. The details of the samples fabrication has been described in section 3.2. The two types of samples are labelled as A type sample and B type sample, for easy reference. A schematic representation of A type sample and B type sample is shown in Figure 6-1.

Figure 6-1: Schematic diagram of the two types of samples presented in this chapter. a) A type Sample which is a single layer of SiO_2 matrix co-doped with ZnO-nc and Eu^{3+} ions b) B type Sample which is a three-layer thin film sample in which the ZnO-nc and Eu^{3+} ions are doped in separate layers of SiO_2 with a buffer layer of plane SiO_2 between them.

The first type of samples namely A type sample, shown in Figure 6-1(a), is a single layer of SiO_2 matrix co-doped with ZnO-nc and Eu^{3+} ions. Four different samples of this type with varying Eu^{3+} concentration ranging from 4 mol% to 16 mol% were fabricated. The four different A type samples are referred as A_x (where x refers to mole fraction of Eu^{3+} ions calculated using
$$x = \frac{\text{moles of } (\text{Eu}^{3+})}{\text{moles of } (\text{Eu}^{3+} + \text{Zn} + \text{Si})}$$
 and it ranges from 0.04 to 0.16). Table 6-1 shows a summary of the different A_x samples. The four different A_x samples are exactly the same samples as those presented in chapter 4. The second type of sample

namely, B type sample is three-layer thin film samples which were prepared using a combination of sol-gel process with spin coating and RF sputtering deposition. The schematic representation of this three-layer thin film sample is shown in Figure 6-1(b). Five different samples with varying thickness of the second layer ranging from 0 to 8 nm were fabricated to study the effect of interaction distance on the energy transfer process from the ZnO-nc to the Eu^{3+} ions. The five different three-layer thin film samples are referred as B_d (where d refers to the thickness, in nm, of the second layer which varies from 0 to 8 nm) samples in this work. The summary of the different B_d samples is also shown in Table 6-1. The detailed fabrication steps of sample B has been presented in section 3.2.3. While the author has presented the chemistry of sol-gel process and the working principle of radio-frequency (RF) magnetron sputtering in detail in section 3.2.1 and 3.2.3, respectively.

Table 6-1: . A summary showing the names of the four different A_x samples and the five different B_d samples.

A Type Sample	Name	Eu^{3+} Concentration
Single Layer $\text{Eu}^{3+}_m\text{:ZnO-nc:SiO}_2$ Sample	$A_{0.04}$	4 mol%
	$A_{0.08}$	8 mol%
	$A_{0.12}$	12 mol%
	$A_{0.16}$	16 mol%
B Type Sample	Name	Spacer Distance
Three Layer $\text{Eu}^{3+}\text{:SiO}_2\text{/SiO}_2\text{/ZnO-nc:SiO}_2$	B_0	0 nm
	B_2	2 nm
	B_4	4 nm

Sample	B ₆	6 nm
	B ₈	8 nm

6.3. Characterisation

The samples presented in this chapter were analysed by measuring the room-temperature photoluminescence (PL) emission spectra. A spectrofluorometer (SPEX Fluorolog-3 Model FL3-11) was used to excite the sample at 325 nm and the PL emission from the sample was measured at wavelengths ranging from 340 nm to 635 nm. The schematic of the SPEX Fluorolog-3 Model FL3-11 along with its working principle has been discussed in detail section 3.3.1.

6.4. Theoretical Calculation

The energy transfer from the ZnO-nc to Eu³⁺ ions depends significantly on the interaction distance between them and also the interaction distance between two Eu³⁺ ions. The author calculates this interaction distance between the ZnO-nc and Eu³⁺ ions and the interaction distance between two Eu³⁺ ions using the ratio of Zn, Si and Eu³⁺ ions in the sample along with the density and molecular mass of ZnO and SiO₂. In this section, the author presents a detailed description of the modeling of the thin film samples and the calculation of interaction distance.

6.4.1. A Type Sample

In this section, first the interaction distance between ZnO-nc and the Eu³⁺ ions and then the interaction distance between two Eu³⁺ ions in A type sample is derived. As mentioned, A type sample is a single layer thin film sample with the Eu³⁺ ions and ZnO-nc co-doped in the same SiO₂ matrix which was prepared using the sol-gel process. In these samples, the ratio of Eu³⁺:Zn:Si and the size of the ZnO-nc are known values. The ratios of Eu³⁺:Zn:Si was calculated from the amount of Eu³⁺, Zn and Si precursors chemicals used which are controlled

during the fabrication process. On the other hand, the size or the radius of the ZnO-nc was calculated from the TEM images of ZnO-nc in SiO₂ which was studied in detail and published in a previous work on ZnO-nc in SiO₂ [95] by pita *et. al.*. It is important note here that the shape of the ZnO-nc in the TEM images is not all spherical, nonetheless it is observed that they are nearly spherical. Thus, in order to analyze the interaction distances among the ZnO-nc and the Eu³⁺ ions presented in this chapter, the shape of ZnO-nc is assumed to be a regular geometric shape which is, in this work, taken as spherical. This spherical shape of ZnO-nc is further supported by studies by other groups where the ZnO-nc was fabricated using the sol-gel process with zinc acetate dihydrate (Zn(CH₃COO).2H₂O) as the precursor, similar to this work, and the shape of ZnO-nc is shown to be spherical [13, 169-171]. Furthermore, the size of the ZnO-nc in these studies are in the range of 3 nm to 7 nm [13, 170, 171] which is very close to the nanocrystals from this work which has a size of 4.83 nm [95]. Thus, using these known values the author first calculates the number of ZnO-nc in one cm³ of the film and the number of Eu³⁺ in one cm³ of the film which are subsequently used to calculate the interaction distances.

The author begins by calculating the volume of one ZnO nanocrystal, denoted by the symbol V_{ZnO-nc}^A (the superscript A indicates A type samples), using the radius of the nanocrystal with the following equation:

$$V_{ZnO-nc}^A = \frac{4}{3}\pi r_{ZnO-nc}^3 \text{ cm}^3 \quad (6.1)$$

where r_{ZnO-nc} refers to the radius of the ZnO nanocrystal. The total volume occupied by the ZnO molecules in one cm³ of the film, denoted by the symbol V_{ZnO}^A , can be then calculated using the equation as follows:

$$V_{ZnO}^A = N_{ZnO-nc}^A \times \frac{4}{3}\pi r_{ZnO-nc}^3 \text{ cm}^3 \quad (6.2)$$

where N_{ZnO-nc}^A is the total number of ZnO-nc in one cm^3 of the film. Similar to the total volume occupied by the ZnO molecules in one cm^3 of the film, the author also calculates the total volume occupied by the SiO_2 molecules in one cm^3 of the film, denoted by the symbol $V_{SiO_2}^A$. The total volume of SiO_2 in one cm^3 of the film is the volume remaining after subtracting the volume of ZnO molecules, which is given by the following equation:

$$V_{SiO_2}^A = 1 - V_{ZnO}^A = 1 - \left(N_{ZnO-nc}^A \times \frac{4}{3} \pi r_{ZnO-nc}^3 \right) \text{ cm}^3 \quad (6.3)$$

It is important to note here that the volume of the Eu^{3+} ions in the film is ignored in equation 6.3 as it is negligible. Now, with the total volume of ZnO and SiO_2 , the total mass of these molecules in one cm^3 of the film is obtained by multiplying the density of these materials with their respective volumes. For instance, the mass of ZnO molecules in one cm^3 of the film, denoted by the symbol m_{ZnO}^A , is given by the formula:

$$m_{ZnO}^A = V_{ZnO}^A \times \rho_{ZnO} = N_{ZnO-nc}^A \times \frac{4}{3} \pi r_{ZnO-nc}^3 \times \rho_{ZnO} \text{ g} \quad (6.4)$$

where ρ_{ZnO} is the density of ZnO molecules. Similarly, the mass of SiO_2 molecules in one cm^3 of the film, denoted by the symbol $m_{SiO_2}^A$, is given by the formula:

$$m_{SiO_2}^A = V_{SiO_2}^A \times \rho_{SiO_2} = \rho_{SiO_2} \left[1 - \left(N_{ZnO-nc}^A \times \frac{4}{3} \pi r_{ZnO-nc}^3 \right) \right] \text{ g} \quad (6.5)$$

where ρ_{SiO_2} is the density of SiO_2 molecules. Next the author calculates the total number of moles of ZnO molecules and SiO_2 molecules in one cm^3 of the film by dividing the mass of these materials with their respective molecular weight. The mathematical formula for the calculation of the total number of moles of ZnO molecules in one cm^3 of the film, denoted by the symbol N_{ZnO}^A ,

and the total number of moles of SiO_2 molecules in one cm^3 of the film, denoted by the symbol $N_{\text{SiO}_2}^A$, is shown in equation 6.6 and 6.7, respectively.

$$N_{\text{ZnO}}^A = \frac{m_{\text{ZnO}}^A}{M_{\text{ZnO}}} = \frac{N_{\text{ZnO-nc}}^A \times \frac{4}{3} \pi r_{\text{ZnO-nc}}^3 \times \rho_{\text{ZnO}}}{M_{\text{ZnO}}} \text{ mol} \quad (6.6)$$

$$N_{\text{SiO}_2}^A = \frac{m_{\text{SiO}_2}^A}{M_{\text{SiO}_2}} = \frac{\rho_{\text{SiO}_2} \left[1 - \left(N_{\text{ZnO-nc}}^A \times \frac{4}{3} \pi r_{\text{ZnO-nc}}^3 \right) \right]}{M_{\text{SiO}_2}} \text{ mol} \quad (6.7)$$

In the above equations M_{ZnO} and M_{SiO_2} refer to the molecular weight of ZnO and SiO_2 respectively. Finally equation 6.6 and 6.7 are related to each other using the ratio of Zn:Si, denoted by the symbol $R_{\text{Zn:Si}}^A$, which is nothing but the ratio of $N_{\text{ZnO}}^A : N_{\text{SiO}_2}^A$. This is mathematically written as follows:

$$R_{\text{Zn:Si}}^A = \frac{N_{\text{ZnO}}^A}{N_{\text{SiO}_2}^A} = \frac{N_{\text{ZnO-nc}}^A \times \frac{4}{3} \pi r_{\text{ZnO-nc}}^3 \times \rho_{\text{ZnO}}}{M_{\text{ZnO}}} \bigg/ \frac{\rho_{\text{SiO}_2} \left[1 - \left(N_{\text{ZnO-nc}}^A \times \frac{4}{3} \pi r_{\text{ZnO-nc}}^3 \right) \right]}{M_{\text{SiO}_2}} \quad (6.8)$$

From equation 6.8, $N_{\text{ZnO-nc}}^A$ can be calculated which can be represented by rearranging equation 6.8 as follows:

$$N_{\text{ZnO-nc}}^A = \frac{R_{\text{Zn:Si}}^A \times M_{\text{ZnO}} \times \rho_{\text{SiO}_2}}{\frac{4}{3} \pi r_{\text{ZnO-nc}}^3 (\rho_{\text{ZnO}} \times M_{\text{SiO}_2} + R_{\text{Zn:Si}}^A \times M_{\text{ZnO}} \times \rho_{\text{SiO}_2})} \quad (6.9)$$

All the values of the parameters on the right hand side of equation 6.9 are known constants, with $R_{\text{Zn:Si}}^A$ equal to 0.5 as determined during sample fabrication and $r_{\text{ZnO-nc}}$ equal to 4.83 nm which was taken from the TEM images of ZnO-nc in SiO_2 annealed at 450°C published in the previous work on ZnO-nc in SiO_2 by the author's group [95]. The values of M_{ZnO} , ρ_{ZnO} , M_{SiO_2} and

ρ_{SiO_2} are material constants of ZnO and SiO_2 molecules which were also used to calculate the value of N_{ZnO-nc}^A .

Figure 6-2. Schematic diagram of ZnO-nc uniformly distributed in SiO_2 matrix.

Next the author calculates the average distance between two ZnO-nc from the total number of ZnO-nc in one cm^3 of the film. For this, the author first assumes that the ZnO-nc are uniformly distributed in the SiO_2 matrix as shown in Figure 6-2. Thus, with this assumption the volume occupied by one ZnO-nc in one cm^3 of the film can be calculated, which is mathematically written as:

$$\begin{aligned} \text{Volume occupied by one ZnO-nc in one } cm^3 \text{ of the film} &= \frac{1}{N_{ZnO-nc}^A} \\ &= \frac{\frac{4}{3}\pi r_{ZnO-nc}^3 (\rho_{ZnO} \times M_{SiO_2} + R_{Zn:Si}^A \times M_{ZnO} \times \rho_{SiO_2})}{R_{Zn:Si}^A \times M_{ZnO} \times \rho_{SiO_2}} \text{ cm}^3 \quad (6.10) \end{aligned}$$

Finally, assuming the volume occupied by one ZnO-nc in one cm^3 of SiO_2 film is a perfect cube as shown in Figure 6-2, the average distance between the

centres of two ZnO-nc, denoted as d_{ZnO-nc}^A , corresponds to the length of the cube. d_{ZnO-nc}^A was calculated by taking the cube root of equation 6.10, which is mathematically shown as follows:

$$d_{ZnO-nc}^A = \sqrt[3]{\frac{\frac{4}{3}\pi r_{ZnO-nc}^3 (\rho_{ZnO} \times M_{SiO_2} + R_{Zn:Si}^A \times M_{ZnO} \times \rho_{SiO_2})}{R_{Zn:Si}^A \times M_{ZnO} \times \rho_{SiO_2}}} \text{ cm} \quad (6.11)$$

An important assumption in this calculation is that, all the Zn atoms incorporated in the samples during the fabrication process combine to form ZnO-nc. This assumption represents an ideal case and the author notes that it is quite unlikely that all the Zn atoms in the sample combine to form ZnO-nc. However, for simplification in this work the author has assumed that all the Zn atoms in the sample combine to form ZnO-nc.

Now, for the calculation of interaction distance between ZnO-nc and Eu^{3+} ions the average distance between the centers of two Eu^{3+} ions also need to be calculated. Hence, similar to the average distance between the centres of two ZnO-nc, first the number of Eu^{3+} ions in one cm^3 of the film is calculated, which is subsequently used to calculate the average distance between the centers of two Eu^{3+} ions.

The number of moles of Eu^{3+} ions in one cm^3 of the film was calculated from the ratio of $Eu^{3+}:Si$ in the film and the number of moles of SiO_2 molecules in one cm^3 of the film which was calculated using equation 6.7. This relation is mathematically shown in the following equation:

$$R_{Eu^{3+}:Si}^A = \frac{N_{Eu^{3+}}^A}{N_{SiO_2}^A} = \frac{N_{Eu^{3+}}^A \times M_{SiO_2}}{\rho_{SiO_2} \left[1 - \left(N_{ZnO-nc}^A \times \frac{4}{3}\pi r_{ZnO-nc}^3 \right) \right]} \quad (6.12)$$

where $R_{Eu^{3+}:Si}^A$ is the ratio of $Eu^{3+}:Si$ in the film and $N_{Eu^{3+}}^A$ is the number of moles of Eu^{3+} ions in one cm^3 of the film. The ratio of $Eu^{3+}:Si$ in A type sample is determined in the experiment from the concentration of Eu^{3+} ions, Si atoms and Zn atoms from the sample fabrication step. $R_{Eu^{3+}:Si}^A$ is varied from 1:16 in $A_{0.04}$ sample to 2:7 in $A_{0.16}$ sample (refer to section 6.2 for details). Thus rearranging equation 6.12, the total number of moles of Eu^{3+} ions in in one cm^3 of the film, $N_{Eu^{3+}}^A$ can be written as:

$$N_{Eu^{3+}}^A = \frac{(\rho_{SiO_2} \times R_{Eu^{3+}:Si}^A) \left[1 - \left(N_{ZnO-nc}^A \times \frac{4}{3} \pi r_{ZnO-nc}^3 \right) \right]}{M_{SiO_2}} \text{ mol} \quad (6.13)$$

In the above equation 6.13, the parameters on the right hand side are known constants, with $R_{Eu^{3+}:Si}^A$ determined during sample fabrication, r_{ZnO-nc} equal to 4.83 nm obtained from previous work on ZnO-nc in SiO_2 by the author's group [95] and N_{ZnO-nc}^A determined from equation 6.9. Thus these values along with M_{SiO_2} and ρ_{SiO_2} , which are material constants of SiO_2 molecules were used to calculate the value of $N_{Eu^{3+}}^A$.

Now, to calculate the average distance between two Eu^{3+} ions from the total number of moles of Eu^{3+} ions in one cm^3 of the film the author again assumes that the Eu^{3+} ions are distributed uniformly in the SiO_2 matrix similar to the ZnO-nc. It is important to note here that the Eu^{3+} ions are embedded in the volume occupied by SiO_2 , which is $1 - \left(N_{ZnO-nc}^A \times \frac{4}{3} \pi r_{ZnO-nc}^3 \right)$, and not in the entire volume of the film which includes the volume occupied by the ZnO-nc along with SiO_2 . Thus, with this assumption the author calculates the volume occupied by one Eu^{3+} ion in one cm^3 of the film, which is mathematically written as:

Volume occupied by one Eu^{3+} ion in one cm^3 of the film

$$\begin{aligned}
 &= \frac{1 - \left(N_{\text{ZnO-nc}}^A \times \frac{4}{3} \pi r_{\text{ZnO-nc}}^3 \right)}{N_{\text{Eu}^{3+}}^A \times N_A} \\
 &= \frac{M_{\text{SiO}_2}}{R_{\text{Eu}^{3+}:\text{Si}}^A \times \rho_{\text{SiO}_2} \times N_A} \text{ cm}^3
 \end{aligned} \tag{6.14}$$

where N_A is Avogadro's constant. Next, assuming that the volume occupied by one Eu^{3+} ion in one cm^3 the film is a perfect cube as shown in Figure 6-1(a), the average distance between the centres of two Eu^{3+} ions, denoted as $d_{\text{Eu}^{3+}}^A$, corresponds to the length of the cube. This can be calculated by finding the cube root of the volume occupied by one Eu^{3+} ion, which is mathematically written as:

$$d_{\text{Eu}^{3+}}^A = \sqrt[3]{\frac{M_{\text{SiO}_2}}{R_{\text{Eu}^{3+}:\text{Si}}^A \times \rho_{\text{SiO}_2} \times N_A}} \text{ cm} \tag{6.15}$$

Finally, the interaction distance between the ZnO-nc and Eu^{3+} ions in A type sample, denoted by the symbol $d_{\text{Eu}^{3+}/\text{ZnO-nc}}^A$, can be calculated from the above derived interaction distances. $d_{\text{Eu}^{3+}/\text{ZnO-nc}}^A$ depends on the radius of ZnO-nc and the average distance between Eu^{3+} ions which is illustrated in Figure 6-1(a). $d_{\text{Eu}^{3+}/\text{ZnO-nc}}^A$ is mathematically written as:

$$d_{\text{Eu}^{3+}/\text{ZnO-nc}}^A = r_{\text{ZnO-nc}} + \frac{1}{2} d_{\text{Eu}^{3+}}^A \text{ cm} \tag{6.16}$$

6.4.2. B Type Sample

Having calculated the interaction distance between ZnO-nc and Eu^{3+} ions and the interaction distance between two Eu^{3+} ions in A type sample, next the author calculates these interaction distance values in B type sample. B type sample, unlike A type sample, is a three layer sample with the ZnO-nc and Eu^{3+}

ions doped in separate layers of SiO₂ with a buffer layer of SiO₂ between them. However, the initial steps of calculation of interaction distances in B type sample are similar to A type sample. In fact the derivation of average distance between the centres of two ZnO-nc in B type sample, denoted by the symbol d_{ZnO-nc}^B (the superscript B indicates B type samples), is the same as in A type sample and it can be derived using the exact same steps as shown in equation 6.1 to 6.11. The average distance between the centres of two ZnO-nc in B type sample, d_{ZnO-nc}^B is mathematically written as:

$$d_{ZnO-nc}^B = \sqrt[3]{\frac{\frac{4}{3}\pi r_{ZnO-nc}^3 (\rho_{ZnO} \times M_{SiO_2} + R_{Zn:Si}^B \times M_{ZnO} \times \rho_{SiO_2})}{R_{Zn:Si}^B \times M_{ZnO} \times \rho_{SiO_2}}} \quad (6.17)$$

where $R_{Zn:Si}^B$ is the ratio of Zn:Si in the third layer of B type sample. This ratio is the same as the ratio of Zn:Si in A type sample which is 1:2. Thus, $R_{Zn:Si}^A = R_{Zn:Si}^B$ which means that the average distance between the centers of two ZnO-nc in A type sample and B type sample is exactly the same.

For the calculation of average distance between the centers of two Eu³⁺ ions, the derivation is slightly different from A type sample even though the final result is the same. For this calculation the author first derives the number of moles of SiO₂ molecules in one cm³ of the first layer of B type sample, which is the Eu³⁺:SiO₂ layer. Then using the number of moles of SiO₂ molecules in one cm³ of the film along with the ratio of Eu³⁺:Si in the film, the number of moles of Eu³⁺ ions in one cm³ of the film is derived. This is similar to the derivation of number of moles of Eu³⁺ ions in A type sample and subsequently using number of moles of Eu³⁺ ions in one cm³ the average distance between the centers of two Eu³⁺ ions in Eu³⁺:SiO₂ layer of the B type sample is derived.

The derivation of average distance between the centers of two Eu^{3+} ions in B type sample begins from the volume of SiO_2 molecules in one cm^3 of the $\text{Eu}^{3+}:\text{SiO}_2$ film, denoted by the symbol $V_{\text{SiO}_2}^B$. $V_{\text{SiO}_2}^B$ is equal to 1 cm^3 as the volume of Eu^{3+} ions in the film is ignored in the sample as it is negligible. Next, the total mass of these SiO_2 molecules in one cm^3 of the film, denoted by the symbol $m_{\text{SiO}_2}^B$, is obtained by multiplying the density of SiO_2 with volume of SiO_2 . $m_{\text{SiO}_2}^B$ is mathematically given by the formula:

$$m_{\text{SiO}_2}^B = V_{\text{SiO}_2}^B \times \rho_{\text{SiO}_2} = 1 \times \rho_{\text{SiO}_2} \text{ g} \quad (6.18)$$

The total number of moles of SiO_2 molecules in one cm^3 of $\text{Eu}^{3+}:\text{SiO}_2$ film is then calculated by dividing the mass of SiO_2 with its molecular weight. Mathematically it is written as:

$$N_{\text{SiO}_2}^B = \frac{m_{\text{SiO}_2}^B}{M_{\text{SiO}_2}} = \frac{1 \times \rho_{\text{SiO}_2}}{M_{\text{SiO}_2}} \quad (6.19)$$

where $N_{\text{SiO}_2}^B$ is the number of moles of SiO_2 molecules in one cm^3 of the $\text{Eu}^{3+}:\text{SiO}_2$ film.

Next step in the calculation of average distance between the centers of two Eu^{3+} ions is the derivation of the number of moles of Eu^{3+} ions in one cm^3 of $\text{Eu}^{3+}:\text{SiO}_2$ film. As mentioned above, it is calculated from the ratio of $\text{Eu}^{3+}:\text{Si}$ in the film and the number of moles of SiO_2 molecules in one cm^3 of the film. This is mathematically shown in the following equation:

$$R_{\text{Eu}^{3+}:\text{Si}}^B = \frac{N_{\text{Eu}^{3+}}^B}{N_{\text{SiO}_2}^B} = \frac{N_{\text{Eu}^{3+}}^B}{1 \times \rho_{\text{SiO}_2} / M_{\text{SiO}_2}} \quad (6.20)$$

where $N_{Eu^{3+}}^B$ is the number of moles of Eu^{3+} ions in one cm^3 of the film. The ratio of $Eu^{3+}:Si$, denoted by the symbol $R_{Eu^{3+}:Si}^B$, in the B type sample is maintained at 9:44 which is the same ratio of $Eu^{3+}:Si$ in the $A_{0.12}$ sample, as mentioned in the method section. Thus, rearranging equation 6.20, the number of moles of Eu^{3+} ions in one cm^3 of the film can be calculated as:

$$N_{Eu^{3+}}^B = \frac{R_{Eu^{3+}:Si}^B \times \rho_{SiO_2}}{M_{SiO_2}} \text{ mol} \quad (21)$$

The number of moles of Eu^{3+} ions in one cm^3 of $Eu^{3+}:SiO_2$ film in the B type sample can be easily calculated by substituting in equation 6.21, the value of $R_{Eu^{3+}:Si}^B$ determined from the sample fabrication and the values of M_{SiO_2} and ρ_{SiO_2} , which are material constants of SiO_2 molecules.

Figure 6-3: Schematic diagram of Eu^{3+} ions uniformly distributed in SiO_2 matrix.

Now, for the calculation of average distance between the centers of two Eu^{3+} ions from $N_{Eu^{3+}}^B$, the author assumes that the Eu^{3+} ions are uniformly distributed in the SiO_2 matrix, which is similar to the assumption in A type

sample, and this is illustrated in Figure 6-3. With this assumption, the volume occupied by one Eu^{3+} ion in one cm^3 of the film can be calculated using the following equation:

$$\begin{aligned} \text{Volume occupied by one } \text{Eu}^{3+} \text{ ion in one } \text{cm}^3 \text{ of the film} &= \frac{1}{N_{\text{Eu}^{3+}}^B \times N_A} \\ &= \frac{M_{\text{SiO}_2}}{R_{\text{Eu}^{3+}:\text{Si}}^B \times \rho_{\text{SiO}_2} \times N_A} \text{ cm}^3 \quad (6.22) \end{aligned}$$

It is interesting to note here that the final results of equation 6.14 and equation 6.22, which show the volume occupied by one Eu^{3+} ion in one cm^3 of the film in A type sample and B type sample, respectively, are exactly the same. The volume occupied by one Eu^{3+} ion in one cm^3 of the film in both sample depend only on the ratio of $\text{Eu}^{3+}:\text{Si}$ in the respective samples.

Lastly, the average distance between the centres of two Eu^{3+} ions in B type sample, denoted by the symbol $d_{\text{Eu}^{3+}}^B$, is calculated from the volume occupied by one Eu^{3+} ion in one cm^3 of the film. For this, it is assumed that the volume occupied by one Eu^{3+} ion in one cm^3 of the film is a perfect cube as shown in Figure 6-3 and so the average distance between the centres of two Eu^{3+} ions corresponds to the length of the cube. This average distance between the centres of two Eu^{3+} ions, can be calculated as follows:

$$d_{\text{Eu}^{3+}}^B = \sqrt[3]{\frac{M_{\text{SiO}_2}}{R_{\text{Eu}^{3+}:\text{Si}}^B \times \rho_{\text{SiO}_2} \times N_A}} \text{ cm} \quad (23)$$

Finally, the interaction distance between the ZnO-nc and Eu^{3+} ions in B type sample which is denoted by the symbol $d_{\text{Eu}^{3+}/\text{ZnO-nc}}^B$ is calculated from the above derived interaction distance. The distance $d_{\text{Eu}^{3+}/\text{ZnO-nc}}^B$ depends on the average distance between the centres of two Eu^{3+} ions, the average distance between the centres of two ZnO-nc and also on the thickness of the middle

SiO₂ buffer layer. $d_{Eu^{3+}/ZnO-nc}^B$ is schematically shown in Figure 6-1(b) and is mathematically written as:

$$d_{Eu^{3+}/ZnO-nc}^B = \frac{1}{2}d_{Eu^{3+}}^B + d_{SiO_2}^B + \frac{1}{2}d_{ZnO-nc}^B \quad (24)$$

where $d_{SiO_2}^B$ is the thickness of the middle SiO₂ buffer layer of the film.

6.5. Results and Discussion

In this work, the PL emission from the four different A type samples and the five different B type samples, as tabulated in Table 6-1, were analysed to study the effect of interaction distance between ZnO-nc and Eu³⁺ ions on the energy transfer process from ZnO-nc to Eu³⁺ ions. The PL spectra were measured by exciting the samples using 325 nm excitation wavelengths and observing the samples emission using a photo detector. The PL emission spectra of the four different A_x samples have been reported and presented in detail in chapter 4. In this chapter the author extends the analysis of the PL emission from A_x samples, especially at 614 nm due to energy transfer from ZnO-nc to Eu³⁺ ions. The author presents the PL emission from the Eu³⁺ ions at 614 nm based on the interaction distance between ZnO-nc and Eu³⁺ ions and the interaction distance between two Eu³⁺ ions, which greatly affect the energy transfer from ZnO-nc to Eu³⁺ ions.

Figure 6-4 shows the 614 nm emission intensity from the four different A_x samples as a function of the Eu³⁺ ion concentration, which was also presented in chapter 4 along with the interaction distance between ZnO-nc and Eu³⁺ ions in these samples which has not been presented earlier. The 614 nm emission intensity increases significantly in these single layer thin film samples with increasing Eu³⁺ ion concentration from 4 mol% to 12 mol% (also reported in chapter 4 section 4.4.1). This is due to the fact that the interaction distance

between ZnO-nc and Eu^{3+} ions reduces with increasing Eu^{3+} ion concentration resulting in higher energy transfer from excited ZnO-nc to Eu^{3+} ions. Specifically, as the interaction distance between ZnO-nc and Eu^{3+} ions reduces the non-radiative energy transfer between donor (ZnO-nc in this work) and acceptor (Eu^{3+} in this work) species increases [77, 172, 173]. The radiative energy transfer process on the other hand is an interaction distance independent process, i.e. it is independent of the distance between ZnO-nc and Eu^{3+} ions.

Figure 6-4: 614 nm PL emission intensity from the four different A_x samples along with the interaction distance between ZnO-nc and Eu^{3+} ions in these samples.

The interaction distance between ZnO-nc and Eu^{3+} ions in A_x samples, which is shown in Figure 6-4, was calculated using equation 6.16. It is evident from the figure that as the interaction distance between ZnO-nc and Eu^{3+} ions reduces from 5.25 nm in $A_{0.04}$ sample to 5.11 nm in $A_{0.12}$ sample, the red emission at 614 nm increases due to increased non-radiative energy transfer from ZnO-nc to Eu^{3+} ions in the sample. However, as the Eu^{3+} ion concentration is further

increased to 16 mol%, the red emission at 614 nm does not increase even though the interaction distance between the ZnO-nc and Eu^{3+} ions reduces to 5.08 nm in $A_{0.16}$ sample. In fact the 614 nm PL emission in $A_{0.16}$ sample reduces and this is attributed to a competing process known as Eu^{3+} ion concentration quenching which has been explained in detail in section 2.2.3.3. Eu^{3+} ion concentration quenching is the non-radiative dissipation of energy from the Eu^{3+} ions through the quenching sites in the sample as a result of migration of energy between neighbouring Eu^{3+} ions [158]. This migration of energy between the Eu^{3+} ions increases with decreasing distance between the Eu^{3+} ions. In the four A type samples the interaction distance between two Eu^{3+} ions decreases as the Eu^{3+} ion concentration increases from 4 mol% to 16 mol%, which is shown in Figure 6-5 along with the 614 nm PL emission intensity from these samples. The interaction distance between two Eu^{3+} ions in A type sample was calculated using equation 6.15. The interaction distance reduces from 0.84 nm in $A_{0.04}$ sample to 0.51 nm in $A_{0.16}$ sample and at distances less than 0.57 nm (which is the interaction distance between two Eu^{3+} ions in $A_{0.12}$ sample), the migration of energy between the adjacent Eu^{3+} ions start to become stronger. This leads to the quenching of energy transferred from the ZnO-nc to the Eu^{3+} ions and thus reducing the PL emission at 614 nm. Thus, in conclusion 5.11 nm is optimum interaction distance between ZnO-nc and Eu^{3+} ions and 0.57 nm is the optimum interaction distance between adjacent Eu^{3+} ions to maximise the red emission at 614 nm from the Eu^{3+} ions in A type sample.

To further understand the effect of the interaction distance between ZnO-nc and Eu^{3+} ions on the energy transfer from ZnO-nc to Eu^{3+} ions and its subsequent effect on the 614 nm emission from the Eu^{3+} ions, the PL emission from the five different B type samples, namely B_0 , B_2 , B_4 , B_6 and B_8 were

analysed. Figure 6-6 shows the PL emission spectra of the five different B_d samples with a spacer distance of 0, 2, 4, 6 and 8 nm. A broadband emission from all the five samples ranging from 340 to 635 nm is clearly observed. This PL emission is very similar to the PL emission from the four A_x samples reported in chapter 4.

Figure 6-5: 614 nm PL emission intensity from the four different A_x samples along with the interaction distance between two Eu^{3+} ions in these samples.

The emission from 350 to 600 nm is attributed to the ZnO-nc, while the small peak at 614 nm is the signature emission of the Eu^{3+} ions. The author has presented a detailed analyzed of this PL emission from ZnO-nc and Eu^{3+} ions in section 4.4.1.

Figure 6-6: PL emission spectra of five different B_d samples with a spacer distance of 0, 2, 4, 6 and 8 nm.

An important characteristic about the B type samples is that the ratio of $\text{Eu}^{3+}:\text{Si}$ in the $\text{Eu}^{3+}:\text{SiO}_2$ layer of the B_d samples was kept the same as the ratio of $\text{Eu}^{3+}:\text{Si}$ in the $A_{0.12}$ sample at 9:44. This was to ensure that the interaction distance between two Eu^{3+} ions in the B type sample was the same as that in $A_{0.12}$ sample which is 0.57 nm, the optimum interaction distance between two Eu^{3+} ions. The reason for maintaining the ratio of $\text{Eu}^{3+}:\text{Si}$ to control the interaction distance between two Eu^{3+} ions is understood from the formula for the interaction distance between two Eu^{3+} ions in A type sample and B type sample, given by equation 6.15 and equation 6.23 respectively. The interaction distance between two Eu^{3+} ions depend on the ratio of $\text{Eu}^{3+}:\text{Si}$ in the sample along with the density (ρ_{SiO_2}) and molecular weight (M_{SiO_2}) of SiO_2 . Since ρ_{SiO_2} and M_{SiO_2} are known material constants, the interaction distance between two Eu^{3+} ions depend only on the ratio of $\text{Eu}^{3+}:\text{Si}$ in the samples. Thus, by keeping the ratio of $\text{Eu}^{3+}:\text{Si}$ at 9:44 in the $\text{Eu}^{3+}:\text{SiO}_2$ layer of B_d samples and in

the $A_{0.12}$ sample, the interaction distance between two Eu^{3+} ions in these samples is maintained at 0.57 nm.

However, it is important to note here that while the ratio of $\text{Eu}^{3+}:\text{Si}$ is the same in both $A_{0.12}$ sample and B_d samples, the actual number of Eu^{3+} ions is not the same in both the samples. The number of Eu^{3+} ions in $A_{0.12}$ sample is 4.12×10^{21} per cm^3 , calculated using equation 6.13 while the number of Eu^{3+} ions in B_d samples 5.43×10^{21} per cm^3 , calculated using equation 6.21. The lesser number of Eu^{3+} ions in $A_{0.12}$ sample is due to the fact that the Eu^{3+} ions are co-doped with ZnO-nc in the same SiO_2 matrix unlike the B_d samples in which the Eu^{3+} ions and ZnO-nc are doped in separate layers of the sample. The volume occupied by ZnO-nc in $A_{0.12}$ sample in the same SiO_2 matrix results in lesser number of Eu^{3+} ions in one cm^3 of the film (as shown in equation 6.13) as compared to B type samples (as shown in equation 6.21), even though the ratio of $\text{Eu}^{3+}:\text{Si}$ and subsequently the interaction distance between two Eu^{3+} ion is the same in both the samples.

Higher Eu^{3+} ions in B_d samples as compared to $A_{0.12}$ sample means that the 614 nm emission from the Eu^{3+} ions in B_d samples is expected to be higher than that of the 614 nm emission from $A_{0.12}$ sample as B_d samples have more Eu^{3+} ions that can be excited. Interestingly, the PL spectra show that for the B_d samples the 614 nm emission is not strong and intense as that for the $A_{0.12}$ sample. Figure 6-7 shows a graphical representation of this comparison, where it is clearly seen that the 614 nm emission from the $A_{0.12}$ sample is 10 times stronger than the 614 nm emission from the B type samples. This shows that the energy transfer from the ZnO-nc to the Eu^{3+} ions which results in the emission at 614 nm is much higher in $A_{0.12}$ sample as compared to B_d samples.

The reason for this huge difference in PL emission at 614 nm is again due to the interaction distance between ZnO-nc and Eu^{3+} ions in the two different types of samples, which is an important factor in the energy transfer process. At short distances the energy transfer from ZnO-nc and Eu^{3+} ion take place through both radiative and non-radiative process, which is the case in A type samples. However, as the distance between ZnO-nc and Eu^{3+} ions increases the contribution due to non-radiative energy transfer process decreases significantly and beyond a certain distance the energy transfer between ZnO-nc and Eu^{3+} ions will take place only through the radiative process, which is the case in B type samples.

Figure 6-7 also shows the interaction distance between ZnO-nc and Eu^{3+} ions in B_d samples, which was calculated using equation 6.24, along with the 614 nm emission intensity from these samples. It is clearly seen from this figure that even for the 0 nm SiO_2 spacer B_0 sample, the interaction distance between ZnO-nc and Eu^{3+} ions is 6.53 nm which is much higher than the interaction distance between ZnO-nc and Eu^{3+} ions in any of the A type samples. The interaction distance between ZnO-nc and Eu^{3+} ions A_x samples is 5.25 nm or shorter. Thus, the shorter interaction distance between ZnO-nc and Eu^{3+} ions in A type samples mean that there is higher non-radiative energy transfer between ZnO-nc and Eu^{3+} ions in this sample compared to the B type samples. This results in the higher red emission at 614 nm from the Eu^{3+} ions in the A type samples.

Figure 6-7: 614 nm PL emission intensity from the five different B_d samples along with the interaction distance between ZnO-nc and Eu^{3+} ions and the interaction distance between two Eu^{3+} ions in these samples. The graph also shows the 614 nm PL emission intensity from the $A_{0.04}$ and $A_{0.12}$ samples for comparison.

Moreover, it is also seen that the 614 nm red emission values from the five B_d samples is fairly similar even though the interaction distance between ZnO-nc and Eu^{3+} ions in these sample vary greatly from 6.53 nm to 14.53 nm as shown in Figure 6-7. In these samples the energy transfer contribution from ZnO-nc to the Eu^{3+} ions is not affected by the interaction distance between the ZnO-nc and the Eu^{3+} ions, which indicates that the energy transfer through non-radiative process is negligible. The energy transfer from ZnO-nc to Eu^{3+} ions in these samples is predominately through radiative process, which is independent of the interaction distance between the ZnO-nc and Eu^{3+} ions, resulting in almost uniform 614 nm emission from the Eu^{3+} ions. Hence, it can concluded that at distances greater than 6.53 nm between ZnO-nc and Eu^{3+} ions, the energy transfer from ZnO-nc to Eu^{3+} ions is mostly through radiative energy transfer process.

6.6. Chapter Summary

In summary, the author presented the effect of the interaction distance between the ZnO-nc and the Eu^{3+} ions and the interaction distance between two Eu^{3+} ions on the energy transfer processes from the ZnO-nc to the Eu^{3+} ions. In this chapter, two different types of samples were presented, namely a single layer of ZnO-nc and Eu^{3+} ion are co-doped in the same SiO_2 matrix (A_x samples) and a three layer thin film sample with the ZnO-nc and Eu^{3+} ions doped in separate layers of SiO_2 separated by a buffer layer of SiO_2 matrix (B_d samples). The model to calculate the interaction distance between the ZnO-nc and the Eu^{3+} ions and the interaction distance between two Eu^{3+} ions in these samples have been discussed in detail and the equation to calculate these interaction distances was derived based on the ratio of Zn, Si and Eu^{3+} ions in the sample along with the density and molecular mass of ZnO and SiO_2 . It is clearly shown that the energy transfer from ZnO-nc to Eu^{3+} ions is higher in A type samples compared to the B type samples as the interaction distance between the ZnO-nc and Eu^{3+} ions is shorter in A type samples. Furthermore, as the interaction distance between ZnO-nc and Eu^{3+} ions is reduced in A type samples, the energy transfer from the ZnO-nc to Eu^{3+} ions increases resulting in higher red emission at 614 nm due to the $^5\text{D}_0 \rightarrow ^7\text{F}_2$ radiative de-excitation of the excited Eu^{3+} ions. The $A_{0.12}$ sample which has 5.11 nm interaction distance between the ZnO-nc and Eu^{3+} ions has the maximum red emission at 614 nm due to efficient energy transfer from ZnO-nc to Eu^{3+} . At higher concentrations of Eu^{3+} ions even though the interaction distance between ZnO-nc and Eu^{3+} ions decreases, the red emission does not increase due to Eu^{3+} ion concentration quenching effect which occurs as the interaction distance between the Eu^{3+} ions become shorter than 0.57 nm in the sample resulting in migration of energy between the Eu^{3+} ions which is non-radiatively dissipated.

It is also shown that the energy transfer in the B type samples, which have a 6.53 nm or higher interaction distance between the ZnO-nc and Eu^{3+} ions, is mostly due to radiative energy transfer. The results from this work are important and it can be used in the development of energy efficient rare-earth ion light sources which makes use of the energy transfer process from semiconductor nanocrystal sensitizers.

Chapter 7: White light Emission from ZnO Nanocrystals co-doped with Eu^{3+} and Tb^{3+} ions in SiO_2 matrix

7.1. Introduction

In this work, the author fabricates thin film samples of ZnO-nc in SiO_2 co-doped with both Eu^{3+} ions and Tb^{3+} ions with the objective of creating a white light emitting sample that can be excited using a single excitation wavelength. This was achieved by first fabricating various thin film samples of ZnO-nc in SiO_2 with varying concentrations of Eu^{3+} and Tb^{3+} ions, listed in Table 7-1, using the low cost sol-gel process. The photoluminescence (PL) emission intensities from these samples were then used to obtain an empirical equation for the emission intensity as a function of Eu^{3+} ions and Tb^{3+} ions concentration. The empirical emission intensity equation was subsequently used to deduce the concentration of Eu^{3+} ions and Tb^{3+} ions which gives white light emission and orangish-white light emission. Using the deduced values of the Eu^{3+} and Tb^{3+} ion concentration, a white light emitting sample and a orangish-white light emitting sample was then fabricated using the sol-gel process to experimentally confirm the deduction. A white light emission and a orangish-white light emission from the two samples were demonstrated in this work. The knowledge and understanding gained from this work will be beneficial for the development of energy efficient solid state white lighting devices which use the energy transfer process from ZnO-nc to Eu^{3+} and Tb^{3+} ions, to produce light. The study presented in this Chapter has been published in: Materials (Mangalam, V.; Pita, K. White light emission from thin-film samples of zno nanocrystals, Eu^{3+} and Tb^{3+} ions embedded in an SiO_2 matrix. Materials 2019, 12, 1997.)

7.2. Sample

In this work, the sol-gel process was employed in the fabrication of the thin film samples due to the low-cost nature of this chemical process. Twenty-six different samples of ZnO nanocrystals (ZnO-nc) embedded in SiO₂ matrix co-doped with varying concentration of Eu³⁺ ions and Tb³⁺ ions were fabricated which are listed in Table 7-1. The samples in this work are labelled as Eu³⁺_{*m*}:Tb³⁺_{*n*}:ZnO-nc:SiO₂ where *m* is the molar fraction of the concentration of Eu³⁺ ions calculated using the formula $m = \frac{\text{moles of (Eu}^{3+})}{\text{moles of (Eu}^{3+} + \text{Tb}^{3+} + \text{Zn} + \text{Si})}$ and *n* is molar fraction of the concentration of Tb³⁺ ions calculated using the formula $n = \frac{\text{moles of (Tb}^{3+})}{\text{moles of (Eu}^{3+} + \text{Tb}^{3+} + \text{Zn} + \text{Si})}$. Note here that eight of these samples are the samples from our previous work which have been reported elsewhere [45, 153], while the remaining eighteen samples were newly fabricated for this current work as indicated in Table 7-1. Furthermore, out of the total twenty-six different samples listed in Table 7-1, twenty-four of the samples were used to establish the empirical equation in this work, while the remaining two samples (Eu³⁺_{0.012}:Tb³⁺_{0.024}:ZnO-nc:SiO₂ and Eu³⁺_{0.014}:Tb³⁺_{0.084}:ZnO-nc:SiO₂) were used to confirm the empirical equation.

Table 7-1: List of 26 samples fabricated using the sol-gel process.

Samples from Previous Work	Samples Newly Fabricated for Current Work
Eu ³⁺ _{0.04} :Tb ³⁺ ₀ :ZnO-nc:SiO ₂	Eu ³⁺ ₀ :Tb ³⁺ ₀ :ZnO-nc:SiO ₂
Eu ³⁺ _{0.08} :Tb ³⁺ ₀ :ZnO-nc:SiO ₂	Eu ³⁺ _{0.03} :Tb ³⁺ ₀ :ZnO-nc:SiO ₂
Eu ³⁺ _{0.12} :Tb ³⁺ ₀ :ZnO-nc:SiO ₂	Eu ³⁺ _{0.06} :Tb ³⁺ ₀ :ZnO-nc:SiO ₂
Eu ³⁺ _{0.16} :Tb ³⁺ ₀ :ZnO-nc:SiO ₂	Eu ³⁺ _{0.09} :Tb ³⁺ ₀ :ZnO-nc:SiO ₂
Eu ³⁺ ₀ :Tb ³⁺ _{0.04} :ZnO-nc:SiO ₂	Eu ³⁺ ₀ :Tb ³⁺ _{0.03} :ZnO-nc:SiO ₂
Eu ³⁺ ₀ :Tb ³⁺ _{0.08} :ZnO-nc:SiO ₂	Eu ³⁺ ₀ :Tb ³⁺ _{0.06} :ZnO-nc:SiO ₂

The samples were fabricated using an identical recipe described in our previous publications [25, 26, 30]. In all the twenty-six samples the molar ratio of Zn:Si in the samples was maintained at 1:2. The Eu^{3+} ions and Tb^{3+} ions are doped into the SiO_2 matrix by mixing Europium(III) nitrate pentahydrate and Terbium(III) nitrate pentahydrate salts, respectively, in the SiO_2 sol. After a 24 hour ageing of the two different sols, namely SiO_2 sol and ZnO-nc sol, they were mixed together before being spin coated on a Si substrate. These samples were then made into densified thin films by soft baking at 100°C , followed by annealing at 450°C using rapid thermal processing (RTP).

7.3. Characterisation

The thin film samples were characterised by studying the photoluminescence (PL) emission from the sample using SPEX Fluorolog-3 Model FL3-11 spectrofluorometer. The PL spectra was obtained by exciting the samples at

325 nm using the 450-W xenon short arc lamp of the spectrofluorometer attached to a monochromator and then measuring the emission intensity from the sample at each wavelength ranging from 340 nm to 635 nm using a photomultiplier tube (PMT) detector coupled to another monochromator.

7.4. Results and Discussion

As mentioned above, in order to obtain the right concentrations of Eu^{3+} and Tb^{3+} ions together with the ZnO-nc (which is fixed in this work), an empirical equation of the PL intensity as a function of Eu^{3+} and Tb^{3+} ion concentrations need to be established. The empirical equation is derived based on the PL intensity data of the samples listed in Table 7-2. The author shows the PL spectra of some of the samples listed in Table 7-2 in Figure 7-1, 7-2 and 7-3 below. Figure 7-1 shows the PL spectra of the SiO_2 films doped with ZnO-nc and varying concentrations of Eu^{3+} ions, namely $\text{Eu}^{3+}_{0.03}\text{Tb}^{3+}_0\text{ZnO-nc:SiO}_2$, $\text{Eu}^{3+}_{0.06}\text{Tb}^{3+}_0\text{ZnO-nc:SiO}_2$, $\text{Eu}^{3+}_{0.09}\text{Tb}^{3+}_0\text{ZnO-nc:SiO}_2$ and the PL spectra of $\text{Eu}^{3+}_0\text{Tb}^{3+}_0\text{ZnO-nc:SiO}_2$ sample (the SiO_2 film doped with ZnO-nc only). The PL spectra of the other samples doped only with Eu^{3+} ions and ZnO-nc in SiO_2 , namely $\text{Eu}^{3+}_{0.04}\text{Tb}^{3+}_0\text{ZnO-nc:SiO}_2$, $\text{Eu}^{3+}_{0.08}\text{Tb}^{3+}_0\text{ZnO-nc:SiO}_2$, $\text{Eu}^{3+}_{0.12}\text{Tb}^{3+}_0\text{ZnO-nc:SiO}_2$ and $\text{Eu}^{3+}_{0.16}\text{Tb}^{3+}_0\text{ZnO-nc:SiO}_2$ samples have been previously published by our group [45]. From the PL emission spectra, it is clearly see the signature emission peaks of Eu^{3+} ions at 590 nm and 614 nm for the samples with Eu^{3+} ions, corresponding to $^5\text{D}_0 \rightarrow ^7\text{F}_1$ and $^5\text{D}_0 \rightarrow ^7\text{F}_2$ transitions respectively. These emissions which are due to the energy transfer process have been discussed in detail in our previous publication [45]. The PL spectrum of the SiO_2 film containing only ZnO-nc ($\text{Eu}^{3+}_0\text{Tb}^{3+}_0\text{ZnO-nc:SiO}_2$ sample), which is also included in Figure 7-1 shows the characteristic broadband emission of ZnO-nc ranging from 350 nm to 600 nm. The origin of the broadband emission from ZnO-nc together with a detailed discussion on the energy transfer process and

contribution of energy transfer from ZnO-nc to Eu^{3+} ion has been reported in our group's earlier work [45].

Figure 7-1: The PL spectra of $\text{Eu}^{3+}_0:\text{Tb}^{3+}_0:\text{ZnO-nc}:\text{SiO}_2$, $\text{Eu}^{3+}_{0.03}:\text{Tb}^{3+}_0:\text{ZnO-nc}:\text{SiO}_2$, $\text{Eu}^{3+}_{0.06}:\text{Tb}^{3+}_0:\text{ZnO-nc}:\text{SiO}_2$ and $\text{Eu}^{3+}_{0.09}:\text{Tb}^{3+}_0:\text{ZnO-nc}:\text{SiO}_2$ samples upon excitation using 325 nm excitation source.

Figure 7-2 shows the PL spectra of the SiO_2 films doped with ZnO-nc and varying concentration of Tb^{3+} ions, namely $\text{Eu}^{3+}_0:\text{Tb}^{3+}_{0.03}:\text{ZnO-nc}:\text{SiO}_2$, $\text{Eu}^{3+}_0:\text{Tb}^{3+}_{0.06}:\text{ZnO-nc}:\text{SiO}_2$ and $\text{Eu}^{3+}_0:\text{Tb}^{3+}_{0.09}:\text{ZnO-nc}:\text{SiO}_2$. The PL spectra of the SiO_2 film doped only with ZnO-nc ($\text{Eu}^{3+}_0:\text{Tb}^{3+}_0:\text{ZnO-nc}:\text{SiO}_2$ sample) is also included the figure. The PL spectra of the other samples doped only with Tb^{3+} ions and ZnO-nc in SiO_2 , namely $\text{Eu}^{3+}_0:\text{Tb}^{3+}_{0.04}:\text{ZnO-nc}:\text{SiO}_2$, $\text{Eu}^{3+}_0:\text{Tb}^{3+}_{0.08}:\text{ZnO-nc}:\text{SiO}_2$, $\text{Eu}^{3+}_0:\text{Tb}^{3+}_{0.12}:\text{ZnO-nc}:\text{SiO}_2$ and $\text{Eu}^{3+}_0:\text{Tb}^{3+}_{0.16}:\text{ZnO-nc}:\text{SiO}_2$ samples have been published in our earlier work [153]. Once again from the PL spectra the author observes the characteristic emission from the Tb^{3+} ions at 489 nm, 545 nm, 586 nm and 621 nm in samples with Tb^{3+} ions. These emissions correspond to $^5\text{D}_4 \rightarrow ^7\text{F}_6$, $^5\text{D}_4 \rightarrow ^7\text{F}_5$, $^5\text{D}_4 \rightarrow ^7\text{F}_4$ and $^5\text{D}_4 \rightarrow ^7\text{F}_3$ transitions, respectively. This energy transfer process and mechanism of energy transfer from ZnO-nc to Tb^{3+} ions has been reported in detail, in our previous publication [153].

Figure 7-2: The PL spectra of $\text{Eu}^{3+}_0\text{ Tb}^{3+}_0\text{:ZnO-nc:SiO}_2$, $\text{Eu}^{3+}_0\text{ Tb}^{3+}_{0.03}\text{:ZnO-nc:SiO}_2$, $\text{Eu}^{3+}_0\text{ Tb}^{3+}_{0.06}\text{:ZnO-nc:SiO}_2$ and $\text{Eu}^{3+}_0\text{ Tb}^{3+}_{0.09}\text{:ZnO-nc:SiO}_2$ samples upon excitation using 325 nm excitation source.

The main focus of this study, as mentioned above, is to demonstrate a white light emitting sample by incorporating both Eu^{3+} ions and Tb^{3+} ions together with ZnO-nc in thin film samples of SiO_2 . Hence, samples with varying concentrations of both Eu^{3+} ions and Tb^{3+} ions together with fixed concentration of ZnO-nc in SiO_2 matrix were also fabricated. Figure 7-3 shows the PL spectra of some of the samples of SiO_2 doped with Eu^{3+} ions, Tb^{3+} ions and ZnO-nc, namely $\text{Eu}^{3+}_{0.03}\text{ Tb}^{3+}_{0.03}\text{:ZnO-nc:SiO}_2$, $\text{Eu}^{3+}_{0.06}\text{ Tb}^{3+}_{0.06}\text{:ZnO-nc:SiO}_2$ and $\text{Eu}^{3+}_{0.09}\text{ Tb}^{3+}_{0.09}\text{:ZnO-nc:SiO}_2$. Again, the author also include the PL spectra of the sample doped only with ZnO-nc ($\text{Eu}^{3+}_0\text{ Tb}^{3+}_0\text{:ZnO-nc:SiO}_2$ sample). In all of the samples with both Eu^{3+} ions and Tb^{3+} ions co-doped with ZnO-nc in SiO_2 , the author clearly observe the emission peaks from Tb^{3+} ions at 489 nm and 545 nm, the emission peaks from Eu^{3+} ions at 590 nm and 614 nm and the relatively broader emission from ZnO-nc with peak intensity at 372 nm. These

emissions from the Tb^{3+} and Eu^{3+} ions are the radiative de-excitations of the RE ions excited through the energy transfer process from excited ZnO-nc.

Figure 7-3: The PL spectra of $Eu^{3+}_0:Tb^{3+}_0:ZnO-nc:SiO_2$, $Eu^{3+}_{0.03}:Tb^{3+}_{0.03}:ZnO-nc:SiO_2$, $Eu^{3+}_{0.06}:Tb^{3+}_{0.06}:ZnO-nc:SiO_2$ and $Eu^{3+}_{0.09}:Tb^{3+}_{0.09}:ZnO-nc:SiO_2$ samples upon excitation using 325 nm excitation source.

To demonstrate a sample of desired colour (white light in this study), first the physiologically perceived colour of the samples need to be deduced. This is achieved by calculating the xyz chromaticity coordinates of the PL emission from the samples. The xyz chromaticity coordinates are a standard defined by the International Commission on Illumination (CIE) which consists of three values denoted by x, y and z. The CIE x, y and z chromaticity coordinates are essentially normalised fractions which give a quantitative relation between spectrum of emission from the sample and the colour perceived by the three different receptors in the human eye[112]. CIE x, y and z chromaticity values are obtained using the following mathematical equations:

$$X = \int_0^{\infty} I(\lambda) \bar{x}(\lambda) d\lambda \quad (7.1)$$

$$Y = \int_0^{\infty} I(\lambda) \bar{y}(\lambda) d\lambda \quad (7.2)$$

$$Z = \int_0^{\infty} I(\lambda) \bar{z}(\lambda) d\lambda \quad (7.3)$$

$$x = \frac{X}{X + Y + Z} \quad (7.4)$$

$$y = \frac{Y}{X + Y + Z} \quad (7.5)$$

$$z = \frac{Z}{X + Y + Z} = 1 - x - y \quad (7.6)$$

where $I(\lambda)$ is the emission intensity of the thin film sample as a function of wavelength and $\bar{x}(\lambda)$, $\bar{y}(\lambda)$ and $\bar{z}(\lambda)$ are the CIE colour-matching functions for the 1964 standard colorimetric observer which are essentially the spectral response of the three different receptors in the human eye[112]. The x , y and z values, correspond to the degree of red, green and blue colours respectively, as perceived by the human eye. This means, the greater the value of x , the more red the sample looks. Similarly, the greater the value of y , the more green the sample looks and the greater the value of z , the more blue the sample looks.

Table 7-2 shows the x , y and z values for the twenty-four samples used to establish the empirical equation in this work, calculated using the above equations 7.1 to 7.6, which is also graphically represented in CIE 1964 colour space plot shown in Figure 7-4.

Table 7-2: CIE x , y and z chromaticity values of the twenty-four different samples used to establish the empirical equation of the PL intensity as a function of Eu^{3+} and Tb^{3+} ion concentrations.

Samples	x	y	z
---------	-----	-----	-----

$\text{Eu}^{3+}_0\text{:Tb}^{3+}_0\text{:ZnO-nc:SiO}_2$	0.258	0.328	0.414
$\text{Eu}^{3+}_{0.03}\text{:Tb}^{3+}_0\text{:ZnO-nc:SiO}_2$	0.356	0.294	0.35
$\text{Eu}^{3+}_{0.04}\text{:Tb}^{3+}_0\text{:ZnO-nc:SiO}_2$	0.369	0.298	0.333
$\text{Eu}^{3+}_{0.06}\text{:Tb}^{3+}_0\text{:ZnO-nc:SiO}_2$	0.4313	0.281	0.288
$\text{Eu}^{3+}_{0.08}\text{:Tb}^{3+}_0\text{:ZnO-nc:SiO}_2$	0.444	0.306	0.25
$\text{Eu}^{3+}_{0.09}\text{:Tb}^{3+}_0\text{:ZnO-nc:SiO}_2$	0.496	0.33	0.174
$\text{Eu}^{3+}_{0.12}\text{:Tb}^{3+}_0\text{:ZnO-nc:SiO}_2$	0.517	0.321	0.162
$\text{Eu}^{3+}_{0.16}\text{:Tb}^{3+}_0\text{:ZnO-nc:SiO}_2$	0.546	0.314	0.14
$\text{Eu}^{3+}_0\text{:Tb}^{3+}_{0.03}\text{:ZnO-nc:SiO}_2$	0.268	0.352	0.38
$\text{Eu}^{3+}_0\text{:Tb}^{3+}_{0.04}\text{:ZnO-nc:SiO}_2$	0.244	0.309	0.447
$\text{Eu}^{3+}_0\text{:Tb}^{3+}_{0.06}\text{:ZnO-nc:SiO}_2$	0.295	0.41	0.295
$\text{Eu}^{3+}_0\text{:Tb}^{3+}_{0.08}\text{:ZnO-nc:SiO}_2$	0.301	0.431	0.268
$\text{Eu}^{3+}_0\text{:Tb}^{3+}_{0.09}\text{:ZnO-nc:SiO}_2$	0.305	0.419	0.276
$\text{Eu}^{3+}_0\text{:Tb}^{3+}_{0.12}\text{:ZnO-nc:SiO}_2$	0.332	0.458	0.21
$\text{Eu}^{3+}_0\text{:Tb}^{3+}_{0.16}\text{:ZnO-nc:SiO}_2$	0.328	0.447	0.225
$\text{Eu}^{3+}_{0.03}\text{:Tb}^{3+}_{0.03}\text{:ZnO-nc:SiO}_2$	0.414	0.334	0.252
$\text{Eu}^{3+}_{0.03}\text{:Tb}^{3+}_{0.06}\text{:ZnO-nc:SiO}_2$	0.441	0.33	0.229
$\text{Eu}^{3+}_{0.03}\text{:Tb}^{3+}_{0.09}\text{:ZnO-nc:SiO}_2$	0.481	0.321	0.198
$\text{Eu}^{3+}_{0.06}\text{:Tb}^{3+}_{0.03}\text{:ZnO-nc:SiO}_2$	0.465	0.318	0.217
$\text{Eu}^{3+}_{0.06}\text{:Tb}^{3+}_{0.06}\text{:ZnO-nc:SiO}_2$	0.484	0.308	0.208
$\text{Eu}^{3+}_{0.06}\text{:Tb}^{3+}_{0.09}\text{:ZnO-nc:SiO}_2$	0.538	0.307	0.155
$\text{Eu}^{3+}_{0.09}\text{:Tb}^{3+}_{0.03}\text{:ZnO-nc:SiO}_2$	0.49	0.309	0.201
$\text{Eu}^{3+}_{0.09}\text{:Tb}^{3+}_{0.06}\text{:ZnO-nc:SiO}_2$	0.514	0.305	0.181
$\text{Eu}^{3+}_{0.09}\text{:Tb}^{3+}_{0.09}\text{:ZnO-nc:SiO}_2$	0.545	0.3	0.155

Figure 7-4: CIE 1964 colour space plot with x and y points of $\text{Eu}^{3+}_0\text{:Tb}^{3+}_0\text{:ZnO-nc:SiO}_2$, $\text{Eu}^{3+}_m\text{:Tb}^{3+}_0\text{:ZnO-nc:SiO}_2$, $\text{Eu}^{3+}_0\text{:Tb}^{3+}_n\text{:ZnO-nc:SiO}_2$ and $\text{Eu}^{3+}_m\text{:Tb}^{3+}_n\text{:ZnO-nc:SiO}_2$ samples along with the white light point.

After showing, the colour of our samples in the CIE colour space in Figure 7-4, the author will now describe the method to obtain the concentrations of Eu^{3+} and Tb^{3+} ions (ZnO-nc is fixed in this study) to get a white emission which corresponds to $x = y = z = 0.333$. This is the main focus of this paper. In order to do this, an empirical equation to model the emission intensity spectra of the $\text{Eu}^{3+}_m\text{:Tb}^{3+}_n\text{:ZnO-nc:SiO}_2$ samples as a function of Eu^{3+} and Tb^{3+} ion concentrations need to be established based on the PL spectra of the samples listed in Table 7-2. The empirical equation is used here since the emission of $\text{Eu}^{3+}_m\text{:Tb}^{3+}_n\text{:ZnO-nc:SiO}_2$ samples is a complex process which involves energy transfer from ZnO-nc to the two RE ions and the energy transfer among the RE ions and interactions among all the constituents (RE ions and ZnO-nc). The

author has found that the intensity spectra of the $\text{Eu}^{3+}_m\text{:Tb}^{3+}_n\text{:ZnO-nc:SiO}_2$ samples can be described by using a 4th degree polynomial equation in m (the molar fraction of the concentration of Eu^{3+} ions) and n (the molar fraction of the concentration of Tb^{3+} ions). This is mathematically written as

$$\begin{aligned}
 I(\lambda, m, n) &= C_{00}(\lambda) + C_{10}(\lambda)m + C_{01}(\lambda)n + C_{20}(\lambda)m^2 + C_{11}(\lambda)mn + C_{02}(\lambda)n^2 \\
 &+ C_{30}(\lambda)m^3 + C_{21}(\lambda)m^2n + C_{12}(\lambda)mn^2 + C_{03}(\lambda)n^3 + C_{40}(\lambda)m^4 \\
 &+ C_{31}(\lambda)m^3n + C_{22}(\lambda)m^2n^2 + C_{13}(\lambda)mn^3 \\
 &+ C_{04}(\lambda)n^4
 \end{aligned} \tag{7.7}$$

where $I(\lambda, m, n)$ is the emission intensity of the $\text{Eu}^{3+}_m\text{:Tb}^{3+}_n\text{:ZnO-nc:SiO}_2$ sample at wavelength λ and $C_{00}(\lambda), C_{10}(\lambda), C_{01}(\lambda), C_{20}(\lambda), C_{11}(\lambda), C_{02}(\lambda), C_{30}(\lambda), C_{21}(\lambda), C_{12}(\lambda), C_{03}(\lambda), C_{40}(\lambda), C_{31}(\lambda), C_{22}(\lambda), C_{13}(\lambda)$ and $C_{04}(\lambda)$ are the coefficients of the polynomial equation in m and n , which are unique for each wavelength λ .

All the values of the coefficient of the polynomial in equation (7.7), i.e. the values of all C , from $C_{00}(\lambda)$ to $C_{04}(\lambda)$, for each emission wavelength (λ) ranging from 340 nm to 635 nm were obtained using the Matlab parametric fitting optimisation function which employs the linear least squares regression method to find these optimum values. The goodness of the fitting of equation (7) was confirmed by comparing the experimentally obtained PL spectra of the twenty-four samples with those from the empirical equation (7.7), which the author will refer to as simulated spectra. Figure 7-5 shows the simulated and experimental emission intensity spectra of four of the $\text{Eu}^{3+}_m\text{:Tb}^{3+}_n\text{:ZnO-nc:SiO}_2$ samples, namely $\text{Eu}^{3+}_0\text{:Tb}^{3+}_0\text{:ZnO-nc:SiO}_2$, $\text{Eu}^{3+}_{0.09}\text{:Tb}^{3+}_0\text{:ZnO-nc:SiO}_2$, $\text{Eu}^{3+}_0\text{:Tb}^{3+}_{0.09}\text{:ZnO-nc:SiO}_2$ and $\text{Eu}^{3+}_{0.03}\text{:Tb}^{3+}_{0.03}\text{:ZnO-nc:SiO}_2$, and it is clearly seen that the fitting of the simulated emission intensity with the experimental emission intensity spectrum is very good. The fitting of the simulated and the

experimental emission intensity values are good for all the twenty-four samples used to obtain the 4th degree polynomial equation.

Figure 7-5: The simulated and experimental emission intensity spectra of four $\text{Eu}^{3+}_m\text{:Tb}^{3+}_n\text{:ZnO-nc:SiO}_2$ samples, namely a) $\text{Eu}^{3+}_0\text{:Tb}^{3+}_0\text{:ZnO-nc:SiO}_2$, b) $\text{Eu}^{3+}_{0.09}\text{:Tb}^{3+}_0\text{:ZnO-nc:SiO}_2$, c) $\text{Eu}^{3+}_0\text{:Tb}^{3+}_{0.09}\text{:ZnO-nc:SiO}_2$ and d) $\text{Eu}^{3+}_{0.03}\text{:Tb}^{3+}_{0.03}\text{:ZnO-nc:SiO}_2$.

Having obtained the empirical equation for the emission intensity of the $\text{Eu}^{3+}_m\text{:Tb}^{3+}_n\text{:ZnO-nc:SiO}_2$ sample as a function of Eu^{3+} ions concentration (m) and Tb^{3+} ions concentration (n), the author then used the empirical equation (7.7) to generate the emission intensity spectra of $\text{Eu}^{3+}_m\text{:Tb}^{3+}_n\text{:ZnO-nc:SiO}_2$ samples for every value of m and n ranging from 0 to 0.090 with a difference of 0.001. The CIE x , y and z chromaticity values were then calculated for each of the simulated emission intensity using equations 7.1 to 7.6. The author found that for a white light emission corresponding to $x = y = z = 0.333$ in the CIE colour space, the values of $m = 0.012$ and $n = 0.024$. The author also

determined the Eu^{3+} ions and Tb^{3+} ions concentrations for CIE chromaticity values (chosen arbitrarily), $x = 0.451$, $y = 0.354$ and $z = 0.194$, which was found to be $m = 0.014$ and $n = 0.084$. The author then fabricated two sample, namely $\text{Eu}^{3+}_{0.012}\text{Tb}^{3+}_{0.024}\text{ZnO-nc:SiO}_2$ for a white light sample and $\text{Eu}^{3+}_{0.014}\text{Tb}^{3+}_{0.084}\text{ZnO-nc:SiO}_2$ sample. The measured PL spectra are shown in Figure 7-6 and 7-7, respectively. As expected, a white light emission from the white light sample, $\text{Eu}^{3+}_{0.012}\text{Tb}^{3+}_{0.024}\text{ZnO-nc:SiO}_2$ was obtained as shown in Figure 7-6. Figure 7-6 and 7-7 also shows that the stimulated and the experimental spectra fit very well. In short, the author has successfully demonstrated that the author is able to design and fabricate $\text{Eu}^{3+}_m\text{Tb}^{3+}_n\text{ZnO-nc:SiO}_2$ samples which emit light of any desired colours in the CIE colour space, using a single wavelength excitation.

Figure 7-6: The simulated and experimental emission intensity spectra of $\text{Eu}^{3+}_{0.012}\text{Tb}^{3+}_{0.024}\text{ZnO-nc:SiO}_2$ sample. The inset shows the image of the sample emitting white light upon exciting the sample using 300 nm UV led light.

Figure 7-7: The simulated and experimental emission intensity spectra of $\text{Eu}^{3+}_{0.014}\text{Tb}^{3+}_{0.084}\text{ZnO-nc:SiO}_2$ sample.

7.5. Chapter Summary

In conclusion, in this work the author have developed a method to determine the concentration of Eu^{3+} ions and Tb^{3+} ions in a thin film sample of SiO_2 co-doped with ZnO-nc ($\text{Eu}^{3+}_m\text{Tb}^{3+}_n\text{ZnO-nc:SiO}_2$ samples) to produce a white light emitting sample or a sample emitting any desired colour in the CIE colour space. Based on the PL data of our samples having various Eu^{3+} and Tb^{3+} ion concentrations and fixed ZnO-nc concentration, a 4th degree polynomial equation in m (the molar fraction of the concentration of Eu^{3+} ions) and n (the molar fraction of the concentration of Tb^{3+} ions) was established to determine the values of m and n to produce a white light or any desired colour emitting sample. The sample combines the red, green and blue emissions from the Eu^{3+} ions, Tb^{3+} ions and ZnO-nc, respectively, to create the white light or any desired colour emission. The emissions from Eu^{3+} ions and Tb^{3+} ions are due to the energy transfer from ZnO-nc to the RE ions. Hence, only a single excitation wavelength, which is used to excite the ZnO-nc, is required to produce various

colour emissions. For a white light emitting sample, the values of m and n are found to be 0.012 and 0.024, respectively. Similarly, for a sample with CIE chromaticity values (chosen arbitrarily), $x = 0.451$, $y = 0.354$ and $z = 0.194$, the values of m and n correspond to 0.014 and 0.084, respectively. The author shows that the stimulated and the experimental spectra of these two samples fit very well. The $\text{Eu}^{3+}_{0.012}\text{:Tb}^{3+}_{0.024}\text{:ZnO-nc:SiO}_2$ sample indeed gives a white light emission. The results presented in this work are important to develop energy efficient solid state lighting devices of any desired colour, such as white light emission, using a single excitation wavelength. In general, this knowledge will help in the development of devices using semiconductor nanocrystals as sensitizers to excite RE ions which have wide ranging application in lasers, optical amplifiers, lighting and display technologies.

Chapter 8: Conclusions and Recommendations

In this Chapter, the author summarizes the main results and conclusions of this thesis, specifically the results and conclusions presented in Chapter 4, 5, 6 and 7. The author also presents the recommendations for future work in the second section of this chapter.

8.1. Conclusion

The main results and conclusions of this thesis are as follows:

- The author has successfully developed processes to fabricate thin film samples of ZnO-nc embedded in SiO₂ matrix co-doped with Eu³⁺ ions using the low-cost sol-gel process. It has been shown that by exciting the ZnO-nc in the sample using an excitation wavelength of 325 nm, a strong red emission from the sample at 614 nm was observed. This emission was the result of the energy transfer from the excited ZnO-nc to the Eu³⁺ ions. The author also showed that the emission from the Eu³⁺ ions as a result of excitation of the ions, through energy transfer from ZnO-nc was around seven times higher than the emission from Eu³⁺ ions as a result of direct excitation of Eu³⁺ ions at 392 nm (highest excitation peak of Eu³⁺ ions). In addition, the dependence of the Eu³⁺ ion red emission on the annealing temperature and also on the Eu³⁺ concentration in the sample were studied and optimised. The annealing temperature of 450°C and Eu³⁺ concentration of 12 mol% gave a maximum red emission from Eu³⁺ ions at 614 nm. Moreover as the concentration of Eu³⁺ ions increased above 12 mol% the red emission from the Eu³⁺ ions at 614 nm reduced due to concentration quenching effect. Then the author presented the results of his study on the contribution of the energy

transfer from the seven different ZnO-nc emission centers to the Eu^{3+} ions. For this, the author calculated and compared the spectral overlap integral of, ZnO-nc emission spectra and lanthanide ion excitation spectra, and the ZnO-nc emission intensity difference integral of the seven ZnO-nc emission centers. For energy transfer from ZnO-nc to Eu^{3+} ions, it was found that the excitonic emission (EE) at 378 nm and Zn defect emission center (Zn_i to V_{Zn}) at 396 nm of the ZnO-nc contributed the greatest in the energy transfer process. On the contrary, the oxygen defect emission centers have low energy transfer contribution to Eu^{3+} ions, but showed high energy loss, as the energy is transferred from the ZnO-nc oxygen defect emission centers to the Eu^{3+} ion induced defects in the sample.

- Similar to the energy transfer from ZnO-nc to Eu^{3+} ions, the energy transfer from ZnO-nc to Tb^{3+} ions was also analysed. The author fabricated thin film samples of Tb^{3+} ions and ZnO-nc embedded in SiO_2 matrix, which gave a strong green emission from the Tb^{3+} ions at 545 nm due to the energy transfer from ZnO-nc to Tb^{3+} ions. The green emission from the Tb^{3+} ions in the sample was also maximised by optimising the Tb^{3+} ion concentration and annealing temperatures. The Tb^{3+} ions samples with 12 mol% Tb^{3+} concentration annealed at 450°C, gave the maximum green emission at 545 nm. Moreover as the concentration of Tb^{3+} ions increased above 12 mol% the green emission from the Tb^{3+} ions at 545 nm also reduced, similar to Eu^{3+} ions, due to concentration quenching effect. The author also presented the results of his study on the contribution of the energy transfer from the seven different ZnO-nc emission centers to the Tb^{3+} ions. This was achieved by calculating the spectral overlap integral and emission intensity integral of the seven

ZnO-nc emission centers. In the case of the energy transfer from ZnO-nc to Tb^{3+} ions, the band edge emission from the smallest ZnO-nc which probably experience quantum confinement (QC) at 360 nm and the ZnO excitonic emission (EE) at 378 nm, showed the highest contribution of energy transfer to the Tb^{3+} ions. The author also showed that the zinc defect and oxygen defect emission centers have low energy transfer contribution to Tb^{3+} ions and high energy loss to the defects induced by the incorporation of Tb^{3+} ions.

- The author then presented the energy transfer efficiencies from the ZnO-nc to Eu^{3+} ions. The transfer efficiencies were calculated by analysing the results of the time-resolved photoluminescence (TRPL) spectra of ZnO-nc:SiO_2 and $\text{Eu}^{3+}_{0.12}\text{:ZnO-nc:SiO}_2$ samples. The author analysed the TRPL spectra of the two samples by calculating the decay time and the stretching exponential coefficient values of the different ZnO-nc emissions centers at 360, 378, 396, and 417 nm using the stretched exponential decay function. The author found that the decay time of the samples with Eu^{3+} ions are faster than those of the samples without Eu^{3+} ions. This is due to the energy transfer from ZnO-nc to the Eu^{3+} ions, which result in the radiative emission from the Eu^{3+} ions at 614 nm, and the energy transfer from ZnO-nc to the additional new defects created due to the incorporation of the Eu^{3+} ions. The decay time was used to calculate the energy transfer efficiency of the four ZnO-nc emission centers mentioned above. The author also calculated the transfer efficiencies using the steady state photoluminescence emission spectra, and found them to be consistent with the transfer efficiencies calculated using the TRPL emission intensity data. The results showed that the transfer efficiencies of EE and Zn_i to V_{Zn} emission centers

emitting at 378 and 396 nm are high because of the energy transfer from ZnO-nc to Eu^{3+} ions, resulting in an emission at 614 nm. While the energy transfer from the oxygen defect emissions at 417, 450, 500, and 575 nm are mostly to the defects created in the $\text{Eu}^{3+}_{0.12}\text{:ZnO-nc:SiO}_2$ sample because of to the incorporation of the Eu^{3+} ions. This result in the high energy transfer efficiency values of the oxygen defect emission centers of ZnO-nc, even though the energy transfer from these emission centers to the Eu^{3+} ions is low. Furthermore, the stretching exponential coefficient values obtained from the TRPL spectra showed that the 360 nm band edge emission (QC) experienced lesser interactions compared to the EE, Zn_i to V_{Zn} , and O_i (oxygen interstitial defect) emissions centered at 378, 396, and 417 nm, respectively.

- The author also calculated the energy transfer efficiencies from the ZnO-nc emission centers to Tb^{3+} ions using the steady-state PL emission intensity data. These results showed that the QC and EE emission centers emitting at 360 and 378 nm, respectively, were mostly due to the energy transfer from ZnO-nc to Tb^{3+} ions resulting in an emission at 545 nm. While the energy transfer from the ZnO-nc defect emissions at 396, 417, 450, 500, and 575 nm were mostly to the defects created because of to the incorporation of the Tb^{3+} ions in the $\text{Tb}^{3+}_{0.12}\text{:ZnO-nc:SiO}_2$ sample. Again similar to Eu^{3+} ions, this result in the high energy transfer efficiency values of the ZnO-nc defect emissions centers even though the energy transfer from these emission centers to the Tb^{3+} ions is low.
- The author then presented the effect of the interaction distance between the ZnO-nc and the Eu^{3+} ions and the interaction distance between two Eu^{3+} ions on the energy transfer process from the ZnO-nc

to the Eu^{3+} ions. A single layer of ZnO-nc and Eu^{3+} ions co-doped in the same SiO_2 matrix (A_x samples), and a three layer thin film sample with the ZnO-nc and Eu^{3+} ions doped in separate layers of SiO_2 separated by a buffer layer of SiO_2 matrix (B_d samples), were fabricated for this study. The equation to calculate the interaction distances between the ZnO-nc and Eu^{3+} ions and the interaction distance between two Eu^{3+} ions, was derived based on the ratio of Zn, Si and Eu^{3+} ions in the sample along with the density and molecular mass of ZnO and SiO_2 . The author showed that the energy transfer from ZnO-nc to Eu^{3+} ions is higher in A type samples compared to B type samples as the interaction distance between the ZnO-nc and Eu^{3+} ions is shorter in A type samples. Moreover, as the interaction distance between ZnO-nc and Eu^{3+} ions was reduced in A type samples, the energy transfer from the ZnO-nc to Eu^{3+} ions increased, resulting in a higher red emission at 614 nm from the Eu^{3+} ions. The A type sample with 12 mol% Eu^{3+} ions which has 5.11 nm interaction distance between the ZnO-nc and Eu^{3+} ions has the maximum red emission at 614 nm. It was noted that at higher concentrations of Eu^{3+} ions, even though the interaction distance between ZnO-nc and Eu^{3+} ions decreases, the red emission does not increase. This is due to the Eu^{3+} ion concentration quenching effect which occurs as the interaction distance between the Eu^{3+} ions become shorter than 0.57 nm in the sample resulting in the migration of energy between the Eu^{3+} ions which is non-radiatively dissipated. In this study, the author also showed that the energy transfer in B type samples, which have a 6.53 nm or higher interaction distance between the ZnO-nc and Eu^{3+} ions, is mostly due to radiative energy transfer.

- Lastly, in the final results chapter, the author combined the red, green and blue emissions from the Eu^{3+} ions, Tb^{3+} ions and ZnO-nc, respectively, to create a white light emission from the samples. The emissions from Eu^{3+} ions and Tb^{3+} ions were due to the energy transfer from ZnO-nc. Hence, using only a single excitation wavelength to excite the ZnO-nc, a white light emission from the thin film sample was achieved. In this study, a method was developed to determine the concentration of Eu^{3+} ions and Tb^{3+} ions, in a thin film sample of SiO_2 co-doped with ZnO-nc and the two RE ions ($\text{Eu}^{3+}_m\text{:Tb}^{3+}_n\text{:ZnO-nc:SiO}_2$ samples), to produce a white light emitting sample or a sample of any desired colour (in the CIE colour space). For this, the author established a 4th degree polynomial equation in m (the molar fraction of the concentration of Eu^{3+} ions) and n (the molar fraction of the concentration of Tb^{3+} ions) based on the PL data of the samples with various Eu^{3+} and Tb^{3+} ion concentrations (but fixed ZnO-nc concentration). This equation was then used to determine the values of m and n to produce a white light or any desired colour emitting sample. Specifically, for a white light emitting sample, the values of m and n were found to be 0.012 and 0.024, respectively. Similarly, for a sample with CIE chromaticity values (chosen arbitrarily), $x = 0.451$, $y = 0.354$ and $z = 0.194$, the values of m and n correspond to 0.014 and 0.084, respectively. The author has shown that the stimulated and the experimental spectra of these two samples agree very well. The $\text{Eu}^{3+}_{0.012}\text{:Tb}^{3+}_{0.024}\text{:ZnO-nc:SiO}_2$ sample indeed gave a white light emission. Thus, the author successfully demonstrated that $\text{Eu}^{3+}_m\text{:Tb}^{3+}_n\text{:ZnO-nc:SiO}_2$ samples of any desired colour in the CIE colour space that can be excited using a single excitation wavelength, can be fabricated.

8.2. Recommendations for future research

In this section, the author outlines the recommendations for further research that can be carried, based on the studies presented in this work.

1. To study the quantum efficiency of emission from the lanthanide ions, namely Eu^{3+} and Tb^{3+} , excited through the energy transfer process from ZnO-nanocrystals. The quantum efficiency can be calculated by measuring the number of photons that are absorbed by ZnO-nc during the excitation process and the number of photons emitted from the ZnO-nc and lanthanide ion during the emission process. Determining the quantum efficiency can be valuable information that can help in understanding the energy transfer from ZnO-nc to lanthanide ions better.
2. To develop electroluminescence devices of ZnO-nc and lanthanide ions by electrically exciting ZnO-nc. The ZnO-nc can be electrically excited by injecting electrons and holes. The recombination of these electrons and holes can then excite the lanthanide ions through the energy transfer process. Further studies need to be done to understand this energy transfer process from ZnO-nc to lanthanide ions as the excitation process of ZnO-nc electrically is different from the excitation process of ZnO-nc optically, which was discussed in this work.
3. To study energy transfer from ZnO-nc to other lanthanide ions such as Ho^{3+} and Tm^{3+} ions to obtain emission at 2.21 μm and 1.7 μm , respectively. The broadband emission from ZnO-nc ranging from 350 nm to 600 nm overlaps with the excitation peaks of Ho^{3+} ions at 360 nm, 455 nm, 468 nm and 538 nm and the excitation peak of Tm^{3+} ions at 480 nm. This leads to an energy transfer process from ZnO-nc to Ho^{3+} and Tm^{3+} ions resulting in emissions at 2.21 μm and 1.7 μm , respectively. These 2

micron emissions are of interest because of their use as light sources for various biological and environmental sensing applications. Thus, studies similar to the ones presented in this work can be carried out to understand the energy transfer contribution and efficiency of energy transfer from ZnO-nc to Ho^{3+} and Tm^{3+} ions.

4. To study optical gain in ZnO-nc and Eu^{3+} ion system. As mentioned in this work, the 614 nm emission from Eu^{3+} ions as a result of excitation through the energy transfer from ZnO-nc is almost seven times higher than the highest direct excitation of Eu^{3+} . This opens up the possibility to have optical gain and to subsequently develop a laser, based on ZnO-nc and Eu^{3+} ion system.

Author's Publication

[Paper-I] V. Mangalam, K. Pita, and C. Couteau, "Study of energy transfer mechanism from ZnO nanocrystals to Eu^{3+} ions," *Nanoscale Research Letters*, journal article vol. 11, no. 1, pp. 1-9, 2016.

[Paper-II] V. Mangalam and K. Pita, "Energy transfer from ZnO nanocrystals to Terbium (3+) ions: A spectral overlap study," presented at the 2016 IEEE Photonics Conference (IPC), Hawaii USA, 2-6 Oct. 2016, 2016.

[Paper-III] V. Mangalam and K. Pita, "Energy Transfer Efficiency from ZnO-Nanocrystals to Eu^{3+} Ions Embedded in SiO_2 Film for Emission at 614 nm," *Materials*, vol. 10, no. 8, p. 930, 2017.

[Paper-IV] V. Mangalam and K. Pita, "Effect of the interaction distance on 614 nm red emission from Eu^{3+} ions due to the energy transfer from ZnO-nc to Eu^{3+} ions," *Optical Materials Express*, vol. 8, no. 10, pp. 3115-3132, 2018/10/01 2018.

[Paper-V] Mangalam, V.; Pita, K. White light emission from thin-film samples of zno nanocrystals, Eu^{3+} and Tb^{3+} ions embedded in an SiO_2 matrix. *Materials* 2019, 12, 1997.

Bibliography

- [1] "Dektak 3 Surface Profile Measuring System (Installation, Operation and Maintenance Manual), Veeco Sloan Technology.."
- [2] C. J. Brinker and G. W. Scherer, "CHAPTER 13 - Film Formation," in *Sol-Gel Science*, C. J. Brinker and G. W. Scherer, Eds. San Diego: Academic Press, 1990, pp. 786-837.
- [3] Y. Dwivedi and S. C. Zilio, "Advances in rare earth spectroscopy and applications," *Journal of Nanoscience and Nanotechnology*, vol. 14, no. 2, pp. 1578-1596, 2014.
- [4] S. V. Eliseeva and J. C. G. Bünzli, "Rare earths: Jewels for functional materials of the future," *New Journal of Chemistry*, vol. 35, no. 6, pp. 1165-1176, 2011.
- [5] D. A. Atwood, *The Rare Earth Elements: Fundamentals and Applications* Wiley, 2012, p. 605.
- [6] K. Moskalik, A. Kozlov, E. Demin, and E. Boiko, "The Efficacy of Facial Skin Cancer Treatment with High-Energy Pulsed Neodymium and Nd:YAG Lasers," *Photomedicine and Laser Surgery*, vol. 27, no. 2, pp. 345-349, 2009/04/01 2009.
- [7] J.-C. Bünzli and S. Eliseeva, "Basics of Lanthanide Photophysics," in *Lanthanide Luminescence*, vol. 7, P. Hänninen and H. Härmä, Eds. (Springer Series on Fluorescence: Springer Berlin Heidelberg, 2011, pp. 1-45.
- [8] S. H. Bowden, Christiana. (16th July). *Absorption Coefficient / PVEducation*. Available: <http://www.pveducation.org/pvcdrom/pn-junction/absorption-coefficient>
- [9] Y. Yu, Y. Wang, D. Chen, P. Huang, E. Ma, and F. Bao, "Enhanced emissions of Eu(3+) by energy transfer from ZnO quantum dots

- embedded in SiO₂ glass," *Nanotechnology*, vol. 19, no. 5, p. 055711, Feb 6 2008.
- [10] A. A. Bol, R. van Beek, and A. Meijerink, "On the Incorporation of Trivalent Rare Earth Ions in II–VI Semiconductor Nanocrystals," *Chemistry of Materials*, vol. 14, no. 3, pp. 1121-1126, 2002/03/01 2002.
 - [11] N. O. Dantas, E. O. Serqueira, A. P. Carmo, M. J. V. Bell, V. Anjos, and G. E. Marques, "Energy transfer between CdS nanocrystals and neodymium ions embedded in vitreous substrates," *Optics Letters*, vol. 35, no. 9, pp. 1329-1331, 2010/05/01 2010.
 - [12] F. Ben Slimen *et al.*, "Effect of CdS nanocrystals on the photoluminescence of Eu³⁺-doped silicophosphate sol gel glass," *RSC Advances*, 10.1039/C7RA01313B vol. 7, no. 24, pp. 14552-14561, 2017.
 - [13] S. Panigrahi, A. Bera, and D. Basak, "Ordered dispersion of ZnO quantum dots in SiO₂ matrix and its strong emission properties," *Journal of Colloid and Interface Science*, vol. 353, no. 1, pp. 30-38, 1/1/ 2011.
 - [14] H. Haiping, W. Yuxia, and Z. Youming, "Photoluminescence property of ZnO–SiO₂ composites synthesized by sol–gel method," *Journal of Physics D: Applied Physics*, vol. 36, no. 23, p. 2972, 2003.
 - [15] D. H. Zhang, Z. Y. Xue, and Q. P. Wang, "The mechanisms of blue emission from ZnO films deposited on glass substrate by r.f. magnetron sputtering," *Journal of Physics D: Applied Physics*, vol. 35, no. 21, p. 2837, 2002.
 - [16] L. Schmidt-Mende and J. L. MacManus-Driscoll, "ZnO – nanostructures, defects, and devices," *Materials Today*, vol. 10, no. 5, pp. 40-48, 5// 2007.

- [17] Q. Shi *et al.*, "Enhancing blue luminescence from Ce-doped ZnO nanophosphor by Li doping," *Nanoscale Research Letters*, journal article vol. 9, no. 1, pp. 1-7, 2014.
- [18] F. Xiao *et al.*, "Efficient Energy Transfer and Enhanced Infrared Emission in Er-Doped ZnO-SiO₂ Composites," *The Journal of Physical Chemistry C*, vol. 116, no. 24, pp. 13458-13462, 2012/06/21 2012.
- [19] G. L. Kabongo, G. H. Mhlongo, T. Malwela, B. M. Mothudi, K. T. Hillie, and M. S. Dhlamini, "Microstructural and photoluminescence properties of sol-gel derived Tb³⁺ doped ZnO nanocrystals," *Journal of Alloys and Compounds*, vol. 591, no. 0, pp. 156-163, 4/5/ 2014.
- [20] S. Ningthoujam Surajkumar, S. Shougaijam Dorendrajit, and M. Sanoujam Dhiren, "Structural and photoluminescence properties of terbium-doped zinc oxide nanoparticles," *Chinese Physics B*, vol. 23, no. 5, p. 058104, 2014.
- [21] P. S. Mbule, G. H. Mhlongo, S. S. Pitale, H. C. Swart, and O. M. Ntwaeaborwa, "Sensitizing effects of ZnO quantum dots on red-emitting Pr³⁺-doped SiO₂ phosphor," *Physica B: Condensed Matter*, vol. 407, no. 10, pp. 1607-1610, 5/15/ 2012.
- [22] H. Li, K. Luo, M. Xia, and P. W. Wang, "Synthesis and optical properties of Pr³⁺-doped ZnO quantum dots," *Journal of Non-Crystalline Solids*, vol. 383, no. 0, pp. 176-180, 1/1/ 2014.
- [23] S. S. Ashtaputre *et al.*, "Investigations of white light emitting europium doped zinc oxide nanoparticles," *Journal of Physics D: Applied Physics*, vol. 41, no. 1, p. 015301, 2008.
- [24] A. Ishizumi, S. Fujita, and H. Yanagi, "Influence of atmosphere on photoluminescence properties of Eu-doped ZnO nanocrystals," *Optical Materials*, vol. 33, no. 7, pp. 1116-1119, 2011.

- [25] Y. Liu, W. Luo, R. Li, G. Liu, M. R. Antonio, and X. Chen, "Optical Spectroscopy of Eu³⁺ Doped ZnO Nanocrystals," *The Journal of Physical Chemistry C*, vol. 112, no. 3, pp. 686-694, 2008/01/01 2008.
- [26] L. Luo *et al.*, "Efficient Doping and Energy Transfer from ZnO to Eu³⁺ Ions in Eu³⁺-Doped ZnO Nanocrystals," *Journal of Nanoscience and Nanotechnology*, vol. 12, no. 3, pp. 2417-2423, 2012.
- [27] Y. Zhang, Y. Liu, X. Li, Q. J. Wang, and E. Xie, "Room temperature enhanced red emission from novel Eu(3+) doped ZnO nanocrystals uniformly dispersed in nanofibers," *Nanotechnology*, vol. 22, no. 41, p. 415702, Oct 14 2011.
- [28] T. Lin *et al.*, "Luminescence enhancement due to energy transfer in ZnO nanoparticles and Eu³⁺ ions co-doped silica," *Thin Solid Films*, vol. 520, no. 17, pp. 5815-5819, 6/30/ 2012.
- [29] J. Lang *et al.*, "Effect of annealing temperature on the energy transfer in Eu-doped ZnO nanoparticles by chemical precipitation method," *Journal of Materials Science: Materials in Electronics*, vol. 24, no. 11, pp. 4542-4548, 2013.
- [30] H. Shahroosvand and M. Ghorbani-asl, "Solution-based synthetic strategies for Eu doped ZnO nanoparticle with enhanced red photoluminescence," *Journal of Luminescence*, vol. 144, no. 0, pp. 223-229, 12// 2013.
- [31] R. Das, N. Khichar, and S. Chawla, "Dual mode luminescence in rare earth (Er³⁺/Ho³⁺) doped ZnO nanoparticles fabricated by inclusive co precipitation technique," *Journal of Materials Science: Materials in Electronics*, journal article vol. 26, no. 9, pp. 7174-7182, 2015.

- [32] Y. Liu, W. Luo, R. Li, H. Zhu, and X. Chen, "Near-infrared luminescence of Nd³⁺ and Tm³⁺ ions doped ZnO nanocrystals," *Optics Express*, vol. 17, no. 12, pp. 9748-9753, 2009/06/08 2009.
- [33] L. Luo, F. Y. Huang, G. S. Dong, Y. H. Wang, Z. F. Hu, and J. Chen, "White Light Emission and Luminescence Dynamics in Eu³⁺/Dy³⁺ Codoped ZnO Nanocrystals," *Journal of Nanoscience and Nanotechnology*, vol. 16, no. 1, pp. 619-625, // 2016.
- [34] L. Luo *et al.*, "Strong luminescence and efficient energy transfer in Eu³⁺/Tb³⁺-codoped ZnO nanocrystals," *Optical Materials*, vol. 37, pp. 470-475, 2014/11/01/ 2014.
- [35] G. L. Kabongo, G. H. Mhlongo, T. Malwela, B. M. Mothudi, K. T. Hillie, and M. S. Dhlamini, "Microstructural and photoluminescence properties of sol–gel derived Tb³⁺ doped ZnO nanocrystals," *Journal of Alloys and Compounds*, vol. 591, pp. 156-163, 4/5/ 2014.
- [36] A. S. Marfunin, *Spectroscopy, Luminescence and Radiation Centers in Minerals*. Berlin: New York: Springer-Verlag, 1979.
- [37] G. Blasse and B. C. Grabmaier, *Luminescent Materials*. Berlin: New York: Springer-Verlag, 1994.
- [38] B. Henderson and G. F. Imbusch, *Optical Spectroscopy of Inorganic Solids*. Oxford, New York:: Clarendon Press, 1989.
- [39] G. H. Dieke, *Spectra and Energy Levels of Rare Earth Ions in Crystals*. New York: InterScience, Johan Wiley and Sons, 1968.
- [40] K. S. Sohn, *Handbook of Luminescence, Display Materials and Devices*. California: American Scientific Publishers, 2003.
- [41] A. J. Steckl *et al.*, "Rare-earth-doped GaN: growth, properties, and fabrication of electroluminescent devices," *IEEE Journal of Selected Topics in Quantum Electronics*, vol. 8, no. 4, pp. 749-766, 2002.

- [42] K. J. Laidler, J. H. Meiser, and B. C. Sanctuary, *Physical Chemistry 4th Edition*. Boston: Houghton Mifflin, 2003.
- [43] C. A. Morrison and R. P. Leavitt, "Chapter 46 Spectroscopic properties of triply ionized," in *Handbook on the Physics and Chemistry of Rare Earths*, vol. 5: Elsevier, 1982, pp. 461-692.
- [44] I. B. Bersuker, "Electronic structure and properties of transition metal compounds : introduction to the theory," ed. New York :: Wiley, 1996, pp. 76-83.
- [45] V. Mangalam, K. Pita, and C. Couteau, "Study of energy transfer mechanism from ZnO nanocrystals to Eu³⁺ ions," *Nanoscale Research Letters*, journal article vol. 11, no. 1, pp. 1-9, 2016.
- [46] S. O. Kasap, *Principles of Electronic Materials and Devices, 2nd ed.* Boston: McGraw-Hill, 2003.
- [47] J. G. Solé, Bausá, L. and Jaque, D. , in *An Introduction to the Optical Spectroscopy of Inorganic Solids*Hoboken, NJ: John Wiley, 2005, pp. 153-207.
- [48] J. García Solé, "An introduction to the optical spectroscopy of inorganic solids," L. E. Bausá and D. Jaque, Eds., ed. Hoboken, NJ :: J. Wiley, 2005, pp. 153-159, 182, 188-191, 190, 193, 200-205, 207.
- [49] N. Yamada, S. Shionoya, and T. Kushida, "Phonon-Assisted Energy Transfer—Comparison between Theory and Experiment," *Journal of the Physical Society of Japan*, vol. 30, no. 5, p. 1507, 1971.
- [50] G. Blasse, *Energy Transfer in Oxidic Phosphors*. 1969, pp. 131-144.
- [51] Q. Xiang, "Research and development of rare earth doped materials by sol-gel process for photonics applications," *Nanyang Technological University, Singapore*, Ph.D thesis p. 63, 2002.

- [52] J. Lucas, P. Lucas, T. L. Mercier, A. Rollat, and W. Davenport, "1.2 Uses," in *Rare Earths - Science, Technology, Production and Use*: Elsevier, p. 3.
- [53] J. Lucas, P. Lucas, T. L. Mercier, A. Rollat, and W. Davenport, "15.1.1 Introduction to the Luminescence," in *Rare Earths - Science, Technology, Production and Use*: Elsevier, p. 251.
- [54] K. Toeda. (2011, 2018, September 3). *Rare earth elements, a key for 21st century technology and industry*. Available:
http://www.spring8.or.jp/en/news_publications/research_highlights/no_56/
- [55] Y. H. Ko, S. H. Lee, and J. S. Yu, "Luminescence Properties of Europium Ions-Doped Yttrium Silicate (Y₂SiO₅:Eu³⁺) Nanocrystalline Phosphors: Effect of Eu³⁺ Ion Concentration and Thermal Annealing," *Journal of Nanoscience and Nanotechnology*, vol. 13, no. 5, pp. 3230-3235, // 2013.
- [56] W. Ran, L. Wang, M. Yang, X. Kong, D. Qu, and J. Shi, "Enhanced energy transfer from Bi³⁺ to Eu³⁺ ions relying on the criss-cross cluster structure in MgMoO₄ phosphor," *Journal of Luminescence*, vol. 192, pp. 141-147, 2017/12/01/ 2017.
- [57] L. Li *et al.*, "Enhancing luminescence of Lu₂MoO₆:Eu³⁺ phosphors by doping with Li⁺ ions for near ultraviolet based solid state lighting," *Materials Research Bulletin*, vol. 78, pp. 26-30, 2016/06/01/ 2016.
- [58] K. Park, J. W. Pi, and D. A. Hakeem, "Effect of alkaline metal ions on the photoluminescence properties of Eu³⁺-doped Ca₃Al₂O₆ phosphors," *Journal of Rare Earths*, vol. 34, no. 12, pp. 1193-1198, 2016/12/01/ 2016.
- [59] M. Kalidasan, K. Asokan, and R. Dhanasekaran, "Luminescence properties of 100MeV W⁸⁺ ion irradiated GdCa₄O(BO₃)₃:Eu³⁺ and GdCa₄O(BO₃)₃:Tb³⁺ phosphors," *Journal of Luminescence*, vol. 180, pp. 241-250, 2016/12/01/ 2016.

- [60] W. Zeng, Y. Wang, S. Han, W. Chen, and G. Li, "Enhancement of CdSiO₃: Tb³⁺ green long-lasting phosphors by co-doping with Re³⁺ (Re³⁺=Gd³⁺, Y³⁺, La³⁺) ions," *Journal of Luminescence*, vol. 152, pp. 210-213, 2014/08/01/ 2014.
- [61] J. A. Wani, N. S. Dhoble, and S. J. Dhoble, "Novel RGB emission of Tb³⁺ ion in Li₂BaP₂O₇ phosphor for near-UV LEDs," *Optik - International Journal for Light and Electron Optics*, vol. 127, no. 24, pp. 11927-11931, 2016/12/01/ 2016.
- [62] L. K. Bharat, Y. I. Jeon, and J. S. Yu, "RE³⁺ (RE³⁺ = Tm³⁺, Tb³⁺ and Sm³⁺) ions activated Y₆WO₁₂ phosphors: Synthesis, photoluminescence, cathodoluminescence and thermal stability," *Journal of Alloys and Compounds*, vol. 685, pp. 559-565, 2016/11/15/ 2016.
- [63] S. S. Reddy, K. R. Nagabhushana, and S. Fouran, "Mechanism of thermoluminescence in high energy carbon ion irradiated Tb³⁺ doped Al₂O₃ phosphor for carbon ion beam dosimetry," *Materials Research Express*, vol. 4, no. 9, p. 095023, 2017.
- [64] N. P. Singh, N. R. Singh, N. R. Singh, and N. M. Singh, "Effect of doping ion concentration on the photoluminescence behavior of CdWO₄:Tb³⁺ phosphor synthesized via co-precipitation method," *Indian Journal of Physics*, vol. 92, no. 11, pp. 1461-1466, 2018/11/01 2018.
- [65] M. Fujii, M. Yoshida, Y. Kanzawa, S. Hayashi, and K. Yamamoto, "1.54 μ m photoluminescence of Er³⁺ doped into SiO₂ films containing Si nanocrystals: Evidence for energy transfer from Si nanocrystals to Er³⁺," *Applied Physics Letters*, vol. 71, no. 9, pp. 1198-1200, 1997.
- [66] A. M. Smith and S. Nie, "Semiconductor Nanocrystals: Structure, Properties, and Band Gap Engineering," *Accounts of Chemical Research*, vol. 43, no. 2, pp. 190-200, 2010/02/16 2010.

- [67] A. L. Rogach, T. A. Klar, J. M. Lupton, A. Meijerink, and J. Feldmann, "Energy transfer with semiconductor nanocrystals," *Journal of Materials Chemistry*, 10.1039/B812884G vol. 19, no. 9, pp. 1208-1221, 2009.
- [68] M. D. Lumb, *Luminescence Spectroscopy*. San Diego, United States: Elsevier Science Publishing Co Inc, 1978.
- [69] B. Valeur, *Molecular fluorescence : principles applications*. Weinheim: : Wiley- VCH, 2002.
- [70] S. O. Kasap and S. O. Kasap, *Principles of electronic materials and devices*, 2 ed. Boston: McGraw-Hill, 2002.
- [71] C. R. Ronda, *Luminescence : from theory to applications*. Weinheim:: Wiley- VCH, 2008.
- [72] C. b. A. D. M. a. A. Wilkinson, *IUPAC. Compendium of Chemical Terminology, 2nd ed. (the "Gold Book")*. Oxford: Blackwell Scientific Publications, 1997.
- [73] T. Förster, "Zwischenmolekulare Energiewanderung und Fluoreszenz," *Annalen der Physik*, vol. 437, no. 1-2, pp. 55-75, 1948/01/01 1948.
- [74] D. L. Dexter, "A Theory of Sensitized Luminescence in Solids," *The Journal of Chemical Physics*, vol. 21, no. 5, pp. 836-850, 1953.
- [75] P. G. Kik, M. L. Brongersma, and A. Polman, "Strong exciton-erbium coupling in Si nanocrystal-doped SiO₂," *Applied Physics Letters*, vol. 76, no. 17, pp. 2325-2327, 2000.
- [76] P. G. Kik and A. Polman, "Exciton–erbium energy transfer in Si nanocrystal-doped SiO₂," *Materials Science and Engineering: B*, vol. 81, no. 1, pp. 3-8, 2001/04/24/ 2001.
- [77] J. Heitmann, M. Schmidt, M. Zacharias, V. Y. Timoshenko, M. G. Lisachenko, and P. K. Kashkarov, "Fabrication and photoluminescence properties of erbium doped size-controlled silicon nanocrystals,"

Materials Science and Engineering: B, vol. 105, no. 1, pp. 214-220, 2003/12/15/ 2003.

- [78] M. Fujii, K. Imakita, K. Watanabe, and S. Hayashi, "Coexistence of two different energy transfer processes in SiO₂ films containing Si nanocrystals and Er," *Journal of Applied Physics*, vol. 95, no. 1, pp. 272-280, 2004.
- [79] A. Polman and F. C. J. M. van Veggel, "Broadband sensitizers for erbium-doped planar optical amplifiers: review," *Journal of the Optical Society of America B*, vol. 21, no. 5, pp. 871-892, 2004/05/01 2004.
- [80] O. Savchyn, P. G. Kik, R. M. Todi, and K. R. Coffey, "Effect of hydrogen passivation on luminescence-center-mediated Er excitation in Si-rich SiO_2 with and without Si nanocrystals," *Physical Review B*, vol. 77, no. 20, p. 205438, 05/30/ 2008.
- [81] K. Pita and Q. V. Vu, "Energy Transfer from Silicon Nanocrystals to Er³⁺ Ions Embedded in Silicon Oxide Matrix," in *Nanocrystal*, Y. Masuda, Ed.: IntechOpen, 2011.
- [82] G. Franzò, F. Iacona, V. Vinciguerra, and F. Priolo, "Enhanced rare earth luminescence in silicon nanocrystals," *Materials Science and Engineering: B*, vol. 69-70, pp. 335-339, 2000/01/14/ 2000.
- [83] O. Savchyn *et al.*, "Luminescence-center-mediated excitation as the dominant Er sensitization mechanism in Er-doped silicon-rich SiO_2 films," *Physical Review B*, vol. 76, no. 19, p. 195419, 11/15/ 2007.
- [84] L. Sun, C. Yan, C. Liu, C. Liao, D. Li, and J. Yu, "Study of the optical properties of Eu³⁺-doped ZnS nanocrystals," *Journal of Alloys and Compounds*, vol. 275-277, pp. 234-237, 1998/07/24/ 1998.

- [85] T. Hayakawa, S. T. Selvan, and M. Nogami, "Energy Transfer Between Eu³⁺ Ions and CdS Quantum Dots in Sol-Gel Derived CdS/SiO₂ : Eu³⁺ Gel," *Journal of Sol-Gel Science and Technology*, vol. 19, no. 1, pp. 779-783, 2000/12/01 2000.
- [86] "Bendre BS, Mahamuni S. Luminescence in ZnO quantum particles. *Journal of Materials Research*. 2004;19(03):737-40. doi:10.1557/jmr.2004.19.3.737," ed.
- [87] D. W. Hamby, D. A. Lucca, M. J. Klopstein, and G. Cantwell, "Temperature dependent exciton photoluminescence of bulk ZnO," *Journal of Applied Physics*, vol. 93, no. 6, pp. 3214-3217, 2003.
- [88] S. B. Zhang, S. H. Wei, and A. Zunger, "Intrinsic n-type versus p-type doping asymmetry and the defect physics of ZnO," *Physical Review B*, vol. 63, no. 7, p. 075205, 01/31/ 2001.
- [89] A. Teke *et al.*, "Excitonic fine structure and recombination dynamics in single-crystalline ZnO," *Physical Review B*, vol. 70, no. 19, p. 195207, 11/12/ 2004.
- [90] A. B. Djurišić *et al.*, "Defect emissions in ZnO nanostructures," *Nanotechnology*, vol. 18, no. 9, p. 095702, 2007.
- [91] P. A. Rodnyi and I. V. Khodyuk, "Optical and luminescence properties of zinc oxide (Review)," *Optics and Spectroscopy*, vol. 111, no. 5, pp. 776-785, 2011/11/01 2011.
- [92] D. H. Zhang, Z. Y. Xue, and Q. P. Wang, "The mechanisms of blue emission from ZnO films deposited on glass substrate by r.f. magnetron sputtering," *Journal of Physics D: Applied Physics*, vol. 35, 2002.
- [93] S. Mahamuni, K. Borgohain, B. S. Bendre, V. J. Leppert, and S. H. Risbud, "Spectroscopic and structural characterization of electrochemically

- grown ZnO quantum dots," *Journal of Applied Physics*, vol. 85, no. 5, pp. 2861-2865, 1999.
- [94] A. Janotti and C. G. Van de Walle, "Native point defects in ZnO," *Physical Review B*, vol. 76, no. 16, p. 165202, 10/04/ 2007.
- [95] K. Pita, P. Baudin, Q. Vu, R. Aad, C. Couteau, and G. Lerondel, "Annealing temperature and environment effects on ZnO nanocrystals embedded in SiO₂: a photoluminescence and TEM study," *Nanoscale Research Letters*, vol. 8, 2013.
- [96] O. M. Ntwaeaborwa, S. J. Mofokeng, V. Kumar, and R. E. Kroon, "Structural, optical and photoluminescence properties of Eu³⁺ doped ZnO nanoparticles," *Spectrochimica Acta Part A: Molecular and Biomolecular Spectroscopy*, vol. 182, no. Supplement C, pp. 42-49, 2017/07/05/ 2017.
- [97] H. V. S. Pessoni, L. J. Q. Maia, and A. Franco, "Eu-doped ZnO nanoparticles prepared by the combustion reaction method: Structural, photoluminescence and dielectric characterization," *Materials Science in Semiconductor Processing*, vol. 30, no. Supplement C, pp. 135-141, 2015/02/01/ 2015.
- [98] A. M. Klonkowski, M. Zalewska, and B. Kościelska, "Emission enhancement of Eu(III) and/or Tb(III) ions entrapped in silica xerogels with ZnO nanoparticles by energy transfer," *Journal of Non-Crystalline Solids*, vol. 352, no. 40, pp. 4183-4189, 2006/11/01/ 2006.
- [99] P. P. Pal and J. Manam, "Photoluminescence and thermoluminescence studies of Tb³⁺ doped ZnO nanorods," *Materials Science and Engineering: B*, vol. 178, no. 7, pp. 400-408, 2013/04/20/ 2013.

- [100] N. Jin, H. Li, F. Liu, and Y.-H. Xie, "Microstructure and Luminescence Properties of Tb³⁺ Doped ZnO Quantum Dots," *Journal of Nanoscience and Nanotechnology*, vol. 16, no. 4, pp. 3592-3596, // 2016.
- [101] M. Najafi and H. Haratizadeh, "The effect of growth conditions and morphology on photoluminescence properties of Eu-doped ZnO nanostructures," *Solid State Sciences*, vol. 41, no. Supplement C, pp. 48-51, 2015/03/01/ 2015.
- [102] F. Xiao *et al.*, "Infrared emission properties and energy transfer in ZnO–SiO₂:Yb³⁺ composites," *Journal of Alloys and Compounds*, vol. 509, no. 29, pp. 7794-7797, 7/21/ 2011.
- [103] V. Kumar, V. Kumar, S. Som, M. M. Duvenhage, O. M. Ntwaeaborwa, and H. C. Swart, "Effect of Eu doping on the photoluminescence properties of ZnO nanophosphors for red emission applications," *Applied Surface Science*, vol. 308, no. Supplement C, pp. 419-430, 2014/07/30/ 2014.
- [104] M. Najafi and H. Haratizadeh, "Investigation of intrinsic and extrinsic defects effective role on producing intense red emission in ZnO:Eu nanostructures," *Materials Research Bulletin*, vol. 65, no. Supplement C, pp. 103-109, 2015/05/01/ 2015.
- [105] L. Singh, "Photoluminescence Studies of ZnO, ZnO:Eu and ZnO:Eu Nanoparticles Covered with Y₂O₃ Matrix," *Materials Sciences and Applications*, vol. 6, pp. 269-278, 2015.
- [106] J. Huang *et al.*, "Synthesis and Optical Properties of Eu³⁺ Doped ZnO Nanoparticles Used for White Light Emitting Diodes," *Journal of Nanoscience and Nanotechnology*, vol. 14, no. 4, pp. 3052-3055, // 2014.
- [107] V. Mangalam and K. Pita, "Energy Transfer Efficiency from ZnO-Nanocrystals to Eu³⁺ Ions Embedded in SiO₂ Film for Emission at 614 nm," *Materials*, vol. 10, no. 8, p. 930, 2017.

- [108] P. Kumar, A. K. Yadav, A. G. Joshi, D. Bhattacharyya, S. N. Jha, and P. C. Pandey, "Influence of Li co-doping on structural property of sol-gel derived terbium doped zinc oxide nanoparticles," *Materials Characterization*, vol. 142, pp. 593-601, 2018/08/01/ 2018.
- [109] V. Mangalam and K. Pita, "Energy transfer from ZnO nanocrystals to Terbium (3+) ions: A spectral overlap study," presented at the 2016 IEEE Photonics Conference (IPC), Hawaii USA, 2-6 Oct. 2016, 2016.
- [110] V. Kumar *et al.*, "Tunable and white emission from ZnO:Tb³⁺ nanophosphors for solid state lighting applications," *Chemical Engineering Journal*, vol. 255, pp. 541-552, 2014/11/01/ 2014.
- [111] W. D. Wright, *The Measurement of Colour*. A. Hilger Limited, 1944.
- [112] R. W. G. Hunt and M. R. Pointer, *Measuring Colour, 4th Edition*. West Sussex, United Kingdom: John Wiley & Sons Ltd, 2011, p. 469.
- [113] K. Seshan, "Handbook of Thin-Film Deposition Processes and Techniques - Principles, Methods, Equipment and Applications (2nd Edition)," ed: William Andrew Publishing/Noyes.
- [114] C. P. Dietrich and M. Grundmann, "Pulsed-Laser Deposition of ZnO Nanowires," in *Wide Band Gap Semiconductor Nanowires 1*, V. Consonni and G. Feuillet, Eds., 2014.
- [115] B. Pandey and D. L. Weathers, "Temperature dependent formation of ZnO and Zn₂SiO₄ nanoparticles by ion implantation and thermal annealing," *Nuclear Instruments and Methods in Physics Research Section B: Beam Interactions with Materials and Atoms*, vol. 332, pp. 359-363, 2014/08/01/ 2014.
- [116] J. Rashid, M. A. Barakat, N. Salah, and S. S. Habib, "ZnO-nanoparticles thin films synthesized by RF sputtering for photocatalytic degradation of

- 2-chlorophenol in synthetic wastewater," *Journal of Industrial and Engineering Chemistry*, vol. 23, pp. 134-139, 2015/03/25/ 2015.
- [117] S.-H. Park, J.-W. Park, S.-M. Yang, K.-H. Kim, and N.-M. Hwang, "Effect of Electric Bias on the Deposition Behavior of ZnO Nanostructures in the Chemical Vapor Deposition Process," *The Journal of Physical Chemistry C*, vol. 119, no. 44, pp. 25047-25052, 2015/11/05 2015.
- [118] L. Xu *et al.*, "Photoluminescent behavior of ZnO nanoparticles in a sandwich-like structure SiO_x/ZnO/SiO_x," *Optik - International Journal for Light and Electron Optics*, vol. 137, pp. 142-147, 2017/05/01/ 2017.
- [119] E. M. Elsayed, A. E. Shalan, and M. M. Rashad, "Preparation of ZnO nanoparticles using electrodeposition and co-precipitation techniques for dye-sensitized solar cells applications," *Journal of Materials Science: Materials in Electronics*, journal article vol. 25, no. 8, pp. 3412-3419, August 01 2014.
- [120] Y. Y. Peng, T. E. Hsieh, and C. H. Hsu, "White-light emitting ZnO-SiO₂ nanocomposite thin films prepared by sputtering method," in *Materials Research Society Symposium Proceedings*, 2006, vol. 891, pp. 533-538.
- [121] P. Panprom *et al.*, "Nanocrystal-ZnO thin film deposition by a novel reactive gas-timing RF magnetron sputtering provided for UV photodetectors," in *Advanced Materials Research* vol. 93-94, ed, 2010, pp. 537-540.
- [122] V. V. Siva Kumar, F. Singh, S. Ojha, and D. Kanjilal, "Influence of Zn concentration on the size and optical properties of ZnO nanocrystals in silica matrix grown by RF co-sputter deposition," *Advanced Materials Letters*, vol. 4, no. 5, pp. 343-346, 2013.

- [123] V. V. S. Kumar and D. Kanjilal, "Enhancement in visible luminescence from nanocomposite ZnO-SiO_x thin films due to annealing," *Functional Materials Letters*, vol. 7, no. 2, 2014, Art. no. 1450007.
- [124] H. Amekura, O. A. Plaksin, N. Umeda, Y. Takeda, N. Kishimoto, and C. Buchal, "A short review and present status of ZnO nanoparticle formation by ion implantation combined with thermal oxidation," in *Materials Research Society Symposium Proceedings*, 2005, vol. 908, pp. 87-92.
- [125] Z. Z. Zhi, Y. Qi, H. Z. Yang, J. H. Wang, X. M. Yu, and B. S. Zhang, "Effects of annealing temperature on optical properties of ZnO nanocrystals embedded in SiO₂ matrix thin films," *Journal of Physics D: Applied Physics*, vol. 40, no. 14, p. 4281, 2007.
- [126] L. Armelao, M. Fabrizio, S. Gialanella, and F. Zordan, "Sol-gel synthesis and characterisation of ZnO-based nanosystems," *Thin Solid Films*, vol. 394, no. 1-2, pp. 90-96, 2001.
- [127] L. Znaidi, "Sol-gel-deposited ZnO thin films: A review," *Materials Science and Engineering B: Solid-State Materials for Advanced Technology*, vol. 174, no. 1-3, pp. 18-30, 2010.
- [128] Y. M. Huang, Q. L. Ma, and B. G. Zhai, "Wavelength tunable photoluminescence of ZnO/porous Si nanocomposites," *Journal of Luminescence*, vol. 138, pp. 157-163, 2013.
- [129] K. Pita, P. Baudin, Q. Vu, R. Aad, C. Couteau, and G. Lerondel, "Annealing temperature and environment effects on ZnO nanocrystals embedded in SiO₂: a photoluminescence and TEM study," *Nanoscale Research Letters*, vol. 8, no. 1, p. 517, 2013.

- [130] D. M. de Leeuw, W. K. Zwicker, and R. N. Bhargava, "Sol-gel process for producing liminescent thin film, and film so produced and devices utilizing same," ed: Google Patents, 1990.
- [131] C.-Y. Tsay, K.-S. Fan, S.-H. Chen, and C.-H. Tsai, "Preparation and characterization of ZnO transparent semiconductor thin films by sol-gel method," *Journal of Alloys and Compounds*, vol. 495, no. 1, pp. 126-130, 2010/04/09/ 2010.
- [132] L. Znaidi, "Sol-gel-deposited ZnO thin films: A review," *Materials Science and Engineering: B*, vol. 174, no. 1, pp. 18-30, 2010/10/25/ 2010.
- [133] N. B. Ibrahim, S. M. Al-Shomar, and S. H. Ahmad, "Effect of aging time on the optical, structural and photoluminescence properties of nanocrystalline ZnO films prepared by a sol-gel method," *Applied Surface Science*, vol. 283, pp. 599-602, 2013/10/15/ 2013.
- [134] Y. Li, L. Xu, X. Li, X. Shen, and A. Wang, "Effect of aging time of ZnO sol on the structural and optical properties of ZnO thin films prepared by sol-gel method," *Applied Surface Science*, vol. 256, no. 14, pp. 4543-4547, 2010/05/01/ 2010.
- [135] T. Ivanova, A. Harizanova, T. Koutzarova, and B. Vertruyen, "Study of ZnO sol-gel films: Effect of annealing," *Materials Letters*, vol. 64, no. 10, pp. 1147-1149, 2010/05/31/ 2010.
- [136] D. Raoufi and T. Raoufi, "The effect of heat treatment on the physical properties of sol-gel derived ZnO thin films," *Applied Surface Science*, vol. 255, no. 11, pp. 5812-5817, 2009/03/15/ 2009.
- [137] C. J. Brinker and G. W. Scherer, "Sol-gel Science: The Physics and Chemistry of Sol-gel Processing," in *Sol-Gel Science*, C. J. B. W. Scherer, Ed. San Diego: Academic Press, 1990, pp. 838-880.

- [138] G. Wilson and A. Patel, "Recent advances in sol-gel processing for improved materials synthesis," *Materials Science and Technology*, vol. 9, no. 11, pp. 937-944, 1993.
- [139] C. J. Brinker and G. W. Scherer, "CHAPTER 1 - Introduction," in *Sol-Gel Science*, C. J. Brinker and G. W. Scherer, Eds. San Diego: Academic Press, 1990, pp. xvi-18.
- [140] C. J. Brinker and G. W. Scherer, "CHAPTER 9 - Structural Evolution during Consolidation," in *Sol-Gel Science*, C. J. Brinker and G. W. Scherer, Eds. San Diego: Academic Press, 1990, pp. 514-615.
- [141] G. Wilson and A. Patel, "Recent advances in sol-gel processing for improved materials synthesis," *Materials Science and Technology*, vol. 9, no. 11, pp. 937-944, 1993/11/01 1993.
- [142] C. N. R. Rao, "Chemical synthesis of solid inorganic materials," *Materials Science and Engineering: B*, vol. 18, no. 1, pp. 1-21, 1993/02/01/ 1993.
- [143] C. A. Milea, C. Bogatu, and A. DuȚĂ, "THE INFLUENCE OF PARAMETERS IN SILICA SOL-GEL PROCESS," *Bulletin of the Transilvania University of Brasov, Series I: Engineering Sciences*, Article vol. 4, no. 1, pp. 59-66, 2011.
- [144] S. Chakrabarti, D. Ganguli, and S. Chaudhuri, "Substrate dependence of preferred orientation in sol-gel-derived zinc oxide films," *Materials Letters*, vol. 58, no. 30, pp. 3952-3957, 2004/12/01/ 2004.
- [145] J. E. Mahan, *Physical vapor deposition of thin film*. New York: Wiley, 2000.
- [146] J. E. Greene, "Review Article: Tracing the recorded history of thin-film sputter deposition: From the 1800s to 2017," *Journal of Vacuum Science & Technology A: Vacuum, Surfaces, and Films*, vol. 35, no. 5, p. 05C204, 2017.

- [147] J. L. Vossen and W. Kern, *Thin film processes II*. Boston: Academic Press, 1991, p. 178.
- [148] *Jobin Yvon Fluorolog-3 Manual*.
- [149] J. G. Solé, L. Bausá, and D. Jaque, "Monochromators and Detectors," in *An Introduction to the Optical Spectroscopy of Inorganic Solids*: Wiley, 2005, pp. 77-112.
- [150] J. G. Solé, L. Bausá, and D. Jaque, "Light Sources," in *An Introduction to the Optical Spectroscopy of Inorganic Solids*: Wiley, 2005, pp. 39-75.
- [151] "Guide to Streak Camera by Hamamatsu," ed.
- [152] M. S. Dhlamini, O. M. Ntwaeaborwa, H. C. Swart, J. M. Ngaruiya, and K. T. Hillie, "Sensitized luminescence through nanoscopic effects of ZnO encapsulated in SiO₂:Tb³⁺ sol gel derived phosphor," *Physica B: Condensed Matter*, vol. 404, no. 22, pp. 4406-4410, 12/1/ 2009.
- [153] V. Mangalam and K. Pita, "Energy transfer from ZnO nanocrystals to Terbium (3+) ions: A spectral overlap study," in *2016 IEEE Photonics Conference (IPC)*, Waikoloa, HI, USA, 2016, pp. 190-191: IEEE.
- [154] L. Yu and M. Nogami, "Local structure and photoluminescent characteristics of Eu³⁺ in ZnO–SiO₂ glasses," (in English), *Journal of Sol-Gel Science and Technology*, vol. 43, no. 3, pp. 355-360, 2007/09/01 2007.
- [155] M. Shwetha and B. Eraiah, "Influence of europium (Eu³⁺) ions on the optical properties of lithium zinc phosphate glasses," *IOP Conference Series: Materials Science and Engineering*, vol. 310, p. 012033, 2018/02 2018.
- [156] A. d. Bettencourt-Dias, "The Electronic Structure of the Lanthanides," in *The Rare Earth Elements Fundamentals and Applications*, D. A. Atwood, Ed. First Edition ed.: Wiley, 2012, p. 30.

- [157] M. K. Chong, K. Pita, and C. H. Kam, "Photoluminescence of sol–gel-derived Y2O3:Eu3+ thin-film phosphors with Mg2+ and Al3+ co-doping," (in English), *Applied Physics A*, vol. 79, no. 3, pp. 433-437, 2004/08/01 2004.
- [158] M. K. Chong, K. Pita, and C. H. Kam, "Photoluminescence of Y2O3:Eu3+ thin film phosphors by sol–gel deposition and rapid thermal annealing," *Journal of Physics and Chemistry of Solids*, vol. 66, no. 1, pp. 213-217, 1// 2005.
- [159] J. W. Shin, J. Y. Lee, Y. S. No, T. W. Kim, and W. K. Choi, "Formation mechanisms of ZnO nanocrystals embedded in an amorphous Zn2xSi1–xO2 layer due to sputtering and annealing," *Journal of Alloys and Compounds*, vol. 509, no. 6, pp. 3132-3135, 2/10/ 2011.
- [160] E. A. Meulenkamp, "Synthesis and Growth of ZnO Nanoparticles," *The Journal of Physical Chemistry B*, vol. 102, no. 29, pp. 5566-5572, 1998/07/01 1998.
- [161] D. Denzler, M. Olschewski, and K. Sattler, "Luminescence studies of localized gap states in colloidal ZnS nanocrystals," *Journal of Applied Physics*, vol. 84, no. 5, pp. 2841-2845, 1998.
- [162] I. Musa *et al.*, "Temperature and size dependence of time-resolved exciton recombination in ZnO quantum dots," *Applied Physics Letters*, vol. 99, no. 24, p. 243107, 2011.
- [163] G. Schlegel, J. Bohnenberger, I. Potapova, and A. Mews, "Fluorescence Decay Time of Single Semiconductor Nanocrystals," *Physical Review Letters*, vol. 88, no. 13, p. 137401, 03/14/ 2002.
- [164] G. Zatoryb, A. Podhorodecki, J. Misiewicz, J. Cardin, and F. Gourbilleau, "On the nature of the stretched exponential photoluminescence decay

- for silicon nanocrystals," *Nanoscale Research Letters*, journal article vol. 6, no. 1, p. 106, 2011.
- [165] J. Linnros, N. Lalic, A. Galeckas, and V. Grivickas, "Analysis of the stretched exponential photoluminescence decay from nanometer-sized silicon crystals in SiO₂," *Journal of Applied Physics*, vol. 86, no. 11, pp. 6128-6134, 1999.
- [166] M. L. Brongersma, A. Polman, K. S. Min, E. Boer, T. Tambo, and H. A. Atwater, "Tuning the emission wavelength of Si nanocrystals in SiO₂ by oxidation," *Applied Physics Letters*, vol. 72, no. 20, pp. 2577-2579, 1998.
- [167] G. Franzò, V. Vinciguerra, and F. Priolo, "The excitation mechanism of rare-earth ions in silicon nanocrystals," *Applied Physics A*, vol. 69, no. 1, pp. 3-12, 1999/07/01 1999.
- [168] V. Mangalam and K. Pita, "Effect of the interaction distance on 614 nm red emission from Eu³⁺ ions due to the energy transfer from ZnO-nc to Eu³⁺ ions," *Optical Materials Express*, vol. 8, no. 10, pp. 3115-3132, 2018/10/01 2018.
- [169] H. Benhebal *et al.*, "Photocatalytic degradation of phenol and benzoic acid using zinc oxide powders prepared by the sol–gel process," *Alexandria Engineering Journal*, vol. 52, no. 3, pp. 517-523, 2013/09/01/ 2013.
- [170] A. Layek, S. De, R. Thorat, and A. Chowdhury, "Spectrally Resolved Photoluminescence Imaging of ZnO Nanocrystals at Single-Particle Levels," *The Journal of Physical Chemistry Letters*, vol. 2, no. 11, pp. 1241-1247, 2011/06/02 2011.
- [171] M. Vafaei and M. S. Ghamsari, "Preparation and characterization of ZnO nanoparticles by a novel sol–gel route," *Materials Letters*, vol. 61, no. 14, pp. 3265-3268, 2007/06/01/ 2007.

- [172] T. Forster, "10th Spiers Memorial Lecture. Transfer mechanisms of electronic excitation," *Discussions of the Faraday Society*, 10.1039/DF9592700007 vol. 27, no. 0, pp. 7-17, 1959.
- [173] J. R. Lakowicz, *Principles of Fluorescence Spectroscopy*. Springer, Boston, MA, 2006.