

SPECTROSCOPY OF TRIVALENT NEODYMIUM IONS (Nd^{3+}) IN ZINC OXIDE (ZnO) THIN FILMS AND POWDERS

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DECLARATION

I, the undersigned, declare that this dissertation is a product of my original work carried under the guidance of Dr. M. Mujaji (Supervisor) and Prof. D. Wamwangi (Co-supervisor). Any work done by others previously has been referenced and acknowledged accordingly. This dissertation is hereby being submitted for a Master of Science in Physics degree at the University of the Witwatersrand, Johannesburg and has not been submitted before for any degree examination at any other University.

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ABSTRACT

Intrinsic defects with energy levels which lie within the wide band gap of ZnO play an important role in the excitation of incorporated trivalent rare-earth (RE^{3+}) ions, in $\text{ZnO}:\text{RE}^{3+}$. In the present study, low-temperature (10 K – 75 K) photoluminescence studies of trivalent neodymium (Nd^{3+}) ions doped into ZnO were conducted using argon-ion laser lines (457.9 nm, 476.5 nm, 488.0 nm and 514.5 nm) and a dye-laser tunable in the 570 nm – 640 nm region, as excitation sources. $\text{ZnO}:\text{Nd}^{3+}$ samples in the form of films and compressed powders were used, with Nd^{3+} concentration of 1.5mol% and 1mol%, respectively.

Nd^{3+} -doped ZnO films suitable for photoluminescence studies were deposited on quartz substrates by the radio-frequency magnetron sputtering method using 100 W power and a 30% O_2 :70%Ar chamber-gas ratio. Deposition times of 3 hours were used in order to achieve acceptable photoluminescence signal to noise levels and some of the films were annealed at 600 °C. For powder samples, the $\text{ZnO}-\text{Nd}_2\text{O}_3$ mixture was ground and compacted into pellets which were then sintered at 600 °C, 750 °C and 950 °C, in air. Some of the powder samples were co-doped with Nd^{3+} and lithium (Li^+) in the ratios 1:1, 1:5 and 1:10.

X-ray diffraction (XRD) peak positions confirmed the hexagonal wurtzite structure for both the films and the powder samples. Scanning electron microscopy (SEM) and energy dispersive spectroscopy (EDS) results revealed an even distribution of Nd^{3+} ions in the films. In the powder samples, the Nd^{3+} distribution was even only in samples sintered at 600 °C and 750 °C whilst in samples sintered at 950 °C, the Nd^{3+} ions are mainly situated at grain boundaries. The higher sintering temperature also encouraged grain growth.

Photoluminescence spectra of both films and powder samples showed a broad emission band spanning the 500 nm – 875 nm range. This emission arises from transitions between energy levels of the ZnO intrinsic defects, which include vacancies, interstitials and antisites. In $\text{ZnO}:\text{Nd}^{3+}$ powders, Nd^{3+} ions give rise to narrow and discrete absorption bands superposed on the broad emission band. The absorption bands are a result of the Nd^{3+} ions absorbing specific wavelength portions of the broadband radiation emitted by intrinsic defects. Coincidence of the defect transition energies and Nd^{3+} multiplet energy positions is testament to this. In addition, sharp Nd^{3+} emission transitions were observed in the 880 nm to 920 nm ($11\,364\text{ cm}^{-1}$ – $10\,670\text{ cm}^{-1}$) range for the films as well as for the $\text{Nd}^{3+}:\text{Li}^+$ co-doped powders sintered at 950 °C. This emission is attributed to the $^4\text{F}_{3/2} \rightarrow ^4\text{I}_{9/2}$ transitions of Nd^{3+} ions. Two different Nd^{3+} centres were identified in both films and powder samples. The Nd^{3+} centre present in annealed films is different from that in the unannealed films, showing a changed crystal-field environment for the Nd^{3+} ion. However, two different Nd^{3+} centres co-exist in $\text{ZnO}:\text{Nd}^{3+}:\text{Li}^+$ powder samples, with

distinctly different fluorescence life-times of 202 μ s and 380 μ s. Crystal-field energy levels of the D ($^2G_{7/2};^4G_{5/2}$), R ($^4F_{3/2}$) and Z ($^4I_{9/2}$) Nd^{3+} multiplets have been deduced for each of the centres and comparisons were made. The site-selective technique was key in the separation of the two centres.

The near-infrared Nd^{3+} emission studied in this work has potential applications in bio-imaging because biological tissues have maximum transmittance in the near-infrared region while the re-absorption characteristic can be applied on welding goggles to block the yellow-flame glow, for example. Additionally, doped ZnO pellets such as prepared and used for this study have potential use as cost-effective targets for thin-film deposition by the pulsed laser technique.

DEDICATION

To my beloved parents, lovely sister – Nyasha Christy and brother – Tatenda Channely; and to my High School Physics teacher – Mr. C. Chiguware.

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TABLE OF CONTENTS

Contents	Page
DECLARATION.....	i
ABSTRACT	ii
DEDICATION	iv
ACKNOWLEDGEMENTS	v
TABLE OF CONTENTS	vii
LIST OF FIGURES	ix
LIST OF TABLES	xvi
CHAPTER 1 INTRODUCTION	1
1.1. Motivation.....	1
1.2. Background.....	3
1.3. Problem statement.....	4
1.4. Study objectives	5
1.5. Structure of dissertation	6
CHAPTER 2 LITERATURE REVIEW	7
2.1. Introduction.....	7
2.2. Fundamental properties of ZnO	7
2.2.1. Crystal structure and lattice parameters.....	7
2.2.2. Band structure and optical properties	9
2.2.3. ZnO intrinsic defects emission	10
2.3. The Rare-earths (REs)	13
2.3.1. Neodymium	15
2.4. Rare-earth doping in ZnO	16
2.4.1. Rare-earth centres and crystal-field effects	17
2.4.2. Theoretical considerations for the dopant Nd ³⁺ ions	19
2.4.3. Direct and indirect excitation of Nd ³⁺ ions.....	20
2.5. Phonon modes in wurtzite ZnO	22
CHAPTER 3 EXPERIMENTAL TECHNIQUES.....	25
3.1. Introduction.....	25
3.2. Sample preparation	25
3.2.1. Thin-film deposition by RF magnetron sputtering.....	25
3.2.2. Preparation of powder samples.....	28
3.3. Characterization techniques	35

3.3.1.	X-ray Diffraction (XRD).....	35
3.3.2.	Scanning Electron Microscopy (SEM).....	37
3.3.3.	Energy-Dispersive X-ray Spectroscopy (EDS).....	39
3.4.	Photoluminescence (PL).....	40
3.4.1.	Emission and excitation spectral measurements	41
3.4.2.	Life-time measurements	44
CHAPTER 4	RESULTS AND DISCUSSION FOR ZnO:Nd ³⁺ FILMS	45
4.1.	Introduction.....	45
4.2.	Sample characterization.....	45
4.2.1.	Grazing incidence X-ray diffraction studies.....	46
4.2.2.	Scanning electron microscopy and energy dispersive X-ray spectroscopy studies..	48
4.3.	Photoluminescence (PL) studies with Ar ⁺ laser excitation.....	52
4.3.1.	Emission from ZnO intrinsic defects.....	56
4.4.	Photoluminescence (PL) studies of Nd ³⁺ ions in ZnO films with dye laser excitation.....	58
4.4.1.	Emission and excitation spectra of Nd ³⁺ ions in ZnO films	58
4.5.	Summary.....	65
CHAPTER 5	RESULTS AND DISCUSSION FOR ZnO AND ZnO:Nd ³⁺ POWDERS.....	67
5.1.	Introduction.....	67
5.2.	Sample characterization.....	67
5.2.1.	Powder X-ray diffraction studies.....	67
5.2.2.	Scanning electron microscopy and energy dispersive X-ray spectroscopy studies	71
5.3.	Photoluminescence (PL) studies with Ar ⁺ laser excitation.....	77
5.3.1.	Emission from ZnO intrinsic defects.....	77
5.3.2.	Absorption of intrinsic defect emission by Nd ³⁺ ions	83
5.3.3.	Impurity Fe ³⁺ emission in ZnO.....	87
5.4.	Photoluminescence (PL) studies of Nd ³⁺ ions with dye laser excitation	90
5.4.1.	Emission and excitation spectra of Nd ³⁺ ions in ZnO powders.....	90
5.4.2.	Phonon modes observed in the emission and excitation spectra	103
5.4.3.	Life-time studies	104
5.5.	Summary.....	105
CHAPTER 6	CONCLUSIONS AND SUGGESTIONS FOR FURTHER WORK	107
REFERENCES		110
PRESENTATIONS		117

LIST OF FIGURES

Figure 2.1 The hexagonal wurtzite structure of ZnO.	8
Figure 2.2 Band structure of wurtzite ZnO. ³⁶	9
Figure 2.3 Typical photoluminescence spectrum of ZnO. ³⁷	10
Figure 2.4 Schematic presentation of the defect energy levels in the ZnO band gap and the inter-defect transitions that yield green to infra-red emission.....	12
Figure 2.5 Transitions from some of the common impurities in ZnO. The transitions for copper and cobalt are inter-configurational whilst that for iron is intra-configurational.	13
Figure 2.6 Energy levels (multiplets) of free Nd ³⁺ ions that fall within the band gap of ZnO. The ^{2S+1} L _J notation used is explained in the text. The crystal-field splits each multiplet into J + 1/2 crystal-field levels.....	18
Figure 2.7 Typical room-temperature absorption (a) and emission (b) spectra for Nd ³⁺ ions. ⁵⁹	19
Figure 2.8 Crystal-field energy levels of the ground Z (⁴ I _{9/2}) and excited R (⁴ F _{3/2}) multiplets illustrating the observable transitions at 10 K and at 75 K for (a) ΔE ≤ 7 cm ⁻¹ and (b) ΔE ≅ 52 cm ⁻¹ . The double arrows identify both absorption (from Z ₁ and Z ₂) and emission (from R ₁ and R ₂).	20
Figure 2.9 Energy transfer mechanisms for excitation of Nd ³⁺ ions. (a) Emission transitions from some of the ZnO intrinsic defects (as in Figure 2.4) contributing to the Nd ³⁺ absorption in (b). (c) Direct excitation of Nd ³⁺ ions through use of resonant energy.....	21
Figure 2.10 (a) Brillouin zone of ZnO showing the high symmetry points ⁶² and the primitive unit cell (shaded section). (b) Phonon dispersion curves of ZnO along the high symmetry directions. Data obtained from INS measurements – ♦ ♦ °, Raman measurements – ◻ and <i>ab initio</i> calculations – solid lines. ⁶¹ r.l.u. – reciprocal lattice units.....	23
Figure 3.1 Illustration of the sputtering process. ⁶⁴	26
Figure 3.2 (a) Schematic of the RF sputtering system: 1 – substrate holder, 2 – substrate, 3 – target, 4 – magnet, and 5 – RF powered electrode. ⁶⁷ (b) Pictorial view of the RF sputtering system: (i) – pressure gauge, (ii) – gas inlet system, (iii) – pump system, (iv) – observation window, and (v) – RF power control.....	27
Figure 3.3 Schematic of processes involved in the preparation of a powder sample.....	28

Figure 3.4 Apparatus and sequence of steps used in preparing the pellet: (a) (i) – agate mortar and pestle loaded with starting powder materials, (b) dampening of fine ground powder, (c) preparation of die with (ii) the bottom paper cover in place, (d) mould loaded with powder and the top paper cover (i) showing and (ii) the base of the mould.	29
Figure 3.5 The Specac Manual Hydraulic Press, with the pellet moulding die in place. (a) the leadscrew, (b) the pressure release valve, (c) pump handle and (d) pressure/load gauge.	30
Figure 3.6 A ZnO pellet just after compaction (green body).	31
Figure 3.7 The competing phenomena during sintering and the effect(s) expected on resultant sintered bodies. ⁷³	32
Figure 3.8 (a) The schematic illustration of diffusion mechanisms for a two-particle system and (b) the three sintering stages showing changes in pore structure during sintering. ⁷⁴	33
Figure 3.9 The appearance of (a) undoped ZnO, (b) Nd ₂ O ₃ and (c) ZnO:Nd:Li pellets sintered at 950 °C. Each pellet prepared with 0.400 g of ZnO had the dimensions of 1 cm diameter and 0.1 cm thickness.	34
Figure 3.10 Diffraction of X-rays by a crystal. ⁷⁷	35
Figure 3.11 The theta-two theta (θ -2 θ) geometry of an X-ray diffractometer. ⁷⁷	37
Figure 3.12 (a) The basic building blocks of a scanning electron microscope. ⁷⁸ (b) Zeiss GeminiSEM system used for SEM sample characterization: (i) – microscope column, (ii) – detectors, and (iii) – controls and screens.....	38
Figure 3.13 The origin and information depth of secondary electrons (SE), backscattered electrons (BSE), Auger electrons (AE) and X-ray quanta (X) in the diffusion cloud of electron range R for normal incidence of the primary electrons (PE). ⁷⁹	39
Figure 3.14 Schematic of the setup for EDS detection. ⁷⁸	40
Figure 3.15 The schematic diagram of the PL system used in this study.....	41
Figure 3.16 (a) Pictorial view of the setup used for PL measurements. (i) – laser source, (ii) – laser console, (iii) – dye laser, (iv) – mirror, (v) – photo-cooler, (vi) – high voltage power supply, (vii) – optical chopper controller, (viii) – monochromator controller, (ix) – pre-amplifier, (x) – photon counter, (xi) – multi-channel analyzer and (b) (i) – monochromator, (ii) – He compressor, (iii) – cryostat, (iv) – sample temperature controller, (v) – mirror, (vi) – 90° prism, (vi) – lense, (vii) – high-pass filter.	42

Figure 4.1 XRD patterns for (i) undoped ZnO film (0% O ₂) annealed at 600 °C, (ii) ZnO:1.5mol%Nd ³⁺ film (30% O ₂) annealed at 600 °C and (iii) unannealed ZnO:1.5mol%Nd ³⁺ (30% O ₂) film. Planes corresponding to the peaks observed for ZnO sample are labelled. A copper X-ray source of wavelength 0.154 nm was used.	46
Figure 4.2 SEM images (i) and the corresponding line scans (ii) for Nd ³⁺ doped and undoped ZnO films. (a) unannealed ZnO:1.5mol%Nd ³⁺ film, (b) ZnO:1.5mol%Nd ³⁺ film annealed at 600 °C and (c) undoped ZnO film annealed at 600 °C.....	49
Figure 4.3 Cross-sectional view of (i) blank quartz substrate coated with gold-palladium, (ii) unannealed ZnO:1.5mol%Nd ³⁺ film, (iii) ZnO:1.5mol%Nd ³⁺ film annealed at 600 °C and (iv) higher magnification (30 000x) of the unannealed film in (ii).	50
Figure 4.4 EDS spectra of (i) unannealed ZnO:1.5mol%Nd ³⁺ film, (ii) ZnO:1.5mol%Nd ³⁺ film annealed at 600 °C and (iii) ZnO film annealed at 600 °C. These spectra correspond to SEM images in Figure 4.2.	51
Figure 4.5 Emission spectra recorded at 10 K for unannealed ZnO:1.5mol%Nd ³⁺ films deposited for 3 hours, using 100 W power and varying O ₂ partial pressure. Spectra for a blank quartz substrate and an undoped ZnO film are included for reference. The excitation wavelength was 457.9 nm.	54
Figure 4.6 Emission spectra recorded at 10 K for ZnO and ZnO:1.5mol%Nd ³⁺ films, unannealed as well as annealed at 600 °C. The 457.9 nm excitation line was used.....	55
Figure 4.7 Emission spectra recorded at 10 K for ZnO:1.5mol%Nd ³⁺ films: (a) unannealed and (b) annealed at 600 °C. Four Ar ⁺ laser wavelengths were used for excitation, as shown.	56
Figure 4.8 Emission spectrum recorded at 10 K for the ZnO:1.5mol%Nd ³⁺ film annealed at 600 °C, excited with the 457.9 nm wavelength. Deconvolution assumes Gaussian peak for each individual peak. The Nd ³⁺ emission is excluded from the fit and will be discussed separately in Section 4.4.1.	57
Figure 4.9 Emission spectra recorded at 10 K for unannealed and annealed ZnO:1.5mol%Nd ³⁺ films depicting Nd ³⁺ emission obtained with (a) indirect excitation at 457.9 nm (Ar ⁺ laser) and (b) direct excitation at 599.100 nm and 607.900 nm wavelengths (dye laser).....	59
Figure 4.10 Emission spectra recorded at 10 K – 75 K for (a) centre A in ZnO:1.5mol%Nd ³⁺ films annealed at 600 °C, using the 599.100 nm excitation wavelength and (b) centre B in unannealed ZnO:1.5mol%Nd ³⁺ films, using the 607.900 nm excitation wavelength. Electronic transitions observed at 10 K and at 75 K are labelled R ₁ → Z _i and R ₂ → Z _i , (i = 1, 2, 3) in (i) and (iv), respectively. Scales on the right are for the magnified spectra.	61

Figure 4.11 Excitation spectra recorded at 10 K and 50 K for (a) centre A in ZnO:1.5mol%Nd³⁺ films annealed at 600 °C, while monitoring the R₁ → Z₂ transition at 895.608 nm and (b) centre B in unannealed ZnO:1.5mol%Nd³⁺ films, while monitoring R₁ → Z₁ transition at 897.929 nm. Transitions from the Z₁ level to the D multiplet levels (D₁ to D₇) are labelled in the 10 K spectra while those from the Z₂ level of centre B are identified in the 50 K spectrum. 63

Figure 4.12 Energy level schemes deduced from transitions observed in the 10 K – 50 K excitation spectra and the 10 K – 75 K emission spectra for ZnO:1.5mol%Nd³⁺. (a) centre A in films annealed at 600 °C and (b) centre B in unannealed films. 64

Figure 5.1 XRD patterns for Nd³⁺ doped and Nd³⁺:Li⁺ co-doped ZnO powders. Patterns are labelled by the sample constituents and sintering temperature; for example, ZnO:1Nd-600 stands for ZnO:1mol%Nd³⁺ sintered at 600 °C. Unsintered samples (green body) are labelled by the constituents only, e.g. ZnO. The ZnO planes are as indicated. Peaks labelled with asterisks (*) are from Fe³⁺ present as an impurity. Cobalt radiation source of wavelength 0.179 nm was used. 68

Figure 5.2 XRD patterns for Nd³⁺ doped and Nd³⁺:Li⁺ co-doped ZnO samples sintered at 950 °C. Patterns are labelled by the sample constituents and sintering temperature; for example, ZnO:1Nd:1Li-950 stands for ZnO:1mol%Nd³⁺:1mol%Li⁺ sintered at 950 °C. Planes corresponding to the peaks observed for Nd₂O₃ are labelled in (vii) while peaks for the ZnO based samples are as in Figure 5.1. Asteriks (*) indicate peaks associated with presence of iron. 70

Figure 5.3 SEM images of Nd³⁺ doped and Nd³⁺:Li⁺ co-doped ZnO powder samples. Images (i), (iii) and (v) are for unsintered samples (green body) while images (ii), (iv) and (vi) are for samples sintered at 600 °C.....72

Figure 5.4 SEM images of Nd³⁺ doped and Nd³⁺:Li⁺ co-doped ZnO samples sintered at 950 °C. A ZnO:10mol%Li⁺ sample, also sintered at 950 °C, is included for reference.....73

Figure 5.5 Line scans for (a) ZnO:1mol%Nd³⁺ samples sintered at (i) 600 °C and (ii) 950 °C and (b) (i) ZnO:1mol%Nd³⁺:10mol%Li⁺ and (ii) ZnO:10mol%Li⁺ samples sintered at 950 °C. Maps for the line scans in (b) (i) and (ii) are shown on the SEM images in (b) (iii) and (iv), respectively. 74

Figure 5.6 EDS spectra for Nd³⁺ doped and Nd³⁺:Li⁺ co-doped ZnO powder samples. Images (i), (iii) and (v) are for unsintered samples (green body) while images (ii), (iv) and (vi) are for samples sintered at 600 °C. The spectra correspond to the cumulative scans of SEM images in Figure 5.3.....75

Figure 5.7 EDS spectra for Nd^{3+} doped and $\text{Nd}^{3+}:\text{Li}^{+}$ co-doped ZnO powder samples sintered at 950 °C. A ZnO:10mol% Li^{+} sample, also sintered at 950 °C, is included for reference. The spectra correspond to the SEM images in Figure 5.4.	76
Figure 5.8 Emission spectra recorded at 10 K with the 457.9 nm excitation line, showing the effect of doping ZnO with 1mol% Nd^{3+} and sintering the samples at different temperatures.	78
Figure 5.9 Deconvolution of the broad emission band from ZnO intrinsic defects in the ZnO:1mol% Nd^{3+} sample sintered at 600 °C, as measured at 10 K using the 457.9 nm wavelength for excitation. Gaussian curve profiles were assumed for the individual peaks and the absorption bands were not included in the fit.....	80
Figure 5.10 Emission spectra of ZnO:1mol% Nd^{3+} samples measured at 10 K with different excitation wavelengths to show the effect of varying excitation wavelengths on the emission, for samples sintered at (a) 600 °C and (b) 950 °C.....	81
Figure 5.11 Emission spectra measured at 10 K with 457.9 nm excitation, showing the effect of co-doping ZnO powders with Nd^{3+} and Li^{+} ions and sintering at (a) 600 °C and (b) 950 °C. Inserts in (b) show (i) regions with Nd^{3+} absorption at lower wavelengths and (ii) Nd^{3+} emission observed in the ZnO:1mol% Nd :10mol% Li sample. Spectra for ZnO and ZnO:10mol% Li are included for reference.....	82
Figure 5.12 The effect of varying the amount of Li^{+} doped into ZnO:1mol% $\text{Nd}^{3+}:\text{Li}^{+}$ samples sintered at 950 °C on the intensity of Nd^{3+} emission. Spectra recorded with 457.9 nm wavelength excitation, at 10 K. Insert shows the Li^{+} concentration dependence for the transition at 893.890 nm.	83
Figure 5.13 Absorption features observed at 10 K in Nd^{3+} -doped and $\text{Nd}^{3+}:\text{Li}^{+}$ co-doped ZnO powder samples sintered at 600 and 950 °C. The spectra were recorded with the 457.9 nm excitation wavelength except for Nd600-dl in (c) for which a dye laser was used. Φ and Θ label peaks observed for samples sintered at 600 °C only and 950 °C only, respectively while peaks labelled Ω were present for both sintering temperatures.....	85
Figure 5.14 Emission spectrum of Fe^{3+} ions in ZnO measured with 457.9 nm excitation at 10 K. The Nd-absorption band has been discussed earlier in Section 5.3.2. The deconvolution of the underlying broadband is reproduced from Figure 5.9.	87
Figure 5.15 Emission spectra for ZnO:1mol% Nd^{3+} :10mol% Li^{+} sample sintered at 950 °C recorded at 10 K with (a) indirect excitation at 457.9 nm and direct excitation at (b) 606.400 nm and (c) 602.100 nm, respectively. Spectra (b) and (c) have been magnified by 30x and 25x, respectively.....	91

Figure 5.16 Emission spectra recorded at 10 K for the two different Nd^{3+} centres in the $\text{ZnO:1mol}\text{Nd}^{3+}\text{:10mol}\%\text{Li}^+$ sample sintered at 950 °C excited with a dye laser set at (a) 606.400 nm and (b) 602.100 nm. Electronic transitions are labelled $R_1 \rightarrow Z_i$ ($i = 1$ to 5) and vibronic transitions are labelled v_j and vb_j ($j = 1, 2, \dots$). 93

Figure 5.17 Emission spectra of centre A in $\text{ZnO:1mol}\text{Nd}^{3+}\text{:10mol}\%\text{Li}^+$ samples sintered at 950 °C. PL spectra collected at different temperatures using the excitation wavelength 606.400 nm. Transitions from the R_1 and R_2 levels of the R multiplet to the Z multiplet levels (Z_1 to Z_5) are labelled in the 10 K and 75 K spectra, respectively. Vibronic transitions are labelled v_j ($j = 2 - 6$) in (i) and v_0 in (iii). β is from an impurity in Nd_2O_3 while C identifies cluster centre transitions. 95

Figure 5.18 Emission spectra of centre B in $\text{ZnO:1mol}\text{Nd}^{3+}\text{:10mol}\%\text{Li}^+$ samples sintered at 950 °C measured at different sample temperatures using the excitation wavelength 602.100 nm. Transitions from the R_1 and R_2 levels of the R multiplet to the Z multiplet levels (Z_1 to Z_5) are labelled in the 10 K and 75 K spectra, respectively. vb_1 in (i) is a vibronic transition. Labels A and C identify breakthrough emission from centre A and the cluster centre(s), respectively....96

Figure 5.19 Shift of the $R_1 \rightarrow Z_1$ peak with temperature for (a) centre A and (b) centre B in $\text{ZnO:1mol}\text{Nd}^{3+}\text{:10mol}\%\text{Li}^+$ samples sintered at 950 °C.....97

Figure 5.20 Changes in linewidths (FWHM) of the $R_1 \rightarrow Z_1$ and $R_1 \rightarrow Z_2$ peaks with temperature for (a) centre A and (b) centre B in $\text{ZnO:1mol}\text{Nd}^{3+}\text{:10mol}\%\text{Li}^+$ samples annealed at 950 °C. .98

Figure 5.21 Excitation spectra recorded at 10 K for (a) centre A and (b) centre B in $\text{ZnO:1mol}\text{Nd}^{3+}\text{:10mol}\%\text{Li}^+$ samples. The monitored wavelengths are 893.890 nm and 899.310 nm for centre A and centre B, respectively. Electronic transitions are labelled $Z_1 \rightarrow D_i$ ($i = 1$ to 7) and vibronic transitions are identified as y_j ($j = 1, 2, 3$). C identifies breakthrough emission from the cluster centre(s).....99

Figure 5.22 Excitation spectra for centre A in $\text{ZnO:1mol}\text{Nd}^{3+}\text{:10mol}\%\text{Li}^+$ samples sintered at 950 °C measured at different sample temperatures (10 K – 75 K) while monitoring the $R_1 \rightarrow Z_1$ transition at 893.890 nm. Transitions from Z_1 and the higher Z levels (Z_2, Z_3) to the D levels (D_1 to D_7) are identified in the 10 K and 75 K spectra, respectively. Vibronic transitions are labelled w_i ($i = 1$ to 6) in (iii) and C identifies the cluster centre transitions. 100

Figure 5.23 Excitation spectra for centre B in $\text{ZnO:1mol}\text{Nd}^{3+}\text{:10mol}\%\text{Li}^+$ samples sintered at 950 °C measured at different sample temperatures (10 K – 75 K) while monitoring the $R_1 \rightarrow Z_1$ transition at 899.310 nm. Transitions from Z_1 and the higher Z levels (Z_2, Z_3) to the D levels (D_1 to D_7) are identified in the 10 K and 75 K spectra, respectively. Vibronic transitions are labelled y_i ($i = 1, 2, 3$) in (i) and C identifies the cluster centre transitions. 101

Figure 5.24 Energy level schemes deduced from transitions in the excitation spectra and emission spectra recorded at 10 K – 75 K temperatures for (a) centre A and (b) centre B, in ZnO:1mol%Nd³⁺:10mol%Li⁺ samples sintered at 950 °C. 102

Figure 5.25 Life-time curves recorded at 10 K for the ⁴F_{3/2} multiplet of (a) centre A with 606.400 nm excitation and (b) centre B with 602.100 nm excitation for Nd³⁺ ions in ZnO:1mol%Nd³⁺:10mol%Li⁺ samples sintered at 950 °C. 105

LIST OF TABLES

Table 2.1 Rare-earth elements and ions with their respective electronic configurations.	15
Table 2.2 Phonon modes present in wurtzite ZnO.....	23
Table 3.1 Information on all samples prepared in this study. RT under sintering temperature identifies green body pellets used as references.....	34
Table 3.2 Relative densities of the as-prepared (green body) and sintered samples.	35
Table 4.1 Peak positions of the (002) plane and the calculated crystallite sizes (S) and lattice parameters.....	47
Table 4.2 Elemental compositions as detected by energy dispersive X-ray spectroscopy.....	52
Table 4.3 Peak positions of the deconvoluted broad-band emission observed in ZnO:1.5mol%Nd ³⁺ films annealed in air at 600 °C and their corresponding defect transitions. References used to determine the defect levels shown in Figure 2.4 are as indicated.	58
Table 4.4 Peak positions and electronic transitions observed for centre A and centre B in ZnO:Nd ³⁺ films at 10 K and at 75 K.	62
Table 4.5 Energy levels obtained for the Z (⁴ I _{9/2}), R (⁴ F _{3/2}) and D (² G _{7/2} ; ⁴ G _{5/2}) multiplets of Nd ³⁺ ions in the centre A and centre B configurations in ZnO films.....	65
Table 5.1 Peak positions of the (100) plane and the calculated crystallite sizes (S) and lattice parameters. A Nd ₂ O ₃ sample is included for reference.	69
Table 5.2 Elemental compositions as detected by energy dispersive X-ray spectroscopy.....	77
Table 5.3 Peak positions of the deconvoluted broad-band emission observed in ZnO:1mol%Nd ³⁺ powder samples sintered at 600 °C and their corresponding defect transitions. References used to determine the defect levels shown in Figure 2.4 are as indicated.	81
Table 5.4 Excited multiplet and absorption peak positions in Nd ³⁺ -doped and Nd ³⁺ :Li ⁺ co-doped ZnO powder samples sintered at 600 °C and 950 °C. Ω labels transitions present for all samples whilst Φ and Θ label transitions present for samples sintered at 600 °C only and 950 °C only, respectively.....	86
Table 5.5 Peak positions of Fe ³⁺ emission in ZnO and the associated phonon modes. av = average of and prefix * in the first column indicates shoulder peaks which could not be separately indicated in Figure 5.14. References used to identify the phonon modes are in the last column.	89

Table 5.6 Peak positions and electronic transitions assigned to each peak observed for centre A and centre B in the ZnO:1mol%Nd ³⁺ :10mol%Li ⁺ powder sample, at 10 K and at 75 K.....	94
Table 5.7 Energy levels of the Z (⁴ I _{9/2}) and R (⁴ F _{3/2}) and D (² G _{7/2} ; ⁴ G _{5/2}) multiplets of the two Nd ³⁺ centres obtained from the energy level schemes in Figure 5.24.....	103
Table 5.8 Phonon modes from emission and excitation spectra for centre A and centre B in Figures 5.17, 5.18, 5.22 and 5.23.	104

CHAPTER 1

INTRODUCTION

1.1. Motivation

Rare-earth doped materials have received widespread research attention due to their impact in several applications, including phosphors^{1,2}, solar cells^{2,3} and medical imaging⁴. Among the materials adopted as hosts for the rare-earth ions are direct wide band gap semiconductors (WBGSCs) such as silicon carbide (SiC), gallium nitride (GaN) and zinc oxide (ZnO). Of these, ZnO is the most utilized and a comprehensive review of optical studies conducted on ZnO doped with various rare-earth ions is reported by Daksh and Agrawal.⁵ Preference of ZnO to other WBGSCs is based on its merits which include:

- (i) high transparency in the visible and near-infrared (NIR) regions of the electromagnetic spectrum⁶ – this property is useful in applications such as making transparent ohmic contacts and as a host for rare-earth ions that show near-infrared luminescence for example Nd³⁺ ions, which can be used for medical imaging;
- (ii) large exciton binding energy of 60 meV at 300 K which is relatively high compared to its thermal energy of 25 meV and to the exciton binding energy of GaN (25 meV) – this makes ZnO a suitable candidate for optoelectronic applications, mostly in the blue and ultraviolet regions of the spectrum, such as in diodes and optically pumped lasers⁷;
- (iii) availability in abundance and non-toxicity – this implies that bulk ZnO can be produced cost-effectively and is environment friendly;
- (iv) high radiation hardness and a high melting temperature of 2 248 K – useful in manufacturing devices which can operate in harsh and hot-temperature environments as those needed for gas sensing or in space and high altitudes.⁸

The wide band gap of ZnO (with energy of 3.44 eV at 4 K) is useful for doping with rare-earth ions. Several energy level states of rare-earth ions (as shown on the Dieke diagram⁹) lie within the band gap of ZnO. This provides ways of exciting the different levels of the rare-earth ions by exciting the intrinsic defects of ZnO first and then relying on energy transfer to the rare-earth ion. ZnO, in the wurtzite structure, is considered a good host for rare-earth ions although there are incorporation challenges due to differences in ionic radii of the Zn²⁺ ion (74.0 pm) and the rare-earth ions (84.8 pm – 103.4 pm).¹⁰ In the literature¹¹, however, it is reported that the rare-earth ions are located at the grain boundaries of the ZnO lattice and hence allow for interaction between the host and the rare-earth dopant.

Rare-earth ions are mainly considered as dopants due to their relatively intense atomic-like luminescent characteristics which arise from $4f$ - $4f$ electronic transitions.^{9,10} These $4f$ electrons are electrically shielded by the fully-occupied $5s^2$ and $5p^6$ shells of the rare-earth ion. The optical emission and absorption spectra of the rare-earth ions comprise sharp transitions (known as spectral lines) and are largely independent of the host matrix, as a result of shielding. However, despite this independence, the intra- $4f$ -shell transitions are sensitive to the local symmetry of the host matrix, hence different optically-active centres have different site symmetries. By comparison of the emission spectra from the different centres of the host or of the dopant, optical signatures corresponding to each centre can be identified.⁹

ZnO and rare-earth doped ZnO materials are fabricated in different forms and dimensions.^{12,13} The one-dimensional (1-D) and two-dimensional (2-D) forms of the materials such as nanorods and nanowires (1-D), thin films (2-D) and powders (3D) have received extensive attention in recent years, compared to bulk structures.¹³ These are less expensive, easy to fabricate, reduced in size, and they have novel electrical, mechanical, chemical and optical properties compared to most three dimensional (3-D) structures.^{13,14} For example, the effective ability of 1-D materials to absorb, scatter and emit light has been useful in applications such as in solar cells and lasers as well as in biomedical detection and sensing.¹⁵ On the other hand, the high surface to volume ratio of the 2-D materials makes them efficient in sensing gases and chemicals by providing a large specific surface area for the adsorption of molecules.¹⁴ The physical properties of these materials are dependent on the types of impurities and defects introduced into them whilst the structural, morphological and optical properties depend on the surface area and surface energy changes. Consequently, to fully utilize the films and powders in different applications, their structural, morphological and luminescence properties need to be fully documented. These properties are influenced by a number of factors which include the preparation techniques and conditions, type of intentional impurities added to the ZnO material and any post-preparation treatments. For example, the photoluminescence properties of unannealed and annealed films are different.¹⁶ Also, the band gap of ZnO varies when doped with transitional metals.¹⁷ As such, there should be systematic and detailed investigations on how these parameters affect the properties of the ZnO-based materials.

In this study, visible-region radiation (457.9 nm – 514.5 nm and 590 nm – 640 nm) is used to excite undoped as well as neodymium doped ZnO films and powders. The films were deposited by radio-frequency magnetron sputtering while powders were sintered. Effects of factors such as parameters adopted for sample preparation, heat treatment and sample temperature as well as the wavelength of the incident radiation on the emission were investigated.

1.2. Background

ZnO is a wide band gap material with band-gap energy of 3.37 eV at room temperature and 3.44 eV at 4 K.⁶ Within its band gap lies the intrinsic (native) defects states which are positioned at distinct levels. The intrinsic defects are imperfections within the lattice and these include vacancies (V_{Zn} and V_{O}), interstitials (Zn_i and O_i) and antisites (Zn_{O} and O_{Zn}) of the constituent zinc and oxygen ions.¹⁸ Interstitials are extra atoms occupying positions which are not usually occupied in the lattice while vacancies arise from missing atoms at regular lattice positions and antisites refer to oxygen atoms occupying the positions of Zn atoms, and vice versa. Upon excitation, the defects emit the energy radiatively in the ultraviolet, visible or near-infrared regions of the electromagnetic spectrum. It is worth noting that these emissions are not characteristic of the excitation radiation or its source, instead they give information about the excited material and its constituents. Because of the wide variety of intrinsic defects in ZnO, the corresponding emission tends to span a wide spectral range (blue to infrared), hence the name broadband emission.

The intentional doping of ZnO with impurities such as transition metals, alkali ions or rare-earth ions gives rise to extrinsic defects which introduce new levels within the band gap of ZnO. These levels are at different energy positions depending on the chosen impurity. Sometimes the impurities exist naturally in the ZnO material and the common ones include iron, copper and cobalt.¹⁹ The extrinsic defects energy levels in the band gap can be excited indirectly or directly. Indirect excitation involves exciting the intrinsic defects of the host and relying on energy transfer to the extrinsic defects which then becomes excited. There are two ways in which such energy transfer can occur. One option is for the extrinsic defect to absorb specific wavelengths (energies) from the radiative emission of the excited intrinsic defect. Alternatively, the excited ZnO intrinsic defects might not emit the energy radiatively. Instead, they will undergo non-radiative relaxation to lower-lying defect states by giving off some energy which is then captured by the extrinsic defects. In either case, the extrinsic defects get excited and can then emit the energy radiatively. The direct excitation process involves using energy, from an external source, which matches the multiplet or defect levels of the extrinsic defects for excitation. Upon excitation of the specific levels, emission then originates from the same excited level or from lower energy levels after some non-radiative relaxations. This results in signature emission due to the extrinsic impurity, in addition to the broadband emission arising from the ZnO intrinsic defects. Such signatures are used to investigate the effect of varying doping parameters such as concentration, the type of impurity and even the types of optical centers present in the prepared samples. This indicates that the wide band gap nature of ZnO and the inherent intrinsic defects play an important role in the excitation of extrinsic defects through energy transfer mechanisms.

Also, the wide band gap exposes more levels, of the rare-earth ions for example, for more efficient and possibly multi-channel energy transfer from intrinsic defects.

1.3. Problem statement

When rare-earth ions are doped into ZnO they improve its luminescence by either enhancing the intrinsic defects emission or the rare-earth's characteristic emission or absorption which is superposed on the broad extrinsic-defects related emission band in the UV-VIS-NIR regions of the electromagnetic spectrum.^{5,16,20,21} Emission and absorption signatures from rare-earth ions including Pr^{3+} ⁵, Nd^{3+} ^{21–26}, Sm^{3+} ^{5,27}, Eu^{3+} ^{2,16,25}, Gd^{3+} ^{5,28}, Tb^{3+} ^{16,21}, Dy^{3+} ^{21,25}, Ho^{3+} ^{5,23}, Er^{3+} ^{2,20,21}, Tm^{3+} ^{21,29} and Yb^{3+} ^{21,30} in the ZnO lattice have been reported. The reported studies were conducted on various forms of the material including films²² and powders^{21,24}, at temperatures ranging from room temperature down to 4.2 K,^{2,5,16,21,22,29} using UV^{2,20–24} and visible^{16,21,22,24} excitation wavelengths. The resulting rare-earth related emission or absorption was sharp and discrete due to the $4f$ - $4f$ intra-shell transitions of the trivalent rare-earth (RE^{3+}) ions, as discussed in Section 1.1.

In the literature, recent spectroscopic studies of ZnO:Nd^{3+} include room temperature photoluminescence measurements by Balestrieri *et al.*²² The 1.6mol% Nd^{3+} doped ZnO films used in their studies were prepared by the reactive sputtering technique and both UV and visible radiations were used for excitation. In the present study, ZnO films doped with 1.5mol% Nd^{3+} were deposited by the magnetron sputtering technique and the photoluminescence measurements were conducted at low temperatures (10 K – 75 K), using visible-region laser radiation for excitation. Use of a tunable dye laser enabled determination of the distinct Nd^{3+} sites in ZnO films and their crystal-field energy levels, thereby adding to the information available in the literature.

Most of the reported studies of Nd^{3+} -doped ZnO powders, are for chemically synthesized samples with 0.8mol%, 1.0mol% and 2.8mol% Nd^{3+} dopant concentrations.^{21,23–25} Photoluminescence measurements on these samples were conducted at room temperatures using UV radiation for excitation. In the work presented here, the aim is to utilize the sintering technique to synthesize 1mol% Nd^{3+} -doped ZnO samples. The manual grinding, pressing and sintering provide a cost-effective method for preparing the samples. Compacted powder samples were used for the low temperature (10 K – 75 K) photoluminescence measurements presented in this work. Site-selective studies enabled determination and characterization of the Nd^{3+} centres in powder samples.

When films are prepared by the sputtering technique, a dense sputter target is required and this is usually a commercial target of ZnO doped with a fixed amount (concentration) of

rare-earth dopants. Such targets are prepared according to the customer's specifications, rather than off the shelf, and are therefore available at relatively expensive costs. For this reason, it is difficult, financially, to purchase several targets with different dopant concentrations in order to deposit the range of films required for research purposes. It is for this reason that dense and less expensive targets, made from the raw powder materials by using appropriate compaction and heat treatment must be considered for depositing thin films for research purposes. With these locally-made targets there is full control of variables such as dopant type and dopant concentrations for depositing suitable films. Since the preparation conditions also affect the optical outcomes of the prepared powder materials, variations in the preparation conditions for the targets will provide different targets for different optical purposes. These potential targets, if made in proper dimensions and densities, can be used for preparing thin films by pulsed laser deposition (PLD). Thus, in addition to the important spectroscopic contribution, the other primary aim of this study is to establish a working method of preparing these potentially cost-effective targets for thin film deposition. Besides their potential application as targets for thin-film deposition, doped powder samples have proved to be very useful matrices for studies of the behavior of Nd^{3+} ions doped into them. This study therefore entails optical spectroscopic studies of Nd^{3+} ions doped into ZnO films as well as powders, at low temperatures of 10 K to 75 K. Nd^{3+} emission, which is mostly observed in the near-infrared region, has applications in the medical imaging field as well as laser sources.^{4,31} On the other hand, if used in coatings of welding goggles, Nd^{3+} absorbs the yellow glow which is harmful to the eyes.³²

1.4. Study objectives

The main objectives of this research are to prepare films and powder samples of Nd^{3+} doped ZnO suitable for optical spectroscopic studies, and to carry out photoluminescence studies at low temperatures (10 K – 75 K) using visible laser radiation for excitation. In order to achieve this, the study is split into two parts i.e. firstly for the films and then for the powders. As such, the main objectives of the study will be outlined separately. For the films, the objectives are as follows:

- ❖ To determine suitable conditions (power, duration for deposition and deposition ambient gases) for depositing ZnO:Nd^{3+} films of good quality and thickness suitable for photoluminescence studies.
- ❖ To identify transitions responsible for the broad emission band associated with intrinsic defects and consider mechanisms of energy transfer to the extrinsic (Nd^{3+}) defects.
- ❖ To examine the effect of post-preparation annealing of the films on the emission

characteristics.

- ❖ To use both the argon ion laser and the dye laser as excitation sources to investigate the spectroscopic behaviour of Nd^{3+} ions doped into ZnO films and then deduce energy level schemes relating to the emissions.

The main objectives for the powders are:

- To establish a working procedure for preparing doped powder samples from raw materials by using a hydraulic press and the sintering technique. This is focused on producing good-quality samples which give significant-intensity emission, for both the host material and the Nd^{3+} ions.
- To compare the emission due to ZnO intrinsic defects in powders and films.
- To investigate the effect of varying the sintering temperature on the distribution of defects present and the resulting photoluminescence.
- To investigate the effect of co-doping Nd^{3+} ions and Li^{+} ions on the emission from both the ZnO intrinsic defects and the extrinsic (Nd^{3+}) defects.
- To investigate the spectroscopic properties of Nd^{3+} ions doped into ZnO powders using both the argon ion laser and the dye laser as excitation sources and then deduce energy level schemes relating to the emission.

For both types of samples, structural and morphological characterization is conducted using X-ray diffraction, scanning electron microscopy and energy dispersive X-ray spectroscopy techniques, in order to assess the effects of the various sample preparation conditions on the sample quality.

1.5. Structure of dissertation

This dissertation is comprised of six chapters. The introduction (Chapter 1) contains motivation and background to the research conducted in this study as well as the specific aims. Chapter 2 contains the literature review, mainly of the existing studies of ZnO, the properties of rare-earth ions and ZnO doped with rare-earth ions while Chapter 3 presents the experimental techniques used. Results of the structural, morphological and the spectroscopic studies conducted on film samples are presented in Chapter 4 while those for powder samples are in Chapter 5. Finally, conclusions from this study and suggestions for further work are given in Chapter 6.

CHAPTER 2

LITERATURE REVIEW

2.1. Introduction

In the early nineteenth century (1810), ZnO was discovered as a red oxide of zinc by Bruce in Franklin city in New Jersey, USA.³³ Today, this semiconducting material exists naturally as the mineral zincite formed by zinc and oxygen and can be found in many places in the world including USA, Italy, Spain and Namibia.³³ In addition, zinc and oxygen are available in abundance in the world, hence reduced costs of bulk ZnO production on large scales.³⁴ Zinc oxide possesses several outstanding properties including those outlined in Chapter 1, hence it is regarded as a potential candidate for future applications in semiconductor nanotechnology. Since most of the optical advantages of ZnO utilize its fundamental properties, some of the properties which are linked to its optical characteristics will be briefly discussed in Section 2.2. The discussion on how ZnO luminescence properties can be improved by the intentional addition of impurities – doping, is the subject matter of Section 2.3. Attention will be given to trivalent rare-earth ions, and to Nd^{3+} ions in particular as a dopant in ZnO. The vibrational properties of ZnO are also discussed in Section 2.5.

2.2. Fundamental properties of ZnO

It is important to appreciate that as sizes of materials are reduced, some of their physical properties may change, relative to those of the bulk materials. For example, when ZnO and related materials are produced in small dimensions such as nanowires, films or nanopowders, they exhibit slightly different optical properties including changed emission characteristics and increased band gap energies. It is worthy, therefore, to understand the fundamental properties for each ZnO material intended for use in optical applications, to cater for any changes that may be brought about by changes in sizes of the material. Also, understanding of the physical properties of ZnO is necessary especially when considering designing materials that can operate under specific conditions such as at high altitudes where high radiation hardness is required. Some of the fundamental properties of ZnO will be discussed in the following sub-sections.

2.2.1. Crystal structure and lattice parameters

ZnO is one of the group II-VI semiconductors with substantial ionic character, that is, its ionicity is borderline between ionic and covalent semiconductors. The ionic radius of Zn^{2+} is 74.0 pm whilst that for O^{2-} is 140.0 pm.²⁰ ZnO crystallizes in three forms, which are wurtzite (hexagonal), zinc blende (cubic) and rock salt. Zinc blende is only stable if grown on cubic structures while the rock salt stabilizes only at high pressures of about 10 GPa.⁶ However, at

ambient conditions, the wurtzite structure is the most thermodynamically-stable phase and is of interest in this study. The unit cell of the hexagonal ZnO structure is depicted in Figure 2.1 with the polar hexagonal axis parallel to the z-axis as shown. Labels a, b and c in Figure 2.1 are the

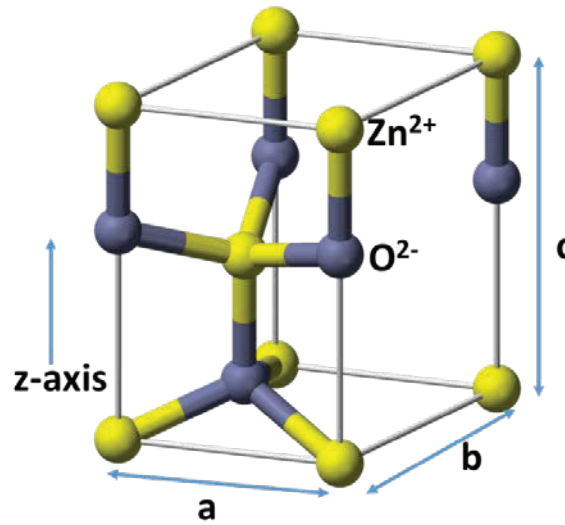


Figure 2.1 The hexagonal wurtzite structure of ZnO.

dimensions of the cell. Sides a and b have equal lengths and lie in the x-y plane with an angular separation of 120° , while c is along the z-axis. The hexagonal wurtzite structure is characterized by lattice parameters $a = b$ which vary between 0.32475 nm and 0.32501 nm while lattice parameter c varies between 0.52042 nm and 0.52075 nm.⁶ According to Morkoç and Ozgür⁶, in real ZnO crystals there is a deviation from atom arrangements in the ideal wurtzite structure and this is observed by changes in the ratios c/a . Several factors contribute to such variations in the lattice parameters of semiconductors such as ZnO. These include (i) strain (external or internal) introduced by impurities, and (ii) concentration or amount of defects and impurities and differences in their ionic radii relative to the radii of the substituted ions of the matrix.⁶ In addition, intrinsic point defects such as oxygen vacancies and zinc antisites may also increase the lattice constants. The lattice parameters of crystalline materials such as ZnO are measured by the X-ray diffraction (XRD) technique discussed in Chapter 3.

The hexagonal wurtzite ZnO structure belongs to the $6mm$ point group and the C_{6v}^{46} space group.⁶ In the configuration presented in Figure 2.1, each zinc ion is tetrahedrally surrounded by four oxygen ions and vice versa. Also, there are alternating planes of tetrahedrally coordinated Zn^{2+} ions and O^{2-} ions which are stacked along the z-axis, making the entire structure lack central symmetry. The polar symmetry along the z-axis is responsible for characteristics of ZnO such as piezoelectricity and is a contributing factor in crystal growth and defect formation.⁷

2.2.2. Band structure and optical properties

The band structure of hexagonal wurtzite ZnO, as shown in Figure 2.2, is important in explaining its properties which include the optical and electrical behaviour. ZnO is classified as a direct wide bandgap semiconductor because the highest point in its valence band (VB) and the lowest point in its conduction band (CB) occur at the same wavevector position in the Brillouin zone (the Γ point in Figure 2.2) where the momentum value, k , is zero. The band gap of ZnO, and all other wide band gap semiconductors, changes with temperature.⁶ For example, a decrease in temperature results in shrinkage of the crystal lattice which strengthens the interatomic bonds and thus widening the band gap. At 4 K, the band gap energy of ZnO is 3.44 eV whilst at 300 K it is 3.37 eV.³⁵ The advantages of the wide band gap include enabling ZnO to withstand high temperatures, pressures and electric fields. This band gap is also tunable by the process of doping, especially with transitional metals.¹⁷ Changes effected in the band gap of ZnO by doping can be assessed by comparing the luminescence characteristics of the material before and after doping.

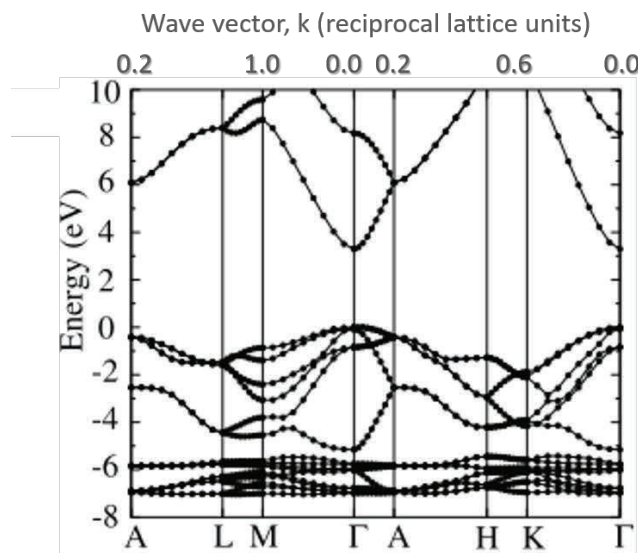


Figure 2.2 Band structure of wurtzite ZnO.³⁶

Luminescence describes the outcome of a process that involves the absorption of energy and the subsequent emission of light. ZnO is one of the materials that, when excited with radiation, absorbs it and then emits the energy in the form of light. Upon excitation, the incident photon is absorbed by the material and the energy is transferred to an electron in the valence band. The excited electron will move to either a higher energy defect level in the band gap or to the conduction band. Through a sequence of processes, the excited electron will be de-excited back to the ground state (valence band). If light is emitted during the de-excitation, the process is termed ‘radiative emission’ and if not, the process is ‘non-radiative relaxation’. The source of excitation identifies the type of luminescence that results. For example, when a material is excited by radiation in the form of light (‘photo-’), then the luminescence process is known as

photoluminescence (PL) or when an applied voltage is the source, then the process is called electroluminescence. In this work, photoluminescence type studies were conducted. Photoluminescence measurement is a non-destructive and efficient experimental technique used to study the optical properties of semiconductors such as ZnO. This technique helps in identifying defect levels and types of impurities in the material as well as their emission properties, through analysis of the optical transitions.

In the literature^{16,20,21,30}, photoluminescence has proved useful in studying the emission from ZnO. The observed emission can be categorized as band-edge emission or defects-related emission.^{6,20,35,36} The band-edge emission is associated with conduction band – valence band transitions. It extends from about 360 nm to about 425 nm and usually peaks at 380 nm as shown in Figure 2.3. Experimental investigations established that this band is richly excitonic in nature.⁶ Defects-related emission arises from transitions between the deep-level intrinsic defects within the bandgap of ZnO or between the deep-level defects and the valence band. Emission from these defects is broad and extends from the blue to the near-infrared region of the electromagnetic spectrum as shown in Figure 2.3. In this study, this broad emission band is of interest.

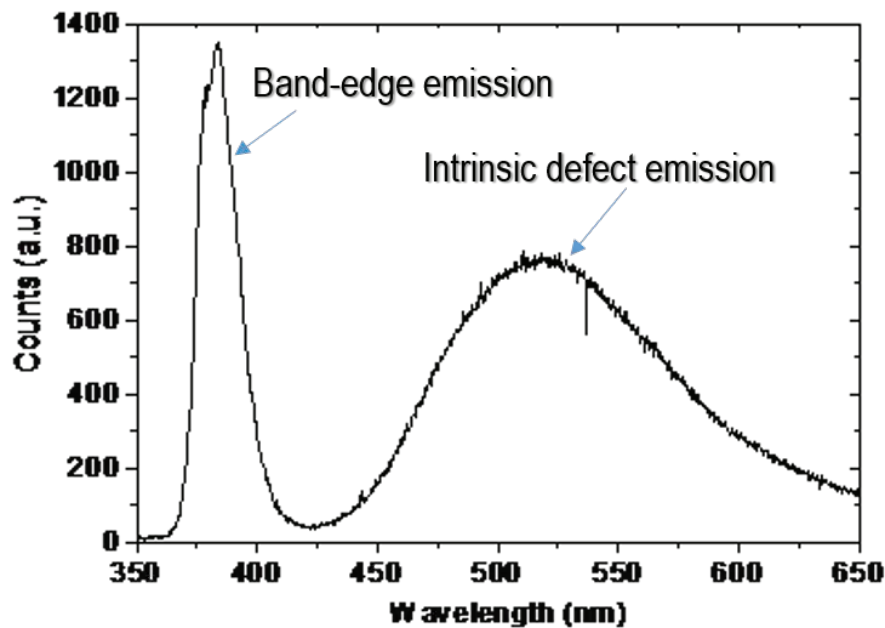


Figure 2.3 Typical photoluminescence spectrum of ZnO.³⁷

2.2.3. ZnO intrinsic defects emission

The nature and exact energy positions within the ZnO band gap of defects responsible for the broad emission are still not fully understood. Assignments of specific inter-defect transitions to sections of the emission in the 450 nm – 900 nm range of the spectrum are only tentative, as there is no consensus among researchers. It is generally believed however that recombination of radiative centres such as V_O , V_{Zn} , O_i , Zn_i , O_{Zn} and Zn_o are the origins of the broad emission

band.^{6,12,16,35–40} There is therefore growing interest in investigating the constituency, characteristics and origins of the broad emission band in ZnO particularly because of the scope of potential applications in fields such as optical-electronics and optical lasing.^{36,37,41}

The broad-emission band spanning the blue to near-infrared region is considered to comprise an overlap of (i) transitions between intrinsic defect levels within the band gap of ZnO, which are formed by the constituent ions of the material (Zn^{2+} , O^{2-}) and (ii) transitions involving some intentionally-introduced impurities (extrinsic defects) with energy levels falling within the band gap of ZnO. Both the intrinsic and extrinsic defect levels generate discrete electronic states in the band gap of ZnO. Intrinsic defects such as antisites (O_{Zn} , Zn_{O}), vacancies (V_{O} , V_{Zn}) and interstitials (O_{i} , Zn_{i}) can contribute to the broad emission band through the possible transitions depicted in Figure 2.4. The energy positions of the defect levels in Figure 2.4 were obtained from different references as indicated on each defect level. All the energy values on the defect levels are in wavenumbers (cm^{-1}); the units are omitted from within the figure for better presentation and clarity. Where positions of the defects levels vary from one reference to another, a block was used instead of a line to show a range of energies that are associated with the specific defect state. Emission transitions in the green - infrared (513 nm – 857 nm) range are shown. These could potentially contribute to the broad band emission characteristics of ZnO and will be used in the analyses in Chapters 4 and 5. The excitation transitions (457.9 nm, 476.5 nm, 488.0 nm and 514.5 nm) are included to show the portion of the bandgap accessible with each Ar^+ laser line. This will also become relevant in Chapters 4 and 5 while the Li^+ defect level at $6\,452\text{ cm}^{-1}$ will be useful in Section 5.3.1.

Although the green luminescence which appears in the 500 nm – 560 nm region is the most investigated section of the emission band, its origins are not fully understood. Several studies aimed at determining the source of this luminescence band have been conducted using a variety of experimental techniques and samples prepared by different methods.^{2,12,16,18,35} In a recent study¹⁶ conducted on ZnO films deposited by radio frequency (RF)-magnetron sputtering, the green-emission band was attributed to a $\text{Zn}_{\text{i}}^+ \rightarrow \text{V}_{\text{Zn}}^-$ transition. However, considering that the $\text{V}_{\text{Zn}}^{2-}$ defect ($21\,097\text{ cm}^{-1} - 22\,221\text{ cm}^{-1}$) have almost the same energy position as that of the Zn_{i}^+ defect ($21\,094\text{ cm}^{-1} - 21\,774\text{ cm}^{-1}$) and there is a V_{Zn} defect level at $2\,742\text{ cm}^{-1}$, the green emission band could also be attributed to the $\text{V}_{\text{Zn}}^{2-} \rightarrow \text{V}_{\text{Zn}}$ and $\text{Zn}_{\text{i}} \rightarrow \text{V}_{\text{Zn}}$ transitions as indicated in Figure 2.4.

The yellow section of the emission band, in the 560 nm – 600 nm region, is attributed to the $\text{O}_{\text{i}} \rightarrow \text{VB}$ transition¹⁶; the corresponding transition in Figure 2.4 is at 575 nm ($17\,401\text{ cm}^{-1}$). It will be shown in Sections 4.3.1 and 5.3.1 that the linewidths (FWHM) of these inter-defect transitions are of the order of 60 nm and so the single transition easily accounts for the yellow emission band. The energy level positions of the $\text{V}_{\text{Zn}}^{2-}$, O_{i} , V_{Zn}^- and V_{Zn} defects in

Figure 2.4 are such that the orange-red emission in the 600 nm – 700 nm comprises two distinct transitions. These are $V_{Zn}^{2-} \rightarrow V_{Zn}^-$ and $O_i \rightarrow V_{Zn}$. This orange-red emission band was found to be enhanced by annealing in air¹², supporting the association of this emission with excess oxygen (O_i) defects.

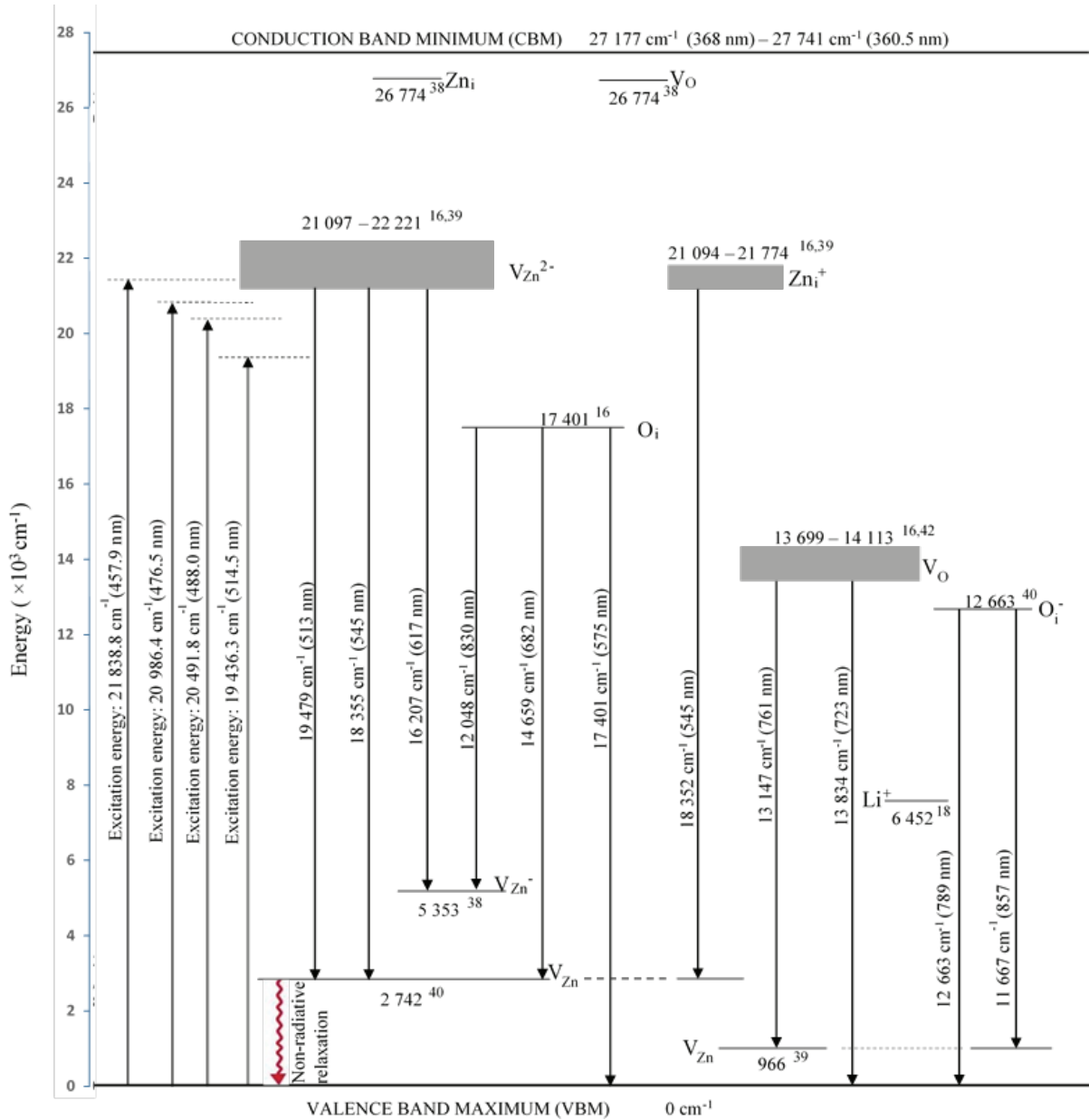


Figure 2.4 Schematic presentation of the defect energy levels in the ZnO band gap and the inter-defect transitions that yield green to infra-red emission.

Emission in the near-infrared region (700 nm – 900 nm) was also reported before and is assigned to the $V_O \rightarrow VB$ and $O_i \rightarrow V_{Zn}^-$ transitions^{16,42} at 13 834 cm^{-1} (723 nm) and 12 048 cm^{-1} (830 nm) in Figure 2.4. Further to this, the V_{Zn} and O_i^- defect levels positioned at 966 cm^{-1} and 12 663 cm^{-1} , respectively, in Figure 2.4 allow for the $V_O \rightarrow V_{Zn}$ (13 147 cm^{-1} ; 761 nm), $O_i^- \rightarrow VB$ (12 663 cm^{-1} ; 789 nm) and $O_i^- \rightarrow V_{Zn}$ (11 667 cm^{-1} ; 857 nm) transitions as shown.

Common accidental impurities found in ZnO include copper, cobalt and iron. These impurities change the optical luminescence of the pure ZnO through the transitions indicated in Figure 2.5. Copper impurities contribute to the green luminescence observed in ZnO.⁶ Although the $\text{Cu}^{2+} \rightarrow \text{Cu}^+$ transition is at 434 nm, its phonon replicas contribute to the broad green emission band centred at ~510 nm.^{37,43} The Co^{3+} and Co^{2+} ions, through the transition shown in Figure 2.5, are the source of emission observed around 661 nm in ZnO:Co samples.^{44–46} Fe^{3+} impurities, with the d^5 electronic configuration, on the other hand form deep traps in the band

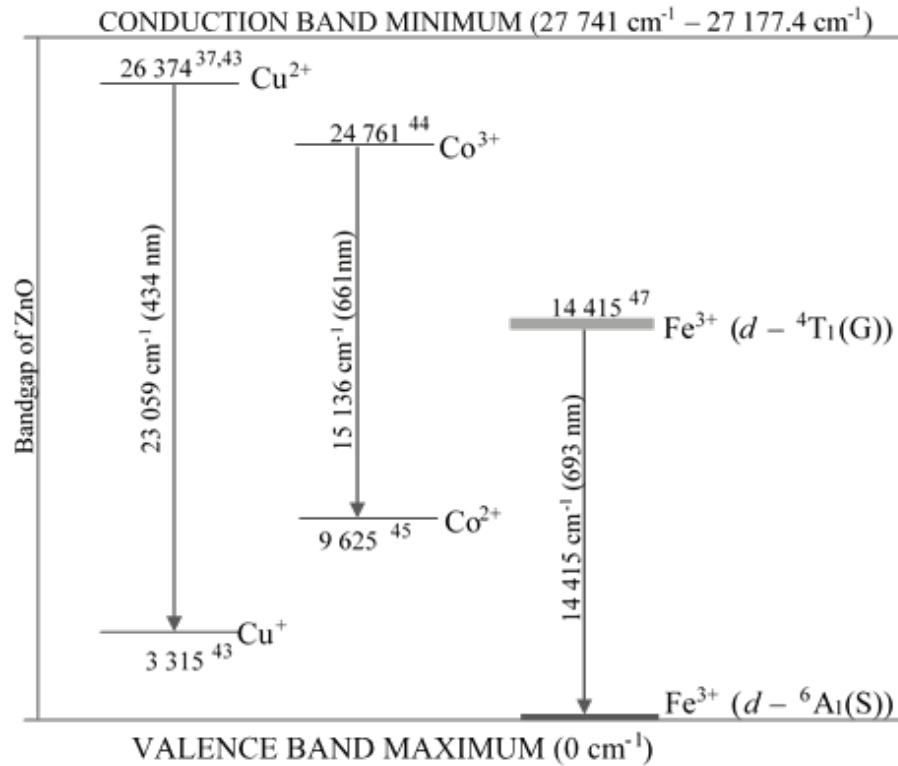


Figure 2.5 Transitions from some of the common impurities in ZnO. The transitions for copper and cobalt are inter-configurational whilst that for iron is intra-configurational.

gap of ZnO which result in near-infrared emission bands ($14\,415\text{ cm}^{-1}$; 693.733 nm).⁴⁷ The $d - d$ Fe^{3+} electronic transition in Figure 2.5 originates from the first excited state (${}^4T_1(\text{G})$) at $14\,415.1\text{ cm}^{-1}$ (693.717 nm) to the ground state (${}^6A_1(\text{S})$).

2.3. The Rare-earths (REs)

About 85% of the rare-earth resources are mined in China and the remaining 15% is from countries that include Brazil, Malaysia, Japan, California and Russia.¹⁰ Rare-earths, hereafter referred to as REs, are not “rare” as their name suggests. Instead, they are called “rare” because they are difficult to extract and separate from their sources. According to Sir Humphry Davy¹⁰, REs are compounds of metallic elements with oxygen.¹⁰ REs were discovered in the period from late 18th century (1794) to mid-20th century (1947). In 1794 Gadolin discovered ytterbia¹⁰, which was later renamed yttria and in 1803 another RE called ceria was discovered by Berzelius

*et al.*¹⁰ Two elements were extracted from the two oxides (yttria and ceria) and they were named yttrium and cerium, respectively.¹⁰ Forty years later, two new oxides were found in yttria and were named erbia and terbia and an additional two were found in ceria, subsequently named lanthana and didymia.¹⁰ Several new oxides were afterwards discovered in didymia, namely: samarium–1879, praseodymium and neodymium–1885 and europium–1896. On the other hand, five more oxides were found in terbia and erbia: ytterbium and holmium–1878, thulium–1879, dysprosium–1886, and lutetium–1907. Scandia was discovered in gadolinite in 1879 and gadolinium was discovered in a purer state in 1880 and was named after the mineral gadolinite.¹⁰ Promethium was discovered in 1947 as a fission product in a nuclear reaction.¹⁰

All rare earth elements extracted from the discovered oxides form the 17 elements of Group III b in Row 6 of the periodic table.¹⁰ Among these 17, is a special group classified as “lanthanides” which constitutes all the rare-earth elements excluding scandia, yttrium and lanthana. The lanthanides are named after lanthanum which is the third element in Row 6, however for simplicity, the generic name rare-earths (REs) will be used in this work, as commonly done in optical spectroscopy. Generally, this group is considered distinct from all the other periods on the periodic table because all properties of the elements in this group are dependent upon the 4*f* electrons. They have the same chemical properties but unique electronic and magnetic properties for each element. The REs, which are associated with the progressive filling of the 4*f*-shell, start with cerium ending with lutetium.

The neutral REs possess the common feature of a xenon core of 54 electrons [Xe], a partially filled 4*f* -orbital and two or three outer electrons in the 6*s* or 5*d* 6*s* orbitals.⁴⁸ Ionic form of the REs is obtained by successive removal of electrons starting from the 6*s* orbital followed by the 5*d* and then 4*f* electrons in that order.^{48,49} The trivalent state of a RE ion (RE³⁺) is formed when a RE element loses three electrons, but when only two are lost, a divalent RE ion (RE²⁺) is formed. The RE³⁺ is the most stable ionic state. Table 2.1 contains the electronic configurations of the 14 rare earth elements and their trivalent ions. The electronic configuration of a trivalent rare-earth ion (RE³⁺) is [Xe] 4*f*^{*n*} where *n*, the number of electrons in the 4*f* shell, varies from 1 for Ce³⁺ to 14 for Lu³⁺. Each trivalent RE ions from Ce³⁺ to Yb³⁺ shows characteristic transitions between energy levels of its 4*f*^{*n*} electronic configuration and the intra 4*f*- 4*f* transitions of Nd³⁺ ions are central to a large portion of this project. Lu³⁺ is excluded as its 4*f* shell is fully occupied.

The last column of Table 2.1, shows a gradual decrease in ionic radius as the number of 4*f* electrons increases from one in Ce³⁺ to fourteen in Lu³⁺. This is due to an accompanying increase in the nuclear charge which results in poor shielding of the 4*f*-shell by the 5*s* 5*p* electron shells. A stronger force then draws the 4*f* electrons closer to the nucleus thereby causing the reduction in the size of the RE elements. This contraction is reflected in the decreasing ionic

radii of the ions (Table 2.1). The shielding of the $4f$ electrons by the $5s^2 5p^6$ closed shells weakens interactions between the electrons in the $4f$ shell and the crystal-field due to the surroundings. This results in a distinct and well-resolved crystal-field energy level structure for

Table 2.1 Rare-earth elements and ions with their respective electronic configurations.

Atomic number	Rare-earth element	Symbol	Electron configuration		RE ³⁺ ion radius (pm)
			Neutral element (RE)	Trivalent ion (RE ³⁺)	
58	Cerium	Ce	[Xe] $4f^2 6s^2$	[Xe] $4f^1$	103.4
59	Praseodymium	Pr	[Xe] $4f^3 6s^2$	[Xe] $4f^2$	101.3
60	Neodymium	Nd	[Xe] $4f^4 6s^2$	[Xe] $4f^3$	99.5
61	Promethium	Pm	[Xe] $4f^5 6s^2$	[Xe] $4f^4$	97.9
62	Samarium	Sm	[Xe] $4f^6 6s^2$	[Xe] $4f^5$	96.4
63	Europium	Eu	[Xe] $4f^7 6s^2$	[Xe] $4f^6$	95.0
64	Gadolinium	Gd	[Xe] $4f^7 5d^1 6s^2$	[Xe] $4f^7$	93.8
65	Terbium	Tb	[Xe] $4f^9 6s^2$	[Xe] $4f^8$	92.3
66	Dysprosium	Dy	[Xe] $4f^{10} 6s^2$	[Xe] $4f^9$	90.8
67	Holmium	Ho	[Xe] $4f^{11} 6s^2$	[Xe] $4f^{10}$	89.4
68	Erbium	Er	[Xe] $4f^{12} 6s^2$	[Xe] $4f^{11}$	88.1
69	Thulium	Tm	[Xe] $4f^{13} 6s^2$	[Xe] $4f^{12}$	86.9
70	Ytterbium	Yb	[Xe] $4f^{14} 6s^2$	[Xe] $4f^{13}$	85.8
71	Lutetium	Lu	[Xe] $4f^{14} 5d^1 6s^2$	[Xe] $4f^{14}$	84.8

each RE³⁺ ion which is nearly unchanged from host to host. It is for this reason that transitions in trivalent lanthanide ions are very sharp and exhibit weak phonon relations. Absorption and emission spectra due to the inner shell $4f$ - $4f$ transitions are sensitive to the local symmetry of the host crystal which results in different spectral characteristics. Therefore, different optically-active RE³⁺ centres can be identified due to different site symmetries. The surroundings of the lanthanide atom or ion are insignificant chemically, i.e., a $4f$ -electron has little tendency to participate in any chemical-bond formation.

In this work, the luminescent characteristics of trivalent neodymium ions (Nd³⁺) doped into the ZnO host lattice are studied, and so the specific properties of neodymium will be discussed next. Effects of the site symmetry and the local crystal field on the emission characteristics of RE³⁺ ions will be discussed in Section 2.4.

2.3.1. Neodymium

Neodymium has a bright silvery metallic lustre and is one of the more reactive RE metals. It tarnishes in air, forming an oxide and as such, neodymium should be stored under a light mineral oil or sealed in plastic.³² This element is the second most abundant RE element after cerium and is found in all lanthanide minerals such as bastnasite, monazite and allanite.²⁰

Industrially, neodymium is manufactured in the form of an oxide, neodymium oxide (Nd_2O_3). This oxide has a double z-axis hexagonal close-packed structure and lattice parameters $a = 0.383 \text{ nm}$ and $c = 0.600 \text{ nm}$.⁵⁰ Neodymium has many applications including

- (i) in the making of strong permanent magnets - the incorporation of neodymium ions into alloys to make neodymium-iron-boron provides a way of making excellent permanent magnets that can decelerate a fast moving train or car within a short period of time. Large wind turbines also use generators that contain strong permanent magnets composed of neodymium-iron-boron.
- (ii) in lasers - Nd^{3+} ions, like other RE^{3+} ions which include Er^{3+} , Tm^{3+} and Ho^{3+} have been efficiently used in solid-state lasers which emit in the near-infrared.⁵¹ The well-known laser neodymium-yttrium-aluminium garnet ($\text{Nd}:\text{YAG}$) laser is used in optical studies and in the treatment of bronchial cancer.^{52,53}
- (iii) in data storage - the unique emission properties of the Nd^{3+} ions have also been employed in making optical data storage media.⁵¹ This is achievable by the multiplexing of the spectral data and then storing lots of data on the same location.
- (iv) in lighting - when doped into wide band gap semiconductors such as ZnO , Nd^{3+} enhances emission of different desired colours (in the visible region) through creation of more intrinsic defects involved in the emission.⁵⁴ Co-doping ZnO with Nd^{3+} and one other or more RE^{3+} ions produces multi-coloured emission.² The emission has applications in plasma displays and the manufacturing of white light sources, for example.
- (v) in absorption of light - Nd^{3+} ions have the ability to absorb bright yellow light glow and so can be used to coat welding goggles in order to protect the eyes.³² The human eye is most sensitive in the yellow spectral region.

2.4. Rare-earth doping in ZnO

Unique semiconductor properties are sometimes achieved in solid-state device fabrication by the process of doping. The dopants are chosen depending on their oxidation state stability, type of host lattice, and the intended application. They can be metal elements^{17,55} or rare-earth elements^{5,51} and they modify the physical properties⁶ of the host material as well as behavioural properties such as magnetism^{8,47,56} or luminescence.^{5,16,51} For example, in terms of magnetic properties, ZnO is considered a non-magnetic material. Thus, addition of Fe^{3+} -ion dopants can introduce some magnetic properties (local magnetic moments) into the ZnO lattice and hence ZnO becomes a dilute magnetic semiconductor material.⁸ In the case of the luminescence properties of ZnO , addition of rare-earth ions increases the intensity of the broad band emission

of ZnO as well as introducing sharp luminescence features characteristic of the RE^{3+} ions as discussed in Section 2.3. Application areas of this sharp emission include medical imaging⁴, fibre optics⁵⁷, phosphor-based light-emitting diodes^{1,2}, and communication devices like military radars, among others.^{10,51}

Much of fluorescence spectroscopic studies focus on elucidating the effects of the crystal field and the resulting modifications of the characteristic sharp-line emission. For such studies, the free ion energy level schemes of RE^{3+} ions, as summarized in the Dieke diagram, provide an invaluable starting point as outlined below (Subsection 2.4.1).

2.4.1. Rare-earth centres and crystal-field effects

Several studies have shown that absorption and emission spectra of the trivalent rare-earth ions doped into solids approximate those of the free ions.^{48,58} The energy level scheme of free Nd^{3+} ions presented in Figure 2.6 is extracted from the Dieke diagram⁵⁸ and these were derived from studies of $\text{LaCl}_3:\text{RE}^{3+}$ conducted by Dieke *et al.*⁵⁸ The Russell-Saunders notation ($^{2S+1}L_J$) for energy levels is used to identify the multiplets as indicated in Figure 2.6, for Nd^{3+} ions. S is the total spin, L is the total orbital angular momentum and J is the total angular momentum and is the magnitude of the vector sum of $\vec{S}$ and $\vec{L}$.

Absorption of radiation is indicated by transitions from a level at lower energies to one at higher energies (e.g. $^4\text{I}_{9/2} \rightarrow ^4\text{G}_{7/2}$) whilst emission originates from the higher level (e.g. $^4\text{F}_{3/2} \rightarrow ^4\text{I}_{9/2}$). For trivalent rare-earth ions, studies of the electronic transitions within the 4f-orbitals are important since they are the sources of absorption and emission signatures. Although 4f-4f transitions are forbidden as electric-dipole transitions by the parity selection rule, they are however observed due to interaction of the 4f electrons with the host crystal which introduces other odd-parity wavefunctions such as from the 5d orbitals.⁴⁸

For a free RE^{3+} ion, spherical symmetry exists and each level is $(2J + 1)$ -fold degenerate. If the rare-earth ion is introduced into a crystal, the 4f electrons interact weakly with the crystal and experience an inhomogeneous electrostatic field which is known as the crystal field. This field is produced by the charge distribution in the crystal and its effect is to distort the closed shells of the RE^{3+} ions. That is, the spherical symmetry is destroyed and the degeneracy of the free RE^{3+} levels removed. Each multiplet level is thus split into a number of crystal-field levels (Figure 2.6) due to the influence of the electric field produced by the environment. According to Kramer's theorem⁴⁸, for odd-electron systems, there is a two-fold degeneracy in the energy states that cannot be removed by any electric fields.

The effect of the crystal field on the free-ion energy levels can be understood by applying the potential produced by the host crystal on the free ion wavefunctions. Therefore, the Hamiltonian for an ion placed in a crystal field is given by⁴⁹

$$H = H_F + V_{cryst} \quad [2.1]$$

where H_F is the Hamiltonian of the free ion and V_{cryst} is derived from the potential due to the crystal environment on the rare-earth ion. The H_F component includes the effects from the Coulomb and spin-orbit interactions.^{48,49} The crystal field at the rare-earth ion site is usually expressed as a linear combination of spherical tensors $C_q^{(k)}$ in the form

$$V_{cryst} = \sum_{k,q,i} B_q^k (C_q^{(k)})_i \quad [2.2]$$

where the summation over i caters for all the $4f$ electrons of the RE^{3+} ion. The k and q values which are governed by the type of electron orbitals being considered and the symmetry of the

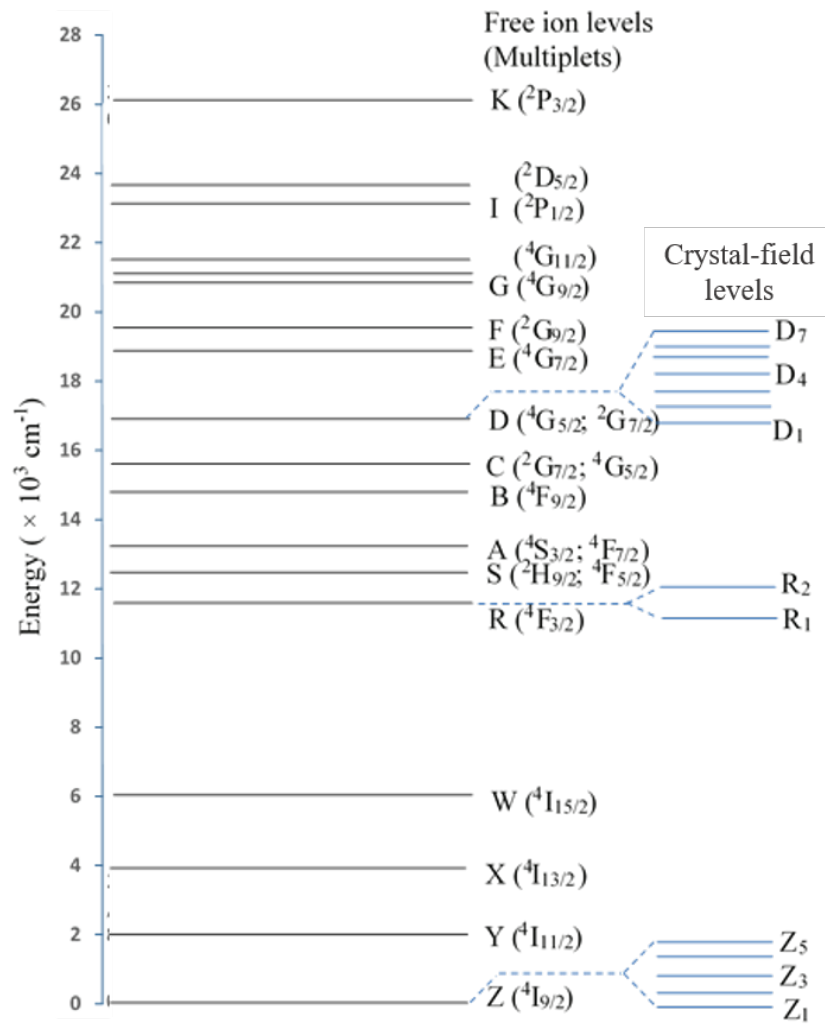


Figure 2.6 Energy levels (multiplets) of free Nd³⁺ ions that fall within the band gap of ZnO. The ^{2S+1}L_J notation used is explained in the text. The crystal-field splits each multiplet into $J + 1/2$ crystal-field levels.

point group, are such that $k \leq 6$ and even while $q \leq k$ for f electrons. The parameters B_q^k depend on the symmetry of the RE^{3+} ion site in the host lattice and are derived from minimization of the standard deviation between experimentally-determined levels (i.e. derived from the observed transitions) and the corresponding calculated values. The number of levels obtained

from this study were too few for the minimization procedure. The degree of splitting of the levels is determined by the symmetry and strength of the crystal field. Whether transitions between specific crystal-field levels of different multiplets are observed (allowed) or not observed (forbidden) is governed by the electric dipole selection rules.

A typical Nd^{3+} absorption spectrum in Figure 2.7 (a) shows transitions from the ground multiplet ($^4\text{I}_{9/2}$) to some of the excited multiplets indicated in Figure 2.6. Nd^{3+} emission in most cases originates from the $^4\text{F}_{3/2}$ multiplet near $12\,000\text{ cm}^{-1}$ ($\sim 900\text{ nm}$) to the lower lying $^4\text{I}_{9/2}$, $^4\text{I}_{11/2}$ and $^4\text{I}_{13/2}$ multiplets as shown in Figure 2.7 (b).

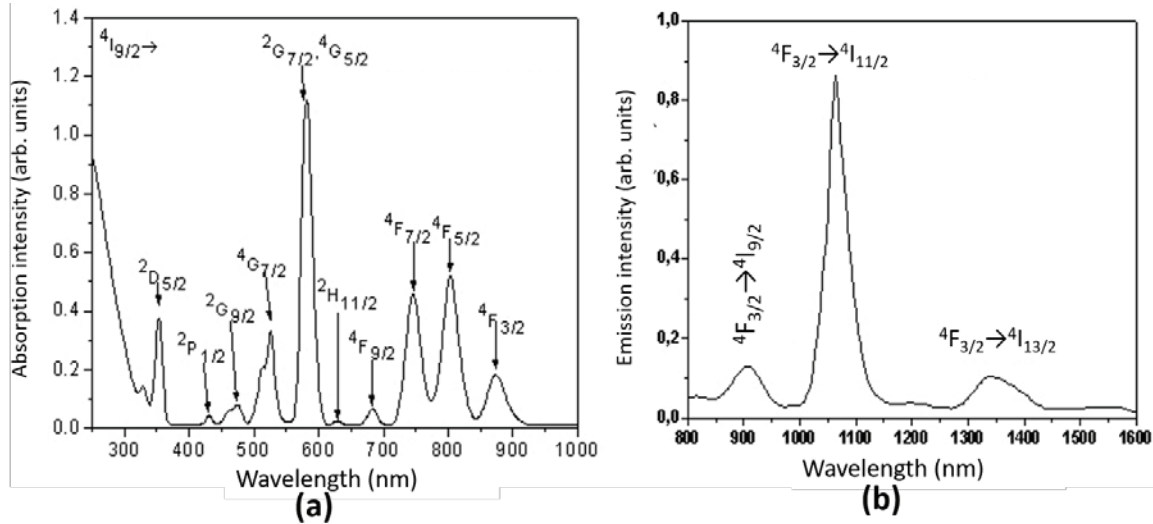


Figure 2.7 Typical room-temperature absorption (a) and emission (b) spectra for Nd^{3+} ions.⁵⁹

2.4.2. Theoretical considerations for the dopant Nd^{3+} ions

Free ion energy levels of Nd^{3+} ions (up to $26\,000\text{ cm}^{-1}$) which lie within the band gap of ZnO are presented in Figure 2.6. When introduced into a crystal, the energy levels will no longer be single-lines as indicated for free ions in Figure 2.6. Since Nd^{3+} has three $4f$ electrons (odd number) each multiplet level in Figure 2.6 has half integer J and will be split into $J + 1/2$ crystal-field levels.⁹ Each of the resulting crystal-field levels is doubly degenerate. For example, the $^4\text{I}_{9/2}$ multiplet level with $J = 9/2$, will be split into $(9/2 + 1/2)$, which is five levels, by the crystal field. The levels are labelled Z_1 to Z_5 , where Z_1 , the ground state is at energy, $E = 0\text{ cm}^{-1}$. Z_2 to Z_5 are the excited states of the ground multiplet as shown in Figure 2.6. Similarly, the $^4\text{F}_{3/2}$ multiplet will have two crystal-field energy levels, R_1 and R_2 , and so forth.

Since the number of electrons in the f -orbital of Nd^{3+} is odd and Nd^{3+} resides in a C_{3v} symmetry (Zn^{2+}) site in ZnO, transitions are allowed between any two inter-multiplet crystal field levels.^{48,49} As such, there will be ten possible transitions between the $^4\text{F}_{3/2}$ and $^4\text{I}_{9/2}$ multiplets of Nd^{3+} , for example. Statistically, the highest energy, ΔE , above the ground level, that can have a reasonable electron population at temperature T is equal to kT where k is the Boltzmann's constant. At 10 K , $\Delta E \cong 7\text{ cm}^{-1}$ and this increases to 52 cm^{-1} at 75 K . This means

that at 10 K, the Z_2 level contains electrons only if it lies within 7 cm^{-1} of Z_1 as shown in Figure 2.8 (a). In that case, absorption transitions from both Z_1 and Z_2 levels are observed. If however the Z_2 level is at 52 cm^{-1} as in Figure 2.8 (b), then transitions from Z_2 can only occur at 75 K and there will be none at 10 K.

Similarly, at 10 K, emission emanates from level R_1 of the R ($^4F_{3/2}$) multiplet only if the $R_1 - R_2$ separation is greater than 7 cm^{-1} and from both R_1 and R_2 , at 75 K (Figure 2.8). The double arrows in Figure 2.8 identify cases for which both absorption and emission transitions are observable. For the ZnO:Nd³⁺ results presented here, the $Z_1 - Z_2$ and $R_1 - R_2$ separations are about 50 cm^{-1} and 95 cm^{-1} , respectively. Following on from the above arguments, it means that the absorption and emission spectra recorded at 10 K, are wholly due to transitions from the ground state (Z_1) level and from the lower level R_1 of the emitting R ($^4F_{3/2}$) multiplet, respectively. Transitions that appear at raised temperatures are therefore associated with the higher energy levels, originating from Z_2 or even Z_3 in the absorption spectra and from the R_2

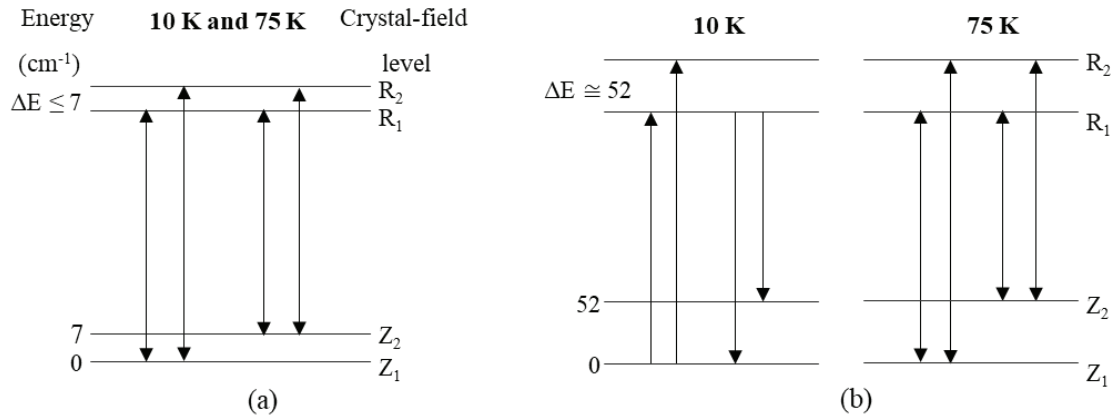


Figure 2.8 Crystal-field energy levels of the ground Z ($^4I_{9/2}$) and excited R ($^4F_{3/2}$) multiplets illustrating the observable transitions at 10 K and at 75 K for (a) $\Delta E \leq 7 \text{ cm}^{-1}$ and (b) $\Delta E \approx 52 \text{ cm}^{-1}$. The double arrows identify both absorption (from Z_1 and Z_2) and emission (from R_1 and R_2).

level in the emission spectra. This line of reasoning will be used in Chapters 4 and 5 to analyse the absorption and emission transitions recorded at low and raised temperatures, in order to deduce energy-level schemes.

2.4.3. Direct and indirect excitation of Nd³⁺ ions

Spectroscopic studies of Nd³⁺ ions doped into ZnO give valuable information on the optical properties of Nd³⁺ ions such as the energy-level structure and the site-configurations of the ions. A comprehensive analysis of the resulting Nd³⁺ ion luminescence can only be made with clear understanding of the theoretical considerations discussed in Section 2.4.2. In this sub-section (Section 2.4.3), two mechanisms by which Nd³⁺ ions can be excited are discussed together with

the relaxation channels. These are indirect excitation and direct excitation as illustrated in Figure 2.9.

The process of exciting the Nd^{3+} ions indirectly relies on excitation of the intrinsic defects of ZnO first, and subsequent energy transfer to the extrinsic Nd^{3+} defects, as highlighted earlier (Section 2.2.3). As shown in Figure 2.4, when the intrinsic defects are excited they will emit the energy radiatively in the 500 nm – 900 nm region. When the energy of the emitted radiation

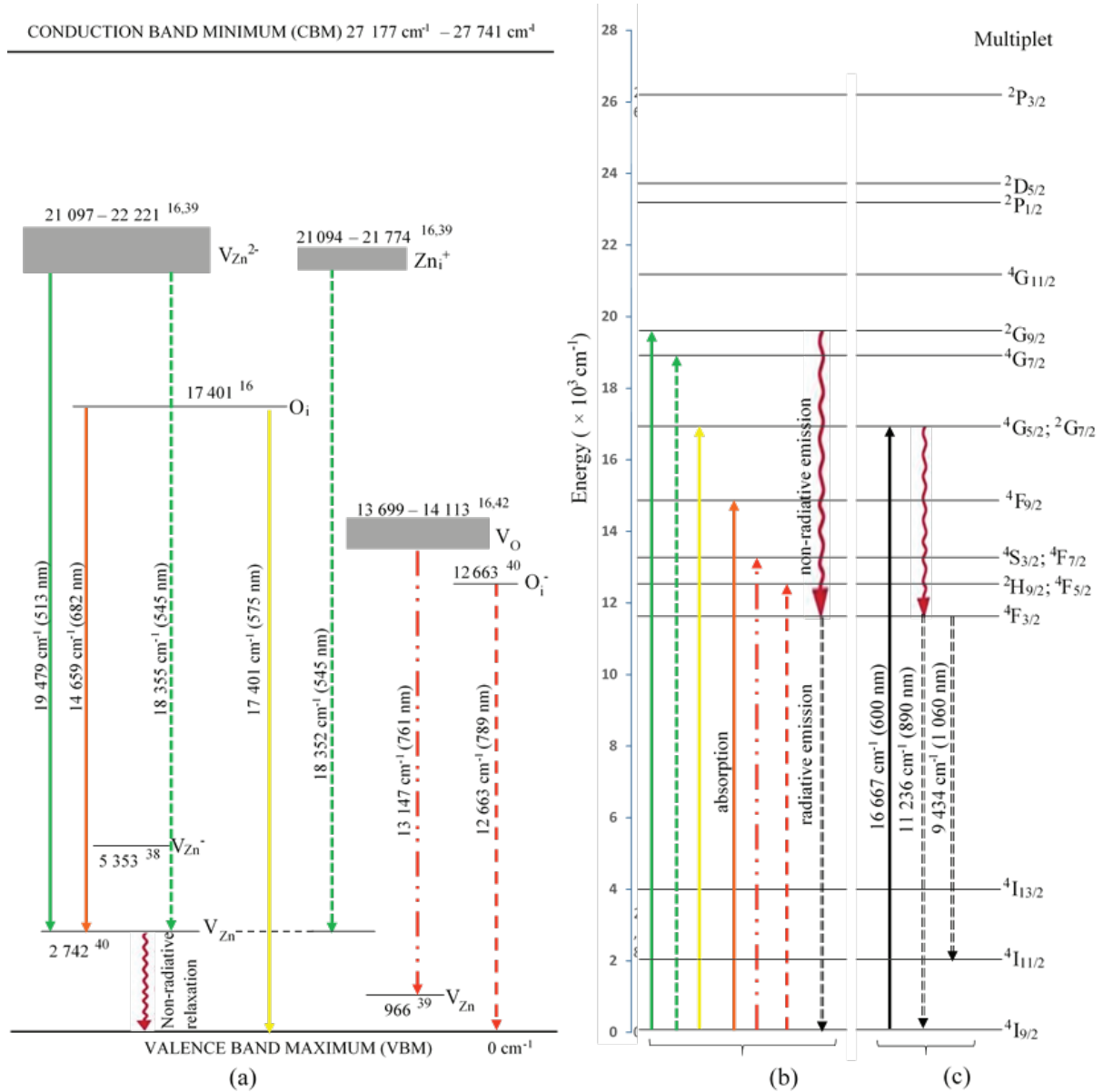


Figure 2.9 Energy transfer mechanisms for excitation of Nd^{3+} ions. (a) Emission transitions from some of the ZnO intrinsic defects (as in Figure 2.4) contributing to the Nd^{3+} absorption in (b). (c) Direct excitation of Nd^{3+} ions through use of resonant energy.

matches or is nearly resonant with the energy of a Nd^{3+} multiplet, the Nd^{3+} ions can absorb the energy. For example, the defect transitions shown in Figure 2.9 (a) overlap with the F ($^2G_{9/2}$), D ($^2G_{7/2}$; $^4G_{5/2}$) and B ($^4F_{9/2}$) multiplet energies above the ground Z ($^4I_{9/2}$) multiplet. Therefore, crystal-field levels in each of these Nd^{3+} multiplets could become populated as electrons absorb matching radiation from the intrinsic defect emission, as indicated. This type of energy transfer

is more likely to occur at high doping levels.¹¹ Alternatively, non-radiative decay processes in populated defect levels could also lead to energy transfer to Nd³⁺ ions. The indirect excitation of Nd³⁺ ions through the absorption or transfer of radiation from intrinsic defects of the host material is important as it provides several channels through which Nd³⁺ ions could be excited.

In the case of direct excitation of Nd³⁺ ions, resonant excitation energy from sources such as tunable dye lasers is used. This excitation process is illustrated in Figure 2.9 (c). Incident radiation of energy of about 16 667 cm⁻¹ (~600 nm wavelength) for example, can be used to directly populate crystal-field levels of the D (²G_{7/2}; ⁴G_{5/2}) multiplet as shown.

It is a common characteristic of Nd³⁺ ions that either excitation process is followed by non-radiative relaxation down to the R (⁴F_{3/2}) multiplet from where emission is almost always observed.^{21,24} Nd³⁺ ions have dominant emission near the 1 060 nm and 890 nm wavelengths, which is attributed to the ⁴F_{3/2} → ⁴I_{11/2} and ⁴F_{3/2} → ⁴I_{9/2} transitions, respectively. The emission cross-section for the ⁴F_{3/2} → ⁴I_{11/2} transitions is much larger (3 times) than that for the ⁴F_{3/2} → ⁴I_{9/2} transitions.⁶⁰ This means that emission from the ⁴F_{3/2} multiplet at ~11 500 cm⁻¹ to the first excited multiplet (⁴I_{11/2}) at ~2 000 cm⁻¹ is much stronger than that to the ground (⁴I_{9/2}) multiplet, in general. A visible region detector which cuts off at 950 nm was used for the work presented in this dissertation and so, unfortunately, it was not possible to record the stronger ⁴F_{3/2} → ⁴I_{11/2} emission. It should therefore be borne in mind that the results presented here (Chapters 4 and 5) are for the weaker set of transitions, particularly in cases where no ⁴F_{3/2} → ⁴I_{9/2} emission is observed.

2.5. Phonon modes in wurtzite ZnO

The vibrational properties of ZnO are essential to understanding the thermal and electronic properties which impede some of its applications. The thermal properties of ZnO can be determined from the quantum vibrations of the lattice, as described by the phonon dispersion relations.

Wurtzite ZnO, with four atoms per unit cell, has twelve phonon modes⁶ which are listed in Table 2.2. The acoustic modes (LA and TA) result from in-phase vibrations of the lattice atoms parallel or perpendicular to the z-axis. Optical modes on the other hand, result from coordinated anti-phasal vibrations of the basis Zn and O atoms.⁶ In the literature⁶, it is reported that the phonon dispersion relations of ZnO have been probed by several techniques including Raman spectroscopy, inelastic neutron scattering (INS) and infrared spectroscopy. *Ab initio* calculations⁶¹ were also performed and the values found are consistent with the experimental data in the literature. An optical mode can be Raman active only, infrared (IR) active only or both Raman and IR active depending on the symmetry properties of the unit cell and the Brillouin zone. The experimental geometry determines which of the allowed modes are

observable. Further, IR-active modes can couple to electronic transitions leading to the vibronic (vibrational-electronic) transitions which are sometimes observable in photoluminescence spectra. The vibronic transitions are often observed accompanying the strong intensity electronic transitions as the coupling is weak. Phonon modes are therefore deduced from the energy difference between an electronic transition and the associated vibronic transitions.

Table 2.2 Phonon modes present in wurtzite ZnO.

Type of modes	Number of modes
Transverse acoustic (TA)	2
Longitudinal acoustic (LA)	1
Transverse optical (TO)	6
Longitudinal optical (LO)	3

The centre of the Brillouin zone of ZnO is the Γ point which is at (0,0,0) (Figure 2.10 (a)). Other common points of high symmetry on the Brillouin zone boundary include A, M, K and H which are at the $(0, 0, \pi/c)$, $(\pi/a, -\pi/\sqrt{3}a, 0)$, $(4\pi/3a, 0, 0)$ and $(4\pi/3a, 0, \pi/c)$ points as shown in Figure 2.10 (a). Figure 2.10 (b) shows the calculated and the experimentally determined dispersion curves in ZnO along the high symmetry directions shown in (a). The acoustic modes (TA and LA) have energies ranging between 0 cm^{-1} (0 meV) and 260 cm^{-1} (32.3 meV) while the optical mode (TO and LO) energies are between 395 cm^{-1} (49.0 meV) and 605 cm^{-1} (75 meV).

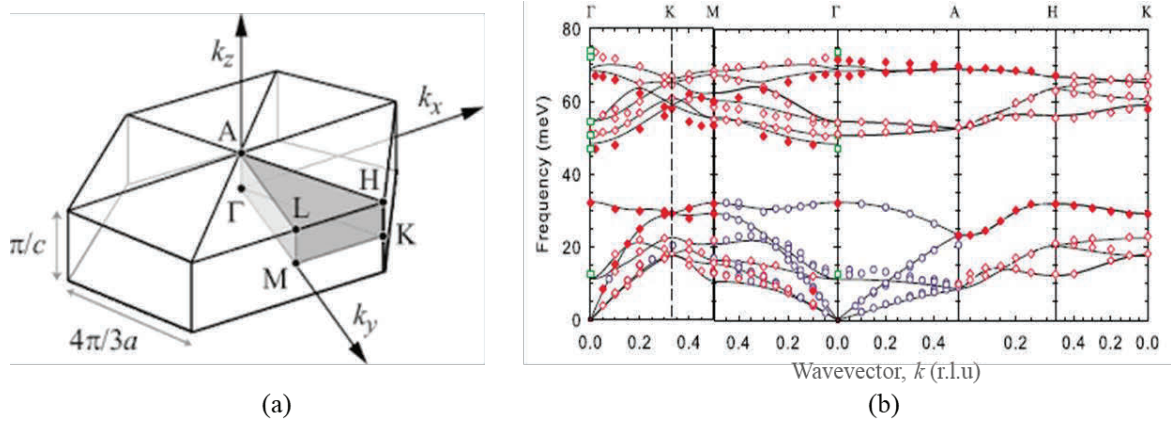


Figure 2.10 (a) Brillouin zone of ZnO showing the high symmetry points⁶² and the primitive unit cell (shaded section). (b) Phonon dispersion curves of ZnO along the high symmetry directions. Data obtained from INS measurements – $\diamond$, Raman measurements – $\square$ and *ab initio* calculations – solid lines.⁶¹ r.l.u. – reciprocal lattice units.

The strong bond between Zn and O atoms tends to cause high phonon frequencies and limit the range of possibly observable local vibrational modes (LVMs) related to any impurities in the lattice.⁶ Local vibrational modes of Fe^{3+} , for example, present as an impurity in ZnO (discussed in Section 2.2.3) are located in the regions where there is negligible density of modes

of the ZnO host lattice. That is, the LVMs of Fe^{3+} fall within the $260 \text{ cm}^{-1} - 395 \text{ cm}^{-1}$ energy range and above 605 cm^{-1} .^{61,63}

In this study, vibronic transitions have been observed in conjunction with the Fe^{3+} electronic transition, as indicated in Figure 2.5, as well as with several of the $\text{Z} (^4\text{I}_{9/2}) \rightarrow \text{D} (^2\text{G}_{7/2}; ^4\text{G}_{5/2})$ and $\text{R} (^4\text{F}_{3/2}) \rightarrow \text{Z} (^4\text{I}_{9/2})$ Nd^{3+} crystal-field transitions (Figure 2.9 (c)) in $\text{ZnO}:\text{Nd}^{3+}$ films and $\text{ZnO}:\text{Nd}^{3+}:\text{Li}^+$ powder samples. These will also be discussed in Chapters 4 and 5.

CHAPTER 3

EXPERIMENTAL TECHNIQUES

3.1. Introduction

Samples of undoped and Nd-doped ZnO in two different forms, namely thin films and powders, were used in this study. Thin films were deposited by the radio frequency (RF) magnetron sputtering technique and the powder samples were prepared using the sintering technique. The two methods are outlined in Section 3.2. The structure, morphology and chemical composition of the films and the powders were determined using X-ray diffraction (XRD), scanning electron microscopy (SEM) and energy dispersive X-ray spectroscopy (EDS), respectively. These characterization techniques are discussed in Section 3.3. The photoluminescence (PL) properties of both sets of samples were studied in the 10 K – 75 K temperature range using an argon ion laser and a dye laser as excitation sources. Details of the measurements are presented in Section 3.4.

3.2. Sample preparation

3.2.1. Thin-film deposition by RF magnetron sputtering

Sputtering is a common method for fabricating thin films in industries involved with semiconductor processing, surface finishing by deposition of metals and the production of jewellery.⁶⁴ The basic sputtering mechanism involves the bombardment of high energetic particles (ions) onto a solid target in a knock-on process. The incident particle (mostly an ion) dislodges atoms from the surface or the near-surface region of the target as shown in Figure 3.1. Under suitable conditions, the sputtered atoms accumulate on a substrate that is mounted close to the target. The incident particles are derived from plasmas of either chemically inert gases such as Ar⁺ and Kr⁺ or reactive ions of compounds with low molecular weight such as O₂⁺ and N₂⁺.⁶⁴ Of these, the relatively low cost Ar⁺ ions are typically used.⁶⁴ The kinetic energy of the incident ion is provided by an accelerating potential (self-bias) in the sputter chamber.⁶⁴ This energy determines the quantity of atoms that are displaced from the target in a single encounter.

The ratio of the number of atoms dislodged from the target to that of the atoms incident on it is known as the sputter yield⁶⁴, Y, and it is given by Equation 3.1.

$$Y = \frac{\text{Number of ejected particles (ions or neutrals)}}{\text{Number of incident particles}} \quad [3.1]$$

In order to achieve a high sputter yield, the energy of the bombarding ions should lie within the 0.01 – 1 keV range which is known as the ‘knock-on’ energy range for sputtering.⁶⁴ Energies

in this range are higher than the binding energies of the atoms at and near the surface of the target, and therefore lead to sputtering through atomic movements such as illustrated in Figure 3.1. The energy (E) ranges of $E < 50$ eV and $E > 1$ keV are less effective for sputtering.

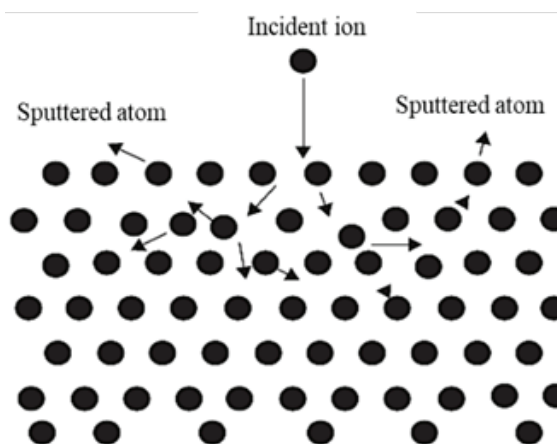


Figure 3.1 Illustration of the sputtering process.⁶⁴

Ions with energies that fall in the lower energy range will not have sufficient energy to eject the strongly bound atoms, but only those loosely attached to the surface of the target.⁶⁴ On the other hand, ions with energies in the higher energy regime result in undesirable deep ion-implantation on the target and a possibility of re-sputtering of the film deposited on the substrate.^{64,65} If the sputtering is performed with suitable energies the sputtered atoms condense on the substrate, forming the desired thin film.⁶⁴ Ad-atom energy of ~ 0.1 eV increase film-substrate adhesion. To improve the efficiency of the deposition process and to prevent contamination of the film, the sputter chamber is evacuated to $\sim 1.0 \times 10^{-5}$ mbar prior to deposition.^{64,65}

The most utilized techniques for deposition of films include the direct current (DC) and the radio frequency (RF) magnetron sputtering. The difference between these two options is in the source of power, i.e. direct current for DC and an alternating current for RF, respectively. The most used RF frequency is 13.56 MHz, with other options being two or three times this value.⁶⁶ The RF setup (Figure 3.2 (a)) has better capability in ionizing the sputtering gas and in sputtering atoms from the target than the DC option.⁶⁴ This technique is suitable for a variety of targets including the conducting and the insulating while DC is suitable for metals only. Other advantages of RF include: (i) excellent deposition rates and (ii) the deposition of films which are of high purity and are highly adhesive to the substrates.⁶⁵

The use of magnetrons in sputtering systems has also significantly enhanced the efficiency of the sputter processes.⁶⁴ In RF magnetron sputtering, a magnet mounted behind the target confines the plasma close to the surface of the target, thereby reducing re-sputtering. In addition, electrons emitted from the target (cathode) also experience a Lorentz force from the magnet and move in a helical loop at a fixed angle. This increases the electron mean free path

in the plasma and thereby enhances the probability of ionization. The increased secondary ionization leads to higher deposition rates.

The RF magnetron sputtering system used to deposit ZnO:Nd³⁺ thin films in this study is shown in Figure 3.2 (b). A high purity (99.99%) target of ZnO/Nd (97:3 wt%) obtained from Semiconductor Wafer, Inc. was used for this work. The target composition ratio is equivalent to about ZnO:1.5mol%Nd³⁺ (calculated with 100% ZnO). The target is 76 mm in diameter and 6 mm thick. The films were deposited on quartz substrates. Prior to deposition, each substrate was thoroughly cleaned using an acetone bath in an Elma Transsonic ultrasonic cleaner (model 470/H) and then carefully dried using a 5N ultra-pure nitrogen gas blower. Several permutations of sputter power and duration of deposition were used in order to establish the optimum

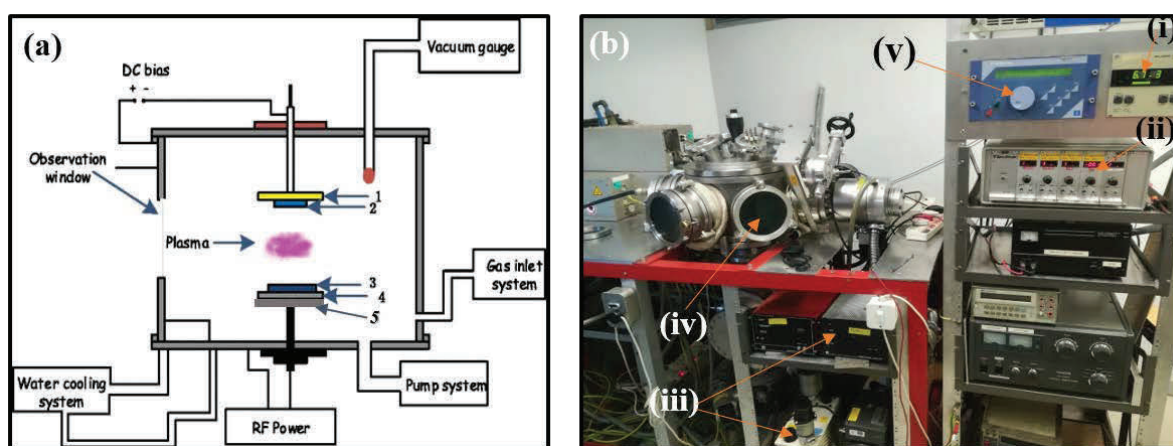


Figure 3.2 (a) Schematic of the RF sputtering system: 1 – substrate holder, 2 – substrate, 3 – target, 4 – magnet, and 5 – RF powered electrode.⁶⁷ (b) Pictorial view of the RF sputtering system: (i) – pressure gauge, (ii) – gas inlet system, (iii) – pump system, (iv) – observation window, and (v) – RF power control.

parameters for deposition of ZnO:Nd³⁺ films usable for photoluminescence studies. From these trials, it was established that the best films were obtainable by depositing for a 3-hour period using the 100 W power setting. Films deposited for shorter durations were too thin and did not yield any photoluminescence. Films deposited with 150 W showed bubbles and some sections had already peeled off by the time the deposition chamber was opened, due to intrinsic stresses. Films were sputtered either in a pure argon environment or in a mixture of O₂ and Ar gases, with the percentage ratio of O₂:Ar varied as 0:100, 30:70 and 50:50. The Ar ion gas flow rate was always fixed at 13 sccm (standard cubic centimetres per minute). The best films were obtained in the 30:70 environment. For reference, undoped ZnO films were also deposited in a pure Argon environment (i.e. 0% O₂) using 100 W and 3-hour settings. Some of the deposited films were annealed at 600 °C; this temperature was established as ideal for thin films intended for photoluminescence studies, in the previous work of Bhebhe.¹⁶

3.2.2. Preparation of powder samples

The preparation of powder samples involved hand-milling of the starting powder materials followed by compaction to form a ‘green body’ which was then sintered. The sequence is illustrated in Figure 3.3. The starting materials were high purity research-grade compounds obtained from Sigma-Aldrich.[†] These are ZnO (99.999%), Nd₂O₃ (99.9%) and Li₂CO₃ (99.997%). The preliminary stages of hand-milling and compaction are discussed in the following sub-section (Section 3.2.2.1) while relevant aspects of the sintering process are presented in Section 3.2.2.2. The milling process results in the reduction of powder particle size, yielding ultra-fine and reasonably agglomerated powders.⁶⁸ The properties of the ground

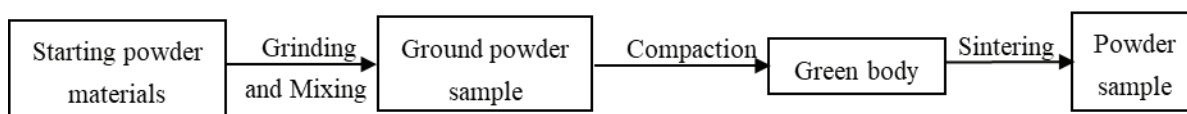


Figure 3.3 Schematic of processes involved in the preparation of a powder sample.

powders depend on parameters such as the duration and the manner of grinding.⁶⁹ These determine the fineness and the level of homogeneity of the ground powders and hence influence the degree of compaction of the powders. In the literature^{21,70}, sintering of rare-earth doped ZnO improves the emission from both the ZnO host and the rare-earth dopant. In addition, other properties such as density, rigidity and crystallinity are improved by the thermal treatment.⁷¹

3.2.2.1. The hand-milling technique and compaction

The hand-milling technique used in this study involves mixing of two or more different types of powders followed by grinding using an agate mortar and pestle. The grinding was performed to encourage interaction between the constituents of the powders and hence form a homogenous mixture. Nd³⁺ doped ZnO (ZnO:Nd³⁺) powders were prepared by first weighing the required masses of the ZnO and Nd₂O₃ starting materials. A typical calculation for determining the mass of Nd₂O₃ required for 1g of ZnO is as follows:

$$\text{Mass of Nd}_2\text{O}_3 = \frac{M_r \text{ of Nd}_2\text{O}_3}{M_r \text{ of ZnO}} \times \frac{x}{2} \times \text{Measured mass of ZnO} \quad [3.2]$$

where M_r is the molar mass (= 336.48 for Nd₂O₃ and 81.39 for ZnO), x is the molar percentage of Nd³⁺ (= 1% for example).

Singh *et al.*⁷² reported that addition of lithium (Li) compounds to rare-earth doped ZnO powders enhances the emission from rare-earth ions. The Li⁺ provides charge compensation in the matrix.⁷² For this reason, lithium carbonate (Li₂CO₃) was added to some of the samples used in this study, at molar concentrations of 1%, 5% and 10%.

[†]<https://www.sigmaaldrich.com/south-africa.html>

The carefully measured masses of the constituent compounds were mixed and ground in an agate mortar as shown in Figure 3.4 (a). As indicated earlier, the purpose of grinding was to

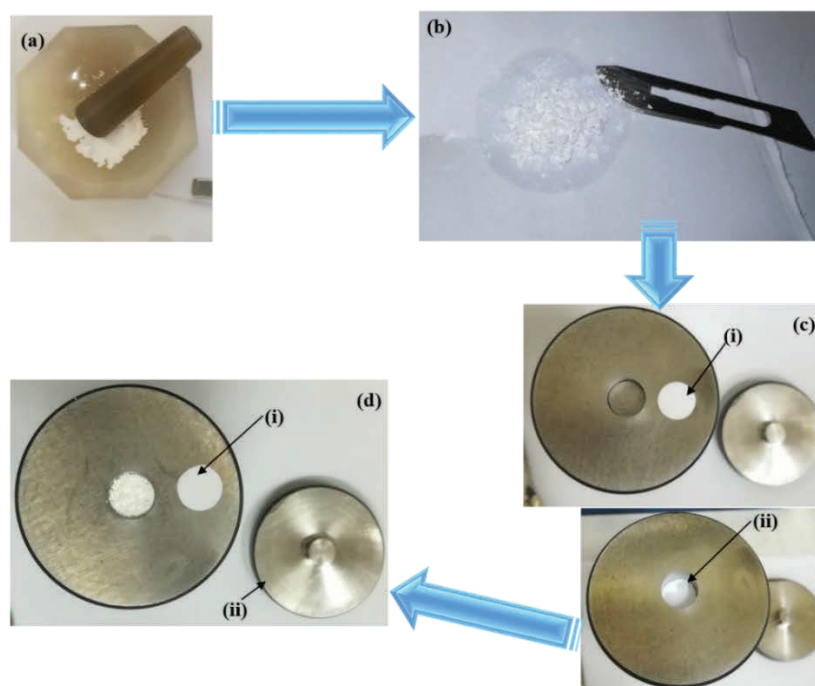


Figure 3.4 Apparatus and sequence of steps used in preparing the pellet: (a) (i) – agate mortar and pestle loaded with starting powder materials, (b) dampening of fine ground powder, (c) preparation of die with (ii) the bottom paper cover in place, (d) mould loaded with powder and the top paper cover (i) showing and (ii) the base of the mould.

obtain a homogeneously doped powder sample. To achieve this, the powder was carefully hand-ground by repetitively moving the pestle against the mortar in an outward spiral manner. This sequence was repeated for a duration of 2 hours per sample. During this process, powder agglomerates were formed as the powders became finer.

For easy handling of the samples, particularly when mounting in a cryostat, the ground powder was compacted to form a pellet, using a manual moulding die and press. This method involves the pressing of the ground powder material whilst it is dry or semi-dry using a moulding die. The procedure of preparing the powder for pressing to form a pellet is illustrated in Figure 3.4 (b) – (d).

The degree of compaction of the powder depends on a number of factors which include the level of agglomeration and the fineness of the ground powder.^{68,73} The agglomerated homogeneous powder formed should not have too big particle sizes as they will hinder the compaction process of the powder. Also, the rate of compaction increases strongly with the decrease in powder particle size.⁶⁸ In this study, in order to minimize the grinding time, nanopowders were used as the starting materials. The optimal grinding time was found to be 2 hours for each sample.

The homogeneous aggregated powder was dampened using a small amount of acetone (Figure 3.4 (b)). This tended to create bigger agglomerates of the powder which were then broken down using a stainless steel scalpel before carefully loading the slightly damp powder into a prepared 10 mm diameter moulding die (Figure 3.4 (c) – (d)).

Loading the damp powder directly into the stainless steel moulding die produced a pellet with undesirable dark spots on its surfaces. To prevent this, for all pellets prepared in this study, two circular shaped pieces (to fit well in the die) of white bond paper (Figure 3.4 (c) (i)) were used as bottom and top covers for the pellet (Figure 3.4 (c) – (d)). Bond paper was chosen over filter paper because it is harder and less fibrous and would not contaminate the sample. These pieces of papers could be easily detached from the pellet after pressing. With the paper discs and the base (Figure 3.4 (d) (ii)) in place, the moulding die was mounted onto the Specac hydraulic press as shown in Figure 3.5, ready for pressing.



Figure 3.5 The Specac Manual Hydraulic Press, with the pellet moulding die in place. (a) the leadscrew, (b) the pressure release valve, (c) pump handle and (d) pressure/load gauge.

The leadscrew (Figure 3.5 (a)) was carefully tightened to hold the moulding die in a central position followed by closing of the pressure release valve (Figure 3.5 (b)). The pump handle (Figure 3.5 (c)) was used to press the pellets uniaxially. The pressing tonnage of 4 T, read from the pressure/load gauge (Figure 3.5 (d)), was achieved by a gradual pump rate of about 1.3 T per minute. The system was held in place for 10 minutes, after which one recovery load (from about 3.5 T back to 4 T) was performed, followed by a 30 minute long hold. The press was then released at the same rate of about 1.3 T per minute. The pellet was carefully removed from the die and the paper covers peeled off. Figure 3.6 shows one of the resulting green body pellets in an annealing boat.



Figure 3.6 A ZnO pellet just after compaction (green body).

3.2.2.2. The sintering technique

Sintering is a process common in powder metallurgy; it involves thermal treatment of powders at a relatively high temperature but below its melting temperature. This heat treatment leads to coarsening and densification of the powders. The combined effect of these changes is improvement in the microstructure of the powders. The most commonly used sintering techniques include solid-state sintering and liquid-phase sintering.⁶⁸ A single phase powder material is used in the former process, whereas a relatively small amount of liquid material (either an additive or one of the starting materials) is required for the latter. The liquid-phase method is more useful for densification, improved rigidity and microstructural homogeneity (compositional, density, grain size) of the powders.⁶⁸ The sintering technique was adopted in this study because of the significant potential benefits of producing doped targets for pulsed laser deposition of thin films as required, easily and at low cost.

The two primary processes that occur during sintering are the densification and the coarsening of the microstructure (grain growth) of the green body, as illustrated in Figure 3.7.⁶⁸ Both processes result from atomic diffusion processes, which will be discussed later in this subsection, and are responsible for the overall reduction in the surface energy of the green body. Densification processes are responsible for the removal of material from the grain boundary regions towards the pores, which results in shrinkage.^{68,74} On the other hand, coarsening involves the re-arrangement of matter between different parts of the pore surfaces without decreasing the pore volume.⁶⁸ In fact, coarsening is the combined effect of grain growth and pore growth, with the associated general decrease in both of their quantities.⁷⁴

The total surface energy of a green body is given by γA , where γ is the specific surface (or interface) energy and A is the total surface (or interface) area of the powder compact. The reduction of the total energy can be expressed as:

$$\Delta(\gamma A) = A\Delta\gamma + \gamma\Delta A \quad [3.3]$$

Here, the change in interfacial energy ($\Delta\gamma$) is due to densification and the change in interfacial area (ΔA) is due to grain coarsening.⁷³ Densification and coarsening often occur concurrently. Coarsening increases the diffusion distance for matter transport leading to a marked reduction

in the densification rate.^{68,74} When densifying diffusion processes are dominant, the sintering process will favour the production of a dense body while the dominance of the coarsening process favours the production of a highly porous body.⁷³

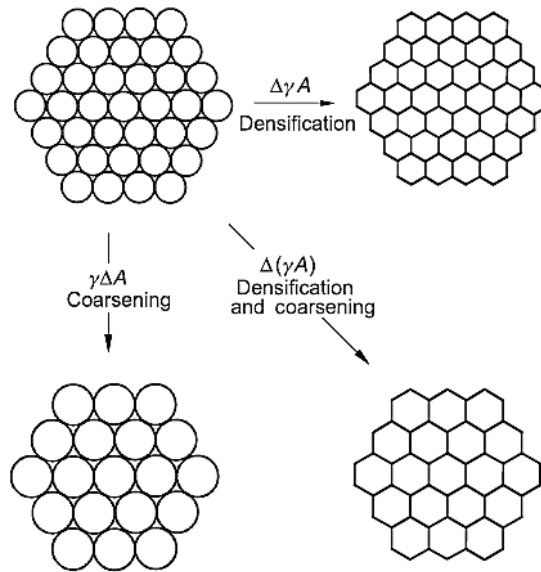


Figure 3.7 The competing phenomena during sintering and the effect(s) expected on resultant sintered bodies.⁷³

As mentioned earlier, densification and coarsening result from diffusion processes. The main diffusion mechanisms involved include surface, volume and grain boundary diffusion. The other mechanisms are vapour transport from evaporation-condensation and plastic flow.⁷⁴ During the diffusion of atoms, there is a significant accumulation of vacancies. This results in the formation of pores observed in the powder compacts. Sintering mechanisms therefore involve the motion and annihilation of vacancies as well. In particular, the motion of vacancies and atoms along the surfaces of grains/particles, grain boundaries and throughout the lattice happens through surface, grain boundary and volume diffusion, respectively, as illustrated in Figure 3.8 (a).⁷⁴ On the other hand, vapour transport mechanism is involved in the movement of atoms and vacancies across the pores and is largely attributed to the formation of necks between grains without any densification or shrinkage. Plastic flow involves the combination of vacancies with dislocations and it plays an important role in compacted powders (green body) where the dislocation density is high. Also illustrated in Figure 3.8 (b) is how the processes in the two-particle system in (a) are translated to a multi-particle system, thereby causing sintering of the material in three stages.^{73,74}

As sintering involves densification, the density of the sample changes through the different stages of the process. The dense random packing of loose powder in (i) of Figure 3.8 (b), prior to compaction, is at a packing density of about 64% of the bulk material density and is not changed noticeably by compaction of the powder.⁷⁴ The initial stage of

sintering as indicated in Figure 3.8 (b) (ii), is characterized by the formation of necks between particles. The inter-particle necks grow to the point where the neck size is less than one-third of the particle size and its contribution to compact shrinkage is limited to 2-3% at most.^{73,74} During the intermediate stage (in Figure 3.8 (b)(iii)), significant densification, up to ~93% of

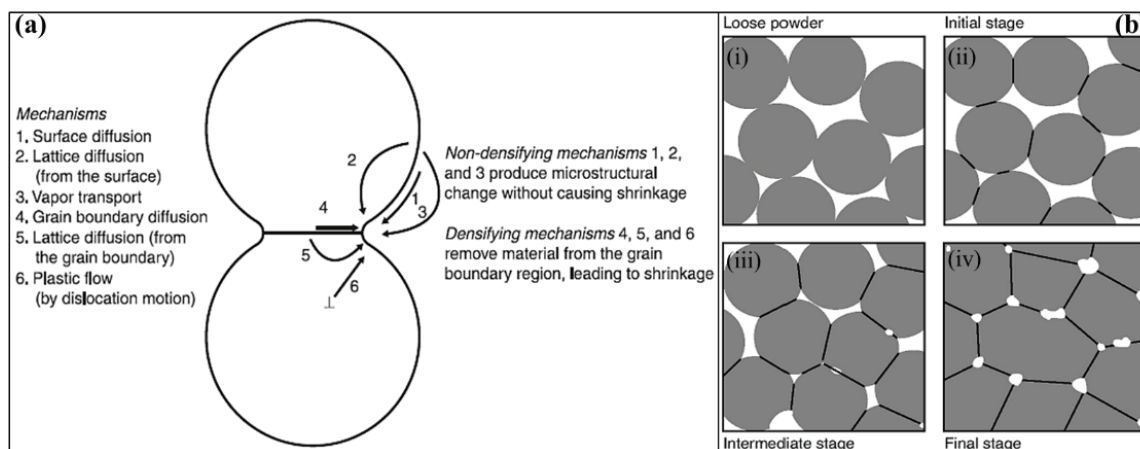


Figure 3.8 (a) The schematic illustration of diffusion mechanisms for a two-particle system and (b) the three sintering stages showing changes in pore structure during sintering.⁷⁴

the relative density, occurs before isolation of the pores.⁷³ This stage is characterized by coalescence between one-third and a half of the particle size.⁷⁴ The final stage, (iv), involves densification from the isolated pore state (elimination of the last 7 – 8% porosity) to the final densification.^{73,74} Apart from the suitable properties of the ground powder and the method of compaction, there are additional variables to be taken into account for better sintering. These variables are largely thermodynamic in nature and they include the rate of heating and cooling the powders, sintering time and the environment in which the sintering is occurring.⁷³

Sintering has been observed to commence between 280 °C and 300 °C in ZnO and is more significant above 500 °C.⁷⁵ Therefore sintering temperatures of 600 °C, 750 °C and 950 °C were adopted for the powder samples used in the work presented here (Table 3.1). All the samples were sintered in air. For the sintering, a pellet (green body) was placed in a porcelain sintering boat as shown in Figure 3.6 and placed at the centre of the furnace, immediately after compaction. A ramping rate of 5 °C per minute was used in each case, followed by a 2-hour dwell time. After the dwell time at a set sintering temperature, samples were allowed to cool down to room temperature naturally before removal from the furnace. The slow ramping rate of 5 °C min⁻¹ was chosen to allow for thermal equilibration of the sample at every stage, as demonstrated in Almotari's work.²⁰

The powder samples prepared for this study are listed in Table 3.1 and images of representative specimens are shown in Figure 3.9. Each pellet had 0.400 ± 0.001 g of ZnO, as measured by a precision balance, and the masses of other constituents were determined

accordingly using Equation 3.1. Three green body (unsintered) pellets identified with RT, for room temperature, (as indicated in Table 3.1) were used for reference measurements.

Table 3.1 Information on all samples prepared in this study. RT under sintering temperature identifies green body pellets used as references.

Composition	Sintering temperatures (°C)
ZnO	RT, 600, 950
ZnO:1mol%Nd	RT, 600, 750, 950
ZnO:1mol%Nd:10mol%Li	RT, 600, 950
ZnO:10mol%Li	600, 950
ZnO:1mol%Nd: <i>n</i> mol%Li (<i>n</i> = 1, 5)	950
Nd ₂ O ₃	950

Visual inspection of the powders at each stage of the process shown in Figure 3.3 showed distinct colour changes. The starting powder material of ZnO (before grinding) and the ground powder (before compaction) was pure white. After compaction, the powder became off-white in colour as shown in Figure 3.6. However, after sintering the undoped ZnO powders became pure white as the starting powder material (Figure 3.9 (a)). Such colour changes have been observed before.⁷⁵ In the case of the doped powders, the pellets had an off-green colour which was intensified by co-doping with Li and annealing at a higher temperature (950 °C). The off-green colour (Figure 3.9 (c)) is as a result of mixing blue and white colours from sintered Nd₂O₃ (Figure 3.9 (b)) and ZnO (Figure 3.9 (a)) powders, respectively.

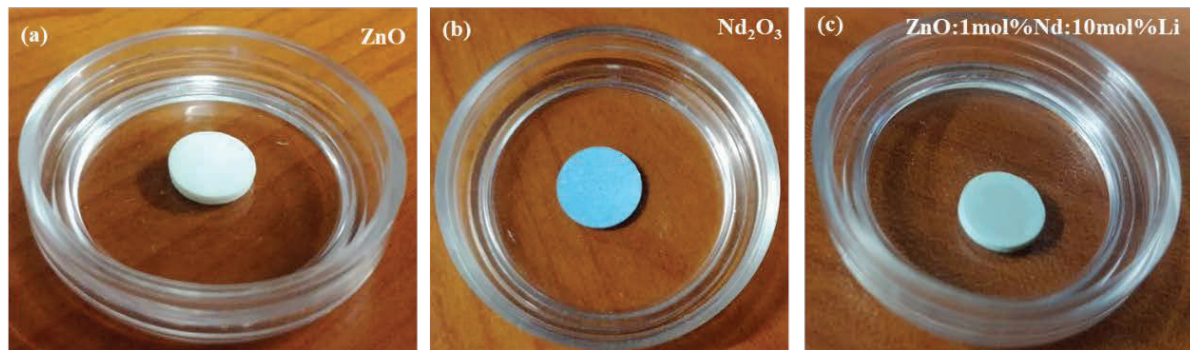


Figure 3.9 The appearance of (a) undoped ZnO, (b) Nd₂O₃ and (c) ZnO:Nd:Li pellets sintered at 950 °C. Each pellet prepared with 0.400 g of ZnO had the dimensions of 1 cm diameter and 0.1 cm thickness.

The densities (ρ_{sample}) of the non-sintered and the sintered pellets were measured using the Archimedes principle. The relative densities of the samples, obtained from the expression $(100 \times (\rho_{\text{sample}} / \rho_{\text{bulk ZnO}}))$ using 5.65 g/cm³ as the density of bulk ZnO²⁰ ($\rho_{\text{bulk ZnO}}$), are presented in Table 3.2. The density values for both unsintered and sintered pellets lie within the acceptable range for an adequately sintered sample.⁷⁴ However, optimization of the sintering parameters (dwell time and ramping rate) may be necessary to further improve the relative densities.

Table 3.2 Relative densities of the as-prepared (green body) and sintered samples.

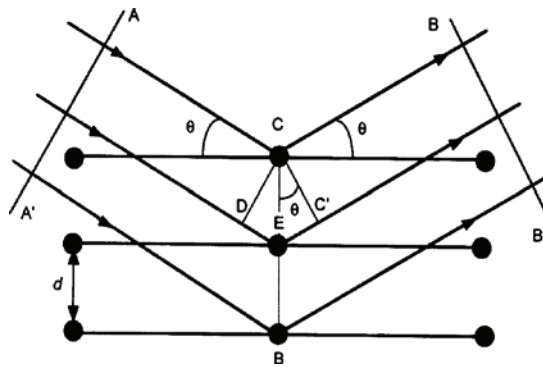
Sample and conditions	Relative density ($\pm 3\%$)
Green-body ZnO; undoped and Nd-doped	66
ZnO; undoped and Nd-doped, annealed at 600 °C	73
ZnO; undoped and Nd-doped, annealed at 750 °C / 950 °C	79
ZnO; Nd and Li co-doped, annealed at 950 °C	92

3.3. Characterization techniques

To characterize the structure, the morphology and chemical composition of both the films and the pellets, the techniques of X-ray diffraction, scanning electron microscopy, energy dispersive X-ray spectroscopy, respectively, were employed. The main features of each technique are highlighted below.

3.3.1. X-ray Diffraction (XRD)

X-ray diffraction (XRD) is useful for determination of structural properties such as crystal structure, orientation and the quality of single crystals as well as polycrystalline films.⁷⁶ The lattice of a crystal in a material consists of regularly spaced atoms, characterized by a particular inter-planar distance or spacing, d , as shown in Figure 3.10. X-rays are electromagnetic waves whose wavelength is of the same order of magnitude as the inter-planar spacing.^{76,77} Each of the individual atoms in the lattice therefore acts as a scattering centre for X-rays. Consideration

**Figure 3.10** Diffraction of X-rays by a crystal.⁷⁷

of the overall scattering effects from a large number of atoms which lie in the path of the incident X-ray beam yields useful information. The X-rays scattered by the atoms have definite phase relations between them. Most directions of the scattering result in destructive interference, but in a few directions constructive interference occurs, which in turn leads to diffraction patterns. Diffraction of the X-rays only takes place at particular angles of incidence which satisfy Bragg's law,^{76,77} given by:

$$n\lambda = 2d \sin \theta \quad [3.4]$$

where n is an integer known as the order of reflection, λ is the wavelength of the incident X-rays and θ is the Bragg angle.^{76,77}

XRD measurements yield crystal structure parameters and the crystallite sizes. These are determined in a two-step process that involves indexing of the pattern and calculation of the lattice parameters. In the indexing part, if the material is known, a measured spectrum is compared to the standard patterns from JCPDS data files or a CIF file of the same material recorded with the same X-ray source. All peaks in the two spectra should match and in cases where different X-ray sources (i.e. not copper source) are used, a correction for shifts in peak positions should be effected before the comparison.⁷⁷ For example, when a cobalt source with

wavelength λ_{Co} is used the peaks are shifted by a factor of $\Delta\theta = 2 \left[\sin^{-1} \left[\frac{\left(\frac{\lambda_{Co}}{\lambda_{Cu}} - 1 \right) \sin \theta_{Cu}}{2 \cos \left(\frac{\theta_{Cu} + \theta_{Co}}{2} \right)} \right] \right]$ to

higher 2θ values compared to values obtained with a Cu X-ray source with wavelength λ_{Cu} .⁷⁷ The Miller indices hkl and the plane corresponding to each peak in the measured spectrum are identified and hence the crystal structure of the material will be known. Assuming a cubic crystal structure of lattice parameter a , the d_{hkl} spacing is related to the lattice parameters by the expression

$$\frac{1}{d_{hkl}^2} = \frac{h^2 + k^2 + l^2}{a^2}, \quad [3.5]$$

where hkl are the indices of the observed Bragg reflexes. Similarly, for a hexagonal crystal system,

$$\frac{1}{d_{hkl}^2} = \frac{4}{3} \left[\frac{h^2 + k^2 + l^2}{a^2} \right] + \frac{l^2}{c^2}, \quad [3.6]$$

where a and c are the lattice parameters.⁷⁷ Secondly, in order to obtain the average size of the crystallites (S) in each sample, the Debye-Scherrer's equation (Equation 3.7) is used.⁷⁷

$$S = \frac{k\lambda}{P_{FWHM} \cdot \cos \theta}, \quad [3.7]$$

where k is equal to 0.9, λ is the wavelength of the X-ray source, P_{FWHM} is the full width at half maximum intensity of each diffraction peak after correction for line broadening using a standard (usually LaB₆) and θ is the diffraction angle. Also, the ratio of the lattice parameters c and a can be calculated. The lattice parameters can also be determined through Rietveld refinement of the data. A crystal information file (CIF) file is used for structure matching.

The primary components of an X-ray diffractometer are the X-ray source, the specimen stage and an X-ray detector. All parts lie on the circumference of a circle, known as the focusing circle, as illustrated in Figure 3.11.⁷⁷ The Bragg angle, θ , is the angle between the plane of the

sample and the source of the X-rays. The angle between the projection of the X-ray source and the detector is 2θ . Hence, the X-ray diffraction patterns obtained with this particular geometry are referred to as θ - 2θ (theta-two theta) scans. In this θ - 2θ geometry, the X-ray source is fixed

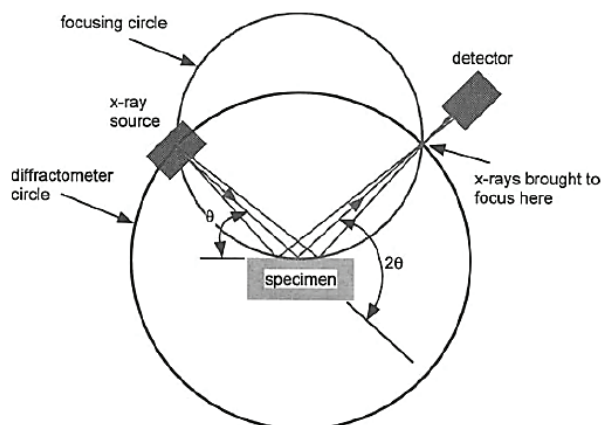


Figure 3.11 The theta-two theta (θ - 2θ) geometry of an X-ray diffractometer.⁷⁷

while the detector and the sample sweep through a range of angles such that the θ - 2θ condition is maintained.⁷⁷ It is important to note that in this Bragg-Brentano geometry, the scattering vector is usually normal to the surface of the sample. The X-ray source can be copper, molybdenum, cobalt or chromium.⁷⁷ However, the most commonly used source is copper.⁷⁷

In this study, a Bruker AXS D2 Phaser desktop diffractometer was used for characterization of the powder samples. The diffractometer employs a sealed tube Co X-ray source and is equipped with a Bruker Lynxeye PSD detector. For beam refinement, a 2.5° secondary beam radial Söller slit and Fe filter are employed as additional optical components. All spectra were recorded with a step size of 0.026° as determined by the equipment. The crystalline phases (structure types) present in the samples were identified and the diffraction peak positions were used to determine the lattice parameters. Changes in the crystallite size were also determined. A Bruker D8 discover equipped with a Cu X-ray source and a Ge022 monochromator was used to measure the grazing incidence X-ray diffraction (GIXRD) of the film samples. Each spectrum was recorded for 2θ values in the range 20 to 80 degrees.

3.3.2. Scanning Electron Microscopy (SEM)

Scanning electron microscopy (SEM) allows for surface and morphology investigations of materials at moderately high magnifications. Figure 3.12 (a) shows the schematic diagram of a general SEM system. Its primary building blocks are (i) the microscope column and (ii) the measurement/imaging controls.⁷⁸

The microscope column houses an electron gun and a couple of lenses which focus the electrons on the specimen (top surface of the sample) and the detector. Electrons are accelerated to energies typically in the 0.1 – 30 keV range. The scan coils are two pairs of electromagnetic

deflection coils that are used to sweep the electron beam across the specimen. The first pair of coils deflects the beam off the optical axis of the microscope and the second pair bends the beam back onto the axis at the focal point of the scan.⁷⁸ This allows the beam to move to a series of discrete locations along a straight line, on a row by row basis, until a rectangular 'raster'

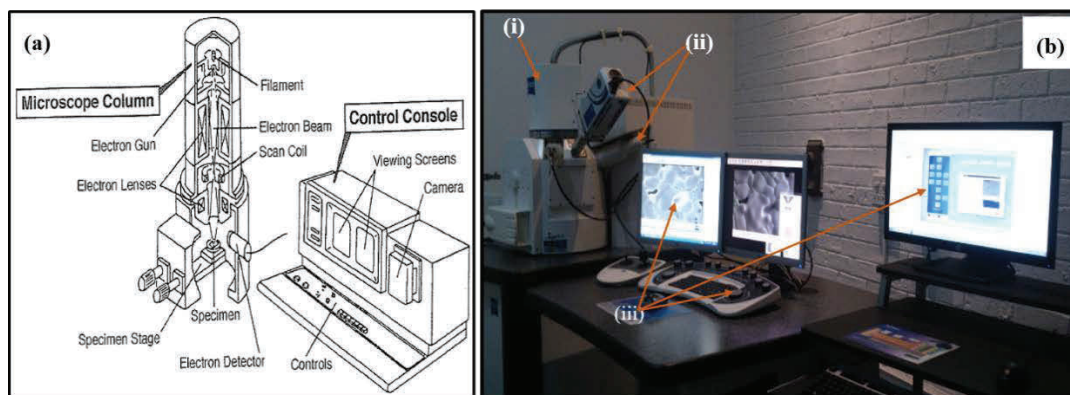


Figure 3.12 (a) The basic building blocks of a scanning electron microscope.⁷⁸ (b) Zeiss GeminiSEM system used for SEM sample characterization: (i) – microscope column, (ii) – detectors, and (iii) – controls and screens.

is generated on the specimen. The raster is displayed on the viewing screen as it builds up. The magnification of the image is the ratio of the length of the raster on the viewing screen to the corresponding length of the raster on the specimen.⁷⁸ Electron lenses de-magnify an otherwise too large starting spot size (from the gun), to produce a much smaller and well-focused electron spot. The small electron spot emerging from the final lens interacts with the sample surface to generate signals used to ultimately form the images. Vertical adjustments to the base of the electron column are made possible by the use of vacuum pumps which can reduce the pressure down to $\sim 10^{-4}$ Pa.⁷⁸ A Zeiss GeminiSEM system, shown in Figure 3.12 (b), was used in this study.

The interaction of the electrons with the specimen, involves elastic and inelastic scattering processes. Inelastic interactions are accompanied by an electron energy loss. In some instances these interactions may give rise to secondary electrons (SE), backscattered electrons (BSE), Auger electrons (AE) and X-rays (X) as illustrated in Figure 3.13.⁷⁹ The image of the specimen is formed as a result of elastic- and inelastic-scattering processes.⁷⁹ After interaction with the specimen, the electrons will have a finite depth range R of the order of 10 nm – 10 μ m (Figure 3.13). This depth range is dependent on the energy of the electron and the density of the target. SEM measurements provide topological, morphological and compositional information of the top surface of the sample.

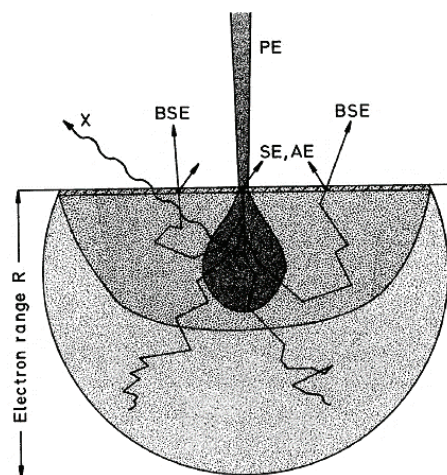


Figure 3.13 The origin and information depth of secondary electrons (SE), backscattered electrons (BSE), Auger electrons (AE) and X-ray quanta (X) in the diffusion cloud of electron range R for normal incidence of the primary electrons (PE).⁷⁹

3.3.3. Energy-Dispersive X-ray Spectroscopy (EDS)

The energy-dispersive X-ray spectrometer (EDS) is a useful tool for determining the elemental composition of a sample. The technique employs X-ray spectrometry and relies on the characteristic X-rays generated from a sample. The EDS capability is now a common feature on most electron beam instruments such as the SEM and transmission electron microscope (TEM).⁷⁸

The EDS detection set-up is as shown in Figure 3.14. A thin Be window isolates the sample chamber from the detector. The probing part of the detector is made up of a reverse-biased p-i-n Si(Li) crystal.⁷⁸ X-ray photons from the sample are transmitted through the Be window into this detector.

The emitted X-rays from the sample are absorbed by the intrinsic region of Si(Li) detector to produce electron-hole (e-h) pairs. The e-h pairs are then swept apart by an applied bias voltage to form a charge pulse which is then converted into a voltage pulse using a charge-to-voltage converter (pre-amplifier). Each voltage pulse is proportional to the energy of the incoming X-ray photon.⁷⁸ Further amplification and shaping of the signal is followed by transmission to a computer for further analysis. Data can be analysed in the form of peak identifications and quantification.⁷⁸

The EDS set-up used in this study formed part of the Zeiss GeminiSEM microscope used for SEM imaging (Section 3.3.2, Figure 3.12). EDS measurements can detect elements with atomic number up to ~ 50 , however becomes less efficient for atoms with atomic numbers lower than 30.⁷⁸ Concentration detection limits for an EDS system depend on factors including the data acquisition time, background corrections and the line energies of the elements in the specimen.⁷⁸ Heavy elements such as Nd have both K and L line energies as compared to the

Zn and O elements with K lines only hence they tend to give higher detection limits due to lower peak-to-background ratio as compared to lighter elements.⁷⁸

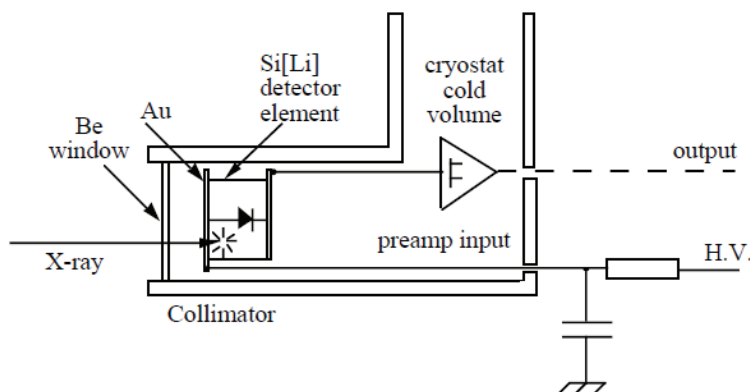


Figure 3.14 Schematic of the setup for EDS detection.⁷⁸

3.4. Photoluminescence (PL)

Photoluminescence (PL) is the emission of light from a material that has been excited by a photon. In this process, an electron absorbs energy from a photon, moves from its ground state to an excited state and subsequently emits energy radiatively.⁹ In radiative emission, light is emitted whereas in non-radiative decay the energy from a photon is dissipated to the lattice as heat through generation of phonons. The wavelength of the emitted light (in the range of UV-VIS-NIR) is characteristic of the luminescent material. Photoluminescence can be further classified as either (a) intrinsic luminescence – emission of light from a nominally pure material (ZnO, for example), or (b) extrinsic luminescence – light emitted by impurities which are intentionally added into a host material (Nd³⁺ ions doped into ZnO, for example).^{9,80}

The duration of the interval between the absorption process and the emission is known as the life-time, τ . This parameter is used to classify the luminescence process as either fluorescence ($\tau < 10^{-8}$ s) or phosphorescence ($\tau > 10^{-8}$ s). Fluorescence emission occurs for as long as the exciting radiation is present and stops immediately when the source of radiation is removed while phosphorescence continues for some time after removal of the radiation source. Both processes are dependent on the types of both the host material and the emitting ion.^{9,80}

In this study, the luminescence properties of intrinsic defects in ZnO and extrinsic Nd³⁺ ion defects in ZnO were studied for samples in the form of films and powders. Low-temperature (10 – 75 K) spectroscopic studies were conducted using excitation wavelengths in the 457 nm – 515 nm range (from the argon-ion laser) and 570 nm – 640 nm range (from a dye laser). The fluorescence life-times of the ⁴F_{3/2} multiplet of Nd³⁺ ions in two different configurations in the ZnO lattice were measured for the powder samples. Due to low signal intensity, it was not possible to measure fluorescence life-times for the films.

3.4.1. Emission and excitation spectral measurements

The components of a PL measurement set-up are the laser source, monochromator, detector and various optical components such as lenses and mirrors for directing the laser and collecting the PL signal. The PL system used in this study is configured as shown in Figure 3.15. A pictorial view of the system is shown in Figure 3.16. The optical chopper and the multi-channel analyzer (Figure 3.15) only form part of the set-up for the life-time measurements to be discussed in Section 3.4.2. For exciting the sample directly with the argon ion laser, the dye laser is removed

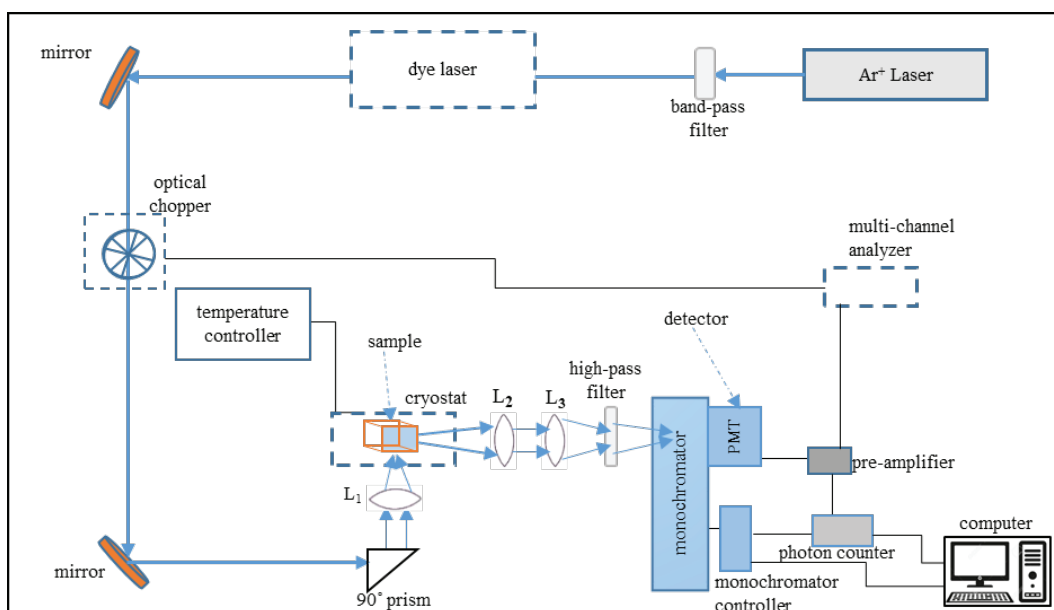


Figure 3.15 The schematic diagram of the PL system used in this study.

from the set-up and the Ar^+ beam of light is passed through an appropriate band-pass laser filter before interacting with the sample in the cryostat. The four Ar^+ laser lines: 457.9 nm, 476.5 nm, 488.0 nm and 514.5 nm were used. For the dye laser excitation studies, the Ar^+ laser set at 514.5 nm was used to pump a dye laser (Spectra-Physics, model 375B) with a continuous flow of Rhodamine 590 dye. The dye laser which is tunable in the 570 nm– 640 nm range was then used to excite the Nd^{3+} ions directly and its wavelength setting was read off a WaveMate wavelength meter. The same optical components as for Ar^+ excitation were used to direct the dye laser output beam to the sample. Using the focusing lens (L_1), the laser beam was made to illuminate the surface of the sample facing the entrance slit of the monochromator (highlighted face, Figure 3.15). Defocusing the laser beam slightly reduced the amount of reflected laser beam collected with the PL signal from the sample. For excitation with the Ar^+ laser lines, laser powers of 35 mW and 50 mW were used for films and powder samples, respectively. A lower value range was used for the thin films in order to prevent damage due to overheating. In the case of excitation with the dye laser, output power of about 70 mW was achievable with 1.0 W Ar^+ laser pump power. Two-thirds of the argon ion laser or dye laser output power was

registered close to the sample due to losses along the nearly 4 m beam path. For consistency, constant power values as well as same laser spot sizes were used in all excitations.

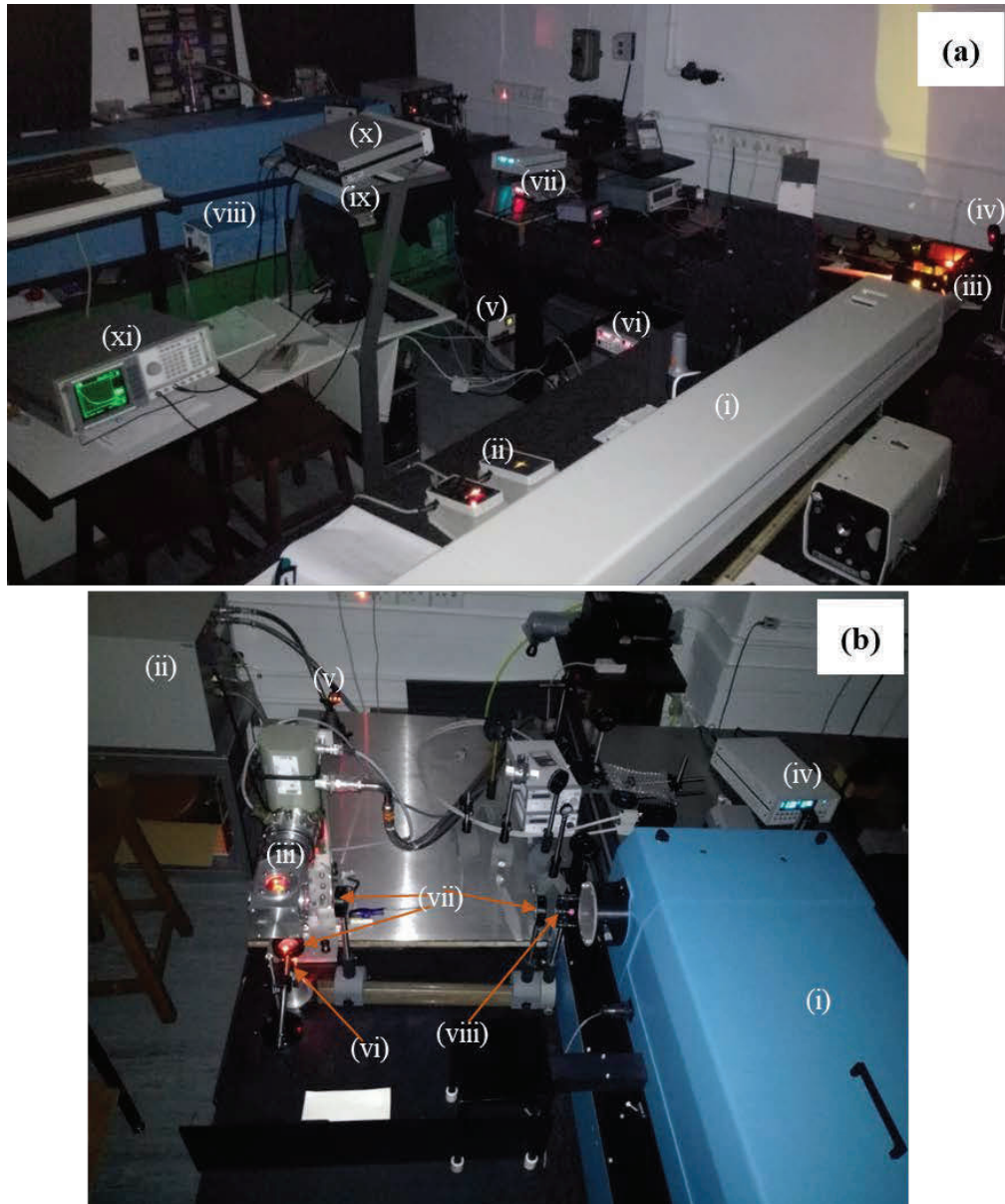


Figure 3.16 (a) Pictorial view of the setup used for PL measurements. (i) – laser source, (ii) – laser console, (iii) – dye laser, (iv) – mirror, (v) – photo-cooler, (vi) – high voltage power supply, (vii) – optical chopper controller, (viii) – monochromator controller, (ix) – pre-amplifier, (x) – photon counter, (xi) – multi-channel analyzer and (b) (i) – monochromator, (ii) – He compressor, (iii) – cryostat, (iv) – sample temperature controller, (v) – mirror, (vi) – 90° prism, (vi) – lense, (vii) – high-pass filter.

The sample was mounted in a Janis CCS-150 closed-cycle cryostat (model 22) shown in Figure 3.16 (b) (iii). The cooling of the sample in the cryostat is achieved by using the compression-expansion of cycled helium gas (Figure 3.16 (b) (ii)) and the temperature of the sample was monitored by a LakeShore temperature controller (model 331) shown in Figure 3.16 (b) (iv). Measurements were conducted with the samples at temperatures ranging from 10 K to 75 K.

Fluorescence was collected with a pair of adjustable lenses (L_2 and L_3) and passed through an appropriate high pass filter before reaching the entrance slit of the monochromator, as shown in Figure 3.15. The 495 nm filter was used with the 457.9 nm, 476.5 nm and 488.0 nm excitation wavelengths whilst a 530 nm filter was selected for the 514.5 nm excitation line. A 2 m McPherson model 2062DP monochromator (Figure 3.16 (b) (i)) fitted with a 1200 grooves per millimetre grating, which is blazed at 500 nm, was used. This monochromator is equipped with a model 789A-3 monochromator controller (Figure 3.16 (a) (viii)). The measured wavelengths are reproducible to 0.005 nm. Slit widths of 150 μm and 500 μm were used for collection of strong and weak PL signals, respectively. Scanning step sizes of 0.200 nm and 0.500 nm were used with the narrow and wider slits, respectively. Longer integration periods of 2 s or 4 s were used in the case of weak signals in order to improve the signal to noise ratio.

The output from the monochromator was detected by a Burle model C31034-A02 photomultiplier tube (PMT) and converted into an electrical signal. The PMT's characteristics which include very low noise, high response rate and high internal gain make it suitable for detection of the low-intensity signals encountered in PL measurements. The photomultiplier tube was cooled to -40 °C with a Photocool™ series photocooler (Figure 3.16 (a) (v)) and was operated at -1350 V using a Stanford model PS325 high voltage power supply (Figure 3.16 (a) (vi)). The electrical signal from the PMT was processed with an SR445A pre-amplifier and an SR400 photon counter, as shown in Figure 3.16. The data was recorded using a McPherson software package.

The Nd^{3+} ions were excited either indirectly or directly as discussed in Section 2.4.3. For indirect excitation, each of the Ar^+ laser lines was used. The Ar^+ laser wavelengths do not match any of the Nd^{3+} multiplet positions. However, both Nd^{3+} and intrinsic defect emissions were observed under these conditions. For direct (resonant) excitation, specific wavelengths from the dye laser emission matching particular $^2G_{7/2}; ^4G_{5/2} \rightarrow ^4I_{9/2}$ transitions of the Nd^{3+} ions were used.

To complement the emission characteristics of the Nd^{3+} ions doped into ZnO films and powders, excitation spectra were measured for the same samples in the 10 K – 75 K temperature range. An excitation spectrum determines the range of wavelengths within the dye range producing a particular emission spectrum from the ion. It is obtained by scanning the dye laser over the dye range (570 nm – 640 nm) while monitoring a particular emission transition. Fluorescence spectra and excitation spectra for the Nd^{3+} ions (i.e. obtained with the dye laser) were recorded at 10 K, 20 K, 50 K and 75 K. The temperature dependence in both types of spectra is useful for the analysis, especially for deducing the energy level scheme. Peaks decreasing in intensity with increasing temperature are assigned to transitions from the lowest level of the emitting multiplet to the levels of the ground multiplet while those increasing with

increasing temperature are from the higher level of the emitting multiplet to the ground multiplet levels, as discussed in Section 2.4.2.

Although the resolution of the monochromator used in this study is limited to ± 0.05 nm by the grating, the monochromator wavelength positions are to four decimal places. In the results presented in this work, the wavelengths are used to calculate energies in either wavenumbers or electronvolts. The wavelength readings are therefore truncated to three decimal places so as to minimize rounding-off errors in the resulting crystal-field level and phonon energies. The wavenumber and electronvolt units are required for deducing energy levels and phonon modes.

3.4.2. Life-time measurements

Since the samples used in this study emitted light only with the incident radiation present, it was clear that there was no phosphorescence. All the observed emission is therefore fluorescence. The life-time of the $^4F_{3/2} \rightarrow ^4I_{9/2}$ fluorescence for the ZnO:Nd³⁺ powder samples was measured while exciting the $^2G_{7/2}; ^4G_{5/2} \rightarrow ^4I_{9/2}$ transitions with the dye laser. Fluorescence from the ZnO:Nd³⁺ films was too weak for life-time measurement. The life-time of a multiplet is the time an excited ion spends in the particular excited state before emitting a photon and returning to the ground state. This parameter can be measured in either the frequency or the time domains⁸¹. The time domain approach, which was used in this study, involves the illumination of a sample with a short-duration pulse of light ($\sim$ ns, ps, fs), followed by measuring the emission intensity as a function of time. The life-time is then determined from the equation of the fitted exponential decay curve.

The dye laser option of the set-up in Figure 3.15 with the optical chopper and the multi-channel analyzer in place was used. The chopper was set to a frequency of 40 Hz and the life-time measurements were conducted for powder samples at 10 K only due to much reduced intensity at the higher temperatures. Fitting an exponential decay curve to the measured data enabled determination of the life-times of the $^4F_{3/2}$ multiplet.

CHAPTER 4

RESULTS AND DISCUSSION FOR ZnO:Nd³⁺ FILMS

4.1. Introduction

For above band-gap excitation, emission from ZnO intrinsic defects is characterized by a UV band-edge emission peak and a broad peak in the visible to near-infrared region.⁶ Below band-gap (370 nm – 515 nm) excitation does not yield the band-edge emission.¹² The broad-band (visible to near-infrared) is a result of contributions from many defects with emission peaks in the blue, green, yellow, orange, red and near-infrared regions.^{12,16,18} Transition mechanisms for the visible emission involve the intrinsic defect centres of ZnO, as discussed in Section 2.2.3, and the unintentional impurities such as copper or iron.¹² Also included are donor-acceptor and deep-shallow level transitions.¹² The nature of defects responsible for photoluminescence in ZnO may vary in different samples, dependent on the type of sample (film or powder, for example) and the method of preparation. Radio-frequency magnetron sputtering was used to deposit films for this study and the effects of varying the gas environment for deposition on the photoluminescence and on the type of defects contributing to the photoluminescence profile were investigated.

Films that were used in this study can be classified into two categories namely, the unannealed and the annealed ZnO:3wt%Nd³⁺ (= ZnO:1.5mol%Nd³⁺) films. Annealing of some samples was performed in order to improve intrinsic-defects emission intensities, as reported by Bhebhe.¹⁶ The annealing temperature was 600 °C and the procedure was the same as for sintering, as described in Section 3.2.2.2. The sample characterization results from X-ray diffraction (XRD), scanning electron microscopy (SEM) and energy dispersive X-ray spectroscopy (EDS) are presented in Section 4.2 and the photoluminescence results in the two subsequent sections (Sections 4.3 and 4.4).

As indicated in Section 3.2.1, all the films were deposited for 3 hours, using 100 W power. A varied O₂ environment (0%, 30%, 50%) was used for the doped films while an Ar-only environment was used for undoped ZnO films. Due to subsequent vacuum chamber problems attributed to higher O₂ concentrations, sputtering of undoped ZnO in O₂ atmospheres was not carried out.

4.2. Sample characterization

The driving force for nanotechnology is in the design and fabrication of scalable devices with higher performance benchmarks. Two-dimensional samples with outstanding properties such as those of ZnO films or rare-earth doped ZnO films are of key importance to the field. As such,

it is vital to understand the related structural, morphological and photoluminescence properties of ZnO and ZnO-based nanomaterials in order to fully utilize the samples. The structural characterization and morphological characterization results of films studied will be discussed in Sections 4.2.1 and 4.2.2, respectively.

4.2.1. Grazing incidence X-ray diffraction studies

XRD results obtained for undoped ZnO films deposited in 0% O₂ and for 1.5mol%Nd³⁺ doped ZnO films deposited in a 30% O₂ atmosphere are presented in Figure 4.1. The diffraction peaks at 31.79°, 34.35°, 36.33°, 47.42°, 56.36°, 62.91°, 66.61°, 68.46°, 68.96° and 77.03° observed for the undoped ZnO sample (Figure 4.1 (i)) correspond to the (100), (002), (101), (102), (110), (103), (200), (112), (201) and (004) Bragg planes of wurtzite ZnO.⁸² The XRD patterns of Nd-doped ZnO do not show any additional peaks indicating that there are no new chemical phases relating to the Nd³⁺ dopant. Comparison of spectra (i) and (ii) of Figure 4.1 shows reduced intensity for Nd-doped ZnO films compared to the undoped ZnO films. This indicates that addition of Nd³⁺ ions into ZnO distorted the crystal structure of ZnO due to the macro stresses attributed plausibly to the large ionic radius mismatch between the Zn²⁺ and Nd³⁺ ions.

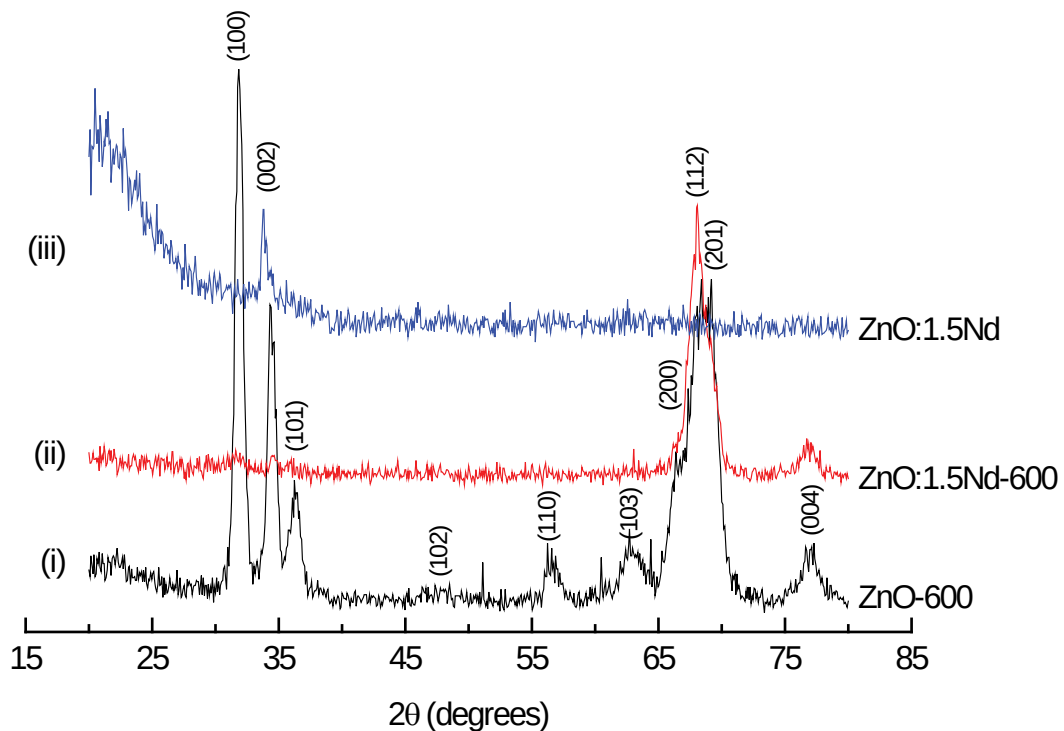


Figure 4.1 XRD patterns for (i) undoped ZnO film (0% O₂) annealed at 600 °C, (ii) ZnO:1.5mol%Nd³⁺ film (30% O₂) annealed at 600 °C and (iii) unannealed ZnO:1.5mol%Nd³⁺ (30% O₂) film. Planes corresponding to the peaks observed for ZnO sample are labelled. A copper X-ray source of wavelength 0.154 nm was used.

Although with weak intensities, observable peaks in the ZnO:1.5mol%Nd³⁺ sample annealed at 600 °C correspond to the (100), (002), (200), (112), (201) and (004) Bragg planes.

The spectra show changes in the preferred growth directions of the films as a result of adding Nd^{3+} dopants to the ZnO host. Whilst the preferred growth directions for the undoped film are (100), (002), (112) and (201), only the (002) direction is preferred in unannealed doped films. Annealing also induced changes in growth directions; comparison of spectra (ii) and (iii) in Figure 4.1 shows that the (112), (201) and (004) are the preferred growth directions post-annealing. The decrease in intensity of the (002) peak after annealing of the doped sample could possibly indicate the prevalence of texture or preferred orientation. This can however be determined from Bragg-Brentano geometry. The spectrum for the unannealed film ($\text{ZnO:1.5mol\%Nd}^{3+}$) shows poor signal to noise ratio compared to the other two spectra in Figure 4.1, which could be ascribed to the amorphous state of the unannealed sample. That is, annealing improves the crystallinity of the samples.^{83,84}

Lattice parameters calculated for the unannealed $\text{ZnO:1.5mol\%Nd}^{3+}$ as well as the annealed ZnO and $\text{ZnO:1.5mol\%Nd}^{3+}$ samples are presented in Table 4.1. Here, the results show that the lattice parameters a and c are not changed significantly by either doping or annealing. The values of a and c obtained for the samples used in the present study are also close to the theoretical values of 0.325 nm and 0.521 nm,⁶ respectively. Comparison between the unannealed and annealed Nd^{3+} -doped samples shows that annealing at 600 °C results in an insignificant shrinkage of up to 2% for the lattice parameters. Since it is known that there is a significant population of intrinsic defects in the as-deposited ZnO films, annealing leads to removal of some of the defects, hence the lattice contracts. In addition, Malevu and Ocaya⁸⁵ suggested that dangling bonds on the surface of ZnO interact with oxygen in the atmosphere and the resulting electrostatic attraction induces some lattice contraction.

Table 4.1 Peak positions of the (002) plane and the calculated crystallite sizes (S) and lattice parameters.

Film sample	2 θ ± 0.01 (°)	Linewidth (2 θ) ± 0.02 (°)	Plane spacing, d ± 0.001 (nm)	Lattice parameters		S ± 1 (nm)	c/a ± 0.01
				a ± 0.001 (nm)	c ± 0.001 (nm)		
ZnO-600	34.45	0.72	0.260	0.325	0.520	12	1.60
ZnO1.5Nd-600	34.41	0.78	0.260	0.325	0.520	11	1.60
ZnO1.5Nd	33.86	0.53	0.264	0.329	0.528	15	1.60

The particle sizes were calculated using the Debye-Scherrer method described in Section 3.3.1 and the results are included in Table 4.1. Comparing crystallite sizes for the unannealed and annealed Nd^{3+} doped ZnO films shows that there is a decrease in the crystallite sizes from annealing. In general, the crystallite sizes tend to increase on annealing due to

smaller crystallites coalescing. However, in Nd³⁺-doped ZnO films, the high concentration of the Nd³⁺ dopants may be hindering the recrystallization process, hence the decrease.

The interplanar spacing of the samples used here is consistent with the experimentally determined value for the (002) plane of wurtzite ZnO (0.260 nm).⁵⁵ From comparison of the experimental interplanar spacing of unannealed wurtzite ZnO⁵⁵ and the spacing of the ZnO:1.5mol%Nd³⁺ film (0.264 nm), it can be deduced that doping increases the spacing slightly. This is due to the incorporation of Nd³⁺ ions which have higher ionic radius of the (99.5 pm) compared with the Zn²⁺ ions (74.0 pm) of the host lattice. Variation in the *c/a* ratios are ways of compensating the changes in the tetrahedral distance between the atoms in the ZnO lattice (Figure 2.1).⁶ This ratio, for ZnO, was not changed by doping with Nd³⁺ ions or by annealing at 600 °C indicating that any induced changes in the tetrahedral coordination were insignificant.

4.2.2. Scanning electron microscopy and energy dispersive X-ray spectroscopy studies

Scanning electron microscopy (SEM) was used to investigate the surface morphologies of undoped and Nd³⁺-doped ZnO films. The SEM images were measured with the same magnification (5 000x) for better comparison and the results are presented in Figure 4.2, together with the corresponding line-scan spectra obtained from energy dispersive spectroscopy, showing constituents in the surface layer of the samples. The graphs in (a)(ii), (b)(ii) and (c)(ii) of Figure 4.2 were obtained by rastering the electron-beam along an 8 µm lateral section on the ZnO:1.5mol%Nd³⁺ and ZnO sample surfaces. The effect of annealing films at 600 °C is illustrated in SEM images (a)(i) and (b)(i) in Figure 4.2 for which a significant increase in sample smoothness is observed. The corresponding line-scan spectra in a(ii) and b(ii) show an even distribution of compositional constituents across the scanned region in both samples, with very low but uniform neodymium (Nd) levels. Uniform distribution indicates that Nd³⁺ ions are uniformly doped into the ZnO films. As explained in Section 3.3.3, the Nd elements were the least detected due to the reduced sensitivity of the line-scan detector to the low energy L lines of Nd. An undoped sample in (c)(i) shows some cracked sections and unevenly distributed layers. Annealing changes the surface energy of the ZnO films, thus enhancing the packing fraction. This leads to variation in tensile stresses in the films during and after annealing and could be responsible for the presence of cracks and vein-like contours in the ZnO films. Cracking of ZnO films deposited by RF sputtering on silicon substrates and annealed at high temperatures was reported in the literature.⁸⁶ Otieno *et al.*⁸⁶ attributed the cracks to tensile stress due to mismatch in anisotropic contraction and thermal expansion of the

ZnO film and the substrate during annealing and after annealing, as the films cool to room temperature. It is not clear why only the undoped film cracked. Besides the points of low intensity which correspond to the cracks, the line scan spectrum of the undoped ZnO film (Figure 4.2 (c)(ii)) does not show any material variations compared to the doped film annealed at the same temperature ((b)(ii)).

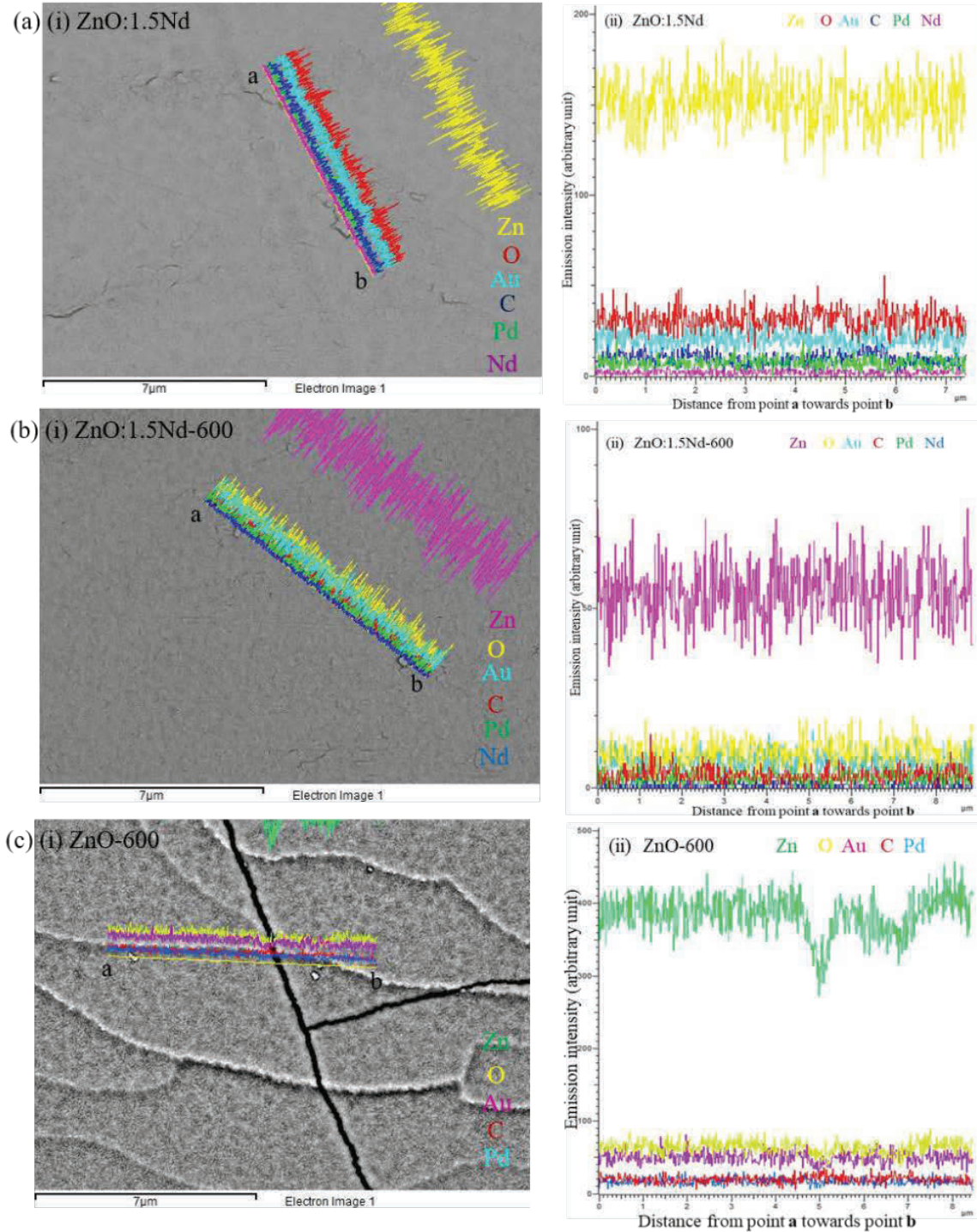


Figure 4.2 SEM images (i) and the corresponding line scans (ii) for Nd³⁺ doped and undoped ZnO films. (a) unannealed ZnO:1.5mol%Nd³⁺ film, (b) ZnO:1.5mol%Nd³⁺ film annealed at 600 °C and (c) undoped ZnO film annealed at 600 °C.

The same SEM facility was used to obtain information on the thickness of the ZnO:1.5mol%Nd³⁺ films. Figure 4.3 shows the cross-sectional views of both the unannealed film and the film annealed at 600 °C. A corresponding view of a substrate that is coated the same way as the samples is included for reference. The appearance of the quartz substrate and the coating in image (i) enabled identification of the film in images (ii) and (iii) of Figure 4.3. Image (iv) shows a section of the film in image (ii) at higher magnification of 30 000x for a clearer view of the cross-section.

Using ImageJ software, at least six readings were taken in order to obtain an average thickness of the sample. One of the lines used to estimate the film thickness is shown in image (iv) of Figure 4.3. The thickness of the unannealed film was deduced to be $2.4 \pm 0.3 \mu\text{m}$. Similar thickness measurements were conducted on the film annealed at 600 °C in order to determine the effect of annealing. The annealed ZnO:1.5mol%Nd³⁺ film however could not be magnified

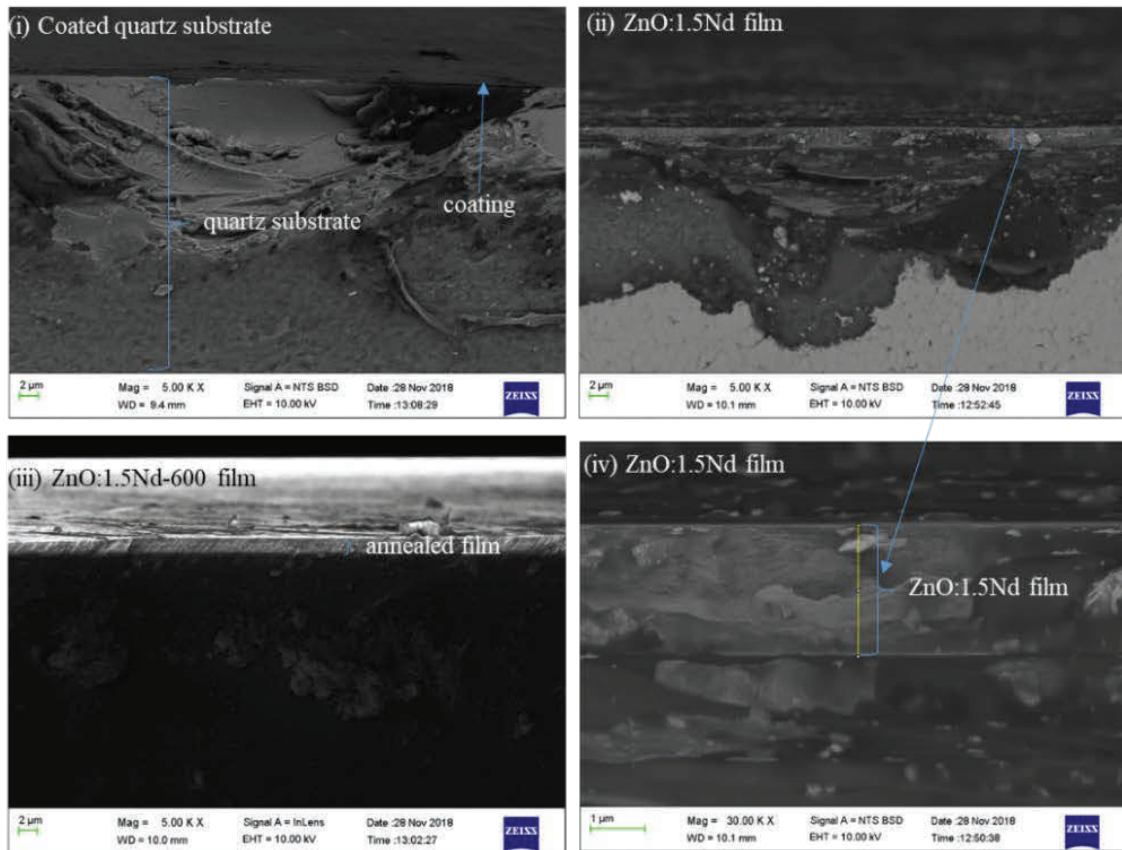


Figure 4.3 Cross-sectional view of (i) blank quartz substrate coated with gold-palladium, (ii) unannealed ZnO:1.5mol%Nd³⁺ film, (iii) ZnO:1.5mol%Nd³⁺ film annealed at 600 °C and (iv) higher magnification (30 000x) of the unannealed film in (ii).

beyond 5 000x as the sample image started showing distortions. With this highest possible magnification (5 000x), the image obtained to show the film is in Figure 4.3 (iii). The thickness of the film after annealing at 600 °C was $1.5 \pm 0.3 \mu\text{m}$. This indicates that annealing of the doped film samples at 600 °C causes a cross-sectional shrinkage of 38% possibly due to removal

of voids. Although undoped films were not considered further because of the poor quality, similar film thickness and shrinkage effects are expected for undoped films deposited under similar conditions.

The elemental composition results obtained from the energy dispersive X-ray spectroscopy (EDS) of samples whose SEM images are presented in Figure 4.2, are shown in Figure 4.4. These EDS spectra are for 25 μm^2 specimen sections and were reproducible for

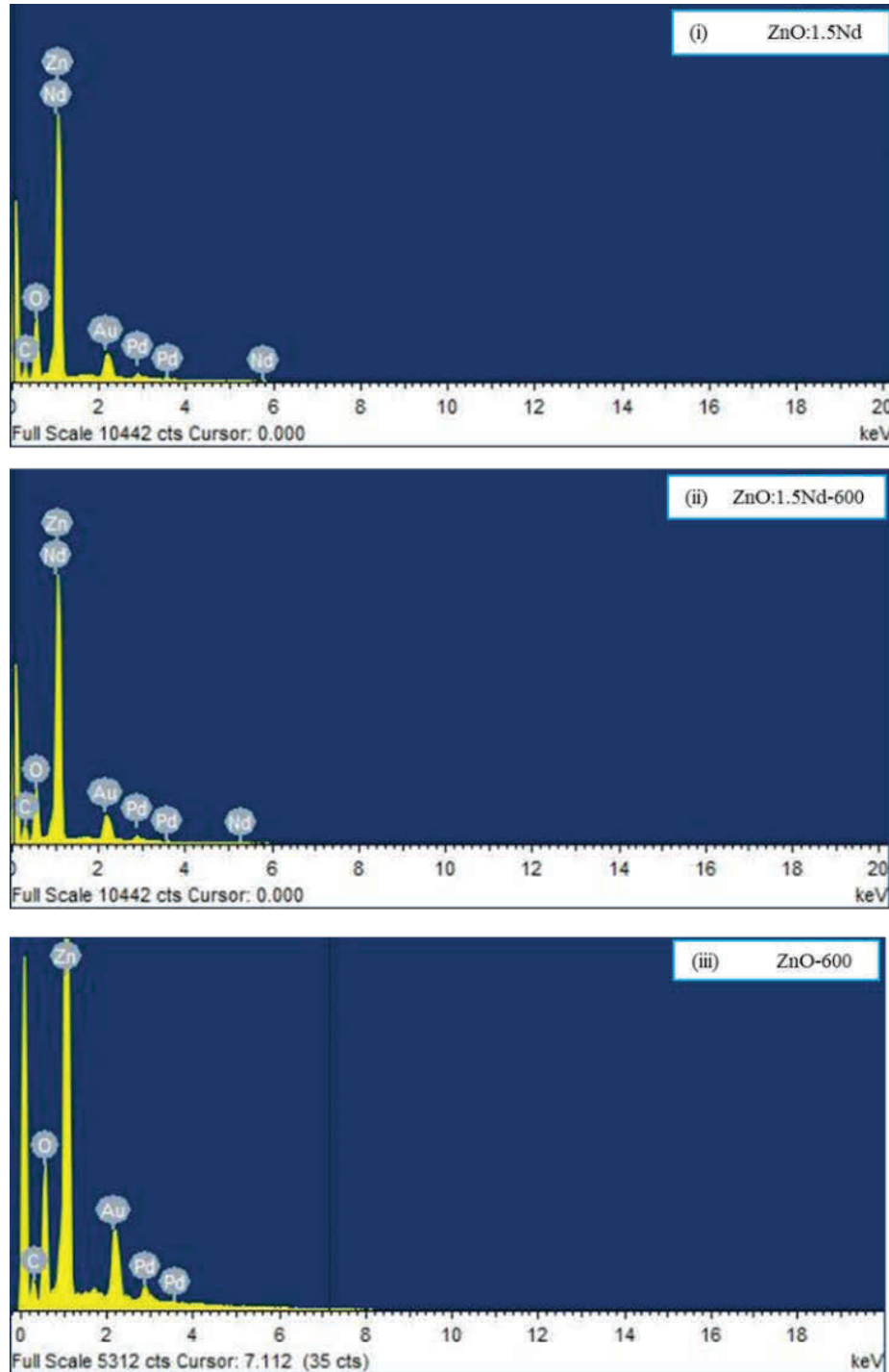


Figure 4.4 EDS spectra of (i) unannealed ZnO:1.5mol%Nd³⁺ film, (ii) ZnO:1.5mol%Nd³⁺ film annealed at 600 °C and (iii) ZnO film annealed at 600 °C. These spectra correspond to SEM images in Figure 4.2.

different sections of the sample. The peak at 0 keV in Figure 4.4 is a reference peak from the detector while the one labelled C is for the carbon tape used to mount the samples onto the stage. Au and Pd peaks are from the gold-palladium coating used to reduce sample charging. This gives improved signal to noise ratio. As expected, Nd peaks were only detected in samples doped with Nd³⁺ ions ((i) and (ii)). The compositional percentages of these samples are presented in Table 4.2; the values have been re-normalized to exclude the C, Au and Pd content.

While a target of ZnO:1.5mol%Nd³⁺ was used for deposition, only about 1.1% was detected in the resulting films, with the EDS system. Since the Nd–O is not a volatile system, losses of Nd through sputtering are unlikely. Furthermore, the films have been sputtered for longer time making any compositional deviation unlikely due to compensation effect. Therefore, the under-reporting of Nd points to the sensitivity of the EDS measurement to the low energy L line of Nd. The EDS system used for this work under-detects the concentration of the dopant by 30%.

Table 4.2 Elemental compositions as detected by energy dispersive X-ray spectroscopy.

Film samples	Elemental composition (mol%)			Film thickness ($\pm 0.3 \mu\text{m}$)
	O	Zn	Nd	
ZnO-600	47.60	52.40	--	--
ZnO1.5Nd	52.47	46.49	1.04	2.4
ZnO1.5Nd-600	49.36	49.47	1.17	1.5

4.3. Photoluminescence (PL) studies with Ar⁺ laser excitation

Radio-frequency magnetron sputtering is mostly used in the manufacture of ZnO films of high quality, tunable morphology and thickness.^{65,66,87} Deposition parameters, including oxygen partial pressure and radio-frequency power, are used to control the physical and structural properties of films. After establishing the RF power of 100 W, the effects of varied oxygen partial pressure were investigated. Photoluminescence spectra for unannealed ZnO:3wt%Nd³⁺ (= ZnO:1.5mol%Nd³⁺) films deposited in 0%, 30% and 50% oxygen partial pressure environments are presented in Figure 4.5. The spectra were measured at 10 K with the 457.9 nm excitation wavelength. Laser power of 25 mW near the sample was maintained for all measurements with the Ar⁺ laser excitation. Doped films show two main results: (i) the broad emission band in the 500 nm – 875 nm region which is from the intrinsic defects in ZnO and (ii) the sharp Nd³⁺ emission transitions in the 875 – 925 nm region.

Figure 4.5 shows that an O₂ partial pressure of 30% resulted in Nd³⁺ emission and had three effects on the broad emission band. Nd³⁺ emission at high oxygen atmosphere was

reported before for Nd^{3+} -doped ZnO films.⁸⁸ For the broad emission, firstly, green-yellow emission in the 500 nm – 600 nm region was decreased by almost half. The green emission component spans from 500 nm to 560 nm and obtains from the $\text{V}_{\text{Zn}}^{2-}$, Zn_i^+ and V_{Zn} defects through the $\text{V}_{\text{Zn}}^{2-} \rightarrow \text{V}_{\text{Zn}}$ and $\text{Zn}_i^+ \rightarrow \text{V}_{\text{Zn}}$ transitions, as shown in Figure 2.4. The yellow emission component extending from 560 nm to 600 nm is due to a transition from the O_i defect, which has an energy level at $17\,041\text{ cm}^{-1}$, to the valence band (Figure 2.4). Decrease in green emission may be due to reduced Zn_i defects as they bond with the added oxygen to form ZnO while reduced yellow emission may indicate that the added oxygen is forming an oxide than occupying interstitial sites. Secondly, emission in the 600 nm – 700 nm region (Figure 4.5) due to the $\text{V}_{\text{Zn}}^{2-} \rightarrow \text{V}_{\text{Zn}}^-$ and $\text{O}_i \rightarrow \text{V}_{\text{Zn}}$ transitions (Figure 2.4) was almost unchanged by depositing in oxygen-rich environments indicating that this orange-red emission is not at all influenced by the excess oxygen. The involvement of the O_i and V_{Zn} defects in the formation of an oxide may be the reason of unchanged intensities. The same effect was reported by Lv and Fang⁸⁹ for ZnO films. Thirdly, a significant increase in emission was observed for the 700 nm – 875 nm region of the broad band. Contributions to this band are mostly from transitions involving oxygen vacancies (V_O) and zinc vacancies (V_{Zn} and V_{Zn}^-) as well as oxygen interstitials (O_i and O_i^-) as shown in Figure 2.4. The increase in this red – near-infrared emission band is attributed to an increased density of the zinc vacancies formed as the zinc combines with the introduced oxygen to form ZnO.¹⁸ It is reported in the literature⁸⁷ that more V_{Zn} , V_O and O_i type defects are generated in films deposited in O_2 environments. In Figure 4.5 the spectrum recorded at 50% O_2 partial pressure has lower intensities than the 30% O_2 . There may therefore be an optimal O_2 partial pressure for harnessing maximum emission intensity for both the Nd^{3+} -ion defects and the intrinsic defects in ZnO.

A spectrum for an undoped ZnO film deposited in an Ar^+ only atmosphere (i.e. 0% O_2 , 100% Ar) is included in Figure 4.5 in order to show the effect of doping on the emission profile. As expected, this sample did not show any Nd^{3+} emission. Also, the broad emission band for this sample did not contain intrinsic-defects emission in the 500 nm – 700 nm as in the doped sample, indicating that emission in this region benefits from additional defects generated by the added Nd^{3+} ions. The spectrum for a blank quartz substrate is included for reference and does not have any peaks.

It is documented in the literature that annealing of undoped ZnO^{16} and Nd^{3+} -doped ZnO^{90} films in air improves their emission intensities due to increased density of deep level states in both cases during the annealing process. With the aim of further improving both Nd^{3+} emission

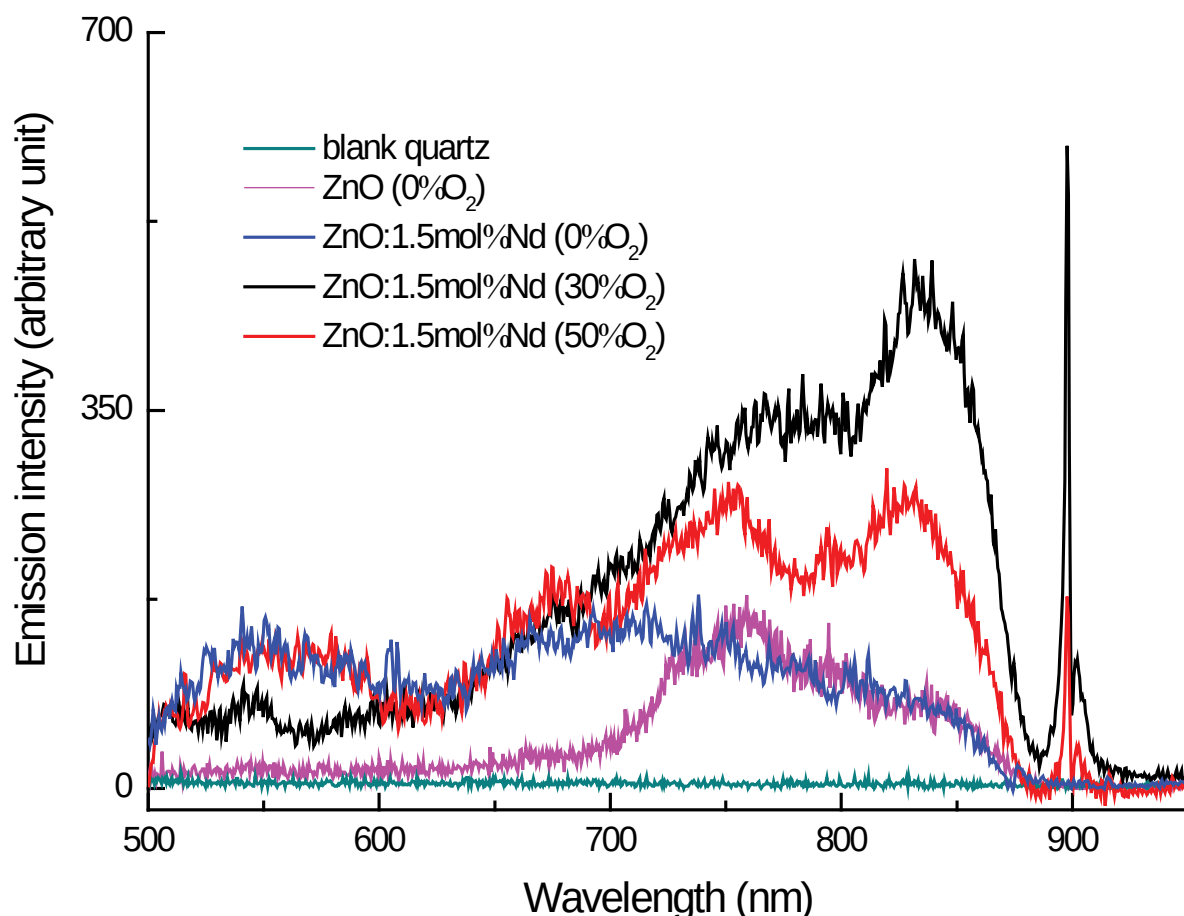


Figure 4.5 Emission spectra recorded at 10 K for unannealed ZnO:1.5mol%Nd³⁺ films deposited for 3 hours, using 100 W power and varying O₂ partial pressure. Spectra for a blank quartz substrate and an undoped ZnO film are included for reference. The excitation wavelength was 457.9 nm.

and intrinsic defects emission, the doped-films deposited in a 30% O₂ environment were annealed at 600 °C – an optimum temperature determined by Bhebhe.¹⁶ The results are presented in Figure 4.6. For reference, an undoped sample was also annealed under the same conditions.

Upon annealing the films at 600 °C, the emission maintained the broad profile while the band intensity was improved by eight times in the 650 nm – 875 nm range (Figure 4.6). The increase in emission intensities in this range is due to increased O_i and O_i⁻ defects generated by annealing in air through oxygen adsorption.⁸³ In addition, annealing improved the Nd³⁺ emission observed in the 875 nm – 925 nm. This could be due to increased density of defects responsible for the population of the emitting Nd³⁺ multiplet (⁴F_{3/2}) as illustrated in Figure 2.9.

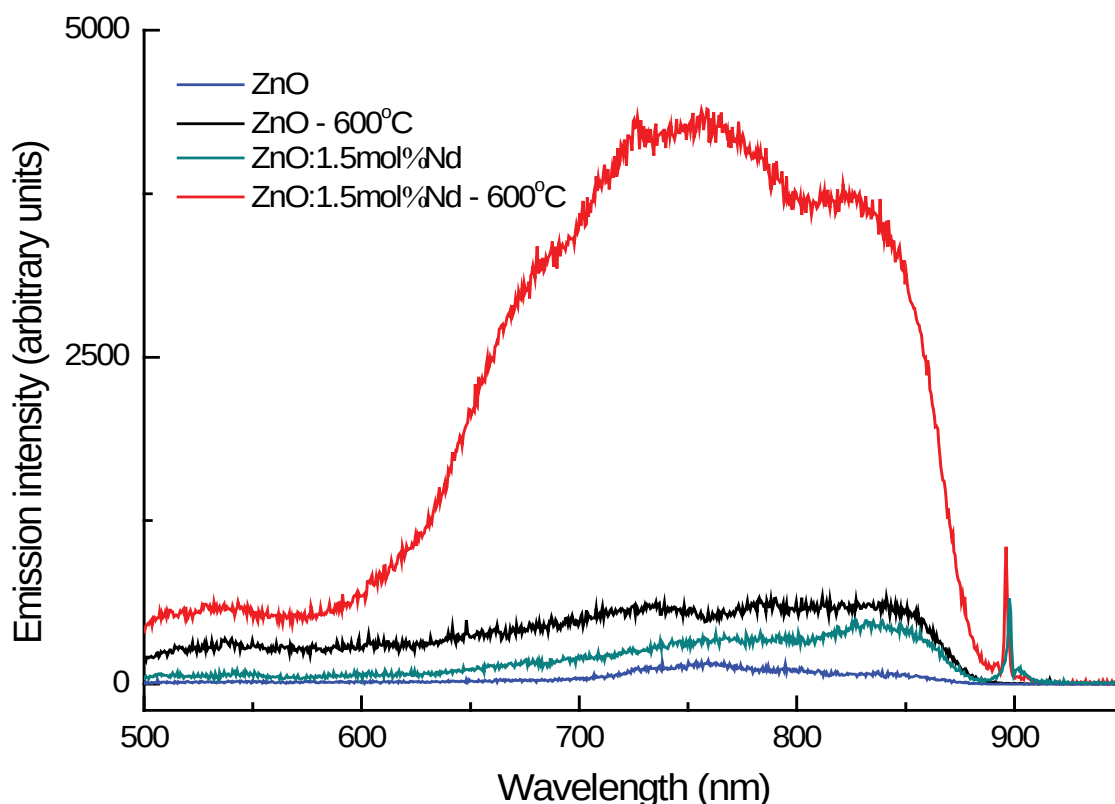


Figure 4.6 Emission spectra recorded at 10 K for ZnO and ZnO:1.5mol%Nd³⁺ films, unannealed as well as annealed at 600 °C. The 457.9 nm excitation line was used.

The effect of varying the excitation wavelength on the emission of both intrinsic defects and Nd³⁺ ions was investigated at 10 K using four excitation lines (457.9 nm, 476.5 nm, 488.0 nm and 515.5 nm) of the Ar⁺ laser. The laser power as well as the laser spot size were kept constant for all measurements. ZnO:1.5mol%Nd³⁺ films, both unannealed and those annealed at 600 °C, were excited with each line in turn and the results are presented in Figure 4.7. Both unannealed and annealed films were used since their emission profiles are different in terms of their intrinsic defects to Nd³⁺ peak intensity ratios. Highest emission intensities for both sample groups (unannealed and annealed) were obtained with the 457.9 nm excitation line (Figure 4.7). The intensities for the other three excitation lines were not significantly different for the unannealed film (Figure 4.7 (a)) while for the annealed film (Figure 4.7 (b)), emission intensities decreased with decreasing excitation energy.

In Figure 4.7, it can be seen that the 457.9 nm excitation wavelength results in enhanced emission in the 650 nm – 875 nm range. Since the emission arises from the O_i → V_{Zn}, V_O → V_B, V_O → V_{Zn}, O_i⁻ → V_B and O_i⁻ → V_{Zn} transitions (Figure 2.4), it means that this shorter wavelength better matches the energies of defect levels contributing to the emission than the other excitation lines. From the intrinsic defects energy level scheme in Figure 2.4, the V_{Zn}²⁻ and Zn_i⁺ defects occur in the 21 094 cm⁻¹ – 22 221 cm⁻¹ energy range and can only therefore, be populated by the 457.9 nm (21 838.8 cm⁻¹) line. Resonant excitation of these two

defect levels will add to the 650 nm – 875 nm emission by non-radiatively populating the O_i , V_O and O_i^- defect states at 17 401, in the range 13 699 cm^{-1} – 14 113 cm^{-1} and at 12 663 cm^{-1} , respectively, as shown in Figure 2.4. The contributing transitions are from the O_i , V_O and O_i^- defect levels to V_{Zn} defects at lower energies and to the VB. There was significant improvement in the intensity of this red – near-infrared emission after annealing. The improvement could be attributed to increased density of V_{Zn} defects with annealing since zinc is volatile. Because of the improved intrinsic-defects emission, the spectrum recorded for the $\text{ZnO}:1.5\text{mol}\%\text{Nd}^{3+}$ film annealed at 600 °C was used for further analysis of the intrinsic defect emission to be discussed in Section 4.3.1.

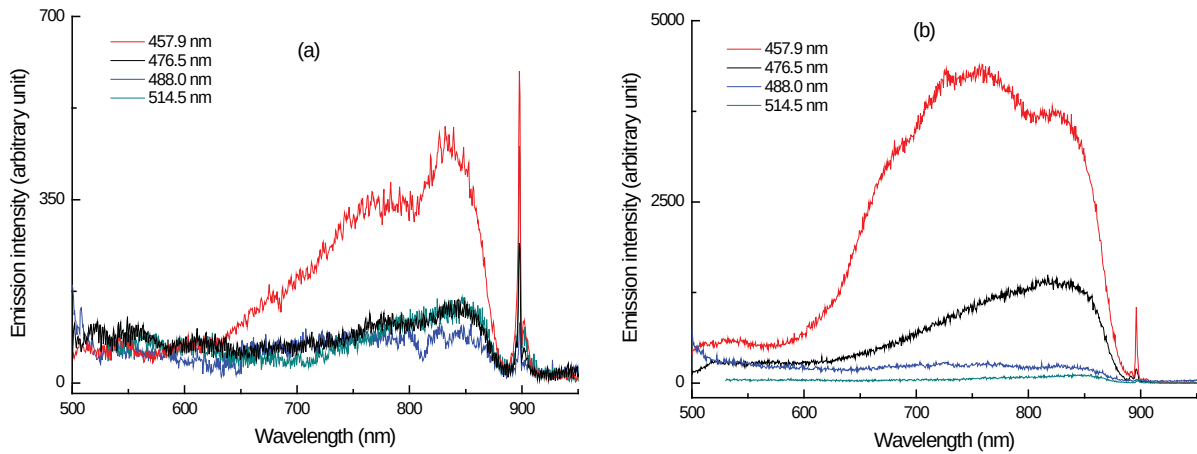


Figure 4.7 Emission spectra recorded at 10 K for $\text{ZnO}:1.5\text{mol}\%\text{Nd}^{3+}$ films: (a) unannealed and (b) annealed at 600 °C. Four Ar^+ laser wavelengths were used for excitation, as shown.

For the Nd^{3+} emission in the 875 nm – 925 nm region, it was observed that the transitions are not at exactly the same wavelength (energy) positions for the unannealed films and those annealed at 600 °C. This apparent anomaly will be explained in Section 4.4.

4.3.1. Emission from ZnO intrinsic defects

Different transitions involving defects with energy levels within the band gap of ZnO (Figure 2.4) are believed to be largely responsible for the broad ZnO emission band which extends from the green to the near-infrared region of the electromagnetic spectrum.^{6,36,37} The defects involved include vacancies (V_O and V_{Zn}) and interstitials (O_i and Zn_i). The broad band's intensity profile is influenced by the concentration of particular defects present in the sample. The higher the quantity of defects, the greater their effect or contribution to the band. Defect emission from undoped and rare-earth doped ZnO is useful in applications such as solar-cells and light emitting diodes.²

Deconvolution of the broad band into distinct transitions enables identification of the defect levels responsible for the emission peaks. Gaussian-shaped transitions are chosen here

for the deconvolution because the transitions are inhomogeneously broadened due to non-equivalent static distortions in the crystalline environment of the point defects.⁹ These distortions may arise from dislocations, unintentional impurities or growth strains, for example. The 10 K PL spectrum for ZnO:1.5mol%Nd³⁺ films annealed at 600 °C obtained with the 457.9 nm excitation wavelength (Figure 4.6), and the defect energy level scheme presented in Figure 2.4 are used for the analysis.

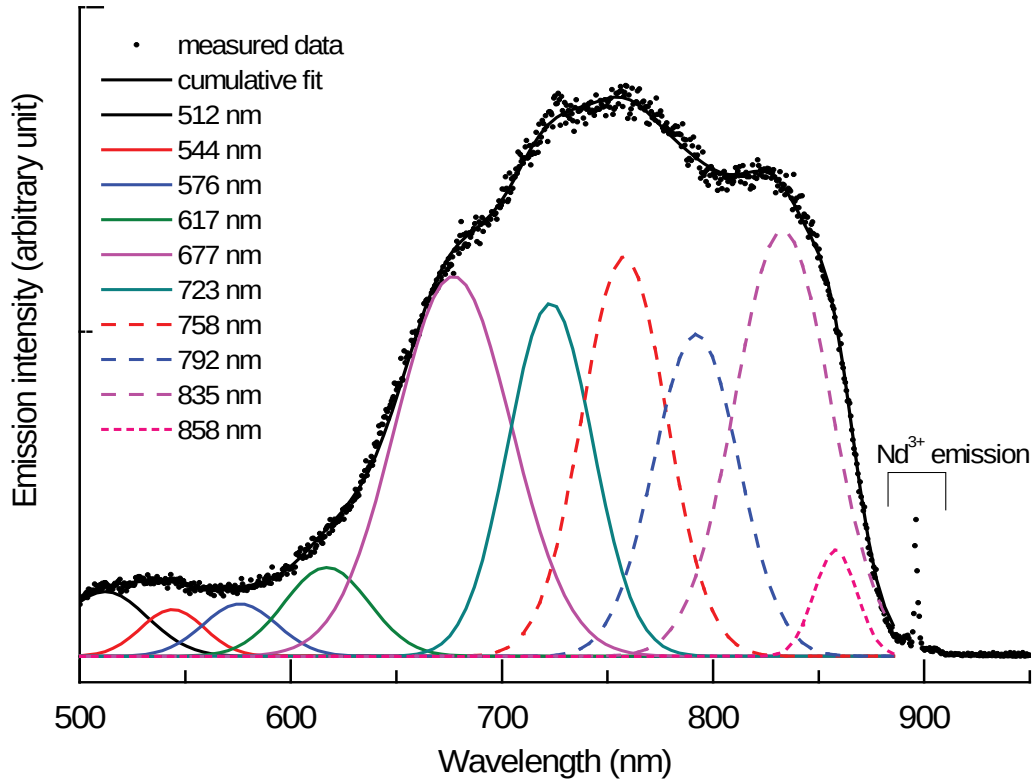


Figure 4.8 Emission spectrum recorded at 10 K for the ZnO:1.5mol%Nd³⁺ film annealed at 600 °C, excited with the 457.9 nm wavelength. Deconvolution assumes Gaussian peak for each individual peak. The Nd³⁺ emission is excluded from the fit and will be discussed separately in Section 4.4.1.

Transitions responsible for the deconvoluted emission peaks shown in Figure 4.8 are indicated in Table 4.3. The error estimate given for the energy positions in the second column of Table 4.3 is an average of values obtained for the lowest and highest wavelength peaks. Variations of up to 5 nm in the fitted transitions could be due to the fact that room temperature transitions (Figure 2.4) are being compared here to low temperature (10 K) transitions (Figure 4.8). Two possible transitions are assigned to the 544 nm fitted peak (Table 4.3) purely because of matching transition energies. It is not possible to make any determination of transition probabilities with the available equipment. In all cases, only the possible transitions based on other published work are given. Although the last two peaks are overlapping, the presence of the less intense peak at 858 nm is justified as its omission leads to discrepancies in the cumulative fit as compared to the measured data.

Table 4.3 Peak positions of the deconvoluted broad-band emission observed in ZnO:1.5mol%Nd³⁺ films annealed in air at 600 °C and their corresponding defect transitions. References used to determine the defect levels shown in Figure 2.4 are as indicated.

Peak position		Corresponding inter-defect transitions
Wavelength (± 1 nm)	Energy (± 25 cm ⁻¹)	
512	19 531	$V_{Zn}^{2-} \rightarrow V_{Zn}^{39,40}$
544	18 382	$V_{Zn}^{2-} \rightarrow V_{Zn}^{39,40}$ $Zn_i^+ \rightarrow V_{Zn}^{39,40}$
576	17 361	$O_i \rightarrow VB^{16}$
617	16 207	$V_{Zn}^{2-} \rightarrow V_{Zn}^{-16,38}$
677	14 771	$O_i \rightarrow V_{Zn}^{40}$
723	13 831	$V_O \rightarrow VB^{39,40,42}$
758	13 193	$V_O \rightarrow V_{Zn}^{40}$
792	12 626	$O_i^- \rightarrow VB^{40}$
835	11 976	$O_i \rightarrow V_{Zn}^{-16}$
858	11 655	$O_i^- \rightarrow V_{Zn}^{39,40}$

4.4. Photoluminescence (PL) studies of Nd³⁺ ions in ZnO films with dye laser excitation

In applications such as photovoltaics, rare-earth ions like Nd³⁺ when doped into ZnO, are used to achieve down-shifting effects⁸⁸ whereas for NIR solid-state lasers, the emission is used as a source of excitation.⁹¹ It is therefore important to determine and fully characterize the emission of Nd³⁺ ions doped into ZnO films or any other host. To this end, the dye laser was used to excite the unannealed and the annealed ZnO:1.5mol%Nd³⁺ films for further insight. The resulting emission is compared with that obtained using Ar⁺-laser excitation in the following sub-section (Section 4.4.1).

4.4.1. Emission and excitation spectra of Nd³⁺ ions in ZnO films

Emission spectra of Nd³⁺ ions in both the unannealed and the annealed ZnO:1.5mol%Nd³⁺ films excited with a 457.9 nm Ar⁺ laser line (extracted from Figure 4.6) are presented in Figure 4.9 (a). It is clear that the peaks obtained for an unannealed film are different, in terms of their wavelength positions, from those obtained for an annealed film. Clearly, there was need to ascertain that the peak shift is a real effect resulting from annealing.

For this investigation, a dye laser was used to directly excite the ²G_{7/2}; ⁴G_{5/2} (D) multiplet of Nd³⁺ ions at ~16 670 cm⁻¹ (600 nm) in Figure 2.9 (c), in unannealed and annealed films. With the monochromator set at the emission transition position identified with the Ar⁺ laser, for the annealed film (895.608 nm in Figure 4.9 (a)), the dye-laser wavelength was manually varied across the dye range of 570 nm – 640 nm. In this way, dye-laser wavelengths which give emission at the monochromator wavelength position were identified. After identifying an

excitation wavelength that results in relatively strong emission, the dye-laser wavelength was then fixed at that excitation wavelength while the monochromator was scanned to obtain a spectrum known as a centre-selective or site-selective emission spectrum, shown in Figure 4.9 (b). Comparison of the recorded centre-selective emission spectra with the spectrum obtained using the Ar^+ laser revealed a perfect match for the annealed sample transitions only. The shifted transitions in Figure 4.9 (a) observed for the unannealed sample, with Ar^+ laser excitation, were completely absent. Dotted vertical lines in Figure 4.9 guide the eye to this correspondence.

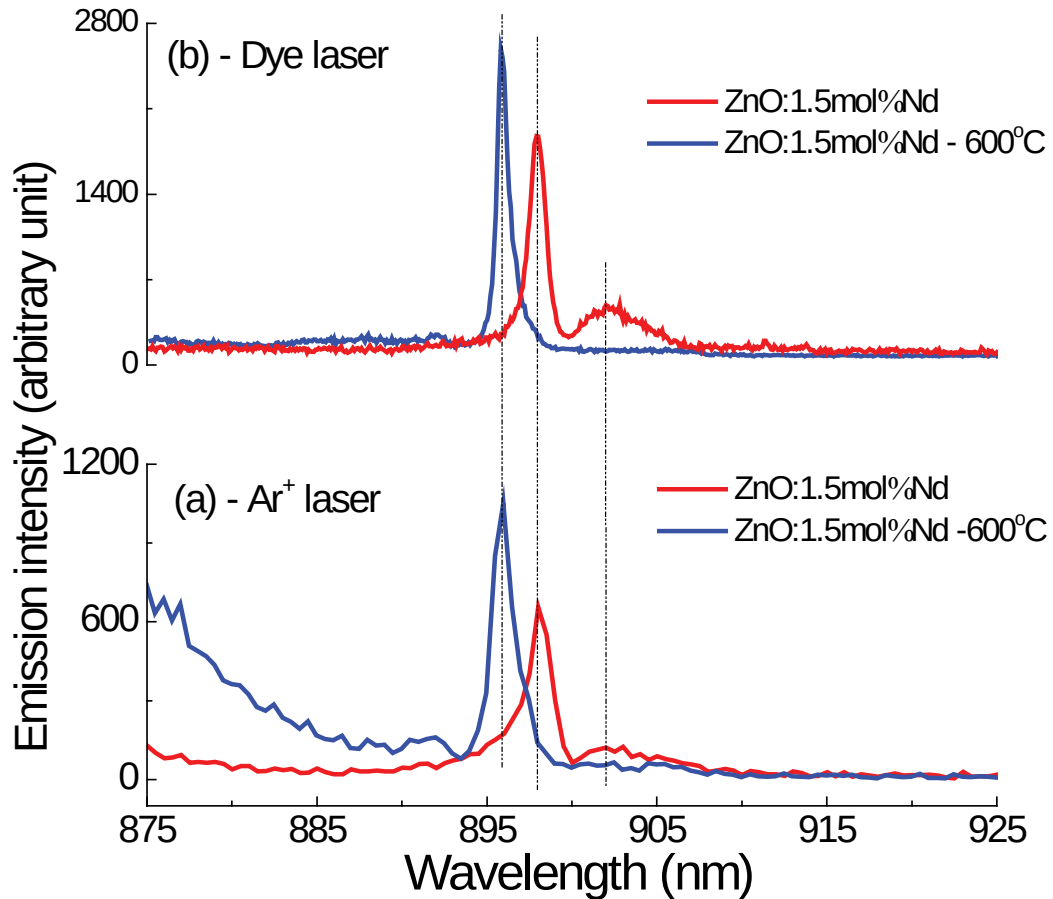


Figure 4.9 Emission spectra recorded at 10 K for unannealed and annealed ZnO:1.5mol%Nd³⁺ films depicting Nd³⁺ emission obtained with (a) indirect excitation at 457.9 nm (Ar^+ laser) and (b) direct excitation at 599.100 nm and 607.900 nm wavelengths (dye laser).

The above procedure was then repeated for the unannealed sample, with the monochromator set on the transition for this film at 897.929 nm in Figure 4.9 (a). Also, peaks in the resulting centre-selective emission spectrum included in Figure 4.9 (b) matched those observed with Ar^+ -laser excitation of the unannealed film perfectly.

A comparison of the peak wavelengths in the spectra obtained with dye-laser excitation (Figure 4.9 (b)) clearly shows that the two spectra are different. This can be interpreted as being due to the presence of two slightly different Nd³⁺ ion sites (centres) in the film samples, depending on the post-deposition heat treatment. The Nd³⁺ centre present in unannealed films

transitions to a slightly different centre on annealing. This indicates that annealing alters the crystal field surrounding the Nd^{3+} ions in a way that changes the transition energies (wavelengths). Both spectra in Figure 4.9 show well resolved Nd^{3+} emission lines, indicating well-ordered crystal-field surroundings of the Nd^{3+} ions.²⁹ For the purposes of this discussion, the centres are considered different; the centre which occurs in annealed films is labelled A and that in the unannealed films is labelled B. The centre A transition at 895.608 nm is marginally stronger and narrower than the centre B transition at 897.929 nm. The ~35% reduction in the linewidths (FWHM) and ~150% increase in intensities of the directly (dye-laser) excited spectra shows less phonon involvement, compared to the indirectly (Ar^+ laser) excited spectra. Also, it can be seen in Figure 4.9 (b) that unlike in the case of Ar^+ -laser excitation, there are no intrinsic defects excited with the dye laser hence there is no emission background related to ZnO intrinsic defects. The overall low intensities in either case are partially due to reduced cross sections for the ~890 nm emission compared to the 1 060 nm emission, as alluded to in Section 2.4.3. Also, weak rare-earth emission in ZnO has been cited as a drawback⁹²; a deeper investigation into the emission quenching mechanisms is warranted and will be suggested for further work.

The observed Nd^{3+} emission peaks are assigned to radiative transitions from the $^4\text{F}_{3/2}$ multiplet at ~895 nm (Figure 2.9) to the ground multiplet ($^4\text{I}_{9/2}$). Following the discussion in Section 2.4.2 regarding transitions observable at low temperature (10 K), the few Nd^{3+} ion emission transitions are assigned as shown in Figure 4.10 (a)(i) for centre A and (b)(i) for centre B, respectively. That is, $\text{R}_1 \rightarrow \text{Z}_i$ ($i = 1, 2, 3$) transitions are labelled in these spectra. Scales on the right side of the graphs in Figure 4.10 are magnified to show the peaks with low intensities. Further spectra were recorded for both annealed and unannealed $\text{ZnO:1.5mol\%Nd}^{3+}$ films at higher temperatures of 20 K, 50 K and 75 K in order to identify emission transitions from the higher R_2 level in the $^4\text{F}_{3/2}$ multiplet to the ground state ($^4\text{I}_{9/2}$) multiplet levels. These are presented in Figure 4.10 (a) and (b) for centre A and centre B, respectively, together with the spectra measured at 10 K. Line-broadening in the $\text{R}_1 \rightarrow \text{Z}_1$ transition with increasing sample temperature, is due to increased phonon activity. The increase in the linewidths (FWHM) recorded at 75 K is 74% for centre A and 50% for centre B, of the values of 0.7 nm and 1.1 nm recorded at 10 K, respectively. The peak positions of the transitions in Figure 4.10 are given in Table 4.4.

In order to detect the $\text{Z} (^4\text{I}_{9/2}) \rightarrow \text{D} (^2\text{G}_{7/2}; ^4\text{G}_{5/2})$ transitions (Figure 2.6) associated with each emission spectrum (i.e. centre), the monochromator was set to the $\text{R}_1 \rightarrow \text{Z}_1$ transition wavelength in each emission spectrum. The dye laser was then mechanically scanned through its lasing range (570 nm – 640 nm) to obtain a spectrum of all possible excitation wavelengths

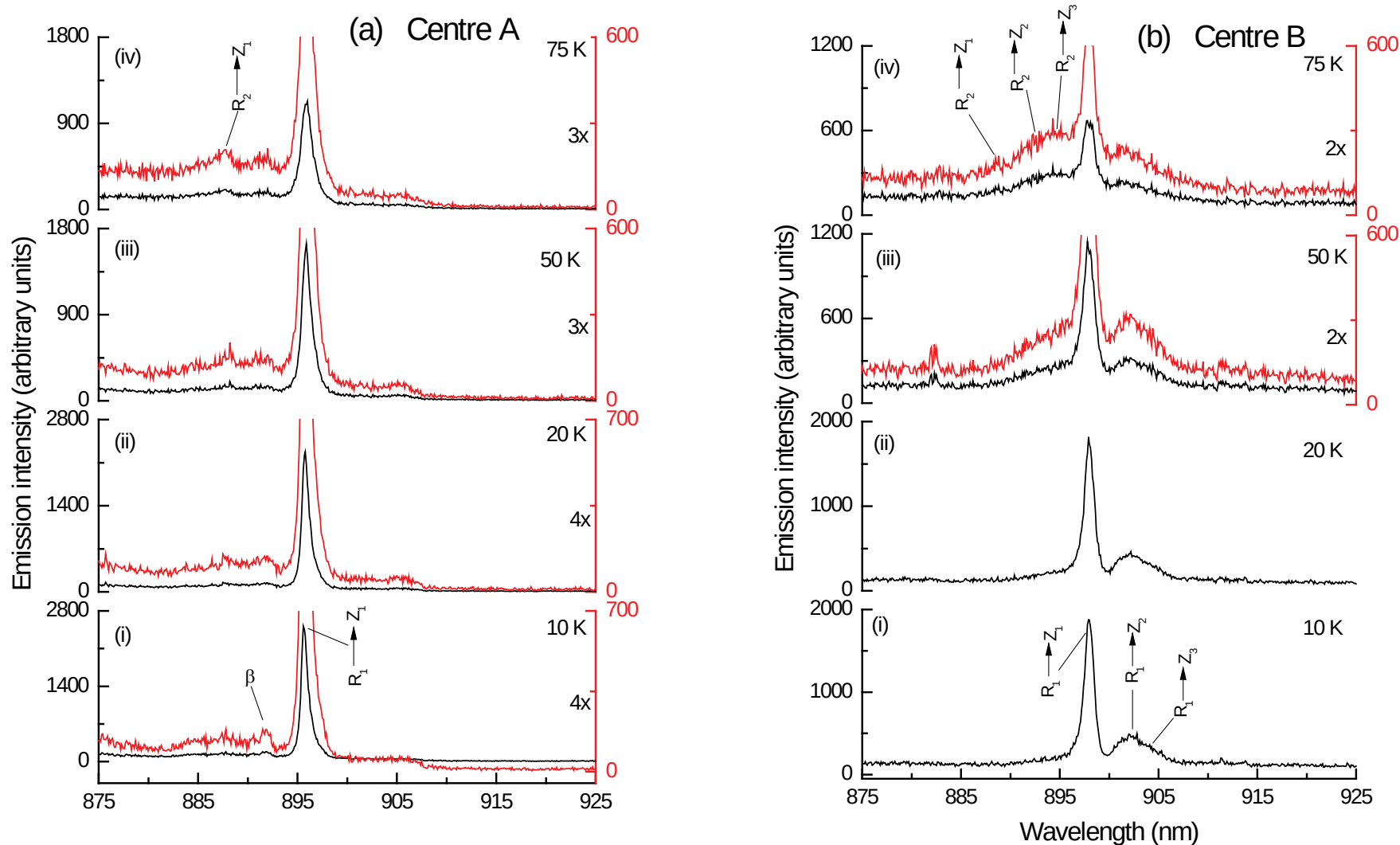


Figure 4.10 Emission spectra recorded at 10 K – 75 K for (a) centre A in ZnO:1.5mol%Nd³⁺ films annealed at 600 °C, using the 599.100 nm excitation wavelength and (b) centre B in unannealed ZnO:1.5mol%Nd³⁺ films, using the 607.900 nm excitation wavelength. Electronic transitions observed at 10 K and at 75 K are labelled $R_1 \rightarrow Z_i$ and $R_2 \rightarrow Z_i$, ($i = 1, 2, 3$) in (i) and (iv), respectively. Scales on the right are for the magnified spectra.

Table 4.4 Peak positions and electronic transitions observed for centre A and centre B in ZnO:Nd³⁺ films at 10 K and at 75 K.

Sample temperature	Centre A peak position,		Centre B peak position		Electronic transition
	Wavelength (± 0.008 nm)	Energy (± 0.1 cm ⁻¹)	Wavelength (± 0.008 nm)	Energy (± 0.1 cm ⁻¹)	
10 K	895.608	11 165.6	897.929	11 136.7	R ₁ → Z ₁
			902.028	11 086.1	R ₁ → Z ₂
			903.791	11 064.5	R ₁ → Z ₃
75 K	887.854	11 263.1	888.739	11 252.0	R ₂ → Z ₁
			892.745	11 201.4	R ₂ → Z ₂
			894.486	11 179.6	R ₂ → Z ₃

for each case. Such a spectrum is called an excitation spectrum. As with the emission spectra, the two excitation spectra were different, confirming the altered Nd³⁺ site in annealed ZnO:1.5mol%Nd³⁺ films. The excitation spectra obtained at 10 K while monitoring the R₁ → Z₁ transitions of the A centre and the B centre at 895.608 nm and 897.929 nm, respectively, are presented in Figure 4.11 (a)(i) and (b)(i), respectively. At 10 K, all the excitation transitions are expected to be from the lowest level (Z₁) of the ground Z (⁴I_{9/2}) multiplet to the seven levels of the excited D multiplet as discussed earlier in Section 2.4.2. Excitation transitions to the D₁ to D₇ levels are indicated for each centre in Figure 4.11 (a) and (b). The peak positions (energies) identify the seven levels (three from ⁴G_{5/2} and four from ²G_{7/2}) that make up the D multiplet of each centre.

Included in Figure 4.11 (a) and (b) is the temperature variation of the excitation peaks. Transitions labelled in spectrum (ii) of Figure 4.11 (b) are from the Z₂ level for the B centre at 50.6 cm⁻¹ which is weakly populated at 50 K, as discussed in Section 2.4.2. The Z₂ → D transitions grow with temperature. Because of the low intensities for centre A (Figure 4.11 (a)), transitions from the Z₂ level could not be unambiguously identified. The diminished intensities in the centre A excitation spectrum are a result of dye-laser instability on the day of measurement. Since the peaks were identifiable, the experiment was not repeated due to time constraints. At 75 K, the excitation transitions were too weak and broad for any new transitions to be identifiable, the measurements were therefore abandoned. Energy level schemes obtained from the 10 K – 50 K excitation spectra and the 10 K – 75 K emission spectra of both centre A and centre B are presented in Figure 4.12.

From these energy level schemes, it can be seen that although the D (²G_{7/2}; ⁴G_{5/2}) multiplet of Nd³⁺ is excited directly, non-radiative processes occur in the lattice until the ⁴F_{3/2} multiplet is populated as illustrated in Figure 2.9 (c). Emission from Nd³⁺ was therefore observed from the ⁴F_{3/2} multiplet, as discussed in Section 2.4.3. The energy levels (in cm⁻¹) for the Z (⁴I_{9/2}), R (⁴F_{3/2}) and D (²G_{7/2}; ⁴G_{5/2}) multiplets obtained from Figure 4.12 are presented in Table 4.5. The two centres have comparable separations between the R₁ and R₂ levels; the separation for centre A is 97.5 cm⁻¹ whilst that for centre B is 17.8 cm⁻¹ more. For the D multiplet, the levels are spread over 724 cm⁻¹ in the

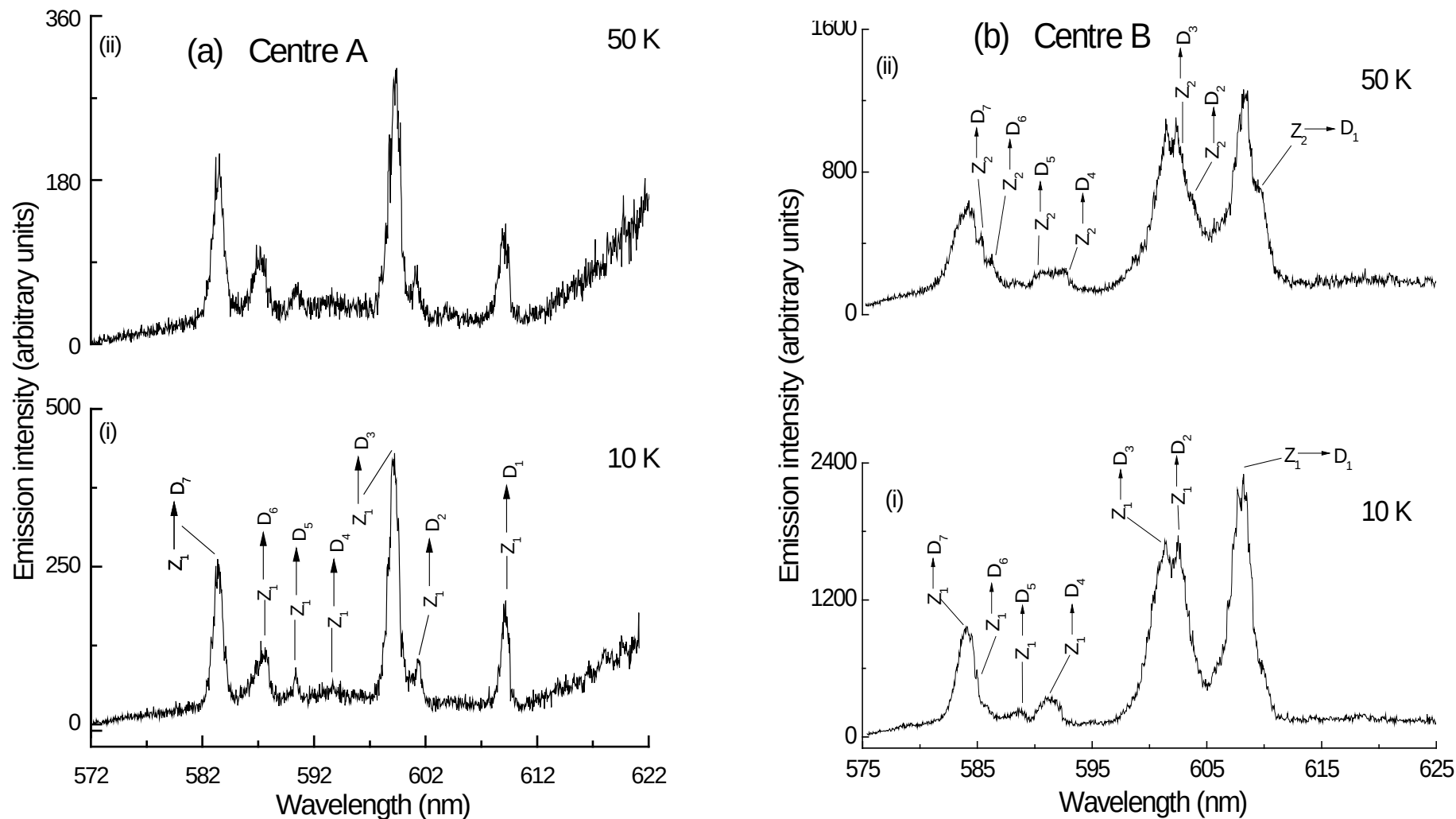


Figure 4.11 Excitation spectra recorded at 10 K and 50 K for (a) centre A in ZnO:1.5mol%Nd³⁺ films annealed at 600 °C, while monitoring the $R_1 \rightarrow Z_2$ transition at 895.608 nm and (b) centre B in unannealed ZnO:1.5mol%Nd³⁺ films, while monitoring $R_1 \rightarrow Z_1$ transition at 897.929 nm. Transitions from the Z_1 level to the D multiplet levels (D_1 to D_7) are labelled in the 10 K spectra while those from the Z_2 level of centre B are identified in the 50 K spectrum.

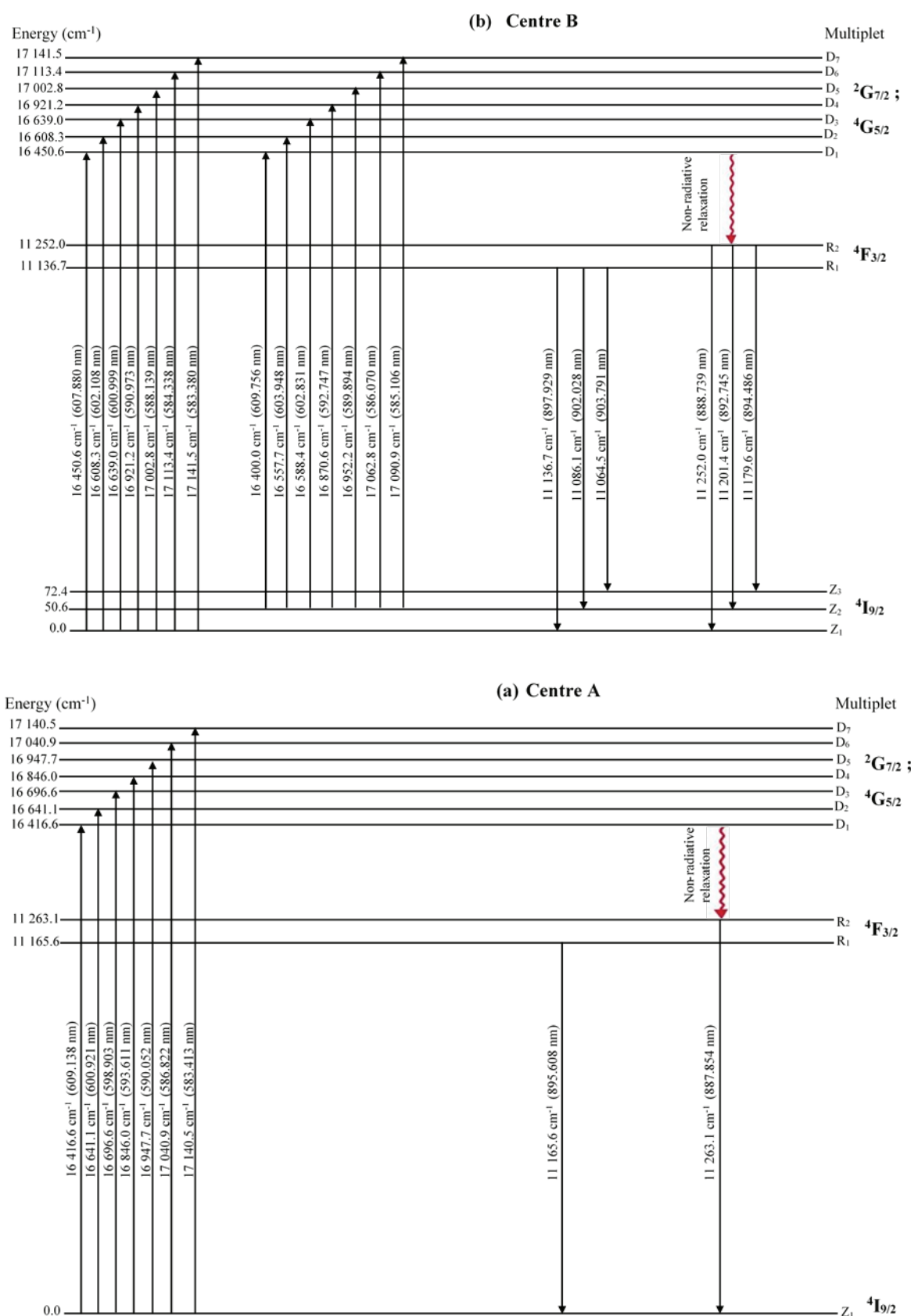


Figure 4.12 Energy level schemes deduced from transitions observed in the 10 K – 50 K excitation spectra and the 10 K – 75 K emission spectra for ZnO:1.5mol%Nd³⁺. (a) centre A in films annealed at 600 °C and (b) centre B in unannealed films.

annealed films (centre A) compared to 691 cm^{-1} in the unannealed films (centre B). While the $R_1 - R_2$ separation has decreased slightly with annealing, the spread of the D multiplet levels has increased by some 33 cm^{-1} . With a complete set of energy levels for only two multiplets, it is not possible to deduce the exact nature of the changes in the crystal-field. However, the slight reduction in both lattice parameters discussed in Section 4.2.1 could be sufficient to cause variations in the more sensitive components of the crystal-field. Energy levels for several multiplets would be required, for each centre, for further crystal-field analysis. Due to low emission intensities for both Nd^{3+} centres in the film samples, life-time measurements did not produce meaningful results and are therefore not presented here.

Table 4.5 Energy levels obtained for the Z ($^4\text{I}_{9/2}$), R ($^4\text{F}_{3/2}$) and D ($^2\text{G}_{7/2}; ^4\text{G}_{5/2}$) multiplets of Nd^{3+} ions in the centre A and centre B configurations in ZnO films.

Multiplet	Label	Energy levels	
		Energy ($\pm 0.1\text{cm}^{-1}$)	
		Centre A	Centre B
Z ($^4\text{I}_{9/2}$)	Z ₁	0.0	0.0
	Z ₂	--	50.6
	Z ₃	--	72.4
R ($^4\text{F}_{3/2}$)	R ₁	11 165.6	11 136.7
	R ₂	11 263.1	11 252.0
D ($^2\text{G}_{7/2}; ^4\text{G}_{5/2}$)	D ₁	16 416.6	16 450.6
	D ₂	16 641.1	16 608.3
	D ₃	16 696.6	16 639.0
	D ₄	16 846.0	16 921.2
	D ₅	16 947.7	17 002.8
	D ₆	17 040.9	17 113.4
	D ₇	17 140.5	17 141.5

4.5. Summary

The main outcomes of the thin-film studies presented in this chapter are:

- ❖ XRD results confirmed the hexagonal wurtzite nature of both the undoped and the doped films. The crystallinity of the samples was improved by annealing.
- ❖ SEM images and line-scans showed a homogeneous distribution of the Nd^{3+} dopant ions in both unannealed and annealed $\text{ZnO:1.5mol\%Nd}^{3+}$ films.
- ❖ EDS scans detected about 30% lower Nd^{3+} concentration.
- ❖ Annealing caused minimal shrinkage of the film and improved the smoothness.
- ❖ Better emission intensities were obtained for films deposited in a 70% Ar : 30% O₂ atmosphere. These films showed both the broad emission band in the 500 nm – 875 nm region attributed to intrinsic defects in ZnO and Nd^{3+} emission in the 885 nm – 925 nm

region, attributed to the $^4F_{3/2} \rightarrow ^4I_{9/2}$ transitions. Both of these emissions were improved by annealing the films in air at 600 °C.

- ❖ Use of the dye laser for excitation confirmed that the Nd^{3+} environment in the annealed samples (centre A) differs from that in the unannealed sample (centre B). The small lattice shrinkage detected in XRD results could be responsible for the changed crystal-field at the Nd^{3+} site on annealing.

CHAPTER 5

RESULTS AND DISCUSSION FOR ZnO AND ZnO:Nd³⁺ POWDERS

5.1. Introduction

The sintered powder samples that were studied are separated into three categories, namely: undoped ZnO, Nd³⁺-doped ZnO and Nd³⁺:Li⁺ co-doped ZnO. The sintering conditions are summarized in Table 3.1. Additionally, a Nd₂O₃ sample was studied as a control sample to demonstrate the incorporation of Nd³⁺ ions into the ZnO lattice in Nd³⁺ doped ZnO. The sample characterization results are presented in Section 5.2 and the photoluminescence results follow in Section 5.3.

5.2. Sample characterization

The photoluminescence (PL) and life-time characteristics are strongly dependent on the methods used to synthesize undoped and rare-earth doped ZnO. Thus, structural and morphological properties of these materials are bound to determine the nature of PL emission and its life-time. The characterizations of these properties were carried out for powder samples used and the results are presented in Sections 5.2.1 and 5.2.2.

5.2.1. Powder X-ray diffraction studies

The effects of doping ZnO powders with Nd³⁺ ions, co-doping with Nd³⁺ and Li⁺ ions and varying the sintering temperature on their structural properties were investigated using powder XRD and the results are presented in Figures 5.1 and 5.2. In Figure 5.1, XRD patterns for undoped, Nd-doped and Nd:Li-doped ZnO samples sintered at 600 °C are presented together with patterns for the unsintered samples (green body). Additionally, the XRD patterns for samples sintered at 950 °C are presented in Figure 5.2 for comparison. Reitveld refinement of the XRD pattern showed the appearance of diffraction peaks at $2\theta = 37.08^\circ, 40.23^\circ, 42.38^\circ, 55.87^\circ, 66.84^\circ, 74.57^\circ, 78.96^\circ, 80.95^\circ, 82.44^\circ$ and 86.85° , for the undoped ZnO powders sintered at 600 °C. These were indexed to a single phase hexagonal wurtzite structure as reported in the literature.⁹³ According to the crystal information file (CIF) of ZnO used in the refinement, the observed peaks correspond to the (100), (002), (101), (102), (110), (103), (200), (112), (201) and (004) Bragg planes, respectively.

By comparing patterns (i) and (ii) as well as (iii) and (iv) in Figure 5.1, it was established that sintering of samples at 600 °C improved the crystallinity of the samples compared to the green body, as evidenced by narrower peaks and relatively higher peak intensities. The decrease in linewidths (FWHM) was 20% for undoped samples and almost 200% for the ZnO:1mol%Nd

samples (Table 5.1). For samples co-doped with Nd^{3+} and Li^+ ions, the crystallinity decreased as shown by the 70% increase in the linewidths.

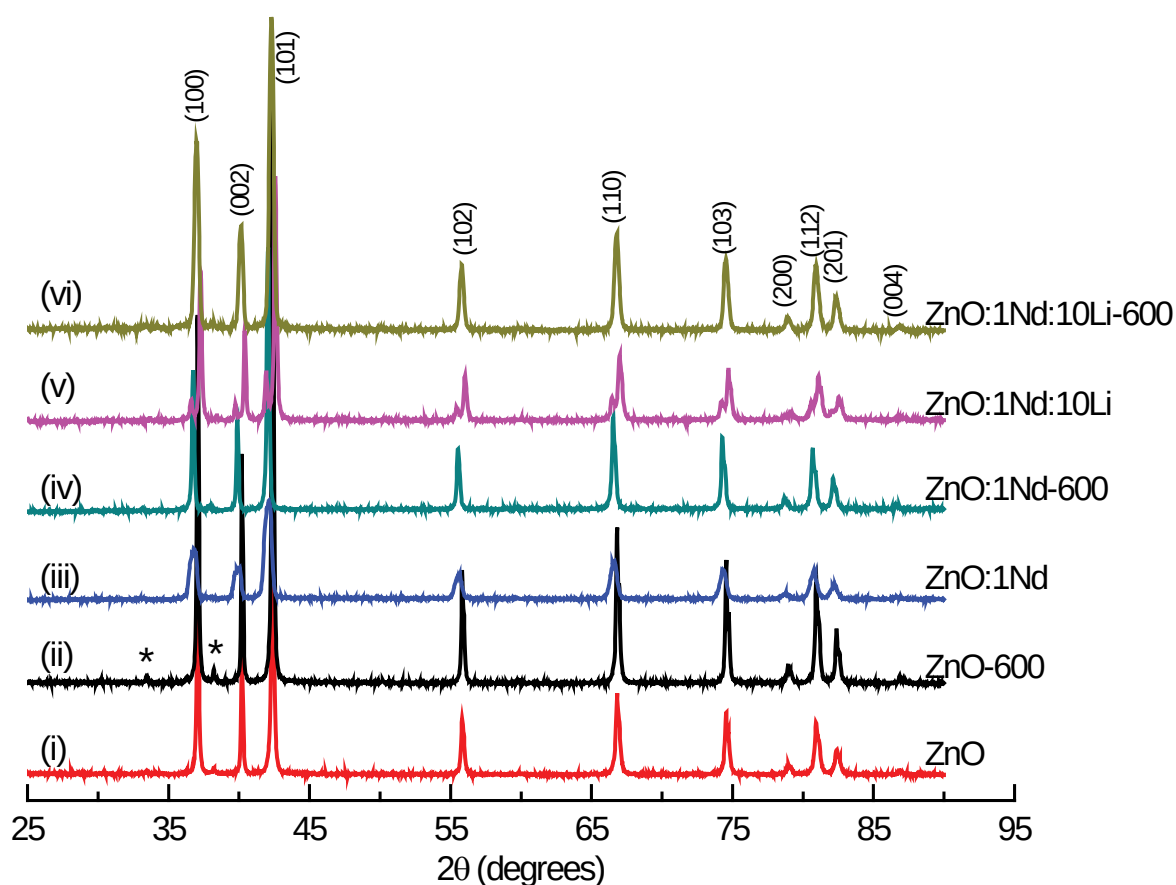


Figure 5.1 XRD patterns for Nd^{3+} doped and $\text{Nd}^{3+}:\text{Li}^+$ co-doped ZnO powders. Patterns are labelled by the sample constituents and sintering temperature; for example, ZnO:1Nd-600 stands for ZnO:1mol% Nd^{3+} sintered at 600 °C. Unsintered samples (green body) are labelled by the constituents only, e.g. ZnO. The ZnO planes are as indicated. Peaks labelled with asterisks (*) are from Fe^{3+} present as an impurity. Cobalt radiation source of wavelength 0.179 nm was used.

Doping ZnO powders with Nd^{3+} ions results in peak shifts to lower angles accompanied with peak broadening (graphs (i) and (iii) or (ii) and (iv) of Figure 5.1). These peak shifts indicate that an ion with larger ionic radius (Nd^{3+} , radius = 99.5 pm) replaced an ion with a relatively smaller radius (Zn^{2+} , radius = 74.0 pm).⁷⁷ The peak broadening can also be construed to represent lattice distortions and reduced crystallinity in the sample.⁷⁷ For samples co-doped with Nd^{3+} and Li^+ ions, peaks shifted to higher angles. This is shown in Figure 5.1 (v) and (vi) and is due to the replacement of some Zn^{2+} ions by Li^+ ions which have the same radii (74.0 pm); the same effect was reported in the literature.⁹⁴ Further, the ionic valence state differences between the Zn^{2+} and the dopant ions (Nd^{3+} and Li^+) lead to lattice distortions and stresses, which in turn, contributes to the peak shifts to higher 2θ angles.

Two sets of peak splittings are apparent in Figure 5.1. The first peak splitting of about 0.2° in all XRD patterns is attributed to the angle dependent resolution of the two components ($K\alpha_1$

and $K\alpha_2$) of the $K\alpha$ X-ray radiation.⁷⁷ Each XRD peak contains two closely-spaced components, whose separation increases slightly with increasing value of θ . The second splitting which occurs in $\text{ZnO}:1\text{mol}\%\text{Nd}^{3+}:10\text{mol}\%\text{Li}^+$, in graph (v), arises from an additional set of Bragg peaks which appear at about 0.5° on the lower angle side of the $K\alpha_1$ related peaks. These additional peaks which disappeared on sintering are possibly from the formation of a segregated monoclinic Nd_2O_3 phase with the addition of Li^+ .²⁶ Alternatively, they are due to the presence of Fe^{3+} and Li^+ ions in the same sample as reported in $\text{Li}^+:\text{Fe}^{3+}$ phosphate precursors.⁹⁵ The disappearance of the cubic phases formed in either case indicates that the new phases formed are less stable and hence dissociate on sintering as compared to the hexagonal wurtzite phases of the ZnO and Nd_2O_3 starting materials.

The additional peaks marked with an asterisk (*) observed for both undoped and doped ZnO are likely to be due to impurities in the starting ZnO precursor. By comparing results from this work with XRD spectra for common impurities in ZnO such as Fe^{3+} ^{96,97} or Cu^{2+} ⁹⁸ ions, it can be concluded that the possible source, in our case is Fe^{3+} . These peaks were reported before in ZnO ⁹⁹ and are consistent with observation of Fe^{3+} emission (to be presented in Section 5.3.3).

The lattice spacing, d , linewidths (FWHM) and lattice parameters (a and c) determined from the Rietveld refinement are presented in Table 5.1. It is evident that the values of the lattice parameters, a and c , are independent of doping and sintering. This is plausible given the low concentration of the dopants and their ionic characteristics. Average crystallite sizes, S , for the

Table 5.1 Peak positions of the (100) plane and the calculated crystallite sizes (S) and lattice parameters. A Nd_2O_3 sample is included for reference.

Sample	2 θ	Linewidth (2 θ)	Plane spacing, d	Lattice parameters		S	c/a
	± 0.01 ($^\circ$)	± 0.02 ($^\circ$)	± 0.001 (nm)	a	c		
ZnO	37.08	0.11	0.281	0.325	0.521	98.9	1.60
ZnO-600	37.08	0.09	0.282	0.325	0.520	111.5	1.60
ZnO1Nd	36.83	0.30	0.284	0.325	0.520	72.0	1.60
ZnO1Nd-600	36.73	0.10	0.284	0.325	0.520	96.7	1.60
ZnO1Nd10Li	37.28	0.10	0.280	0.325	0.521	74.6	1.61
ZnO1Nd10Li-600	36.97	0.17	0.282	0.325	0.520	112.7	1.60
ZnO1Nd-950	37.21	0.09	0.281	0.325	0.520	140.0	1.60
ZnO1Nd1Li -950	37.05	0.09	0.280	0.325	0.520	160.3	1.60
ZnO1Nd5Li -950	37.06	0.07	0.281	0.325	0.520	253.5	1.60
ZnO1Nd10Li -950	37.07	0.07	0.281	0.325	0.521	250.6	1.60
ZnO10Li-950	37.07	0.07	0.282	0.325	0.521	258.2	1.60
ZnO-950	37.14	0.09	0.281	0.325	0.520	132.1	1.60
Nd_2O_3 -950	31.24	0.08	0.332	0.383	0.601	98.2	1.57

samples were also determined. The ratio c/a , in the last column of Table 5.1 is an important parameter to show straining of the c-axis or rotational distortions. Sintering of samples at 600 °C, generally increased the sizes of the crystallites indicating that sintering promotes crystal growth.

The effect of co-doping ZnO with Nd^{3+} and Li^+ ions and sintering at 950 °C is depicted in Figure 5.2. The concentration of Li^+ ions was varied from 0mol% to 10mol% for a constant Nd^{3+} concentration of 1mol% (Figure 5.2 (i) – (iv)). A comparison of graph (iv) in Figure 5.1 and graph (i) in Figure 5.2 as well as the values in Table 5.1 shows that sintering of $\text{ZnO:1mol\%Nd}^{3+}$ samples at a higher temperature marginally further improved the crystallinity of the sample by about 5%. There was almost no effect on the undoped ZnO samples (Figure 5.1 (ii) and Figure 5.2 (vi)). For the co-doped samples, the relative intensities of the peaks from planes (002),

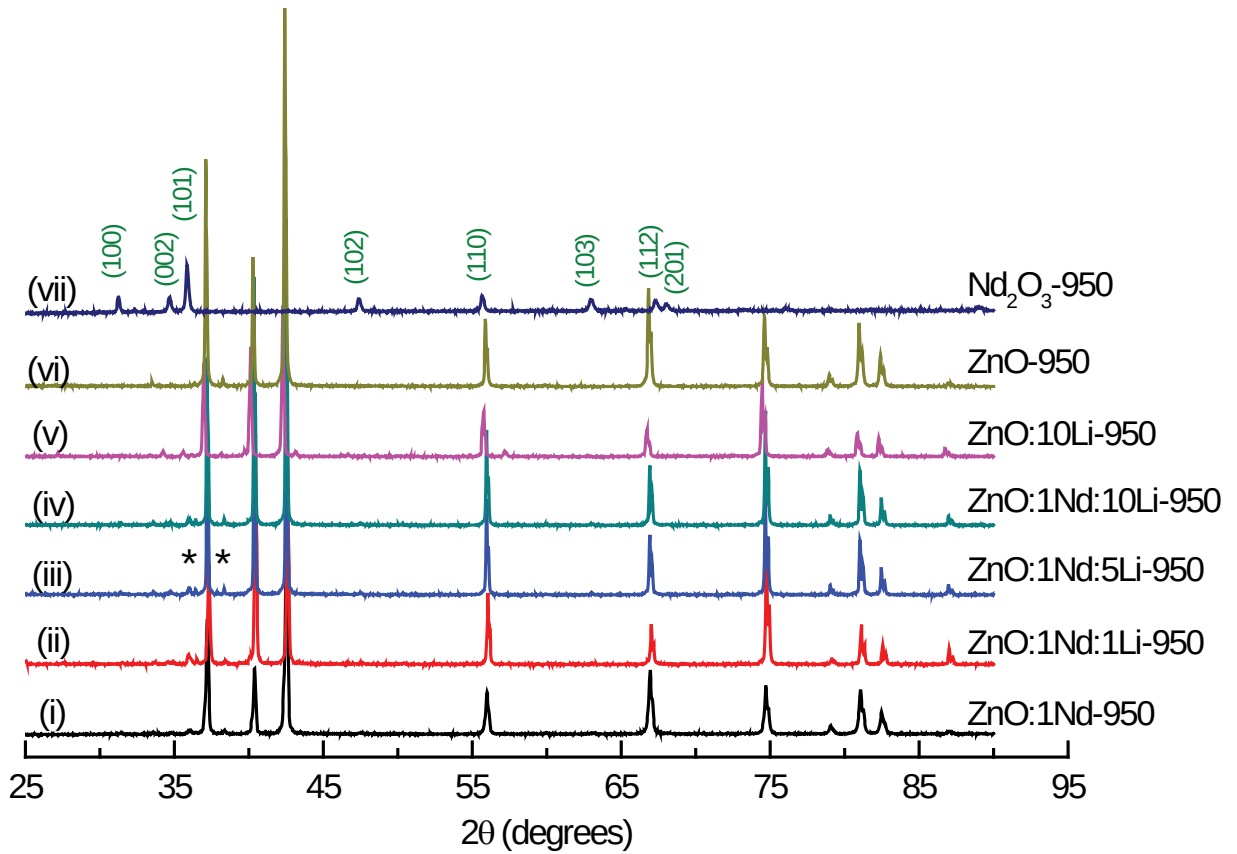


Figure 5.2 XRD patterns for Nd^{3+} doped and $\text{Nd}^{3+}:\text{Li}^+$ co-doped ZnO samples sintered at 950 °C. Patterns are labelled by the sample constituents and sintering temperature; for example, ZnO:1Nd:1Li-950 stands for $\text{ZnO:1mol\%Nd}^{3+}:\text{1mol\%Li}^+$ sintered at 950 °C. Planes corresponding to the peaks observed for Nd_2O_3 are labelled in (vii) while peaks for the ZnO based samples are as in Figure 5.1. Asteriks (*) indicate peaks associated with presence of iron.

(102) and (103) increased with increasing Li^+ concentration (Figure 5.2 graphs (i) – (iv)). This is an indication of changed preferential growth direction or texture formation. For comparison, XRD patterns for the $\text{ZnO:10mol\%Li}^+$ and Nd_2O_3 powders are included (graphs (v) and (vii) in Figure 5.2). The planes from Nd_2O_3 match those reported in literature¹⁰⁰ and have confirmed a

hexagonal wurtzite structure of lattice constants $a = 0.383 \pm 0.001$ nm and $c = 0.601 \pm 0.001$ nm (Table 5.1). There was a significant increase in the sizes of crystallites of the samples co-doped with Nd^{3+} and Li^+ ions as compared to samples with Nd^{3+} only ($\text{ZnO:1mol\%Nd}^{3+}$) which were sintered at 950 °C. The increases were 15% for 1mol% Li^+ and about 80% for both 5mol% Li^+ and 10mol% Li^+ .

The calculated values for lattice parameters for the undoped ZnO powder samples of $a = 0.325 \pm 0.001$ nm and $c = 0.521 \pm 0.001$ nm (Table 5.1) are consistent with values reported in the literature³⁵ for bulk ZnO ($a = 0.325$ nm, $c = 0.521$ nm). Therefore, lattice parameters did not change significantly from doping and co-doping of the ZnO material with Nd^{3+} and Li^+ ions. The shift in the Bragg reflexes upon doping could be possibly attributed to the contributions of ionic sizes and valence states.

5.2.2. Scanning electron microscopy and energy dispersive X-ray spectroscopy studies

The surface morphologies of undoped, Nd^{3+} -doped and $\text{Nd}^{3+}:\text{Li}^+$ co-doped ZnO powders were examined using a scanning electron microscope and the results are presented in Figure 5.3. and Figure 5.4. Comparison between images (ii), (iv) and (vi) of Figure 5.3 shows that when sintering at 600 °C, doping with Nd^{3+} ions or co-doping with Nd^{3+} and Li^+ ions does not significantly change the surface morphologies. For $\text{ZnO:1mol\%Nd}^{3+}:\text{10mol\%Li}^+$, this is consistent with the 1% increase in crystallite size (S) while for $\text{ZnO:1mol\%Nd}^{3+}$ there is a decrease of 13%. In addition, by comparing morphology of the green bodies (images (i), (iii) and (v)) and the corresponding sintered samples of the same composition in Figure 5.3, it can be concluded that sintering caused particle agglomeration or clustering. This is consistent with the crystallite growths of 13%, 34% and 51% for the sintered ZnO, $\text{ZnO:1mol\%Nd}^{3+}$ and $\text{ZnO:1mol\%Nd}^{3+}:\text{10mol\%Li}^+$ samples, respectively (Table 5.1). This indicates that sintering of samples encourages crystal growth.

The effect of sintering ZnO and $\text{ZnO:1mol\%Nd}^{3+}$ samples at the higher temperature of 950 °C is shown by comparing images in Figure 5.3 (ii) and (iv) with images of similar samples in Figure 5.4 (i) and (iii), respectively. It is evident that sintering at 950 °C promotes crystal-growth with potential linkage of the grains at the boundary. This result is consistent with the further grain growth of 18% and 45% compared to sintering at 600 °C for the ZnO and $\text{ZnO:1mol\%Nd}^{3+}$ samples, respectively (Table 5.1).

The effect of sintering samples co-doped with Nd^{3+} and Li^+ ions at 950 °C was also investigated. Figure 5.3 (vi) and Figure 5.4 (vi) show that the higher sintering temperature facilitates the formation of large grains with well-defined grain boundaries. The same grain

growth and grain-boundary definition was observed for ZnO:10mol%Li⁺ (Figure 5.4 (ii)). According to XRD results (Table 5.1), the additional growth of grains in these samples as a direct

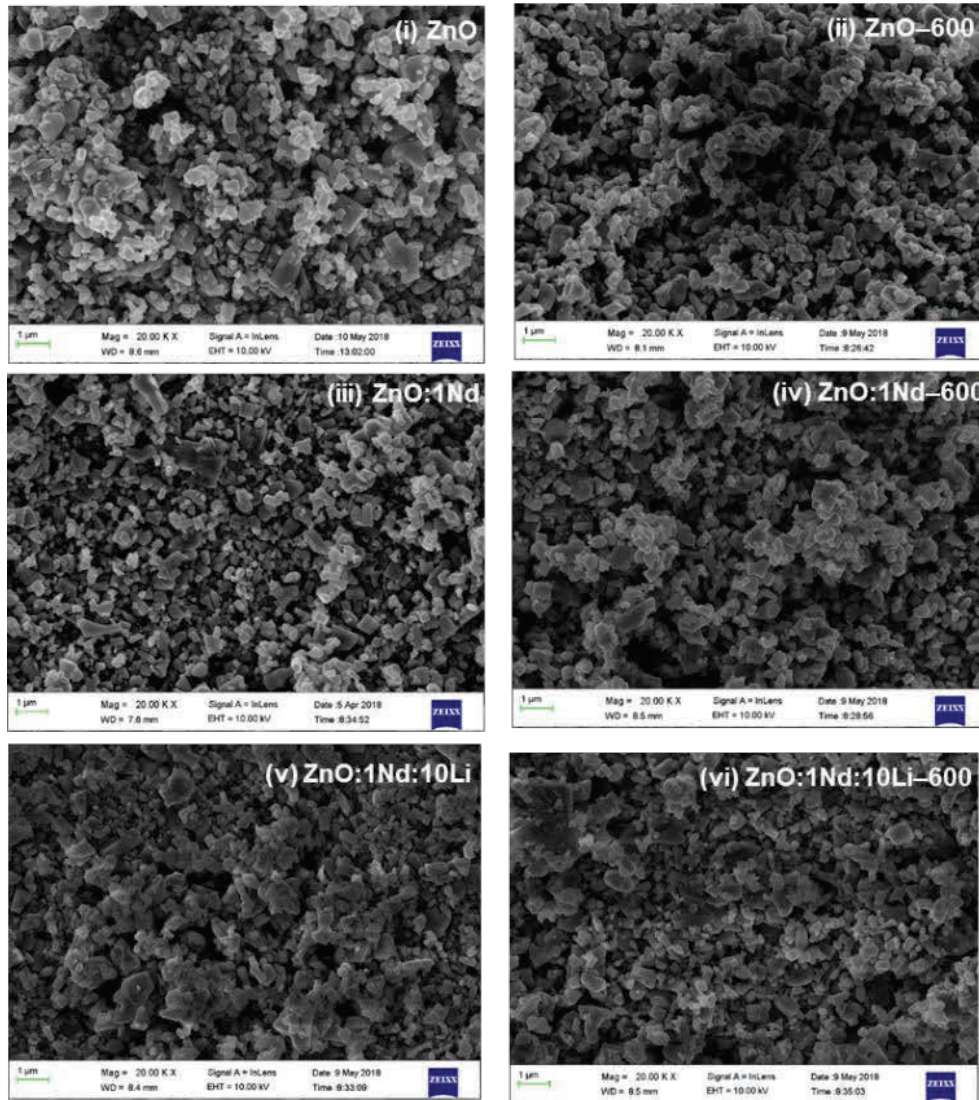


Figure 5.3 SEM images of Nd³⁺ doped and Nd³⁺:Li⁺ co-doped ZnO powder samples. Images (i), (iii) and (v) are for unsintered samples (green body) while images (ii), (iv) and (vi) are for samples sintered at 600 °C.

effect of sintering the co-doped samples at 950 °C compared to 600 °C is about 122 %. The effect of co-doping ZnO with Nd³⁺ and Li⁺ ions for Li⁺ concentration varying from 0 – 10mol% is shown in images (iii) – (vi) of Figure 5.4. The sizes of grains increased further with increasing Li⁺ ions concentration.

To determine the distribution of constituent elements of samples with large morphological changes, elemental line scans were performed on randomly selected sections. Each scan was rastered between two points (point **a** to point **b**) across the grains via the grain boundaries. Results for ZnO:1mol%Nd³⁺ powder samples sintered at 600 °C and 950 °C as well as ZnO:1mol%Nd³⁺:10mol%Li⁺ and ZnO:10mol%Li⁺ samples sintered at 950 °C are presented in Figure 5.5. Line scans (a)(i) and (a)(ii) in Figure 5.5 were obtained along any 10 μm and 15 μm

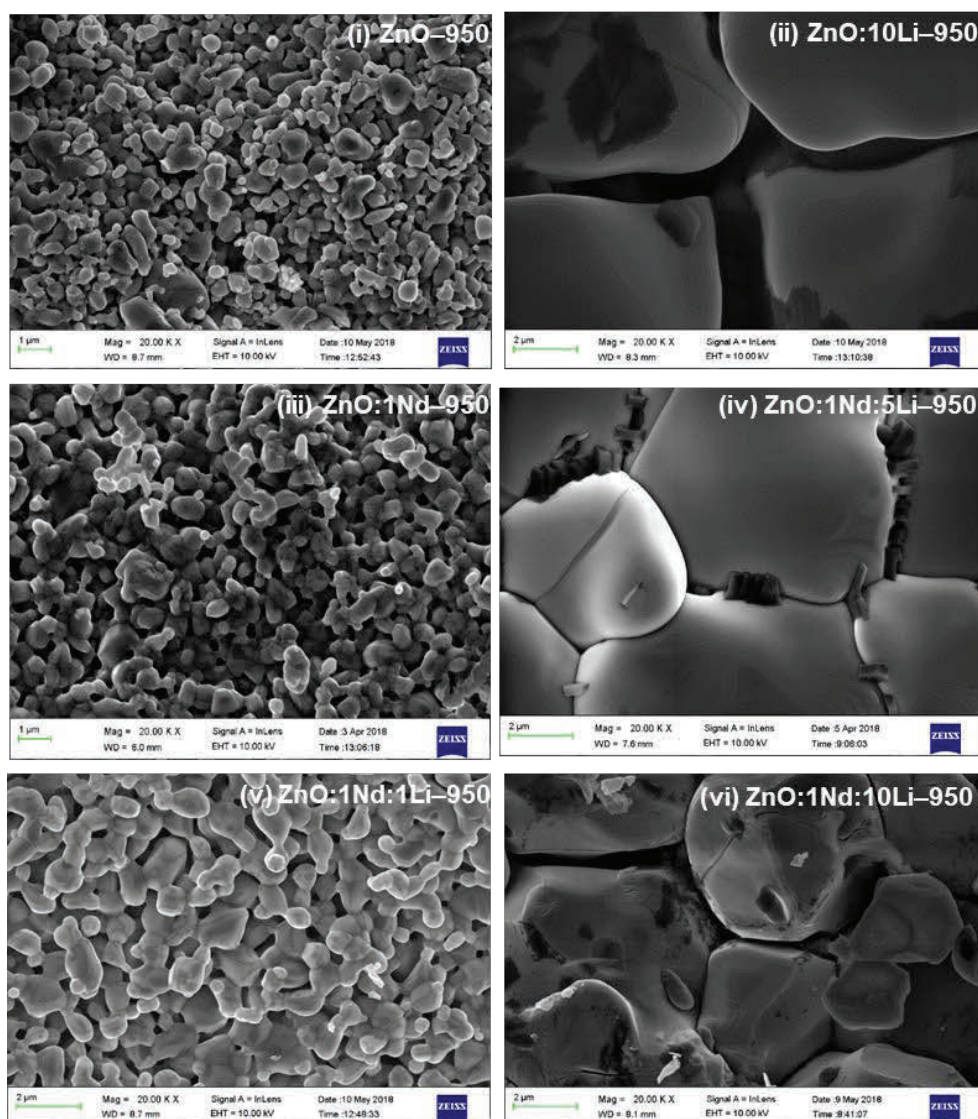


Figure 5.4 SEM images of Nd^{3+} doped and $\text{Nd}^{3+}:\text{Li}^+$ co-doped ZnO samples sintered at 950 °C. A $\text{ZnO}:\text{10mol}\%\text{Li}^+$ sample, also sintered at 950 °C, is included for reference.

lateral direction of the SEM images in Figure 5.3 (iv) and Figure 5.4 (iii), respectively. The line scans show that there is uniform distribution of constituent elements in the samples. Despite the low concentration of neodymium (Nd) due to the low sensitivity of EDS as discussed in Sections 3.3.3 and 4.2.2, its homogeneous distribution across the selected scan areas was observed. The crystallites are close to each other, leaving a few gaps; the gaps are shown by points of low emission intensities (almost zero) on the graphs. There are relatively larger gaps for sample (ii) than in sample (i) indicating that the grains for the $\text{ZnO}:\text{1mol}\%\text{Nd}^{3+}$ are larger when the sample is sintered at 950 °C than at 600 °C. The results are consistent with SEM images in Figure 5.3 (iv) and Figure 5.4 (iii). With addition of $\text{10mol}\%\text{Li}^+$ to the $\text{ZnO}:\text{1mol}\%\text{Nd}^{3+}$ and sintering at 950 °C, the grain boundary gaps were further increased and the level of Nd was no longer uniform (Figure 5.5 (b)(i)). There were positions along the line of scan with relatively higher Nd concentration. At these points, the concentrations of Zn and O were relatively low.

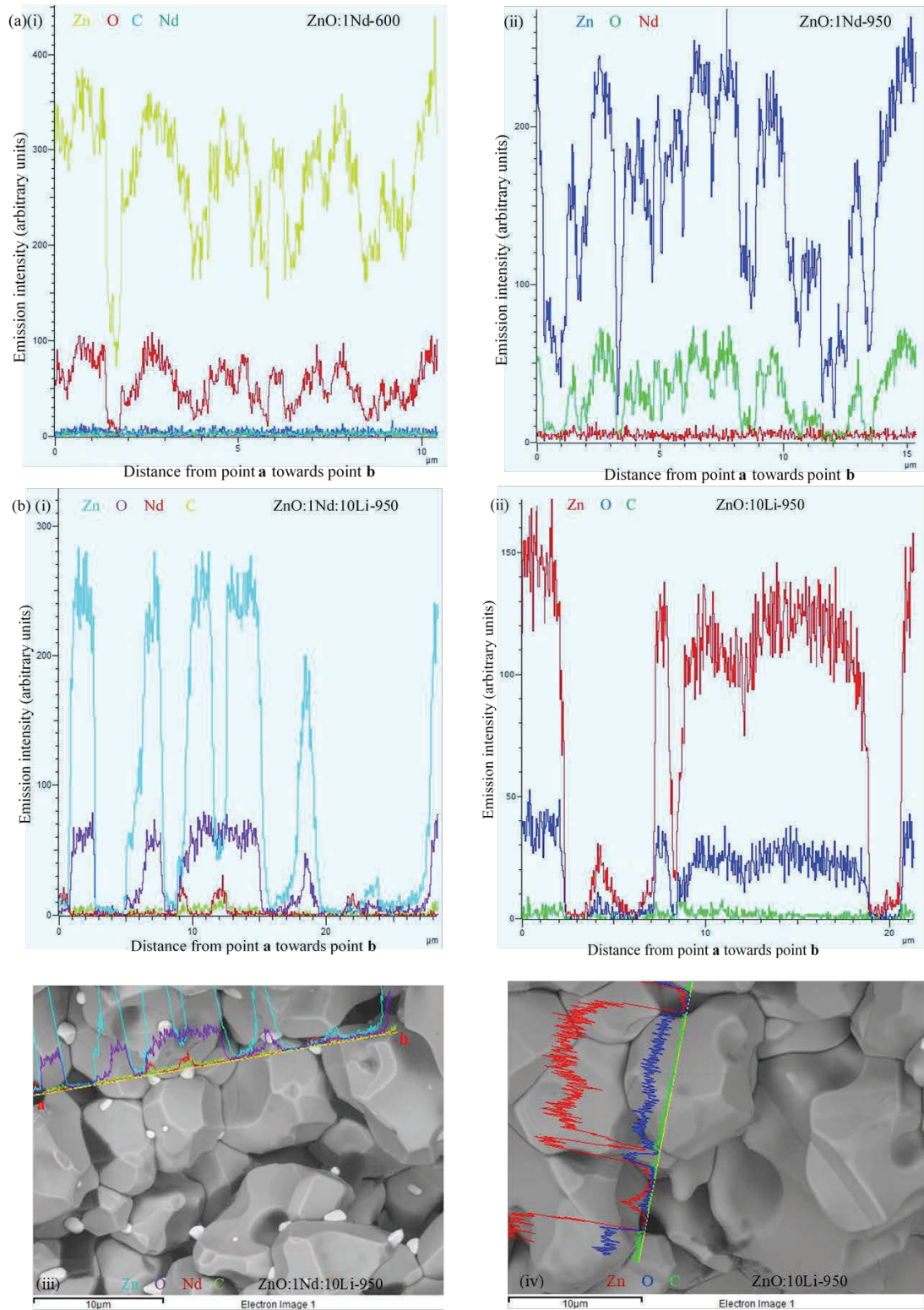


Figure 5.5 Line scans for (a) ZnO:1mol%Nd³⁺ samples sintered at (i) 600 °C and (ii) 950 °C and (b) (i) ZnO:1mol%Nd³⁺:10mol%Li⁺ and (ii) ZnO:10mol%Li⁺ samples sintered at 950 °C. Maps for the line scans in (b) (i) and (ii) are shown on the SEM images in (b) (iii) and (iv), respectively.

Looking at the map in (b)(iii) of Figure 5.5 for this line-scan, the regions with relatively high concentration of Nd are found on the small particles within the boundary regions. From comparing maps (iii) and (iv) in Figure 5.5 (b), it can be concluded that these small particles

contain Nd since they are absent in the $\text{ZnO:10mol\%Li}^+$ sample. In the literature¹¹, it is reported that trivalent rare-earth ions and lithium ions associate with each other and are mainly located near the grain boundaries. This is an effect of the high diffusion coefficient of lithium at a sintering temperature of 950 °C as compared to 600 °C. As a result, the migration of rare-earth ions and lithium ions to the grain boundaries is caused by the lithium acting as an interstitial donor.¹⁰¹

The energy-dispersive X-ray spectroscopy (EDS) results presented in Figures 5.6 and 5.7 correspond to the SEM images in Figures 5.3 and 5.4, respectively. The detector generates a reference peak at 0 keV while the carbon tape used for mounting samples onto the stage is responsible for the one labelled C. As expected, Nd^{3+} peaks were only detected in samples doped with Nd^{3+} ions ((iii) – (vi)). Figure 5.7 shows that there was an increase in the amount of Nd detected in the $\text{Nd}^{3+}:\text{Li}^+$ co-doped samples sintered at 950 °C.

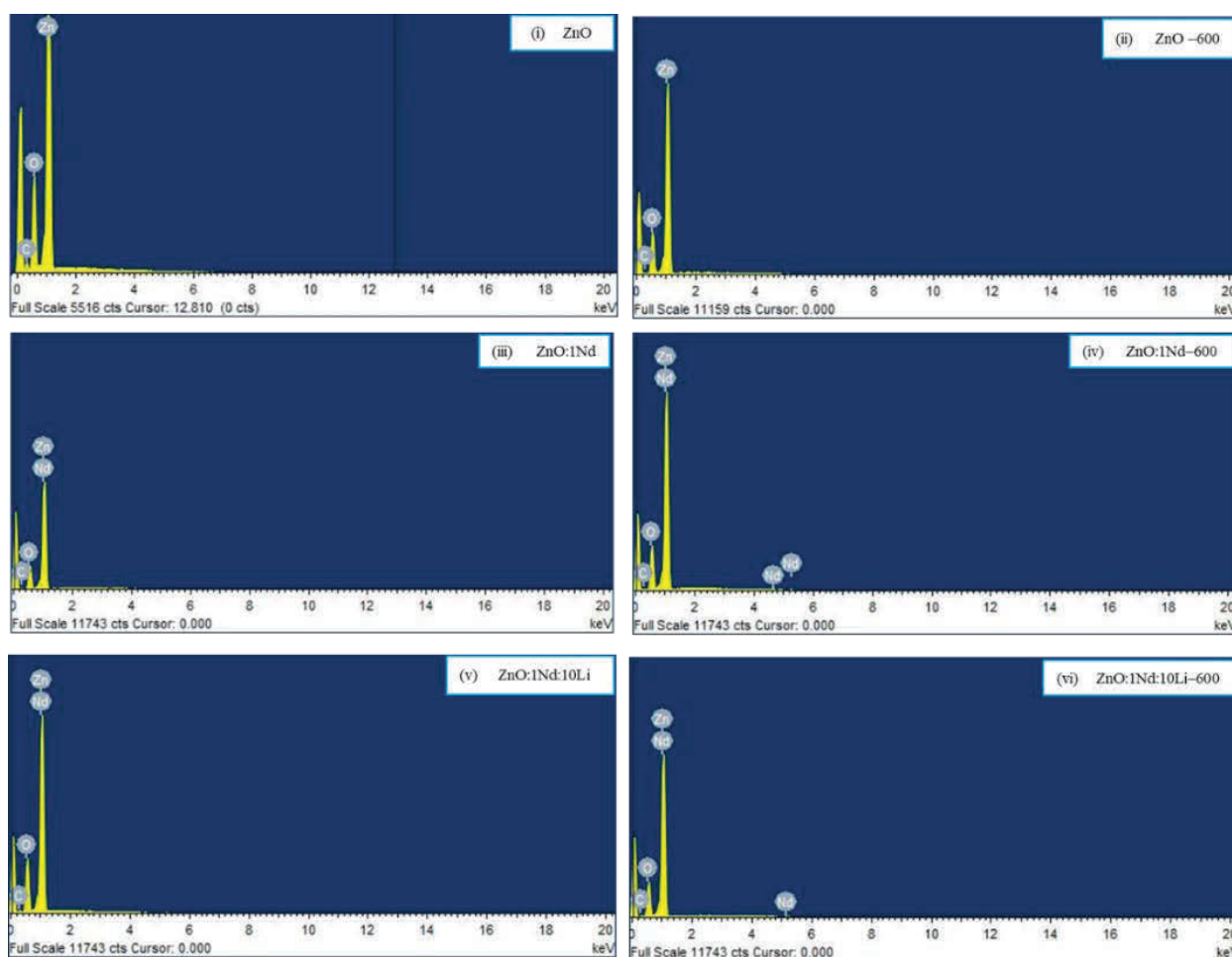


Figure 5.6 EDS spectra for Nd^{3+} doped and $\text{Nd}^{3+}:\text{Li}^+$ co-doped ZnO powder samples. Images (i), (iii) and (v) are for unsintered samples (green body) while images (ii), (iv) and (vi) are for samples sintered at 600 °C. The spectra correspond to the cumulative scans of SEM images in Figure 5.3.

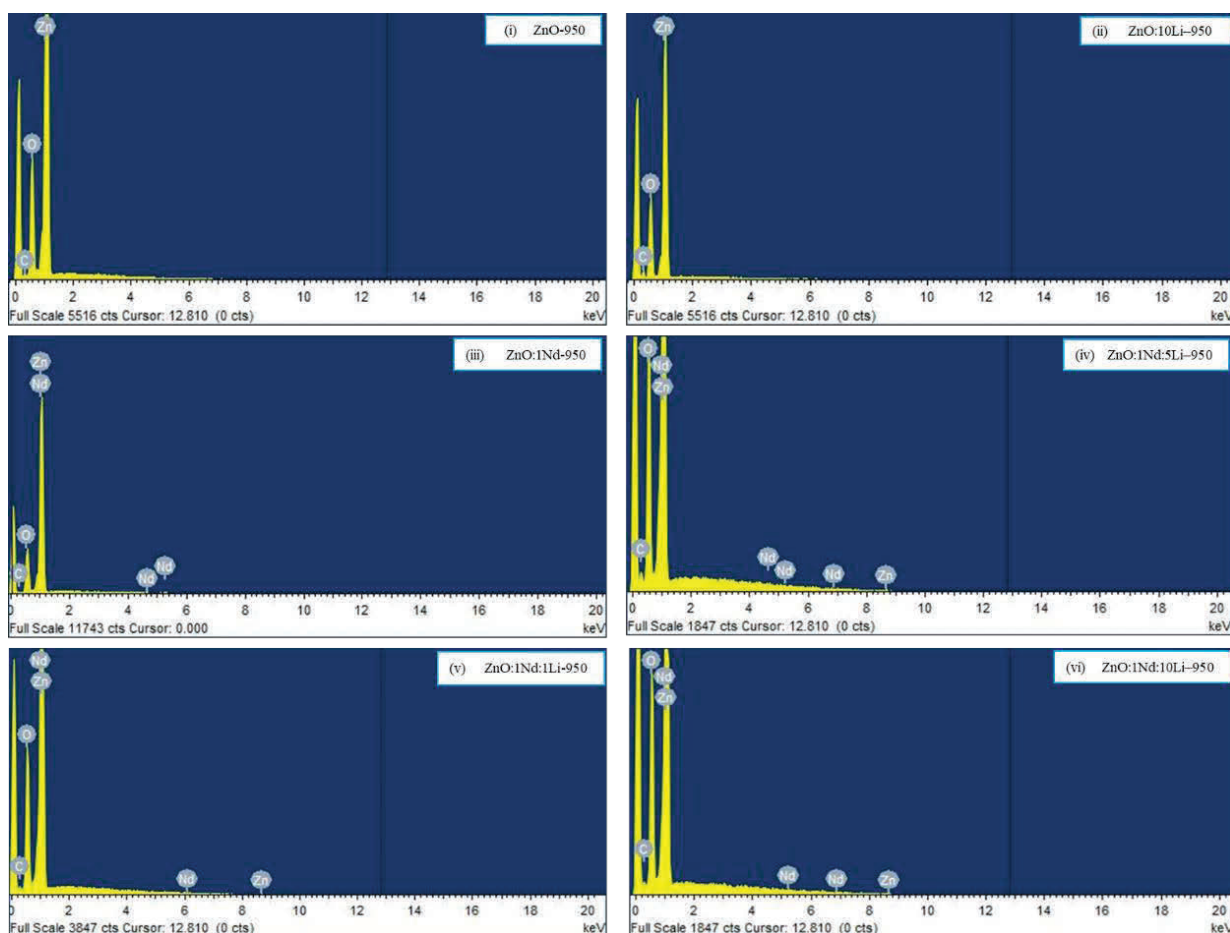


Figure 5.7 EDS spectra for Nd^{3+} doped and $\text{Nd}^{3+}:\text{Li}^{+}$ co-doped ZnO powder samples sintered at 950 °C. A ZnO:10mol% Li^{+} sample, also sintered at 950 °C, is included for reference. The spectra correspond to the SEM images in Figure 5.4.

The compositional percentages presented in Table 5.2 have been re-normalized to exclude the C from the mounting tape. Li^{+} ions could not be detected with this system due to the limited sensitivity to Li ($Z = 3$). In addition, though XRD results (Figures 5.1 and 5.2) showed peaks for impurity Fe in the samples, no Fe was detected in the EDS scans (Figures 5.6 and 5.7). This is most likely due to their relatively low concentration as the minimum detectable concentration in EDS is 0.1%.¹⁰² The EDS detected concentration of 0.17% Nd^{3+} in the ZnO:1mol% Nd^{3+} :5mol% Li^{+} sample (Table 5.2) appears to be anomalous. The measurement was repeated and this value was confirmed. The under-detection of Nd is due to the limited sensitivity of the EDS measurements to the Nd elements. The Nd concentration values for the other samples are acceptable for the 1mol% starting amount, given that the system under-detects by ~30% (Section 4.2.2).

Table 5.2 Elemental compositions as detected by energy dispersive X-ray spectroscopy.

Sample	Elemental composition (mol%)		
	O	Zn	Nd
ZnO	48.41	51.59	
ZnO-600	48.64	51.36	
ZnO1Nd	47.44	51.98	0.58
ZnO1Nd-600	49.84	49.46	0.70
ZnO1Nd10Li	53.41	46.13	0.46
ZnO1Nd10Li-600	48.81	51.13	0.56
ZnO1Nd-950	48.98	50.51	0.51
ZnO1Nd1Li-950	49.60	49.92	0.48
ZnO1Nd5Li-950	54.95	44.94	0.17
ZnO1Nd10Li-950	51.74	47.45	0.81
ZnO10Li-950	58.38	41.62	
ZnO-950	51.00	49.00	

5.3. Photoluminescence (PL) studies with Ar⁺ laser excitation

In 2017, rare-earth doped ZnO was confirmed to be the potential material for solid state lighting and solar cells.² As such, there is need to fully understand and document the photoluminescence characteristics of the powders before they can be considered for any applications. The emission results of ZnO intrinsic defects in the Nd³⁺-doped ZnO powders studied here will be discussed in the following sub-section (Section 5.3.1). For the purposes of the analysis of the results presented in Section 5.3.1, the defect energy level scheme presented in Figure 2.4 will be relied on. Photoluminescence properties of the Nd³⁺ ions will follow in Sections 5.3.2 and 5.4.

5.3.1. Emission from ZnO intrinsic defects

Low-temperature (10 K) spectra of undoped and Nd-doped ZnO powder samples that were unsintered (green body) and those sintered at different temperatures (600 °C, 750 °C and 950 °C) are shown in Figure 5.8. These spectra were obtained using the 457.9 nm laser line and the laser power near the sample was ~35 mW. For the undoped ZnO powders, a broad asymmetrical band extending from 500 nm to 875 nm was observed. For samples sintered at 600 °C, the intensity improved by about two-fold compared to the green body. This effect is consistent with the improvement in crystallinity of the samples as shown by the decreasing linewidths (FWHM) of the XRD peaks (Table 5.1). The increased particle sizes in the SEM images (Figures 5.3 and 5.4) further support the assertion. This broad emission is attributed to native (intrinsic) defects in ZnO and it also exists for green body samples.

The Nd-doped samples showed four main characteristics. Firstly, the broad-band profile characteristic of the undoped ZnO is present and is improved by sintering at 600 °C. Further,

sintering at 600 °C showed a changed intensity ratio in the emission peaks at ~650 nm and ~550 nm with the former increased, in comparison to the green body, whilst the latter decreased.

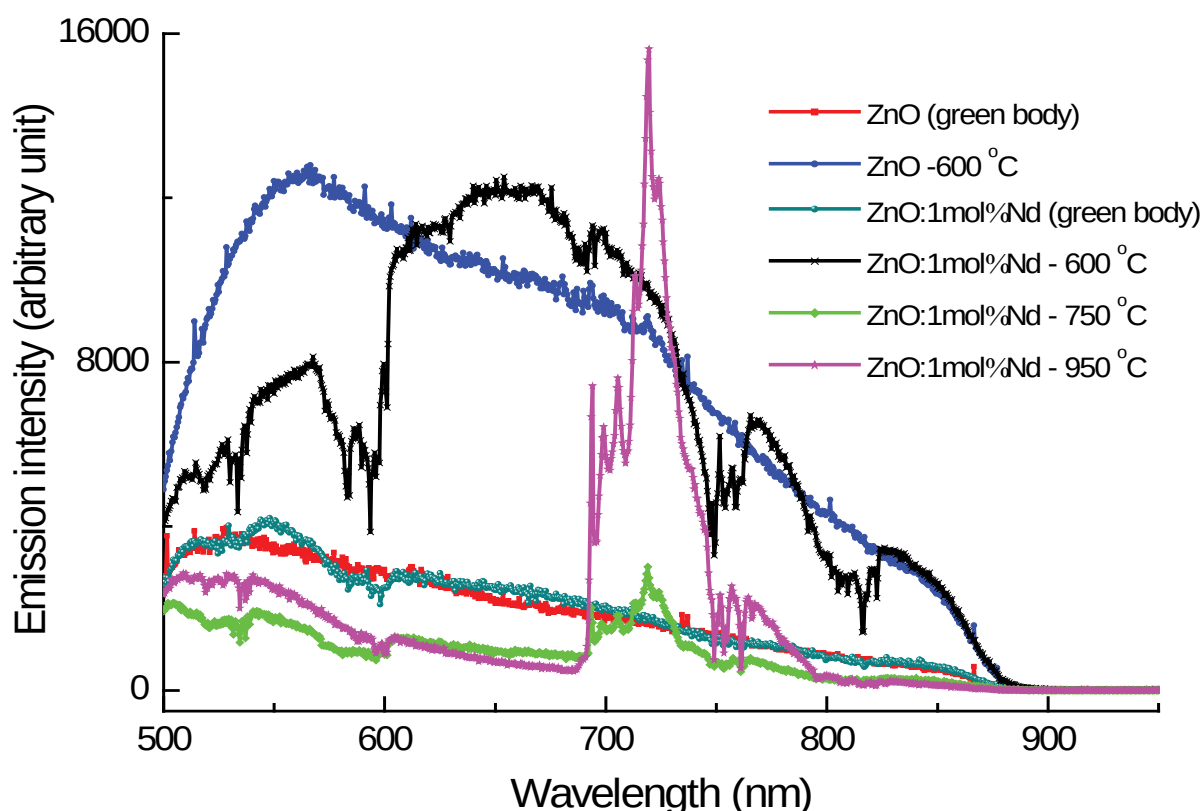


Figure 5.8 Emission spectra recorded at 10 K with the 457.9 nm excitation line, showing the effect of doping ZnO with 1mol%Nd³⁺ and sintering the samples at different temperatures.

This could be attributed to defect annihilation and formation of defect complexes and vacancies during the sintering. It is reduced in samples sintered at higher temperatures (750 °C and 950 °C). Secondly, narrower absorption bands appear superposed on the broad emission band for all sintered samples, regardless of the sintering temperature. The positions of the narrow-band absorption features coincide with the Nd³⁺ multiplet positions shown in Figure 2.6, and will be analysed in Section 5.3.2. Thirdly, a strong narrow-line emission band appears in the 690 nm – 760 nm region for samples sintered at 750 °C and 950 °C (Figure 5.8). The intensity of this feature in the sample sintered at 950 °C was four times that of the samples sintered at 750 °C. This feature, which dominates the spectrum at 950 °C, turns out to be characteristic of an Fe³⁺ centre in ZnO. The centre will be discussed further in Section 5.3.3. Lastly, no Nd³⁺ emission was detected in the region from 500 nm up to 950 nm accessible with the available photomultiplier tube (PMT) for all the ZnO:1mol%Nd³⁺ samples, in contrast to the film samples (Section 4.3).

The green-yellow emission in the 500 nm – 600 nm region, observed for green body ZnO and ZnO:1mol%Nd³⁺ powders, is similar to that observed for the ZnO and ZnO:1.5mol%Nd³⁺

film samples (Section 4.3, Figure 4.6). This indicates that the presence of the specific defects (V_{Zn}^{2-} , Zn_i^{+} , O_i and V_{Zn}) which are responsible for the emission in this region (Figure 2.4) is less dependent on the method used to fabricate the samples. This nature of the emission characteristics was observed to be the same in both the powder samples and the film samples. The increased intensities after sintering or annealing of the powder or film samples, respectively, at 600 °C, results from loss of Zn and creation of more zinc-vacancy defects on the surface of the samples with heat treatment. Also, O_i defects are increased due to adsorption of oxygen on the surface of the samples during annealing or sintering in air. These V_{Zn} and O_i defects contribute to the green-yellow emission band through $V_{Zn}^{2-} \rightarrow V_{Zn}$, $Zn_i^{+} \rightarrow V_{Zn}$ and $O_i \rightarrow VB$ transitions as indicated in Figure 2.4. Sintering of powders at 600 °C, however, changed other sections of the broad-emission band, differently. There was significant improvement in the 600 nm – 700 nm emission band intensity compared to the films and less so for the region with wavelengths higher than 750 nm. Based on the defects assigned to the band in Section 4.3.1, it can be suggested that more zinc-vacancy defects are created and more oxygen interstitials are adsorbing on the powder samples sintered at 600 °C than on the film samples, leading to this increase. The overall increase in the intrinsic defect emission is reversed at higher sintering temperatures (750 °C and 950 °C) because at the higher temperatures, there is recovery of stoichiometry due to evaporation of zinc on the surfaces and also annihilation of oxygen interstitial defects.

The luminescence spectra comprising both the ZnO intrinsic defect emission band and the overlapping absorption regions are similar to those reported by others^{11,23,25,103} with the only difference being the relative intensities of the signals and the pronounced Fe^{3+} emission. Spectra of the unsintered ZnO and ZnO:1mol% Nd^{3+} samples (green body) are included in Figure 5.8 as reference.

Using the 457.9 nm laser line for excitation, there is a general decrease in intrinsic defect emission as the sintering temperature is raised from 600 °C to 750 °C and then to 950 °C (Figure 5.8). This has been observed before.³⁷ Since the two extreme sintering temperatures of 600 °C and 950 °C gave samples with differing emission properties, further studies on samples sintered at these two temperatures were carried out. These include:

- (i) identification of the intrinsic defects through deconvolution of the broad band spectrum,
- (ii) investigation of the dependence of emission characteristics on excitation energies ($457 \text{ nm} < \lambda_{ex} < 515 \text{ nm}$),
- (iii) studying the effects of co-doping ZnO powders with Nd^{3+} and Li^{+} ions.

Contributions of transitions between specific pairs of intrinsic defect levels in the ZnO band gap, to the broad-band emission, can be evaluated using the defect level scheme of Figure 2.4, as done for the films in Section 4.3.1. That is, the broad emission band is deconvoluted into individual peaks which are then assigned to the transitions between specific defects. Figure 5.9 shows the individual peaks, their peak wavelengths and the best-fit curve that results from cumulative addition of the deconvoluted profiles, for the ZnO:1mol%Nd³⁺ sample sintered at 600 °C. Absorption features have not been taken into account in the fit as these will be considered separately in Section 5.3.2. The cumulative fit therefore shows the intrinsic defects emission profiles only. The peak positions and the tentative defect transitions responsible for the deconvoluted emission bands presented in Table 5.3 are as presented in Table 4.3 for the ZnO:1.5mol%Nd³⁺ films. Although the emission band profile (Figure 5.9) is different from that

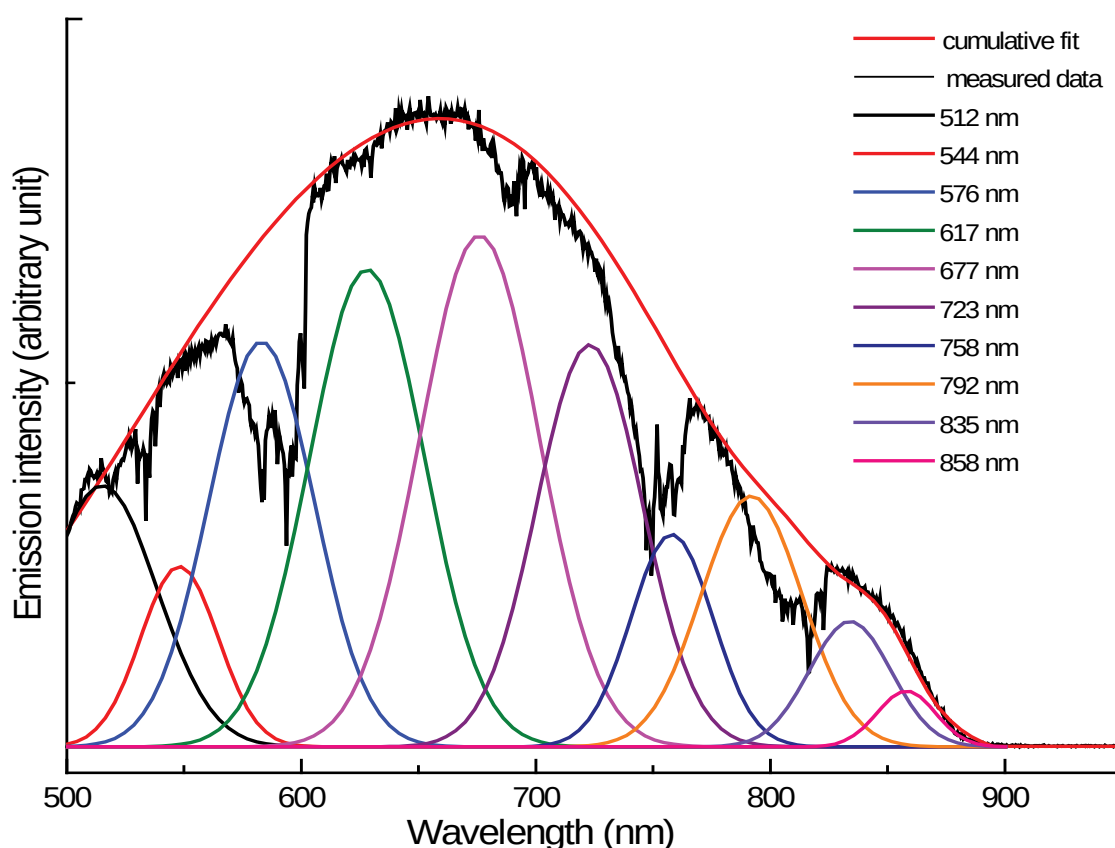


Figure 5.9 Deconvolution of the broad emission band from ZnO intrinsic defects in the ZnO:1mol%Nd³⁺ sample sintered at 600 °C, as measured at 10 K using the 457.9 nm wavelength for excitation. Gaussian curve profiles were assumed for the individual peaks and the absorption bands were not included in the fit.

of films (Figure 4.8), the fitted peak positions are the same within the 1 nm fitting error margin. The nature of the intrinsic defects in ZnO are therefore the same in powders and films although their relative concentrations are different.

Table 5.3 Peak positions of the deconvoluted broad-band emission observed in ZnO:1mol%Nd³⁺ powder samples sintered at 600 °C and their corresponding defect transitions. References used to determine the defect levels shown in Figure 2.4 are as indicated.

Peak position		Corresponding inter-defect transitions
Wavelength (± 1 nm)	Energy (± 25 cm ⁻¹)	
512	19 531	$V_{Zn}^{2-} \rightarrow V_{Zn}^{39,40}$
544	18 382	$V_{Zn}^{2-} \rightarrow V_{Zn}^{39,40}$ $Zn_i^+ \rightarrow V_{Zn}^{39,40}$
576	17 361	$O_i \rightarrow VB^{16}$
617	16 207	$V_{Zn}^{2-} \rightarrow V_{Zn}^{-16,38}$
677	14 771	$O_i \rightarrow V_{Zn}^{40}$
723	13 831	$V_O \rightarrow VB^{39,40,42}$
758	13 193	$V_O \rightarrow V_{Zn}^{40}$
792	12 626	$O_i^- \rightarrow VB^{40}$
835	11 976	$O_i \rightarrow V_{Zn}^{-16}$
858	11 655	$O_i^- \rightarrow V_{Zn}^{39,40}$

The effect of varying the excitation wavelength, on the observed emission, was also investigated and the results are shown in Figure 5.10. The use of different excitation wavelengths

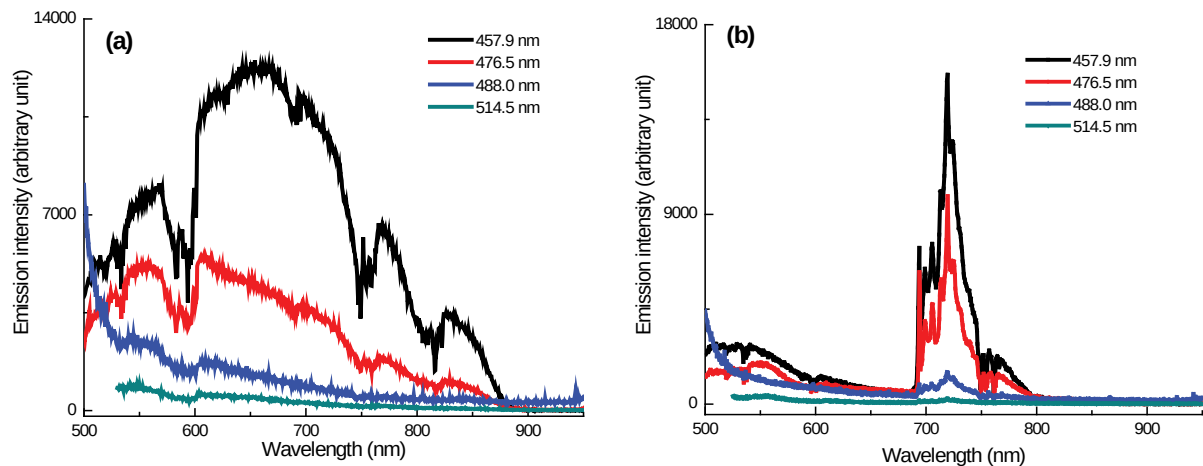


Figure 5.10 Emission spectra of ZnO:1mol%Nd³⁺ samples measured at 10 K with different excitation wavelengths to show the effect of varying excitation wavelengths on the emission, for samples sintered at (a) 600 °C and (b) 950 °C.

is important in selective studying of the luminescence spectra of materials containing multiple defect levels, such as ZnO, since different centres would exhibit emission characteristics that could be excitation-wavelength dependent. Excitation with energies below the bandgap energy of ZnO ($< 27\,180$ cm⁻¹) enables more direct population of defect levels from which radiative transitions emanate. Figure 5.10 shows that the general profiles of the Ar⁺-laser excited defect emissions were not changed by varying the excitation wavelengths. As found for the films, there

was an overall increase in intensity with increasing excitation energies, that is, the 457.9 nm line gave the highest emission intensities at both sintering temperatures.

Figure 5.11 shows that adding Li^+ ions to $\text{ZnO:1mol\%Nd}^{3+}$ resulted in (i) significantly reduced defect emission in the 600 nm – 750 nm region for the sample sintered at 600 °C, (ii) observation of Nd^{3+} emission in the 885 nm – 935 nm region, for samples sintered at 950 °C and (iii) increased Fe^{3+} emission in samples with or without Nd^{3+} , that were sintered at 950 °C. The energy levels attributed to the added Li^+ ions are positioned at $6\,452\text{ cm}^{-1}$ in the band gap of ZnO^{18} (Figure 2.4) and they act as traps to the emission from O_i and V_O defects, hence the emission quenching observed in the 600 nm – 750 nm region. In the case of Nd^{3+} emission, it is documented in the literature⁷² that alkali ions modify the matrix of the host materials in several ways that support the radiative transfer processes (to the rare-earth ions) thereby improving the luminescence intensity. The explanation of enhanced emission is that when a trivalent rare-earth ion (e.g. Nd^{3+}) substitutes a divalent ion (e.g. Zn^{2+}), charge imbalances as well as vacancies are generated.⁷² Alkali ions such as Li^+ are used to compensate for the charge imbalance and the vacancy defects too and as a result, the luminescence intensity is improved.⁷² In some instances,

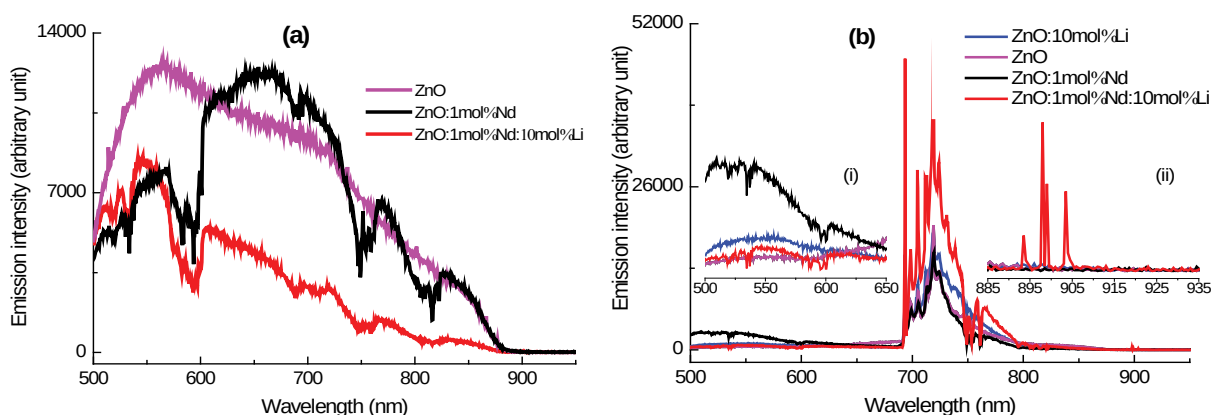


Figure 5.11 Emission spectra measured at 10 K with 457.9 nm excitation, showing the effect of co-doping ZnO powders with Nd^{3+} and Li^+ ions and sintering at (a) 600 °C and (b) 950 °C. Inserts in (b) show (i) regions with Nd^{3+} absorption at lower wavelengths and (ii) Nd^{3+} emission observed in the $\text{ZnO:1mol\%Nd:10mol\%Li}$ sample. Spectra for ZnO and $\text{ZnO:10mol\%Li}$ are included for reference.

due to its low melting temperature, lithium works as a flux thus improving the crystallinity of the doped material⁶⁸ and increases the grain sizes (Table 5.1 and Figure 5.4). In addition, co-doping $\text{ZnO:1mol\%Nd}$ with Li^+ and sintering at 950 °C improved the Fe^{3+} emission in the 690 nm – 760 nm region. This may also be a direct result of the charge compensation.

To investigate the effect of the quantity of Li^+ used on the emission from the Nd^{3+} ions, the doping concentration of Li^+ was varied from 0mol% to 10mol% and the resulting spectra are shown in Figure 5.12. It can be seen that the intensity of the emission from Nd^{3+} ions increases

with increasing Li^+ concentration; this is consistent with line-scan results (Figure 5.5) which show that more neodymium is incorporated (together with Li^+) in the smaller grains of the sample found in the crevices at 10mol% Li^+ concentration. The 600% increase in intensity caused by raising the Li^+ concentration from 1% to 5% is much more than that caused by the 5% to 10% Li^+ increase (35%). This implies high concentration of Li^+ (~10mol%) results in emission quenching as shown by the saturation tendency illustrated in the insert of Figure 5.12.

Although the 457.9 nm laser line only was used to study this Nd^{3+} emission, it is expected that the other argon laser lines would give the same spectrum though much weaker, in consistency with the intrinsic defect emission findings (Figure 5.10). The sharp emission lines shown in Figure 5.12 are the $^4\text{F}_{3/2} \rightarrow ^4\text{I}_{9/2}$ transitions of Nd^{3+} ions. This Nd^{3+} photoluminescence was investigated further using direct excitation of the $^2\text{G}_{7/2}; ^4\text{G}_{5/2}$ multiplets accessible with the dye laser and is discussed in Section 5.4. The absorption bands and the impurity- Fe^{3+} emission in ZnO will however be considered first.

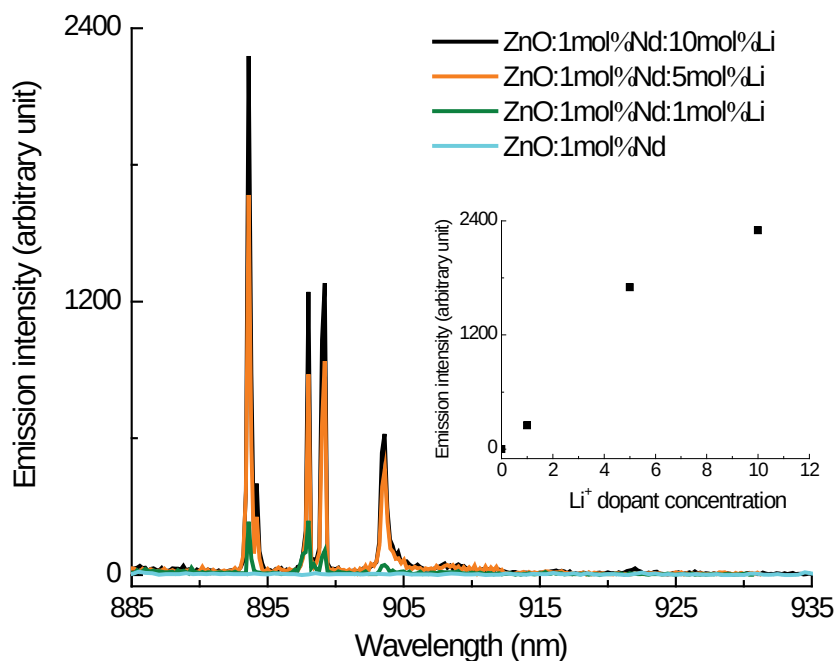


Figure 5.12 The effect of varying the amount of Li^+ doped into $\text{ZnO:1mol\%Nd}^{3+}:\text{Li}^+$ samples sintered at 950 °C on the intensity of Nd^{3+} emission. Spectra recorded with 457.9 nm wavelength excitation, at 10 K. Insert shows the Li^+ concentration dependence for the transition at 893.890 nm.

5.3.2. Absorption of intrinsic defect emission by Nd^{3+} ions

All the powder samples doped with Nd^{3+} ions showed absorption bands characteristic of Nd^{3+} ions, irrespective of (i) the sintering temperature used and (ii) whether or not lithium was added. The $\text{ZnO:1mol\%Nd}$ sample sintered at 600 °C gave the most intense absorption bands compared to the other samples. As such, the spectrum recorded with this sample was used for analysis of the absorption bands.

The broad emission peak obtained for ZnO:1mol%Nd powder samples sintered at 600 °C can be considered to be the combined effect of a number of intrinsic defect transitions as shown in Figure 5.9. Clearly, the superposed Nd³⁺-absorption transitions are in near-resonance with the 512 nm, 544 nm, 576 nm, 677 nm, 752 nm and 792 nm intrinsic defect peaks. It is therefore quite possible that photons emitted by the intrinsic defects at these wavelengths are absorbed by Nd³⁺ ions in the sample, leading to the effects observed in this work. This form of radiative energy transfer between the host matrix and the Nd³⁺ ions is favourable at high Nd³⁺ concentrations such as used here (1mol%).^{21,24} The absorption transition groups are assigned to the Z (⁴I_{9/2}) → F (²G_{9/2}), Z (⁴I_{9/2}) → E (⁴G_{7/2}), Z (⁴I_{9/2}) → D (²G_{7/2}; ⁴G_{5/2}), Z (⁴I_{9/2}) → B (⁴F_{9/2}), Z (⁴I_{9/2}) → A (⁴S_{3/2}, ⁴F_{7/2}) and Z (⁴I_{9/2}) → S (⁴F_{5/2}; ²H_{9/2}) transitions, using Figure 2.9, and are presented separately in Figure 5.13. The absorption peaks and the corresponding excited multiplets for the identified transitions are presented in Table 5.4. Transitions observed only for the sample sintered at 600 °C are labelled Φ, those present in the samples sintered at 950 °C only are identified by Θ while transitions present at both sintering temperatures are labelled with Ω.

Similar absorption profiles are reported in the literature for Nd-doped ZnO powders excited with wavelengths in the UV^{23,25,103} and visible – NIR regions (500 nm – 850 nm).^{11,21} They were attributed to Nd³⁺ absorption of the light emitted by ZnO defects. Although Jadwisieniczak *et al.*¹¹, claimed that there is no correlation between the emission peaks for intrinsic defects in ZnO and the absorption bands for the rare-earth ion, no alternative explanation for the absorption was proffered. However, from the results presented here in Figure 5.9, there is clear matching between some of the ZnO intrinsic defect emission peaks and the Nd³⁺ absorption bands. Absorption by the Nd³⁺ ions only occurs for selected emission peaks where the position of the emission peak matches the position of the Nd³⁺ multiplets (Figure 2.9). This, therefore indicates that the Nd³⁺ absorption captures the emission from the intrinsic defects of ZnO in particular energy regions.

Absorption peak positions for the Nd³⁺ doped and Nd³⁺:Li⁺ co-doped ZnO powders are compared in Figure 5.13. In Figure 5.13 (b), the absorption bands coincide with most of the peaks in the Nd³⁺ excitation spectra for the two centres (labelled A and B) and will be reconciled with the dye-laser excitation results later in this chapter (in Section 5.4). The absorption signal was too weak for any further quantitative analysis. The ZnO:1mol%Nd³⁺ sample sintered at 600 °C which showed the most intense absorption bands with argon-laser excitation, also had an absorption band in the 675 nm – 705 nm region with dye-laser excitation. The recorded spectrum labelled Nd 600 – dl is included in Figure 5.13 (c). In this region, the absorption in samples sintered at 950 °C was overshadowed by the emission from the Fe³⁺ impurity and the spectrum is therefore not included. The additional peaks in the 680 nm – 688 nm (Figure 5.13 (c)) region

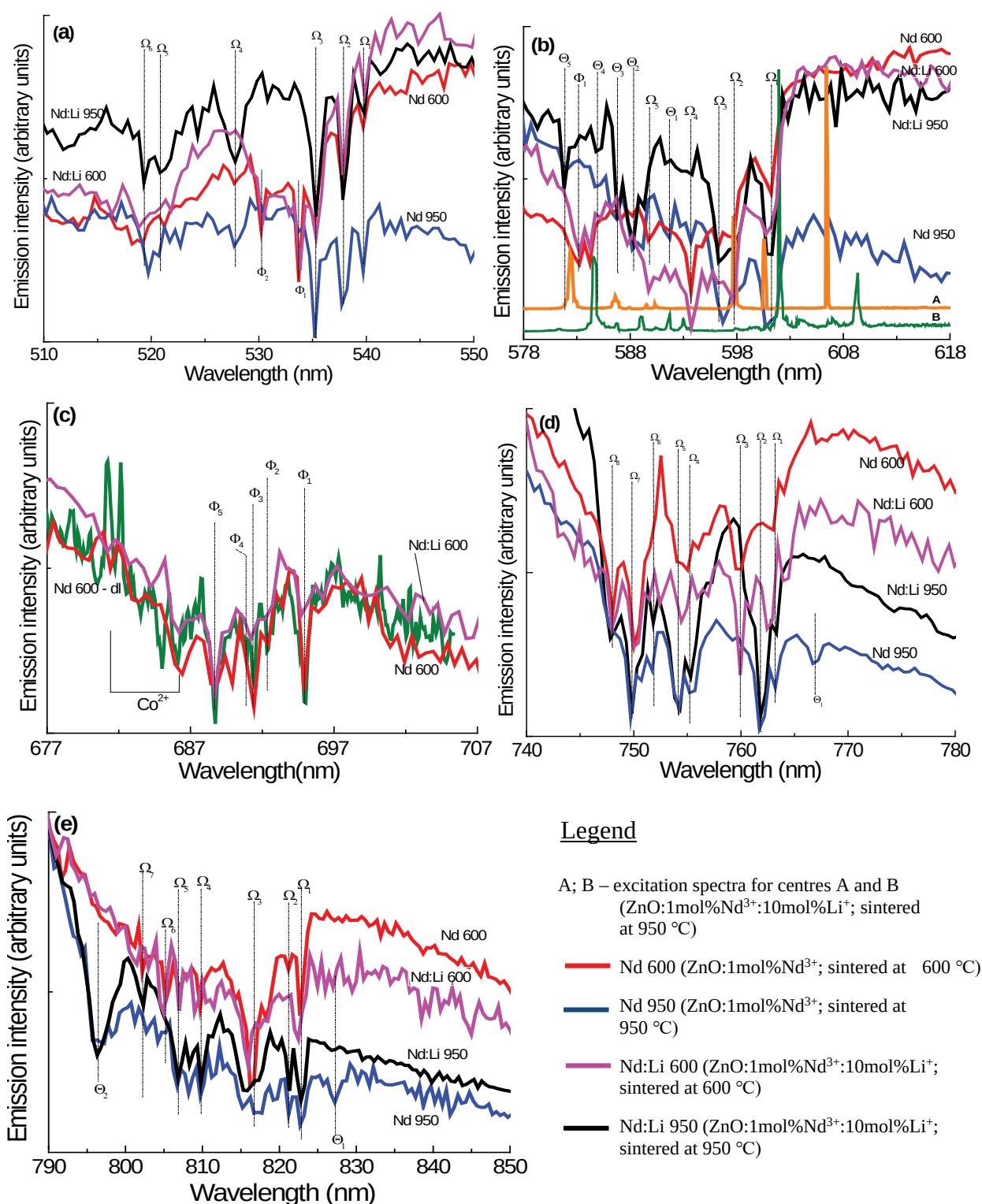


Figure 5.13 Absorption features observed at 10 K in Nd³⁺-doped and Nd³⁺:Li⁺ co-doped ZnO powder samples sintered at 600 and 950 °C. The spectra were recorded with the 457.9 nm excitation wavelength except for Nd600-dl in (c) for which a dye laser was used. Φ and Θ label peaks observed for samples sintered at 600 °C only and 950 °C only, respectively while peaks labelled Ω were present for both sintering temperatures.

Table 5.4 Excited multiplet and absorption peak positions in Nd³⁺-doped and Nd³⁺:Li⁺ co-doped ZnO powder samples sintered at 600 °C and 950 °C. Ω labels transitions present for all samples whilst Φ and Θ label transitions present for samples sintered at 600 °C only and 950 °C only, respectively.

Excited multiplet	Peak label (Fig. 5.13)	Absorption peak position	
		wavelength	energy
		(± 0.008 nm)	(± 0.1 cm ⁻¹)
E (⁴ G _{7/2}) + F (² G _{9/2})	Ω_1	539.527	18 534.8
	Ω_2	537.650	18 599.5
	Ω_3	535.195	18 684.8
	Φ_1	533.504	18 744.0
	Φ_2	530.153	18 862.5
	Ω_4	527.688	18 950.6
	Ω_5	521.202	19 186.4
	Ω_6	519.358	19 254.5
D (² G _{7/2}) + (⁴ G _{5/2})	Ω_1	601.208	16 633.2
	Ω_2	597.566	16 734.6
	Ω_3	596.399	16 767.3
	Ω_4	593.701	16 843.5
	Θ_1	591.701	16 900.4
	Ω_5	589.713	16 957.4
	Θ_2	588.324	16 997.4
	Θ_3	586.823	17 040.9
	Θ_4	584.948	17 095.5
	Φ_1	583.446	17 139.5
B (⁴ F _{9/2})	Θ_5	581.856	17 186.4
	Φ_1	694.991	14 388.7
	Φ_2	692.386	14 442.8
	Φ_3	691.399	14 463.4
	Φ_4	690.906	14 473.7
A (⁴ S _{3/2}) + (⁴ F _{7/2})	Φ_5	688.727	14 519.5
	Θ_1	767.021	13 037.5
	Ω_1	763.188	13 102.9
	Ω_2	761.820	13 126.5
	Ω_3	759.630	13 164.3
	Ω_4	755.186	13 241.8
	Ω_5	754.007	13 262.5
	Ω_6	751.869	13 300.2
S (⁴ F _{5/2}) + (² H _{9/2})	Ω_7	749.920	13 334.8
	Ω_8	747.830	13 372.0
	Θ_1	827.277	12 087.8
	Ω_1	822.819	12 153.3
	Ω_2	821.273	12 176.2
	Ω_3	816.634	12 245.4
	Ω_4	809.711	12 350.1
	Ω_5	806.916	12 392.9
	Ω_6	805.353	12 416.9
	Ω_7	802.248	12 465.0
	Θ_2	796.359	12 557.2

were obtained in undoped ZnO as well as ZnO:1mol%Nd samples with both argon laser and dye-laser excitations. These peaks could be due to presence of Co²⁺ impurities in the ZnO starting material⁴⁶ which results in Co²⁺ $\leftrightarrow$ Co³⁺ absorption and emission transitions, as indicated in Figure 2.5.

5.3.3. Impurity Fe^{3+} emission in ZnO

The prominent emission feature observed in the 690 nm – 780 nm region (Figure 5.10 (b) and Figure 5.11 (b)) for the undoped and doped ZnO samples sintered at 950 °C was reported before for ZnO doped with transitional metals.^{47,56,63,104} After careful comparison of results from this work with those in the literature, it was established that this feature derives from Fe^{3+} ions.^{47,56,63} There is perfect matching of both the peak intensity ratios and the separations between the peaks. There is a logical source of the Fe^{3+} ions in the samples used for this work. One of the common impurities in ZnO is Fe^{2+} ions which converts to Fe^{3+} upon excitation with radiation.⁵⁶ The Fe_2O_3 impurity phase was detected in XRD spectra for samples sintered at 950 °C (Figure 5.2). However, the concentration must be really low given that the purity of ZnO was given as 99.99% and the low intensity of the XRD peaks. The sharp peaks (690 nm – 750 nm) superposed on the broad emission band which is from ZnO defects (Figure 5.14) are attributed to the Fe^{3+} intra-

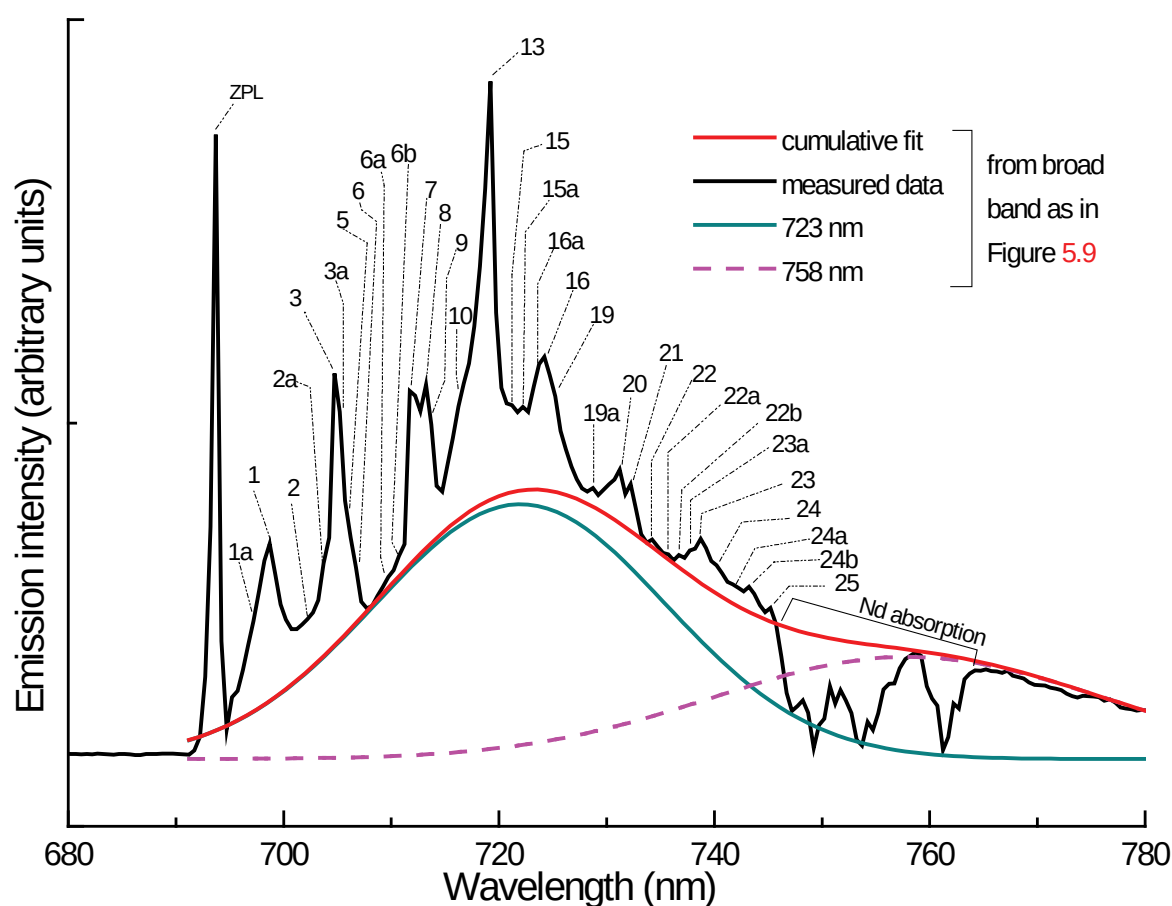


Figure 5.14 Emission spectrum of Fe^{3+} ions in ZnO measured with 457.9 nm excitation at 10 K. The Nd-absorption band has been discussed earlier in Section 5.3.2. The deconvolution of the underlying broadband is reproduced from Figure 5.9.

centre ${}^4\text{T}_1(\text{G}) \rightarrow {}^6\text{A}_1(\text{S})$ electronic transition presented in Figure 2.5 and the associated vibronic transitions. The position of the Fe^{3+} emission overlaps with the $\text{O}_i \rightarrow \text{V}_{\text{Zn}}$ transition centred at 677 nm. Therefore, the depletion in the intrinsic defects emission in this region suggests that this

defects emission is responsible for excitation of the ${}^4T_1(G)$ level of Fe^{3+} . The broad background overlapping the vibronic transitions in Figure 5.14 is associated with the $V_O \rightarrow VB$ and $V_O \rightarrow V_{Zn}$ emission transitions, as shown in Figure 5.9 and listed in Table 5.3. The sharp high-energy Fe^{3+} emission transition at 693.717 nm ($14\,415.1\text{ cm}^{-1}$) is the electronic transition or zero phonon line (ZPL). Its energy of $14\,415.1\text{ cm}^{-1}$ is equivalent to 1.7875 eV which is very similar to values in the literature.^{47,56} The well-structured low-energy sideband is made up of vibronic transitions labelled as 1a to 25 in Figure 5.14. Their wavelengths and energy positions are presented in Table 5.5.

These vibronic transitions show the main couplings between the electronic transition (ZPL) and the phonons in the host lattice⁵⁶ as discussed in Section 2.5. In the presence of an impurity such as Fe^{3+} ion in the regular ZnO lattice, the normal vibrations of the host lattice are perturbed leading to the presence of local vibrational modes (LVMs) around the impurity atom (ion). The perturbation depends on the properties of the impurity such as its mass and effective charge state.⁶³ For an Fe^{3+} ion, the energies of the local vibronic modes fall within regions of low density of phonon states of the ZnO lattice.⁶³ In the literature⁴⁷, the sharp intense vibronic transitions are assigned to optical phonons at the centre of the Brillouin zone (Γ -point) of ZnO whilst weaker intensities or lower energies indicate coupling with acoustical phonons, multi-phonon modes, or non-zero wave-vector phonon modes (at the A, K, or M points of the Brillouin zone shown in Figure 2.10).

The vibrational modes of energy 237.4 cm^{-1} , 260.7 cm^{-1} , 601.2 cm^{-1} and 625.3 cm^{-1} are assigned to local vibrational modes (LVMs) occurring in the neighbouring environment of the transitional metal (Fe^{3+})⁶³ while the most intense vibronic at 513.5 cm^{-1} and its shoulder at 509.7 cm^{-1} are from defect complexes formed by interstitial Zn and O ions (Zn_i-O_i).¹⁰⁵ The modes localised around an impurity can have significant impact especially when the mass of the impurity ion is very different from the substituted ion. Since the molar mass of Fe^{3+} (55.85 g) is 15% less than that of Zn^{2+} (65.38 g) the local vibrational modes (LVMs) of Fe^{3+} can be distinct. As expected⁶³, the LVMs of the Fe^{3+} ion were detected in the region (within the experimental error) between 30.0 meV (242.0 cm^{-1}) and 50.0 meV (403.3 cm^{-1}) as well as the region above 73.0 meV (588.8 cm^{-1}). The values obtained in this work for the LVMs of Fe^{3+} ions are in good agreement with those reported in the literature.^{47,63} The vibrational modes with energies of 372.0 cm^{-1} , 404.9 cm^{-1} , 568.9 cm^{-1} and 589.4 cm^{-1} are optical modes at the Γ point of ZnO; these have been identified in earlier infrared studies.^{106,107} Acoustic modes of energy 77.5 cm^{-1} , 102.9 cm^{-1} , 179.5 cm^{-1} , 225.6 cm^{-1} , 241.6 cm^{-1} and 271.7 cm^{-1} were detected as shown in Table 5.5. Although predicted in *ab initio* calculations⁶¹, the mode of 77.5 cm^{-1} is not often detected in measurements.

Table 5.5 Peak positions of Fe³⁺ emission in ZnO and the associated phonon modes. av = average of and prefix * in the first column indicates shoulder peaks which could not be separately indicated in Figure 5.14. References used to identify the phonon modes are in the last column.

Peak i	Wavelength, λ_i $\pm 5 \times 10^{-3}$ (nm)	Energy, E_i		$\Delta E (E_A - E_i)$			Phonon modes (references as indicated)
		± 0.1 (cm ⁻¹)	± 0.2 (eV)	± 0.2 (cm ⁻¹)	± 0.4 (meV)	Heitz <i>et al.</i> ⁴⁷ (meV)	
ZPL	693.717	14415.1	1.7875	0.0	0.0	0.00	ZPL ^{47,56}
1a	697.468	14337.6	1.7779	77.5	9.6	--	TA (A) ^{61,108}
1	698.706	14312.2	1.7747	102.9	12.8	12.74	TA (M) ^{56,104,109}
2	702.466	14235.6	1.7652	179.5	22.3	22.26	TA (A) ^{61,104}
2a	703.769	14209.2	1.7619	205.9	25.6	--	2 × [1]
3	704.745	14189.5	1.7595	225.6	28.0	--	LA (K, M) ⁶¹
3a	705.335	14177.7	1.7580	237.4	29.5	29.44	LVM _{Fe} ⁶³
*4	705.541	14173.5	1.7575	241.6	30.0	29.91	LA (M) ¹⁰⁹
5	706.493	14154.4	1.7551	260.7	32.4	32.28	LVM _{Fe} ^{56,63}
6	707.046	14143.4	1.7538	271.7	33.7	33.71	LA (M) ^{104,105}
6a	709.954	14085.4	1.7466	329.7	40.9	--	[1] + [3]
6b	710.870	14067.3	1.7443	347.8	43.2	--	[1] + [4]
7	712.092	14043.1	1.7413	372.0	46.2	46.15	TO (Γ) ^{106,107}
8	713.190	14021.5	1.7387	393.6	48.8	48.05	surface optical phonon ¹¹⁰
9	713.765	14010.2	1.7373	404.9	50.2	49.50	TO (Γ) ^{106,107}
10	716.730	13952.3	1.7301	462.8	57.4	56.76	2 × av {[3] and [3a]}
*11	718.395	13919.9	1.7261	495.2	61.4	61.35	[3a] + [5]
*12	719.145	13905.4	1.7243	509.7	63.2	63.25	LVM _{Zn(i)-O(i)} ^{105,111}
13	719.342	13901.6	1.7238	513.5	63.7	63.64	LVM _{Zn(i)-O(i)} ^{105,111}
*14	719.797	13892.8	1.7227	522.3	64.8	64.75	2 × [5]
15	721.111	13867.5	1.7196	547.6	67.9	67.85	LO (A) ⁶¹ , 2 × [6]
15a	722.218	13846.2	1.7169	568.9	70.6	--	LO (Γ) ^{106,107}
16a	723.292	13825.7	1.7144	589.4	73.1	--	LO (Γ) ^{106,107}
16	723.911	13813.9	1.7129	601.2	74.6	74.55	LVM _{Fe} ^{56,63}
*17	724.330	13805.9	1.7119	609.2	75.6	75.50	[3a] + [7]
*18	724.720	13798.4	1.7110	616.7	76.5	76.42	[1] + [13]
19	725.176	13789.8	1.7099	625.3	77.6	77.52	LVM _{Fe} ⁶³
19a	728.732	13722.5	1.7016	692.6	85.9	--	[1] + [16a]
20	731.411	13672.2	1.6954	742.9	92.1	92.12	2 × [7]
21	732.817	13646.0	1.6921	769.1	95.4	95.42	[7] + [8]
22	734.311	13618.2	1.6887	796.9	98.8	98.84	2 × av{[8] and [9]}
22a	735.756	13591.5	1.6853	823.6	102.2	--	2 × [3] + [7]
22b	736.741	13573.3	1.6831	841.8	104.4	--	[1] + 2 × [7]
23a	737.657	13556.4	1.6810	858.7	106.5	--	[5] + [16], [6] + [15b]
23	738.917	13533.3	1.6781	881.8	109.4	109.39	[1] + [7] + [9], [5] + [19]
24	740.420	13505.9	1.6747	909.2	112.8	112.73	[8] + [13]
24a	741.891	13479.1	1.6714	936.0	116.1	--	[5] + [6] + [9]
24b	743.139	13456.4	1.6686	958.7	118.9	--	[8] + [15a], 2 × [3] + [13]
25	745.671	13410.7	1.6629	1004.4	124.6	124.54	[3a] + [7] + [8], [9] + [16]

5.4. Photoluminescence (PL) studies of Nd³⁺ ions with dye laser excitation

A potential application of the near-infrared Nd³⁺ emissions in the 890 nm ($^4F_{3/2} \rightarrow ^4I_{9/2}$) and 1060 nm ($^4F_{3/2} \rightarrow ^4I_{11/2}$) regions is in biological imaging since biological tissues have maximum transmittance in these same regions.²⁴ For further studies of the emission obtained from Nd³⁺ ions in ZnO, the $^2G_{7/2}; ^4G_{5/2}$ (D) multiplet was directly excited using a dye laser. This is in contrast to the indirect excitation mechanism associated with the Ar⁺ laser, which involves Nd³⁺ ions harvesting some of the intrinsic defects emission (Section 5.3). Only samples co-doped with Li⁺ ions and sintered at 950 °C showed Nd³⁺ emission for both Ar⁺ and dye-laser excitations. The dye-laser excitation results obtained for the ZnO:1mol%Nd³⁺:10mol%Li⁺ sample will be discussed here. Of the three Li⁺ co-doped samples, this sample showed the highest Nd³⁺ emission intensities with the Ar⁺ laser (Figure 5.12), hence this choice. The emission spectra were recorded using the same laser power as for the Ar⁺ laser excitation (35 mW).

5.4.1. Emission and excitation spectra of Nd³⁺ ions in ZnO powders

The procedure for site-selective excitation studies described in Section 4.4.1 was followed in order to determine the Nd³⁺ sites (centres) present in ZnO powders. The monochromator was set to one of the emission transition positions in Figure 5.12 obtained with the Ar⁺ laser for the ZnO:1mol%Nd³⁺:10mol%Li⁺ sample. The dye-laser wavelength was then manually varied over the dye range in order to determine all the excitation wavelengths responsible for the particular emission. As for the films, the excitation wavelength that results in strong emission was then used to obtain a site-selective emission spectrum. When the emission spectrum was compared with the Ar⁺-laser excited emission spectrum (Figure 5.15), it was observed that the site-selective emission spectrum matched some but not all the Ar⁺ laser excited emission transitions. The above process was then repeated with the monochromator set to one of the transitions in the Ar⁺-laser spectrum that were absent from the first site-selective emission. The resulting emission spectrum contained all the missing transitions of reasonably strong intensity corresponding to a second Nd³⁺ site. Due to low emission intensities, weaker peaks (in the wavelengths positions higher than 905 nm) were not detected with the Ar⁺ laser (Figure 5.15 (a)). The two site-selective emission spectra obtained with dye laser excitation are compared to the earlier Ar⁺-laser excited spectrum (Figure 5.12) in Figure 5.15. The site-selective emission spectra in Figure 5.15 (b) and (c) are clearly different which means that there are two distinct Nd³⁺ configurations (centres) co-existing in the powder samples. These have been labelled centre A and centre B corresponding to spectra (b) and (c) respectively, in Figure 5.15. The transition labelled α in Figure 5.15 (a) could not be separately monitored as it is too close to the stronger A centre transition to be resolved. Dotted vertical lines shown in Figure 5.15 guide the eye to the peaks which are

corresponding in spectra recorded with both the indirect (Ar^+ laser) and direct (dye-laser) excitation mechanisms. The spectrum recorded with the Ar^+ laser contains a superposition of

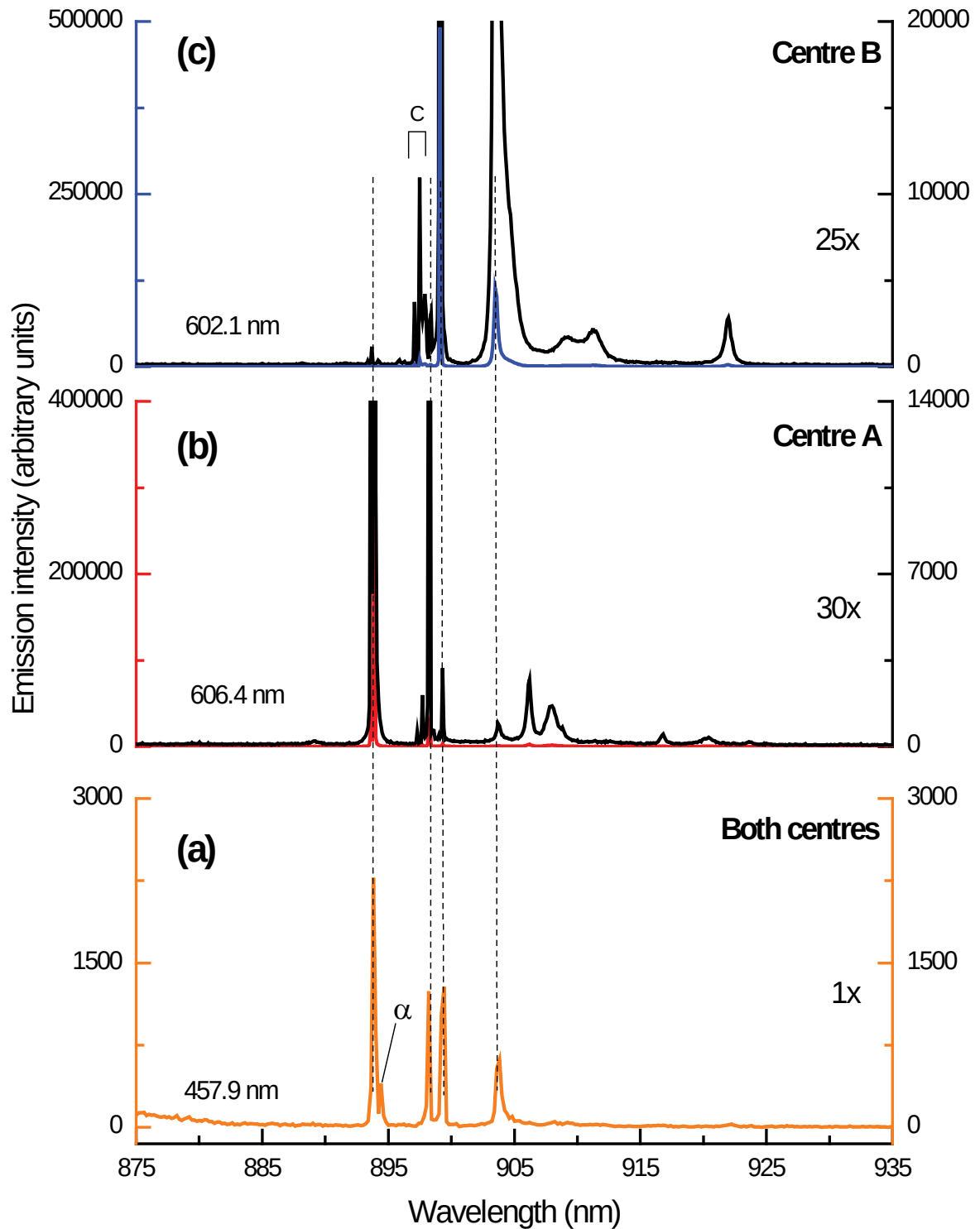


Figure 5.15 Emission spectra for $\text{ZnO:1mol\%Nd}^{3+}\text{:10mol\%Li}^+$ sample sintered at 950 °C recorded at 10 K with (a) indirect excitation at 457.9 nm and direct excitation at (b) 606.400 nm and (c) 602.100 nm, respectively. Spectra (b) and (c) have been magnified by 30x and 25x, respectively.

emission from different centres but distinction is not possible. The centre A and centre B emission spectra also show weaker multiple peaks in the 897.000 nm – 900.000 nm

(11 148.3 cm⁻¹ – 11 111.1 cm⁻¹) region and these were reproducible under both direct excitations. These peaks, labelled C in Figure 5.15 (c), may arise from some Nd³⁺ clusters within the lattice.

As shown in Figure 5.15, upon excitation with either (a) an Ar⁺ laser or (b, c) a dye laser, sharp Nd³⁺ emission lines were observed in the same region. The group of observed emission lines corresponds to radiative transitions from the ⁴F_{3/2} (R) multiplet at ~895 nm (Figure 2.9) to the lowest ⁴I_{9/2} (Z) multiplet. The spectra show some intense and well resolved Nd³⁺ emission lines, indicating well-ordered crystal-field surroundings of the Nd³⁺ ions.²⁹ While the emission from broadband excitation of intrinsic defects (Figure 5.15 (a)) has been reported before,^{11,24,29} to the best of my knowledge this study is among the first few site-selective excitation studies of Nd³⁺ ions doped into ZnO powders. As discussed in Section 2.4.2, there are five crystal-field levels in the Z (⁴I_{9/2}) multiplet, two in the R (⁴F_{3/2}) multiplet and seven (4 + 3) in the dye-laser excited D (²G_{7/2}; ⁴G_{5/2}) multiplet. Consequently, all the Nd³⁺ ion emission transitions in Figure 5.16 are present at 10 K and are therefore from the lower level (R₁) of the ⁴F_{3/2} multiplet to each of the Z₁ to Z₅ levels of the ground multiplet (⁴I_{9/2}). Scales on the right side in Figures 5.15 and 5.16 are magnified by up to 50X to show low intensity peaks. An emission peak from impurities is labelled β in Figure 5.16. This peak could not be assigned to any transition related to Nd³⁺ ions. One reason is that the linewidth of this peak relative to the peak labelled R₁ → Z₁ is large and therefore forbids it to be the first transition. Linewidths increase with wavelength for emission transitions to the ground multiplet, due to further relaxation from the higher levels (Z₂ – Z₅) to the lowest level (Z₁). Secondly, the peak β is present in both centre A and centre B spectra. However, basing on its appearance in spectra recorded for Nd-doped materials, this peak can be assigned to emission from an impurity which is always present in the Nd₂O₃ powder. In addition, peaks associated with vibrational modes coupled to the strongest electronic transitions are also present in the spectra. These are labelled v₁ – v₇ for centre A and vb₁ and vb₂ for centre B in Figure 5.16 and will be discussed further in Section 5.4.2. Labels A and B in the spectra (a) and (b) indicate weak peaks which are a result of emission breaking through from the centre A or centre B, respectively, due to small overlap in the excitation transition profiles in conjunction with the laser linewidth. The emission intensities of the most intense peaks, which correspond to the R₁ → Z₁ transitions of centre A and centre B were found to be of 2.5 : 1 ratio. Electronic transitions obtained from the two centres are presented in Table 5.6.

Further experiments were performed at higher temperatures of 20 K, 50 K and 75 K in order to identify emission transitions originating from the higher level, R₂, in the ⁴F_{3/2} multiplet to the ground multiplet levels. The spectra are presented in Figures 5.17 and 5.18 for centre A and centre B, respectively. Additional peaks obtained for the two centres at the higher

temperatures are also listed in Table 5.6. The upper limit temperature was selected to be 75 K because beyond this, thermal broadening prevented identification of any individual transitions. Generally, the intensity of the emission lines observed at 10 K decreased with increasing sample

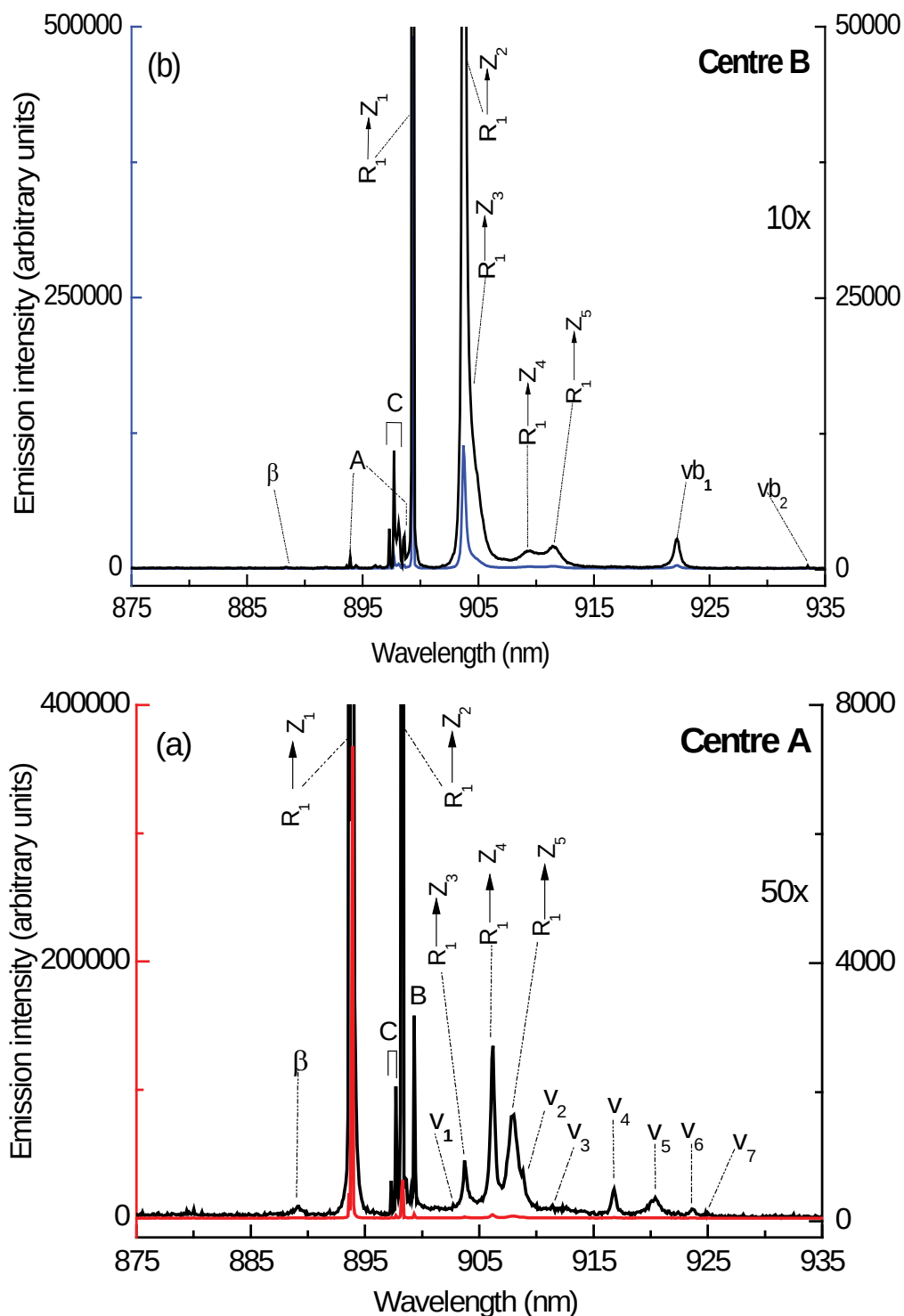


Figure 5.16 Emission spectra recorded at 10 K for the two different Nd^{3+} centres in the $\text{ZnO:1molNd}^{3+}:10\text{mol\%Li}^{+}$ sample sintered at 950 °C excited with a dye laser set at (a) 606.400 nm and (b) 602.100 nm. Electronic transitions are labelled $R_1 \rightarrow Z_i$ ($i = 1$ to 5) and vibronic transitions are labelled v_j and vb_j ($j = 1, 2, \dots$).

Table 5.6 Peak positions and electronic transitions assigned to each peak observed for centre A and centre B in the ZnO:1mol%Nd³⁺:10mol%Li⁺ powder sample, at 10 K and at 75 K.

Sample temperature	Centre A peak position		Centre B peak position		Electronic transition
	Wavelength (± 0.008 nm)	Energy (± 0.1 cm ⁻¹)	Wavelength (± 0.008 nm)	Energy (± 0.1 cm ⁻¹)	
10 K	893.890	11 187.1	899.310	11 119.6	R ₁ → Z ₁
	898.242	11 132.9	903.715	11 065.4	R ₁ → Z ₂
	903.738	11 065.2	904.425	11 056.7	R ₁ → Z ₃
	905.948	11 038.2	909.446	10 995.7	R ₁ → Z ₄
	907.938	11 014.0	911.486	10 971.1	R ₁ → Z ₅
75 K	886.380	11 281.8	891.709	11 214.4	R ₂ → Z ₁
	890.663	11 227.6	896.040	11 160.2	R ₂ → Z ₂
	896.062	11 159.9	896.740	11 151.5	R ₂ → Z ₃
	898.242	11 132.9	901.670	11 090.5	R ₂ → Z ₄
	900.196	11 108.7	903.677	11 065.9	R ₂ → Z ₅

temperature whilst the emerging emission lines from the higher level of the R multiplet grew. As the temperature changed from 10 K to 75 K, the intensity of the R₁ → Z₁ emission line for each Nd³⁺ centre decreased by a factor of ten for centre A and 30 for centre B. Transitions from the R₂ level of the ⁴F_{3/2} multiplet are labelled on the 75 K spectra for each centre and can be seen to increase in intensity from 20 K while those from R₁ become weaker. The position of transition R₂ → Z₄ coincides with that of the R₁ → Z₂ transition hence the intensity of the latter is not decreasing at the same rate as other peaks present at 10 K. This is due to influence from a growing peak for the R₂ → Z₄ transition. For easy comparison of peaks observed at 10 K and 75 K, R₁ → Z spectra (Figure 5.16) are reproduced in (i) of both figures. Magnified scales on the right show peaks with low intensities. The energy separation between the lowest level (Z₁) and the highest level (Z₅) of the ground multiplet (⁴I_{9/2}) was found to be ~180 cm⁻¹ for centre A and ~150 cm⁻¹ for centre B. These values lie within the range of values obtained for Nd³⁺-doped lanthanum chloride presented on the Dieke diagram.⁵⁸ This gives confidence in the identification of the five transitions.

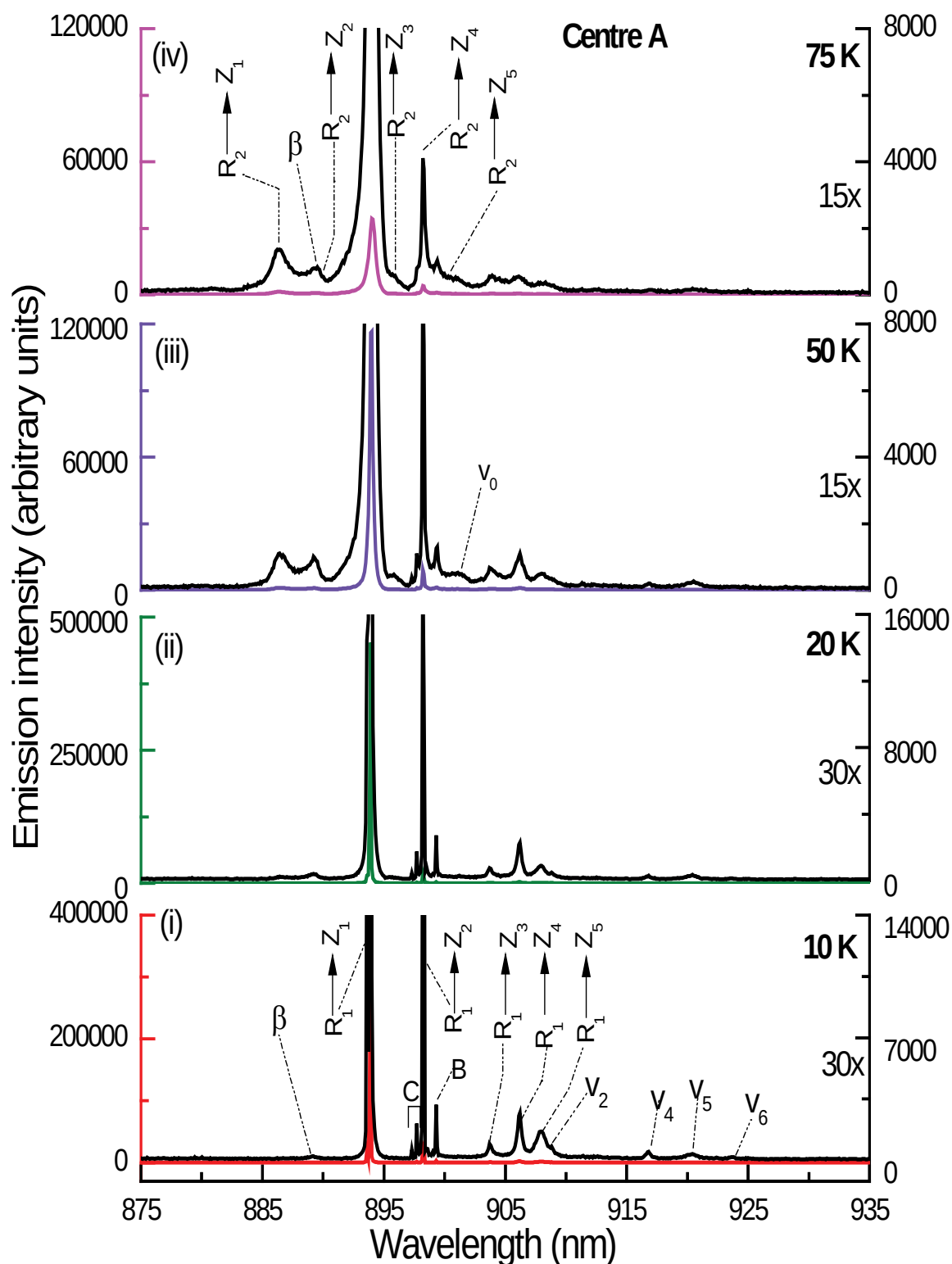


Figure 5.17 Emission spectra of centre A in ZnO:1mol%Nd³⁺:10mol%Li⁺ samples sintered at 950 °C. PL spectra collected at different temperatures using the excitation wavelength 606.400 nm. Transitions from the R₁ and R₂ levels of the R multiplet to the Z multiplet levels (Z₁ to Z₅) are labelled in the 10 K and 75 K spectra, respectively. Vibronic transitions are labelled v_j (j = 2 – 6) in (i) and v₀ in (iii). β is from an impurity in Nd₂O₃ while C identifies cluster centre transitions.

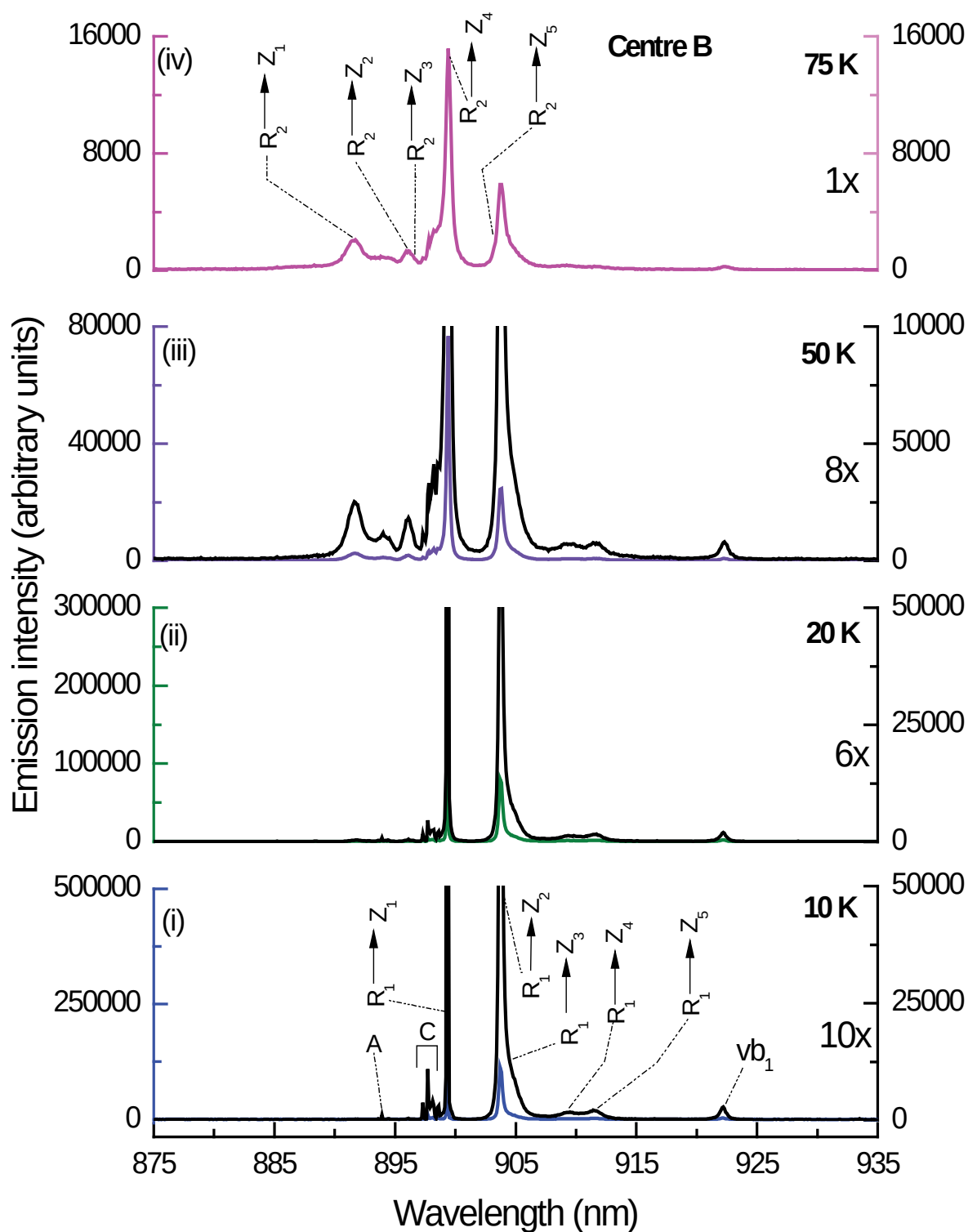


Figure 5.18 Emission spectra of centre B in ZnO:1mol%Nd³⁺:10mol%Li⁺ samples sintered at 950 °C measured at different sample temperatures using the excitation wavelength 602.100 nm. Transitions from the R₁ and R₂ levels of the R multiplet to the Z multiplet levels (Z₁ to Z₅) are labelled in the 10 K and 75 K spectra, respectively. vb₁ in (i) is a vibronic transition. Labels A and C identify breakthrough emission from centre A and the cluster centre(s), respectively.

In addition, there was a slight shift in the position of the most intense peak ($R_1 \rightarrow Z_1$) to higher wavelengths for both centres A and B as shown in Figure 5.19. This transition shifted by 0.182 nm (2.0%) for centre A and by 0.151 nm (1.7%) for centre B whereas the second intense peak ($R_1 \rightarrow Z_2$) remained almost at the same peak position in both cases as shown (Figure 5.19).

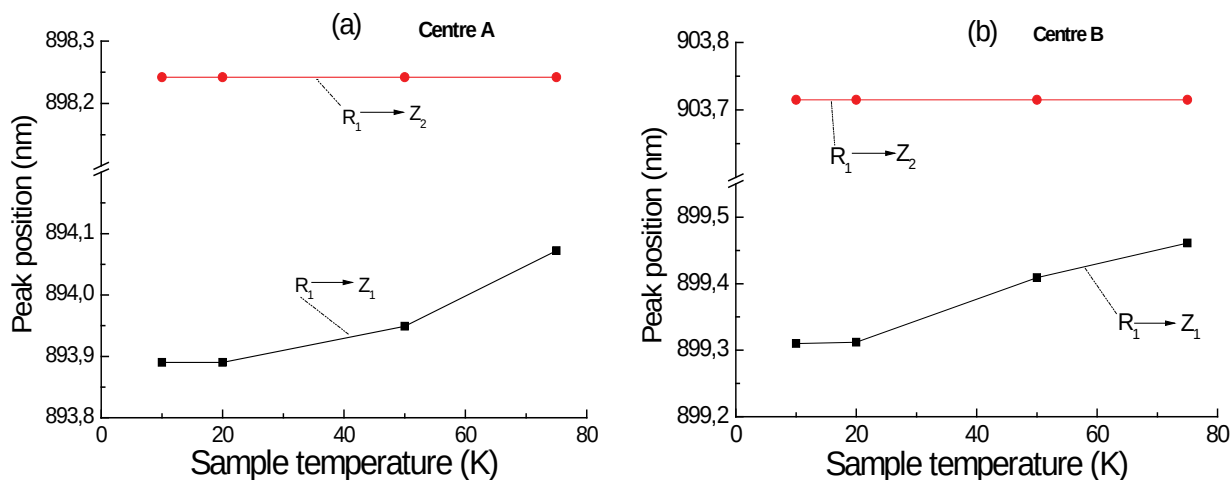


Figure 5.19 Shift of the $R_1 \rightarrow Z_1$ peak with temperature for (a) centre A and (b) centre B in $\text{ZnO:1molNd}^{3+}\text{:10mol\%Li}^+$ samples sintered at 950 °C

A peak shift towards the lower energies may indicate involvement of the emission peak in electron–phonon coupling.¹¹² The stronger coupling effect is due to the fact that at higher temperatures there are more vibrational modes of the host lattice and these affect the local environment of the doped rare earth ion. Therefore, some of the emission energy intended to be in the emission of the ion is lost to the system through these vibrations.¹¹²

Broadening of emission lines with increasing temperature was also observed in the spectra as another effect of the electron-phonon interaction due to increasing electron mobility with increasing temperature. The changes observed in the linewidths (FWHM) of $R_1 \rightarrow Z_1$ and $R_1 \rightarrow Z_2$ peaks are shown in Figure 5.20. The $R_1 \rightarrow Z_2$ transition is much narrower for centre A than for centre B. In general, the centre B transitions and the $R_1 \rightarrow Z_1$ transition of centre A broadened at the same rate while the $R_1 \rightarrow Z_2$ transition of centre A responded rather weakly to the temperature increases (Figure 5.20). This may indicate poor coupling of this electronic transition to the lattice modes even at the raised temperatures; it is not immediately clear why this is so.

In order to obtain the $Z \rightarrow D$ excitation spectrum for each centre, the monochromator was set to the $R_1 \rightarrow Z_1$ transition which is the strongest in each emission spectrum and the dye laser scanned through its lasing range (570 nm – 640 nm). Again, the two excitation spectra were different, confirming the presence of two distinct Nd^{3+} sites in the ZnO powders.

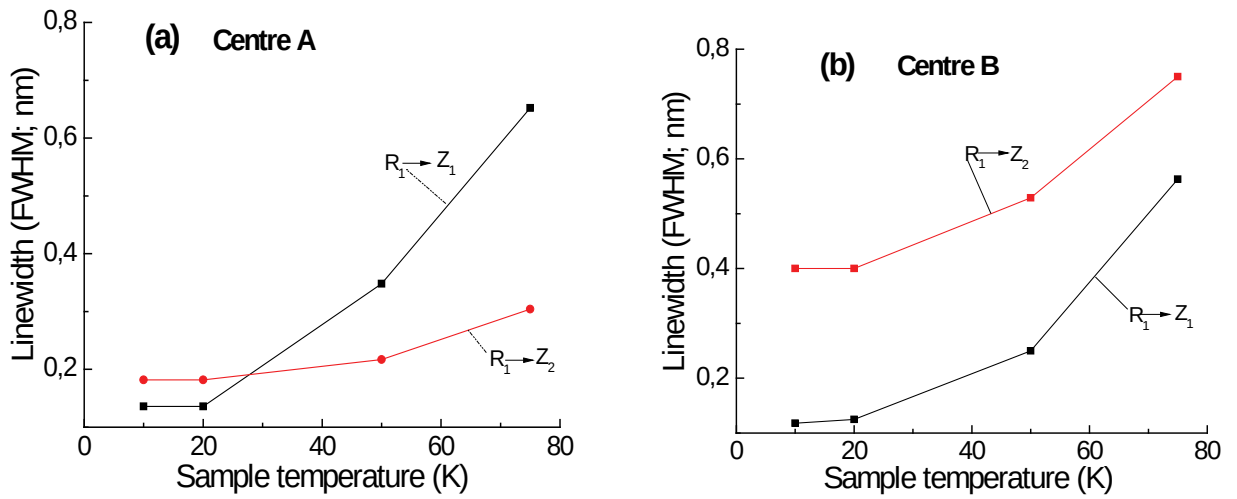


Figure 5.20 Changes in linewidths (FWHM) of the $R_1 \rightarrow Z_1$ and $R_1 \rightarrow Z_2$ peaks with temperature for (a) centre A and (b) centre B in $\text{ZnO:1molNd}^{3+}\text{:10mol\%Li}^+$ samples annealed at 950 °C.

The excitation spectra obtained at 10 K while monitoring the $R_1 \rightarrow Z_1$ transition of both centre A and centre B at 893.890 nm and 899.310 nm, respectively, are presented in Figure 5.21. At 10 K, all the excitation transitions are expected to be from the lowest level (Z_1) of the ground multiplet ($^4I_{9/2}$) to the seven levels of the excited D ($^2G_{7/2}, ^4G_{5/2}$) multiplet, as discussed in Section 2.4.2. Excitation transitions to the D_1 to D_7 levels are indicated on Figure 5.21, for each centre. The transition wavelengths (energies) identify the levels that make up the D multiplet of each centre. In each figure, the peaks appear as a combination of a group of three and then another group of four transitions, as for the films (Figure 4.11). These therefore, correspond to the three levels of the $^4G_{5/2}$ multiplet and the four levels of the $^2G_{7/2}$ multiplet, respectively.

Additional peaks labelled y_i ($i = 1, 2, 3$) are associated with phonon modes of the lattice (to be discussed later in Section 5.4.2). The peaks identified with C can be related to the cluster centre(s) which give the weak emission at ~898 nm in Figures 5.17 and Figure 5.18. The peaks in the excitation spectra of both centres overlap with absorption features in the indirectly excited spectrum as shown in Figure 5.13 (b). This clearly shows that both Nd^{3+} centres benefit from the absorption of intrinsic defect emission. However, the $Z_1 \rightarrow D_1$ peaks near 608 nm for both centres were not detected in the absorption spectra presented in Figure 3.13 (b) probably because there is no simple direct relationship between absorption and emission peak intensities, in general.

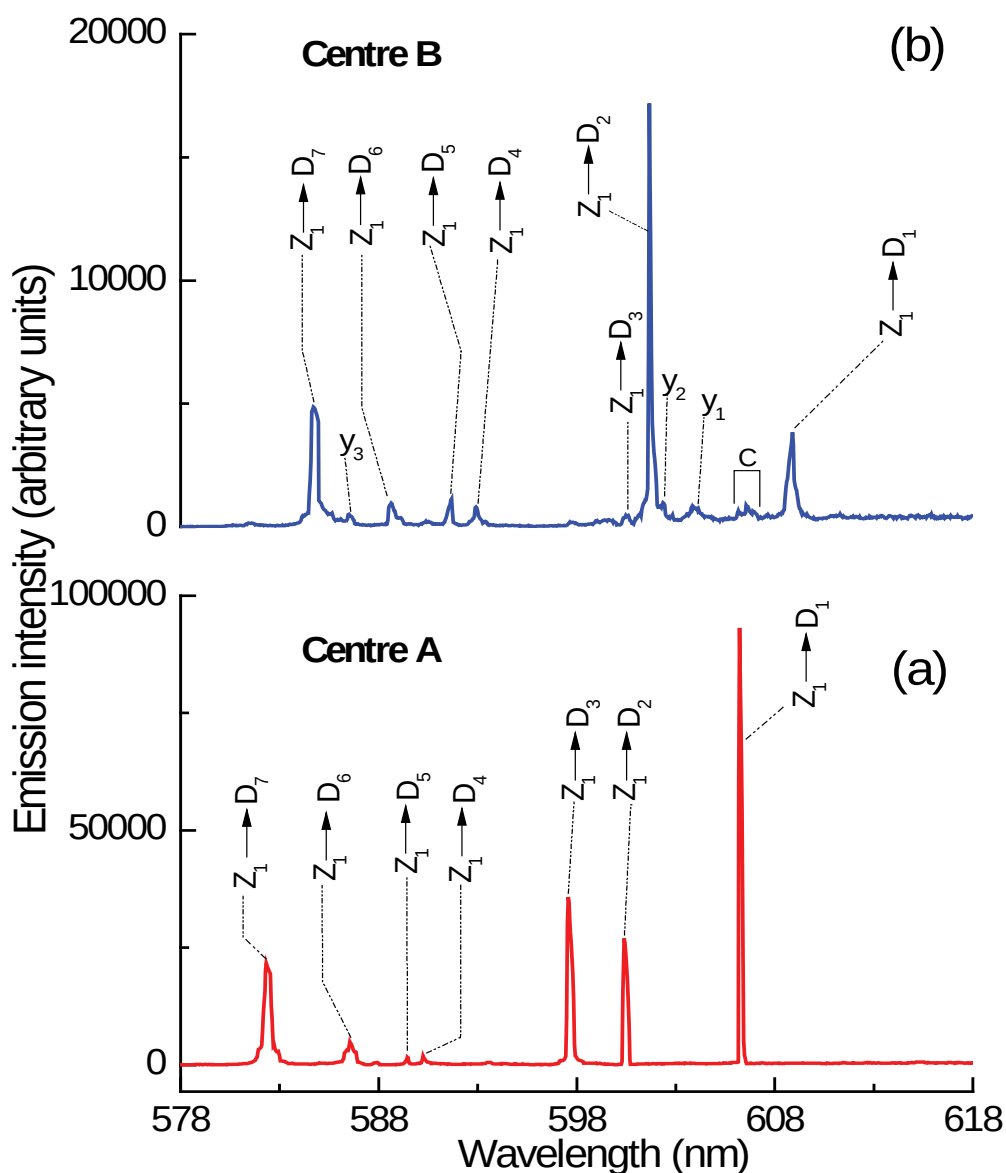


Figure 5.21 Excitation spectra recorded at 10 K for (a) centre A and (b) centre B in ZnO:1mol%Nd³⁺:10mol%Li⁺ samples. The monitored wavelengths are 893.890 nm and 899.310 nm for centre A and centre B, respectively. Electronic transitions are labelled $Z_1 \rightarrow D_i$ ($i = 1$ to 7) and vibronic transitions are identified as y_j ($j = 1, 2, 3$). C identifies breakthrough emission from the cluster centre(s).

Figures 5.22 and 5.23 show variations in the excitation transitions for centre A and centre B, respectively, with increasing sample temperature. For both centres (Figures 5.22 and 5.23), transitions labelled on spectrum (i) are all from the Z_1 level (as in Figure 5.21) whereas those labelled in spectrum (iv) are from the Z_2 and Z_3 levels which start to become populated above 20 K. The $Z_2 \rightarrow D$ and $Z_3 \rightarrow D$ transitions grow with temperature. Peaks labelled with a w in the 50 K spectrum of Figure 5.22 are vibronic transitions while that labelled C is unassigned and could belong to a cluster centre. Because of the smaller $Z_2 - Z_3$ separation for centre B, the $Z_3 \rightarrow D$ transitions always appear as shoulders to the $Z_2 \rightarrow D$ transitions (spectrum (iv) in Figure 5.23).

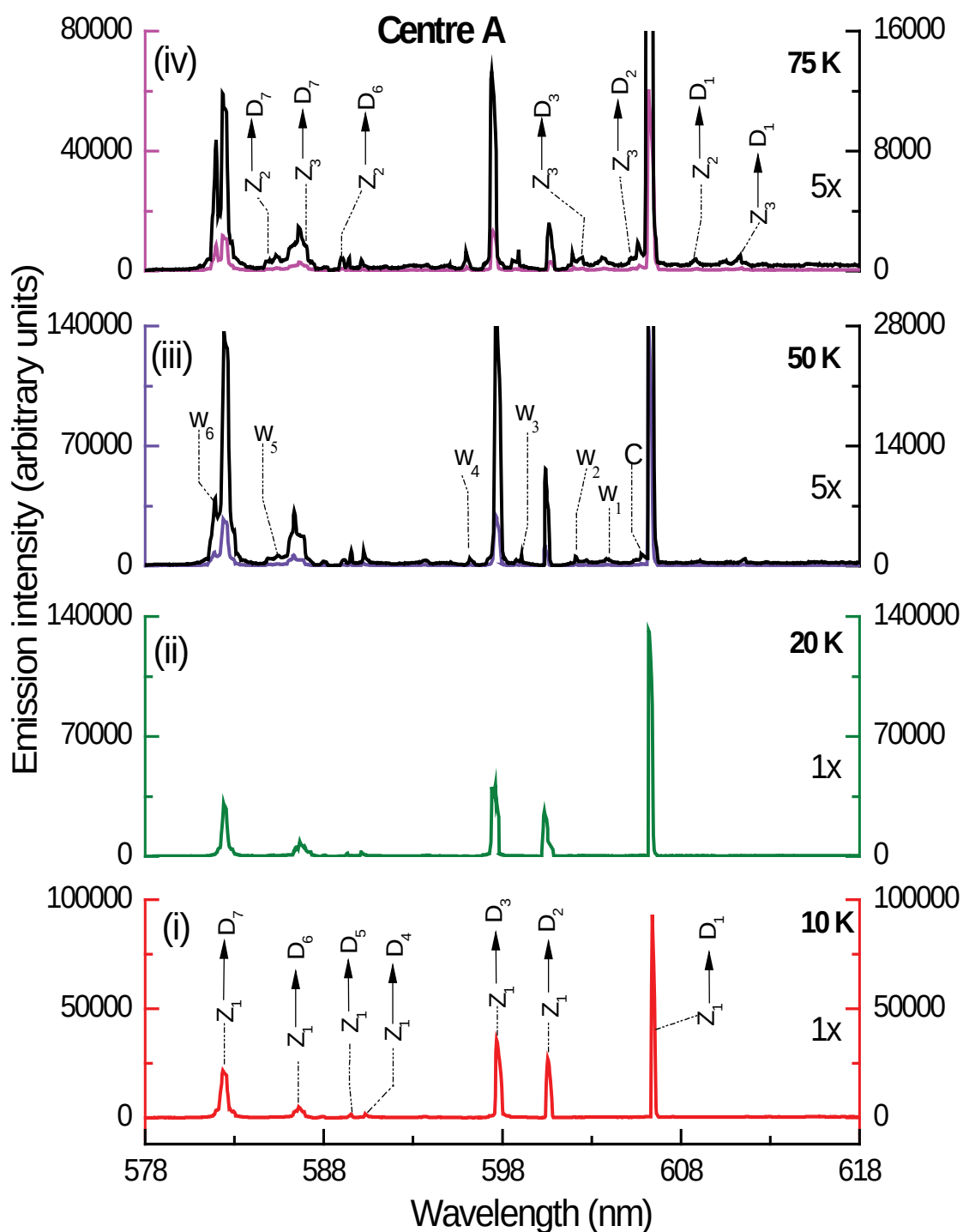


Figure 5.22 Excitation spectra for centre A in ZnO:1mol%Nd³⁺:10mol%Li⁺ samples sintered at 950 °C measured at different sample temperatures (10 K – 75 K) while monitoring the R₁ → Z₁ transition at 893.890 nm. Transitions from Z₁ and the higher Z levels (Z₂, Z₃) to the D levels (D₁ to D₇) are identified in the 10 K and 75 K spectra, respectively. Vibronic transitions are labelled w_i (i = 1 to 6) in (iii) and C identifies the cluster centre transitions.

Energy level schemes obtained from the 10 K – 75 K excitation and emission spectra of centre A and centre B are presented in Figure 5.24. What distinguishes the two centres is the separation between their Z₂ and Z₃ levels, which is about 70 cm⁻¹ for centre A and 15 cm⁻¹ for centre B. Also, the ⁴F_{3/2} multiplet for the centre A is at about 70 cm⁻¹ higher than that for the

centre B. Both pairs of levels of the $^4F_{3/2}$ multiplet are separated by about 95 cm^{-1} , which is approximately equal to the 97.5 cm^{-1} for centre A in the films but is lower by about 20 cm^{-1} than that for centre B in the films.

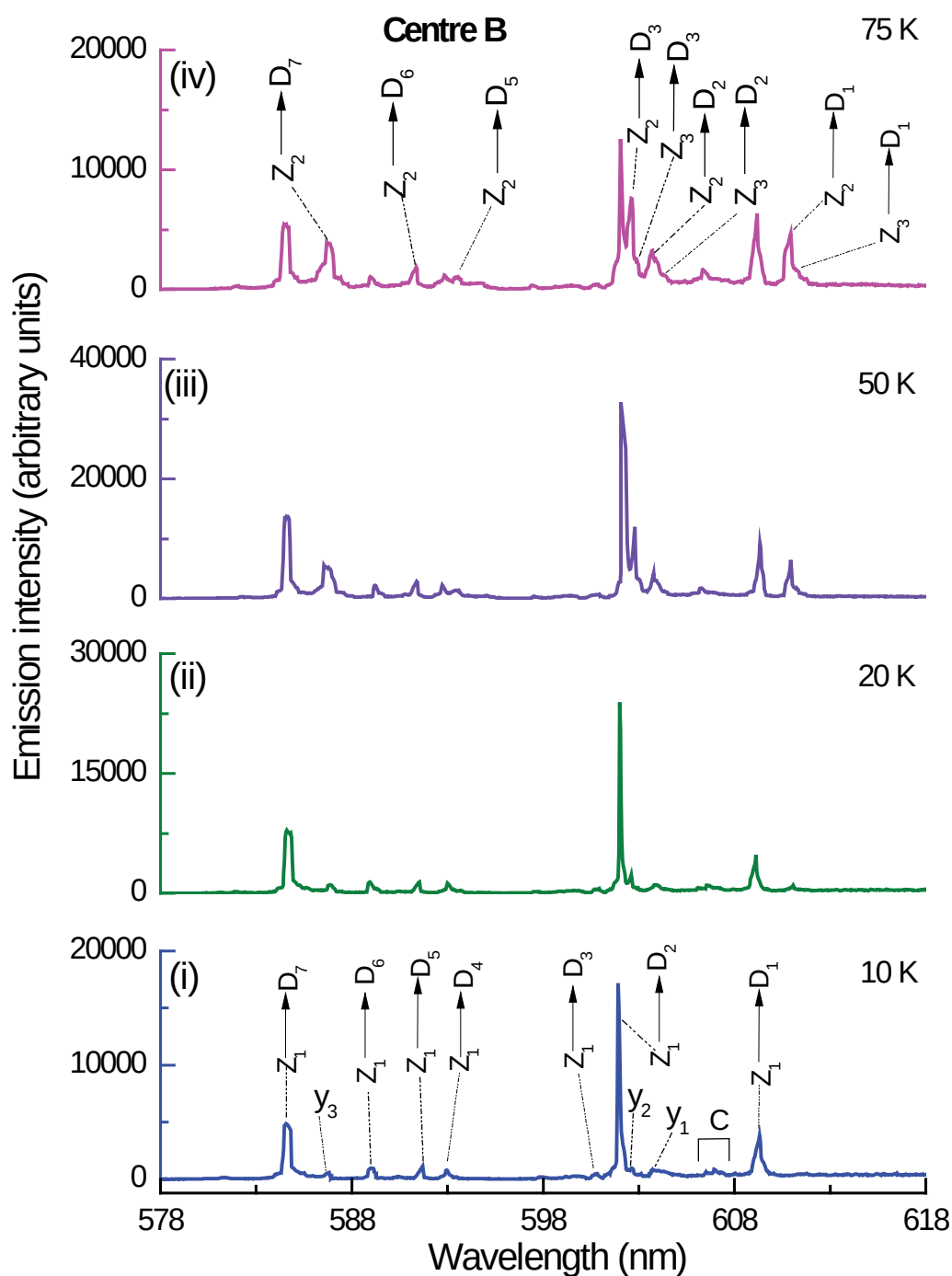


Figure 5.23 Excitation spectra for centre B in $\text{ZnO:1mol\%Nd}^{3+}\text{:10mol\%Li}^+$ samples sintered at 950°C measured at different sample temperatures (10 K – 75 K) while monitoring the $R_1 \rightarrow Z_1$ transition at 899.310 nm . Transitions from Z_1 and the higher Z levels (Z_2 , Z_3) to the D levels (D_1 to D_7) are identified in the 10 K and 75 K spectra, respectively. Vibronic transitions are labelled y_i ($i = 1, 2, 3$) in (i) and C identifies the cluster centre transitions.

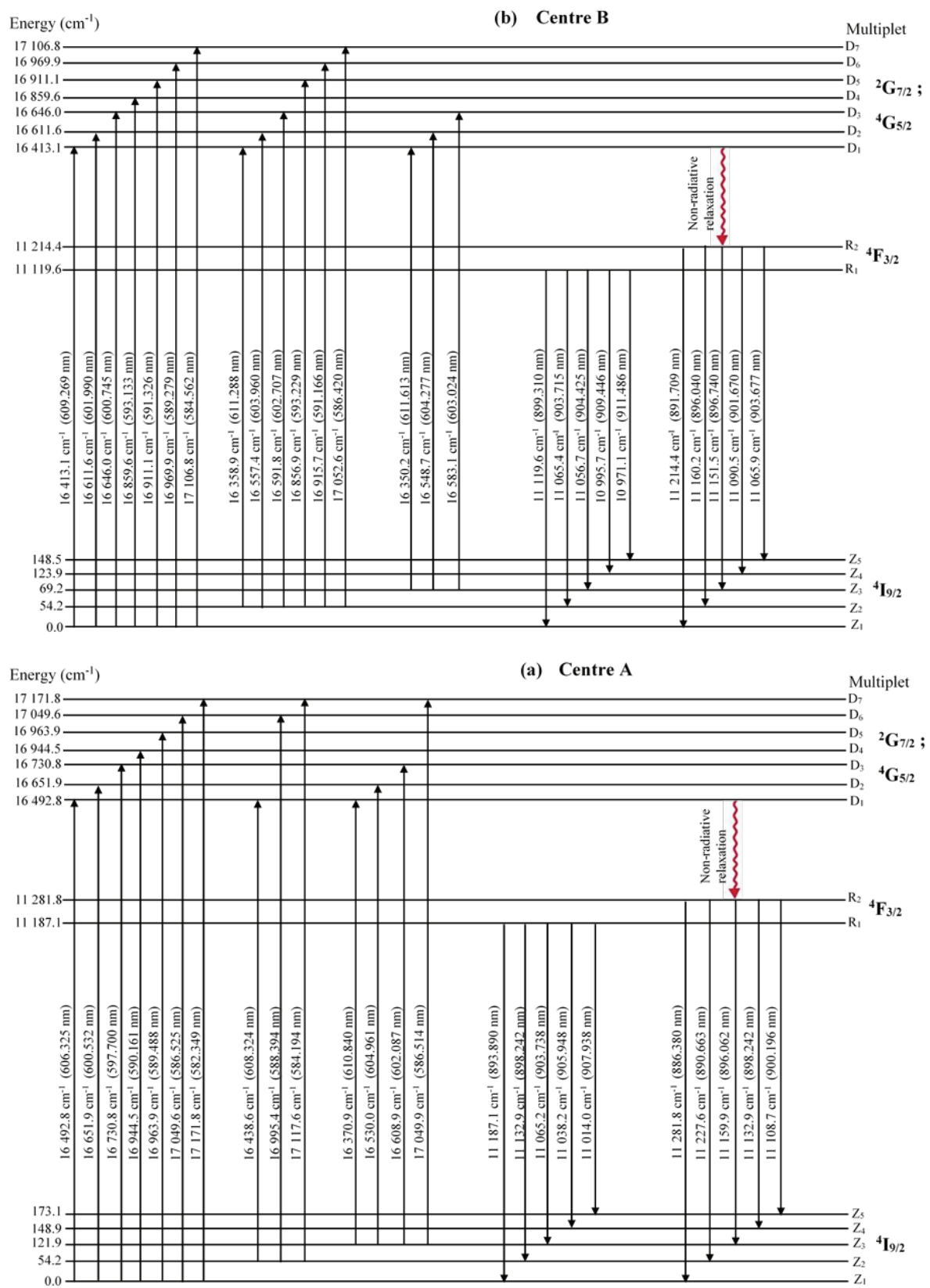


Figure 5.24 Energy level schemes deduced from transitions in the excitation spectra and emission spectra recorded at 10 K – 75 K temperatures for (a) centre A and (b) centre B, in $\text{ZnO:1mol\%Nd}^{3+}\text{:10mol\%Li}^+$ samples sintered at 950 °C.

The energy positions of levels in the excited multiplet (D ($^2G_{7/2}; ^4G_{5/2}$)), emitting multiplet ($^4F_{3/2}$) and the ground multiplet ($^4I_{9/2}$) as deduced from the energy level schemes in Figure 5.24 are summarized in Table 5.7.

Table 5.7 Energy levels of the Z ($^4I_{9/2}$) and R ($^4F_{3/2}$) and D ($^2G_{7/2}; ^4G_{5/2}$) multiplets of the two Nd^{3+} centres obtained from the energy level schemes in Figure 5.24.

Multiplet	Energy levels		
	Label	Energy ($\pm 0.1\text{cm}^{-1}$)	
		Centre A	Centre B
Z ($^4I_{9/2}$)	Z ₁	0.0	0.0
	Z ₂	54.2	54.2
	Z ₃	121.9	69.2
	Z ₄	148.9	123.9
	Z ₅	173.1	148.5
R ($^4F_{3/2}$)	R ₁	11 187.1	11 119.6
	R ₂	11 281.8	11 214.4
D ($^2G_{7/2}; ^4G_{5/2}$)	D ₁	16 492.8	16 413.1
	D ₂	16 651.9	16 611.6
	D ₃	16 730.8	16 646.0
	D ₄	16 944.5	16 859.6
	D ₅	16 963.9	16 911.1
	D ₆	17 049.6	16 969.9
	D ₇	17 171.8	17 106.8

5.4.2. Phonon modes observed in the emission and excitation spectra

The emission spectra (Figures 5.16, 5.17 and 5.18) and excitation spectra (Figures 5.22 and 5.23), recorded at sample temperatures ranging from 10 K to 75 K, included some vibronic peaks. The vibrations are either due to ions of the host lattice or the impurities. Effective coupling of an electronic transition and the vibrations of the lattice usually occurs with the most intense electronic transitions because it is a very weak effect. The peak positions and types of phonons (with the corresponding Brillouin zone points) involved are indicated in Table 5.8. Vibronic modes with energy of about 275 cm^{-1} are strongest in emission spectra of both centres.

Almost all of the phonon modes observed in the emission and excitation spectra of the two Nd^{3+} centres (Table 5.8) were observed also in the impurity- Fe^{3+} emission spectrum (Table 5.5). As discussed in Section 5.3.3, these are phonon modes of the ZnO host. The modes observed in this section however were shifted to higher energies by about 10 cm^{-1} . In addition, new modes which are transverse in nature and are at the M point of the Brillouin zone (Figure 2.10 (b)) appeared at 451.2 cm^{-1} and 444.7 cm^{-1} for the Nd^{3+} centres (Table 5.8). The vibronic transitions observed here are weaker than those observed in the case of the impurity Fe^{3+} ion (Section 5.3.3, Figure 5.14). This is expected since phonon coupling is stronger to $3d$ (Fe^{3+}) electrons than to $4f$

(Nd³⁺) electrons.⁵⁵ According to the Franck-Condon principle⁹, the intensity of a vibronic transition is proportional to the square of the overlap integral between the vibrational wavefunctions of the two states that are involved in the transition. Since there are different ions involved (Fe³⁺ and Nd³⁺) and different electronic transitions involved, the vibrational wavefunctions will differ and hence the related intensities of the vibronic transitions.

Table 5.8 Phonon modes from emission and excitation spectra for centre A and centre B in Figures 5.17, 5.18, 5.22 and 5.23.

Centre and Label	Electronic transitions		Associated vibronic transitions			Phonons	
	Wavelength (± 0.008 nm)	Energy (± 0.1 cm ⁻¹)	Label	Wavelength (± 0.008 nm)	Energy (± 0.1 cm ⁻¹)	Energy (± 0.2 cm ⁻¹)	Modes
Centre A	R ₁ →Z ₁	11 187.1	v ₀	900.576	11 104.0	83.1	TA (A) ^{61,108}
			v ₁	902.684	11 078.1	109.0	TA(M) ^{56,104,109}
			v ₂	908.775	11 003.8	183.3	TA (A) ^{61,104}
			v ₃	911.373	10 972.5	214.6	2 × v ₁
			v ₄	916.819	10 907.3	279.8	LA (M) ^{104,105}
			v ₅	920.319	10 865.8	321.3	3 × v ₁
			v ₆	923.612	10 827.1	360.0	2 × v ₂
	Z ₁ →D ₁	16 492.8	v ₇	924.941	10 811.5	375.6	TO (Γ) ¹⁰⁶
			w ₁	603.285	16 575.9	83.1	TA (A) ^{61,108}
			w ₂	601.568	16 614.9	122.1	TA(M) ⁶¹
			w ₃	598.868	16 698.2	205.4	w ₁ + w ₂
	Z ₁ →D ₃	16 730.8	w ₄	596.147	16 774.4	281.6	LA (M) ^{104,105}
			w ₅	585.433	17 081.4	588.6	LO (Γ) ^{106,107}
			w ₆	582.004	17 182.0	451.2	TO (M) ⁶¹
Centre B	R ₁ →Z ₁	11 119.6	vb ₁	922.134	10 844.4	275.2	LA (M) ^{104,105}
			vb ₂	936.692	10 675.9	443.7	TO (M) ¹⁰⁹
	Z ₁ →D ₁	16 413.1	y ₁	604.175	16 551.5	138.4	TA (M) ^{104,109}
			y ₂	602.850	16 587.9	174.8	TA (A) ^{61,104}
	Z ₁ →D ₂	16 611.6	y ₃	586.319	17 055.6	444.0	TO (M) ¹⁰⁹

5.4.3. Life-time studies

Figure 5.25 shows the fluorescence decay curves for the ⁴F_{3/2} → ⁴I_{9/2} transitions measured for (a) centre A and (b) centre B. The most intense (R₁ → Z₁) peaks at 893.890 nm and 899.310 nm were monitored for the measurements while dye-laser wavelengths of 606.400 nm and 602.100 nm were used to excite the two centres, respectively. The life-time of this (⁴F_{3/2}) multiplet has been widely reported for Nd³⁺ ions doped into different hosts.^{21,29} However, in all the conducted studies there was no separate measurements of life-times for the two different

Nd^{3+} centres. Thus, the life-time curves obtained with broad-band excitation could be for either centre or for a mixture of the two centres present in ZnO. On the contrary, in this work the life-time for each centre was measured individually. From exponential decay curves of the form $y = Ae^{\left(\frac{-t}{\tau}\right)} + y_0$ fitted to the measured data (Figure 5.25), it was deduced that the life-time τ of

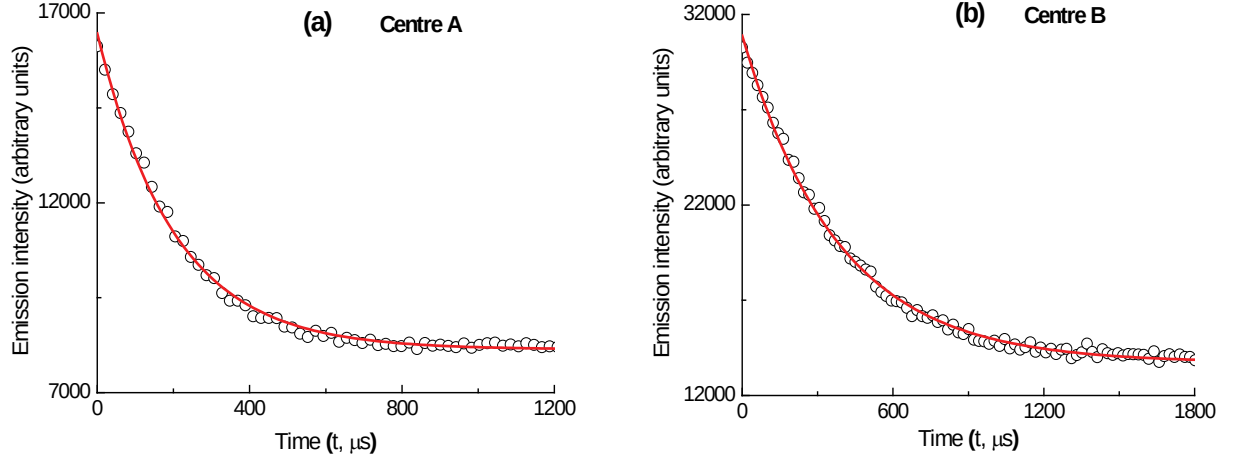


Figure 5.25 Life-time curves recorded at 10 K for the $^4\text{F}_{3/2}$ multiplet of (a) centre A with 606.400 nm excitation and (b) centre B with 602.100 nm excitation for Nd^{3+} ions in $\text{ZnO:1mol\%Nd}^{3+}\text{:10mol\%Li}^+$ samples sintered at 950 °C.

centre A is $202 \pm 4 \mu\text{s}$ whilst that for centre B is $380 \pm 4 \mu\text{s}$. The values of $328 \mu\text{s}$ ²⁹ and $305 \mu\text{s}$ ²¹ reported in the literature for the same form of host (i.e. ZnO powders) are comparable to the value of the B centre only and the average value for the two centres, respectively.

5.5. Summary

There are a number of important outcomes from this chapter. Firstly, when co-doped into ZnO with Li^+ ions, Nd^{3+} ions are located in the boundary regions of the ZnO grains. XRD analysis supports that there was incorporation of Nd^{3+} ions in the ZnO lattice as shown by XRD peak shifts in positions and broadening of linewidths. Crystallinity of the samples was improved by sintering at the higher temperature of 950 °C.

Secondly, there was a broad emission band extending from 500 nm to 875 nm which is attributed to intrinsic defects of ZnO. This emission is attributed to the combined emission between defects positioned at states within the bandgap of ZnO. This type of emission was enhanced in powders sintered at 600 °C compared to those sintered at higher temperatures (750 °C and 950 °C) due to associated defect density changes.

Thirdly, Nd^{3+} absorption bands were superposed on the broad emission band from ZnO defects. Though present in all samples with Nd^{3+} ions, the sharp absorption features were most intense in the $\text{ZnO:1mol\%Nd}^{3+}$ sample sintered at 600 °C. That is, the level of absorption strongly depends on the sintering temperature. The absorption bands match the energy states of

the Nd^{3+} ions and show correspondence between absorption by Nd^{3+} ions and radiation emitted by specific intrinsic defects in ZnO.

Fourthly, there was emission in the region from 690 nm to 750 nm due to the impurities emitting in the Fe^{3+} state. This emission band comprised an electronic transition from the Fe^{3+} ions and vibronic transitions due to the local vibrations of Fe^{3+} , the Zn and O interstitials as well as modes of the host lattice. The Fe^{3+} emission increased in intensity with increasing sintering temperature and addition of Li^+ ions to the samples.

Lastly, a group of emission lines observed in the 885 nm – 915 nm region is attributed to emission from the $^4\text{F}_{3/2}$ multiplet to the ground ($^4\text{I}_{9/2}$) multiplet of Nd^{3+} ions. While Nd^{3+} absorption was observed in all samples containing Nd^{3+} ions, Nd^{3+} emission was only observed in samples co-doped with Nd^{3+} and Li^+ ions for both Ar^+ -laser and dye-laser excitation. The Nd^{3+} emission intensities strongly depended on the doping concentration of the Li^+ , as it increased with the Li^+ amount (studied up to 10mol%). The slower rate of increase of Nd^{3+} emission from 5mol% Li^+ to 10mol% Li^+ doping suggests that saturation might occur just above 10mol% as shown in the insert of Figure 5.12. From this it can be concluded that addition of appropriate quantities of lithium compounds together with Nd^{3+} ions to ZnO enhances the Nd^{3+} emission. However, it is important to note that sintering temperatures also played a crucial role in enhancing the emission as only co-doped samples sintered at 950 °C showed Nd^{3+} emission. Further, it was established that there are two dominant Nd^{3+} centres in the ZnO lattice, named centre A and centre B. The two centres have different crystal fields as shown by differences in their emission lines and energy levels. Emission intensity was stronger for centre A than for centre B. From the emission and excitation spectra recorded with the site-selective excitation technique and the temperature dependence studies, energy level schemes for the two centres were generated. Vibronic peaks arising from vibrations of the host matrix and the defects were also observed close to Nd^{3+} peaks in the emission and excitation spectra. In addition, the life-times for the $^4\text{F}_{3/2}$ multiplet for the two centres were measured separately and the centre B life-time (380 μs) is almost 90% more than that for centre A.

CHAPTER 6

CONCLUSIONS AND SUGGESTIONS FOR FURTHER WORK

The structural, morphological and luminescence properties of zinc oxide (ZnO) films and powder samples doped with trivalent neodymium (Nd^{3+}) ions have been investigated. The ZnO host and the rare-earth neodymium were chosen due to their unique properties which suit novel applications in many important fields including in optical communications, biological imaging and lasers. In addition, due to its high melting temperature and its high radiation hardness, ZnO is useful in the manufacture of devices for applications in harsh conditions such as in space, high altitude or extreme temperature environments.

XRD measurements confirmed that both the films and the powders have the hexagonal wurtzite structure. SEM studies showed that crystallinity of both forms of samples is improved by heat treatment. For the films annealed at 600 °C and powder samples sintered at 600 °C and 750 °C, the Nd^{3+} ions are evenly distributed in the sample while for the powder samples sintered at 950 °C, the Nd^{3+} ions are confined to the grain boundaries.

Photoluminescence measurements revealed that although the samples are in different forms (films and powders), the intrinsic defects emission have similar spectral characteristics thus implying that the emission originates from similar defect transitions. Unlike for the Nd^{3+} -doped powders, no absorption was observed for the Nd^{3+} -doped films. In the powders, absorption bands were observed in all powders and their positions match selected Nd^{3+} multiplets. Sintering of powders at all temperatures did not change the crystal field significantly, resulting in no change in the energy position of the absorption transitions.

Nd^{3+} emission was observed from the $^4\text{F}_{3/2} \rightarrow ^4\text{I}_{9/2}$ transitions. In the films, this emission was present for both unannealed and annealed Nd^{3+} -doped films. But for the powders, only samples co-doped with Nd^{3+} and Li^+ ions and sintered at 950 °C yielded Nd^{3+} emission. There are two different Nd^{3+} centres in both films and powders; the single centre present in unannealed films is different from that in the annealed films while two different centres co-exist in the powder samples. Nd^{3+} emission from the $^4\text{F}_{3/2} \rightarrow ^4\text{I}_{9/2}$ inter-multiplet transitions was undetected in the other powder samples which however showed Nd^{3+} absorption transitions overlapping the broad intrinsic-defects emission band. This is possibly because of emission intensities that are lower than the detection limit of the spectrometer used. This could have been verified if it were possible to measure emission from the $^4\text{F}_{3/2} \rightarrow ^4\text{I}_{11/2}$ transitions near 1 060 nm since the $^4\text{F}_{3/2} \rightarrow ^4\text{I}_{9/2}$ transitions observed here have a two-third lower emission cross-section, in general,

compared to the $^4F_{3/2} \rightarrow ^4I_{11/2}$ transitions.⁶⁰ Unfortunately, the available detector cuts off at 950 nm.

Due to different crystal-field environments around the Nd^{3+} ions in the powders, the energy levels are also different. The two Nd^{3+} centres that co-exist in $ZnO:1mol\%Nd^{3+}:10mol\%Li^+$ powder samples have the same separation between the Z_1 and Z_2 levels of their ground Z ($^4I_{9/2}$) multiplets. The higher multiplet levels of centre A are about 70 cm^{-1} more than for centre B and there is comparable spread of the crystal-field levels in each multiplet. Although levels for the R ($^4F_{3/2}$) and D ($^2G_{7/2}; ^4G_{5/2}$) multiplets for the films are in the same energy range as for the powders, there is no clear relationship between the energy levels of the two centres in the films. This indicates a changed crystal field in the films as a result of the annealing.

A common feature for both films and powders is that more than 95% of the energy, judging by the intensities, is in a single transition ($R_1 \rightarrow Z_1$) even at high temperatures (75 K). This is useful for applications such as in lasers, where a single wavelength is usually required. The specific transition ($R_1 \rightarrow Z_1$) will have most of the energy, thereby significantly reducing energy losses via undesired transitions.

Although the Nd^{3+} emission in the NIR region and the corresponding excitation in the yellow to red regions has been reported before, for the first time, this study enabled the separation of spectra for different-configuration Nd^{3+} centres. It can be conclusively stated, from this study, that the emission in the 885 nm – 915 nm region from the Nd^{3+} doped ZnO films and powders is a superposition of emission from two major Nd^{3+} centres. The site-selective technique has proved useful in this study for clearly identifying the two centres, namely centre A and centre B as well as documenting their different spectral (both emission and excitation) and life-time characteristics. These differences indicate variation in the crystal-field environments of the Nd^{3+} centres present in the ZnO samples. Clearly, there is need for systematic investigations of the variety of rare-earth sites in ZnO and other semiconductor hosts and stability of the resulting centres with heat treatment as well as their optical transition characteristics. Such studies can provide means for tuning the sample preparation conditions in order to favour a specific rare-earth centre for improved optical output efficiency.

This work can be extended by

- (i) investigating the effect of annealing the films at different temperatures on the Nd^{3+} centres present. There may be an annealing temperature at which the two centres co-exist in the films.
- (ii) studying the effect of varying the Nd^{3+} dopant concentration in $ZnO:Nd^{3+}:Li^+$ co-doped powder samples with the aim of improving the Nd^{3+} emission.

- (iii) co-doping ZnO with Nd^{3+} ions and another rare-earth ion such as erbium (Er^{3+}) or terbium (Tb^{3+}) in the hope of either increasing the transition intensities or varying the transition energies (wavelengths) in the near-infrared region, which are usable for biomedical imaging.
- (iv) exploring of the powder sample preparation technique established here to prepare targets suitable for depositing films using the pulsed laser technique. The aim is to obtain low-cost targets that will produce good quality films with different optical properties.
- (v) investigating the Nd^{3+} -emission quenching mechanisms involved in ZnO:Nd^{3+} powders.

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PRESENTATIONS

1. “Spectroscopy of trivalent neodymium ions (Nd^{3+}) in zinc oxide (ZnO) thin films and powders” (Poster), *DST-NRF Centre of Excellence in Strong Materials annual students workshop*, University of the Witwatersrand, Johannesburg, South Africa, 2018.
2. “Spectroscopy of trivalent neodymium ions (Nd^{3+}) in zinc oxide (ZnO) thin films and powders” (Poster), *63rd South African Institute of Physics Conference*, University of the Free State, Bloemfontein, South Africa, 2018.
3. “Site-selective spectroscopy of Nd^{3+} in $\text{ZnO:Nd}^{3+}\text{:Li}^+$ powders” (Poster), *DST-NRF Centre of Excellence in Strong Materials annual students workshop*, University of the Witwatersrand, Johannesburg, South Africa, 2019.