Spectroscopy of trivalent neodymium ions (Nd^{3+}) in zinc oxide (ZnO) powders and thin films

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1. INTRODUCTION AND MOTIVATION

Trivalent rare-earth ions (RE^{3+}) doped ZnO

- ZnO is a wide-band-gap semiconductor with a wurtzite structure with potential for RE incorporation.
- Intrinsic point defects (vacancies, antisites, interstitials) in ZnO are responsible for its broad emission band(s) in the VIS-NIR region.
- RE^{3+} ions doped into ZnO yield narrow and discrete absorption and emission peaks superposed on the broad ZnO emission band.
- RE^{3+} ions emission finds application in bio-imaging, lasers and colored-light production while absorption is useful on welder's goggles for blocking the yellow glow.
- Most of the reported ZnO:Nd^{3+} emission is for UV excitation and at room temperature. [1]

Research Aim

- Spectroscopic study of Nd^{3+} ions in ZnO powders and thin films using VIS excitation and at sample temperature of 10 K.

2. BACKGROUND

- The energy levels of intrinsic defects in ZnO lie within its energy gap (Figure 1).
- Some energy levels of the Nd^{3+} ions lie within the ZnO energy gap (0–27 700 cm^{-1} (361 nm)) .[1]
- Indirect excitation of the Nd multiplet within the ZnO gap is possible through excitation of the intrinsic defects and subsequent energy transfer to the Nd^{3+} ions.
- Co-doping with lithium (Li) enhances the Nd emission.
- Laser spectroscopy is a non-destructive method for studying the photoluminescence properties of rare-earth ions doped into ZnO.[2]

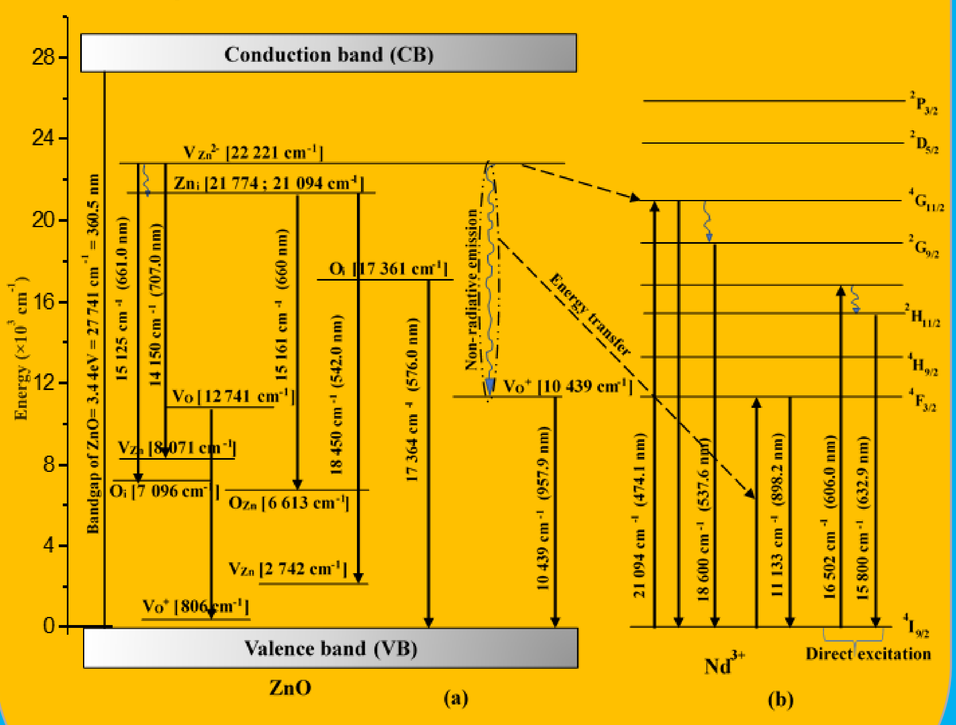

Figure 1: (a) Some defects states which lie within the bandgap of ZnO and (b) energy states of Nd^{3+} ions.

3. EXPERIMENTAL

a. Samples preparation

- Powder samples were prepared by the sintering technique (grinding, compaction by pressing and annealing).
- Thin films were prepared by radio-frequency magnetron sputtering technique using a 3mol%Nd doped ZnO target.
- Samples (both powders and films) were annealed at varying temperatures (600–950℃), in air and for 2 hrs. A ramping rate of 5℃ per/min was adopted.

b. Structural characterization

- Surface morphology and elemental composition was investigated by SEM and EDS, respectively.

c. Spectroscopy

- Four Ar^+ laser lines (457.9 nm, 476.5 nm, 488.0 nm and 514.5 nm) were used for excitation.
- Samples were cooled to 10 K in a closed-cycle cryostat.
- Emission was detected by a high resolution monochromator and a PMT.

4. RESULTS AND ANALYSIS

Structural characterization of the powders

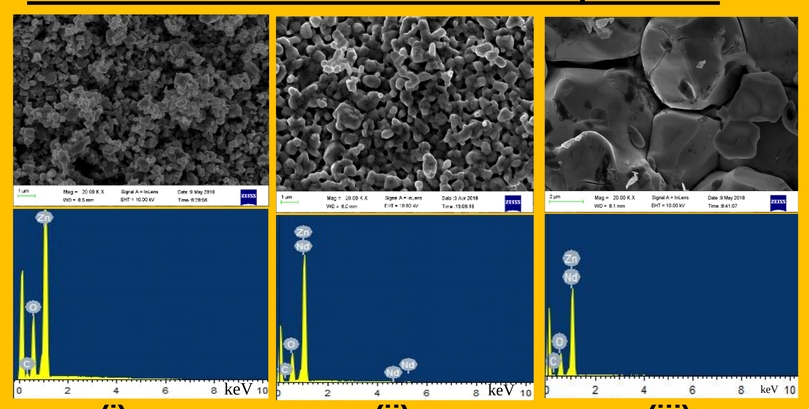

Figure 2: SEM images and EDS spectra of:
i. ZnO:1mol%Nd annealed at 600℃,
ii. ZnO:1mol%Nd annealed at 950℃
iii. ZnO:1mol%Nd:10mol%Li annealed at 950℃

- The combined effect of Li co-doping and annealing at 950℃ is larger grains (1000%) and aggregation of Nd^{3+} ions at the grain boundaries.
- From EDS spectra, the average surface concentration of Nd is 0.6 at.%.

II. Fluorescence from ZnO intrinsic defects

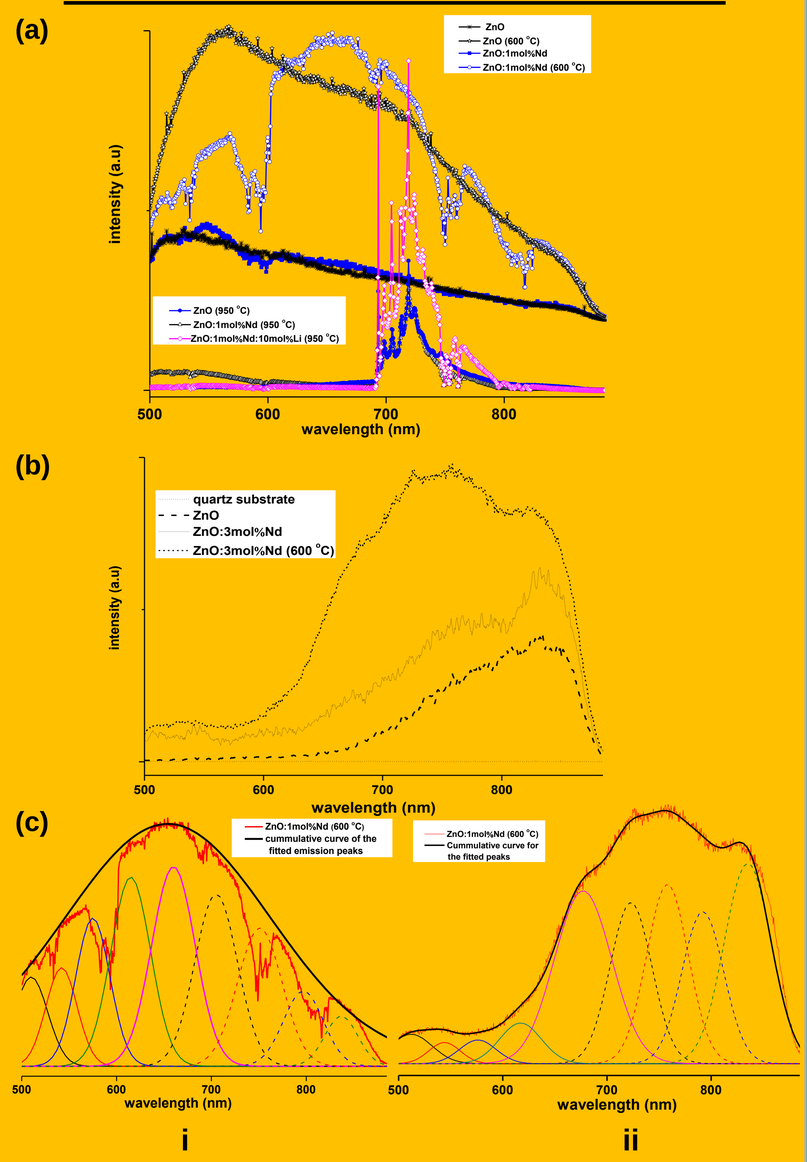

Figure 3: Effects of doping and annealing on fluorescence from (a) powders and (b) films. The deconvoluted intrinsic-defect peaks are shown in (c) i and (c) ii for the powders and thin films, respectively.

Table 1: Intrinsic defects emission peak positions, the corresponding transitions and the near-resonant Nd^{3+} ion multiplet (Figure 1).

Peak position ± 5 (nm)		Corresponding transitions	Near-resonant Nd multiplet(s)
Powders	Films		
510	512	$Zn_i^+ \rightarrow O_i$ or V_{Zn}	$^2G_{9/2}$
542	544		
576	576	$O_i \rightarrow VB$;	$^2G_{7/2}$
615	617	$Zn_i^+ \rightarrow V_{Zn}^-$	$^4G_{5/2}$
660	677	$Zn_i^+ \rightarrow O_{Zn}$ or O_i	$^2H_{11/2}$
705	723	$V_{Zn}^{2-} \rightarrow O_i$ or V_{Zn}, $V_O \rightarrow VB$, $V_{Zn}^{2-} \rightarrow V_{Zn}$, $Zn_i \rightarrow V_{Zn}$	$^4F_{9/2}$
751	758	$V_O \rightarrow V_O^+$ or V_{Zn} ,	$^4S_{3/2}$; $^4F_{7/2}$
797	792		
837	835	$V_{Zn}^{2-} \rightarrow O_i$	$^2H_{9/2}$; $^4F_{5/2}$

- Both the powders and the films gave the same emissions attributed to intrinsic defects.
- The 457.9 nm excitation wavelength gave much higher emission intensities than other Ar^+ laser lines.
- Absorption features in the broad ZnO emission profile indicate the Nd^{3+} ions absorbed near-resonant energy emitted by the ZnO intrinsic defects.
- Annealing causes re-distribution of intrinsic defects as shown by the changed emission intensity distribution (Figure 3).

III. Fluorescence:Nd^{3+} extrinsic defects

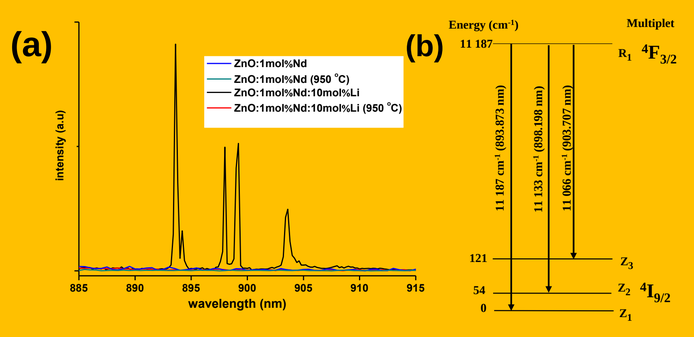

Figure 4: (a) Emission spectrum and (b) energy levels for ZnO:1mol%Nd:10mol%Li powder annealed at 950℃.

- Co-doping with Li^+ ions and annealing at 950℃ promotes the population of V_O^+ defects which are linked to the population of the $^4F_{3/2}$ multiplet (Figure 1).

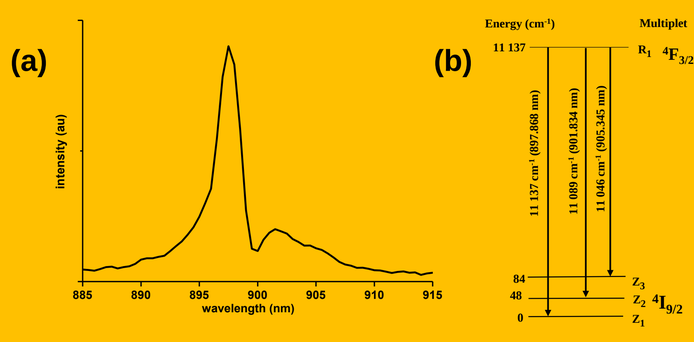

Figure 5: (a) Emission spectrum and (b) energy levels for ZnO:3mol%Nd thin films

5. CONCLUSION

- Intrinsic defect emission and Nd^{3+} absorption is observed in the 500-850 nm region.
- Nd^{3+} emission is only observed near 900 nm ($^4F_{3/2} \rightarrow {}^4I_{9/2}$) in the Li co-doped samples annealed at 950℃ and the films.
- The energy level positions of Nd^{3+} ions are in the same region in the films and the powders; the broader film transitions could be an indication of the quality of the films.
- Doped sintered-powders can be cost-effective targets for thin film deposition by the pulsed laser technique.
- XRD analysis will be done to assess effects of doping and annealing.

6. ACKNOWLEDGEMENTS

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7. REFERENCES

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