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 (RE^{3+}) doped ZnO

- Wide-band-gap semiconductor with wurtzite structure.
- Energy gap of 3.4 eV at 4 K and high melting temperature (2248 K) hence regarded as a strong material.
- Most reported emission from ZnO:Nd^{3+} was obtained with UV excitation at room temperature (300 K). [1]

Research Aim

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

2. EXPERIMENTAL
Laser Spectroscopy

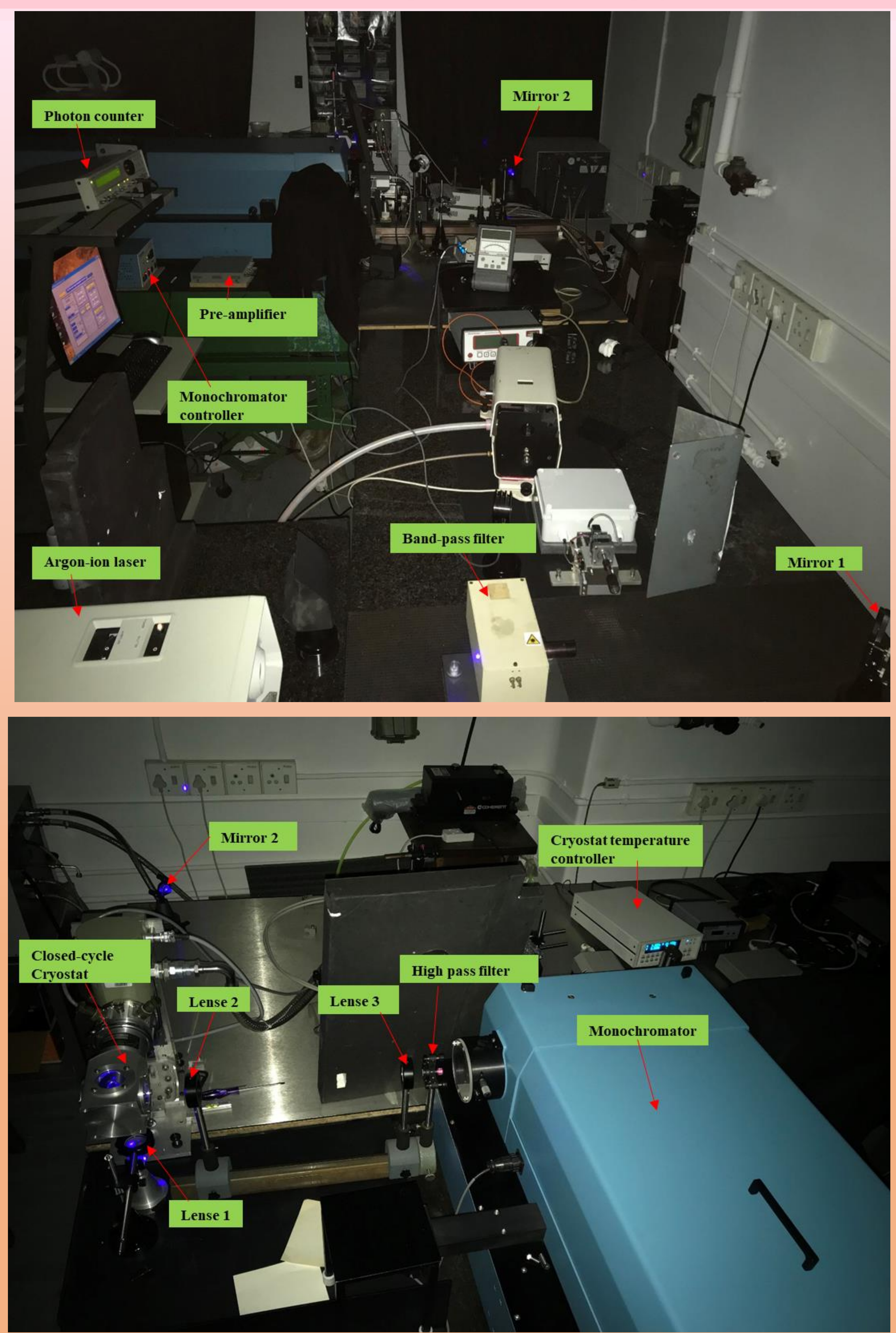

Figure 1: Setup for fluorescence spectroscopy measurements

3. THEORY

- ZnO has intrinsic point defects namely: vacancies (V_o and V_{Zn}), interstitials (O_i and Zn_i) and antisites (O_{Zn} and Zn_O). [2]
- Both the extrinsic and intrinsic defects affect the optical behaviour of ZnO.
- Rare-earth extrinsic defects enhance the photoluminescence properties of ZnO.
- Spectroscopy is a non-destructive method for studying the photoluminescence properties of doped materials. [3]
- Transitions between the intrinsic defect levels are broad while the rare-earth transitions are narrow and discreet.

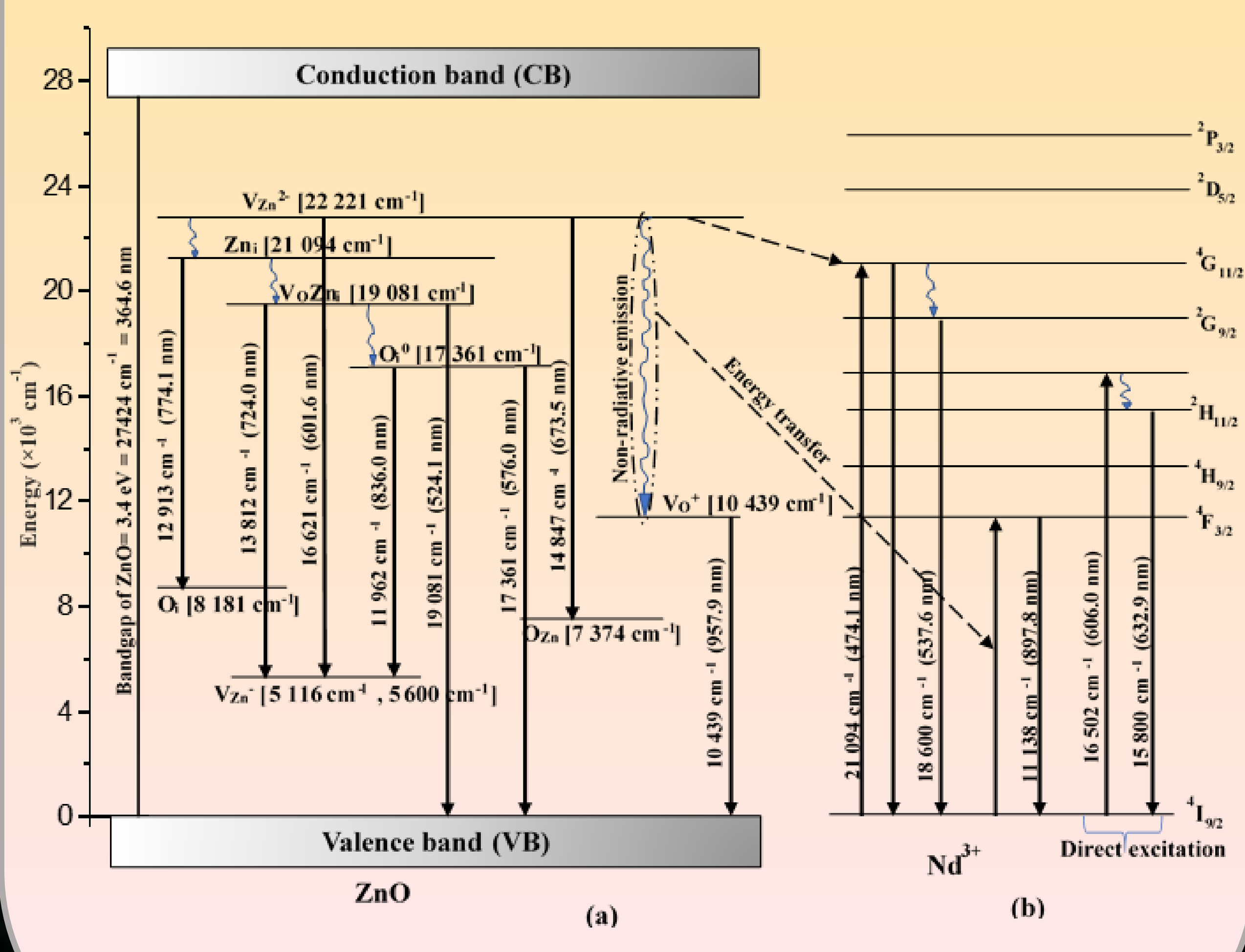

Figure 2: (a) Some defects states which lie within the bandgap of ZnO and (b) energy states of Nd^{3+} ions.

4. RESULTS AND DISCUSSION

4.1 Fluorescence from ZnO intrinsic defects

a. Powders

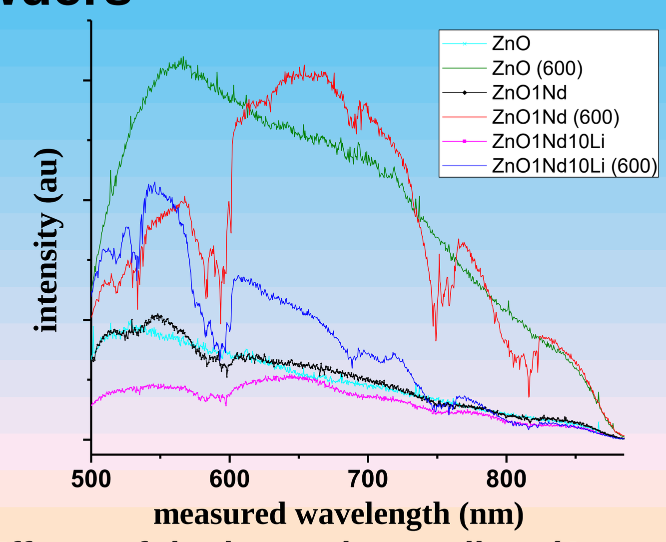

Figure 3: Effects of doping and annealing. (Annealing: 600 ℃; air; 2 hrs; RMP = 5 ℃/min).

- Reabsorption features in the broad ZnO emission profile indicate energy transfer between the extrinsic and ZnO intrinsic defects.
- The positions of the reabsorption features match the energy levels of Nd^{3+} ions.
- Decrease in the intrinsic defects emission after co-doping ZnO:Nd^{3+} with Li^+ and annealing indicates redistribution of the intrinsic defects.

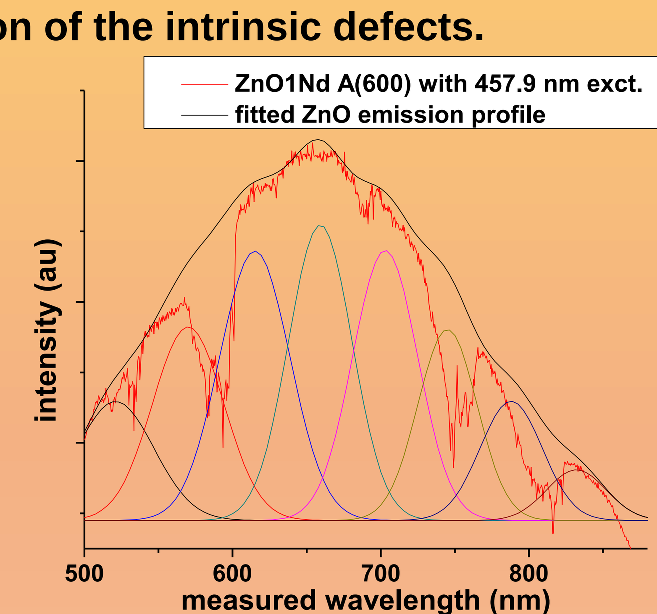

Figure 4: Gaussian fitting on the defects emission

b. Thin Films

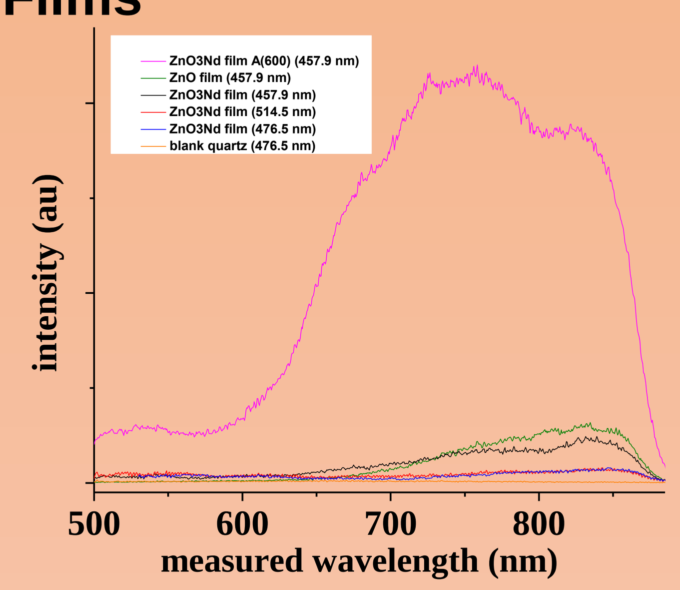

Figure 5: Effects of doping, annealing and varying the excitation wavelength. (Annealing: 600 ℃; air; 2 hrs; RMP = 5 ℃/min).

- Same emission profile with different excitation wavelengths with highest intensity from highest excitation energy (457.9 nm)
- Annealing improved emission peaks at 639 nm, 678 nm, 722 nm and 767 nm due to introduced oxygen defects

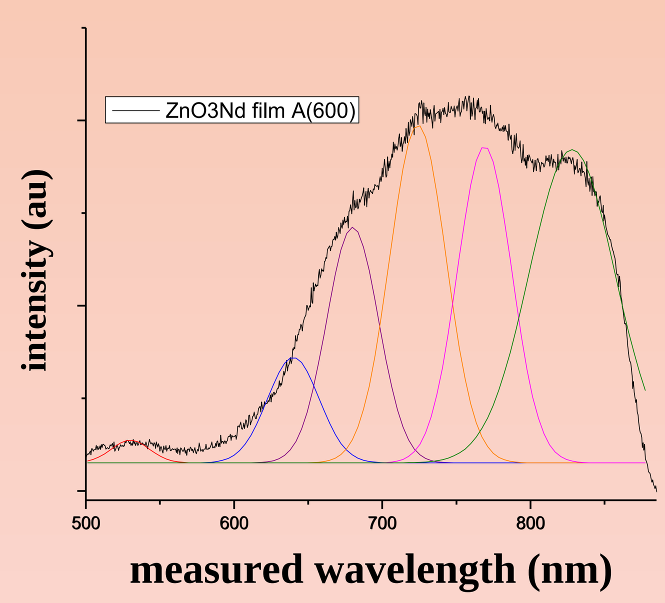

Figure 6: Gaussian fitting of defects emission

- The Gaussian peak positions for the powders and the films are given in Table 1 with the corresponding transitions as illustrated in Figure 2 (a)

Table 1 Peak positions and transitions

Peak positions (nm) Powders	Thin films	Corresponding Transition (Figure 2(a))
521	530	$V_OZn_i \rightarrow VB$
570	--	$O_i^0 \rightarrow VB$
615	639	$V_{Zn}^{2-} \rightarrow V_{Zn}^-$
659	678	$V_{Zn}^{2-} \rightarrow O_{Zn}$
703	722	$V_OZn_i \rightarrow V_{Zn}^-$
745	--	$V_OZn_i \rightarrow V_{Zn}^-$
788	767	$Zn_i \rightarrow O_i$
832	836	$O_i^0 \rightarrow V_{Zn}^-$

4.2 Fluorescence from Nd^{3+} extrinsic defects in ZnO

a. Powders

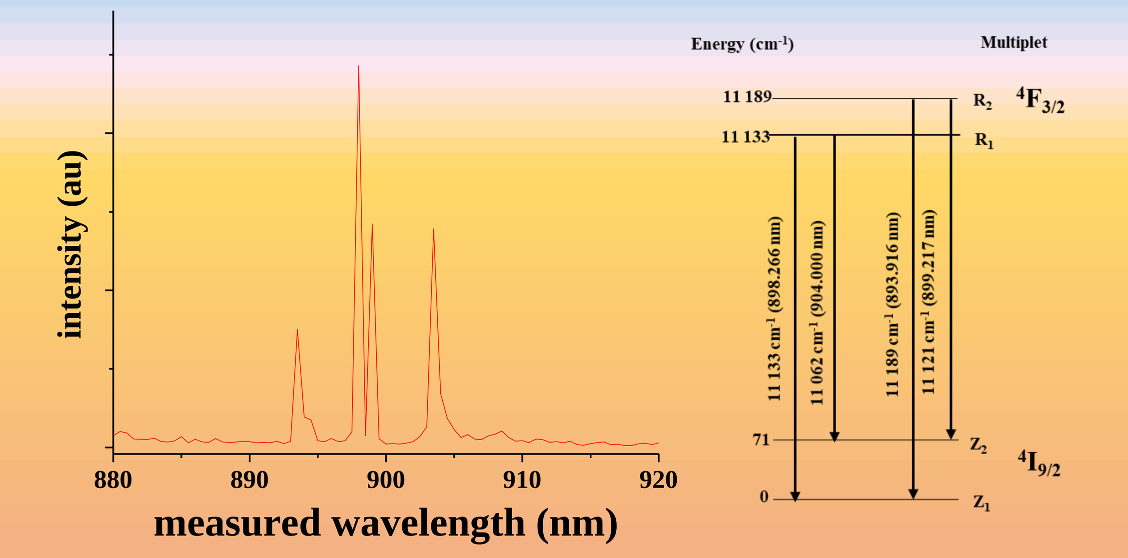

Figure 7: Emission and energy level scheme.

- Co-doping with Li^+ ions and annealing at 950 ℃ encourages the existence of V_o^+ defects which are linked to the population of the $^4F_{3/2}$ multiplet.
- Channels for energy transfer from the intrinsic to extrinsic defects are shown in Figure 2.

b. Thin Films

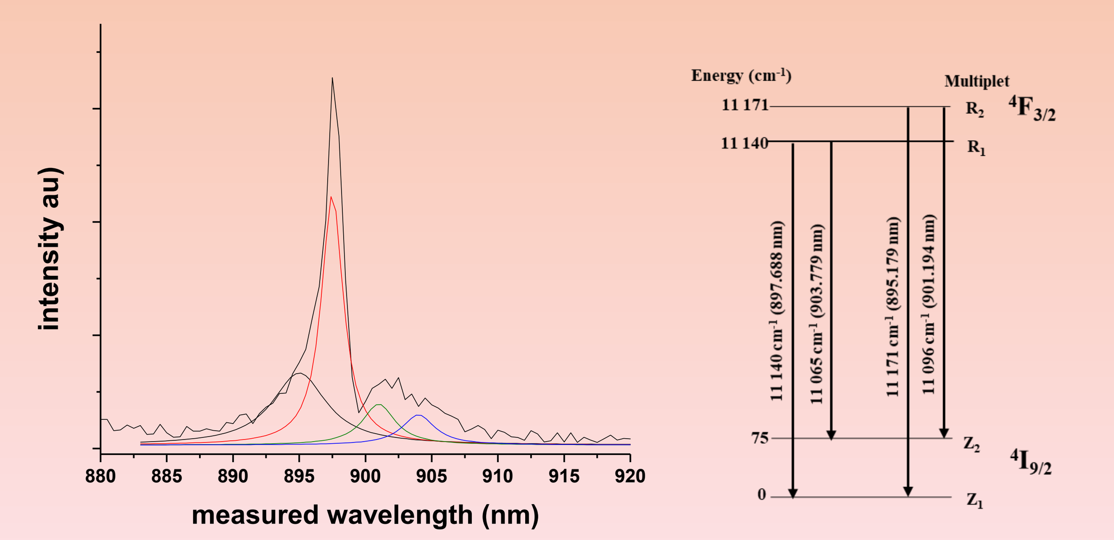

Figure 8: Emission and the corresponding energy level scheme

5. CONCLUSION

- Although several Nd^{3+}-reabsorption features are observed in the region from 500 nm to 850 nm, emission is only observable from ~ 900 nm (from the $^4F_{3/2}$ multiplet).
- The energy level positions of Nd^{3+} ions are similar in the films and the powders; the broader film transitions could be an indication of the quality of the films.
- Applications
  - ✓ NIR emission: bio-imaging, NIR lasers and colored-light emission.
  - ✓ Reabsorption: absorbing the yellow-flame glow on welder's goggles
  - ✓ Doped sintered-powders: cost-effective targets for thin film deposition by the pulsed laser technique.

6. WORK IN PROGRESS

- Structural characterization
- Direct excitation of Nd^{3+} ions (Figure 2 (b)) using dye lasers.

7. REFERENCES

[1] Balestrieri, M. *et al. J. Mater. Chem. C* **2,** 9182–9188 (2014).

[2] Janotti, A. and Van De Walle, C. G. (2009) Fundamentals of zinc oxide as a semiconductor', *Reports on Progress in Physics*, 72(12).

[3] Garc´ıa Sol´e, J., et.al. (2005) *An Introduction to the Optical Spectroscopy*. England: John Wiley & Sons Ltd.

8. ACKNOWLEDGEMENTS

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