# Characterization of MBE grown $\{Zn(Mg)O/ZnCdO\}_m$ superlattices doped in-situ with Eu

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## INTRODUCTION

- $Zn_{y-1}Mg_yO$ ternary alloys can significantly increase the band gap up to ~ 6 eV, whereas $Zn_{1-x}Cd_xO$ alloys reduce the band gap to ~ 2.35 eV with increasing Mg/Cd content (**Fig.1**)[1].
- The deposition of high-quality thin films with a high Cd and Mg content is complicated by the difference in crystal structures, CdO and MgO crystalize in the cubic phase, while ZnO has a wurtzite phase.
- Doping of ZnO-based materials with rare-earth elements (Sc, La, Eu, etc.) is a popular method for manipulating their optical properties (**Fig.2**)[2].
- We report of in-situ Eu-doped $\{ZnCdO/ZnMgO\}_{22}$ superlattices (SLs) grown by molecular beam epitaxy (MBE).

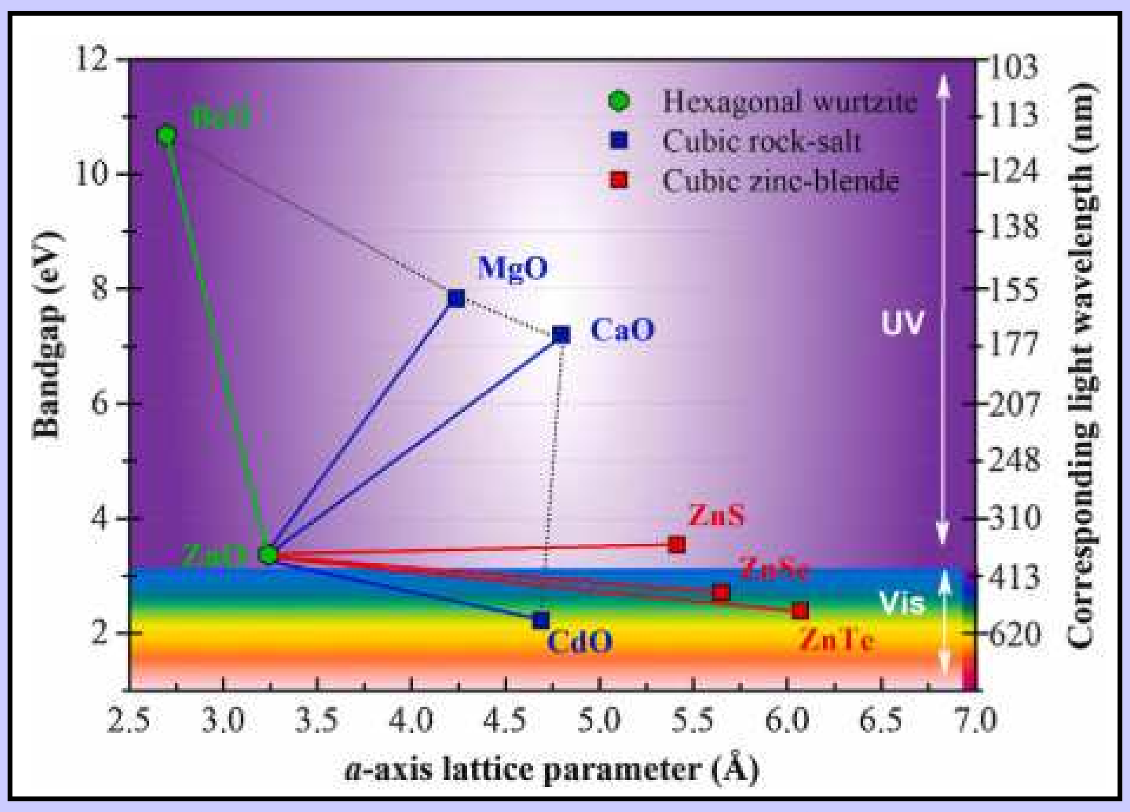



**Fig.1**. Bandgap versus lattice constant a for the typical II-VI compound semiconductors[1].

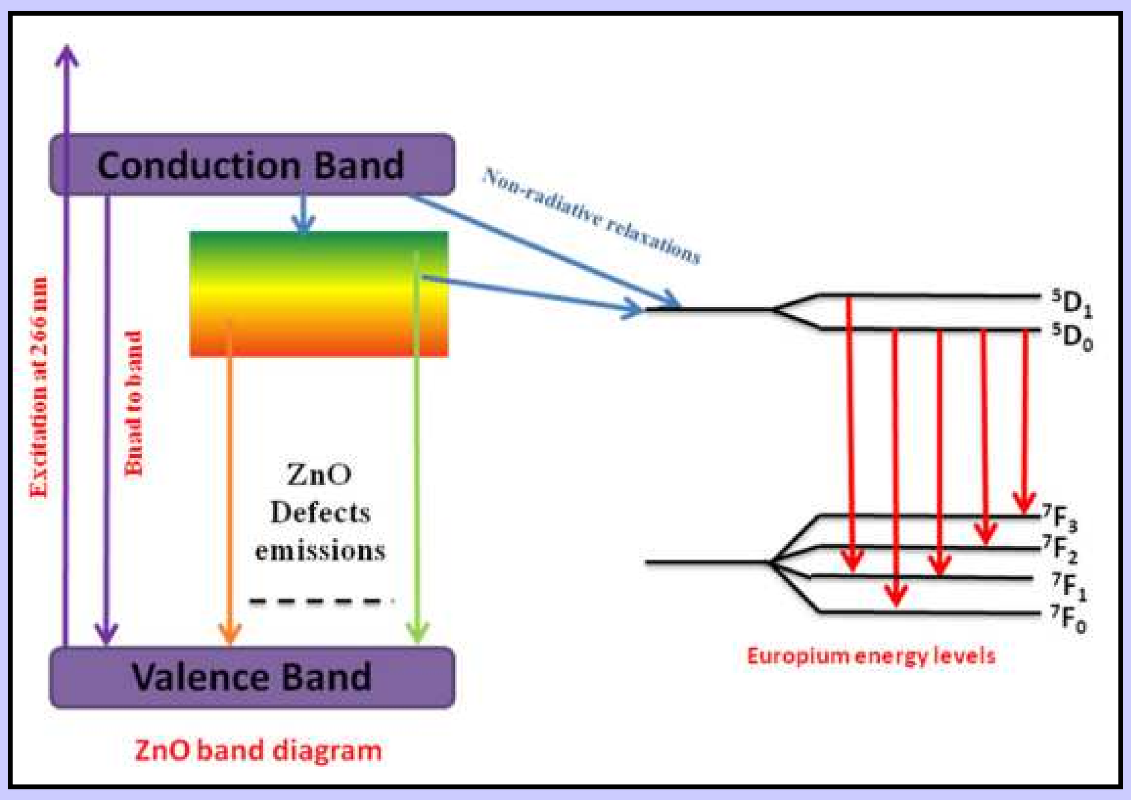



**Fig. 2.** Schematic band diagram illustrating the ZnO and $Eu^{3+}$ ions emissions and the energy transfer mechanism between them[2].

## METHODS

- ➢ In situ Eu-doped $\{ZnCdO/ZnMgO\}_{22}$ short-period SLs with different Zn content were grown on *m*-plane (10-10 ) sapphire substrates ($Al_2O_3$) by plasma-assisted MBE (**Fig. 3**):
  - ❖ sample A: $\{ZnCdO{:}Eu_{13nm}/ZnMgO_{12.5nm}\}_{22}$;
  - ❖ sample B: $\{ZnCdO{:}Eu_{10.5nm}/ZnMgO_{9.5nm}\}_{22}$.
- ➢ The growth temperature was 360°C.
- ➢ Eu dopant was introduced into ZnCdO quantum wells.
- ➢ The temperature of the Mg, Cd and Eu effusion cells were fixed (534, 340 and 475°C, respectively).
- ➢ A rapid thermal processing (RTP) system was applied to the SLs at 700, 800 and 900°C for 1 minute in an oxygen ($O_2$) environment.

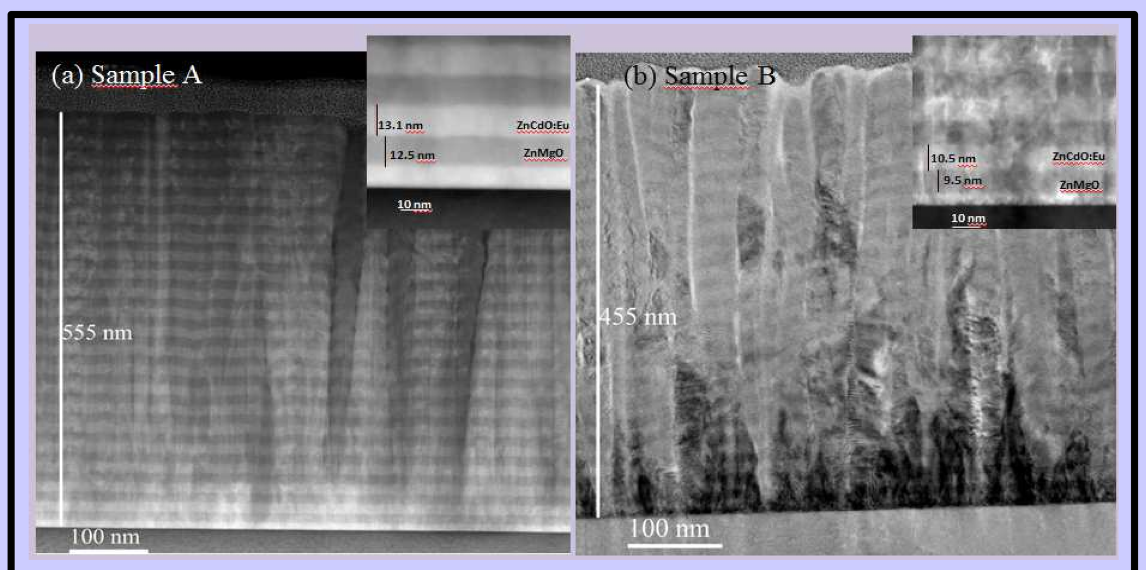



**Fig. 3.** HT-TEM cross-sectional of (a) $\{ZnCdO{:}Eu_{13nm}/ZnMgO_{12.5nm}\}_{22}$ SL and (b) $\{ZnCdO{:}Eu_{10.5nm}/ZnMgO_{9.5nm}\}_{22}$ SL

## SIMS vs CL MEASUREMENTS

The depth distribution of Cd, Eu, Mg; Zn and O elements for as grown and annealed Eu doped $\{ZnCdO/ZnMgO\}_{22}$ SLs are shown in **Fig. 4 a, d**.

Individual ZnCdO:Eu and ZnMgO sublayers are clearly visible for as grown samples and confirm the good quality of structures.

A decrease in the amplitude of the oscillations or their disappearance on the SIMS depth profile with an increase in the annealing temperature is associated with a rise of elements diffusion into the samples.

A relatively homogeneous Cd, Eu, Mg; Zn and O profiles are observed for both as grown and annealing at of 700-900°C superlattices.

Atomic percentages of Eu, Cd and Mg atoms were estimated (**Table 1**).

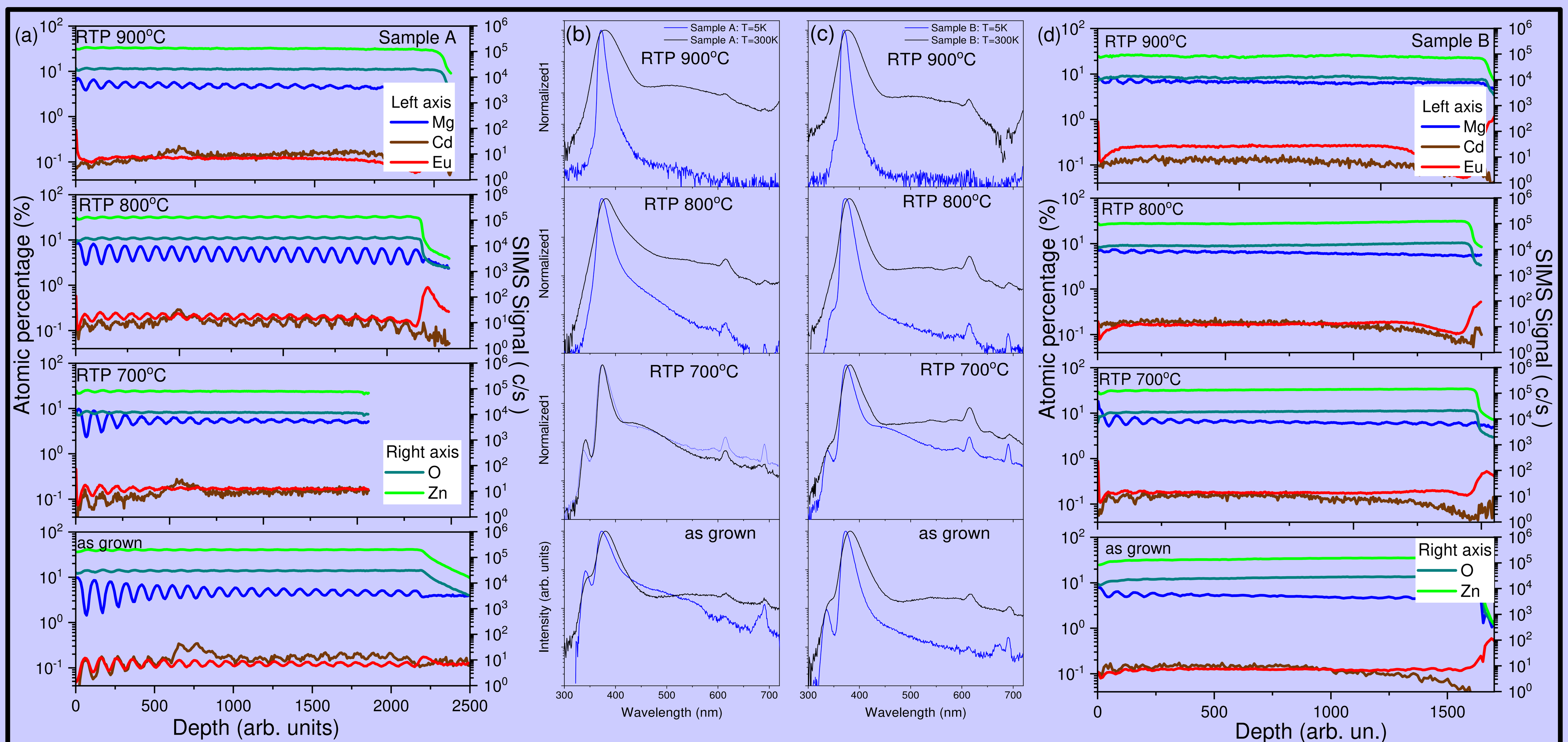



**Fig. 4.** (a) SIMS depth profile of as grown and annealed at different temperatures $\{ZnCdO{:}Eu_{13nm}/ZnMgO_{12.5nm}\}_{22}$ SL; (b) normalized CL spectra of $\{ZnCdO{:}Eu_{13nm}/ZnMgO_{12.5nm}\}_{22}$ SL before and after annealing; (c) normalized CL spectra of $\{ZnCdO{:}Eu_{10.5nm}/ZnMgO_{9.5nm}\}_{22}$ SL before and after annealing; (d) SIMS depth profile of as grown and annealed at different temperatures $\{ZnCdO{:}Eu_{10.5nm}/ZnMgO_{9.5nm}\}_{22}$ .

CL spectra for all $\{ZnCdO/ZnMgO\}_{22}$ SLs doped with Eu demonstrate near-band-edge (NBE) emission and deep level emissions (DLE).

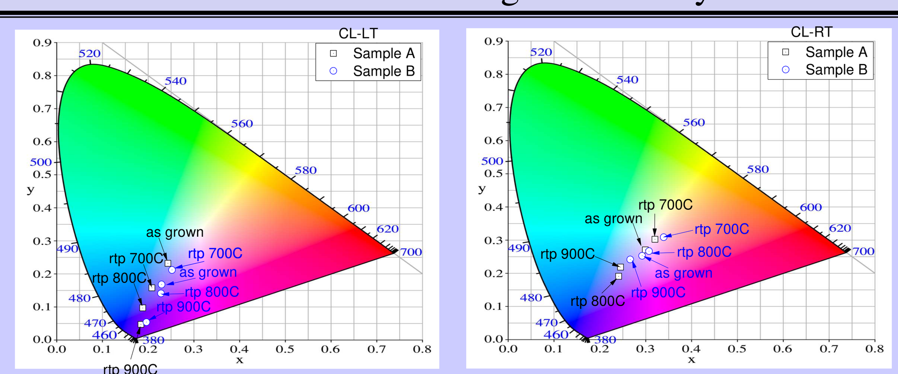
A red shift as well as an increase in the full-width-half-maximum (FWHM) ) of the NBE peak are observed for all superlattices in CL measurements at room temperature (**Fig. 4 b, c**).

The peak at 3.65±4 eV observed for as grown and annealed at 700°C samples corresponds to the CL emission of the ZnMgO barrier layers.

CL spectra for as grown in situ Eu-doped $\{ZnCdO/ZnMgO\}_{22}$ SLs showed emission bands at ~615 nm, due to the $^5D_0$ – $^7F_2$ intra-4f-shell transition of $Eu^{3+}$ ions (**Fig. 4 a, b**).

In the case of SL after RTP at 700°C, relatively narrow emission peaks at 593, 615, 654, and 691 nm were revealed, due to the $^5D_0$-$^7F_{1,2,3,4}$ intra-4f transitions (**Fig 2**).

Upon annealing at temperatures above 700°C, the emission intensity at ~615 nm decreases. Perhaps this is due to the destruction of the superlattice structure due to the Cd and Mg diffusion[3].



## X-RAY ANALYSIS

The X-ray diffraction patterns showed for as grown samples A and B several diffraction peaks indicate that the films are polycrystalline with planes corresponding of the hexagonal structure of ZnO (**Fig. 5 a**).

Formation of foreign phases from CdO, MgO or $Eu_2O_3$ 3 wasn't observed.

For sample B characteristic satellites were determined, which confirm the good quality periodic structure of the sample (**Fig. 5 b**).

The Zn concentration affects the lattice parameters *a* and *c* (**Table 2**).

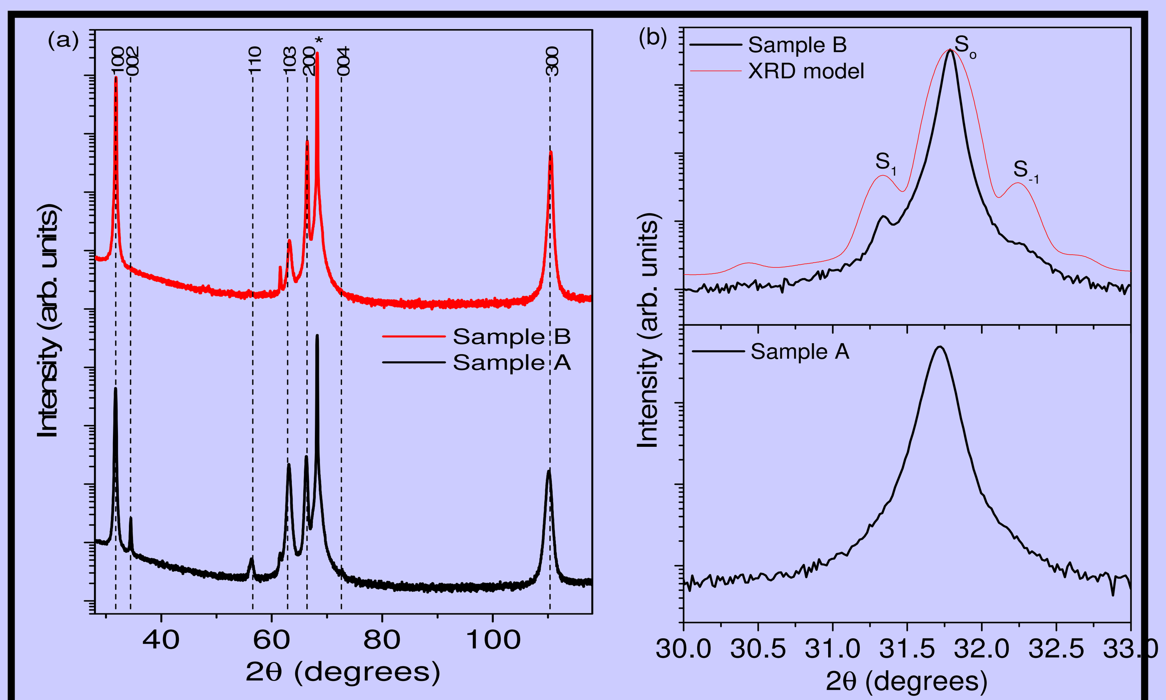



**Fig. 5.** (a) XRD patterns of as-grown in sute Eu-doped $\{ZnCdO/ZnMgO\}_{22}$ SLs (black vertical dotted line corresponds to the peak positions of wurtzite ZnO and * indicates the peak originated from the $Al_2O_3$ substrate); (b) HR-XRD 2θ-ϖ scans of the 10.0 peaks.

## ENERGY GAP

The Tauc method is used to determine the band gap of the as grown Eu-doped $\{ZnCdO/ZnMgO\}_{22}$ SLs (**Fig. 6a**).

The band gap varies in the range from ~3.304 to ~3.313 eV (**Table 2**).

Structural disorder in the crystal lattice of the as grown samples corresponds to the so-called Urbach tail (**Fig. 6b**).

The Urbach energy varies in the range from ~233 to ~214 meV (**Table 2**) .

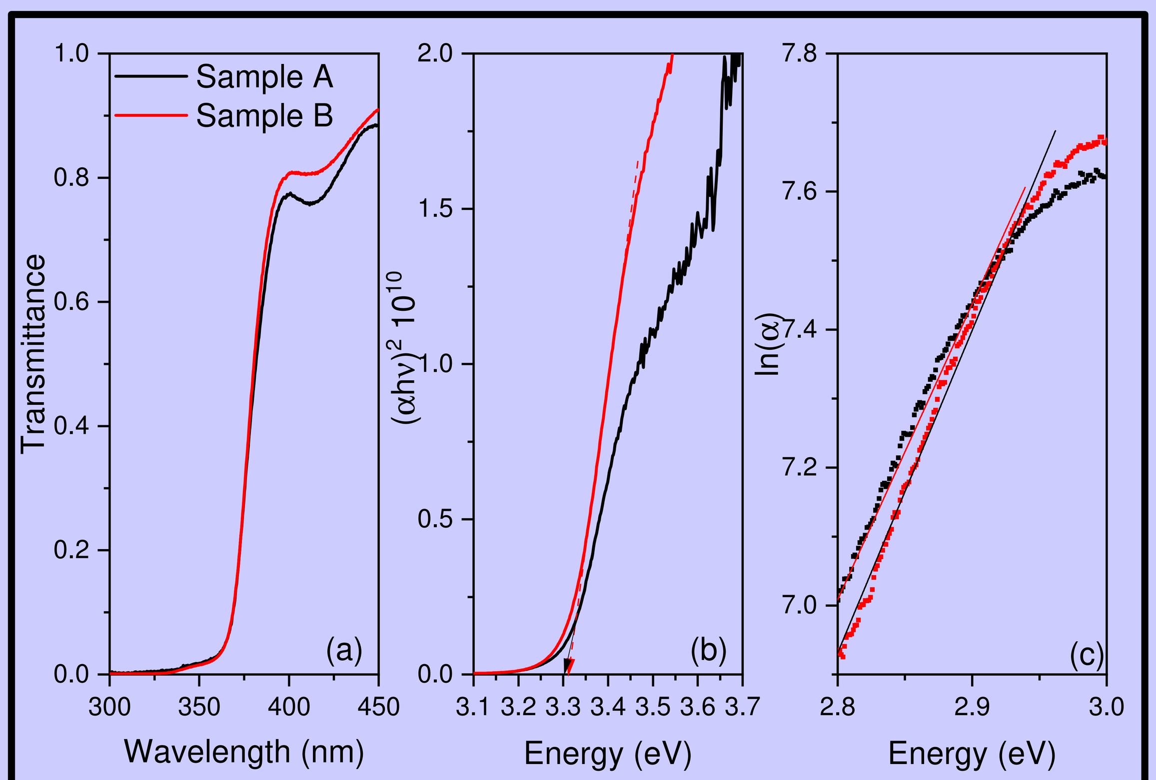



**Fig. 6.** (a) The transmission spectra of the as grown Eu-doped $\{ZnCdO/ZnMgO\}_{22}$ SLs; (b) Tauc's plots of as grown samples; (c) semilog dependence of the absorption coefficient on photon energy for $\{ZnCdO/ZnMgO\}_{22}$ SLs doped with Eu.

**Table 2**

| Sample | $T_{Zn}$ °C | Thickness ZnCdO:Eu layer | Thickness ZnMgO layer | $a_{10.0}$ (Å) | $c_{103}$ (Å) | $E_g$ eV | $E_U$ meV |
|---|---|---|---|---|---|---|---|
| Sample A | 548 | 13±2 nm | 12.5±1 nm | 3.253 | 5.18 | 3.304 | 233 |
| Sample B | 544 | 10.5±1 nm | 9.5±1 nm | 3.247 | 5.174 | 3.313 | 214 |

## CONCLUSIONS

- ❖ In situ Eu-doped $\{ZnCdO/ZnMgO\}_{22}$ SLs were obtained by PA-MBE on *m*-plane $Al_2O_3$ substrate.
- ❖ The formation of good quality SLs was confirmed by TEM and XRD measurements.
- ❖ CL spectra for as grown and annealed at different temperatures $\{ZnCdO/ZnMgO\}_{22}$ SLs doped with Eu showed NBE and DLE band as well as red emission line from the dopant $Eu^{3+}$.
- ❖ The optimal conditions for amplifying red radiation were determined.
- ❖ The highest intensity of the $^5D_0$ – $^7F_2$ peak was observed after annealing at 700°C.

## ACKNOWLEDGEMENTS

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## REFERENCES

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