

## Re-dispersible Li<sup>+</sup> and Eu<sup>3+</sup> co-doped CdO nanowires: Luminescence studies

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**Abstract:** Re-dispersible CdO, 5 at.% Eu<sup>3+</sup> doped CdO, 2 at.% Li<sup>+</sup> and 5 at.% Eu<sup>3+</sup> co-doped CdO nanowires in organic solvent are prepared by urea hydrolysis in ethylene glycol medium at low temperature of 150 °C. CdO nanowires have the apical ratio of 50 nm to 2 μm. CdO starts band gap edge at 360 nm and shows luminescence at 430 nm (blue emission). The asymmetric ratio ( $A_{21}$ ) of the integrated intensities of the electrical dipole transition to the magnetic dipole transition for 5 at.% Eu<sup>3+</sup> doped CdO is found to be 1.2 and this ratio is significantly increased for 2 at.% Li<sup>+</sup> and 5 at.% Eu<sup>3+</sup> co-doped CdO ( $A_{12} = 2.2$ ). It establishes that the red emission can be enhanced by Li-doping. Also, the significant energy transfer from host CdO to Eu<sup>3+</sup> is found for 2 at.% Li<sup>+</sup> and 5 at.% Eu<sup>3+</sup> co-doped CdO.

**Keywords:** Re-dispersible; nanowires; luminescence; semiconductors; energy transfer.

### Introduction

II-VI oxide semiconducting materials find increasing application in optoelectronic devices such as flat panel displays (FPD), photovoltaic/solar cells, heat reflectors and energy-efficient windows [1-3]. Among them, CdO is an emerging material for its large direct band gap energy of 2.5 eV, with an indirect band gap of 1.36 eV. Luminescence property of Eu<sup>3+</sup>-doped CdO is rarely studied compared to CdS. However, CdO is more stable as compared to CdS since CdS oxidizes in air. Eu<sup>3+</sup> can substitute Cd<sup>2+</sup> because of similar ionic radii, i.e., ionic radii of Eu<sup>3+</sup> and Cd<sup>2+</sup> are 0.94 and 0.97 Å respectively. But positive charges in both are not same. To compensate charge balance, it is needed to add a positive ion such as Li<sup>+</sup>, Na<sup>+</sup> and K<sup>+</sup>. Li<sup>+</sup> has high diffusivity and low activation energy because of its small ionic radius (0.59 Å). Studies of Li<sup>+</sup> and Eu<sup>3+</sup> co-doped in CdO have not been widely reported. But there has been reports in the literature regarding the enhancement of luminescence intensity by Li<sup>+</sup> and Eu<sup>3+</sup> co-doped semiconducting materials were reported [4-6].

In addition to doping effect, the electronic and optical properties of semiconducting materials can be modified by the shape of particles [2,3,7-10]. Another challenge is

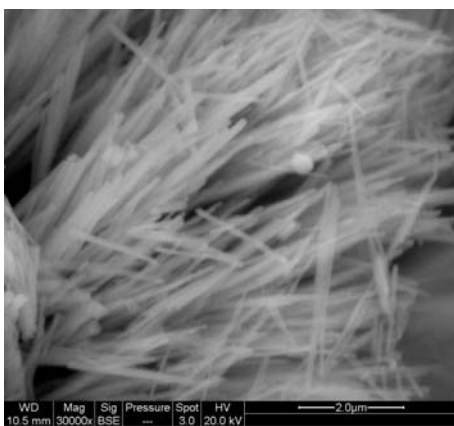
the preparation of materials, which can be re-dispersible in organic solvent. Such materials can be incorporated in polymer based materials and optical fibres.

In the present work, we have prepared the re-dispersible CdO, Li<sup>+</sup> and Eu<sup>3+</sup> doped CdO nanowires in organic solvent by urea hydrolysis at low temperature of 150 °C and their luminescence properties are studied. To the best of our knowledge, there is no report on luminescence studies of Li<sup>+</sup> and Eu<sup>3+</sup> co-doped CdO nanowires. We propose the mechanism why CdO nanoparticles can be re-dispersed in organic solvent.

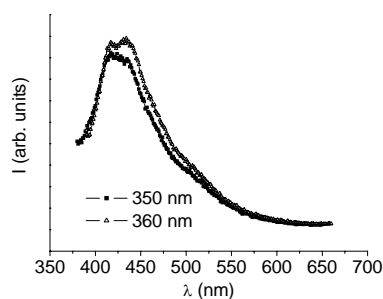
### Experimental

CdO and Li<sup>+</sup> and Eu<sup>3+</sup> co-doped CdO particles are prepared by urea hydrolysis in ethylene glycol medium. For preparation of CdO, 10 ml of 0.1 M cadmium sulfate is mixed with 2 g of urea into the two necked round bottom flask. 50 ml of ethylene glycol is added into it. It is refluxed at 150 °C for 2 h. A white precipitate appears and is collected using centrifugation. To remove excess ethylene glycol, it is again centrifuged by addition of methanol and acetone alternatively. Also, 5 at.% Eu<sup>3+</sup> doped CdO and 2 at.% Li<sup>+</sup> and 5 at.% Eu<sup>3+</sup> co-doped CdO particles are prepared by similar method. Starting materials used for Eu<sup>3+</sup> and Li<sup>+</sup> are Eu<sub>2</sub>O<sub>3</sub> and Lithium acetate respectively.

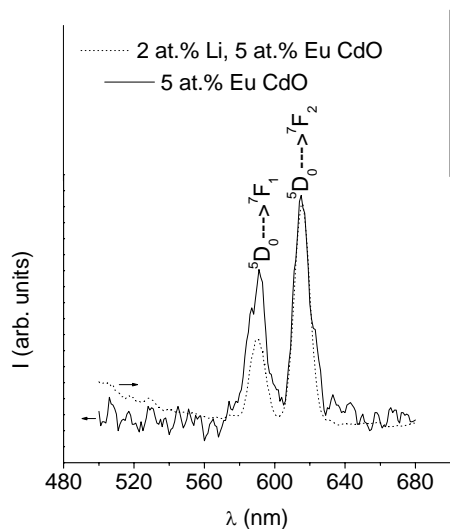
The powder x-ray diffraction (XRD) patterns of the ZnO and Li<sup>+</sup> and Eu<sup>3+</sup> doped ZnO samples are recorded with Cu K<sub>α</sub> radiation and Ni-filter in the 2θ range 35-120° using a Rich Seifert Iodebyflex X-ray unit model 2002. The average crystallite size ( $t$ ) was calculated from the line broadening using the Scherrer's relation:  $t = 0.9\lambda/B\cos\theta$ , where  $\lambda$  is the wavelength of X-rays and  $B$  is the half maximum line width. Scanning electron microscope (SEM), JEOL JSM-840A is used to investigate the particle size distribution and morphology. Luminescence measurements are performed using Fluorolog (R)-3 Spectrofluorometer.



**Figure 1.** SEM image of CdO nanowires



**Figure 2.** Photoluminescence emission spectra of CdO nanowires at 350 and 360 nm excitations.



**Figure 3.** Photoluminescence emission spectra of 5 at.%  $\text{Eu}^{3+}$  doped CdO and 2 at.%  $\text{Li}^+$  and 5 at.%  $\text{Eu}^{3+}$  co-doped CdO nanoparticles at 395 nm excitation.

### III. Results and Discussion

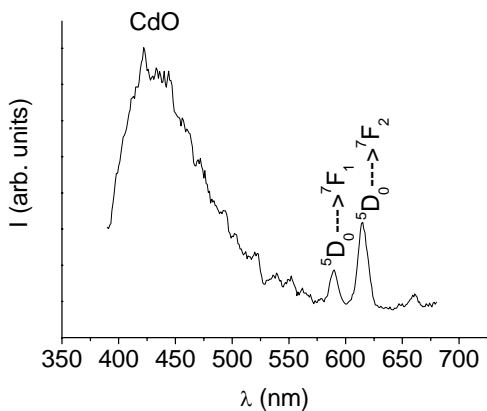
The X-ray diffraction studies on nanoparticles of CdO and  $\text{Eu}^{3+}$  doped CdO and  $\text{Li}^+$  and  $\text{Eu}^{3+}$  co-doped CdO show that they crystalline in cubic structure. The average crystallite size is found to be in 10-30 nm.

Figure 1 shows SEM image of CdO particles. It gives anisotropic nanocrystal, i.e., nanowires with apical ratio of 50 nm to 2  $\mu\text{m}$ . Figure 2 shows the photoluminescence emission spectra of CdO nanowires at 350 and 360 nm excitations. The peak at 430 nm could be seen and it arises from the combination of the electrons from the conduction band and holes from the valence band. It was reported that depending on particle sizes and exciting wavelengths, the different emission peaks and shapes could be seen in the range of 400 – 600 nm peaks [2,3]. CdO nanowires shows the band edge at  $\sim 360$  nm.

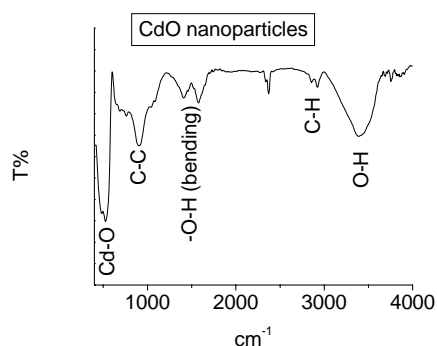
Figure 3 shows the emission spectrum of 5 at.%  $\text{Eu}^{3+}$  doped CdO nanoparticles at 395 nm excitation. The 395 nm excitation corresponds to the main excitation peak of  $\text{Eu}^{3+}$  ions ( $^7\text{F}_0 \rightarrow ^3\text{L}_6$ ). The peaks at 590 and 614 nm could be observed. The peaks at 590 and 614 nm are due to the intra-4f transitions of  $\text{Eu}^{3+}$  ions and correspond to the magnetic dipole transition,  $^5\text{D}_0 \rightarrow ^7\text{F}_1$  and the electronic dipole transition,  $^5\text{D}_0 \rightarrow ^7\text{F}_2$  respectively. Usually, the electronic dipole transition,  $^5\text{D}_0 \rightarrow ^7\text{F}_2$  is hypersensitive to  $\text{Eu}^{3+}$  symmetry.  $\text{Eu}^{3+}$  symmetry could be defined by asymmetric ratio ( $A_{21}$ ) of the integrated intensities of  $^5\text{D}_0 \rightarrow ^7\text{F}_2$  to  $^5\text{D}_0 \rightarrow ^7\text{F}_1$  and  $A_{21}$  is found to be 1.2.

Figure 3 shows the emission spectrum of 2 at.%  $\text{Li}^+$  and 5 at.%  $\text{Eu}^{3+}$  co-doped CdO nanoparticles at 395 nm excitation. The peaks at 590 and 614 nm could be observed.  $A_{21}$  is found to be 2.2. It suggests that symmetry of the co-ordination polyhedron of the  $\text{Eu}^{3+}$  ion is lowered by  $\text{Li}^+$  doping compared to that of undoped 5 at.%  $\text{Eu}^{3+}$  doped CdO nanoparticles. The red emission at 615 nm is significantly enhanced for 2 at.%  $\text{Li}^+$  and 5 at.%  $\text{Eu}^{3+}$  co-doped CdO nanoparticles compared to 5 at.%  $\text{Eu}^{3+}$  doped CdO nanoparticles. In order to check energy transfer between CdO and  $\text{Eu}^{3+}$ , 2 at.%  $\text{Li}^+$  and 5 at.%  $\text{Eu}^{3+}$  co-doped CdO nanoparticles are excited at 360 nm (Fig. 4). There is a strong blue emission at 430 nm along with orange emission at 590 nm and red emission at 615 nm. The peak at 430 nm is due the CdO host. The peak at 590 and 615 nm are due to the  $\text{Eu}^{3+}$  ions. This confirms that the energy can be significantly transferred from the host CdO to  $\text{Eu}^{3+}$ .

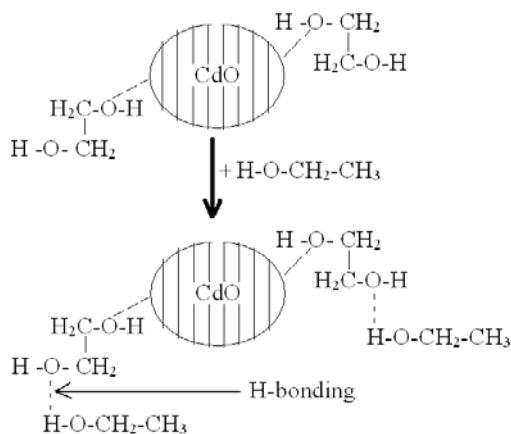
The UV absorption study on CdO nanoparticles, which are re-dispersible in ethanol shows absorption at 310 nm. IR spectrum of CdO nanoparticles is shown in Fig. 5. There are O-H, C-H, C-C functional groups in addition to Cd-O bond. Such extra functional groups are due to incorporation of ethylene glycol molecules, which act as capping. There are two O-H bonds in ethylene glycol molecule. One O-H bond binds with CdO particles. Agglomeration among particles is hindered due



**Figure 4.** Photoluminescence emission spectrum of 2 at.% Li<sup>+</sup> and 5 at.% Eu<sup>3+</sup> co-doped CdO nanoparticles at 360 nm excitation.



**Figure 5.** IR spectrum of CdO nanoparticles.



**Figure 6.** Proposed mechanism for re-dispersible CdO nanoparticles in organic molecules such as methanol and ethanol.

to capping. The other O-H bond can interact with methanol or ethanol (organic solvent) through H-bonding. A broad peak at 3500 cm<sup>-1</sup> indicates that the H-bonding is present in ZnO nanoparticles because capping of ethylene glycol. These materials could be incorporated in polymer based materials and optical fibres, which may be useful in wide number of applications. The proposed mechanism, “how CdO nanoparticles can be re-dispersible in organic solvent such as methanol or ethanol”, is also shown in Fig. 6.

### Conclusions

CdO, Eu<sup>3+</sup> doped CdO, Li<sup>+</sup> and Eu<sup>3+</sup> co-doped CdO nanowires are prepared and are re-dispersible in organic solvent. Red emission is significantly enhanced for Li<sup>+</sup> and Eu<sup>3+</sup> co-doped CdO compared to Eu<sup>3+</sup> co-doped CdO. Also, there is a strong energy transfer from the host CdO to Eu<sup>3+</sup> ions for Li<sup>+</sup> and Eu<sup>3+</sup> co-doped CdO.

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### References

1. Lima S. A. M., F. A. Sigoli, M. R. Davolos, and M. Jafericci Jr. *J. Alloys Comp.* **344**, 280 (2002).
2. Ghosh M., and C. N. R. Rao, *Chem. Phys. Lett.* **393**, 493 (2004).
3. Dong W., and C. Zhu, *Optical Mater.* **22**, 227 (2003).
4. Bachir S., K. Azuma, J. Kossanyi, P. Valat, and J. Lumines. **75**, 35 (1997).
5. Zhang H., X. Fu, S. Niu, G. Sun, and Q. Xin, *J. Lumines.* **115**, 7 (2005).
6. Bae J. S., S. B. Kim, J. H. Jeong, J. C. Park, D. K. Kim, S. H. Byeon, and S. S. Yi, *Thin Solid Films* **471**, 225 (2005).
7. Yan H., R. He, J. Pham, and P. Yang, *Adv. Mater.* **15**, 402 (2003).
8. Alivisatos A. P., *Science* **271**, 933 (1996).
9. Jin S., Y. Yang, J. E. Medvedeva, J. R. Ireland, A. W. Metz, J. Ni, C. R. Kannewurf, A. J. Freeman, and T. J. Marks, *J. Am. Chem. Soc.* **126**, 13787 (2004).
10. Peng X. C., X. F. Wang, Y. W. Wang, C. Z. Wang, G. W. Meng, and L. D. Zhang, *J. Phys. D: Appl. Phys.* **35**, L101 (2002).