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Structural and Optical Properties of Co-Bi doped ZnO nano particles Opto electronic devices

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Abstract: Well crystalline Co-Bi co-doped ZnO nanostructures with various concentration of Bi were synthesized by simple chemical route technique using metal acetate precursors. X-ray diffraction patterns of the pure and Co with Bi doped samples have shown the well crystalline diffraction peaks corresponds to the characteristic wurtzite ZnO crystal structure. Aggregated nano particles have emerged with flower like morphology and it can be seen from the scanning electron microscopy and transmission electron microscopy. The average particle diameter was estimated and found to be 25–35 nm. Tunable optical band gap related to an additional electron state created by dopant was observed from the UV–Visible spectra. Typical PL emission in the UV, visible and continuous deep level emission further demonstrates that the potential application of the material in optoelectronics. From this study it is suggested that this kind of excellent optical tunability of the Bi co-doped ZnO: Co system will be the potential material for future opto-electronic devices.
Keywords: Structural and Optical Properties of Co-Bi doped ZnO nano particles Opto electronic devices.

Introduction:

Zinc oxide (ZnO), a promising II–VI group semiconductor material, has been widely applied in various fields such as transducers, transparent conduction electrodes, solar cells, and wide ultraviolet (UV)opto electronic devices due to its direct band gap of 3.37 eV at room temperature and a large exciton binding energy of 60 meV[1]. ZnO is also inexpensive, abundant in the nature, chemically stable and non toxic. Doping with appropriate elements in ZnO has been reported to be an excellent way to improve its properties to avail this material for various luminescence device fabrications. Al-doped ZnO has shown good electrical and optical properties [2].Near band edge emission in photoluminescence spectrum of Bi-ZnO nano wires is red-shifted relative to that of undoped ZnO nano rods as a result of enhanced carrier concentration [3]. The optical band gap of the nanocrystals can be tuned in the range of 2.9-3.8 eV by the use of the dopants such as Cd, Mg, Mn, and Fe ions [4]. The tailoring of optical band gap in Pb-doped ZnO nano wires could be useful in the fabrication of future optoelectronic nanodevices such as nanosensors, scanning nanoprobes and field emission. The doping of transition metal elements into ZnO offers a feasible means of fine tuning the band gap to make use as UV detector and light emitters. Mn doping causes a large reduction in the intensity of the UV emission and small

reduction in green emission intensity of the PL spectra [6]. The analysis of optical properties in ZnO:Ce nanoparticles showed that, it is a promising material and has potential applications in optoelectronic devices[7]. However, it is believed that the presence of additional carrier introduced by co-doping (simultaneous doping) can induce the good optical property [2,8]. The luminescence properties of Li doped ZnO:Dy nano crystals is approximately ten times more intense than that of ZnO :Dy without Li which shows additional carrier will improve the optical properties[9].In this study we have discussed the ZnO: Co: Bi nano particles by tuning the dopant systematically. The structural and morphological optical features of pure and doped ZnO nano particles with Bi concentration were investigated.

Experimental Techniques:

The stoichiometric amount of precursor sources were dissolved in 20 ml of de ionized water separately under stirring. The typical Co and Bi concentrations are 10% fixed for Co and Bi concentration varied from 1-4% as well. The solutions are rapidly mixed together to form the homogenous mixture. After that 1 M of NaOH solution is added drop wise to the above mixture for over 20 min at room temperature. Finally, the precipitate is washed and consecutively through centrifugation.

Results and Discussions:

Phase Analysis:

XRD pattern of pure and Co with Bi co-doped ZnO nanoparticles are shown in Fig 1. Well defined diffraction peaks have been indexed by hexagonal wurtzite nanostructure. Due to the addition of Co in the Zn lattice there is the peak shift towards higher angle ~0.21° as earlier reports [10,11]. When compared to Co doped ZnO pattern, the Bi co-doped shows the blue shift in the XRD pattern. The observed shift may be due to the large ionic radius Bi induces. The shift in the peaks corresponding to the large Bi^{3+} ion disturbs the Co substituted ZnO lattices. No additional peaks are found in the XRD pattern up to the 4% of Bi co-doping. The average particle size of the pure and doped ZnO nanoparticle is estimated from Scherer equation for maximum peak. It can be seen that of the particle is about 25-30 nm for ZnO nanostructure.

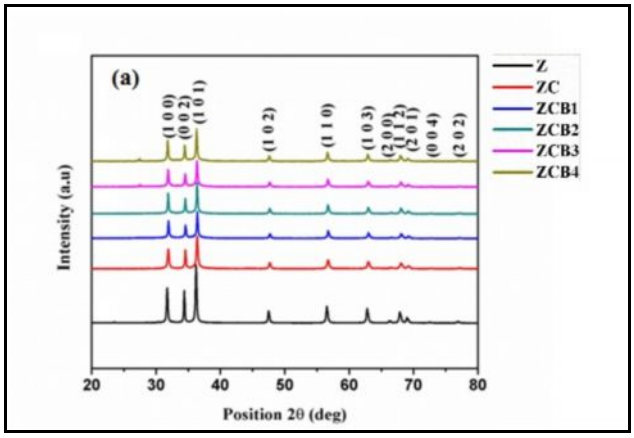

Fig. 1 XRD patterns of pure and Co with Bi co-doped ZnO nano particles

Morphological Studies:

High resolution scanning electron microscopy (HRSEM) images of the resulting Bi co-doped ZnO: Co nanoparticles are presented in Fig 2 (a-h). From the micrograph, it can be seen that the formation of small gillyflower like ZnO crystallites are with severe aggregation. With adding the Co and Bi instead of Zn, there was no change in the morphology. This suggests the complete incorporation of dopant ions into Zn sites. The average crystallite size of 20-30 nm obtained from the TEM for ZnO: Co doped with Bi sample was shown in Fig.3(a-d)

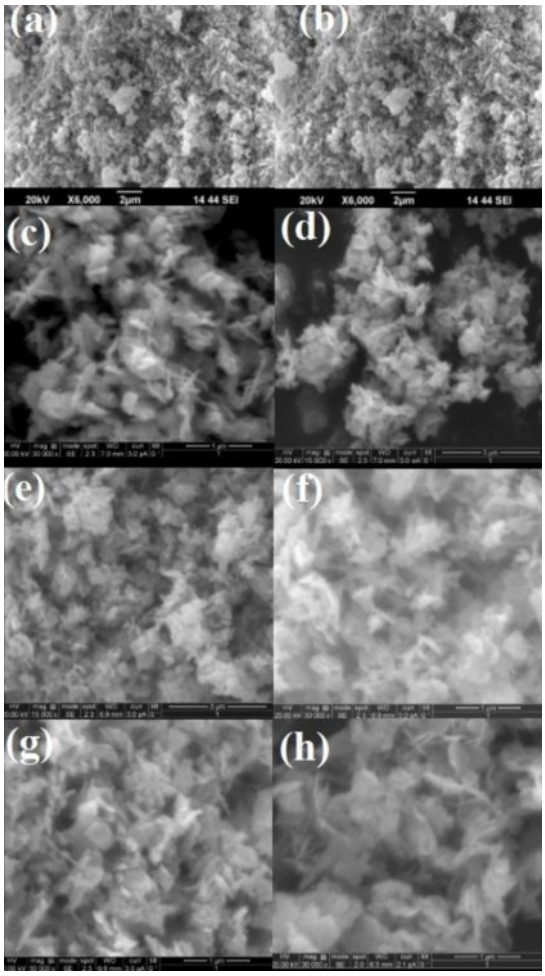

Fig. 2 Scanning electron micrographs of (a&b) pure ZnO (c&d) Co doped (e&f) 1% Bi co-doped (g&h) 3% Bi co-doped ZnO: Co nano particles.

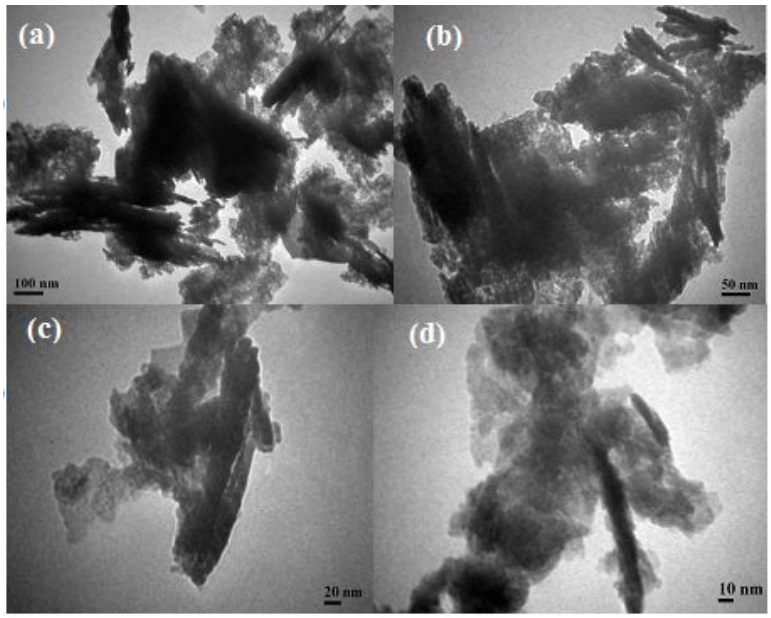

Fig. 3 (a-d) TEM images of ZnO Co doped with 1% Bi nano particles

Optical Absorption Studies:

The UV-Vis absorption spectra of chemically precipitated pure and Co with Bi co-doped ZnO nanoparticle were shown in the Fig 4. The maximum excitonic absorption was found at 350-365 nm for all the samples which imply the lower particle dimension of the ZnO system. With addition of Co^{2+} and Bi^{3+} it was

found that least blue shift in absorption edge indicates the increase in particle diameter [12]. The dopant induced strain causes the blue shift in the absorption spectra by changing the band structure of the doped samples [13].

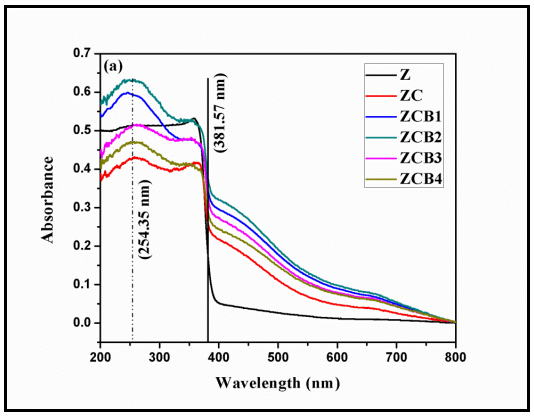

Fig. 4 UV-Vis absorption spectra of pure and Co with Bi co-doped ZnO nano particle

Photoluminescence Studies:

Fig 5a&5b show the PL spectra of the pure and Co with Bi doped ZnO nanoparticles. The near band-edge UV emission peak is found at around 380 nm for all the samples of pure and doped ZnO nanostructures. This is mainly due to the direct recombination of excitons at (n=1) state. The second peak at 250-270 nm is the lower UV region corresponding the first excited (n=2) excitonic state [14]. In addition to the above, the deep-level visible band obtained at around 550 nm attributes the intrinsic defects such as oxygen vacancy and zinc interstitials that are always present in ZnO [13,15]. Furthermore, due to Bi co-doping with Co, the additional violet emission is observed around 430 nm [16]. With increase in Bi concentration, the relative intensity of the violet emission has increased as in Fig 5b.The violet emission in the PL spectra of the Bi co-doped ZnO nanostructure is directly assigned to recombination from the conduction band to the energy level of deep traps or of surface and interface states originating from crystal defects inside or at the surfaces [11].

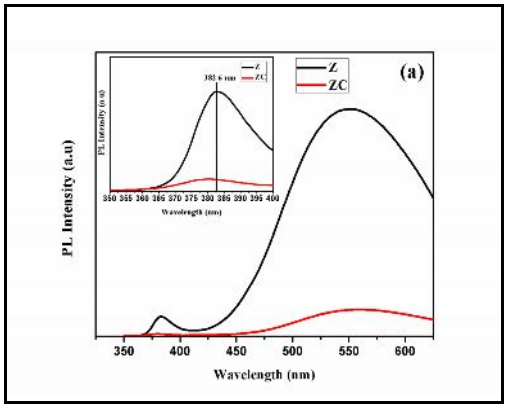

Fig. (5a) PL spectra of pure and Co doped ZnO nano particles.

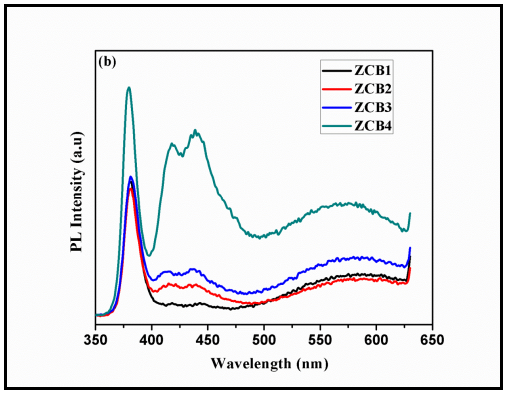

Fig. (5b) PL spectra of Co with Bi co doped ZnO nano particles.

Conclusion

In summary, the XRD pattern shows the pure and Bi co-doped ZnO were in the hexagonal wurtzite crystal structure. HRSEM and TEM observation evidences the flower like nanostructure with stacking and aggregation. The broad and an intense PL emission UV-visible region confirm the optical behavior of the ZnO nanostructure. Further, the tunable optical features of the Bi co-doped ZnO nanostructure could be the promising material for future opto-electronics and spintronics devices.

References:

1. Xiying, M.a., and ZuiWang., The optical properties of rare earth Gd doped ZnO nanocrystals. Materials Science in Semiconductor Processing, 2012, 15: 227-231.
2. H.Y. He*., Q. Liang., Enhancement in the optical transmittance of ZnO:Al powders by Mo co-doping Current Applied Physics 12, 2012, 865-869.
3. Congkang Xu., Junghwan Chun., and Dong Eon Kim., Electrical properties and near band edge emission of Bi-doped ZnO Nanowires, Applied Physics Letters, 90, 2007,083113 .
4. Wang, Y. S., John Thomas, P., and O'Brien, P., Optical Properties of ZnO Nanocrystals Doped with Cd, Mg, Mn, and Fe Ions, The journal of physical chemistry B letters, 110, 2006, 21412-21415.
5. Mashkoor Ahmad., Caofeng Pan., Wang Yan., Jing Zhu., Effect of Pb-doping on the morphology, structural and optical properties of ZnO nanowires synthesized via modified thermal evaporation, Materials Science and Engineering B 174, 2010, 55–58.
6. Maiti, U.N., Ghosh, P.K., Nandy, S., Chattopadhyay, K.K., Effect of Mn doping on the optical and structural properties of ZnO nano/micro-fibrous thin film synthesized by solgel technique Physica B 387, 2007, 103-108.
7. Yun Geng Zhang., Guang Biao Zhang., and Yuan Xu Wanga., First-principles study of the electronic structure and optical properties, of Ce-doped ZnO, Journal of Applied Physics, 109, 2011, 063510
8. Zhang Zhicheng ., Zheng Yongping. , Lai Fachun., Lai Heng., Huang Zhinan ., Huang Zhigao., Effects of Samarium Doping on Optical Properties of $Zn0.9(Co_{1-x}Sm_x)_{0.1}O$ Diluted Magnetic Semiconductor, Journal of rare earths, 24, 2006, p.270.
9. Feng Gu., Shu Fen Wang., Meng Kai Lu., Guang Jun Zhou., Dong Xu., and Duo Rong Yuan.,Structure Evaluation and HighlyEnhanced Luminescence of Dy^{3+} Doped ZnO Nanocrystals by Li^{3+} Doping via Combustion Method, Langmuir, 20, 2004, 3528-3531.
10. Yang, L.W., Wu, X.L., Qiu.T., Siu, G.G., Paul, K., Chu. Synthesis and magnetic properties of Zn1−xCoxO nanorods. J. Appl. Phys., 2006, 99, 074303.
11. Bappaditya Pal., and Giri, P. K., High temperature ferromagnetism and optical properties of Co doped ZnO Nanoparticles, Journal of Applied Physics, 108, 2010, 084322.
12. Guodong Tang., Xiaoqin Shi., Chao Huo., Zhihe Wang. Room temperature ferromagnetism in hydrothermally grown Ni and Cu co-doped ZnO nanorods. J.ceramint, 2012, 11.073.
13. Karthikeyan.B., Suchand Sandeep C.S., Reji Philip., Baesso, M.L., Study of optical properties and effective three-photon absorption in Bidoped ZnO nanoparticles. J. Appl. Phys., 2009, 106, 114304.
14. Bappaditya Pal., Giri P.K., and Room Temperature Ferromagnetism in Co-doped ZnO nanoparticles: Milling time dependence and annealing effect. International Journal of Nanoscience, 2010, 10:1, 1-5.
15. Jungang Hou., Zheng Wang., Shuqiang Jiao., Hongmin Zhu., Bi2O3 quantum-dot decorated nitrogen-doped Bi3NbO7 nanosheets: in situ synthesis and enhanced visible-light photocatalytic activity Cryst. Eng. Comm., 2012, 14, 5923–5928.
16. Hays,J., Reddy, K.M., Graces, N.Y., Engelhard, M.H., Shutthanandan, V., MLuo, Xu.C., Giles ,N.C., Wang, C., Thevuthasan, S., and Punnoose, A., Effect of Co doping on the structural, optical and magnetic properties of ZnO nanoparticles, J. Phys.: Condens. Matter 19, 2007, 266203-24pp.

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