Effect of potassium doping on the optical properties of zinc oxide nanoparticles grown by sol-gel method

M.Balasubrahmaniyam, Gincy Sunny, E.I.Anila*

Department of Physics, Union Christian College Aluva - 683 102, Kerala, (INDIA)

E-mail: anilaei@gmail.com

ABSTRACT

We report the synthesis and optical characterization of ZnO:K nanocrystals of size ~3nm prepared using wet chemical method. The crystals prepared for different pH were characterized by X-ray diffraction, absorption analysis and photoluminescence (PL) measurements. In the photoluminescence spectrum a weak near band edge emission at about 400nm and a strong emission at about 570nm due to K^+ center at Zn site in ZnO:K quantum dots were observed.   © 2010 Trade Science Inc. - INDIA

INTRODUCTION

Semiconductor nanoparticles have been under continuous scientific interest because of their unique quantum nature, which changes the material solid-state properties. ZnO is a wide and direct band gap (3.37eV) II–VI semiconductor with many applications, such as a transparent conductive contact, thin-film gas sensor, solar cell, luminescent material, surface electro acoustic wave device, hetero junction laser diode, ultraviolet laser etc. Although laser diode or light emitting diode using GaN was already reported, ZnO is advantageous over GaN because of it's high free excitonic binding energy (60 meV), higher resistance to radiation damage and easier processing using wet chemical method. Pure ZnO nanoparticles exhibit a UV emission at 370nm and a broad green emission at 520nm[1]. Peak of the broad emission in visible region can be shifted by intentional incorporation of impurities either at cationic site or anionic site. In this paper we report the synthesis of potassium doped ZnO nanocrystals by wet chemical method with special attention given to the effect of pH on the band gap and photoluminescence of these crystals.

EXPERIMENTAL

50ml of 0.1M Zinc acetate dihydrate was prepared in methanol and 25ml of KOH solution in methanol was added to it to attain a desired pH. This solution was stirred for one hour at room temperature. The experiment was repeated for different pH by varying the concentration of KOH. This process introduces potassium ion (K^+) substitution at Zn site for the ZnO Quantum dots.

The powder extracted from a colloid of large particle size was characterized by x-ray diffraction using Rigaku x-ray diffractometer with Cu K_α x-ray. Absorption spectra of different colloidal samples prepared for different pH were recorded using Jasco V500 spectrophotometer. Fluorolog-3 spectrofluorimeter was used for the photoluminescence (PL) measurements of colloidal samples.

RESULTS AND DISCUSSION

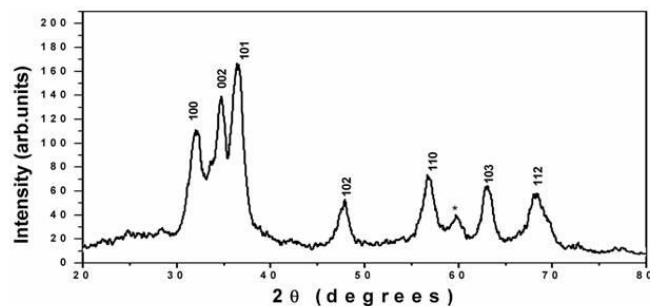XRD pattern ZnO:K nanocrystals prepared for 11.86 pH is shown in Figure 1.

Figure 1 : X-ray diffraction pattern of ZnO:K nanocrystals prepared for 11.86 pH

The peaks obtained from the XRD analysis was in agreement with that of bulk ZnO wurtzite structure. Grain size of the samples calculated using the Debye-Scherrer formula was found to be 2.9nm.

Absorption spectra of different samples prepared for different pH is shown in Figure 2. Blue shift in the absorption edge was found till a pH of 12.16 and thereafter decreased. The direct band gap of ZnO:K quantum dots were estimated by plotting (hν) versus (αhν)² and extrapolating the linear portion near the on set of absorption edge to the energy axis.
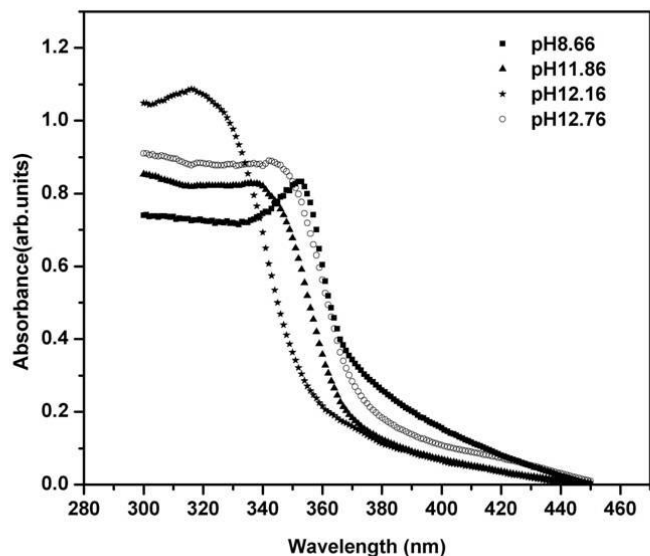

Figure 2 : Absorption spectra of ZnO:K colloids prepared for different pH

The maximum band gap was found to be for ZnO:K quantum dots prepared for a pH of 12.16 (TABLE 1). Blue shift in the Band gap means the particle size is decreasing as predicted by effective mass approximation.

TABLE 1 : pH versus band gap of ZnO:K quantum dots

pH	Band gap (eV)
8.66	3.38
11.86	3.45
12.16	3.56
12.76	3.4

The PL studies give information on the effect of doping in phosphors. The PL spectra of ZnO:K nanocolloid samples for excitation at 340nm is shown in Figure 3. Generally ZnO nano crystals exhibit two kinds of emissions: one is ultraviolet near band-edge emission at approximately 380 nm[2-9] and the other a visible deep level emission with a peak in the range from 450 to 730 nm for excitation around 340nm[10,11].
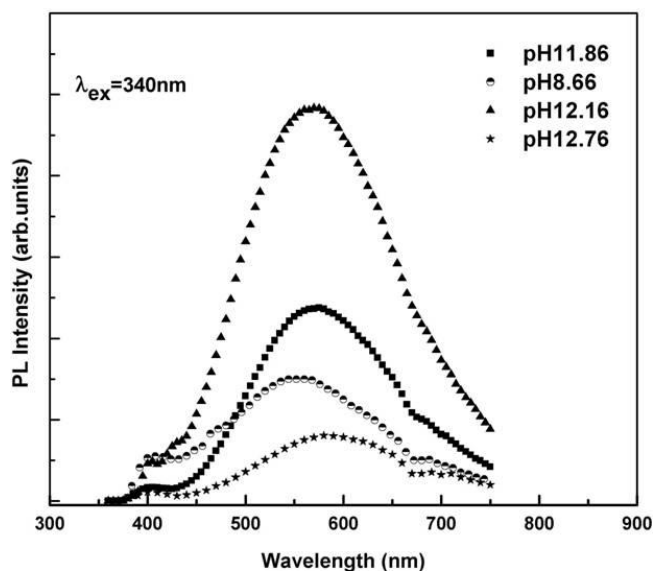

Figure 3 : PL spectra of ZnO: K nanocolloids prepared for different pH

The emission spectra of all samples mainly contain a narrow band around 400nm and a broad band around 570nm. The broad visible emission at 570nm may be thought of as the superposition of three emissions at 520nm, 570nm and 700nm. Transition from a shallow donor level to the valence band causes the emission at 400nm[12]. Zhao et al. attributed emission at 413nm to be due to Zn vacancy[3]. Therefore, the emission at 400nm in this work may be due to transition from Zn vacancy to valence band. There are different explanations for the origin of green luminescence but the most widely accepted one is that due to singly ionized oxygen vacancies[9,13-16]. Different studies suggested the origin of red-NIR (700nm) emission to be due to excess oxygen or Zn interstitials[17]. The prominent emission in potas-

Short Communication

sium doped ZnO nanocolloids was the emission around 570 nm which may be due to recombination at K^+ center. Kshirsagar et al. attributed the emission at 570 nm in ZnO:Na nanocrystals to Na^+ center at Zn site[11]. The emission peak shifts from 549nm to 589nm as the pH is changed from 8.66 to 12.76. This can be explained as due to the greater incorporation K^+ center in to the host lattice thereby increasing the emission due to this center compared to that due to singly ionized oxygen vacancies. Also with increase in pH interstitial Zn will increase thereby enhancing emission at 700nm. The PL emission intensity was found to increase with increasing pH up to 12.16 pH and thereafter decreased. This may be due to concentration quenching. The defect responsible for green emission is located on the surface but not for the yellow emission[10,18]. Figure 4 shows the excitation spectra of ZnO:K nanocolloids with different pH for emission at 565nm which is in agreement with absorption spectra.
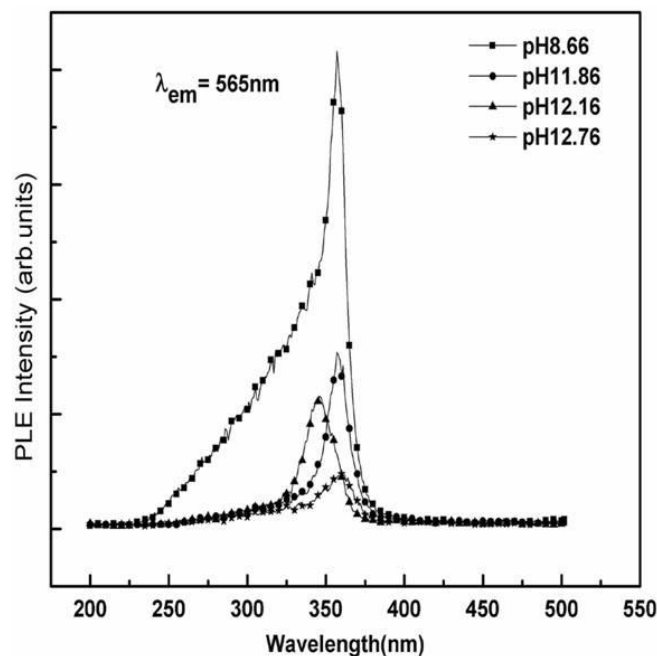

Figure 4 : PLE spectra of ZnO : K colloids for different pH

CONCLUSIONS

Green and yellow emitting ZnO: K quantum dots of size~3nm were prepared by wet chemical method for different pH. Blue shift in absorption edge and a further increase is observed with increase in pH. PL emission consists of two peaks around 400nm and 570nm in which former is near band edge emission and the latter is a broad emission due to K+ at Zn site (yellow), singly ionized oxygen vacancies (green) and Zn

interstitials (red). Emission shifts from green to yellow with increase in pH due to greater incorporation of K+ at Zn site. PLE spectra shows band to band excitation in agreement with absorption spectra

REFERENCES

[1] D.Bera, L.Qian, S.Sabui, S.Santra, P.H.Holloway; Optical Mater., **30**, 1233-1239 **(2008)**.

[2] X.Liu, X.Wu, H.Cao, R.P.H.Chang; J.Appl.Phys., **95**, 3141 **(2004)**.

[3] D.Zhao, C.Andreazza, P.Andreazza, J.Ma, Y.Liu, D.Shen; Chem.Phys.Lett., **399**, 522 **(2004)**.

[4] L.Huang, S.Wright, S.Yang, D.Shen, B.Gu, Y.Du; J.Phys.Chem.B, **108**, 19901 **(2004)**.

[5] F.Wen, W.Li, J.H.Moon, J.H.Kim, S.B.Lee, Y.H.Kwon, T.W.Kang; Opt.Commun., **250**, 111 **(2005)**.

[6] L.E.Greene, M.Law, J.Goldberger, F.Kim, J.C.Johnson, Y.Zhang, R.J.Saykally, P.Yang; Angew. Chem., **115**, 3030 **(2003)**.

[7] H.J.Fan, R.Scholz, F.M.Kolb, M.Zacharias; Appl. Phys.Lett., **85**, 4142 **(2004)**.

[8] H.J.Fan, R.Scholz, F.M.Kolb, M.Zacharias, U.Gosele, F.Heyroth, C.Eisenschmidt, T.Hempel; J.Christen.Appl.Phys.A, **79**, 1895 **(2004)**.

[9] X.Q.Meng, D.Z.Shen, J.Y.Zhang, D.X.Zhao, Y.M.Lu, L.Dong, Z.Z.Zhang, Y.C.Liu, X.W.Fan; Solid State Commun., **135**, 179 **(2005)**.

[10] A.B.Djurisic, W.C.H.Choy, V.A.L.Roy, Y.H.Leung, C.Y.Kwong, K.W.Cheah, T.K.Gundu Rao, W.K.Chan, H.F.Lui, C.Surya; Adv.Funct.Mater., **14**, 856 **(2004)**.

[11] S.D.Kshirsagar, V.V.Nikesh, S.Mahamuni; Appl. Phys.Lett., **89**, 53120 **(2006)**.

[12] H.Zeng, W.Cai, J.Hu, G.Duan, P.Liu, Y.Li; Appl. Phys.Lett., **88**, 171910 **(2006)**.

[13] Y.Q.Chen, J.Jiang, Z.Y.He, Y.Su, D.Cai, L.Chen; Mater.Lett., **59**, 3280 **(2005)**.

[14] R.C.Wang, C.P.Liu, J.L.Huang, S.J.Chen; Appl. Phys.Lett., **87**, 53103 **(2005)**.

[15] H.T.Ng, B.Chen, J.Li, J.Han, M.Meyyappan, J.Wu, S.X.Li, E.E.Haller; Appl.Phys.Lett., **82**, 2023 **(2003)**.

[16] Z.Chen, N.Wu, Z.Shan, M.Zhao, S.Li, C.B.Jiang, M.K.Chyu, S.X.Mao; Scr.Mater., **52**, 63 **(2005)**.

[17] M.Gomi, N.Oohira, K.Ozaki, M.Koyano; Jpn.J. Appl.Phys., **42**, 481 **(2003)**.

[18] D.Li, Y.H.Leung, A.B.Djurišić, Z.T.Liu, M.H.Xie, S.L.Shi, S.J.Xu, W.K.Chan; Appl.Phys.Lett., **85**, 1601 **(2004)**.