Synthesis and photoluminescence of ZnO Nanophosphors

Prinsa Verma*, S. Pandey, Avinash C.Pandey
Nanophosphor Application Center, University of Allahabad
(A DST Funded Project under IRHPA in collaboration with Nano Crystal Technology, NewYork).
*p2_v@rediffmail.com

Abstract*: We demonstrate the significant enhancement of emission characteristics of phosphors from nano-particles[1]. The ZnO nano particles were synthesized by using the wet chemical route by using Zinc acetate di-hydrate and Sodium hydroxide/Potassium hydroxide/Lithium hydroxide solutions. This bottom-up approach is motivated due to the considerable interest in the fabrication of optoelectronic devices[2,3] as the luminescent efficiency drastically changes with the particle size[4,5]. Nanophosphor materials such as ZnO have potential applications in high brightness light emitting diode applications[4]. Effect of size induced emission in visible region, radiative life time shortenings[5] and blinking effects[6] are prominent at nanoscale range. ZnO nanomaterial, having a wide band gap, is one of the promising candidates for general illumination applications due to its high optical transparency and color tunability[7].*
To investigate the crystallinity[6], particle size[7] and efficiency, analytical techniques such as Wide Angle X-ray Scattering (WAXS), Small Angle X-ray Scattering (SAXS) and Photoluminescence (PL) were employed. The WAXS, SAXS and TEM studies revealed the average particle sizes to be between 2 and 15 nm. Crystal growth more controlled by LiOH than KOH/NaOH.

1. Introduction

Zinc Oxide (ZnO), a wide band gap (3.37 eV) semiconductor, is a potentially important for laser diode[1] optical waveguides[2,3] optical switches[4,5], transparent ultraviolet (UV) protection conducting film[6] and acousto-optic and surface acoustic application. At the same time, high exciton binding energy (60 meV) makes it a promising candidate for room temperature laser diodes. Furthermore, ZnO has been well-studied as a sensor material.

Low dimensional semiconductors exhibit novel luminescence behaviour. Size depend luminescent properties have been observed that are useful in various optoelectronic applications. Doped ZnO nano crystals have been observed to yield high luminescent quantum efficiency & shorting in decay life time.

Almost all II-IV semiconductors are direct band gap materials & allow manipulation of properties by controlling the stoichiometry. ZnO is a well known II-VI luminescent material & has a short cathodoluminescent decay time. Very strong green luminescence peaked at about 510 to 530 nm is observable in ZnO. This green luminescence in ZnO has been investigated for a long time.

It has been observed that bulk ZnO crystals prepared under oxidizing conclusions exhibit predominantly a broad band in the green region and a narrow band in Ultraviolet region. Therefore for a long time one origin of the green luminescence has been attributing to the defect levels arising either due to oxygen vacancies or due to Zinc interstitials to explain the green emission in ZnO, Various models have been proposed studies carried out by Van-Heusden et al suggested that the green emission in ZnO is due to recombination of electrons in singly occupied oxygen vacancies with photo excited holes in the valence band.

Liu et al have investigated the green and yellow luminescence in ZnO and Mn-doped ZnO, which was attributed to interstitial Zn & Oxygen. They have also observed quenching of both green & yellow luminescence by Mn doping. In general, it has been observed that surface defects play an active role in the luminescence behaviour of quantum dots. Doping of Cu in ZnO quantum dots, which have OH radical on its surface, is responsible for quenching green luminescence.

2. Experimental: Synthesis of ZnO with LiOH

We prepared ZnO described by Spanhel and Anderson[7] groups were used some of the modifications have been introduced in the preparation. 0.1mol of Zn $(Ac)_2.2H_2O$ (Merck) was dissolved in 50 ml of ethanol at atmospheric pressure and 55^oC. Contrary to Spanhel and Anderson & other workers [7,8] Zn $(Ac)_2.2H_2O$ solution was refluxed for 1/2 hr. and then cooled the above prepared solution to room temperature. 0.14 mol sample of $LiOH.H_2O$ was dissolved in 50 ml of ethanol at room temperature in an ultrasonic bath. Lithium hydroxide solution was added drop wise to the Zn $(Ac)_2$ solution under vigorous stirring. The reaction mixture became transparent and we obtain a bright blue green luminescence in the UV-spectrometer.

Precipitation has been obtained by Heptane preferable because it is less toxic. Typically, the required volume ratio of hexane/heptane to ZnO solution was between 4:1 and 3:1 supernatant was removed by decantation or centrifugation. This procedure could be repeated several times n-heptane was added to a ZnO solution within 1 days after preparation and the mixture was kept at room temperature (RT= 35^0C) until a white powder has been obtained.

Synthesis of Nano-phosphorous ZnO with NaOH

The synthesis has been done by taking Zinc acetate dihydrate and lithium hydroxide[9] in appropriate quantity and then prepares alcoholic solution of individual as mentioned above. The solution of sodium hydroxide was added drop wise in Zinc Acetate solution followed by vigorous stirring maintained at ice bath and the precipitate is obtained by using heptane. A clear contrast has been visualized in both ZnO powders in PL measurement.

Characterization

X-ray Diffraction (XRD) : Crystallite size of the prepared sample was analyzed using XRD technique Sample were preferably orientated along different planes, the "d" valuewere compared with standard JCPDS data card (79-0207) which confirms the wurtzite structure of the materials.

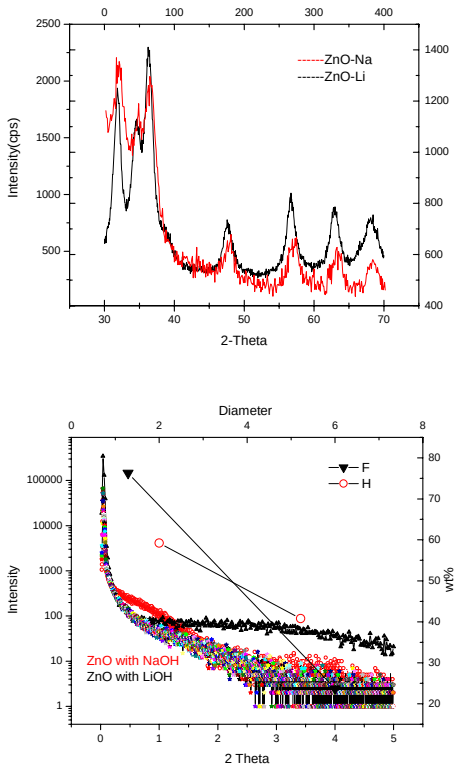

Figure 1. XRD pattern of ZnO with LiOH and with NaOH.

Crystallite size of the ZnO powder sample was calculated form the peak width using Debye- Scherrer formula $D = (0.9\lambda)/(\beta\cos\theta)$ where D is the diameter of the crystallites, λ is the wavelength of Cu K_α line, β is full width at way maximum (FWHM). The particle size was obtained in the range of 10- 30 nm in the case of ZnO with NaOH while in the case of ZnO with LiOH is in the range of 6-10nm which is consistent through SAXS..

Optical Studies

PL measurement were done at room temperature . All samples PL measurements were done at room temperature. All sample showed characteristic peak at 580 nm which corresponds to the blue green emission. These emissions were found to be extremely broad and this broadening may be due to phonon assisted by transition[10].

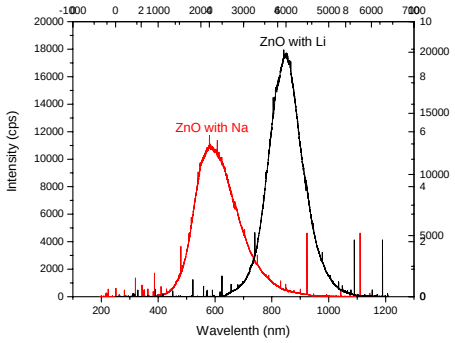

Figure 2. PL spectra of ZnO with LiOH and NaOH

From the different sample preparation a clear contrast in luminescence property has been observed which we are reporting. It is concluded that synthesis of ZnO with LiOH, more luminescence intensity was observed as compared to synthesis of ZnO with NaOH.

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