SYNTHESIS, CHARACTERIZATION AND PHOTOLUMINESCENCE PROPERTIES OF Ce$^{3+}$ DOPED ZnO NANOPHOSPHOR

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Abstract

Rare earth doped metal oxide semiconducting nanophosphors are relevant because of their unique optical properties and promising applications in optoelectronic devices. The present study involves the synthesis of Ce doped ZnO nano particles (NPs) by a combustion method. X-ray diffraction results indicated that the synthesized ZnO and ZnO:Ce nanoparticles have a pure wurtzite (hexagonal phase) structure. The average crystallite size was found to be in the nanometer range. The formation of ZnO:Ce$^{3+}$ nanoparticles was confirmed by Fourier transform infrared and X-ray diffraction spectra. The synthesised nanoparticles exhibit emission peaks in the blue region. The photoluminescence emission spectra of Ce-doped ZnO showed enhanced visible emissions as a result of 5d$\rightarrow$4f transition of cerium.

Keywords: Nanophosphor, wurtzite, SEM, Photoluminescence

1. INTRODUCTION

Nanostructured materials play essential role in the fields of energy sources, health and environments. The relevance of nano-sized material is that their optical, electrical and chemical properties can be tuned by changing the size of the particles. Zinc oxide, a unique attractive metal oxide semiconductor, has been widely used in the field of near-UV emission, gas sensors, transparent conductor and piezoelectric applications [1-5]. It is due to its wide band gap 3.37 eV, large bond strength, and large exciton binding energy (60 meV) at room temperature [6]. Luminescent properties of ZnO can be improved by doping with transition metals or lanthanide ions. It provides modification in the electronic structure of ZnO nanoparticles for enhancing optical, magnetic and catalytic properties. Doping with rare earth elements have vast number of applications in lighting, displays, biomedicine, sensing, and security. They exhibit extremely sharp absorption and emission lines due to 4f-4f intra shell transitions and do not photo bleach [7-13].

ZnO doped with rare earth ion such as Eu, Gd, Sm and Ce were synthesised by various methods. The luminescent properties of Ce doped ZnO have been investigated by number of researchers, since cerium has the super-sensitive f–f transitions in some hosts and unusual interaction between the excited states and the host lattice [14]. In order to change the material properties in a controllable fashion suitable temperature and annealing ambient environment have to be chosen [15,16]. The effect of annealing temperature on the structural and optical properties of cerium(Ce) doped ZnO nanoparticles prepared by simple, low cost solution combustion method was discussed in this paper. The prepared nanopowders were characterized by powder X-ray diffraction (XRD), Scanning electron microscopy (SEM), Fourier transform infrared spectroscopy (FTIR), UV-visible spectroscopy and Photoluminescence spectroscopy (PL).
2. EXPERIMENTAL DETAILS

Ce doped ZnO nanopowders were prepared by combustion method by taking Zinc nitrate hexahydrate, Zn(NO$_3$)$_2$·6H$_2$O and cerium nitrate hexahydrate, Ce(NO$_3$)$_3$·6H$_2$O as oxidant and glycine as fuel. All chemicals are analytical grade. The cylindrical petri dish containing the reaction mixture is placed over a hot plate. Combustion evolves vast amount of heat and non-toxic gases resulting nanocrystalline powders. The prepared samples were annealed at different temperatures. Pure ZnO was also synthesised by combustion method for comparing the properties.

\[
\text{Glycine}\quad \text{Zn(NO}_3\text{)}_2\cdot6\text{H}_2\text{O}+\text{Ce(NO}_3\text{)}_3\cdot6\text{H}_2\text{O} \longrightarrow \text{Zn}_{(1-x)}\text{Ce}_x\text{O}+ \text{gaseous products}
\]

For structural analysis, X-ray diffraction measurements of the samples were recorded using Bruker AXS D8 Advance with Cu target radiation ($\lambda =1.5406$ Å). The particle morphology of phosphors has been examined by JEOL, JSM - 6390LV Scanning electron microscopy. FTIR spectroscopic studies have been performed with a IR Prestige-21. The optical absorption studies were recorded on UV-2450 spectrophotometer. Photoluminescence studies carried out by using LS Fluorescence Spectrometer. Sample codes are entitled in Table 1.

| Sample code | Sample description               |
|-------------|----------------------------------|
| Z1          | Undoped ZnO calcined at 200°C    |
| Z2          | Ce:ZnO calcined at 500°C         |
| Z3          | Ce:ZnO calcined at 700°C         |
3. RESULTS AND DISCUSSION

3.1 X-RAY DIFFRACTION

Fig 1. XRD patterns of (a) Z1, (b) Z2, (c) Z3 nanophosphor

Fig 1 shows the XRD results obtained for Z1, Z2 and Z3 nanophosphor. The crystallite size of the nanoparticles was estimated by applying the Scherrer equation [17]:

$$D = \frac{K\lambda}{\beta \cos \theta}$$  \hspace{1cm} (1)

where $D$ is the average particle size of the crystallite, $K$ the particle shape factor, $\lambda$ is the wavelength of X-ray used which is CuKα radiation ($\lambda = 1.5406 \ \text{Å}$), $\beta$ the calibrated the corrected full width at half maximum (FWHM) of the XRD peaks, and $\theta$ is the Bragg’s angle (half of the peak position angle).

For hexagonal lattice, lattice parameters are obtained by the equation [18]:

$$\left[ \frac{1}{d_{hkl}} \right]^2 = \left[ \frac{h^2 + k^2 + l^2}{a^2} \right] + \frac{l^2}{c^2}$$  \hspace{1cm} (2)

Unit cell volume ($V$) of the products is given by the formula,

$$V = (0.866) \ a^2 c$$

Bond length of the prepared nanocrystalline hexagonal lattice is obtained by,
\[ L = \left( \frac{a^2}{3} + c^2 \left( \frac{1}{2} - u \right) \right)^{0.5} \]  
\[ (3) \]

Where \( u = \frac{a^2}{3c^2} + 0.25 \), \( a \) and \( c \) are lattice parameters of the unit cell.

Dislocation density of the nanoparticle is calculated using the formula,

\[ \delta = \frac{1}{D^2} \]  
\[ (4) \]

**Table 2. Structural parameters of the pure and doped Ce:ZnO nanophosphors**

| Sample details | ‘d’ spacing (Å) | Lattice parameters(Å) | ‘Cell volume ‘V’(Å³) | Bond Length ‘L’ | Crystallite Size ‘D’(nm) | Dislocation density \( \delta \times 10^{-3} \text{(nm)}^2 \) |
|----------------|-----------------|------------------------|----------------------|-----------------|--------------------------|----------------------------------|
|                | 100             | 002                    | 101                  | a               | c                        | c/a                              | 1                                | 5.2149                          | 1.972                           | 16.7664                         | 3.5572                          |
| Z1             | 2.8134          | 2.6090                 | 2.4763               | 3.2486          | 1.972                    | 1.972                           | 5.2149                          | 1.972                           | 16.7664                         | 3.5572                          |
| Z2             | 2.8464          | 2.6296                 | 2.5006               | 3.2867          | 2.0145                   | 2.0145                           | 5.1770                          | 2.0145                         | 21.5294                         | 2.1574                          |
| Z3             | 2.8122          | 2.6013                 | 2.4740               | 3.2472          | 1.9804                   | 1.9804                           | 5.2064                          | 1.9804                         | 26.2430                         | 1.4520                          |

Crystallographic parameters obtained from XRD are enlisted in Table 2. It is clear that crystalline size increases with increasing annealing temperature. The peak width increases with decrease of annealing temperature. This indicates the growth of crystals and construction of larger clusters. Heating process enhances number of collision between particles leads to the coalesce with one another to form a larger particle [19]. Increase of unit cell volume with temperature may due to the rapid decrease in the density of vacant lattice sites, vacancy clusters, and local lattice disorders and a rapid resumption of lattice parameters [20]. Decrease in dislocation density may be due to the increase of crystal growth.

**3.2. SCANNING ELECTRON MICROSCOPY (SEM)**

![Fig 2. SEM image of (a) Z1,(b) Z2,(c) Z3 nanophosphor](image)
Microstructural characterization of the synthesized samples were carried out by SEM analysis. SEM images of final products are shown in Fig 2. Pure ZnO appears like tiny spherical particles. In fig 2(b) and 2 (c), crystalline size increases with temperature such that particles were aggregated and also the attractive force between particles will increases and it appears like agglomerate.

3.3. FTIR SPECTROSCOPY (FTIR)

![FTIR spectra of (a) Z1, (b) Z2, (c) Z3 nanophosphor](image)

Chemical and structural changes of synthesized nanomaterials can be investigated by FTIR spectroscopic analysis. Fig 3 illustrates FTIR spectra of Z1, Z2 and Z3 nanophosphor, studied in the wave number range 400 - 4000 cm\(^{-1}\). The spectra shows the band located at around 450–490 cm\(^{-1}\) can be attributed to the Zn–O stretching mode in the ZnO lattice [21]. The absorption peak at 526 cm\(^{-1}\) ascribed to stretching frequency of ZnO [22]. Sharpening of metal oxide peak with temperature indicate better crystallinity and at higher temperature peak gets broaden may due to size reduction. On Ce doping samples exhibit a peak centred at 892 cm\(^{-1}\) may be due to the presence of Ce-O stretching vibration [23]. As particle size increases, lower vibrational frequency shift arise, may due to repulsive dipolar interactions and increase of bonding frequency may due to quantum confinement effect. The broad absorption band around 3514 cm\(^{-1}\) attributed to the O-H stretching mode of hydroxyl group. It is observed that the area of hydroxial peak diminishes with rise in temperature. Peak at 1369 cm\(^{-1}\) correspond to C=O bending vibrations and will diminish at higher annealed temperature.
3.4. UV-VISIBLE SPECTROSCOPY

**Fig 4.** Absorbance spectra of (a) Z1, (b) Z2, (c) Z3 nanophosphor

**Fig 5.** Tauc plot of (a) Z1, (b) Z2, (c) Z3 nanophosphor
Fig 6. The calcination temperature dependence on the band gap and crystallite size

Table 3. Variation in crystallite size and energy band gap with temperature

| Sample details | Crystallite size (nm) | Band gap (eV) |
|----------------|----------------------|---------------|
| Z1             | 15.0623              | 3.15          |
| Z2             | 22.9682              | 3.13          |
| Z3             | 33.2992              | 3.12          |

The optical properties of synthesized nanopowders were studied by using optical absorption spectrum. Fig 4 exhibits UV-visible spectrum of Z1, Z2, Z3 nanophosphor in the wavelength range 350-550 nm. The fundamental absorption band edge shift towards higher wavelength (red-shift) with calcination temperature. Red shift may be due to the insufficient growth of particle as a result of solid state diffusion process and blue shift is attributed to the quantum size effect [24]. The optical band gap of the nanopowders were calculated using Tauc relation [25]:

$$\alpha = A(h\nu - E_g)^n$$  \( (5) \)

Where \( \alpha \) is the optical absorption co-efficient, \( A \) is a constant, \( h \) is Plank’s constant, \( \nu \) is the photon frequency, and \( E_g \) is the optical band gap and \( n \) is a value that depends on the nature of transition (\( n=2 \) for direct band gap, \( 2/3 \) for direct forbidden gap and \( 1/2 \) for indirect band gap). \( E_g \) might be calculated by plotting \((ah\nu)^2\) on the Y-axis and photon energy \((h\nu)\) on the X-axis as in Fig 5 and tabulated in table 2 for all samples. Band gap studies reveal that
optical band gap undergoes a reduction with increasing temperature. Decrease of band gap may be ascribed to the fact that new defect are introduced after substitution of Ce by Zn atoms in order to electro negativity and ionic radius difference between Zn and Ce. Dopant atoms take up the energy levels located in the bottom of the conduction band. The valence electrons require extra energy to be excited to higher energy states in the conduction band. It weakens the electron and hole wavefunctions, which result from reduction of quantum size effect and enhancement of crystallinity accompanied with increase of particle size.

3.5 PHOTOLUMINESCENCE SPECTROSCOPY

![PL spectra of (a) Z1 (b) Z2 (c) Z3 nanophosphor](image)

Photoluminescence investigation confirms the ability of nanoparticle to absorb incident energy and convert it into visible radiation. Fig 7 represents the photoluminescence spectra of Z1, Z2, Z3 nanophosphors. Luminescence peaks of Z1 nanophosphor were observed at 420 nm, 457 nm and 486 nm excited by 280 nm. The most prominent peak located at 486 nm may due to the transitions from 2D3/2–2F7/2 states. Blue emissions correspond to singly occupied oxygen vacancies in deep trapped holes [van Dijken et al., 2000; Li et al., 2003]. Peak at 420 nm may due to Zn vacancies[27].On cerium doping peak positions shifted to higher wavelength region, which may be due to the energy transfer of conduction band electrons of ZnO to the newly created intermediate levels by Ce3+ ions[28]. Also, on doping, impurity ions reducing electron-or hole-trapped surface levels on ZnO, leading to increase in luminescence intensity [29]. As calcined temperature increases,
prominent and weak peak positions does not changed but intensity get sharply decreased. Reduction in PL intensity may be due to crystal growth.

4. CONCLUSION

The nanocrystalline powders of ZnO:Ce were prepared by combustion method. The wurtzite structure was confirmed from the diffraction patterns of all prepared samples. It is found that structure of synthesized samples remains unaffected by annealing but there is a change in the crystallite size. FTIR showed that various chemical functional groups are present in the synthesized samples. The SEM results reveals the morphological structure and variation in the grain growth. Optical UV-Vis measurements indicate that band gap shifted to higher wavelength with rise in temperature. It is found that PL intensity increases with rise in calcination temperature. Post growth thermal treatment can drastically modify the luminescence behaviour in the blue region of Ce doped ZnO samples.

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