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STRUCTURAL AND OPTICAL INVESTIGATION OF PURE AND LANTHANUM DOPED ZnO NANOPARTICLES SYNTHESIZED BY CO-PRECIPITATION METHOD

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ABSTRACT

Objective: Zinc oxide nanoparticles are assumed to be the foundation for several applications including environmental applications, optical devices, telecommunication, energy storage and so on. Its very crucial to obtain uniform and good quality nanoparticles in their properties point of view.

Materials and Methods: Pure and rare earth material (La) doped ZnO nanoparticles were prepared by co-precipitation route with heating temperature of 200°C and their properties were comparatively studied in this work. The structural properties were carried out by X-Ray diffraction technique and Optical analysis was done by using UV-Vis spectrophotometer.

Results: Structural investigations show that all the crystallites are of hexagonal wurtzite structure with preferred orientation along (101) plane. Further, optical analysis indicates that the average transmittance of the prepared samples is 85 % in visible region of spectrum. Moreover, Energy band gap studies reveal the increase in energy band gap from 3.23eV to 3.24 eV with incorporation of La^{+3} in ZnO lattice.

Conclusion: These analyses indicate that doping Zinc oxide with lanthanum varies and enhances the properties of prepared thin films.

Keywords: - Synthesis,ZnO nanoparticles, Co-precipitation, Structural and Optical Study.

INTRODUCTION

Metal oxide nanoparticle are preeminent materials due to their characteristic properties, one of which is zinc oxide (ZnO). ZnO is an n- type semiconductor material with a wide direct band gap of 3.37 eV and high exciton binding energy of 60 meV at room Temperature [1, 2]. Zinc oxide nanostructures play an important role for their size dependent applications in semiconductor and optoelectronic technologies with unique electrical and catalytic properties, high luminescence yield and low price [3, 4]. Due to its wide range of applications in technical manufacturing, cosmetics, and the pharmaceutical industry, zinc oxide nonmaterial, such as nanoparticles or zinc oxide-based semiconductors, have been studied [5,6]. Not only this butZnO nanoparticles have some commercial applications, such as solar cells, field effect transistors, photo detectors, liquid crystal displays, surface acoustic wave's devices, lasers, photodiodes and ultraviolet light emitting diode [7,15]

To enhance conductivity and transparency of materials and to meet the demands of these applications, ZnO has to be doped with some favourable elements in controlled manner [16,17]. Taking this thing into consideration rare earth elements doped II–IV semiconductornanoparticles have great importance in scientific community because such doping canvary and enhance properties of materials and related devices.

Un-doped and doped Zinc oxide nanomaterials can be formed using several techniques such as co-precipitation method [18, 19], sol–gel method [20], combustion method [21] and hydrothermal method [22]. Co-precipitation method is found to be more significant as it gives better quality material. Apart from that its processing cost is low, relatively low temperature is required and better yield can be achieved.

The main objective of this study is to prepare nanoparticles based on ZnO doping with different La concentrations by the Co-precipitation approach with heating temperature of 200°C. The structural and optical properties of prepared nanoparticles were studied in details.

EXPERIMENTAL DETAILS

In order to prepare pure and Lanthanum doped ZnO nanoparticles, Zinc acetate dehydrate (Zn $(CH_3COO)_2 2H_2O$), Lanthanum Nitrate (La $(NO_3)_3 \cdot 6H_2O$) and NaOH were used as precursors. Due to the high solubility and low decomposition we have chosen Zinc Acetate dehydrate as a precursor. Initially to obtain pure ZnO nanoparticles, aqueous solution of 0.5M zinc acetate is dissolved in 100ml deionized water with vigorous and continuous stirring. About 1.5M of NaOH is dissolved in 100ml deionized water in another beaker which is mixed in Zinc Acetate solution drop by drop until the pH of the solution attains 14.White precipitates are formed. Keep this solution for 15-20 minutes so that precipitate gets settled down at the bottom of the beaker which is then washed 4-5 times with deionized water till the pH value reaches to 7. Finally, precipitates are air dried and heated at 200°C temperature in oven to form oxides and desired nanoparticles are obtained. In order to get lanthanum doped ZnO nanoparticles (2%) the desired amount of lanthanum nitrate was added in the zinc acetate solution and same process is followed as mentioned above to get nanoparticles of doped samples.

RESULT AND DISCUSSION

Structural analysis

The crystalline phase analysis and orientation of pure ZnO and La-doped ZnO nanoparticles were identified using X-ray diffraction. The typical X-ray patterns of un-doped ZnO and La-doped ZnO nanoparticles of La concentration of 2% with heating temperature of 200°C is shown in Figure (a) with 2θ angle ranging from 20° to 80°.The diffraction peaks intensity correspond to the plane such as, [002], [100], [101], [110], [200], [102], and [201] were observed which indicates that all the nanoparticles samples exhibit hexagonal wurtzite crystal structure. No any extra peaks related to crystal phase La were observed which indicates all the nanoparticles are of single phase. XRD pattern also confirms that (101) peak is much stronger than other peaks, indicating preferred orientation.

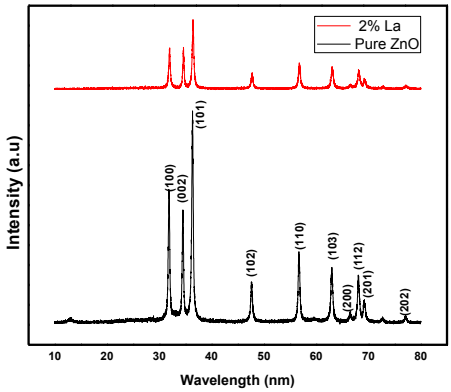

Fig 1: XRD spectra of pure and La doped ZnO nanoparticle

The average crystalline size can be determined with the help of FWHM of X-ray diffraction peak by using Debye-Scherer, s equation,

$$D = \frac{k\lambda}{B\cos\theta} \qquad (1)$$

Where, K indicates shape factor, λ indicates X-ray beam,Bindicates FWHM of the diffraction peak and θ indicates angle of diffraction peak.

The lattice parameters 'a' & 'c' of the deposited nanoparticles were calculated by using,

$$\frac{1}{d^2_{h,k,l}} = \frac{4(h^2+hk+k^2)}{3a^2} + \frac{l^2}{c^2} \qquad (2)$$

Where, $d_{h,k,l}$ is an interplanar spacing distance, h, k and l are miller indices.

The dislocation density (δ)indicates the numberof defects associated with the prepared samples and is given as the length of dislocation lines per unit volume of the crystalalso known as Williamsonand Smallman's relation,

$$\delta = \frac{1}{D^2} \qquad (3)$$

Where D is the grain size.

And micro strain (ε) values is calculated using equation,

$$\varepsilon = \frac{b}{4\cos\theta} \qquad (4)$$

The volume of the crystallites can be determined by,

$$V = \frac{\sqrt{3}}{2}a^2c \qquad (5)$$

All these values are calculated and reported in Table 1. It isobserved that with increase in doping concentration, the intensity of the peaks decreases which in turn decreases the size of the nanoparticles.XRD peak of doped sample is observed to be slightly shifted towards the higher angles may be due the difference in ionic radii ofdopant La^{3+} (1.03 Å) is greater than Zn^{2+} (0.74 Å). It has been found in several researches that when ionic radii of dopant materials are higher than that of host materials, the peak intensity of doped samples decrease and shiftslightly towards higher angles. Similar results were observed by L. V. Devi et.al [23].

Table1: Structural parameter of pure and la doped ZnO nanoparticle.

Doping (%)	a (nm)	c (nm)	c/a	D (nm)	Strain 'ε'	Volume $(nm)^3$	$\delta(nm)^{-2}$
0	0.3246	0.5203	1.6026	38.3738	0.000635	0.047493	0.0006790
2	0.3241	0.5188	1.6009	36.5312	0.000791	0.047208	0.0007493

Optical Analysis

The optical properties of $Zn_{1-x}La_xO$ materials with various doping concentrations wereinvestigated by UV–Vis absorption spectra in the range of 400nm to 800 nm which is shown in Figure (3). From Figure, it canbe seen that the absorption-edge of the synthesized $Zn_{1-x}La_xO$ materials located at around350-400nm. The optical band gap of Eg is calculated using the followingEq. (6).

$$\alpha = \frac{A(hv-Eg)^n}{hv} \qquad (6)$$

Where, 'A' and 'n' are constants, value of 'n' equal to 1/2 for the direct band gap semiconductor.

Optical transmittance spectra of the pure and lanthanum doped ZnO have been mentioned in the Fig. (4). From the spectra it can easily be seen that the nanoparticles have the higher transmittance values up to 85%, showing that the samples produced are transparent especially in the visible region. The Eg values for the nanoparticles have been obtained from the plot of variation of $(\alpha hv)^2$ versus the photon energy. Table (2) shows the band gap results of both pure ZnO and La-doped ZnO. Evidently, the band gap of La-doped ZnO increased gradually from3.23 eV to 3.24eV while La concentration increased from o% to 2%. This result may be associated with the two important certainties;one is that there may be appropriate interactionbetween surface oxidic size ofZnO and La^{3+}. Instead incorporation of La^{3+} in ZnO canmodify the electronic structure.

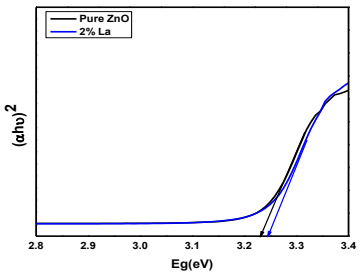

Fig. 2: Tauc plot for La doped ZnO nanoparticle

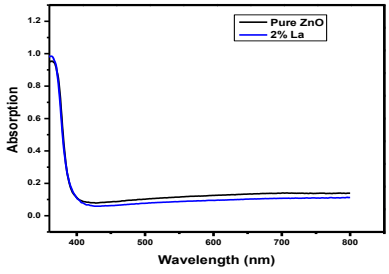

Fig. 3: Absorption spectra of pure and La doped ZnO nanoparticle.

Table 2: Optical bandgap of pure and la doped ZnO nanoparticle

Concentration	Band Gap (Eg)
0%	3.23 eV
2%	3.24 eV

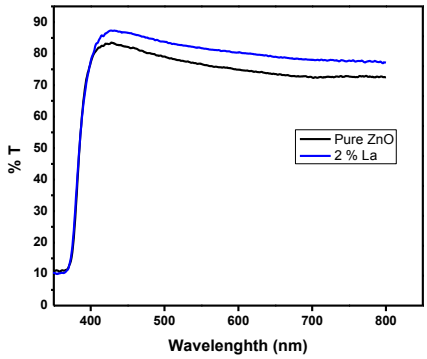

Fig. 4: %Transmission spectra of pure and La doped ZnO nanoparticle

CONCLUSION

Summarizing the work, Un-doped and La doped ZnO nanoparticles were successfully prepared by Co-precipitation route with doping amount of 2%. From XRD results it is confirmed that particles size has been decreased from 38nm to 36 nm with introduction of La content and hexagonal wurtzite structure is formed. The small particle size of La-doped ZnO may indicate high porosity and surface area than pure ZnO. It can also be observed that La doping changed the lattice parameters values but the structure remains unchanged (Hexagonal). Optical analysis shows that transmittance of the nanoparticlesis more than 80 % for both pure and doped nanoparticles. On the other hand, absorbance is visibly decreased with addition of Lanthanum in the crystal lattice. The band gap value is increased with La doping.

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