

Synthesis, X-ray peak broadening studies, morphological and optical properties of ZnO, Ba-doped ZnO and BaCu codoped ZnO nanoparticles

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Abstract

The Zinc oxide (ZnO), Barium (Ba) doped ZnO and Barium-copper co-doped ZnO (BaCu:ZnO) nanoparticles (NPs) have been synthesized by co-precipitation method. From the XRD pattern revealed that the ZnO, Ba:ZnO and BaCu:ZnO samples were exhibits hexagonal wurtzite structure. We also investigate the crystallite improvement in nanostructured ZnO, Ba:ZnO and BaCu:ZnO NPs by X-ray broadening analysis using scherrer formula and Williamson-Hall plot analysis. FESEM images confirmed that, the morphology of the ZnO, Ba:ZnO and BaCu:ZnO NPs formed spherical structure. Chemical composition was identified by EDAX analysis. The optical study was carried out using PL spectra.

Keywords: ZnO; BaCu codoped ZnO; X-ray broadening; scherrer formula and Williamson-Hall analysis.

Introduction

The important II–VI semiconductor ZnO is a direct band gap (3.36 eV at room temperature), n-type semiconductor with a large exciton binding energy γ of 60 meV and piezoelectric coefficients with a predicted curie temperature above room temperature when doped with the impurity [1–3]. Modification of the surface of zinc oxide plays an important role in making the material useful for numerous applications. The modification should improve the performance of materials like photocatalytic activity, conductivity, etc [4]. Co- precipitation is one of the methods used for the synthesis of nanopowders. The major advantages of this method are; reaction temperature is reduced due to homogeneous mixing of reactant precipitates and metal powders formed are highly reactive in low temperature sintering, which lead to the formation of smaller particles [5].

A perfect crystal would extend infinitely in all directions therefore; no crystals are perfect due to their finite size. This deviation from perfect crystallinity leads to a broadening of diffraction peaks. The two main properties extracted from the peak width analysis are the crystallite size and the lattice strain. The crystallite size is a measure of the size of coherently diffracting domains. The crystallite size of the particles is generally not the same as the particle size due to the formation of polycrystalline aggregates [6]. The lattice strain is a measure of the distribution of lattice constants arising from crystal imperfections such as lattice dislocations. The micro-strain analysis is performed for the samples from the X-ray diffraction.

In the present work, ZnO, Ba:ZnO and BaCu:ZnO NPs are synthesized by co-precipitation method. We have studied the structural, morphological, chemical composition and optical properties of the ZnO, Ba:ZnO and BaCu:ZnO NPs.

Experimental methods

The following high purity chemicals such as zinc (II) nitrate hexahydrate ($\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$), Copper (II) nitrate Hexahydrate ($\text{Cu}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$), barium nitrate ($\text{Ba}(\text{NO}_3)_2$) and sodium hydroxide (NaOH) were used as the precursors without further purification.

ZnO nanoparticles was prepared co-precipitation method. In this method, a solution was prepared by dissolving 0.1 M of Zinc nitrate in double distilled water. 0.8 M of NaOH solution was added into the Zinc nitrate solution. Then, the white precipitate was obtained. The solution with the white precipitate was stirred at the temperature of 60 °C for 4 h. Then, a clear solution was obtained, which found to be stable at ambient condition. Thereafter, the solution was washed several times with double distilled water and ethanol. Finally, the precipitate was dried at 120 °C. Thus, ZnO nanopowder was obtained.

In case of Ba doped ZnO NPs, 0.006 M of Barium nitrate ($\text{Ba}(\text{NO}_3)_2$) was dissolving in 100 ml of double distilled water, then added 0.094 M of zinc (II) nitrate hexahydrate ($\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$) solution in barium solution. In order to use NaOH as a precipitating agent, 0.8 M of NaOH was added into the metal (Ba:Zn) metal solution. Then, the black precipitate was obtained. The black precipitate was stirred at room temperature for 20 minutes. The mixture was again stirred at a temperature of 60 °C for 4 hours. The

solution was washed several times with double distilled water and ethanol. The precipitate was dried at 120 °C.

Similarly BaCu codoped ZnO NPs, 0.003 M of Barium nitrate ($\text{Ba}(\text{NO}_3)_2$) and 0.003 M Copper (II) nitrate Hexahydrate ($\text{Cu}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$) of was dissolving in 100 ml of double distilled water, then added 0.094 M of zinc (II) nitrate hexahydrate ($\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$) solution in barium-copper metal solution. In order to use NaOH as a precipitating agent, 0.8 M of NaOH was added into the metal (BaCu:Zn) metal solution. Then, the black precipitate was obtained. The black precipitate was stirred at room temperature for 20 minutes. The mixture was again stirred at temperature of 60 °C for 4 hours. The solution was washed several times with double distilled water and ethanol. The precipitate was dried at 120 °C. The ZnO, Ba:ZnO and BaCu:ZnO NPs samples were annealed at 800 °C for 5 h, because the energy from the heat will enhance the vibration and diffusion of lattice atoms for atomic rearrangement. Also the annealing helped to remove the residual impurities.

Characterization techniques

The ZnO, Ba:ZnO and BaCu:ZnO NPs were characterized by X-ray diffractometer (model: X'PERT PRO PANalytical). The diffraction patterns were recorded in the range of 25°-80° for the ZnO, Ba:ZnO and BaCu:ZnO samples where the monochromatic wavelength of 1.54 Å was used. The samples were analyzed by Field Emission Scanning Electron Microscopy (Carl Zeiss Ultra 55 FESEM) with EDAX (model: Inca). Photoluminescence spectra was taken using a spectrometer JASCO spectrofluorometer FP-8200.

Results and discussions

Figure 1 shows the XRD pattern of ZnO, Ba:ZnO and BaCu:ZnO NPs. The of ZnO, Ba:ZnO and BaCu:ZnO NPs exhibits hexagonal wurtzite structure and space group p63mc. Which is also confirmed by the JCPDS data (Card No: 36-1451). It is worth to mention, there is no impurity phase observed in Ba and BaCu codoped ZnO NPs. The lower angle shift in diffraction peaks for ZnO NPs as compared to the Ba and BaCu

codoped ZnO NPs, this shift may be substituted of impurity phase. Ba and BaCu codoped ZnO intensity are increased as compared to the pure ZnO NPs (Fig. 2.), due to impurity effects.

The micro-strain the breadth of the Bragg peak is a combination of both instrument and sample-dependent effects. To decouple these contributions, it is necessary to collect a diffraction pattern from the line broadening of a standard material such as silicon to determine the instrumental broadening. The instrument-corrected broadening β_{hkl} [7] can be represented by:

$$\beta_{hkl} = [\beta_{hkl}^2 \text{measured} - \beta_{hkl}^2 \text{instrumental}]^{1/2}$$

The particle grain size of ZnO, Ba:ZnO and BaCu:ZnO NPs are determined by the X-ray line broadening method using the Scherrer's equation reported Ramakanth, 2007 [6], the average particles size 44, 53 and 42 nm for ZnO, Ba:ZnO and BaCu:ZnO NPs respectively.

The strain-induced broadening β_ϵ is given by the Wilson formula $\beta_\epsilon = 4\epsilon \tan \theta$, where ϵ is the root mean square value of the micro-strain. Assuming that the particles size and strain contributing to the line broadening and independent of each other and both have a Cauchy like profile, the observed line width is simply the sum of these two, i.e., $\beta_{hkl} = (k\lambda / D \cos \theta) + 4\epsilon \tan \theta$, which becomes as

$$\beta_{hkl} \cos \theta = (k\lambda / D) + 4\epsilon \sin \theta$$

Figures 3 shows the plots of Williamson-Hall equation for ZnO, Ba:ZnO and BaCu:ZnO NPs samples. The calculated strain values are 0.0025, 0.00355 and 0.00285. These effects change the size and shape of the particles.

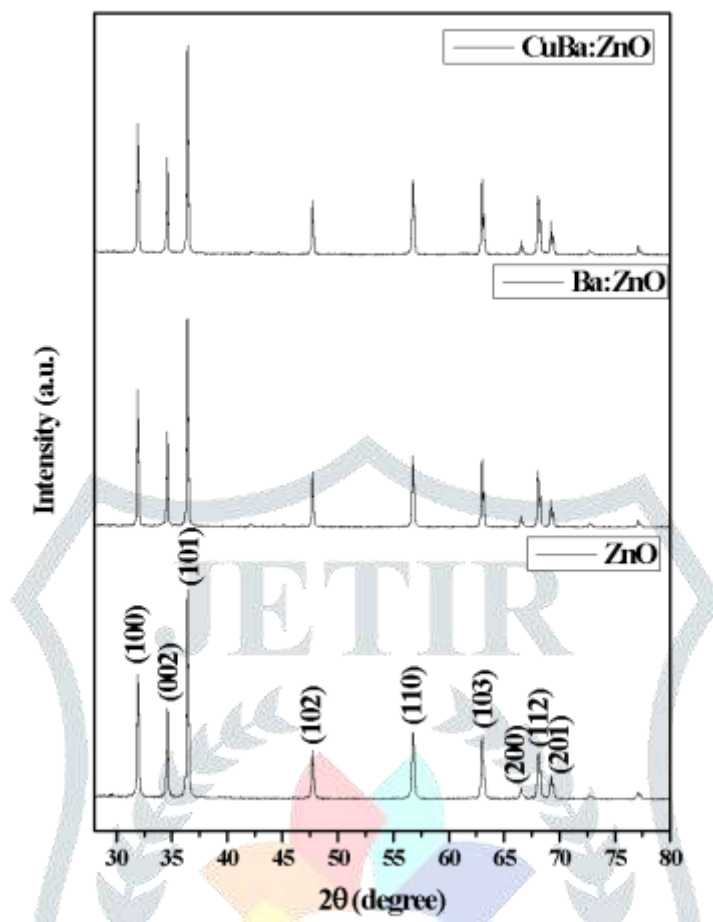


Figure 1 X-ray diffraction pattern of ZnO, Ba:ZnO and BaCu:ZnO NPs.

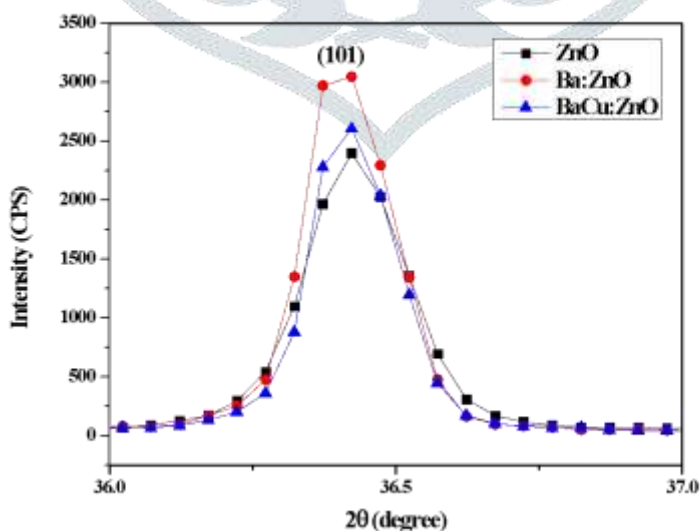


Figure 2 X-ray powder diffraction patterns of the doping-induced peak shift for ZnO, Ba:ZnO and BaCu:ZnO NPs.

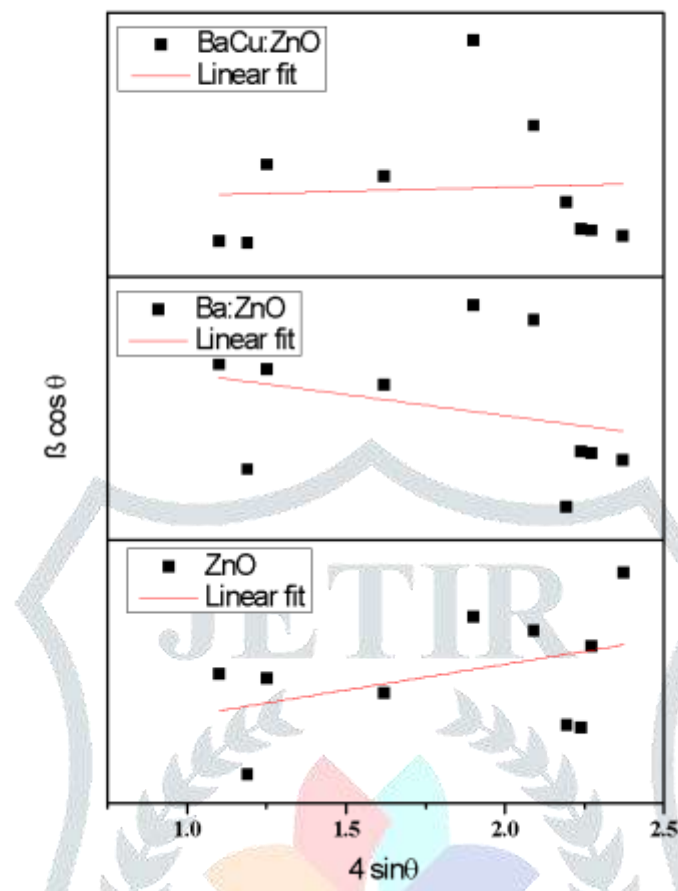


Figure 3 The W-H analysis of ZnO, Ba:ZnO and BaCu:ZnO NPs.

Morphology and chemical composition

Figure shows 4 the surface morphology of the ZnO, Ba:ZnO and BaCu:ZnO NPs were investigated by FESEM analysis. FESEM clearly display the synthesized ZnO, Ba:ZnO and BaCu:ZnO NPs formed spherical structure. The atomic percentage was identified by EDAX spectra is shown in Fig. 4. The EDAX data display the expected elements Zn, Ba, Cu and O are present in the nanoparticles. In the case Ba doped ZnO and BaCu codoped ZnO, there is no impurity peaks observed in the EDAX spectra.

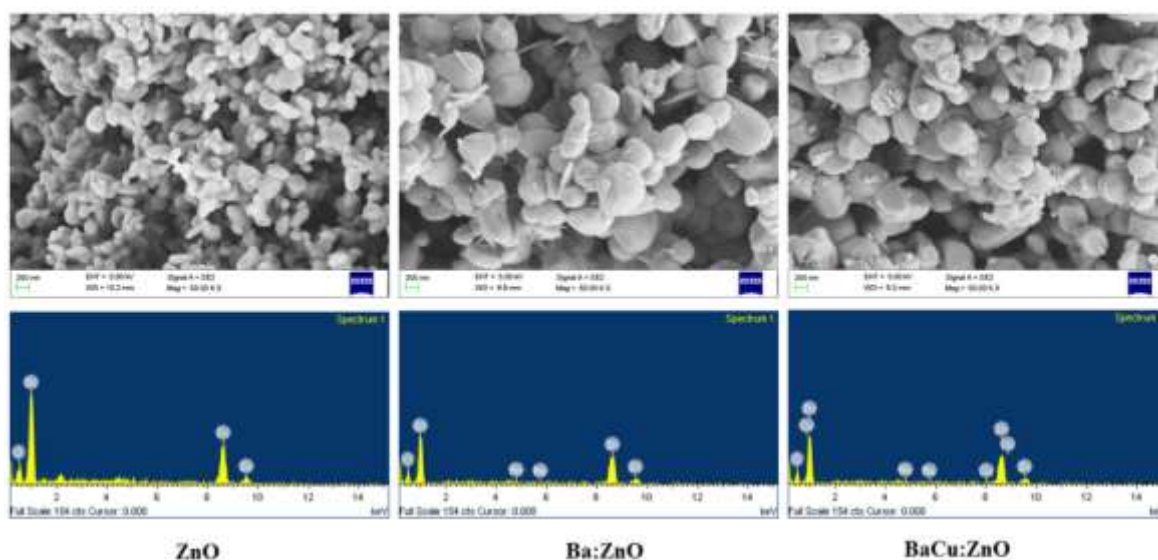


Figure 4 FESEM and EDAX spectra of ZnO, Ba:ZnO and BaCu:ZnO NPs.

Photoluminescence (PL) spectroscopic studies

Photoluminescence (PL) spectra of ZnO, Ba:ZnO and BaCu:ZnO NPs are shown in Fig. 5. Which excitation wavelength at 320 nm. The PL spectra of ZnO, Ba doped ZnO and BaCu Codoped NPs, UV emission observed at 360 nm, (360 nm and 389 nm) and (360 nm and 392 nm) , which is recombination corresponding to the near band edge (NBE) exciton emission of the wide band gap ZnO NPs [8, 9]. The violet emission centered at 415 nm for BaCu codoped ZnO NPs is attributed to radiative defects of interstitial (Zn_i) and Zn vacancies (V_{Zn}) related to the interface traps existing at the grain boundaries [10]. The blue emission observed at 479 and 480 nm for Ba:ZnO and BaCu:ZnO NPs, respectively, which is corresponding to singly ionized Zn vacancies. The green emission peak at 524 nm is ascribed to the recombination of electrons in singly ionized oxygen (V_o) vacancy with photo-excited holes in the valence band [11].

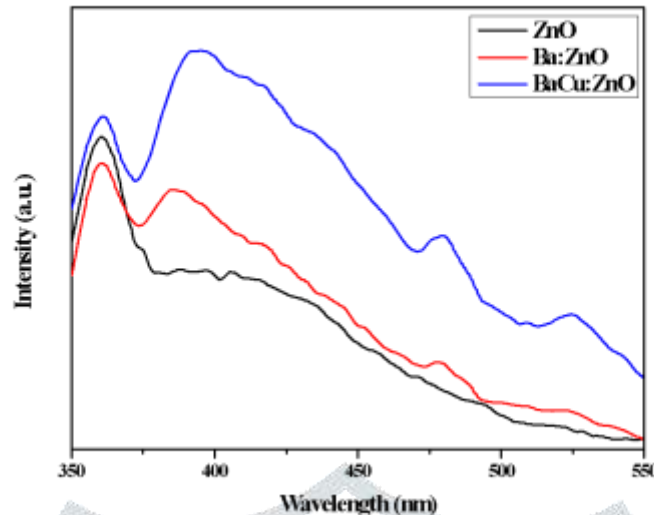


Figure 5 PL spectra of ZnO, Ba:ZnO and BaCu:ZnO NPs

Conclusions

The ZnO, Ba:ZnO and BaCu:ZnO NPs were prepared through co-precipitation method. From the XRD patterns, the synthesis ZnO, Ba:ZnO and BaCu:ZnO NPs exhibits the hexagonal structure. The XRD broadening of ZnO, Ba:ZnO and BaCu:ZnO NPs, barium and copper doping effects which may be small crystallite size and lattice strains. XRD broadening was analyzed through scherrer formula and modified forms of W-H analysis. FESEM images show the synthesized nanoparticles were spherical structure for ZnO, Ba:ZnO and BaCu:ZnO NPs respectively. Chemical composition were identified through EDAX spectra. The photoluminescence studies showed that the ZnO, Ba:ZnO and BaCu:ZnO NPs samples the band emission, which were due to zinc vacancies, oxygen vacancies and surface defects.

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