



RESEARCH ARTICLE

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Pure and SrBa Dual Doped ZnO Nanoparticles Prepared by Co-precipitation Method and Their Structural, Optical and Antimicrobial Properties

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ABSTRACT

The present investigation, the successful preparation of pure ZnO (Z1) NPs and SrBa dual doped ZnO (Z2) NPs by chemical co-precipitation technique without use of any capping agent. The structural and morphological properties of Z1 and Z2 NPs were analyzed using X-ray diffraction (XRD) studies, Field emission scanning electron microscopy (FESEM), Elemental analysis (EDAX), Fourier transform infrared spectroscopy (FTIR). An optical property was studied by UV-Vis spectroscopy and Photoluminescence (PL) spectra. The antimicrobial activity of Z1 and Z2 NPs has been investigated against *Staphylococcus aureus* and *Klebsiella pneumoniae* bacterial strains. It has been interestingly observed that Z2 NPs has enhanced the inhibitory activity than that of Z1 NPs against *S. aureus* and more efficiently than the *K. pneumoniae* bacterial strain.

Keywords: Zinc Oxide, Nanoparticles, XRD, *S. aureus* and Antimicrobial activity.

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INTRODUCTION

Nowadays, one-dimensional (1D) nanostructures like nanowires, nanobelts, nanorods, and nanotubes have paying attention a great deal of interest in academic as well as industrial research. [1-2] These nanostructures find applications in an electronic devices and circuits,

optoelectronic integrated circuits, electrochemical and electromechanical devices, etc. [3-4]

ZnO is an important n-type II-VI semiconductor NPs having direct band gap 3.37 eV, in addition with large excitation energy of 60 meV. Due to this property it has eminent uses such as luminescence, transparent

electronics, optoelectronics, ultraviolet (UV) light emitters, piezoelectric devices etc. [5-6] ZnO is also suitable for UV screening applications, because it has low toxicity, high chemical stability and it is effective to inhibit pathogenic organisms. [7] In previous studies, ZnO reveals the room temperature ferromagnetism (RTFM), when the metallic dopants like Al, Co, Mg and Mn etc., are successfully doped in ZnO. [8] Earlier reports, pure and dual doped (Co, Ag) ZnO NPs were manufactured by co-precipitation method without use of capping agent. [9] In the present investigation, we have planned to prepare pure and SrBa dual doped ZnO NPs by chemical co-precipitation method and their structural, optical and antimicrobial properties have been studied.

MATERIALS AND METHODS

Preparation of pure ZnO (Z1) and SrBa dual doped ZnO NPs (Z2)

To prepare 0.1 M $\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ solution by using double distilled water under constant stirring. While at room temperature, solution of 0.8 M NaOH was added drop by drop. It was stirred constantly at a temperature of $80 \pm 5^\circ\text{C}$ for 4 hours. Afterward end of the reaction, it was allowed to settle for overnight and the supernatant liquid was discarded. The obtained white coloured precipitate was thoroughly washed with double distilled water to remove all the other ions and then centrifuged at 3000 rpm for 10 minutes. The final precipitate was dried in a hot air oven at 80°C for 2 hours. The above resultant dried powders was crushed and calcined at 700°C for 5 hours. The final product ZnO (Z1) was stored in air tight container for further analysis.

Similarly, in the preparation of SrBa dual doped ZnO NPs, the required amount of 0.097 M $\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$, 0.002 M $\text{Sr}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$, 0.001 M $\text{Ba}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ was completely dissolved in deionized water, aqueous NaOH (0.8M) solution was added drop wise to the above aqueous solution and stirred at $80 \pm 5^\circ\text{C}$ for 4 hours. The white colour precipitate was formed slowly, which was washed several times with double distilled water and ethanol. The precipitate was dried at 120°C . Thus, SrBa dual doped ZnO (Z2) nanopowder was obtained. This sample was annealed at 700°C for 5 hours.

Antimicrobial Assay

Antimicrobial activity of the Z1 and Z2 NPs was carried out by agar well diffusion method against two pathogenic bacterial strains namely *S. aureus* (gram positive) and *K. pneumoniae* (gram negative) on Muller-Hinton agar, according to the guidelines of Clinical and Laboratory Standards Institute (CLSI). [10] The media plates (MHA) were streaked with bacteria for 2-3 times by rotating the plate at 60° angle for each streak to ensure homogeneous distribution of the inoculums. Then the agar plates were swabbed with 100 ml each of overnight cultures of *S. aureus* and *K. pneumoniae* using a sterile L-shaped glass rod. Using a sterile cork-borer,

wells (6 mm) were created in each petri plate. The concentration of Z1 and Z2 NPs $1.5\mu\text{g}/\text{ml}$ for both gram positive and gram negative bacteria were loaded onto the petri plates followed by incubation for 24 h at 37°C for bacteria. After the incubation period, the diameter of the zone of inhibition (DZI) was recorded. Amoxicillin (Hi-Media) was used as the positive control against gram negative and gram positive bacteria to compare the efficacy of the test samples. We have simultaneously studied whether the dimethyl sulfoxide (DMSO) without the Z1 and Z2 NPs plays any active role as a biocide or not. As there is no any disc zone of inhibition observed, it confirms that DMSO doesn't show any biocidal property.

Characterization Studies

The Z1 and Z2 NPs were characterized by X-ray diffractometer (model: X'PERT PRO PAN analytical). The diffraction pattern was recorded in the range of 25° - 80° for the Z1 and Z2 NPs, at the monochromatic wavelength of 1.54 \AA . The morphological features of the sample were measured by Field emission scanning electron microscopy (Model: Carl Zeiss 55). The Z1 and Z2 NPs were analyzed by EDAX (model: ULTRA 55). The FT-IR spectrum was recorded in the range of 400 - 4000 cm^{-1} by using Perkin-Elmer spectrometer. Ultraviolet-visible (UV-Vis) spectra of Z1 and Z2 NPs were recorded on a Perkin-Elmer UV-Lambda 25 spectrophotometer (Perkin-Elmer, Norwalk, Connecticut). The PL emission study of the sample was carried out using Horiba Jobin YVON spectrofluorometer (model: FLUOROMAX-4, 450 W high pressure xenon lamp as the excitation source, photomultiplier at a range 325-550 nm).

RESULTS AND DISCUSSION

X-ray diffraction studies

The XRD pattern of Z1 and Z2 NPs are shown in Fig. 1. The XRD peak position of at angles (2θ) of 31.732, 34.320 and 36.354, consistent to the (100), (002) and (101) planes of the ZnO NPs, respectively. Correspondingly, another peak position appeared at angles (2θ) of 47.43, 56.49, 62.57, 66.27, 68.12, 69.04 and 76.99 related to the (102), (110), (103), (112), (201), (004) and (202) planes of the ZnO NPs, respectively. The standard X-ray diffraction peaks show that the hexagonal wurtzite structure of ZnO NPs with space group of $p6_3mc$ and also confirmed by the JCPDS data (card No: 361451). This results are also witnessed that there is no impurity phase found in the Sr^{2+} and Ba^{2+} dual doped ZnO NPs, because of ionic radii of Sr (1.12 \AA) and Ba (1.35 \AA). The average crystallite size of the samples are calculated by Debye Scherrer's relation,

$$\text{Average crystallite size (D)} = \frac{0.9 \lambda}{\beta \cos \theta} \quad \text{--- (1)}$$

Where D is the crystallite size, λ is the wavelength (1.5406 \AA $\text{CuK}\alpha$), θ is the Bragg diffraction angle and β is the full width at half maximum (FWHM). The average crystallite sizes of Z1 and Z2 NPs were calculated to be 42 nm and 35 nm. Because of SrBa dual

doping in ZnO nanostructures, the particles size of its results decreases. It is due to distortion in the ZnO matrix by Sr²⁺, Ba²⁺ dopant ions, which increases the rate of growth of ZnO.

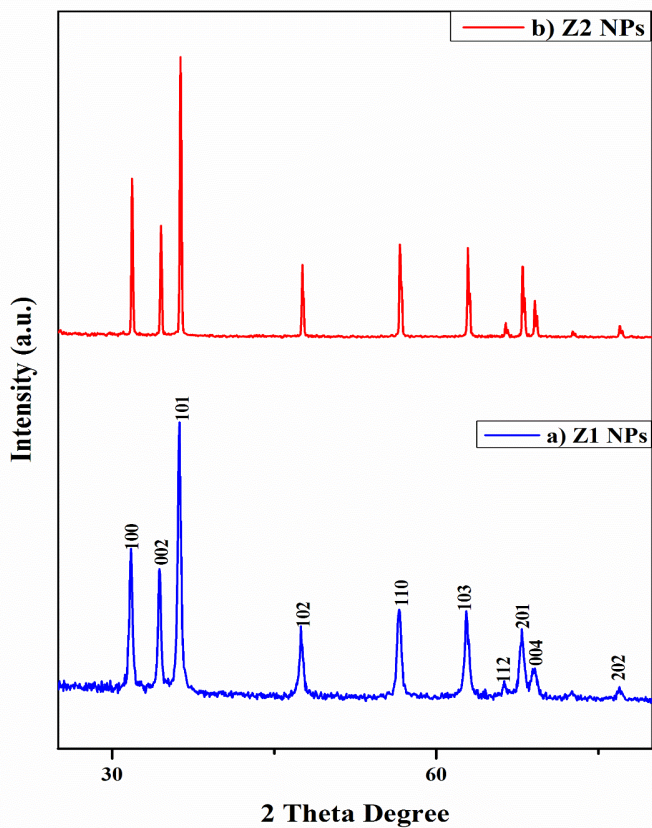


Fig. 1: XRD pattern of a) Z1 NPs b) Z2 NPs

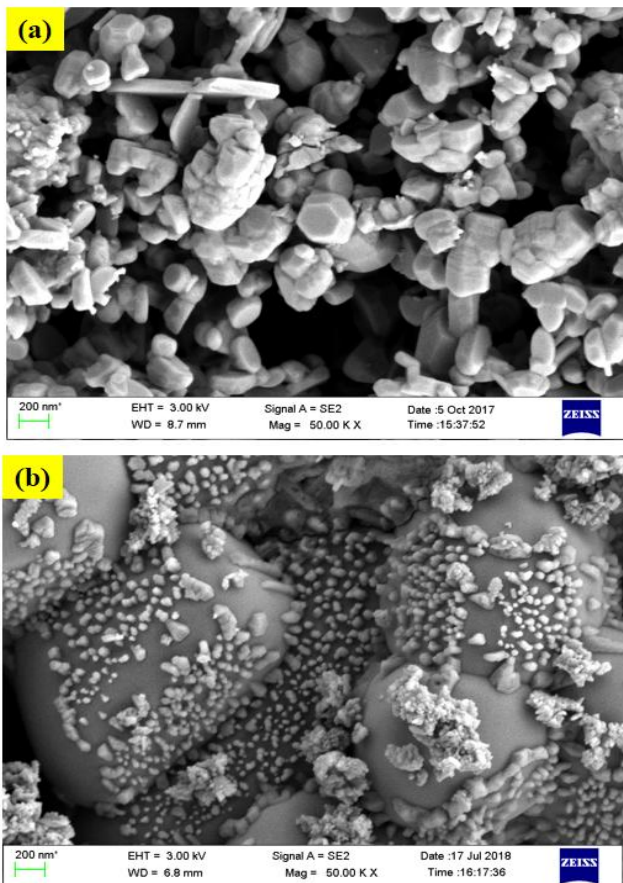


Fig. 2: FESEM images of a) Z1 NPs b) Z2 NPs

Morphological analysis

The surface morphology of the Z1 and Z2 NPs are shown in Fig. 2. From the FESEM images, the spherical and hexagonal like nanostructures were observed in Z1 NPs and Z2 NPs respectively. The average particle sizes were observed at 41 nm and 37 nm for Z1 and Z2 NPs respectively. The thicknesses of the nanoparticles are reduced, because the alkaline metal ions decrease the nucleation and subsequent growth rate of ZnO NPs.

Elemental analysis

The EDAX spectra used to analyse the elemental composition of Z1 and Z2 NPs and it is shown in Fig. 3. In the Z2 sample, Sr and Ba composition is observed at 2.84% and 1.72% and the Zn and O are 67.39% and 21.15% respectively. In the Z1 sample the chemical composition of Zn and O are found as 83.70% and 16.30% respectively. The EDAX spectrum has indicated the existence of Zn, O, Sr, and Ba for the synthesized NPs.

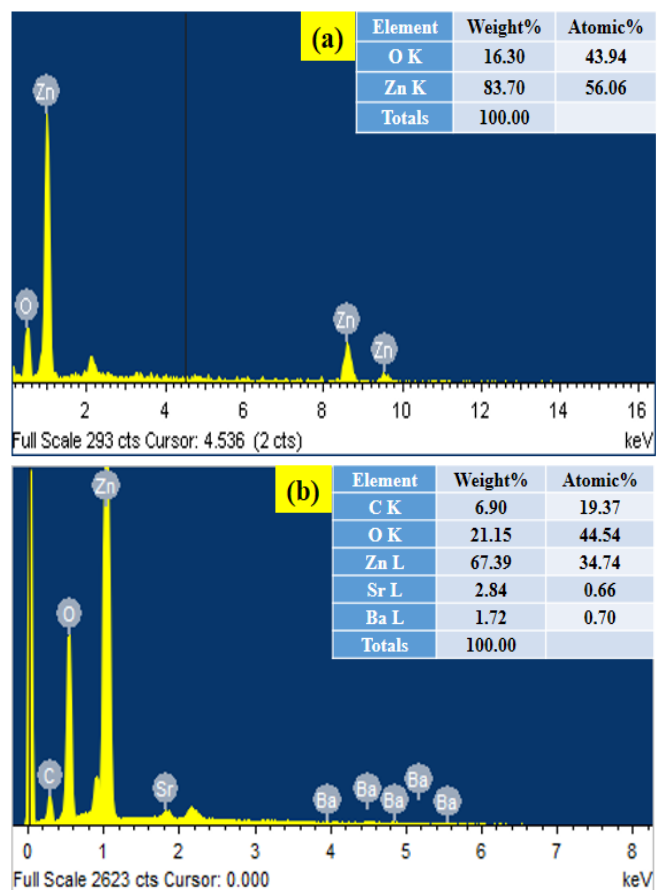


Fig. 3: EDAX spectra of a) Z1 NPs b) Z2 NPs

Functional group analysis

Fig. 4 shows that the FT-IR spectrum of the Z1 and Z2 NPs. The prepared Z1 and Z2 NPs were analyzed by FT-IR spectroscopy in the range from 400 to 4000 cm⁻¹ at room temperature. It comprises several characteristic bands. The vibrational stretching frequency mode of O-H band observed at a peak position in the range of 3020-3650 cm⁻¹. [11] The peak in the range of 445 cm⁻¹ corresponds to Zn-O stretching for Z1 NPs and in the case of Z2 NPs Zn-O stretching found to be 490 cm⁻¹.

Due to H–O–H bending vibration peak is observed at 1635 cm^{-1} which is assigned to a small amount of H_2O in Z1 NPs. [12] The asymmetric C–O stretching bands to be 1112 cm^{-1} and asymmetric C–H bands are observed at 2924 cm^{-1} for Z1 and Z2 NPs.

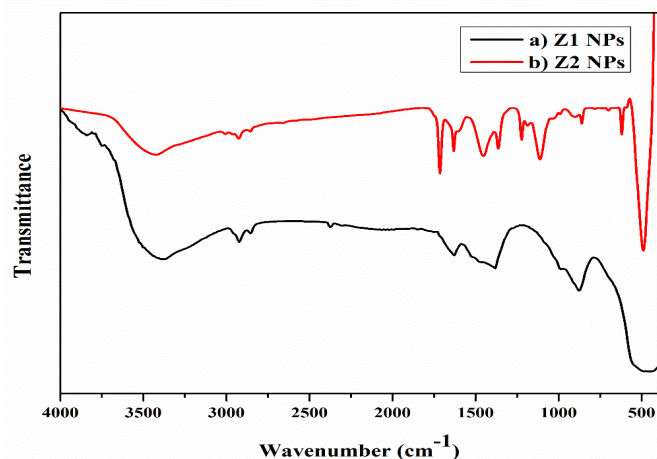


Fig. 4: FT-IR spectra of a) Z1 NPs b) Z2 NPs

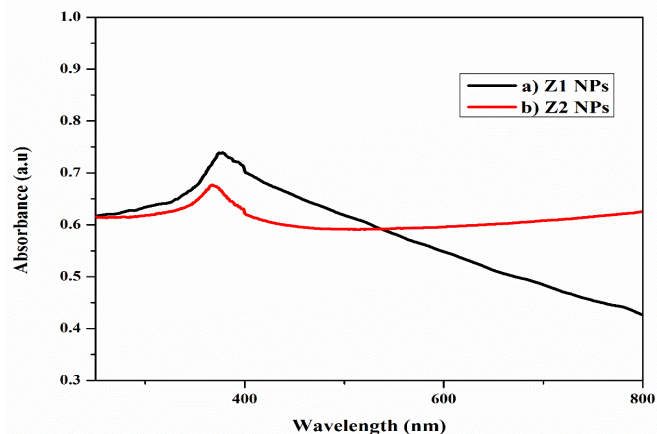


Fig. 5: Absorption spectra of a) Z1 NPs b) Z2 NPs

Optical studies

Fig. 5 shows that UV-visible optical absorption spectra of Z1 and Z2 NPs. From the absorption spectra, the absorption peaks are found at 377 nm for Z1 NPs whereas the peaks are observed at 366 nm for Z2 NPs, which can be attributed to the photo excitation of electrons from valence band to conduction band. It may be due to the photo excitation of electrons from valence band to conduction band. [13]

Photoluminescence (PL) studies

Fig. 6 (a-b) show that the photoluminescence spectra of prepared Z1 and Z2 NPs. The PL emissions of very short wavelength of 350 nm to long wavelength 600 nm are observed for Z1 and Z2 NPs. The seven peaks for both Z1 and Z2 NPs are fitted by Gaussian function. The emission spectra have seven peak positions at 387, 401, 416, 438, 457, 477, 516 nm and 357, 387, 411, 437, 450, 481, 497 nm for Z1 and Z2 NPs respectively. The observed PL bands are one violet emission, three blue emissions, one blue-green emission, two green emissions respectively.

The lowest wavelength of UV emission peaks are observed at 357 and 387 nm, which correspond to the

near-band emission (NBE) of Z1 and Z2 NPs. The four violet emissions centred at 410, 416, 438 and 447 nm is attributed to an electron transition from a shallow donor level of the natural zinc interstitials to the top level of the valence band. [14] The blue green emission observed at 477, 481 and 497 nm is ascribed to the transition between the oxygen vacancy and interstitial oxygen. [15] Finally two green emissions observed at 516 nm, corresponds to the singly ionized oxygen vacancies. [16-17]

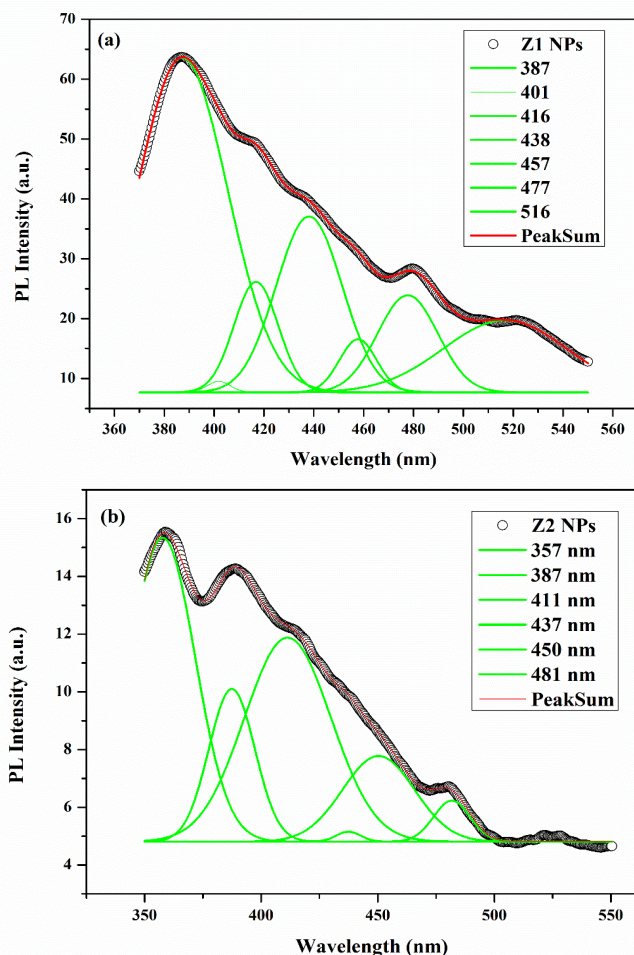


Fig. 6 (a & b): photoluminescence emission spectra of Z1 NPs and Z2 NPs

Table 1: Antimicrobial activities of Z1 and Z2 NPs for against human pathogens

S. No	Concentration of Z1 and Z2 NPs (μL)	Zone of inhibition (mm)	
		Gram positive strains	Gram negative strains
		<i>S. aureus</i>	<i>K. pneumoniae</i>
1	15	1.7	1.4
2	20	1.6	1.5
3	25	1.5	1.3
4	30	1.6	1.4
5	35	1.7	1.4

Antimicrobial Activity

In the present work, the antimicrobial activities of Z1 and Z2 NPs are shown in Fig.7. The antimicrobial activities of prepared Z1 and Z2 NPs were tested against the human pathogens like gram positive (*S. aureus*) and gram negative (*K. pneumoniae*) bacteria with

reference to Amoxicillin. The antimicrobial activity values are listed in Table 1. From the figure, the zones of inhibition values were increased with respect to the Z2 NPs concentration against the tested bacteria. The observed inhibition zone was higher in gram positive bacteria than gram negative bacteria which may be attributed to the difference in their cell wall structure of chemical composition. From these zones of inhibition values, it could be stated that Z2 NPs have higher antimicrobial property when compared to Z1 NPs. The antimicrobial activity of NPs may either directly interact with the microbial cells or produce secondary products that cause damage. [18]

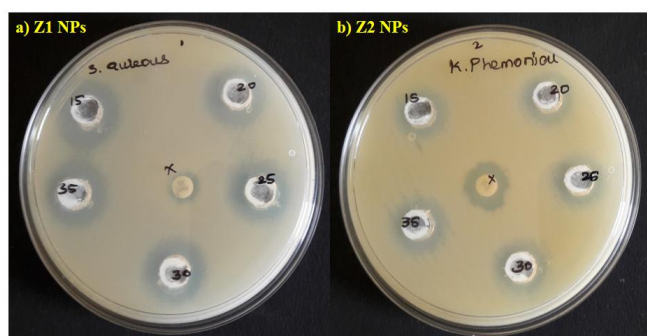


Fig. 7. Zone of inhibition of Z1 and Z2 NPs against *S. aureus* and *K. pneumoniae*

The Z1 and Z2 NPs were prepared successfully through co-precipitation method. The hexagonal wurtzite structure of Z1 and Z2 NPs were confirmed by X-ray diffraction studies. The calculated average crystallite sizes of Z1 and Z2 NPs were 42 and 35 nm respectively. The size of Z2 NPs is smaller when compared to Z1 NPs. This size reduction is mainly due to the distortion in the host ZnO lattice by the foreign impurities like Sr^{2+} and Ba^{2+} ions. From the FESEM images, the morphology of nanoparticles was found spherical and hexagonal in shape. The elemental compositions were identified for the synthesized Z1 and Z2 NPs using EDAX spectra. From the FT-IR spectra, the Zn-O stretching frequency appeared at 445 cm^{-1} and 523 cm^{-1} for Z1 and Z2 NPs. The UV-Vis spectrum showed the absorption peak is found at 377 and 396 nm for Z1 and Z2 NPs respectively. PL spectra showed that doping materials altered the band emission, which is due to zinc vacancy, oxygen vacancy and surface defects. The antimicrobial studies performed against a set of bacterial strains showed that the Z2 NPs possessed more antimicrobial property.

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