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Effect of Fe+F doping on the antibacterial activity of ZnO powder

K. Ravichandran[a,*], R. Rathi[a,b], M. Baneto[c], K. Karthika[a], P.V. Rajkumar[a], B. Sakthivel[a], R. Damodaran[d]

[a]*Post Graduate & Research Department of Physics, AVVM Sri Pushpam College (Autonomous), Poondi, Thanjavur 613 503, Tamil Nadu, India*
[b]*Department of Physics, Sengamala Thayaar Educational Trust Women's College, Mannargudi 614 001, Tamil Nadu, India*
[c]*CUER – UL, Université de Lomé, BP: 1515, Togo*
[d]*Post Graduate & Research Department of Zoology, AVVM Sri Pushpam College (Autonomous), Poondi, Thanjavur 613 503, Tamil Nadu, India*

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Abstract

Undoped and Fe+F doped ZnO powders were prepared using a simple and low cost soft chemical method. The Fe doping level was varied from 0 to 10 at% in steps of 2 at% and the F doping level was kept constant at 10 at%. The XRD studies showed that the prepared powders have hexagonal wurtzite structure of ZnO. The variation in the periodicity of the crystalline ZnO powders as evidenced from the variation in the intensities of the XRD lines is correlated with Fe and F incorporation in the ZnO lattice. The PL and FTIR results supported these incorporations. The SEM images revealed that the grains have perfect hexagonal shape with the side greater than 200 nm up to the Fe doping level of 4 at% and then it decreased drastically to nano level when the doping level is greater than 6 at%. From the antibacterial studies, it is found that the grain size plays a key role in determining the antibacterial efficiency of the prepared ZnO powder.

Keywords: D. ZnO; A. Powders: Chemical preparation; B. Grain size; E. Biomedical application

1. Introduction

Zinc oxide (ZnO) is one of the most promising II–VI n-type semiconductors with direct band gap of 3.3 eV. It exhibits high chemical and thermal stability and high electron mobility [1–3]. Moreover, ZnO is available in abundance, low in cost and is environmentally safe because of its non-toxicity [4]. The properties of ZnO can be tailored by doping with cationic and anionic dopants like Al, Mn, Sn, Ag, Fe, F, Mg and Cu in order to make it suitable for several different applications. ZnO is widely used in food packaging [5], photocatalysis [6] and antibacterial treatment [7].

Different techniques have been employed to synthesize doped ZnO powders, of which, soft chemical method offers several advantages as it is simple and inexpensive which is suitable for the preparation of a large amount of sample with varied nanostructures [8]. In the present work, undoped and Fe+F doped ZnO powders have been synthesized using the soft chemical method. In the present study, Fe is doped with ZnO because of the fact that Fe is one of the most significant magnetic materials and moreover in biomedical applications antibacterial and magnetic properties are very much needed. In our previous study, we found that F doping enhances the antibacterial efficacy of ZnO nanopowders [9]. Hence, we have added F as the second dopant with ZnO in the present work. To the best of our knowledge, this is the first report on the antibacterial properties of doubly (Fe+F) doped ZnO nanopowders.

2. Methods and materials

2.1. Synthesis process

Undoped and Fe+F doped ZnO powders were synthesized using a soft chemical method. Zinc acetate dehydrate [Zn

*Corresponding author. Tel.: +91 9443524180, Mobile: +91 4362 278602; fax: +91 4374 239328.
E-mail addresses: kkr1365@yahoo.com, kkravi1365@gmail.com (K. Ravichandran).

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$(CH_3COO)_2 \cdot 2H_2O]$ (0.2 M) used as the host precursor was dissolved in doubly de-ionized water. Ferric nitrate [$Fe(NO_3)_3 \cdot 9H_2O$] and ammonium fluoride [NH_4F] were used as dopant precursors. The Fe doping level was varied from 0 to 10 at% in steps of 2 at% while the doping level of F was kept constant at 10 at%. Required amount of NaOH solution was added drop wise with the precursor solution to keep the pH value at 8. The prepared solution was magnetically stirred for 2 h at a temperature of 85 °C. After the stirring process, the solution was cooled to room temperature and kept undisturbed for 1 h to obtain the required precipitate. Then, it was filtered and washed separately with a mixture of ethanol and water kept in the ratio of 1:3. Finally, the precipitate was calcined for 3 h at the temperature of 550 °C.

2.2. Characterization of ZnO:Fe:F powders

The crystalline structure of the powders was observed using x-ray powder diffraction method (PANalytical-PW 340/60 X'pert PRO) with Cu-Kα (1.5406 Å) radiation. The luminescence spectra of the powders were analyzed using spectrofluorometer (JobinYvon_FLUROLOG-L3-11) with Xenon Lamp (450 W) as the excitation source of wavelength of 325 nm at room temperature. The fourier transform infrared (FTIR) spectra were recorded using Perkin-Elmer RX-I FTIR spectrophotometer. The surface morphological studies were made using scanning electron microscope (SEM–HITACHIS-3000H).

2.3. Evaluation of antibacterial activity

The antibacterial activity of ZnO:Fe:F powders were examined using agar well diffusion method against *Escherichia coli (E. coli)* and *Pseudomonas aeruginosa (P. aeruginosa)* (Gram negative) bacteria. Nutrient agar medium was used for the bacterial growth which was poured onto the petri plates. Fresh bacterial cultures of both organisms were swabbed onto the agar medium. Using a cork borer, wells were punched on the agar plates and 200 μg/mL of stock solutions were loaded in to the wells. These plates were incubated at 37 °C for 24 h and observed for the inhibition zone around the well. Streptomycin was used as control antibiotic for the comparison in this study.

3. Results and discussion

3.1. Structural studies

Fig. 1 shows the XRD patterns of undoped and Fe+F doped ZnO nanopowders. The diffraction peaks observed are related to the lattice planes (100), (002), (101), (102), (110), (103), (200), (112) and (201) of hexagonal wurtzite structure of ZnO as found in the JCPDS Card no 36–1451. From the observed XRD profiles, it is found that the intensities of the prominent peaks increase up to 4 at% of Fe doping level and then decrease with further increase in the Fe doping level. This increase in the intensities up to 4 at% may be due to the compensation of zinc vacancies by the Fe incorporation. Moreover, the incorporation of F ions into the oxygen vacancies also plays a partial role in

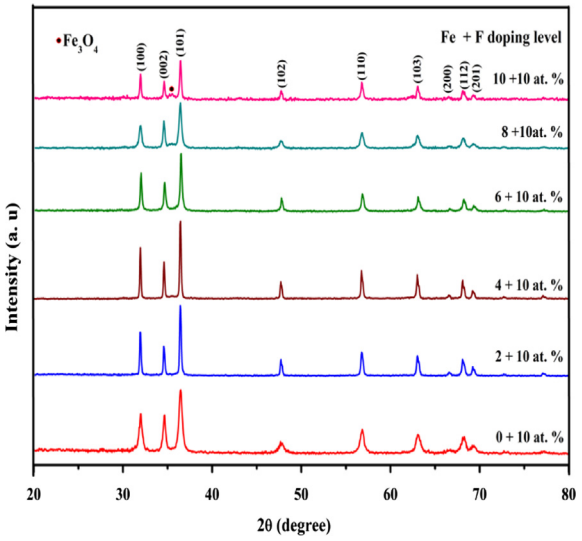

Fig. 1. XRD patterns of undoped and doubly doped ZnO nanopowders.

enhancing the intensities of the peaks as these incorporations improve the periodicity of the crystalline system. The observed decrease in the intensities beyond the 4 at% of Fe doping level may be due to the possible interstitial incorporation of the excess Fe ions into the ZnO matrix causing degradation in the crystallinity of the samples.

It is also observed that the positions of the peaks shift towards higher angles after doping and this trend continues only up to the Fe doping level of 4 at% and beyond that the peaks are found to be shifted towards lower angles (Table 1). The former indicates a decrease in the '*d*' value and this result is a strong evidence for the increasing substitution of Fe^{3+} ions in to the Zn^{2+} sites because it is a well known fact that Fe^{3+} has lower ionic radius (0.64 Å) than that of the host ion (Zn^{2+} – 0.74 Å) [10] whereas the latter indicates an increase in the '*d*' value which may be due to the possible interstitial incorporation of the Fe^{3+} ions into the ZnO lattice.

These variations in the periodicity of the crystal lattice are reflected in the calculated crystallite sizes and lattice parameters also. The crystallite sizes are calculated using the Scherrer's formula [11].

$$D = \frac{0.9\lambda}{\beta \cos \theta} \tag{1}$$

where λ is the wavelength of x-ray (1.5406 Å for Cu-Kα), θ is Bragg's angle and β is the full-width at half-maximum.

The lattice constants '*a*' and '*c*' and the volume of the unit cell (v) are calculated using the formula [12].

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

$$v = \frac{\sqrt{3}}{2}a^2 c \tag{3}$$

The volume of the crystallite (V) and the number of unit cells in a crystallite (N_u) are estimated using the relations [13]

$$V = D^3 \tag{4}$$

$$N_u = V/v \tag{5}$$

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