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# Influence of a novel triple doping (Ag+Mn+F) on the magnetic and antibacterial properties of ZnO nanopowders

K. Ravichandran[a,*], P. Sathish[a], B. Muralidharan[b], B. Sakthivel[a], K. Swaminathan[c], A. Panneerselvam[d], G. Muruganandam[e]

[a]Post Graduate & Research Department of Physics, AVVM Sri Pushpam College (Autonomous), Poondi, Thanjavur 613503, Tamil Nadu, India
[b]Department of Chemistry, BITS PILANI-Dubai Campus, Dubai International Academic City, Dubai, United Arab Emirates
[c]Department of Physics, RKM Vivekananda College (Autonomous), Chennai 600004, Tamil Nadu, India
[d]Post Graduate & Research Department of Botany & Microbiology, AVVM Sri Pushpam College (Autonomous), Poondi, Thanjavur 613503, Tamil Nadu, India
[e]Post Graduate & Research Departmentof Chemistry, AVVM Sri Pushpam College (Autonomous), Poondi, Thanjavur 613503, Tamil Nadu, India

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**Abstract**

In the present study, Ag+Mn and Ag+Mn+F doped ZnO nanopowders were synthesized using a combustion method and their magnetic, structural, surface morphological and antibacterial properties were studied. The magnetic studies reveal that the doped ZnO nanopowders exhibit superparamagnetic behavior. Surface morphological studies show that the grain size of the undoped ZnO is about 250 nm and the size reduces by one order of magnitude (from 250 nm to 23 nm) after doping. The reason for this drastic decrease in the grain size and crystallite size is explained on the basis of Zener Pinning Effect. The antibacterial efficiency of the synthesized nanopowders is tested against two different bacteria *viz. Escherichia Coli* and *Klebsiella Oxytoca* and it is found that the antibacterial efficiency of ZnO nanopowder increases remarkably after multiple doping. All the doped and undoped nanopowders exhibit better efficiency against *K. oxytoca* than *E. coli*. The PL results confirm the presence of certain intrinsic and extrinsic defects in the crystalline structure.


*Keywords:* ZnO:Ag:Mn:F nanopowders; Combustion route; SEM; TEM; Antibacterial activities

## 1. Introduction

Metal oxides have attracted the attention of the scientists owing to their potential applications in various fields, biomedical applications in particular [1]. Zinc oxide, one of the materials of this kind, is promising because of its several advantages like biocompatibility, biodegradability, low-cost and nontoxicity [2–4]. ZnO nanopowders used in food packaging materials are found to control food borne pathogens. It is also applied in the field of photocatalysts [5]. Similarly, the multifaceted antibacterial activity of Ag and magnetic properties of Mn are promising when they are in nanoscale [6,7]. In our previous study, fluorine (F) was added to increase the carrier concentration of ZnO nanopowders and F doping was found to enhance the antibacterial efficiency of ZnO nanopowders [8]. Therefore, F has been added as a third dopant in this work. In the present work, undoped, Ag+Mn and Ag+Mn+F doped ZnO nanopowders are prepared and their magnetic, antibacterial and structural properties are studied and reported.

Several methods are employed for the preparation of doped and undoped ZnO nanopowders such as sol–gel [9], hydrothermal [10], heteropolyometalates [11], precipitation [12], soft chemical [13], and combustion [14]. The combustion method is widely used because of the ease of handling, simplicity and low-cost.

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

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## 2. Materials and methods

### 2.1. Synthesis process

The host precursor zinc nitrate hexahydrate [$Zn(NO_3)_2 \cdot 6H_2O$] (0.2 M) is dissolved in 200 ml of de-ionized water to get an aqueous starting solution. Silver nitrate [$AgNO_3$], manganese acetate tetrahydrate [$Mn(CH_3COO)_2 \cdot 4H_2O$] and ammonium fluoride [$NH_4F$] are used as dopant precursors for Ag, Mn and F, respectively. Double (Ag+Mn) and triple (Ag+Mn+F) doped nanopowder samples are synthesized by adding suitable amounts of dopants (Ag-2 at%, Mn-10 at% and F-10 at%) in the starting solution. Required amount of ammonia solution is added to maintain the pH value of the starting solution at 9. Polyethylene glycol is added as surfactant which can be used to get the gel formation and to achieve the homogeneity in the final product. The resultant mixture is heated at 50 °C and magnetically stirred for 20 min. After the completion of the stirring process, the mixture is shifted to heating mantle, which is maintained at 90 °C for 2 h till the mixture gets ignited. The synthesized powder was finally calcined at 550 °C for 2 h and allowed to attain room temperature to get the final product [8].

### 2.2. Characterization of ZnO:Ag:Mn:F nanopowders

The crystalline structure of the synthesized powders was studied using a x-ray powder diffraction technique (PANalytical-PW 340/60 X' pert PRO) using Cu-Kα radiation ($\lambda = 1.5406$ Å). Fourier transform infrared (FTIR) spectra were observed using a Perkin Elmer RX-I FTIR spectrophotometer. Photoluminescence (PL) spectra were recorded using spectrofluorometer (JobinYvon_FLUROLOG-FL3-11) with xenon lamp (450 W) as the excitation source of wavelength 325 nm. The surface morphology of synthesized ZnO nanopowders was observed using a scanning electron microscope (Carl Zeiss Ultra 55 FE-SEM). Elemental distribution and compositional mapping were studied using electron probe microstructure analyzer (EPMA) and the elemental qualitative analysis was carried out using energy dispersive X-ray analysis (EDAX) attached to EPMA. The microstructure of the synthesized ZnO nanopowders was analyzed using transmission electron microscope (TEM, Hitachi H-7100)

### 2.3. Evaluation of antibacterial activity

The antibacterial activity of the synthesized ZnO nanopowders was tested against *Escherichia Coli* and *Klebsiella Oxytoca* (Gram negative) bacteria using an agar well diffusion method. Nutrient agar medium was used for growth of bacteria. This agar medium was sterilized in an autoclave at 121 °C for 15 min and then loaded into petriplate and allowed to solidify in a laminar air flow chamber. After solidification, using a sterile cotton swab, fresh bacterial culture was spread over the plate using a spread plate technique.

Three wells each of 5 mm in diameter were made in the agar plates with the help of sterile cork borer. The wells were inoculated with 100 µg/mL of stock solution of the product.

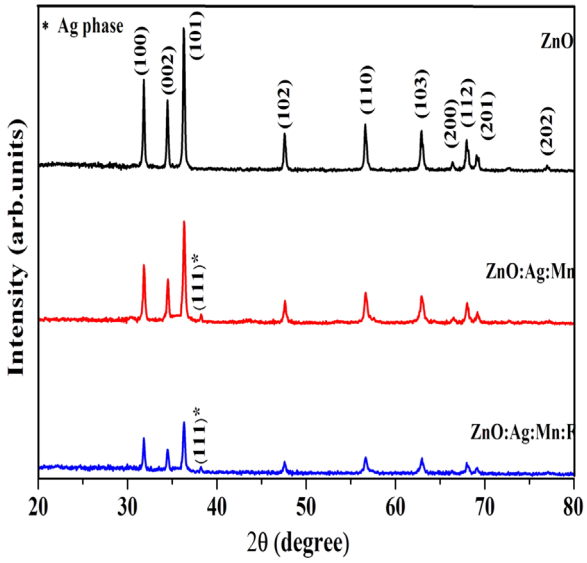


Fig. 1. XRD patterns of undoped, Ag+Mn and Ag+Mn+F doped ZnO nanopowders.

All the plates were incubated at 37 °C for 24 h. After incubation, the plates were observed for the formation of clear inhibition zone around the well. The zone of inhibition was noted by measuring the diameter of the inhibition zone around the well.

## 3. Results and discussion

### 3.1. Structural studies

The XRD patterns of undoped, Ag+Mn and Ag+Mn+F doped ZnO nanopowders synthesized using combustion method are shown in Fig. 1 which reveals that all the synthesized powders have hexagonal wurtzite structure of ZnO (JCPDS Card no. 36-1451 ). The polycrystalline ZnO nanopowders are grown along the planes (100), (002), (101), (102), (110), (103), (201), and (202) with the highest intensity corresponding to the (101) diffraction line.

Similar diffraction patterns but with a reduced intensity are obtained for the Ag+Mn doped and Ag+Mn+F doped ZnO nanopowders which may be due to the degradation in the crystalline quality of the samples caused by the incorporation of dopants into the ZnO matrix. An unmatched diffraction peak is observed at $2\theta = 38.065^\circ$ for both the doped samples which is found to be associated with the (111) plane of face centered cubic structured metal Ag according to the JCPDS Card no. 04-0783, indicating the presence of the secondary phase.

Eventhough the intensities of all the peaks are remarkably reduced after doping, the predominance of (101) peak is not affected by the inclusion of Ag, Mn and F. No noticeable shift in the diffraction angles is observed after doping because one of the dopants Ag is formed as a separate phase and moreover the ionic radii of $Mn^{2+}$ (80 pm) and $F^-$ (133 pm) are comparable to those of their host counterparts $Zn^{2+}$ (74 pm) and $O^{2-}$ (132 pm) [15,16].