Effect of hydrothermal synthesis on physical property modulation and biological activity of ZnO nanorods

Soumyaditya Sutradhar1,5, Atul Bandyopadhyay2, Tanumoy Debnath1,3, Tanmoy Chakraborty1, Sukanta Majumdar4, Shohini Chakraborty4 and Sukhen Das3

1 Department of Physics, Amity University, Rajarhat, Kolkata-700135, West Bengal, India
2 Department of Physics, University of Gour Banga, Malda, West Bengal-732103, India
3 Department of Physics, Jadavpur University, Kolkata-700032, India
4 Department of Botany, University of Gour Banga, Malda, West Bengal-732103, India
5 Author to whom any correspondence should be addressed.

E-mail: sds.phy1@gmail.com

Keywords: hydrothermal synthesis route, ZnO nanorods, bound magnetic polaron, Maxwell-Wagner-Sillars polarization, antibacterial activity, antifungal activity

Abstract

Influence of hydrothermal synthesis route on various defect states of ZnO nanomaterial and this specific synthesis route induced physical property modulation and the biological activity of ZnO nanomaterial has been considered here for the first time ever. X-ray diffraction (XRD) and Field emission scanning electron microscopy (FESEM) reveal the presence of single phase wurtzite structure of ZnO nanomaterial with hexagonal rod like morphology. Photoluminescence (PL) study confirms the presence of structural defects in form of oxygen vacancy defects, zinc vacancy defects, zinc interstitial defects etc in the ZnO nanomaterial. The detail analysis of magnetic response at different temperatures reveals the presence of vacancy mediated room temperature ferromagnetism (RTFM) in rod like ZnO nanomaterial. Dielectric response as a function of frequency has also been measured for ZnO nanorods. The result of this dielectric study shows that the nanomaterial of ZnO exhibits superior dielectric constant due to the grain boundary defect. Hydrothermal synthesis route influences the structure of ZnO nanomaterial mostly towards rod like in nature and the grain boundary defect of rod like structure creates large space charge polarization. In addition to the significant modulation of all these physical properties based on the hydrothermal synthesis route, various biological activities such as antibacterial and antifungal activities of these rod like ZnO nanomaterial has also been observed on the Gram negative clinical isolates like, Escherichia coli, Klebsiella pneumoniae, and plant pathogen Alternaria alternate. Hydrothermal synthesis route creates such an impact on the growth of ZnO nanomaterial that the material evolves with significant modulations of physical properties and biological activities.

1. Introduction

The search of materials with some useful properties has gained both scientific and technological interest of the research community in this present century. These materials are also phrased as ‘multifunctional/smart material’ because one such material can be used effectively in more than one field of applications beneficial for mankind. Among these multifunctional/smart materials, semiconducting ZnO nanomaterial can be found at the forefront of the interdisciplinary research due to its various unique properties like, synthesis process dependent morphological property, defect induced optical and magnetic properties, grain boundary defect induced super dielectric property as well as antibacterial/antifungal property and all these above mentioned properties of ZnO nanomaterial can make it a suitable one for widespread applications in various fields of research [1–4]. In addition, recent research works on room temperature ferromagnetism (RTFM) in nanostructure ZnO creates more excitement to the researchers as it can initiate a wider debate on the origin of...
RTFM. The paramagnetic/diamagnetic properties of ZnO are the most common type herein and these are also very much abundant in literatures [5, 6]. Moreover, the recent studies on the magnetic behaviour of ZnO nanomaterial have concluded that the ferromagnetism (FM) is the characteristic feature of the nanoparticle under certain conditions though the origin of FM in nanostructure ZnO is still under controversy. Thus, in this direction a comprehensive investigation is very much required [7, 8]. It is already established that the structural defects present in ZnO play the crucial role to obtain magnetic ordering in ZnO nanoparticles but the particle size, grain boundary and shape of the nanoparticle are also capable of triggering FM in non-magnetic oxide systems [9, 10]. Thus, understanding of proper reasons behind the presence of FM and the selective tuning of magnetic properties are required to ensure its uses in various spintronic devices. Numerous other reports are now available where the physical property modulation has been done by the selection of single or multiple dopant ions [11, 12]. But so far no one has reported any comprehensive study to show the modulations of the various physical properties not by the choice of dopants but with the proper choice of synthesis route. In this present report the hydrothermal synthesis route has been selected for the preparation of ZnO nanoparticle out of many others like, sol-gel, co-precipitation, solid state reaction etc. The hydrothermal synthesis route can modulate the morphology of ZnO nanoparticle towards hexagonal rod like structure and this particular feature of hydrothermal synthesis route has already been established in our earlier report [13]. ZnO is a very well known n-type semiconductor. So, it contains large number of free electrons. The formation of rod like structure of ZnO nanomaterial can restrict the free motion of the charge carriers inside ZnO by creating grain boundary defect states and due to that a very high electric dipolar effect is expected. Thus, this hydrothermal synthesis route plays the key role for the modulation of morphology and the morphology dependent dielectric property of ZnO nanomaterial. Therefore it is possible to fabricate devices based on ZnO nanoparticle for practical applications. On the other hand, ZnO is a non-toxic material and its bio-safety/biocompatible nature is now an established fact to the entire world of research and hence can be the best option for the applications in bio-medical field [14–16]. However, the effectiveness of ZnO nanomaterial in the field of biological activities mostly depends on its morphology. In this direction the morphology of ZnO nanoparticle can modulate properly and efficiently for better results in biological activity only by the selection of hydrothermal synthesis route. The rod like morphology of ZnO nanoparticle with needle like ends under hydrothermal synthesis route can produce larger damage to the bacteria’s and fungi’s and provides better antibacterial and antifungal activities. Moreover, ZnO nanomaterial is not only stable but also it is safe to human beings. Food and Drug Administration (FDA, USA) has categorized zinc oxide (ZnO) as ‘generally recognized as safe’ (GRAS) (21CFR182.8991) [17]. Thus, these all features of ZnO nanomaterial have motivated us to do comprehensive study on it.

ZnO possess antimicrobial property with a longer life-time than that of other organic-based disinfectants. Though, numerous works have already been reported to investigate the antimicrobial/antibacterial properties of ZnO nanoparticles but most of these works have given their attention on the antimicrobial effect of bulk ZnO or on transition/rare earth metal ions doped ZnO nanomaterials [18, 19]. Also, in the published reports the role of synthesis process dependent morphology on antimicrobial/antibacterial effect has not been considered very significantly. In this paper, we have studied the antimicrobial/antibacterial property of ZnO nanorods on Gram negative clinical isolates viz. Escherichia coli and Klebsiella pneumoniae using Agar disk-diffusion method. This Escherichia coli (E. coli) bacteria usually observes in the body organ i.e. intestines of healthy people and animals. Most varieties of E. coli are moderately dangerous or cause relatively brief diarrhea. But a few are very much dangerous, such as E. coli O157:H7 and these strains are responsible for severe abdominal cramps, bloody diarrhea and vomiting. Also, the Klebsiella pneumoniae (K. pneumoniae) bacteria are harmless when they are found in human body part like intestines. But if they are found to the other parts of human body then they can cause severe diseases. K. pneumoniae can also infect our lungs, bladder, brain, liver, eyes, blood, wounds and cause many serious health issues. The motivation behind the study is that the hydrothermally prepared ZnO nanorods can be found coarser with almost needle like sharp ends as compare to bulk ZnO and thus contribute to the greater mechanical damage of the cell membrane and possess enhanced antimicrobial/antibacterial activity. Also, the production cost of ZnO nanomaterial in this process is low as compare to the doped ZnO nanomaterials and the synthesis technique is also very simple. On the other hand, the larger surface area of hydrothermal synthesis assist rod like ZnO in the nano scale regime will generate a larger number of active oxygen species (released from ZnO on the surface of the colony of bacteria) which will kill bacteria more effectively [20, 21]. The hydrothermal synthesis route produces hexagonal rod like structure of ZnO nanomaterial and this rod like structure increases the surface to volume ratio of each grain. This elevated surface to volume ratio corresponding to each rod like grain can produce active oxygen species more than the nanomaterials in any other form. In this paper, we have also included the antifungal activity of ZnO nanoparticles against fungal plant pathogens like Alternaria alternata (A. alternata) which has been recorded to cause leaf spot and many other diseases over many host species of plant. This pathogen often creates disease on tomato plant and is referred to as Alternaria stem cancer of tomato. It is also an opportunistic plant pathogen and so far a very little attention has been given by the researchers in their earlier literatures. ZnO nanomaterial...
will be a very good choice as antifungal agent against plant pathogens like A. Alternata as well as many others fungal diseases because it cannot affect the fertility of the soil like other antifungal agents. Since it possesses both antimicrobial and antifungal properties with high heat resistant, therefore thin coating of ZnO nanoparticles will be beneficial for preserving precious articles/objects. An effort has been made here to inspect the magnetic, dielectric as well as biological activities of ZnO nanorods and the correlation of these properties with the structural, morphological and photoluminescence properties have also been made successfully. The present research also aims to combine physical and biological activity of ZnO nanoparticles in order to explore its applications in engineering and bio-medical industries for different edges of human life.

2. Experimental

2.1. Materials and preparation technique

The nanomaterial of zinc oxide (ZnO) with rod like morphology was prepared by two stage hydrothermal method. The detail preparation technique was given in our earlier reports. Zinc acetate dehydrate Zn(CH₃COO)₂ · 2H₂O (Sigma Aldrich, 99%), and ammonium hydroxide NH₄OH (concentration ~25%) both were used as the starting materials with AR grade and without any further purification. In two stages of hydrothermal process ZnO nanomaterial was first synthesized by co-precipitation method in aqueous medium. The required precursor salt of zinc acetate was dissolved in triple distilled water in a beaker with proper stoichiometric ratio. The aqueous solution of zinc salt was placed over magnetic stirrer and the temperature was set at 60 °C. After an hour of vigorous stirring NH₄OH was added slowly in the salt solution to begin co-precipitation process and the final pH of the solution was kept at ~10. Stiring was continued for 3 h at 60 °C for complete reaction. After the completion of stirring, the co-precipitated particles were collected from the beaker and it was then transferred into a Teflon jacket. The Teflon jacket was sealed inside a stainless steel autoclave. Finally, the autoclave was placed in an oven at 160 °C for 48 hours. In this hydrothermal synthesis route, the growth mechanism of ZnO nanoparticles inside the Teflon jacket was performed under high pressure and temperature. After 48 hours the autoclave was cooled down to RT and the solid precipitate at the bottom of the Teflon jacket was collected for proper washing. Finally, the dried powders of ZnO were annealed at 400 °C in vacuum furnace. Both these synthesis techniques i.e. hydrothermal synthesis route and heat treatment schedule of ZnO nanomaterial at 400 °C are very much important to get the required crystallographic phase, morphology and the improvement of various physical and biological activities of ZnO nanomaterial. Here it is to be mentioned that, the nanorods of ZnO were synthesized by the one step hydrothermal synthesis method where the chemical process was conducted under high pressures and temperatures over the boiling temperature in aqueous solutions. This is the simplest method by which an amorphous species can be transformed into a crystalline one. This process requires minimum energy consumption and this process also conducted in a closed system due to which the environmental impact on the synthesis procedure is almost negligible. Also this process provides the resultant product with much higher homogeneity than any other solid state processes. The process is very simple and it has been done inside the autoclave without using much difficult setup. After the completion of the hydrothermal synthesis route inside the autoclave the pH value of the final product remains same so the pH of the solution was not regulated at all. The whole course of preparation technique by hydrothermal synthesis route is given by a flow chart in the figure 1.

2.2. Characterization technique

The XRD pattern was recorded in powder x-ray diffractometer, Model D8, BRUKER AXS, using Cu Kα radiation (λ = 1.5405 Å) in the range of 2θ from 20 to 80°. Field emission scanning electron microscope (FESEM) was employed for morphological study using INSPECT F50 (FEI, Netherland). Fourier transformed infrared spectra (FTIR) were recorded on a FTIR spectrometer (8400 S, Shimadzu) in the wavelength range of 350–4000 cm⁻¹. The photoluminescence spectroscopy (PL) study was also done using a spectrofluorimeter, Perkin Elmer Germany with an excitation wavelength (λex) of 320 nm. Magnetization versus applied magnetic field (M-H) data of the powder ZnO samples at RT and at different low temperatures was recorded by a SQUID magnetometer (MPMS XL 7, Quantum Design), where the maximum applied field was 50000 Oe. For magnetic measurement the ZnO pellet was formed and the pellet was placed at the center of the magnetic field in SQUID magnetometer for the study of magnetic response. Here, we want to mention that the as-prepared sample is Zn(OH)₂. The following reaction takes place to produce crystalline ZnO from Zn(OH)₂:

\[ 2\text{Zn(OH)}_2 \rightarrow 2\text{ZnO} + 2\text{H}_2\text{O} \]

As this article deals with physical property modulation and biological activity of ZnO nanorods therefore the magnetic properties of Zn(OH)₂ is not focused here. It is to be noted that Zn(OH)₂ is diamagnetic having magnetic susceptibility −6.70 × 10⁻⁶ cm³ mol⁻¹. Electrical conduction mechanism was investigated by dielectric measurements using Agilent 4294 A Precision Impedance Analyzer. For frequency dependent
dielectric response measurement, the powder ZnO nanomaterial was converted into the pellet form (circular disk of radius 6.5 mm and thickness 1.6 mm) by applying hydraulic palletized with a pressure of 35 kg cm\(^{-2}\). Both the plane surfaces of the ZnO pellet was coated with conductive silver paint (TED PELLA). The metal wires were connected at both the plane surfaces of the ZnO pellet using conductive silver paint and the frequency dependent capacitance measurement, which is used to understand the frequency dependent dielectric behaviour of ZnO nanomaterial, was conducted by using Agilent 4294 A Precision Impedance Analyzer.

### 2.3. Preparation of solution for antibacterial and antifungal studies

For the preparation of ZnO suspension, ZnO nanomaterial was mixed with triple distilled water and it was then placed in an ultra-sonic bath for the breaking of agglomeration between ZnO nanorods. This process will help to get uniform dispersion of ZnO nanomaterial in the aqueous solution. Finally, the master nano fluid was prepared after 30 min of continuous sonication. The antibacterial and antifungal studies were conducted with 1, 0.5, 0.25 and 0.1 mg ml\(^{-1}\) of the final concentration of ZnO nano fluid. These differently concentrated nano fluids were used for the assay of antibacterial and antifungal activity. All the experiments were performed with freshly prepared colloidal suspension of rod like ZnO nanomaterial.

### 2.4. Antibacterial activity study

Antibacterial activity of the rod like ZnO nanomaterial was tested against Gram negative clinical isolates viz *Escherichia coli* (*E. coli*) and *Klebsiella pneumoniae* (*K. pneumoniae*), which were obtained from Microbiology Laboratory, Malda Medical College and Hospital, Malda, West Bengal, India.

Agar disk-diffusion method was used to study the antimicrobial activity of the ZnO nanomaterial. Mueller-Hinton Agar plates were inoculated with standardized inoculums (5 \(\times\) 10\(^6\) CFU/ml) of the tested microorganism. Then, filter paper discs (about 6 mm in diameter), containing the ZnO nanoparticles at the desired concentration, were placed on the agar surface. The Petri plates were incubated at 37 °C for overnight and inhibition zone was also recorded.

The antimicrobial activity of ZnO nanomaterial was also evaluated by the culture turbidity as a qualitative measurement of cell growth. To examine the bacterial growth rate in the presence of the ZnO nanomaterial, the microorganisms were grown in liquid medium supplemented with ZnO nanomaterial colloidal suspensions. Cultures of the nanomaterial-free medium under the same growth conditions were used as a control. The
overnight culture was inoculated into 10 ml of the respective growth medium, which was equivalent to an initial cell and the density of bacterial cells in liquid culture was estimated by a spectrophotometer. The final optical density (OD) was measured at 600 nm wavelength for the tested strains.

2.5. Antifungal activity study
Antifungal activity was also evaluated for ZnO nanomaterial against plant pathogenic fungus Alternaria alternate, procured from the culture collection of Microbiology and Microbial Biotechnology Laboratory, University of Gour Banga, Malda, West Bengal, India. The fungus, Alternaria alternata was replicated and grown in potato dextrose agar (PDA) culture media. PDA plates containing 1 mg ml$^{-1}$ of rod like ZnO nanomaterial were prepared and a fungal disc (1.5 mm in diameter) from the actively growing edge of fungal culture was placed at the center of the PDA plates. Plates were then incubated at 28 °C for approximately 18 days. Percentage (%) of inhibition was calculated by using the following formula [26]

\[
\% \text{ Inhibition} = \frac{\text{Growth of control} - \text{Growth of treatment}}{\text{Growth of control}} \times 100
\]

3. Result and discussions
3.1. XRD diffraction
X-ray diffraction pattern of hydrothermally prepared ZnO nanomaterial is shown in figure 2. The x-ray diffraction peaks appear at Bragg angles $2\theta = 31.715^\circ, 34.366^\circ, 36.196^\circ, 47.484^\circ, 56.535^\circ, 62.806^\circ, 66.302^\circ, 67.896^\circ, 69.053^\circ$ and $76.930^\circ$ which corresponds to (hkl) planes (100), (002), (101), (102), (110), (103), (200), (112), (201) and (202) respectively. The relative intensity of the above mentioned peaks are also exactly matched with the standard XRD pattern of ZnO as given in the JCPDS file (card No. 36–1451). In this direction, Jadav et al have shown the growth of nanorods for ZnO thin film system. In first step the seed layer is made on SiO$_2$/p-Si substrates (100) by RF sputtering method. After that ZnO nanorods were hydrothermally deposited on top of seed layers which make ZnO nanorods to growth in one direction only. This single peak index to (002) in XRD pattern indicates that the RF sputtered ZnO seed layers are preferentially oriented in the (001) direction [27]. But in the present case the mechanism for the synthesis of ZnO powder sample is totally different. The nano crystal of powder ZnO can grow in all directions. There may be preferential growth in any particular direction, but the growth is not 100% in any particular direction like the thin film synthesis. Therefore the presence of multi peaks in XRD pattern is quite obvious for the powder ZnO prepared by hydrothermal synthesis route [28]. The average nanocrystallite diameter of wurtzite structure can be obtained by the following relation [23]

\[
\langle D \rangle_{100} = \frac{0.9 \lambda}{\beta \cos \theta}
\]

Here, D is the average nanocrystallite diameter, $\lambda$ is the x-ray wavelength, $\theta$ is the corresponding Braggs angle of the plane (100), $\beta$ is the full width at half maximum (FWHM) corresponding to the plane (100). The average nanocrystallite diameter (D) estimated for the ZnO nanomaterial is $\sim$29 nm. The corresponding interplaner spacing (d) was calculated from the Bragg’s equation given below [24]
Here ‘n’ is the order of diffraction pattern. The lattice parameters ‘a’ and ‘c’ of hexagonal ZnO nanomaterial was also measured by the equation given below [29, 30]

\[
\frac{1}{d^2} = \frac{4}{3} h^2 + \frac{h k + k^2}{a^2} + \frac{l^2}{c^2}
\]

The corresponding values of ‘a’ and ‘c’ are 3.247 and 5.197 Å respectively. Thus x-ray diffraction pattern indicates that our synthesized nanocrystalline ZnO sample are in single phase without the presence of any significant impurity/contamination. The value of internal lattice strain/micro strain (\(\epsilon\)) for ZnO nanomaterial was also estimated using the formula [29, 30]

\[
\epsilon = \frac{\beta \cos \theta}{4}
\]

The value of lattice strain/micro strain (\(\epsilon\)) for ZnO nanomaterial is \(\sim 12.02 \times 10^{-4}\) and the value is comparatively high [13]. The dislocation density for nanorod arrays are directly proportional to the microstrain and inversely proportional to nanocrystallite diameter and lattice parameter, The dislocation density for nanorod can obtained from the following equation (6) [31]

\[
\delta = \frac{15\epsilon}{aD}
\]

The calculated dislocation density for our sample is \(1.91 \times 10^{11}\) cm\(^{-2}\). The dislocation density is also proportional to defect within the sample. The high value of microstrain and dislocation density obtained from the XRD analysis show that the structural disorder are present in ZnO nanomaterial and these structural disorder inside ZnO appear mainly due to hydrothermal synthesis route. These large variations of structural disorder cannot be observed and obtained in the bulk state that we have achieved in the nanomaterial state of ZnO only under hydrothermal synthesis route and all these along with oxygen vacancy (as evident from PL analysis) will help the ZnO nanomaterial to get significant modulation of its different physical and biological properties enormously in form of magnetic, dielectric, antimicrobial and antifungal activities in comparison to its bulk state.

3.2. FESEM analysis
The grain morphologies of single phase hexagonal ZnO nanomaterial was observed by field emission scanning electron microscopy (FESEM) and the FESEM images are displayed in figures 3(a)–(c) respectively. It is clear from the figure 3(a) that the morphology of the ZnO nano-seeds, before taking them under hydrothermal process, are all spherical in nature. Also, it is very much clear from the Figures 3(b) and (c) that the hydrothermal synthesis route influences the nanomaterial of ZnO to grow into rod like morphology from its initial nano-seed like structure as obtained in co-precipitation method. The crystal growth mechanism of ZnO nanomaterial in hydrothermal synthesis route can be explained on the basis of kinetic concept. Initially, the growth mechanism starts with the formation of growth units and finally, it ends up with the absorption of growth units at the

\[2d \sin \theta = n\lambda\]
interface of the crystal lattice. The formation of rods like morphology of ZnO nanomaterial under this particular synthesis process mostly depends on the pH value of aqueous solution. We have already observed in our previous article that the rods like morphology of ZnO nanomaterial requires pH value close to 9 or 10, which is comparatively very high in comparison to the usual co-precipitation or hydrothermal synthesis route. When the pH is at 10 and the autoclave was placed in the oven at a temperature of 160 °C, growth units in the form of $\text{Zn(OH)}_2^{2-}$ would develop in the aqueous solution. It is to be mentioned that pH value of the solutions was measured by digital pH meter made by ALLIDE SCIENTIFIC PRODUCTS (Model EUTECH INSTRUMENTS pH Tutor). The data is cross verified by the pH indicator strip manufactured by Merck. Now, the diffusion process develops between the growth units in the supersaturation solution under high temperature and pressure and it also deregulates the movement of molecules and ions inside the autoclave. Due to these factors the growth units $\text{Zn(OH)}_2^{2-}$ would finally bounded together in the solution by the dehydration reaction and then they will decompose themselves into a large size cluster of zinc complex. When the size of the zinc complex cluster reaches the critical value necessary for the formation of rod like ZnO nanomaterial, the cluster gets precipitated. In this way growth units are adsorbed in the primary nuclei due to large surface energy and intermolecular force present between the growth units and the ZnO nanoseeds are finally transferred into hexagonal rod like structure. This rod like morphology appears due to formation of growth units and the presence of excessive pressure inside the Teflon jacket under hydrothermal synthesis route. At high pH, close to 10 the solubility of ammonia in the aqueous solution reduces and it comes out from the solution. The liberation of excess ammonia at high temperature from the aqueous solution produces sufficient pressure inside the autoclave. Now, when the pressure is sufficiently high in the autoclave the number of growth units present in the aqueous solution decomposed into a large size grain and forms rod like structure. It is now easier to make the comment that the rod like structure with hexagonal cross-section is the signature morphology of the ZnO nanomaterials prepared under hydrothermal synthesis route. Moreover, all the nanorods in of ZnO nanomaterial are nearly uniform in size and not yet agglomerated.

### 3.3. FTIR studies

The chemical composition of the synthesized ZnO nanomaterial was examined through FTIR spectrum and depicted in figure 4(a). The absorption bands of metal oxides can be found in the fingerprint region (i.e. below 1000 cm$^{-1}$), due to inter-atomic vibrations. The absorption band ~485 cm$^{-1}$ is observed due to stretching mode of Zn–O which is the characteristic feature of hexagonal wurtzite ZnO crystal [32]. The weak doublet at about 2247 and 2467 cm$^{-1}$ is observed due to the presence of CO$_2$ molecule in air [33]. The ZnO nanomaterial might have trapped some CO$_2$ molecule from the atmosphere during FTIR measurement. The peak at 1572 cm$^{-1}$ appears due to the symmetric stretching of COO$^-$ group in acetate complexes [34]. The rest three peaks around 872, 3140 and 3259 cm$^{-1}$ are associated with the characteristic vibration of –OH group [35].

![Figure 4. (a) FTIR and (b) photoluminescence (PL) spectra of ZnO nanomaterials.](image-url)
peaks are attributed to the dissociation of the OH molecule due to annealing of the sample. Even at 400 °C of annealing temperature it is observed in the FTIR spectra that all the surface adsorbed OH groups are not completely removed. In addition, the nanomaterial has been operated for different measurements in the ambient atmosphere so there is a possibility of adsorption of some water molecules by the nanomaterial from the air also. The FTIR spectra clearly indicate the desired phase formation without any contamination/impurities.

3.4. Photoluminescence spectrum
The photoluminescence spectrum of ZnO nanomaterial is displayed in figure 4(b) and it is very important measurement to investigate the optical properties of direct band gap semiconducting materials. Figure 4(b) also shows a sharp peak at 372 nm and a broad peak around 544 nm. The sharp UV-A emission peak at 372 nm of ZnO nanomaterial appears due to the recombination of free excitons through exciton-exciton collision process and this emission peak is assigned as near-band-edge (NBE) emission band [36]. The broad emission band centred at 544 nm of ZnO nanomaterial appears mainly due to the annealing of the ZnO nanomaterial at 400 °C under vacuum environment. The broad emission band centred at 544 nm can be the result of joint contributions from multiple defect states such as oxygen vacancies, zinc interstitials and zinc vacancies as well as their complexes [37]. Among them the donor defects are oxygen vacancy, zinc interstitials and acceptor defect is zinc vacancies. We have annealed our sample in vacuum atmosphere and thus the oxygen vacancies have evolved as the large distinctive defects in our sample. In addition, the hydrothermal synthesis route influences the structure of ZnO nanomaterial towards rod like in nature with high aspect ratio and this particular structure also favours the creation of large quantities of oxygen vacancies inside the nanomaterial. Here in the present case, the oxygen vacancy is the most common type of defects and usually act as radiative center in photoluminescence process.

Three types of charge states corresponding to oxygen vacancies are available therein. Such types are $V_{o}^{−}$, $V_{o}^{++}$ and $V_{o}^{++}$ and they are usually located below the bottom of the conduction band (CB) in the sequence of $V_{o}^{−}$, $V_{o}^{++}$ and $V_{o}^{++}$ from top to bottom. In our cases, the PL emission in the visible region from the nanorods is due to the defect states related deep level emission band. The PL spectrum definitely indicates large number of structural defects present within the sample due to the annealing of ZnO nanomaterial under vacuum environment. It is also to be noted that $V_{o}$ concentration in ZnO samples plays the most significant role for the improvement of the ferromagnetism in ZnO nanomaterial as well as it is also responsible for the generation of $H_{2}O_{2}$ in ZnO nanomaterial and consistently it enhances the biological activity of the nanomaterial [38].

3.5. Magnetic properties
The magnetization versus magnetic field at 300, 150 and 10 K are shown in figures 5(a)–(c). It is evident from the hysteresis loops that ZnO nanorods are ferromagnetic, not only at low temperatures but also at RT. The magnetization tends to saturate from the field 10000 Oe and attain the saturation magnetization ($M_{s}$) ~0.010 emu g$^{-1}$ which is nearly one orders higher than the recently reported values [39, 40]. It is now established that grain boundaries are a determining factor for the ferromagnetic behaviour of ZnO nanocrystals as reported by Straumal et al [41]. He introduced a new parameter named grain boundary specific area $S_{GB}$ defined as the ratio of the grain boundary area to the volume. According to his calculation for nano-powder $S_{GB} = 1.65 \times 10^{-6}$ m$^{-1}$, a aspect ratio, $D$ = average crystallite size. In our case $S_{GB}$ comes out to be $3.1 \times 10^{-7}$ m$^{-2}$ m$^{-3}$ which is far ahead from the threshold value ZnO nanocrystals ($5.3 \times 10^{-7}$ m$^{-2}$ m$^{-3}$) [42]. Therefore, grain boundary defects will not induce the magnetic ordering in ZnO nanomaterial. We believe that this has been achieved by the formation of large number of native defects due to vacuum annealing. It is to be noted that the magnetization at RT in our case is greater/ comparable to that of many publications on transition metal doped/co-doped ZnO system [43, 44]. This result is very much significant in context of biomedical applications of magnetic nanoparticle. In absence of transition-metal the formation of free radicals will be prevented which is very much fatal for human health [9].

The observed magnetism in ZnO nanorods is startling, because neither $Zn^{2+}$ nor $O^{2−}$ is ferromagnetic, thus, in principle; there is no source for magnetism in the present ZnO nanomaterial. Though, several types of native defects, such as oxygen vacancy defects, zinc interstitial defects, zinc interstitial defects, zinc vacancy defects, as well as oxygen interstitial defects contribute behind magnetic ordering as reported but here we propose that magnetic moments can be formed due to anionic vacancy clusters. In this mechanism, an electron trapped in an oxygen vacancy ($V_{o}$) forms the F-center. Ferromagnetism can occur due to either superexchange interaction between vacancy clusters via isolated F-centers or through a limited electron delocalization between vacancy clusters [45]. As per theoretical calculation by Banerjee et al the oxygen vacancy cluster can have large moment with more than three times oxygen vacancies. The oxygen vacancy ($V_{o}$) clusters mediated by the $V_{o}$ with one electron (F-center), contributes to FM while the isolated F-center contributes to the low temperature PM [39]. Thus, the isolated F-centers give rise to a strong paramagnetic like behaviour at low temperature and M–H curve deviates from saturation at 10 K.
The magnetization increases as temperature decreases and curve departs from saturation which indicates that dominance of paramagnetic contribution at lower temperature. Thus we can presume that sample is a mixture of two magnetic components i.e. a FM component which is saturated at low field and a linear component due to PM. Considering this we tried to fit the isothermal curve followed by Langevin function.

Figure 5. Magnetic hysteresis (M-H) loops at (a) 300 K (b) 150 K and (c) 10 K and initial magnetization versus magnetic field curve recorded at (d) 300 K (e) 150 K and (f) 10 K along with the fitted data using BMP model of ZnO nanomaterials.
Dielectric constant (\( \varepsilon' \)) of the sample was calculated using the relation

\[
\varepsilon' = \frac{C_d}{C_0 A}
\]

where, \( C \) is the capacitance of the sample, \( d \) and \( A \) are the thickness and area of the pellet respectively. We have considered the variation of dielectric constant (\( \varepsilon' \)) with frequency in the range of 40 Hz to 100 kHz at RT and the graph is shown in figure 6(a). Also, the dielectric loss tangent (\( \tan \delta \)) as a function of frequency at RT for ZnO nanomaterial was measured and the graph is shown in figure 6(b). It is clear from the figure 6(a) that the dielectric constant (\( \varepsilon' \)) of the ZnO nanomaterial was found to decrease with the increase of frequency of the applied electric field. High value of dielectric constant (\( \varepsilon' \)) at low frequency of the sample appears mainly due to the contributions from the dipolar as well as space charge polarizations present inside the sample (Maxwell-Wagner-Sillars interfacial polarization), though the other types of microscopic polarizations are also present there [48, 49]. Basically, ZnO is an n-type semiconductor that consist free electron as mobile charge carrier. In bulk ZnO these charge carriers can develop conductivity. But if this semiconducting ZnO is formed in the nanoscale range then the charge carriers get bounded by the non-conducting grain boundaries. These charge carriers are able to move inside the conducting grains but they are unable to overcome the barrier of the grain boundary potential and get stuck inside the grains. Now, if this ZnO grains are subjected to the external electric field then these charge carriers get accumulated at the surface or interface of the ZnO grain structures and as a consequence it develops interfacial or space charge polarization effect inside ZnO nanomaterials. Also, in the low frequency region, the permanent dipoles of the sample are able to align themselves with the oscillation of the frequency of the applied electric field and as a result, contribute fully to the dielectric property of the material. In the high frequency region the dipolar and space charge polarizations are not responsive and the dielectric response appears mainly due to the presence of electronic and ionic polarizations. This high value of dielectric constant (\( \varepsilon' \)) at low frequency region and its low value at high frequency region are also in good agreement with Koop’s theory [50]. In the present work, hydrothermally prepared ZnO nanomaterial is found with rod like grain structure. Also it is clear from the FESEM image that the rods like grains are all discrete in nature. Now, each grain is conducting in nature though the individual grains are separated from one another by the non-conducting grain boundaries. N-type semiconductor ZnO contains large number of free electrons. These electrons can move freely inside the each grain but at the grain boundary they come into the bound state due to the non-conducting grain boundaries. These bound electrons at the grain boundary produce large dipolar effect due to space charge polarization. Now, the dipoles when come under the influence of external electric field produce large dipole moment as well as large dielectric constant. Also, it is clearly understood that the hydrothermally prepared ZnO nanomaterial process a large number of defects like dangling bond, zinc interstitial (\( \text{Zn}_i \)), zinc vacancy (\( V_{\text{Zn}} \)) and oxygen vacancy (\( V_{\text{O}} \)) etc inside the structure of ZnO nanomaterial.

| Temperature (K) | BMPS (per cc) | \( \varepsilon'_0 \) (BMPS/emu) | Paramagnetic contribution (emu/g) |
|----------------|--------------|-------------------------------|----------------------------------|
| 300            | \( 4.35 \times 10^{16} \) | \( 5.58 \times 10^{-17} \) | \( 3.33 \times 10^{-8} \) |
| 150            | \( 9.18 \times 10^{16} \) | \( 2.97 \times 10^{-17} \) | \( 4.53 \times 10^{-8} \) |
| 10             | \( 5.58 \times 10^{16} \) | \( 8.31 \times 10^{-19} \) | \( 2.82 \times 10^{-6} \) |

Table 1. Fitting parameters extracted from BMP model.
These defects are also responsible for positive and negative space charge distribution at the interface between the nanostructures and produces further improvement of the dielectric constant of the ZnO nanomaterial. The dielectric loss ($\tan \delta$) represents the energy dissipation in the dielectric system. It can be observed from the Figure 6(b) that the initially dielectric loss ($\tan \delta$) increases with the increase of the frequency, showing relatively higher value and afterwards it decreases with the increase of frequency for the ZnO nanoparticles which might be due to the presence of space charge polarization in the sample. Thus, it can be inferred that the ZnO nanostructure prepared by hydrothermal synthesis route can be applied for the high frequency device applications.

Also, it can be concluded that the hydrothermal synthesis route plays the key role to fabricate the nanomaterials into rod like in nature and this rod like structure modulates various physical properties like optical, magnetic and dielectric properties suitable for many technological applications. Various articles have already been published so far to show the variations of different physical properties where the researchers have given their attention on the influence made by the dopants on the physical properties of ZnO nanomaterials. They have considered transition metal ions, rare earth metal ions as well as their suitable combinations to produce influence on the physical properties but so far no one has shown how the synthesis process itself can modulate the various physical properties of pure ZnO nanomaterials. In this article, first time we have shown the influence of hydrothermal synthesis technique on the physical property in the most comprehensive manner and also it has also been proved that just by selecting the hydrothermal synthesis route a large variation of the physical properties can be made. So regardless of the selection of dopant ions form transition metal or rare earth metal groups if the nanomaterial of ZnO is prepared by hydrothermal synthesis route then the enhancement of various physical properties can also be obtained and this fact has been established in the present report and this hydrothermally prepared ZnO nanomaterial can be made suitable for many applications in the fields of research i.e. this material can be used for the fabrication of gate electrode in electronic MOS devices, multiphase multiferroic devices, piezoelectric nano-generators, capacitors, gas sensors, electrochemical transducers etc [51–54].

3.7. Antibacterial activity

The antibacterial activity of ZnO nanorods was evaluated by measuring the zone of inhibition as well as decrease in cell density. The growth inhibition study against bacteria was monitored with choosing four different concentrations (100, 250, 500 and 1000 μg ml$^{-1}$). The sizes of the zones of growth inhibition are presented in table 2. Result indicated that ZnO nanorods are efficiently inhibited the growth of two Gram negative clinical isolates. A density dependent inhibition of bacterial growth was recorded ($P < 0.05$) and shown in the figure 7. Similar type of observation was also recorded when ZnO nanorods were evaluated by culture turbidity as a qualitative measure of cell growth. In broth culture, along with the increase in concentration of ZnO
nanomaterial growth was depleted. The lowest concentrations of nanoparticles that prevent the growth of the isolates *Escherichia coli* and *Klebsiella pneumoniae* were 800 and 650 μgm l⁻¹ respectively. In this case, antibacterial activity of nanorods may be ascribed to the damage of cell membranes, leakage of cell contents and cell demise. We believe that generation of more H₂O₂ due to presence of large oxygen vacancies by vacuum annealing may have positive influence on the antibacterial properties of ZnO nanomaterial.

### 3.8. Antifungal activity

ZnO nanorods were also tested for their antifungal activity against notorious plant pathogen *Alternaria alternata*. Growth of the *Alternaria alternata* was recorded up to 18 days in presence of ZnO nanomaterial at a concentration of 1000 μgm l⁻¹. It was recorded that ZnO nanomaterial reduced the growth of the pathogen effectively. After 18 days of incubation, inhibition of growth was recorded 38.9% and shown in the figure 8. Not only generation of H₂O₂ but also the electrostatic interaction plays crucial role to damage the cell membrane of microorganism. The abrasive surface of ZnO due to large structural defects (as evident from PL analysis) can damage the cell membrane. Momen *et al* suggested that randomly oriented ZnO nanowires show superior antibacterial activity compared with regularly oriented ZnO nanowires [36]. The FESEM images of ZnO nanorods clearly indicate the different spatial orientation of the rods which may be another reason for antifungal activity. So, from the antifungal activity it is quite clear that the overall effectiveness of the ZnO nanomaterial mostly depends on its rod like shape which on the other hand is the derivative of the hydrothermal synthesis route. Firstly, the rod like structure with needle like ends can produce mechanical damage to the cell membrane of microorganism. Secondly, the large surface to volume ratio of ZnO nanomaterial can absorb large quanta of light due to which large amount of electron-hole pairs are expected in the ZnO nanomaterial. Now, the holes can dissociate water molecules (H₂O) mixed with ZnO nanomaterial into OH⁻ and H⁺ ions. The H⁺ ions can react with the superoxide radical anions ("O²⁻") to generate (HO₂⁻) radicals, which upon successive collisions with electrons present in the system produce hydrogen peroxide anions (HO₂⁻). They then react with H⁺ ions to produce molecules of H₂O₂. The generated H₂O₂ can penetrate into the cell membrane and kills the cell. Therefore, these electron-hole pairs are mainly responsible for the generation of H₂O₂ and thereby the cell death of the microorganism. Many articles so far have shown the antibacterial and antifungal properties of ZnO and

| Microorganisms  | 100 μgm l⁻¹ | 250 μgm l⁻¹ | 500 μgm l⁻¹ | 1000 μgm l⁻¹ |
|----------------|-------------|-------------|-------------|--------------|
| *E. coli*      | 9.4 ± 0.33  | 10.9 ± 0.09 | 11.6 ± 0.10 | 13.6 ± 0.16  |
| *K. pneumonia* | 10.9 ± 0.03 | 11.1 ± 0.115| 11.5 ± 0.45 | 13.0 ± 0.20  |

*a* All experiments were conducted in triplicates; results represent mean ± SD.

**Figure 7.** Antibacterial activity of rod like ZnO nanomaterials against (a) *E. coli* (b) *K pneumonia*.  

**Table 2.** Data of antimicrobial activity of ZnO nanomaterials.
doped-ZnO nanomaterials but in those articles the effect of dopant present in the structure of ZnO mostly influences biological activity of the nanomaterial as a whole. In the present article and for the first time the influence of hydrothermal synthesis process on the various biological activities has been reported.

4. Conclusions

The ZnO nanorods are synthesized via two step hydrothermal method and this particular synthesis process has shown its superior influence on different physical properties as well as on biological activities. The FESEM micrographs confirm the formation of rod like structures with nearly uniform size distributions as well as needle like ends. XRD and FTIR studies confirmed the formation of tetrahedral coordination between zinc and oxygen ions. The enhancement of ferromagnetism has been attributed due to the formation of oxygen vacancy defects due to vacuum annealing. The paramagnetic contribution at low temperature is due to the isolated F-centers present in the nanomaterial. The magnetic phases (PM and FM) are assessed from the analysis explained by FCE mechanism. The high value of dielectric constant of ZnO nanomaterial is also correlated to structural/grain boundary defects appears mainly due to the hydrothermal synthesis process controlled structure modification. Antibacterial activities of synthesized nanorods were tested on Escherichia coli and Klebsiella pneumonia. These nanorods also displayed a better antifungal activity, inhibiting the growth of fungi Alternaria alternate. The concentration of oxygen vacancies in ZnO crystal may have distinct effect on the generation of H₂O₂ and, consistently, the antimicrobial activity. These findings introduce a simple, inexpensive process to synthesize multifunction ZnO nanorods useful for magnetic applications, dielectric application and also in various anti-fungal and anti-bacterial therapeutic treatments. Along with all these it is to be mentioned here that so far many articles have been published on ZnO and doped-ZnO nanomaterials where the enhancement of many physical properties like, optical, magnetic, dielectric as well as biological activities have been reported but this is probably the first report where we have shown how a particular synthesis process i.e., hydrothermal synthesis route can modulate and improves different physical and biological activities without having dopants in the structure of ZnO.

Conflict of interest statement

The authors declare that there is no conflict of interest. Also, the authors declare there is no competing financial interest.

ORCID iDs

Soumyaditya Sutradhar  https://orcid.org/0000-0003-3679-2583
References

[1] Huang X H, Zhang C, Tay C B, Venkatesan T and Chua S J 2013 Green luminescence from Cu-doped ZnO nanorods: role of Zn vacancies and negative thermal quenching Appl. Phys. Lett. 102 111106

[2] Applerot G, Lipovský A, Dror R, Perkas N, Nitzan Y, Lubart R and Gedanken A 2009 Enhanced antibacterial activity of nanocrystalline ZnO due to increased ROS-mediated cell injury Adv. Funct. Mater. 19 842

[3] Weller H 1993 Quantized semiconductor particles: a novel state of matter for material science Adv. Mater. 5 88

[4] Kumar S and Sahare P D 2012 Effects of annealing on the surface defects of zinc oxide nanoparticles NANO: Brief Reports and Reviews 7 1250022

[5] Ravichandran K, Karthika K, Saktivela B, Jalema Begum N, Snegas S, Swaminathan K and Senthambesilv V 2014 Tuning the combined magnetic and antibacterial properties of ZnO nanopowders through Mn doping for biomedical applications J. Magn. Magn. Mater. 358 50

[6] Modak S, Achariya S, Bandyopadhyay A, Karan S, Roy S K and Chakrabarti P K 2010 Micro-structural investigations and paramagnetic susceptibilities of zinc oxide, europium oxide and their nanocomposite J. Magn. Magn. Mater. 322 283

[7] Sundersen A, Bhargavi R, Rangaranjan N, Siddesh U and Rao C N R 2006 Ferromagnetism as a universal feature of nanoparticles of the otherwise nonmagnetic oxides Phys. Rev. B 74 161306

[8] Chaboy J et al 2010 Evidence of intrinsic magnetism in capped ZnO nanoparticles Phys. Rev. B 82 64411

[9] Wang Q, Sun Q, Chen G, Kawazo Y and Jena P 2008 Vacancy-induced magnetism in ZnO thin films and nanowires Phys. Rev. B 77 205411

[10] Hofmann D M, Hofstaetter A, Leiter F, Zhou H, Hennecker F, Meyer B K, Orlinskii S B, Schmidt I and Baranov P G 2002 Hydrogen: a relevant shallow donor in zinc oxide Phys. Rev. Lett. 88 045504

[11] Yan W, Jiang Q, Sun Z, Yao T, Hu F and Wei S 2010 Determination of the role of O vacancy in Co:ZnO magnetic film J. Appl. Phys. 108 013901

[12] Subramanian M, Thakur P, Tanemura M, Hihara T, Ganesan V, Soga T, Chae K H, Jayavel R and Limbo T 2010 Intrinsic ferromagnetism and magnetic anisotropy in Gd-doped ZnO thin films synthesized by pulsed laser deposition method J. Phys. Appl. Phys. 108 053904

[13] Debnath T, Saha P, Patra N, Das S and Sutrathdar S 2018 Hydrothermal process assists undoped and Cr-doped semiconducting ZnO nanorods: frontier of dielectric property J. Appl. Phys. 123 194101

[14] Veiseh O, Gunn J W and Zhang M 2010 Design and fabrication of magnetic nanoparticles for targeted drug delivery and imaging Adv. Drug Delivery Rev. 62 204

[15] Chandra S, Bariic K C and Babadur D 2011 Oxide and hybrid nanostructures for therapeutic applications Adv. Drug Deliv. Rev. 63 1267

[16] Tan K H, Djiurisic A B, Chan C M N, Xi Y Y, Tse C W, Leung Y H, Chan W K, Leung F C C and Au D W T 2008 Antibacterial activity of ZnO nanoparticles prepared by a hydrothermal method Thin Solid Films 516 6167

[17] Kumar R S, Dananjiya S H S, Zosya M D and Yang M 2016 Enhanced antifungal activity of Ni-doped ZnO nanostructures under dark conditions RSC Adv. 6 108648

[18] Yamamoto 2001 Influence of particle size on the antibacterial activity of zinc oxide Int. J. Inorg. Mater. 3 643

[19] Padmavathy N and Vijayaraghavan R 2008 Enhanced bioactivity of ZnO nanoparticles—an antimicrobial study Sci. Technol. Adv. Mater. 9 035004

[20] Brayner R, Dahoumane S A, Djediat C, Meyer M and Fievet F 2010 ZnO nanoparticles: synthesis, characterization, and ecotoxicological studies Langmuir 26 6522

[21] Nel A E, Madler L, Velegder D, Xia T, Hock E M V, Somasundaram P, Castranova V and Thomson M 2009 Understanding biophysicochemical interactions at the nano–bio interface Nat. Mater. 8 543

[22] Gajjar P, Pettee B, Brit D W, Huang W, Johnson W P and Anderson A J 2009 Antimicrobial activities of commercial nanoparticles against an environmental soil microbe, pseudomonas putida KT 2440 J. Biol. Eng. 31 1

[23] Das S, Das S, Das D and Sutrathdar S 2017 Tailoring of room temperature ferromagnetism and electrical properties in ZnO by Co (3d) and Gd (4f) element co-doping J. Alloy. Compd. 691 739

[24] Das S, Bandyopadhyay A, Saha P, Das S and Sutrathdar S 2018 Enhancement of room-temperature ferromagnetism and dielectric response in nanocrystalline ZnO co-doped with Co and Cu J. Alloy. Compd. 749 1

[25] Das S, Bandyopadhyay A, Das, Das D and Sutrathdar S 2018 Defect induced room-temperature ferromagnetism and enhanced dielectric property in nanocrystalline ZnO co-doped with Tb and Co J. Alloy. Compd. 731 591

[26] Himratul-Azni A W, Mohd-Ali-Faisal N and Fathilah A R 2011 Determination of the percentage inhibition of diameter growth (PLDG) of Piper betle crude aqueous extract against oral Candida species Journal of Medicinal Plant Research 5 878

[27] Yadava A B, Parvathib P V L and Shaik R T 2019 Zero bias UV detection and precursor effect on properties of ZnO nanorods grown by hydrothermal method on SiO2/p-Si substrate Thin Solid Films 685 343

[28] Samanta P K and Bandyopadhyay A K 2012 Chemical growth of hexagonal zinc oxide nanorods and their optical properties Applied Nanosciences 2 111

[29] Zak A K, Maidj W H A, Abirshami M E and Yousefi R 2011 X-ray analysis of ZnO nanoparticles by Williamson–Hall and size–strain plot methods Solid State Sci. 13 251

[30] Sharma D and Iha R 2017 Transition metal (Co, Mn) co-doped ZnO nanoparticles: effect on structural and optical properties J. Alloy. Compd. 698 532

[31] Kahraman S, Geitikara H A, Bayansal F, Cakmak H M and Guder H S 2012 Characterisation of ZnO nanorod arrays grown by a low temperature hydrothermal method Philos. Mag. 92 2150

[32] Shob M 2013 ROS-dependent anticandidal activity of zinc oxide nanoparticles synthesized by using egg albumen as a biotemplate Adv. Nat. Sci.: Nanosci. Nanotechnol. 4 035015

[33] Bandyopadhyay A, Bhakta N, Sutrathdar S, Sarkar B J, Deb A K, Kobayashi S, Yoshimura K and Chakrabarti P K 2016 Microstructure investigation optical properties and magnetic phase transition of Tm+3 substituted nanocrystalline ZnO (Zn0.95Tm0.05O) RSC Adv. 6 101818

[34] Liu S M, Liu F Q, Guo H Q, Zhang Z H and Wang Z G 2000 Correlated structural and optical investigation of terbium–doped zinc oxide nanocrystals Physics Letters A 271 128

[35] Coates J 2000 Interpretation of Infrared Spectra, A Practical Approach in Encyclopedia of Analytical Chemistry ed R A Meyers (Chichester: Wiley) 10815
Chen Y, Bagnall D M, Koh H J, Park K T, Hiraga K, Zhu Z Q and Yao T 1998 Plasma assisted molecular beam epitaxy of ZnO on c-plane sapphire: growth and characterization J. Appl. Phys. 84 3912

Studenikin S A, Golego N and Cocivera M 1998 Fabrication of green and orange photoluminescent, undoped ZnO films using spray pyrolysis J. Appl. Phys. 84 2287

Xu X, Chen D, Yi Z, Jiang M, Wang L, Zhou Z, Fan X, Wang Y and Hui D 2013 Antimicrobial mechanism based on H2O2 generation at oxygen vacancies in ZnO crystals Langmuir 29 5573

Banerjee S, Mondal M, Gayathri N and Sardar M 2008 Enhancement of ferromagnetism upon thermal annealing in pure ZnO Appl. Phys. Lett. 91 182501

Xu Q, Wen Z, Jiang H, Qi X, Zhong W, Xu L, Wu D and Xu M 2011 Room temperature ferromagnetism in ZnO prepared by microemulsion AIP Adv. 1 032127

Straumal B B, Mazilkin A A, Protasova S G, Myatiev A A, Straumal P B, Schütz G, Van Aken P A, Goering E and Baretzky B 2009 Magnetization study of nanograined pure and Mn-doped ZnO films: formation of a ferromagnetic grain-boundary foam Phys. Rev. B 79 205206

Straumal B B, Mazilkin A A, Protasova S G, Straumal P B, Myatiev A A, Schütz G, Goering E J, Tietze T and Baretzky B 2013 Grain boundaries as the controlling factor for the ferromagnetic behaviour of Co-doped ZnO Nanocrystals J. Magn. Magn. Mater. 372 37

Basith N M, Vijaya J J, Kenedy L J, Bououdina J, Sadrnezhaad S K and Kaviyarasan V 2014 Co-Doped ZnO nanoparticles: structural, morphological, optical, magnetic and antibacterial studies J. Mater. Sci. Technology 30 1108

Pan D, Xu G, Lv L, Yong Y, Wang X, Wan J, Wang G and Sui Y 2006 Observation and manipulation of paramagnetic oxygen vacancies in Co-doped TiO2 nanocrystals Appl. Phys. Lett. 89 082510

McCabe G H, Fries T, Liu M T, Shapira Y, RamMohan L R, Kershaw R, Wold A, Averous M and McNiff E J 1997 Bound magnetic polarons in p-type Cu2Mn0.9Zn0.1SnS4 Phys. Rev. B 56 6673

Bandyopadhyay A, Sutradhar S, Sarkar B J, Deb A K and Chakraborti P K 2012 Vacancy mediated room temperature ferromagnetism in Co-doped TiO2 Appl. Phys. Lett. 100 252411

Wagner K W 1973 The distribution of relaxation times in typical dielectrics Am. Phys. 40 817

Maxwell J 1973 Electric and Magnetism (New York: Oxford University Press) vol 2

Koops C G 1951 On the dispersion of resistivity and dielectric constant of some semiconductors at audio frequencies Phys. Rev. 83 121

Bazargan A M, Naghavi M, Mazaheri M and Sadramehmad S K 2009 Simultaneous synthesis and single-step sintering of lead magnesium niobate ceramic using mixed nanopowders Ceram. Int. 35 1139

Chang S, Doremus R H, Ajayan P M and Siegel R W 2000 Processing and mechanical properties of C-nanotube reinforced alumina composites Ceram. Eng. Sci. Proc. 21 653

Mukharjee P K and Chakravorty D 2002 Growth of silver nanowires using mica structure as a template and ultrahigh dielectric permittivity of the nanocomposite J. Mater. Res. 17 3127

Yang Y, Guo W, Wang X, Wang Z, Qi J and Zhang Y 2012 Size dependence of dielectric constant in a single pencil-like ZnO nanowire Nano Lett. 12 1919

Li M, Zhu L and Lin D 2011 Toxicity of ZnO Nanoparticles to Escherichia coli: mechanism and the influence of medium components Environ. Sci. Technol. 45 1977

Momen M H, Amadeh A, Sohi M H and Moghanlou Y 2014 Photocatalytic properties of ZnO nanostructures grown via a novel atmospheric pressure solution evaporation method Materials Science and Engineering: B 190 66