



## STRUCTURAL, OPTICAL, MAGNETIC AND ANTIBACTERIAL PROPERTIES OF TRANSITION METAL IONS (Ni, Ca, and Fe) DOPED ZnO NANOPARTICLES PREPARED BY SINGLE-STEP METHOD

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### ABSTRACT

Nanostructures of metal oxides are playing a vital role in determining the characteristics of the properties such as magnetic, optical and electrical properties. In this work, nanostructured ZnO based composites were prepared and their magnetic and optical properties are estimated. The as prepared composite is composed of  $\text{Zn}_{0.090}(\text{Ni}_{0.05}\text{Ca}_{0.05})\text{Fe}_{0.010}\text{O}$  (ZnNiCaFeO) using co-precipitation method followed by sintering process. To distinguish the role of composites, bare ZnO also prepared and their properties were compared with the composite material. Both ZnNiCaFeO exhibited hexagonal wurtzite structure with the grain size of about  $\sim 52$  and  $\sim 46$  nm respectively. Hexagonal nanorod structured morphology and the atomic percentage of the as prepared composites were obtained from the FESEM and EDAX analysis, respectively. UV-Vis absorption spectra of the samples showed absorption peak at 296 (ZnO) and 288 nm for ZnNiCaFeO NPs. Excitation wavelength of the composite materials are also estimated from the PL studies. It was noted that composite ZnNiCaFeO exhibited ferromagnetic behavior with the significant magnetization values of 0.34914 emu/g. The reduction in the viability of all the bacteria to zero using ZnNiCaFeO nanoparticles occurred and it plays a vital role in the increased antibacterial and antioxidant activity performance. Thus, the obtained results indicate the composites can be used in soft magnetic application as well as in various optical applications.

**Keywords:** Zinc Oxide, Co-precipitation, Wurtzite, Optical properties, Ferromagnetic

### 1. INTRODUCTION

Nanotechnology is an important field of existing research dealing with synthesis, strategy, and exploitation of particle's alignment ranging from about 1 to 100nm in size. Within this size range, chemical, physical, and biological properties changed in techniques of both individual atoms/molecules and their consequent size. Novel exploitation of nanoparticles and nonmaterial's are increasing quickly on diverse fronts due to their totally new or improved properties based on their size and morphology [1, 2]. The advancement of green synthesis procedure for the mixture of nanoparticles is forming into a critical part of nanotechnology [3, 4]. The currently synthesized nonmaterial's and their portrayal is a making field of nanotechnology for the earlier two decades, inferable from their vast exploitation in the some fields [5].

Zinc oxide (ZnO) is a multifunctional semiconducting metal oxide having a direct energy band gap of 3.37 eV and high binding energy (60 meV). Therefore it is used enormous applications in various fields such as magnetic, piezoelectric, optical, photocatalysts, gas sensing and

etc., [6, 7]. The polar nature of the hexagonal wurtzite lattice allowed to grow various nano sized morphologies such as rods, wires, spindle, belts, stars etc., by simply controlling the synthesis conditions [8]. Optical properties of nanocrystalline semiconductors were widely investigated due to its peculiar characteristics such as size and large band gap. Currently, a widespread research has been carried out to explore the effect of doping various metal elements such as  $\text{Ni}^{2+}$ ,  $\text{Co}^{2+/3+}$  and  $\text{Fe}^{2+/3+}$  for modifying the electrical, optical and magnetic properties of various metal oxides [9]. For example, magnetic ferrites ( $\text{M}_x\text{Fe}_{3-x}\text{O}_4$ , where  $\text{M}=\text{Fe, Co, Mn, Ni, or Zn}$ ) are versatile nanomaterials having super-paramagnetism and tunable surface properties [10]. Further, optical properties of the above ferrite systems can also be modified due to such doping process [11]. For Miao *et al.*, improve the optical and magnetic properties of the ferrite Zn and Ni doping due to the attribution of defects. Plenty of methods have been reported to synthesis pure and doped ZnO NPs, which can be categorized into either chemical or physical methods such as sol-gel method, solvothermal and co-precipitation

method [12-14]. Among them, the co-precipitation method is one of the versatile simple processes, which is cost effect, giving high yield and homogeneous mixture of reagent precipitates. In addition, it is a simple technique for the synthesis of controlled size and morphology of the metal oxides and metal hydroxides.

In this work, ZnO and Ni, Ca and Fe mixed forms to ZnO matrix, namely, ZNCFO nanoparticles ( $\text{Zn}_{0.090}(\text{Ni}_{0.05}\text{Ca}_{0.05})\text{Fe}_{0.010}\text{O}$ ) via co-precipitation method has been synthesised and characterised. As prepared samples were subjected to various characterizations such as XRD, FTIR, Photo Luminescence (PL), VSM, antibacterial and antioxidant activity.

## 2. MATERIAL AND METHODS

### 2.1. Materials

Zinc (II) nitrate hexahydrate ( $\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ ), Nickel (II) nitrate hexahydrate ( $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ ), Calcium (II) nitrate tetrahydrate ( $\text{Ca}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ ), Iron (III) nitrate nonahydrate ( $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ ) and Sodium hydroxide (NaOH) were purchased from NICE chemicals and used as received.

### 2.2. Synthesis of ZnNiCaFeO NPs

Pure ZnO nano powders were synthesized using formerly reported procedures [13]. Briefly, precursor solution of  $\text{Zn}_{0.090}(\text{Ni}_{0.05}\text{Ca}_{0.05})\text{Fe}_{0.010}\text{O}$  NPs (ZnNiCaFeO), was obtained using co-precipitation process in which 90 mmol Zinc nitrate, 50 mmol Nickel nitrate, 50 mmol Calcium nitrate and 10 mmol Iron nitrate were dissolved separately using distilled water as a common solvent. Further all the precursor solutions were mixed together to get homogenous solution and the solution is continuously stirred and 0.8 M of NaOH solution is prepared and added drop wise to the above solution until obtaining the brown colour precipitate. Thereafter, the precipitate powder was washed several times using double distilled water followed by ethanol solvents until reaching the pH of the washed solution to neutral condition. After washing, the collected powder was dried at 120°C for 6 h in vacuum oven. Eventually, the obtained product was calcinated at 700°C for 5h in a muffle furnace at air medium to get pure ZnO and ZnNiCaFeO samples.

### 2.3. Characterization techniques

ZnO and ZnNiCaFeO NPs were characterized by X-ray diffractometer (model: X'PERT PRO PANalytical) recorded in the range of 20-80° with the monochromatic

wavelength of 1.54 Å. Morphological studies were performed in (Carl Zeiss Ultra 55 FESEM) with EDAX (model: Inca) model. FT-IR spectra of the samples were recorded in the range of 400-4000  $\text{cm}^{-1}$  by using Perkin-Elmer spectrophotometer. Raman spectra were recorded using Burker RFS 25 spectrometer. The absorption spectra of the samples were carried in the range between 200 and 1100 nm by Lambda 35 spectrometer. The vibrating sample magnetometer were recorded 2.17 Tesla using as a Model 7404.

### 2.4. Antibacterial Activity of Nanoparticles

Bacterial strains including *Escherichia coli* and *Bacillus subtilis* were used for experiment. 50ml of LB broth was prepared in 250ml conical flask and the bacterial strains were grown in this medium at 37°C on an orbital shaker. The culture flask was inoculated at 0.1 OD 600nm with freshly prepared LB medium under same culture conditions. The mid log phase bacterial cultures were used for the antibacterial studies. 0.1 OD of overnight different bacterial cultures was swabbed on the 25ml LB agar plates. Then the whatman disk was placed on the plates. About 30ul of ZnO and ZnNiCaFeO nanoparticles samples were add on that whatman disc and incubate for overnight at 37°C.

### 2.5. DPPH Assay

The DPPH scavenging assay of ZnO and ZnNiCaFeO was evaluated after the Rejiniemon et al., 2015 [15]. First we prepared 0.15% DPPH in ice cold methanol. The reaction mixture contains 3.8 ml of methanol add various concentration of ZnO and ZnNiCaFeO and then add 200  $\mu\text{L}$  of DPPH solution then it make incubated at normal temperature for 30min in dark condition. After incubation time the absorbance have make the process at 517nm. Vitamin C has a use of a standard. The DPPH radical scavenging activity was calculated using the given equation.

DPPH radical scavenging activity (%) =  $[(A_0 - A_1) / A_0] \times 100$ , where  $A_0$  is the absorbance of the rule at 30 min and  $A_1$  is the absorbance of the paradigm at 30 min. All paradigms have examined in triplicate.

### 2.6. Hydrogen Peroxide Scavenging Activity

Ethyl acetate extract of ZnO and ZnNiCaFeO of hydrogen peroxide activity was evaluated after the Frank Ngonda 2013 method [16]. 40mm of  $\text{H}_2\text{O}_2$  was taken in phosphate buffer ph 7.4. The reaction mixtures contains various concentration of ZnO and ZnNiCaFeO and add

1ml of distilled water then add 0.6ml of  $\text{H}_2\text{O}_2$  incubated for 10 min at normal temperature. According to incubation, the absorbance was adopted at 560nm. The ascorbic acid was used as a standard. The hydrogen peroxide scavenging activity of ZnO and ZnNiCaFeO was calculated by the equation.

Hydrogen peroxide radical scavenging activity (%) =  $[(A_0 - A_1) / A_0] \times 100$ , where  $A_0$  is the absorbance of the rule at 10 min and  $A_1$  is the absorbance of the paradigm at 10 min. All paradigms are termed in triplicate.

### 3. RESULTS AND DISCUSSION

#### 3.1. XRD analysis

X-ray diffraction patterns of ZnO and ZnNiCaFeO NPs recorded were shown in Fig. 1a. The Characteristic peaks

obtained at angle of ( $2\theta$ ) of 31.8, 34.6, 36.3, 47.6, 56.6, 62.9, 66.4, 67.9 and 69.1° are corresponding to (100) (002) (101) (102) (110) (103) (200) (112) and (201) lattice planes of the ZnO NPs. The standard diffraction peaks confirmed the hexagonal wurtzite structure of ZnO NPs with space group p63mc, which is well matched with the JCPDS data (Card No: 79-2205). In order to examine the effect of ZnO on ZnNiCaFeO composite on the structure is confirmed from the enlarged version of the XRD pattern between 34 to 35° (Fig.1b). In case of ZnNiCaFeO NPs, a new phase has emerged an angle between 37 and 43.1° corresponding to  $\text{Fe}_3\text{O}_4$  along (311) and (400) planes [17], further, the unreacted  $\text{Fe}^{3+}$  present in the final composition is also evidenced from the Fig.1(c-d).

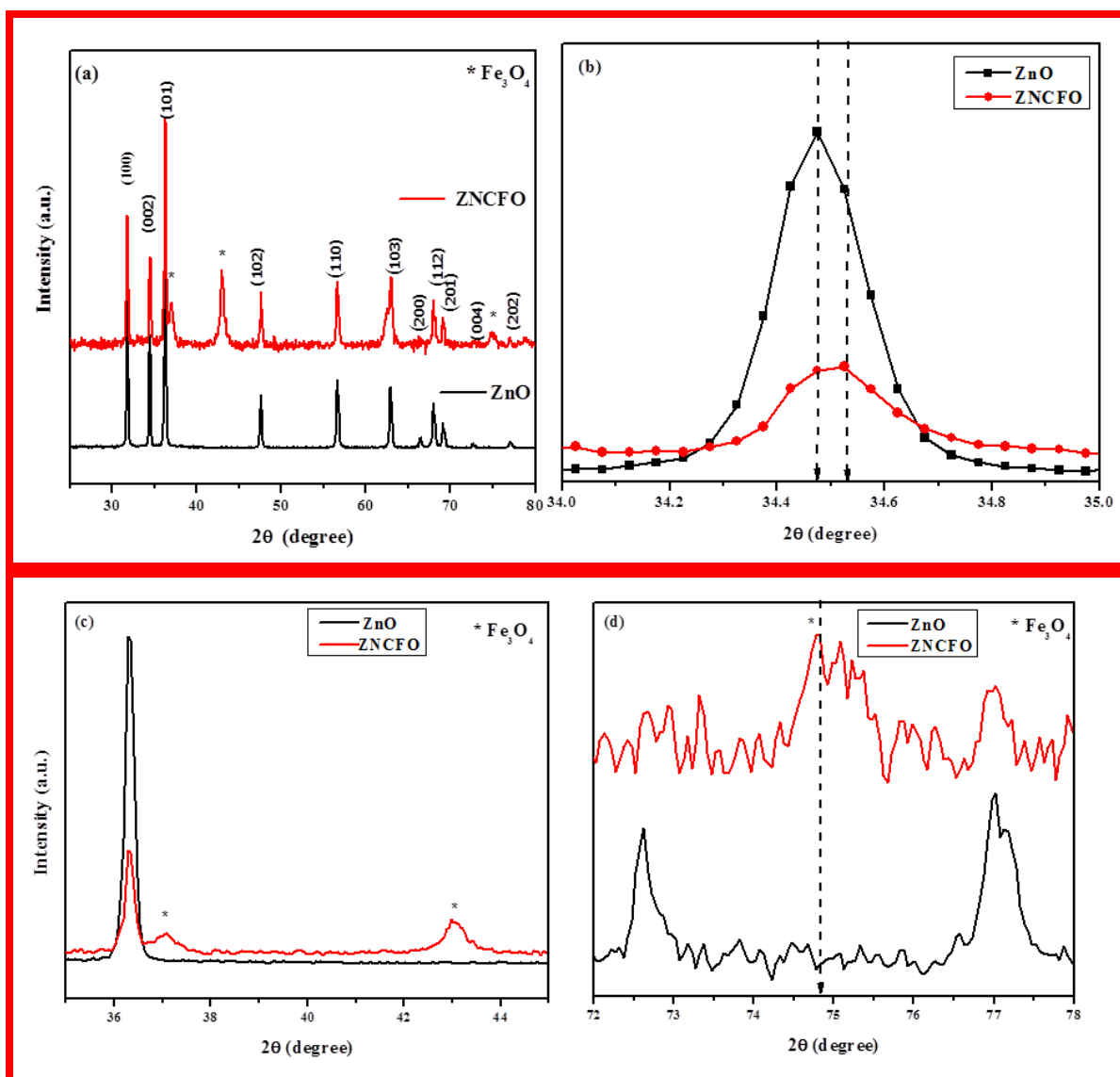


Fig. 1: X-Ray diffraction pattern of (a) ZnO and ZNCFO NPs (b) the doping-induced peak shift for NPs (c and d) enhanced XRD spectra of  $\text{Fe}_3\text{O}_4$  secondary peaks.

**Table 1: Lattice parameters, atomic peak factors, bond length of ZnO and ZNCFO NPs**

| JCPDS<br>Card<br>no: (79-<br>2205) 2θ<br>(degree) | ZnO<br>2θ<br>(degree) | ZNCFO<br>2θ<br>(degree) | JCPDS<br>Card<br>no: (79-<br>2205)<br>d-<br>spacing<br>[Å] | ZnO<br>d-<br>spacing<br>[Å] | ZNCFO<br>d-<br>spacing<br>[Å] | ZnO<br>(hkl) | ZNCFO<br>(hkl) | JCPDS<br>Card<br>no: (79-<br>2205)<br>Rel.<br>Int.<br>[%] | ZnO<br>Rel.<br>Int.<br>[%] | ZNCFO<br>Rel.<br>Int.<br>[%] |
|---------------------------------------------------|-----------------------|-------------------------|------------------------------------------------------------|-----------------------------|-------------------------------|--------------|----------------|-----------------------------------------------------------|----------------------------|------------------------------|
| 31.799                                            | 31.795                | 31.784                  | 2.8146                                                     | 2.81218                     | 2.81309                       | (100)        | (100)          | 56.40                                                     | 61.10                      | 50.57                        |
| 34.419                                            | 34.45                 | 34.479                  | 2.6035                                                     | 2.60123                     | 2.59914                       | (002)        | (002)          | 41.50                                                     | 48.83                      | 32.50                        |
| 36.251                                            | 36.278                | 36.28                   | 2.4760                                                     | 2.47426                     | 2.47414                       | (101)        | (101)          | 99.99                                                     | 100.00                     | 100.00                       |
| -                                                 | -                     | 37                      | -                                                          | -                           | 2.4245                        | -            | (222)*         | -                                                         | -                          | 11.52                        |
| -                                                 | -                     | 43.01                   | -                                                          | -                           | 2.10113                       | -            | (400)*         | -                                                         | -                          | 24.11                        |
| 47.536                                            | 47.566                | 47.58                   | 1.9112                                                     | 1.9101                      | 1.90947                       | (102)        | (102)          | 21.10                                                     | 22.07                      | 20.39                        |
| 56.591                                            | 56.617                | 56.61                   | 1.6250                                                     | 1.62435                     | 1.62456                       | (110)        | (110)          | 30.50                                                     | 33.24                      | 27.01                        |
| 62.851                                            | 62.891                | 62.93                   | 1.4773                                                     | 1.47656                     | 1.47571                       | (103)        | (103)          | 26.80                                                     | 30.36                      | 21.61                        |
| 66.371                                            | 66.4                  | -                       | 1.4073                                                     | 1.40674                     | -                             | (200)        | -              | 4.00                                                      | 4.35                       | -                            |
| 67.942                                            | 67.979                | 67.97                   | 1.3785                                                     | 1.3779                      | 1.37797                       | (112)        | (112)          | 21.70                                                     | 20.32                      | 16.43                        |
| 69.081                                            | 69.106                | 69.1104                 | 1.3585                                                     | 1.35814                     | 1.3592                        | (201)        | (201)          | 10.6                                                      | 11.12                      | 10.70                        |
| 72.560                                            | 72.59                 | -                       | 1.3017                                                     | 1.30124                     | -                             | (004)        | -              | 1.70                                                      | 1.96                       | -                            |
| -                                                 | -                     | 74.7                    | -                                                          | -                           | 1.26929                       | -            | (622)*         | -                                                         | -                          | 4.82                         |
| 76.953                                            | 77                    | 76.9                    | 1.2380                                                     | 1.23745                     | 1.2381                        | (202)        | (202)          | 3.30                                                      | 2.76                       | 4.12                         |

\*Fe<sub>3</sub>O<sub>4</sub> = JCPDS Card No:87-2334

The lattice constants 'a' and 'c' of the wurtzite structure of ZnO NPs is calculated by using the relation,

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

with the first order approximation (n = 1) for the (100) plane. The lattice constant 'a' is obtained through the relation  $a = \frac{\lambda}{\sqrt{3} \sin \theta}$  and lattice constant 'c' is derived for

the plane (002) by the relation  $c = \frac{\lambda}{\sin \theta}$ . The calculated values of 'a' and 'c' are 3.2472 and 5.2024 Å for ZnO NPs whereas ZnNiCaFeO NPs have 3.2282 and 5.1982 Å, respectively (Table 1).

The calculated values showed decrease in lattice constants due to the effect of Fe atoms trapped in the non-equilibrium position were shifted to a more equilibrium position. The lattice parameter values were given in Table 1.

$$V = \frac{\sqrt{3}a^2c}{2} = 0.866a^2c \quad (2)$$

The unit cell volumes calculated by the above relation are found to be 47.5050 Å<sup>3</sup> and 47.4959 Å<sup>3</sup> for pure ZnO and ZnNiCaFeO NPs, respectively. The unit cell volume in

ZnNiCaFeO also decreases with the effect of Ni, Ca and Fe ions in ZnO matrix.

The effect of doping on bond length of Zn-O is calculated by using the relation,

$$L = \sqrt{\left( \frac{a^3}{3} + \left( \frac{1}{2} - u \right)^2 c^2 \right)} \quad (3)$$

where 'a' and 'c' are lattice parameters and 'u' positional parameter which is measured from the amount by which each atom is displaced with respect to the next along the c-axis. The parameter 'u' can be calculated by the formula

$$u = \left( \frac{a^2}{3c^2} \right) + 0.25 \quad (4)$$

Showed a strong correlation between the c/a ratio and 'u'. The c/a ratio decreases with increasing 'u' in such a way that those four tetrahedral distances remain nearly constant through a distortion of tetrahedral angles due to the long-range polar interaction. The c/a ratio decreases in the ZnNiCaFeO NPs as compared to that of the ZnO NPs were observed in Table 2.

The bond length of pure ZnO and ZnNiCaFeO NPs are 1.9758 and 1.9756 Å, respectively, and the change in bond length were attributed to high ionic radius of Fe<sup>3+</sup>.

In hexagonal wurtzite structure, the metal and oxygen ion in ZnO faces directly positioned in “c” axis, but for the “a” and “b” axis, the structure contains only oxygen ions facing each other. Therefore, oxygen ion is diagonally connected to the metal ion so that the variation is significant in “c” axis but not in “a” axis [18]. Debye Scherrer's relation [13] calculates the average crystalline size of the sample.

The average crystallite sizes 52 and 46 nm for ZnO and ZnNiCaFeO NPs, respectively. The reduction in the particles size is mainly due to the distortion in the host ZnO lattice due to the foreign impurity, i.e.  $\text{Ni}^{2+}$ ,  $\text{Ca}^{2+}$  and  $\text{Fe}^{3+}$  ions, which decrease the nucleation and subsequent growth rate of ZnO NPs.

**Table 2: Lattice parameters, atomic peak factors, bond length of ZnO and ZNCFO**

| Samples | Lattice parameters (Å) |        | Atomic peak factor c/a | Bond length (L) Å | Cell volume (V) Å <sup>3</sup> | Average crystalline size (D) nm |
|---------|------------------------|--------|------------------------|-------------------|--------------------------------|---------------------------------|
|         | a                      | c      |                        |                   |                                |                                 |
| ZnO     | 3.2472                 | 5.2024 | 1.6021                 | 1.9758            | 47.5050                        | 52                              |
| ZNCFO   | 3.2282                 | 5.1982 | 1.6003                 | 1.9756            | 47.4959                        | 46                              |

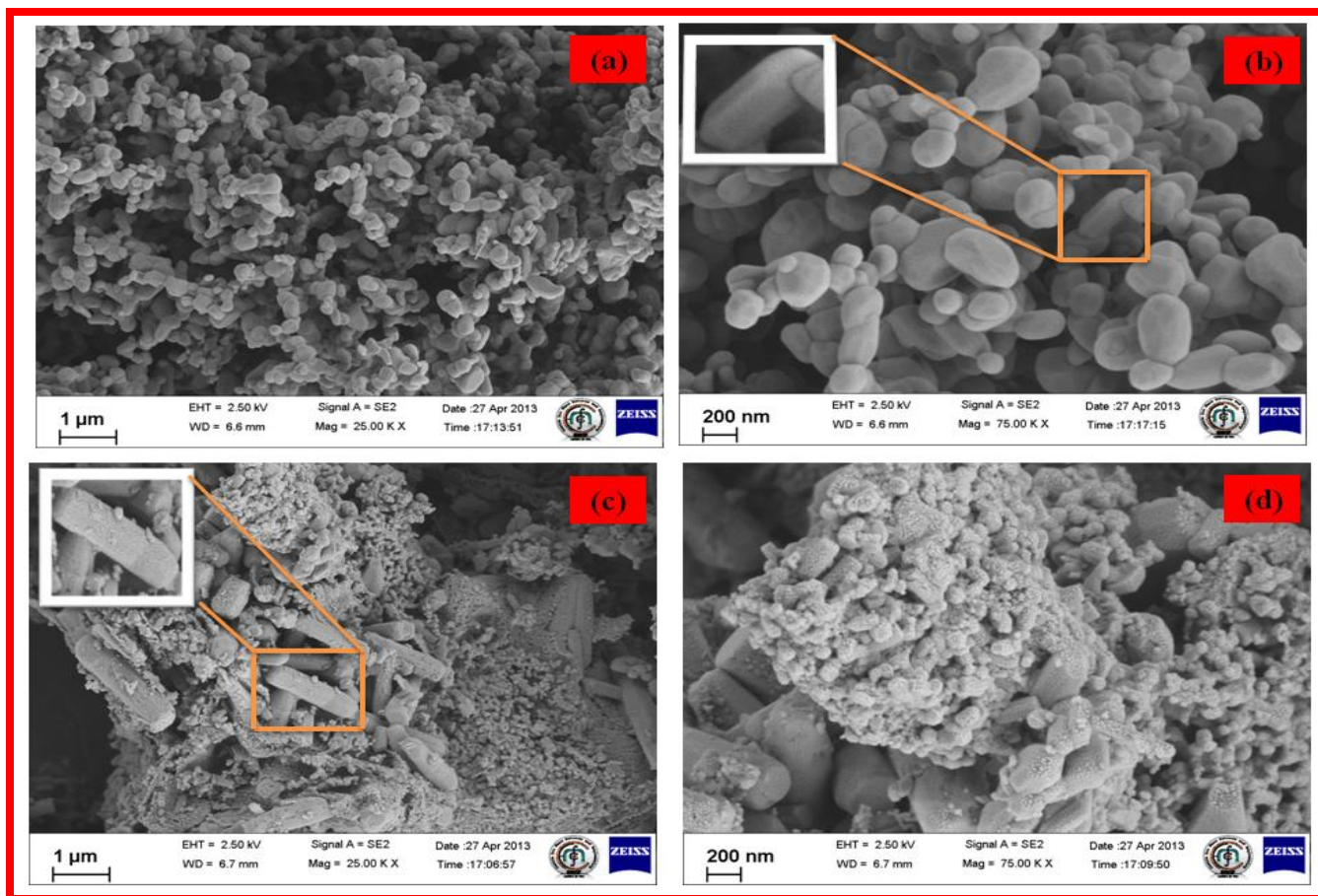


**Fig. 2: FESEM image with low and high resolution for (a-b) ZnO NPs (c-d) ZNCFO NPs**

### 3.2. SEM Analysis

The surface morphology of the ZnO and ZnNiCaFeO NPs are observed from the FESEM analysis at different magnifications (Fig. 2(a-d)). The FESEM image clearly shows the uniform size of the NPs in the order of nanometer size of below 200. The ZnO NPs exhibits

hexagonal spherical like structure with even grain sizes. Whereas in the case of the ZnNiCaFeO composite, there are nanorod shaped particles overlapped on the hexagonal structure of the ZNO confirmed the presence of the other compounds, which is also evidenced from the EDAX spectrum.

### 3.3. EDX spectra

The chemical compositional analysis of ZnO and ZnNiCaFeO NPs carried out using EDX spectra were shown in Fig. 3a and b, respectively. From the EDX analysis, the amounts of Zn, Ni, Ca, Fe and O present in the pure ZnO and ZnNiCaFeO samples were estimated and the observed values were given in the Table 3. In the composite sample, the concentration of Ni, Ca and Fe

were found to be 20.16, 21.31 and 2.02 %, respectively. In the ZnO and ZnNiCaFeO NPs, the chemical composition of Zn and O were found as (52.44% and 47.56%) and (24.69% and 31.82%), respectively which confirmed the effective compound for formation during the synthesis process.

**Table 3: Elemental composition of ZnO and ZnNiCaFeO NPs**

| Element | Weight% | Atomic% | Element | Weight% | Atomic% |
|---------|---------|---------|---------|---------|---------|
| O K     | 21.25   | 52.44   | O K     | 11.91   | 31.82   |
| Zn L    | 78.75   | 47.56   | Ca K    | 19.99   | 21.31   |
|         |         |         | Fe K    | 2.64    | 2.02    |
| Totals  | 100.00  |         | Ni K    | 27.70   | 20.16   |
|         |         |         | Zn L    | 37.77   | 24.69   |
|         |         |         | Totals  | 100.00  |         |

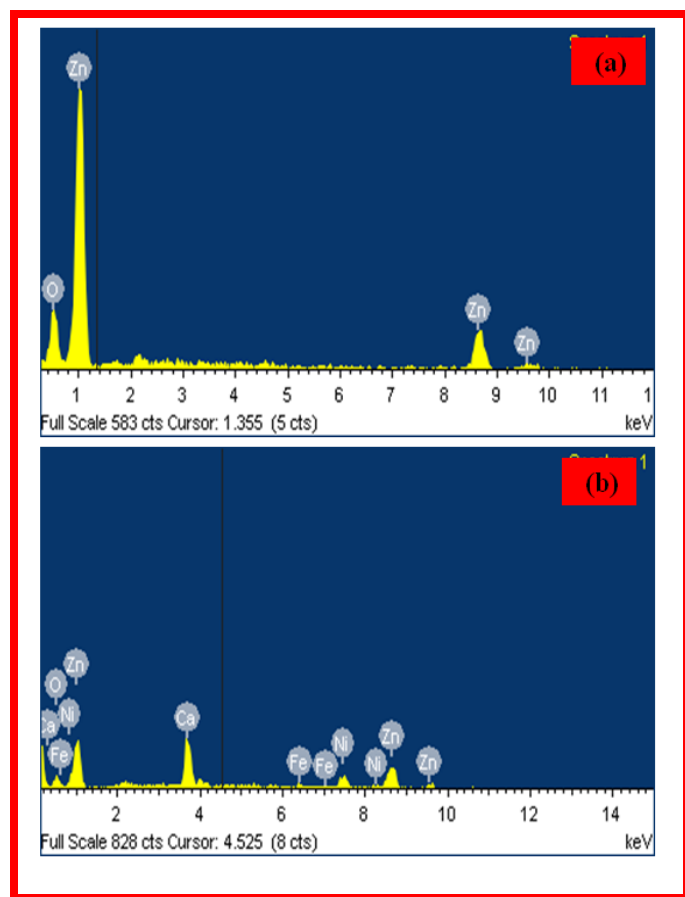


**Fig. 3: EDX spectra of a) ZnO and b) ZNCFO NPs**

### 3.4. FTIR analysis

Further, the b band formation of the composite and the pure ZnO samples are evidenced from the FTIR spectral analysis. Fig. 4 showed FTIR spectra of the ZnO and

ZnNiCaFeO samples; the spectra showed the peaks around at 3443 and 3418  $\text{cm}^{-1}$  which are corresponding to O-H stretching vibration whereas the peaks at 1633  $\text{cm}^{-1}$  and 1618  $\text{cm}^{-1}$  related to O-H bending vibration [19] of the prepared samples. In the ZnO sample, the Zn-O band was observed at at 445  $\text{cm}^{-1}$  [18]. However, the Zn-O band is shifted to 620-550  $\text{cm}^{-1}$  range in the ZnNiCaFeO sample confirmed the the presence of stabilized  $\text{Ni}^{2+}$  and  $\text{Ca}^{2+}$  in the ZnO matrix, whereas  $\text{Zn}^{2+}$  prefers tetrahedral sites because of its ability to form covalent bonds.

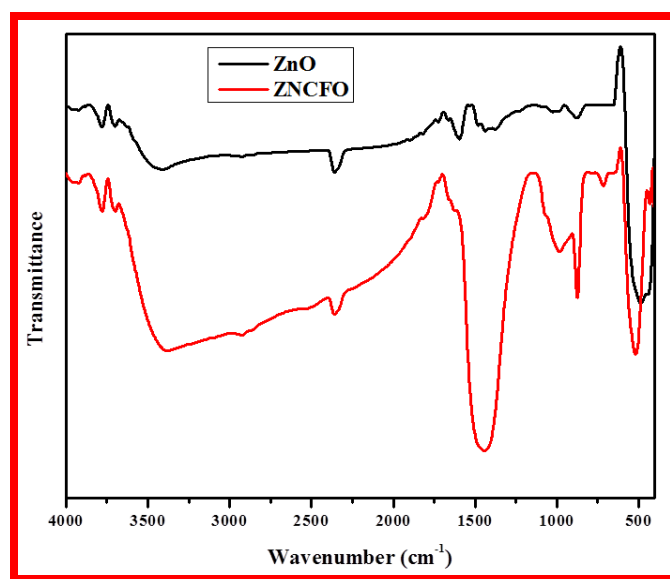


**Fig. 4: FT-IR Spectra of pure ZnO and ZnNiCaFeO NPs**

### 3.5. UV-Vis spectra analysis

UV-Vis optical absorption spectra of ZnO and ZnNiCaFeO NPs have been recorded in the range 190-900 nm and the obtained absorption spectra were shown in Fig. 5. From the UV-Vis spectra, the absorption peaks were found at 296 and 288 nm for ZnO and ZnNiCaFeO NPs, which was attributed to the photo excitation of electron from valence band to conduction band. Thus,

the obtained absorbances of the above samples are depending on several factors including optical band gap, oxygen deficiency, surface roughness and impurity location. Further, the absorption band edge of the ZnNiCaFeO sample has been blue shifted towards the lower wavelength side due to the quantum confinement.

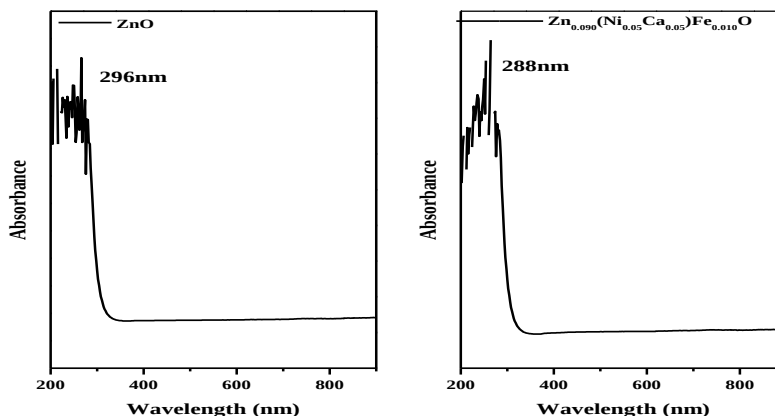


Fig. 5: UV-Vis spectra of (a) pure ZnO and (b) ZnNiCaFeO NPs

The relation between the absorption coefficient ( $\alpha$ ) and the incident photon energy ( $h\nu$ ) can be written as:

$$\alpha h\nu = A(h\nu - E_g)^n \quad (5)$$

where  $E_g$  is the optical bandgap,  $A$  is the constant and the exponent  $n$  depends on the type of transition. The  $n=1/2$  for allowed direct transition, 2 for allowed indirect transition  $3/2$  and 3 for forbidden direct and indirect transitions respectively [20]. Considering direct band transition in ZnO NPs, a plot between  $(\alpha h\nu)^2$  vs. photon energy ( $h\nu$ ) and extrapolating the linear portion of the absorption edge to find the intercept with energy axis is shown in Fig. 6.

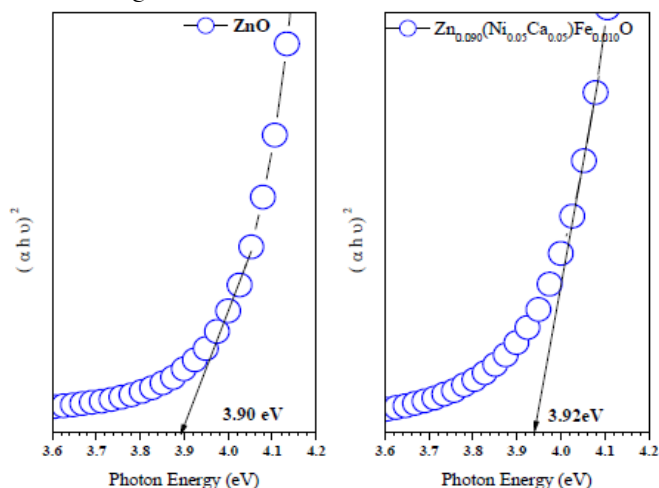


Fig. 6: Band gap of (a) pure ZnO and (b) ZnNiCaFeO NPs

The band gap increases from 3.90 to 3.92 eV in the doped sample due to the effect of metal ions like Ni, Ca and Fe. The reduction in particle size results in increase of surface/ volume ratio. The surface atom has lower coordination number and atomic interaction, which increases the highest valence band energy and decreases the lowest unoccupied conduction band energy.

The Gaussian decomposed photoluminescence emission spectra of the as-synthesized ZnO and ZnNiCaFeO NPs recorded at the excitation wavelength of 350 nm (Fig. 7). The spectra showed a broad emission peaks from 380-580 nm for two samples. Six emission peaks have been obtained from the Gaussian function for the PL spectra of the samples, named as C1-C6 (Table-4).

Table 4: Photoluminescence peak position for pure ZnO and ZnNiCaFeO NPs

| Sample    | Peak position (nm) |     |     |     |     |     |
|-----------|--------------------|-----|-----|-----|-----|-----|
|           | C1                 | C2  | C3  | C4  | C5  | C6  |
| ZnO       | 386                | 395 | 410 | 433 | 459 | 488 |
| ZnNiCaFeO | 388                | 400 | 438 | 458 | 498 | 563 |

The emission spectra of the ZnO NPs with six peaks at 386, 395, 410, 459 and 488 nm are shown in Fig. 7(a). The emission spectra observed at 380 and 395 nm range (band to band transition at UV region) are mainly attributed to radiative recombination of the free

exciton-exciton collision [21], 410 nm (violet emission) electron transition from a shallow donor level of the natural zinc interstitials to the top level of the valence band [22], 433 nm (blue emission) singly ionized Zn vacancies and surface defects in the ZnO NPs[23], 459 and 488 nm (blue-green emission) corresponding to the transition between oxygen vacancy and oxygen interstitial defect vacancies [24,25].

### 3.6. Photoluminescence study

PL emission spectra of ZnNiCaFeO NPs, the red shift were observed compared to ZnO NPs due to various parameters, such as electron phonon coupling, lattice distortion, localization of charge carriers due to interface effects and point defects [26]. A small band shift in the near band edge (388 nm), violet emission (400 nm), blue emission (438 nm), blue green emission (458 and 498 nm) attributed to the dopant effects (Fig. 7(b)).

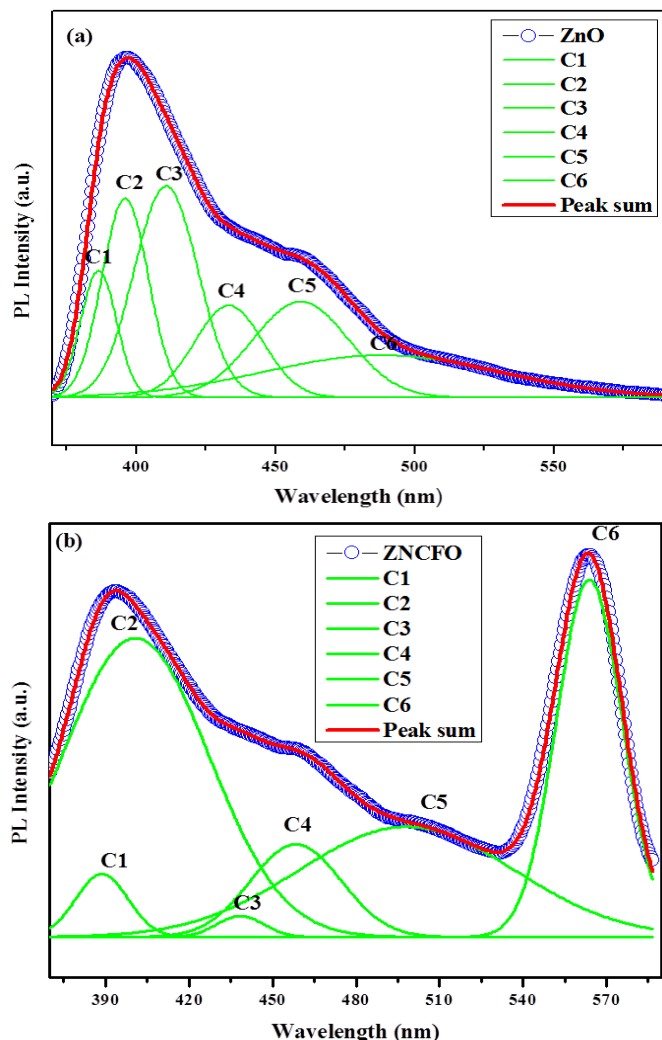


Fig. 7: Gaussian de-composed photoluminescence emission spectra of (a) ZnO NPs and (b) ZNCFO NPs

The yellow emission bands were observed at 563 nm in ZnNiCaFeO sample due to the presence of interstitial oxygen vacancies [27]. The shift and variation in the emission values confirmed the presence of Ni, Ca and Fe into the ZnO matrix.

### 3.7. Magnetic properties

Magnetization versus magnetic field (M-H) curves for ZnO and ZNCFO NPs were shown in Fig. 8. M-H loops were carried out at a temperature of 300 K with maximum applied field  $\pm 20$  kOe, to observed the magnetic properties in the combined effect of  $\text{Ni}^{2+}$ ,  $\text{Ca}^{2+}$  and  $\text{Fe}^{3+}$  in ZnO matrix. The ZnO NPs exhibits the diamagnetic behavior in this sample [28, 29] and ZNCFO sample exhibit ferromagnetic behavior. The magnetization values of about - 0.02722 emu/g and 0.34914 emu/g were observed at 20 kOe for ZnO and ZNCFO NPs respectively.

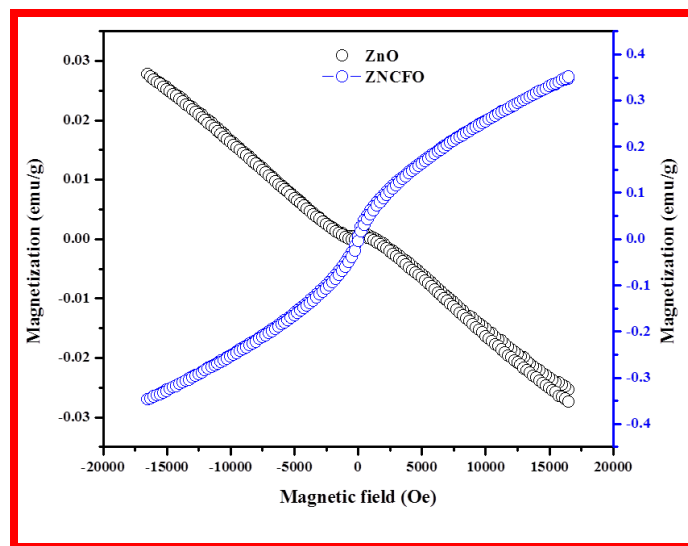


Fig. 8: Magnetic hysteresis (M-H) curves of the pure ZnO and ZNCFO NPs

In the XRD results of ZNCFO sample, secondary phase might exist due to the presence of  $\text{Fe}^{3+}$  ion, which is useful to consider all possible ferromagnetic impurity phase present in the sample. Room temperature ferromagnetism is correlated to Fe-related oxide such as  $\text{Fe}_3\text{O}_4$  or Fe cluster and the presence of oxygen vacancies will change in the band structure of host semiconductors [30]. In literature, the intrinsic defects play vital role in the ferromagnetism of transition metal doped ZnO and the oxygen vacancies with the trapped occupying an orbital overlapping with the d shells of transition metals [31-33]. In our results, PL spectra of ZNCFO sample,

the yellow emission band observed at 563 nm is attributed to the presence of interstitial oxygen vacancies. In case of ZnO NPs, the yellow emissions disappear as compared to ZNCFO sample. The shift and variation in the emission values confirm the presence of metal Ni, Ca and Fe into the ZnO matrix.

### 3.8. Antibacterial activity

Interestingly, ZnO and ZnNiCaFeO NPs is a promising candidate, which shows an excellent antibacterial activity against both bacteria. In this present work, antibacterial activity of ZnO and ZnNiCaFeO NPs against bacterial strains *Escherichia coli* and *Basillus subtilis* were investigated by the disc diffusion agar method. From the fig.9 it is evident that both ZnO and ZnNiCaFeO NPs showed activity towards both pathogens. From the figure 9 it is found that zone of inhibition of ZnNiCaFeO sample is higher than that of the ZnO, which may be due to the reason that the particle size is lower in case of ZnNiCaFeO, sample [34-36].

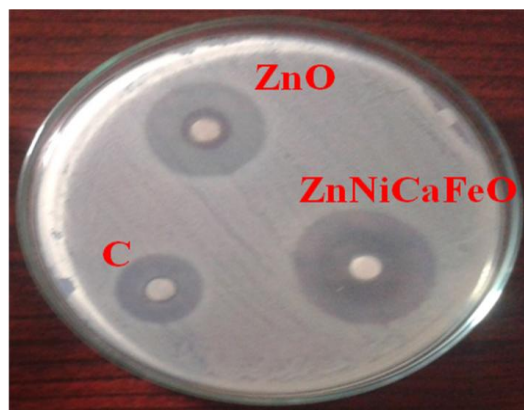


Fig. 9: Antibacterial activity of ZnO and ZnNiCaFeO

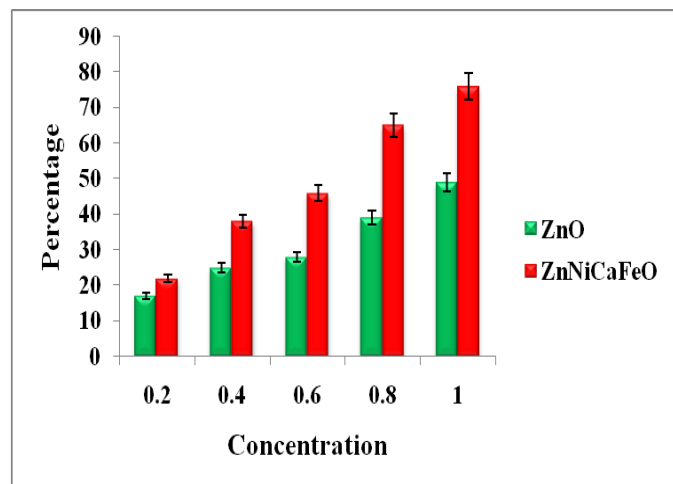


Fig. 10: DPPH Assay

### 3.9. DPPH Assay

DPPH radical scavenging movement is the basic efficient methods for screening the antioxidant activity of ZnO and ZnNiCaFeO nanoparticles. The outcome of DPPH free radical scavenging activity of ZnO and ZnNiCaFeO nanoparticles are viewed in figure 10. From the outcome, they show the comparatively active against standard ascorbic acid. ZnNiCaFeO nanoparticles having activity depend on concentration manner. ZnO nanoparticles 49.2% DPPH activity showed at 100 $\mu$ g/ml and 76.88% at 100 $\mu$ g/ml ZnNiCaFeO [37].

### 3.10. Hydrogen Peroxide Radical Scavenging Activity

Hydrogen peroxide can cross cell membranes promptly, once inside the cell,  $H_2O_2$  can apparently respond with  $Fe^{2+}$ , and conceivably  $Cu^{2+}$  ions to form hydroxyl radical with this might be the root of a larger number of its toxic effects. The hydrogen peroxide radical scavenging activity demonstrated relies upon the grouping of ZnO and ZnNiCaFeO nanoparticles. The increased concentration increased scavenging activity and the outcome is seen in figure 11. The hydrogen peroxide radical scavenging activity showed highest activity in 74.73% at 100 $\mu$ L/ml of ZnNiCaFeO nanoparticles and in 60.07% at 100 $\mu$ L/ml of ZnO. Hydrogen peroxide activity showed more activity 74.73 $\pm$ 2.7 at 100 $\mu$ L/ml of ZnNiCaFeO nanoparticles compared to ZnO [38].

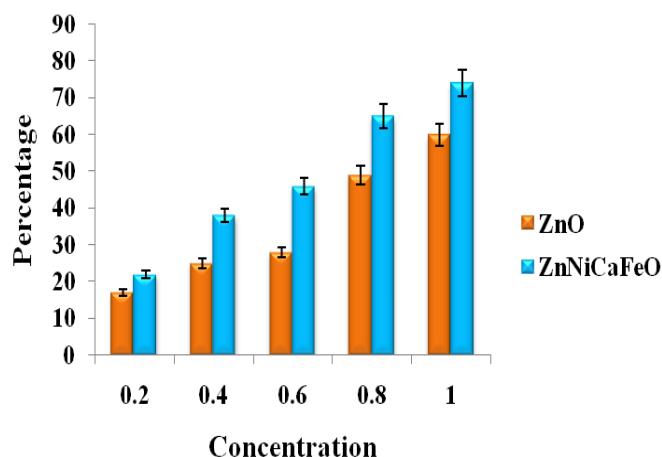


Fig. 11: Hydrogen Peroxide Radical Scavenging Activity

## 4. CONCLUSION

Present study focused on the synthesis of ZnO and ferrite composition ZNCFO using single step co-precipitation method. From the XRD patterns, the synthesized ZnO

and ZNCFO NPs exhibits a hexagonal wurtzite structure. FESEM images showed the synthesis ZnO and ZNCFO NPs formed hexagonal rod like structures and nanorods filled with uniform grain boundaries. From the EDX analysis, the chemical compositions were estimated. FT-IR spectra, the various vibrational frequencies were assigned for ZnO and ZNCFO NPs. The band gap increases from 3.91 to 3.92 eV in the doped sample due to the effect of Ni, Ca and Fe doping effects. Room temperature ferromagnetism is correlated to Fe cluster and the presence of oxygen vacancies in the band structure of host semiconductors. The synthesized ZnO and ZNCFO nanoparticles with strong antibacterial activity were expected to serve in applications in the pharmaceutical and nanocomposite fields. Our work provided a possible way to develop nanomaterials with very attractive properties to be applied in antibacterial activities.

### Conflicts of interest

There are no conflicts to declare.

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