

# Cu- and Ni-Doping Effect on Structure and Magnetic Properties of Fe-Doped ZnO Nanoparticles

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## ABSTRACT

Cu- and Ni-codoped FeZnO particles with the wurzite structure were successfully synthesized at low temperature by a co-precipitation method. The samples were characterized using a vibrating sample magnetometer, X-ray diffraction, energy dispersive X-ray spectroscopy, UV-Vis spectrophotometry and electron spin resonance. The results demonstrated that room temperature ferromagnetic order was observed in both samples and the magnetization was higher than that of Fe-doped ZnO. The correlation between the structural and magnetic properties is discussed.

**Keywords:** Codoped ZnO Nanoparticles; Room-Temperature-Ferromagnetic; Co-Precipitation

## 1. Introduction

Dilute magnetic semiconductors (DMSs) in which some of the cations host lattice are replaced by a transition metal ions have attracted considerable attention due to their potential as spin-polarized carrier sources and their potential applications in spintronic devices [1-5]. The main challenge for practical application of DMSs is the attainment of Curie temperature above room temperature [6]. Following the theoretical prediction of room temperature ferromagnetic by Dietl *et al.* [7], several studies involving magnetic ions doped II-VI semiconductors were performed by different researcher in transition metal doped ZnO. It is known that ZnO has high solubility for transition metals and superior semiconductor properties [8]. Moreover, ZnO is a wideband gap semiconductor with a relative large exciton binding energy. Among transition metal, ZnO doped with Fe ions without any modification of the structure has been the most considerable interest. Ferromagnetism with Curie temperature higher than room temperature has been observed in Fe-doped [9-12], Co-doped [13-15], Mn-doped [16-18], Ni-doped [19-21], Cu-doped [22] and V-doped [23] ZnO nanoparticles. Meanwhile, several codoped ZnO have also been reported with the expectation that codoping can lead to remarkable changes in the properties of the materials [24-26]. Presence of two different kind of transition ions simultaneously in a host material produces magnetic property that can be different from the magnetic property due to single transition metal ions. For instance, Han *et al.* [27] reported that the Curie tem-

perature of bulk  $Zn_{0.94}Fe_{0.05}Cu_{0.01}O$  was above room temperature and the maximum saturation of magnetization was larger than that of the sample without Cu [27,28]. Shim *et al.* [29] also prepared FeCu co-doped ZnO sample and reported that the room temperature ferromagnetic in the sample is due to the secondary phase  $ZnFe_2O_4$  [27,29].

Despite the considerable amount of data a great deal of controversy remains, especially regarding the fundamental issue of whether the system actually exhibits room temperature ferromagnetic at all; and in the case where it does, whether the effect is intrinsic to the material. Further studies suggested that the inconsistencies in the literature regarding the ferromagnetic ordering of transition metal doped ZnO indicate that these materials are very sensitive to the fabrication and processing conditions. Therefore, this paper we attempt to study the effect of Cu- and Ni co-doping on the weakest ferromagnetic Fe-doped ZnO (1 at% of Fe). The co-precipitation method was chosen for the synthesis of these materials because it is cost effective, requires low temperature processing and offers a higher degree of solubility. The effects of Cu and Ni doping on the structural, optical and magnetic properties of nanocrystalline Fe-doped ZnO particles was investigated using X-ray diffraction (XRD), energy dispersive X-ray (EDX), UV-Vis spectroscopy (UV-Vis), electron spin resonance (ESR) and vibrating sample magnetometer (VSM). It was found that the incorporation of Cu and Ni in Fe-doped ZnO nanoparticles not only enhances ferromagnetic properties to the host materials but also changes lattice constant and the optical properties.

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## 2. Experimental

For the synthesis of Cu- and Ni-doping of Fe-doped ZnO nanoparticles in this study the following starting materials were used without further purification: zinc (II) sulfate ( $\text{ZnSO}_4 \cdot 7\text{H}_2\text{O}$ , 99%, Merck), iron (II) sulfate ( $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ , 99%, Merck), copper (II) sulfate ( $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ , 99%, Merck) and nickel (II) nitrate ( $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ , 99% Merck).  $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$  and  $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ ,  $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$  and  $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ , were added simultaneously to the  $\text{ZnSO}_4 \cdot 7\text{H}_2\text{O}$ , solution under continuous stirring to get homogeneous solutions. These mixtures (solution A) were placed in an ultrasonic cleaner operating at 57 kHz for 2 h. Simultaneously, 44 mmol NaOH solution was prepared in 440 ml of deionized water (solution B). Then solution B was added drop wise to solution A with constant stirring for 2 h until a pH of 13 was reached. The mixed solution was allowed to stand at room temperature for 18 h. Subsequently, the solution was centrifuged and washed several times with ethanol and distilled water to remove residual and unwanted impurities. The final product was dried in a vacuum oven at  $200^\circ\text{C}$  for 1 h to yield Fe/Cu and Fe/Ni-codoped ZnO powders.

Elemental analyses of the samples were carried out using scanning electron microscope (SEM) with EDX attachment. To evaluate the phase purity of the samples, XRD measurements were performed using a Philips PW 1710 and monochromatic Cu-K $\alpha$  ( $\lambda = 1.54060 \text{ \AA}$ ) radiation operated at 40 kV and 20 mA in the range of  $10^\circ$  to  $80^\circ$ . The instrumental broadening including the instrumental symmetry was calibrated using a Si powder standard sample. The X-ray diffraction patterns were analyzed by means of the MAUD program using the Rietveld whole profile fitting method to determine the crystal structure and lattice parameters.

To study the electronic interaction near the optical band gap resulting from the addition of dopant atoms, diffuse reflectance UV-Vis measurements were performed using a Shimadzu UV-Vis spectrophotometer with an integrating sphere and a spectral reflectance standard in the wavelength range of 200 - 800 nm. The diffuse reflectance,  $R$ , of the sample is related to the Kubelka-Munk function,  $F(R)$ , according to the following equation:  $F(R) = (1 - R)^2 / 2R$  [30]. The energy band gap of the samples was calculated from the diffuse reflectance spectra by plotting the  $F(R)^2$  as a function of energy and extrapolating to  $F(R)^2 = 0$ .

Magnetic measurements were performed on Oxford Type 1.2 T vibrating sample magnetometer (VSM). These measurements were taken from 0 to  $\pm 1$  Tesla field. To obtain information on electronic structure ESR was carried out using X-band JEOL JES-RE1X at room temperature. The shape and area of the ESR spectra

were analyzed using standard numerical methods.

## 3. Results

To confirm the presence of Fe, Cu and Ni ions in the synthesized nanocrystalline ZnO particles, EDX measurements were performed. Four different random areas in the sample were chosen and about the same Fe, Cu and Ni concentration was obtained for all of them. This result suggested that the distribution of doping is homogeneously. The EDX data from concentrations of Fe, Cu and Ni are listed in **Table 1**. It is seen that the amounts of Fe, Cu and Ni incorporated in the samples are slightly lower than their nominal composition introduced in the synthesis.

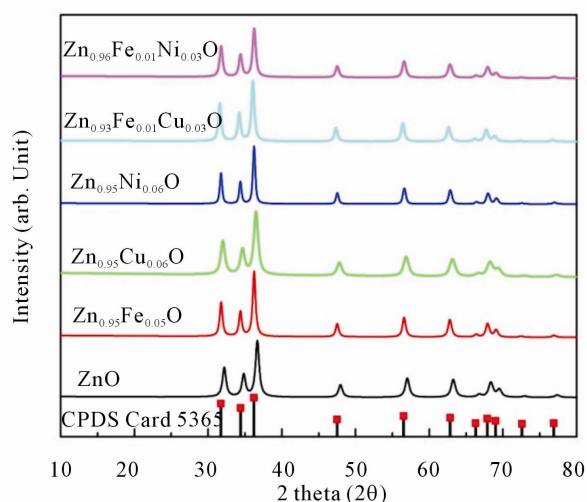
The XRD patterns for  $\text{Zn}_{0.96}\text{Fe}_{0.01}\text{Cu}_{0.03}\text{O}$  and  $\text{Zn}_{0.96}\text{Fe}_{0.01}\text{Ni}_{0.03}\text{O}$  samples are presented in **Figure 1**. Also shown the XRD patterns of  $\text{Zn}_{0.95}\text{Fe}_{0.05}\text{O}$  [31],  $\text{Zn}_{0.94}\text{Cu}_{0.06}\text{O}$  [32],  $\text{Zn}_{0.95}\text{Ni}_{0.05}\text{O}$  [33] and undoped ZnO [34]. It has been observed that all of peaks of XRD pattern belong to the hexagonal lattice of ZnO with three most preferred orientations namely (100), (002) and (101). Most importantly, all of the XRD peaks were attributed to ZnO and no other undesired peaks were observed due to secondary phases or impurity phases within the detection limit of the X-ray diffractometer. From the  $2\theta$  values, the inter-planar spacing  $d$  of the peaks is calculated.

The values are listed in **Table 2**. A good agreement between the observed and the calculated  $d$  values is found to exist indicated a suitability of unit cell parameters and the crystal structure.

The lattice constants, calculated from Rietveld refinement using MAUD programs, unit cell volume, the values ratio ( $c/a$ ) are summarized in **Table 2**. The results are compared with those of Fe-doped ZnO. The average crystallite size and strain were also obtained from Rietveld refinement of the X-ray diffraction patterns of the samples obtained by constructing Williamson-Hall plots [35] with different peaks for the same families. In the present study, (100), (002), (101), (102), (110), (103),

**Table 1. EDX data of Fe-, Cu-, Ni-doped ZnO and Cu- and Ni-codoped FeZnO nanoparticle.**

Sample	Fe (%)	Cu (%)	Ni (%)	Zn (%)	O (%)
$\text{Zn}_{0.95}\text{Fe}_{0.05}\text{O}$	4.64	-	-	32.62	62.74
$\text{Zn}_{0.94}\text{Cu}_{0.06}\text{O}$	-	5.69	-	31.24	63.07
$\text{Zn}_{0.95}\text{Ni}_{0.05}\text{O}$	-	-	4.86	42.32	52.82
$\text{Zn}_{0.96}\text{Fe}_{0.01}\text{Cu}_{0.03}\text{O}$	1.02	2.96	-	42.71	53.31
$\text{Zn}_{0.96}\text{Fe}_{0.01}\text{Ni}_{0.03}\text{O}$	1.35	-	3.23	42.60	52.82



**Figure 1.** XRD patterns of ZnO, Zn<sub>0.95</sub>Fe<sub>0.05</sub>O, Zn<sub>0.94</sub>Cu<sub>0.06</sub>O, Zn<sub>0.95</sub>Ni<sub>0.05</sub>O, Zn<sub>0.96</sub>Fe<sub>0.01</sub>Cu<sub>0.03</sub>O and Zn<sub>0.96</sub>Fe<sub>0.01</sub>Ni<sub>0.03</sub>O nanoparticles.

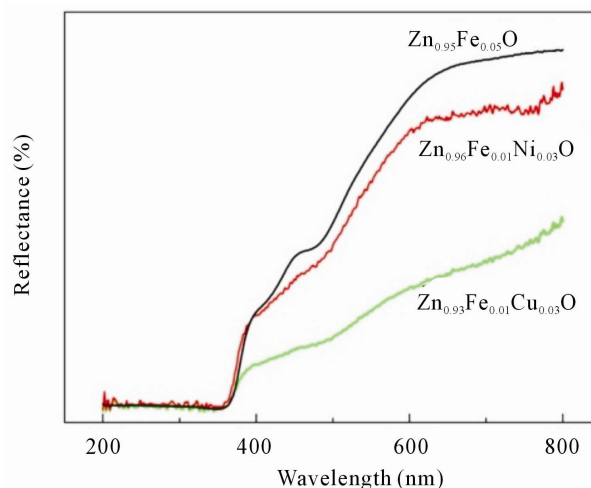
and (112) peaks were used to construct the Williamson-Hall plot. From the linear fit to the data, the average crystallite size,  $\langle D \rangle$ , was extracted from the y-intercept and the strain,  $\varepsilon$ , from the slope of the fit of:

$$\beta \cos \theta = K \lambda / \langle D \rangle + 2\varepsilon \sin \theta$$

In this calculation the strain was assumed to be uniform in all directions of the samples. The average crystallite size,  $\langle D \rangle$  and the strain,  $\varepsilon$ , are shown in **Table 2**. These results indicate that the  $\langle D \rangle$  in the Zn<sub>0.96</sub>Fe<sub>0.01</sub>Cu<sub>0.03</sub>O and Zn<sub>0.96</sub>Fe<sub>0.01</sub>Ni<sub>0.03</sub>O samples have a similar average crystallite size with Zn<sub>0.97</sub>Fe<sub>0.03</sub>O. These data showed that the substitutional doping does not influence the crystal structure significantly.

To study the electronic interactions near the optical band gap region of Zn<sub>0.96</sub>Fe<sub>0.01</sub>Cu<sub>0.03</sub>O and Zn<sub>0.96</sub>Fe<sub>0.01</sub>Ni<sub>0.03</sub>O samples diffuse-reflectance measurements were performed on the samples in the UV-Vis region at room temperature. All spectra were obtained in the range of 200 - 800 nm. **Figure 2** shows the diffuse-reflectance spectra,  $R$ , as a function of wavelength. The band gap energy of the doped ZnO samples was calculated from the diffuse-reflectance spectra by plotting the square of the Kubelka-Munk function  $F(R)^2$  vs. the energy in electron volts. The linear part of the curve was extrapolated to  $F(R)^2 = 0$  to calculate the direct band gap energy. **Table 2** also shows the band of Zn<sub>0.96</sub>Fe<sub>0.01</sub>Cu<sub>0.03</sub>O and Zn<sub>0.96</sub>Fe<sub>0.01</sub>Ni<sub>0.03</sub>O samples. It is seen that the absorption edge is slightly different with the addition of Cu and Ni in Fe-doped ZnO sample compare to Fe-doped ZnO sample itself.

To gain insight into the oxidation state of the dopant cations involved in the spin coupling and site occupancy of the dopant ion in the host material, ESR spectra were



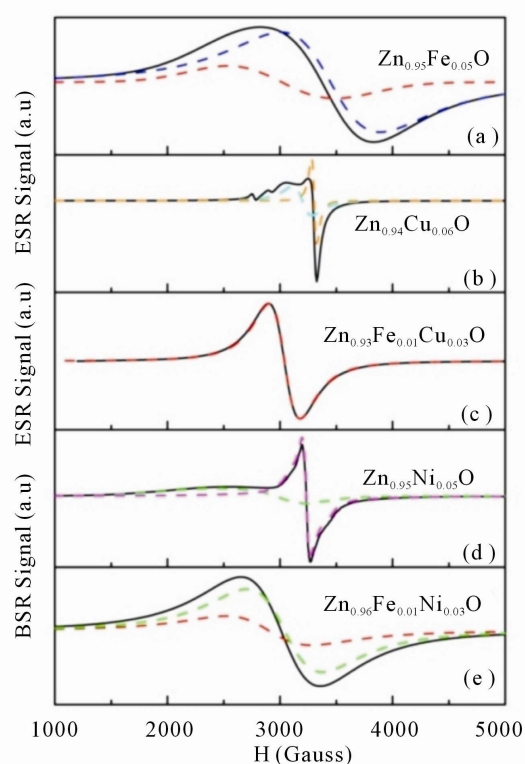
**Figure 2.** The diffuse-reflectance spectra of Zn<sub>0.96</sub>Fe<sub>0.01</sub>Cu<sub>0.03</sub>O and Zn<sub>0.96</sub>Fe<sub>0.01</sub>Ni<sub>0.03</sub>O compared with Zn<sub>0.95</sub>Fe<sub>0.05</sub>O nanoparticles.

measured at room temperature. Typical ESR spectra of both the Zn<sub>0.96</sub>Fe<sub>0.01</sub>Cu<sub>0.03</sub>O and Zn<sub>0.96</sub>Fe<sub>0.01</sub>Ni<sub>0.03</sub>O particles are provided in **Figure 3**. For interpretation of Zn<sub>0.96</sub>Fe<sub>0.01</sub>Cu<sub>0.03</sub>O and Zn<sub>0.96</sub>Fe<sub>0.01</sub>Ni<sub>0.03</sub>O results a comparison with Fe-, Ni- and Cu-doped ZnO ESR spectra was also instructive. In Zn<sub>0.95</sub>Fe<sub>0.05</sub>O the ESR signal can be considered as a superposition of two overlapping signals, a broad and intense signal attributed to Fe<sup>2+</sup> and another weak and narrow signal assigned to Fe<sup>3+</sup> [31,33]. In the case of Zn<sub>0.95</sub>Ni<sub>0.05</sub>O, the ESR spectra had similar features, which exhibited two overlapping resonance peaks. One peak corresponded to the broad resonance while the other peak located at higher magnetic field was much narrower. The linewidth and the g-values of the broad signal in our Zn<sub>0.95</sub>Ni<sub>0.05</sub>O was consistent with the line shape and position of the previously reported Ni-doped ZnO samples [33,36] and have been attributed to a ferromagnetic resonance due to Ni<sup>2+</sup> ions. A comparison of the g-values of the narrow ESR signal with the ESR signals of Ni in Li<sub>1-x</sub>Ni<sub>1+x</sub>O<sub>2</sub> [37,38], SnO<sub>2</sub> [39] and TiO<sub>2</sub> [40], which have g-values in the range of 2.13 - 2.18, suggests that the narrow resonance in our Zn<sub>0.95</sub>Ni<sub>0.05</sub>O samples is attributable to paramagnetic Ni<sup>3+</sup> ion centers.

The electronic configuration of Cu<sup>2+</sup> ion is 3d<sup>9</sup> and the electronic ground state is <sup>3</sup>S<sub>1/2</sub>. The only natural isotope is <sup>63</sup>Cu, which has nuclear spin 3/2. The ESR spectrum of Zn<sub>0.94</sub>Cu<sub>0.06</sub>O sample shown in **Figure 3** revealed the presence of broad signal, which is superimposed on poor-resolved quadruplet signals and a pronounced narrow resonance. The broad signal at g value of 2.05 is associated with Cu<sup>2+</sup> interacting with nearby Cu<sup>2+</sup> via dipole interaction [41] whereas a narrow signal at g value of 1.98 could be attributed to an unpaired electron trap-

**Table 2.** The The lattice constants, unit cell volume, ratio of lattice parameters, interplanar spacing, average crystallite size, strain and band gap energy of  $\text{Zn}_{0.95}\text{Fe}_{0.05}\text{O}$ ,  $\text{Zn}_{0.94}\text{Cu}_{0.06}\text{O}$ ,  $\text{Zn}_{0.95}\text{Ni}_{0.05}\text{O}$ ,  $\text{Zn}_{0.96}\text{Fe}_{0.01}\text{Cu}_{0.03}\text{O}$ , and  $\text{Zn}_{0.96}\text{Fe}_{0.01}\text{Ni}_{0.03}\text{O}$  nanoparticle.

Sample	a = b (Å)	c (Å)	volume (Å <sup>3</sup> )	c/a	d <sub>101</sub> (Å)	<D> nm	$\epsilon(\times 10^{-4})$	E <sub>g</sub> (eV)
$\text{Zn}_{0.95}\text{Fe}_{0.05}\text{O}$	3.2555	5.2184	47.8781	1.6029	2.4805	21	21.2	3.29
$\text{Zn}_{0.94}\text{Cu}_{0.06}\text{O}$	3.2350	5.1810	46.9570	1.6015	2.4644	18	47.0	3.32
$\text{Zn}_{0.95}\text{Ni}_{0.05}\text{O}$	3.2370	5.1890	46.7592	1.6030	2.4664	27	33.9	3.28
$\text{Zn}_{0.96}\text{Fe}_{0.01}\text{Cu}_{0.03}\text{O}$	3.2563	5.2205	47.9388	1.6032	2.4812	19	9.16	3.33
$\text{Zn}_{0.96}\text{Fe}_{0.01}\text{Ni}_{0.03}\text{O}$	3.2553	5.2186	47.8938	1.6031	2.4804	18	13.70	3.36



**Figure 3.** The electron spin resonance spectra of  $\text{Zn}_{0.96}\text{Fe}_{0.01}\text{Cu}_{0.03}\text{O}$  and  $\text{Zn}_{0.96}\text{Fe}_{0.01}\text{Ni}_{0.03}\text{O}$  compared with  $\text{Zn}_{0.95}\text{Fe}_{0.05}\text{O}$ ,  $\text{Zn}_{0.94}\text{Cu}_{0.06}\text{O}$ , and  $\text{Zn}_{0.95}\text{Ni}_{0.05}\text{O}$  nanoparticles.

ped on an oxygen vacancy site [42-52].

Comparing the ESR spectra of  $\text{Zn}_{0.95}\text{Fe}_{0.05}\text{O}$  and  $\text{Zn}_{0.94}\text{Cu}_{0.06}\text{O}$  with that of  $\text{Zn}_{0.96}\text{Fe}_{0.01}\text{Cu}_{0.03}\text{O}$ , the line width and the g-value of  $\text{Zn}_{0.96}\text{Fe}_{0.01}\text{Cu}_{0.03}\text{O}$  can be attributed to  $\text{Fe}^{2+}$ , since the g-value observed here does not agree with the reported value for  $\text{Cu}^{2+}$ . In addition, hyperfine structure due to  $^{63}\text{Cu}$  and  $^{65}\text{Cu}$  nuclei necessary for identification of Cu-related center was not observed. So the peak observed here would not be attributed to the Cu ions themselves.

It is apparent from **Figure 3** that the two resonances of  $\text{Zn}_{0.96}\text{Fe}_{0.01}\text{Ni}_{0.03}\text{O}$  are too close to be separated with confidence. We have carefully studied the line signal and

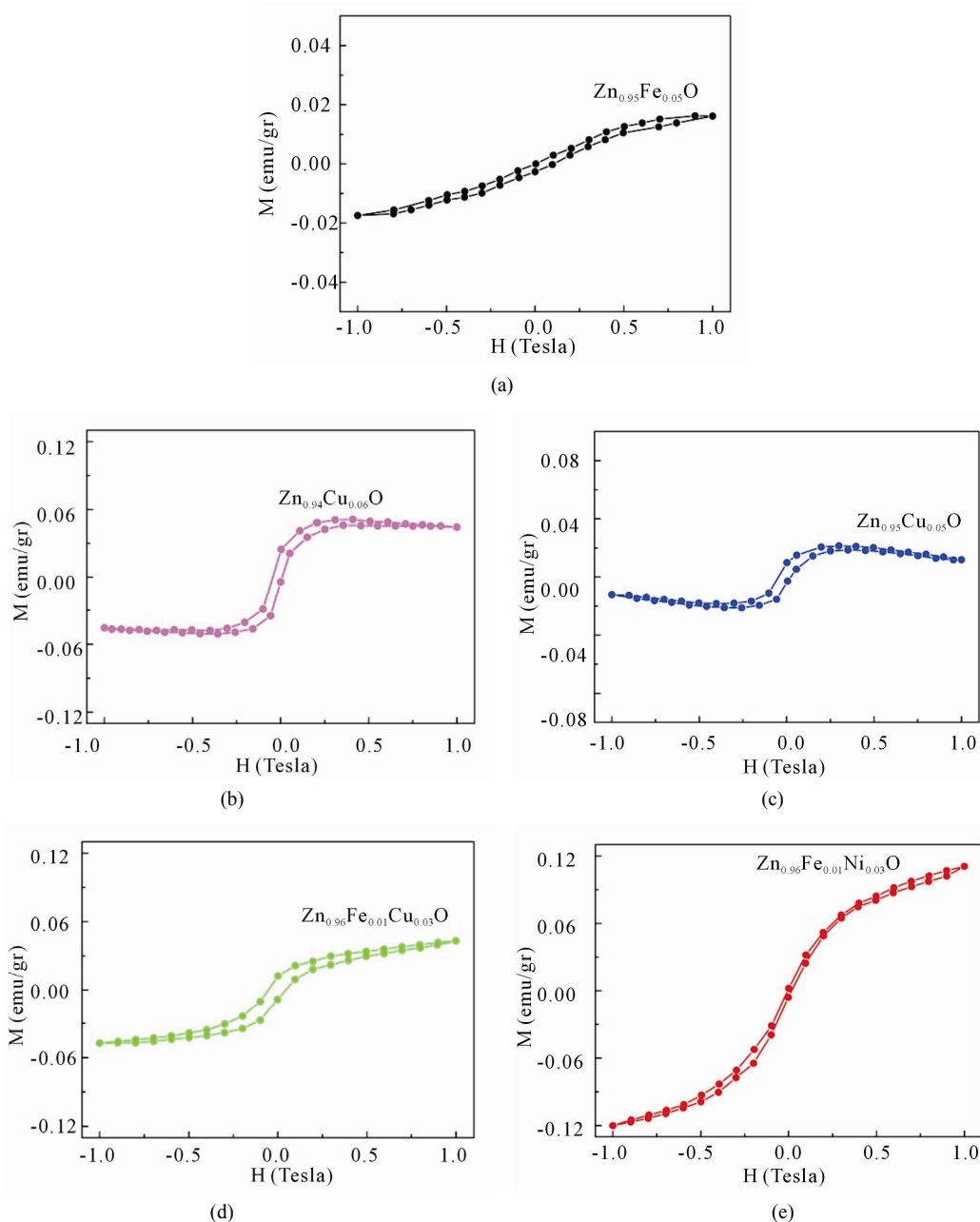
found that the line-width and the line intensity can be deconvoluted in  $\text{Fe}^{2+}$  and  $\text{Ni}^{2+}$  signals. Although, it was reported that the g-value of Ni metallic species is centered at 2.2 [53], the presence of Ni metallic might be ruled out since the line width of this species is much broader than that of our ESR spectra of  $\text{Zn}_{0.96}\text{Fe}_{0.01}\text{Ni}_{0.03}\text{O}$ . The g-values, total number of spins associated with each signals and the line width are quite variable as shown in **Table 3**.

The room temperature ferromagnetic behavior of both the  $\text{Zn}_{0.96}\text{Fe}_{0.01}\text{Cu}_{0.03}\text{O}$  and  $\text{Zn}_{0.96}\text{Fe}_{0.01}\text{Ni}_{0.03}\text{O}$  particles in the magnetic field range from 0 to  $\pm 1$  T using VSM measurements have been shown in **Figure 4**. The magnetization is plotted as a function of magnetic field for different dopant ions incorporated in Fe-doped ZnO particles. The diamagnetic contribution from the sample holder has already been subtracted to estimate the actual ferromagnetic contribution of each sample. Also shown in **Figure 4** the magnetization of  $\text{Zn}_{0.95}\text{Fe}_{0.05}\text{O}$ ,  $\text{Zn}_{0.94}\text{Cu}_{0.06}\text{O}$  and  $\text{Zn}_{0.95}\text{Ni}_{0.05}\text{O}$ . The comparative M(H) loops showed that, the  $\text{Zn}_{0.96}\text{Fe}_{0.01}\text{Ni}_{0.03}\text{O}$  exhibits higher magnetization than that of  $\text{Zn}_{0.97}\text{Fe}_{0.03}\text{O}$  as well as  $\text{Zn}_{0.95}\text{Ni}_{0.05}\text{O}$ . The same result was also observed in  $\text{Zn}_{0.96}\text{Fe}_{0.01}\text{Cu}_{0.03}\text{O}$ . In the case of  $\text{Zn}_{0.96}\text{Fe}_{0.01}\text{Cu}_{0.03}\text{O}$  sample a coercive field ( $H_c$ ) and the remnant magnetization ( $M_R$ ) are found to be 554 Oe and 0.012 emu/g, while for  $\text{Zn}_{0.96}\text{Fe}_{0.01}\text{Ni}_{0.03}\text{O}$  smaller values are observed, namely 120 Oe and 0.004 emu/g. However, the saturation magnetization for Ni incorporation in Fe-doped ZnO is clearly higher than that of Cu co-doping.

The mechanism responsible for the observed ferromagnetism at room temperature in transition metal-doped ZnO is also not clear and has been debated over the years. Several explanations are discussed below. Nevertheless a few researchers have claimed to observe ferromagnetic behavior arising only from a secondary phase and not from the material itself. The results of the XRD and EDX measurements in our samples demonstrate that the dopant ion was incorporated into the wurtzite lattice at Zn sites forming a solid solution instead of precipitates. However, a secondary phase might

**Table 3.** The g value, linewidth ( $\Delta H_{pp}$ ), and peak area of  $Zn_{0.96}Fe_{0.01}Cu_{0.03}O$  and  $Zn_{0.96}Fe_{0.01}Ni_{0.03}O$  compared with  $Zn_{0.95}Fe_{0.05}O$ ,  $Zn_{0.94}Cu_{0.06}O$ , and  $Zn_{0.95}Ni_{0.05}O$  nanoparticle.

Sample	g value	$\Delta H_{pp}$ (Gauss)	Area ( $\times 10^6$ ) (a.u)	g value	$\Delta H_{pp}$ (Gauss)	Area ( $\times 10^5$ ) (a.u)
$Zn_{0.95}Fe_{0.05}O$	2.2378	1074.54	4.73	2.0077	826.38	10.50
$Zn_{0.94}Cu_{0.06}O$	2.1770	312.19	23.90	2.1460	62.35	6.07
$Zn_{0.95}Ni_{0.05}O$	2.5795	801.38	4.71	2.1501	70.32	35.70
$Zn_{0.96}Fe_{0.01}Cu_{0.03}O$	2.2134	286.05	6.78	-	-	-
$Zn_{0.96}Fe_{0.01}Ni_{0.03}O$	2.3208	795.51	14.25	2.2137	698.22	31.41



**Figure 4.** The room temperature ferromagnetic of  $Zn_{0.96}Fe_{0.01}Cu_{0.03}O$  and  $Zn_{0.96}Fe_{0.01}Ni_{0.03}O$  compared with  $Zn_{0.95}Fe_{0.05}O$ ,  $Zn_{0.94}Cu_{0.06}O$ , and  $Zn_{0.95}Ni_{0.05}O$  nanoparticles.

exist in the sample even though it was not detected in our XRD spectra. Thus, it is useful to consider all possible ferromagnetic impurity phases that might be present in both samples. It is known that Cu-related oxides such as CuO, Cu<sub>2</sub>O or Cu clustering could not contribute to the room temperature ferromagnetism, because none of them exhibit ferromagnetism above room temperature [54-56]. Therefore the ferromagnetism behavior observed in our Cu-doped samples studied here does not seem to be related with the presence of any secondary phases or Cu clusters, while Cu clusters and its oxides are generally considered to be non-ferromagnetic and could not contribute to the room temperature ferromagnetic. In the case of Fe-doped samples nearly all possible Fe-based oxides, such as FeO and Fe<sub>2</sub>O<sub>3</sub> are antiferromagnetic with T<sub>N</sub> values of 198 and 963 K, respectively [57,58]. The exception to this is Fe<sub>3</sub>O<sub>4</sub>, which is ferromagnetic with a T<sub>c</sub> of approximately 858 K [59]. Another secondary phase that can be found in Fe-doped ZnO samples is ZnFe<sub>2</sub>O<sub>4</sub>. However, this phase is antiferromagnetic and can be excluded as the origin of room temperature ferromagnetic in our samples. In the case of Ni co-doping, the formation of secondary phase such as NiO is a unlikely source of ferromagnetism as NiO is antiferromagnetic in nature with T<sub>N</sub> values of 523 K [60] and 5 K [61] for bulk- and nanocrystalline NiO, respectively. Accordingly, the ferromagnetism behavior observed in our Zn<sub>0.96</sub>Fe<sub>0.01</sub>Cu<sub>0.03</sub>O and Zn<sub>0.96</sub>Fe<sub>0.01</sub>Ni<sub>0.03</sub>O particles studied here does not seem to be related with the presence of any secondary phases.

There is also an emerging consensus that ferromagnetic behavior in transition metal-doped ZnO is correlated with defects such as oxygen or zinc vacancies [62-64]. Karmakar *et al.* [11] investigated the origin of ferromagnetism in Fe-doped ZnO using local probe measurements such as ESR and Mössbauer spectroscopy. The results revealed that the Fe ions are present in both Fe<sup>2+</sup> and Fe<sup>3+</sup> valence states. The presence of uncoupled Fe<sup>3+</sup> ions is possibly due to hole doping in the system, which was caused by cation (*i.e.*, Zn) vacancies. By comparing the ESR measurements from our sample with the results obtained from Karmakar *et al.* [11] it is confirmed that the ferromagnetism observed in our Zn<sub>0.97</sub>Fe<sub>0.03</sub>O sample was due to the presence of Fe atoms in the form of Fe<sup>2+</sup> ions and Fe<sup>3+</sup> ions.

According to Karmakar *et al.* [11] a cation vacancy near Fe can promote Fe<sup>2+</sup> into Fe<sup>3+</sup> and also mediate the Fe<sup>2+</sup>-Fe<sup>2+</sup> exchange interaction. Moreover, since the transition metal ion is slightly higher side towards cationic percolation threshold, Fe<sup>2+</sup>-Fe<sup>3+</sup> exchange interaction may also possible. Viswanatha *et al.* [65] investigated the origin of ferromagnetism in FeCu-codoped ZnO experimentally as well as theoretically. Their results revealed that the Fe ions are present in both Fe<sup>2+</sup> and Fe<sup>3+</sup> valence

states, with the concentration of trivalent state increased with increasing Cu doping and redox-like pairs Fe<sup>2+</sup> + Cu<sup>2+</sup> ⇌ Fe<sup>3+</sup> + Cu<sup>1+</sup> can be occurred to stabilize the ferromagnetism in codoped system. They believed that the ferromagnetism of this system is ascribed to a double-exchange interaction between the Fe atoms mediated by the Cu atom. It is obvious from ESR spectra of Zn<sub>0.96</sub>Fe<sub>0.01</sub>Cu<sub>0.03</sub>O show the presence of Fe<sup>2+</sup> ion and the absence of Cu<sup>2+</sup> ion. However, our EDX result shows the presence of Cu atom in our Zn<sub>0.96</sub>Fe<sub>0.01</sub>Cu<sub>0.03</sub>O. These results suggested that the oxidation state of Cu is +1, since Cu in the +1 state has no unpaired spin. Usually, a Cu ion will contribute to the net ferromagnetic moment only if it is in the +2 state. Interestingly, the Zn<sub>0.96</sub>Fe<sub>0.01</sub>Cu<sub>0.03</sub>O sample shows an evidence of ferromagnetic order. Therefore we believed that a small amount of Fe<sup>3+</sup> and Cu<sup>2+</sup> ions would be found in our sample to neutralize the charge imbalance, although both ions (Fe<sup>3+</sup> and Cu<sup>2+</sup>) were not detected in our ESR spectra. Comparing the XRD, EDX, VSM and ESR results for Zn<sub>0.96</sub>Fe<sub>0.01</sub>Cu<sub>0.03</sub>O with Zn<sub>0.95</sub>Fe<sub>0.05</sub>O, Zn<sub>0.94</sub>Cu<sub>0.06</sub>O and the results obtained in the literature, we conclude that Fe<sup>2+</sup>, Cu<sup>1+</sup>, Fe<sup>3+</sup> and Cu<sup>2+</sup> are presence in our Zn<sub>0.96</sub>Fe<sub>0.01</sub>Cu<sub>0.03</sub>O sample and have played the important role in obtaining the room temperature ferromagnetism.

In the case of Zn<sub>0.96</sub>Fe<sub>0.01</sub>Ni<sub>0.03</sub>O, the bent nature of the curve exhibits a shallow ferromagnetism in our sample. The ferromagnetism could arise due to possible reason: 1) secondary phase or clustering of metallic or 2) the presence of charge carriers, or 3) the formation of defect structures such as oxygen- and zinc vacancies. It is already discussed above that the formation of secondary phase is unlikely. Moreover, from the ESR spectra of Zn<sub>0.96</sub>Fe<sub>0.01</sub>Ni<sub>0.03</sub>O the presence of Ni metallic might be ruled out. In addition the ESR measurement exhibits superposition of Fe<sup>2+</sup> and Ni<sup>2+</sup> signals. It is also known that the presence of Ni in ZnO nanoparticle could enhance the magnetic d-d exchange interaction between the magnetic moment of Ni<sup>2+</sup> contribute for the ferromagnetic state [66]. Thus the observed ferromagnetism in the Zn<sub>0.96</sub>Fe<sub>0.01</sub>Ni<sub>0.03</sub>O could be considered as a result of the exchange interaction between conductive electron with local spin polarized electron on the Ni<sup>2+</sup> or Fe<sup>2+</sup> ions. In some reported transition metal doped ZnO systems, bound magnetic polaron (BMP) models are widely proposed mechanisms to explain the presence of room temperature ferromagnetism. The BMP model was used to explain room temperature ferromagnetism in semiconducting as well as insulating materials [67]. Other studies reported that defects and oxygen vacancies are common in Ni-doped ZnO nanostructures and are responsible for the formation of BMP [68]. However, the oxygen vacancy signal was not observed in Zn<sub>0.96</sub>Fe<sub>0.01</sub>Ni<sub>0.03</sub>O ESR spectra. Therefore, the conductive electron with local

spin polarized electron exchange interaction is the more probable mechanism in the present investigation.

#### 4. Conclusion

In conclusion, the room temperature ferromagnetism of  $Zn_{0.96}Fe_{0.01}Cu_{0.03}O$  and  $Zn_{0.96}Fe_{0.01}Ni_{0.03}O$  nanoparticles were observed. Several assumptions have been addressed to explain room temperature ferromagnetism: the role of secondary phases, metallic clusters and defect-induced ferromagnetism. A detailed analysis of XRD, EDX, UV-Vis and ESR measurements revealed that the formation of secondary phases and metallic clusters in  $Zn_{0.96}Fe_{0.01}Cu_{0.03}O$  and  $Zn_{0.96}Fe_{0.01}Ni_{0.03}O$  nanoparticles were not responsible for the room temperature ferromagnetism. In  $Zn_{0.96}Fe_{0.01}Cu_{0.03}O$  nanoparticles ESR and EDX analysis revealed that  $Fe^{2+}$  ions and  $Cu^{1+}$  were present. However, to neutralize the charge imbalance we believed that a small amount of  $Fe^{3+}$  and  $Cu^{2+}$  ions would be found in our sample and have played the important role in obtaining the room temperature ferromagnetism. In  $Zn_{0.96}Fe_{0.01}Ni_{0.03}O$  the conductive electron with local spin polarized electron exchange interaction is the more probable mechanism for the origin of room temperature ferromagnetism.

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