EFFECT OF TEMPERATURE TO THE MAGNETIC PROPERTY OF NI$_{0.2}$CO$_{0.1}$ZN$_{0.7}$O NANOPARTICLES

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ABSTRACT
ZnO and Ni$_{0.2}$Co$_{0.1}$Zn$_{0.7}$O nanoparticles were successfully synthesized by microwave assisted combustion synthesis method using urea as a fuel. The structural, morphological, compositional and Magnetic property of Ni$_{0.2}$Co$_{0.1}$Zn$_{0.7}$O nanoparticles were investigated by X-ray diffraction (XRD), Scanning electron microscopes (FE-SEM JEOL-7001), Energy-dispersive X-ray spectroscopy (EDX), and quantum design Vibrating sample magnetometre (QD-VSM) respectively. The structural property showed the formation of Wurtzite structure of ZnO,with nine prominent peaks in which the strong diffraction peaks appear in (100), (002) and (101), respectively, there is a trace related to Ni ions observed. The average size of these nanoparticles was estimated which show that there is a little decrease in the average size of the particles compared to ZnO. Scanning electron microscopes (SEM) showed that the samples have sizes smaller than 100nm, no indication of phase separation and little agglomeration was observed. Energy-dispersive X-ray spectroscopy (EDX) results tallies with the synthesis results. Magnetic measurement reveal that at all temperature the sample present a ferromagnetic behavior with a clear S shape hysteresis loop however the behavior is decreasing with an increase in temperature but still the sample room temperature ferromagnetic behavior was maintained.
Keywords: Nanoparticles, Zinc oxide, Dilute magnetic semiconductor, ferromagnetism, curie temperature.

INTRODUCTION

Dilute magnetic semiconductor (DMS) have attracted considerable attention of researches due to their promising applications in spintronic as microelectronic technology (Limaye *et al.* 2*0*11). Moreover its ability to use spin degrees of freedom and charge manipulation, makes them useful to worked as functionality of memory, detectors, light-emitting sources, spin-valve transistors, spin light-emitting diodes, non-volatile storage, logic devices (Chattopadhyay, 2009; Caglar, (2013); Mandal and Nath, 2006). The greatest challenge for these materials is that the above mentioned technological applicatıons can only be possible when the materials retain their magnetic character at room temperature (Sharma *et al.* 2012). Among the dilute magnetic semiconductors Zinc Oxide semiconductor emerge to be the best applicant because of its wide band gap of 3.37 eV and large exciting binding energy of approximately 60meV at 300 K. (Fern, 2006; Abdullahi, 2015).With these exceptional and intresting properties a number of research was foccussed on. Recent discovery shows that room temperature ferromagnetic materials (RTFM) can be increased when doped with transition metal (TM), (Ni, Fe, Mn,Cu Co, V,) (Koseoglu, 2013). in which magnetic ions are employed as a substitute to a small percentage metallic ions in the parent semiconductor materials thereby hosting sp transition metal in the dilute magnetic semiconductors and eventually increase the curie temperature of the materials (Koseoglu *et al.* 2012). It has been reported by Koseoglu Y that Co$_{0.2}$Zn$_{0.8}$O sample is found to exhibit a clear RT ferromagnetism with a large coercivity of 560Oe (Koseoglu, 2013). Glaspel *et al.* (2005) also reported a paramagnetic behavior of 10% Co doped ZnO sample although room temperature ferromagnetism was observed by hydrogenating the samples at 573K for 6h . Similar observation was made for other transition metals like Mn, as Junhao reported the display of room-temperature ferromagnetism as well as paramagnetism, in 2.5% and 5% Mn-doped ZnO samples while the 10% and 15% samples exhibit paramagnetic effects.

The observed ferromagnetic behaviors likely originate from cooperative effect of intrinsic and extrinsic magnetisms (Jiang, 2011). Interestingly co doping process are now involved to enhance the magnetic ordering and better optical and magnetic properties of the nanoparticles (Abdullahi *et al*. 2015). Abdullahi *et al*. (2015) reported an observation of room temperature ferromagnetic behavior with coercive field and remanent magnetization of 47.70 Oe and 1.8×10^{-1} emu/g, in 15% Mn of $Mn_xCo_{0.1}Zn_{0.9-x}O$ nanoparticles. In this paper we report effect of temperature to the magnetic property of $N_{0.2}Co_{0.1}Zn_{0.7}O$ nanoparticles prepared by microwave synthesis method.

Synthesis

ZnO and $Ni_{0.2}Co_{0.1}Zn_{0.7}O$ nanostructured materials were prepared using Nickel (II) nitrate hexa hydrate $(Ni(NO_3)_2.6H_2O)$, mixed with an appropriate ratio of Cobalt(II) nitrate hexahydrate $(Co(NO_3)_2.6H_2O)$ and Zinc nitrate hexahydrate $(Zn(NO_3)2.6H_2O)$ respectively as in table 1 were dissolved in 10 mL of doubly distilled water, using urea as a fuel, the mixture is stirred with a magnetic stirrer until it dissolved completely. Then it was poured into a curicible which was taken in to a kichen type microwave oven that operates with 800 watts for 15 minutes. The solution boils and dehydrates followed by combustion resulting from the evolution of gas in form of spark, the solution burns completely with the release of much amount of heat and gas, where by obtained the desired solid phase.

Table1: Amounts of Metal Nitrates used to synthesize ZnO and $Ni_{0.2}Co_{0.1}Zn_{0.7}O$ Nanopowders.

Sample	Ni(II)nitrate (g)	Co(II)nitrate (g)	Zn(II)nitrate (g)	Urea (g)
ZnO	0.000	0.000	5.940	6.00
$Ni_{0.2}Co_{0.1}Zn_{0.7}O$	1.163	0.582	4.158	6.00

RESULTS AND DISCUSSION

XRD measurement

Structural characterization of the samples was carried out using Rigaku X-ray diffraction (XRD) spectrometer, Figure1 shows the combined XRD patterns taken from both the samples. The diffraction patterns indicate wurtzite structure of ZnO where all the diffraction peaks can be pointed out to the hexagonal phase ZnO as reported in JCPDS card (No. 36-1451, a = 0.3249 nm, c = 0.5206 nm) with nine prominent peaks 100, 002, 101, 102,110,103,200,112, and 201. Where the strong diffraction peaks appear in (100), (002) and (101), respectively. (Jayakumar *et al*. 2006; Pan *et al*. (2013) For the $Ni_{0.2}Co_{0.1}Zn_{0.7}O$ sample there is a trace of single peak level X observed around 2θ degree of 42.3, which is likely to be NiO, this implies that not all Ni ions can substitute Zn^{2+} without changing the structure (Khatoon and Ahmad, (2012);Vallalperuman *et al*. (2014).
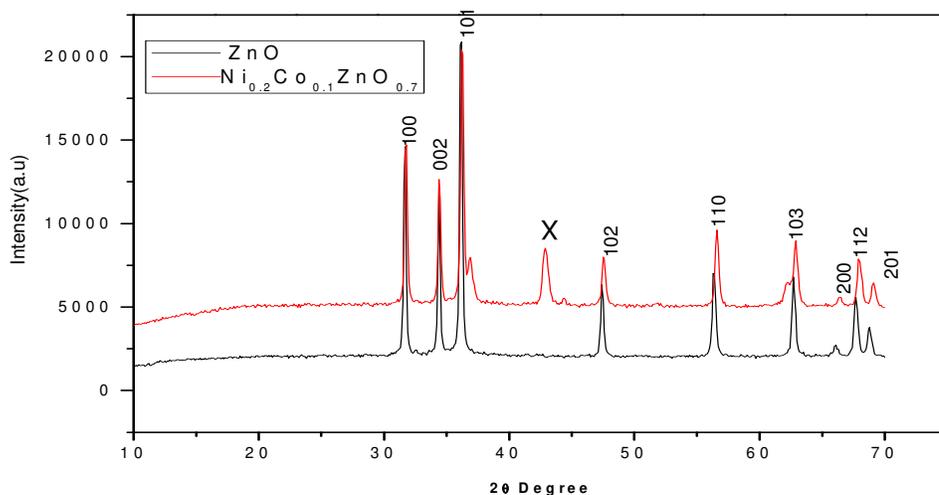
Figure 1: XRD patterns for ZnO and $Ni_{0.2}Co_{0.1}Zn_{0.7}O$.

To find the sizes of the particles we used Scherrer equation written as (Koseoglu *et al.* 2012).

$$D = \frac{k\lambda}{\beta cos\theta} \qquad (1)$$

Where, D is the grain size, K is a dimensionless shape factor with a value (0.9) which varies with the actual shape of the crystallite, λ is the wavelength of the X-ray used (1.5402A) . β is the full width of the half maximum of the most intense peak, θ is the Bragg angle corresponding to maximum X-ray diffraction peak (Chattopadhyay *et al.,* 2009; Sharma *et al.,* 2003).

The calculation of the lattice constant a and c can be done by using the formula for hexagonal system as.

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

Using Bragg's law we can rewrite the above equation as follows

$$\frac{4sin^2\theta}{\lambda} = \frac{4}{3}\left(\frac{h^2+hk+k^2}{a^2}\right) +\frac{l^2}{c^2} \qquad (3)$$

Where d is the lattice spacing, a and c are lattice constants, hkl are miller indices. To calculate a, we used the peak of the form (hk0) so that c will vanish in the equation, similarly to get c we used the peak of the form (00l) so that we have only c and l as our variable. The equation derived for a and c are respectively given as (Pan *et al.,* 2013).

$$a = \frac{\lambda\sqrt{(h^2+hk+k^2)}}{\sqrt{3}sin\theta} \qquad (4)$$

$$c = \frac{\lambda l}{2sin\theta} \qquad (5)$$

Table 2: Particles size and Lattice parameters of ZnO and $Ni_{0.2}Co_{0.1}Zn_{0.7}O$ Nanoparticles

Sample	D(101)nm	a (11 0)nm	c (002)nm
ZnO	32.65	3.2614	5. 2085
$Ni_{0.2}Co_{0.1}Zn_{0.7}O$	31.77	3.2488	5.2079

The crystallite sizes of the samples were calculated with Scherrer's equation using the most intense peak (101), the crystal size changes from 32.65 to 31.77 as dopant ions are involved. As shown in Table 2. These indicate that the growth of the parent compound has been suppressed as a result of the strain induced by the dopant that ultimately reduce the intensity of the diffraction peak and increase its width (Omri *et al.,* 2013).

Moreover, the lattice parameters a and c decreases with an increase in the dopant content these results from the difference in the ionic radii of Zn^{2+} Ni^{2+} Co^{2+}, of with 74 64 and 72pm respectively. Where the ionic radius of the Ni^{2+} is far less than that of Zn^{2+} these account for the difference in their lattice parameter (Siddheswaran *et al.* 2013; Köseoğlua *et al.* 2014).

SEM measurement

SEM images reveals that all samples consist of almost spherical shaped nanoparticles, no any indication of phase separation and little agglomeration was observed in $Ni_{0.2}Co_{0.1}Zn_{0.7}O$ sample though there is a sign of porosity in the sample that might be as a result of evolution of gases like Co_2, N_2 and water vapor during the synthesis(Köseoğlu, 2016). A close view of all sample shows that smaller crystallites have sizes smaller than 100 nm which confirm the XRD results. Moreover, the nanoparticles were dense and distributed evenly on the whole area however, a clear distinct boundary between neighboring crystallites can still be observed.[8] The FE-SEM images of all samples are shown in Figure 2

(a) ZnO
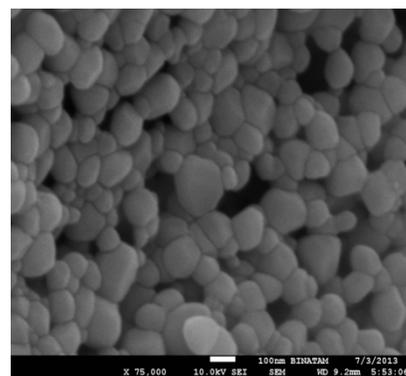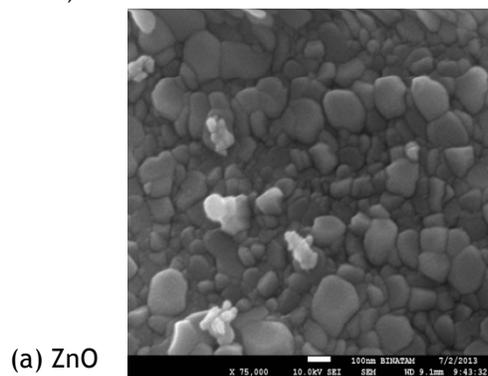
(b)$Ni_{0.2}Co_{0.1}Zn_{0.7}O$

Figure2 Field emission scanning electron micro-graphs (FE-SEM) of ZnO and $Ni_{0.2}Co_{0.1}Zn_{0.7}O$ Nanoparticles

EDX measurement

The EDX measurement results is shown in fig.3(a),and (b). The results comply with what is expected from the synthesis where by the mass ratios of the chemical composition of the samples tallies with the outcomes of the EDX spectra. The spectrum contains all the expected elements and no impurity was found.
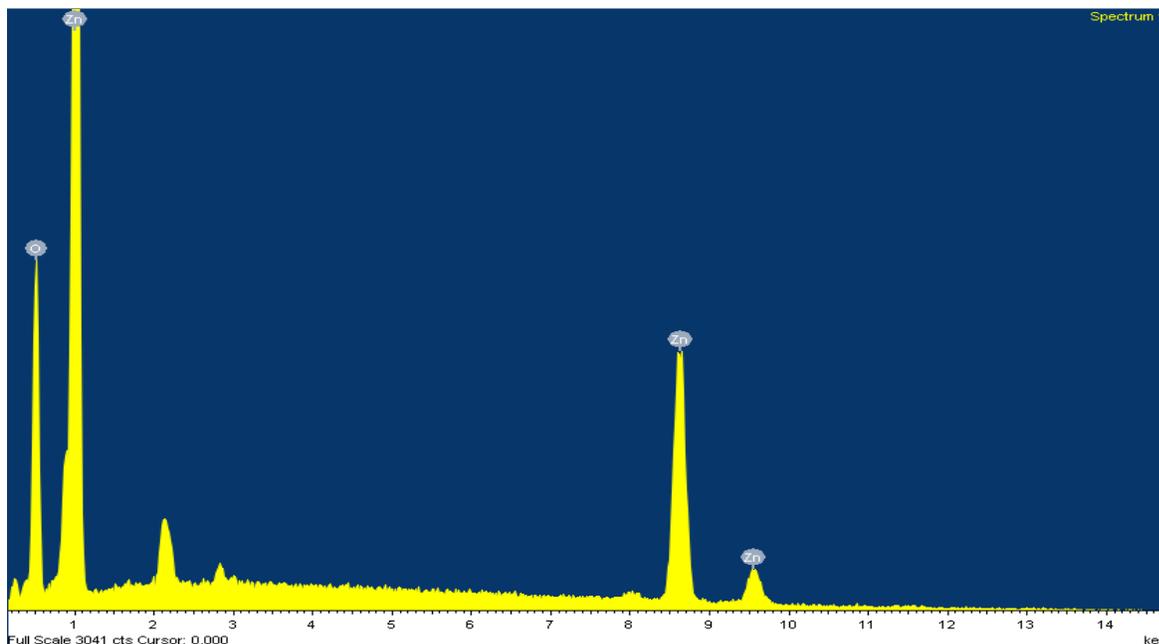
(a) ZnO
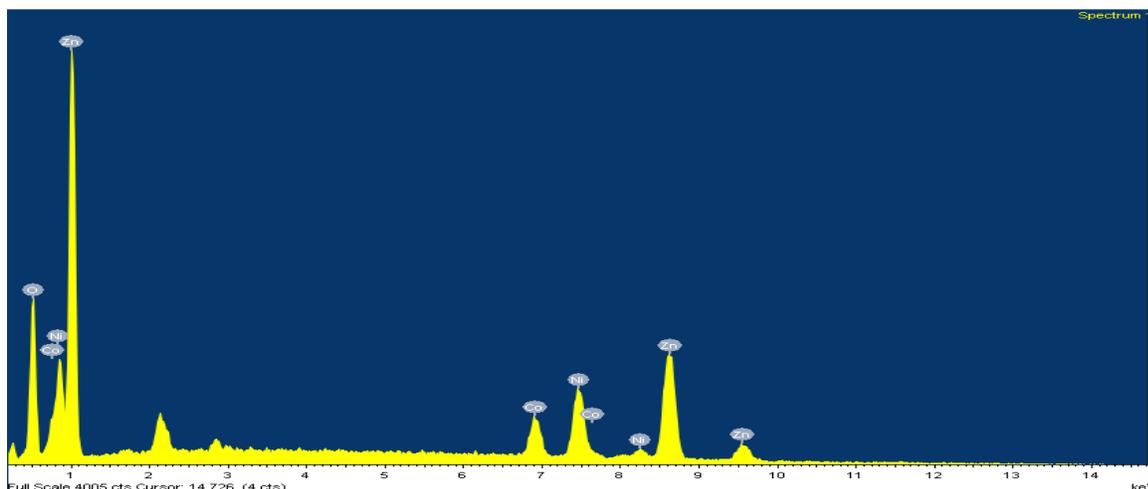
(b)$Ni_{0.2}Co_{0.1}Zn_{0.7}O$

Figure 3: EDX graph of (a) ZnO (b) $Ni_{0.2}Co_{0.1}Zn_{0.7}O$ Nanoparticles

Table 3: Elemental Percentage for ZnO and $Ni_{0.2}Co_{0.1}Zn_{0.7}O$ Nanoparticles

| Element | ZnO | | $Ni_{0.2}Co_{0.1}Zn_{0.7}O$ | |
	Weight %	Atomic %	Weight %	Atomic %
O K	6.59	56.24	5.19	39.55
Co K	0.000	0.000	3.94	8.15
Ni K	0.000	0.000	8.86	18.41
Zn L	20.94	43.76	18.17	33.89
Total	27.53	100	36.16	100

The spectra of Nanoparticles is shown in Figure3. It can be observed that the most abundant element in both samples is Zinc then oxygen followed by the respective element. In both samples the appearance of un named peak at almost 2.0eV indicate the presence of carbon atom which result from the carbon coating applied before the Edx measurement (Köseoğlu, 2016). Moreover, from table 3 the percentage weight of each element is shown which is related with the number of elements in the sample similarly the atomic percentage of oxygen indicates that there is oxygen vacancies in both the sample's only that the vacancy is more presented in $Ni_{0.2}Co_{0.1}Zn_{0.7}O$ compared to ZnO sample which may result in increasing the ferromagnetic behavior of the samples (Sharma *et al.* 2003).

Magnetic measurement

Magnetic measurements were carried out by quantum design magnetometer (QD-VSM). The sample were cooled either in the presence of an external magnetic field (Field cooling case -FC) or in zero field (zero field cooling case ZFC). The magnetic behaviors were recorded by sweeping the external field between ±10kOe at different temperature fig.4(a) shows the magnetic property of $Ni_{0.2}Co_{0.1}Zn_{0.7}O$ sample at different temperature. It reveal that at all the temperature the sample presents a ferromagnetic behavior with a clear S shape hysteresis loop however the behavior is decreasing with an increase in temperature but still the sample exhibit room temperature ferromagnetic behavior as indicated by fig. 4 (b) where it clearly shows that the curie temperature (TC) is above room temperature since the field diverges at 295K (Ajwafi, 2013). Table 4 gives the magnetic parameters of $Ni_{0.2}Co_{0.1}Zn_{0.7}O$ sample at 10K, 100K and 200K, the saturation magnetization M_s, Coercive field H_c, and remanence magnetization of M_r is presented which shows that increase in temperature reduce the ferromagnetic property of the sample.
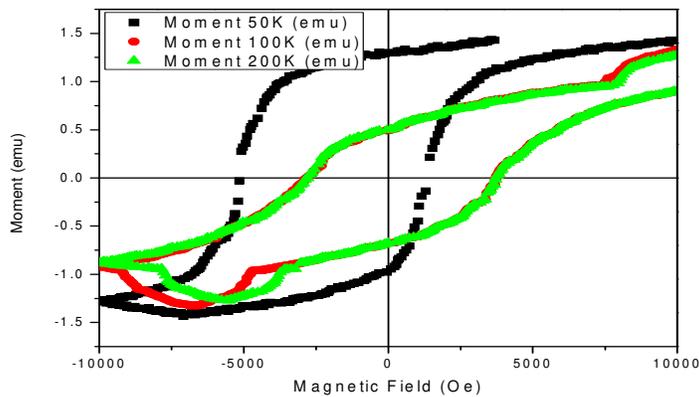
Figure 4(a) M-H Curve of $Ni_{0.2}Co_{0.1}Zn_{0.7}O$ Nanoparticles at different temperature
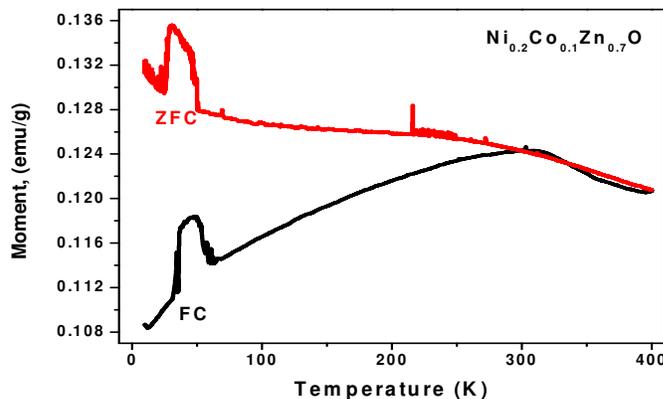
Figure 4(b) Zero Field Cooling (ZFC) and Field Cooling (FC) at room temperature.$Ni_{0.2}Co_{0.1}Zn_{0.7}O$ Nanoparticles

Table 4: magnetic measurement of ZnO and $Ni_{0.2}Co_{0.1}Zn_{0.7}O$ Nanoparticles

$Ni_{0.2}Co_{0.1}Zn_{0.7}O$	M_s (emu/g)	H_c (Oe)	M_r (emu/g)
50K	1.457	5292.10	1.339
100K	1.358	3037.54	0.543
200K	1.293	2937.58	0.534

CONCLUSION

ZnO and $Ni_{0.2}Co_{0.1}Zn_{0.7}O$ nanoparticles were successfully synthesized by microwave assisted combustion synthesis method using urea as a fuel. The structural property showed the formation of Wurtzite structure of ZnO,with nine prominent peaks in which the strong diffraction peaks appear in (100), (002) and (101), respectively, with addition peak observed for $Ni_{0.2}Co_{0.1}Zn_{0.7}O$. The average size of $Ni_{0.2}Co_{0.1}Zn_{0.7}O$ decrease compared to that of ZnO. Scanning electron microscopes (SEM) showed that the samples have sizes smaller than 100nm, no indication of phase separation and little agglomeration was observed. Energy-dispersive X-ray spectroscopy (EDX) results tallies with the synthesis results. Magnetic measurement reveal that at all temperature the sample present a ferromagnetic behavior with a clear S shape hysteresis loop however the behavior is decreasing with an increase in temperature but still room temperature ferromagnetic behavior was maintained.

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