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Properties of Co/Ni codoped ZnO based nanocrystalline DMS

Rezq Naji Aljawfi, S. Mollah*

Department of Physics, Aligarh Muslim University, Aligarh 202002, India

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ABSTRACT

Nanoparticles of Co and Ni codoped zinc oxide, $Zn_{0.9}Co_{0.1-x}Ni_xO$ (x=0.0, 0.03, 0.06 and 0.09), diluted magnetic semiconductors (DMSs) are synthesized by the sol–gel method at annealing temperature of 500 °C. X-ray diffraction (XRD) patterns confirm the single phase character of the samples with x=0.0 and 0.03. However, minor NiO secondary phase is detected in the samples with x=0.06 and 0.09. All of them possess the hexagonal wurtzite structure. There is no significant change in the lattice parameters due to variation of doping concentration. The average particle size is found to be 19.31–25.71 nm. FTIR and UV-vis spectroscopic results confirm the incorporation of the dopants into the ZnO lattice structure. Magnetization data reveal the presence of room temperature ferromagnetism (RTFM). The XRD patterns rule out the formation of secondary phase are a concern in any DMS system as a source of spurious magnetic signals. Therefore, we carried out the XPS studies from which the oxidation states of Co and Ni are found to be Co^{2+} and Ni^{2+} , respectively. Moreover, XPS O 1s spectra show evidence of the presence of the oxygen vacancy in the ZnO matrix.

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1. Introduction

Diluted magnetic semiconductor (DMS) is referred to a semiconductor in which a small fraction of host cations are replaced by transition metal ions (TMI) as magnetic elements [1]. In the recent years, large efforts have been devoted to the investigation of DMS due to their potential application in spintronic devices [2] for which the basic requirements are room temperature ferromagnetism (RTFM) and good optical transmittance. Zinc oxide (ZnO) is an attractive semiconductor for numerous applications and a building block material for many advanced device technologies because of its large band gap (3.35 eV) at room temperature. It has large excitonic binding energy (60 meV), optical transparency, chemical stability, hardness and piezo-electric properties [5,6]. Doping of ZnO with magnetic ions such as Fe, Co, Ni, etc. introduces magnetic properties forming DMS [7]. Dietl et al. [3] have predicted that p-type ZnO-based DMS may exhibit RTFM. Later, it is suggested theoretically that the RTFM may also exist in n-type doped ZnO systems [1,4]. These findings prompt the intense investigations on ZnO-based DMS. Ferromagnetism in TMI doped ZnO is proved by theoretical calculations and experimentally, RTFM has been reported in V-, Co-, Ni-, Fe-, Cu- and Mn-doped ZnO systems [8]. Though there are many reports on structural, optical and magnetic characteristics of TMI-doped or

E-mail address: smollah@rediffmail.com (S. Mollah).

codoped ZnO, the origin of RTFM in DMS materials is not understood completely. There are still some reports showing no indication of RTFM or suggesting the presence of secondary phases as the origin of RTFM in DMS [9]. A number of studies indicate that the RTFM may originate from the precipitation of magnetic clusters or from the secondary magnetic phases [10]. Some of these are valuable contributions to the magnetization mechanism in the DMS system. For example Cr/Co doped ZnO thin film has been studied by Yan et al. [11], who showed that Zn_{0.92}Co_{0.08}O film consists of substitutional Co ions and Co metallic clusters. But in the case of codoped of Co and Cr, the Co metallic clusters and all the Co ions located at Zn sites disappear. Therefore, the codoped Cr plays an important role in mediating the atomic distribution of Co ions in ZnO lattice. Lathiotakis et al. [12] have demonstrated that in codoped Zn(Co-Cu)O, the Cu⁺ ions act as superexchange mediators by causing a remote delocalization through the hybridization of the Cu $d_3z^2 - r^2$ spin majority state with the O-p states.

Pure ZnO in nanoscale exhibits ferromagnetic properties due to the presence of oxygen vacancy on the surface of nanoparticles [13]. This underscores the fact that the magnetization is not necessarily resulted from Co metallic culster in DMS. Since the intrinsic defects form donor states in ZnO, it is concluded that (Zn,Co)O and (Zn,Ni)O are promising candidates for high transition temperature (T_c) ferromagnetic materials [14]. Stirred from the above mentioned facts, it would be quite interesting to synthesize and investigate the properties exhibited by Co and Ni codoped ZnO. The present article reports the effect of Co/Ni

^{*} Corresponding author. Tel./fax: +91 571 2701001.

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codoped on structural, optical and magnetic properties of ZnO based DMS in the series of $Zn_{0.9}Co_{0.1-x}Ni_xO$ (x=0.0, 0.03, 0.06 and 0.09) which are synthesized by the sol-gel method at annealing temperature of 500 °C. The total percentage of dopants (Co/Ni) is kept constant at 10%; only Ni doping gives rise to secondary phases. The samples show RTFM. Ni and Co have been chosen as doping elements since these are important transition metals with ionic radii close to that of Zn^{2+} , which leads to an easy incorporation of Ni²⁺ and Co²⁺ ions into the ZnO lattice.

2. Experimental procedure

All $Zn_{0.9}Co_{0.1-x}Ni_xO$ (x=0.0, 0.03, 0.06 and 0.09) samples were synthesized by the sol-gel method [15]. Analytical reagents (AR) grade zinc nitrate [Zn $(NO_3) \cdot 6H_2O$], nickel nitrate [Ni $(NO_3)_2$.6 \cdot H₂O], cobalt nitrate [Co $(NO_3)_2$.6 \cdot H₂O] and citric acid $[C_6H_8O_7]$ were used as the raw materials without any special treatment. These were taken at the desired stoichiometric ratio. Nitrates were dissolved in distilled water to get homogeneous solution by using magnetic stirrer at 70 °C. Citric acid had been dissolved separately in distilled water for 30 min and then added to the nitrate solution. Slowly, the color of nitrate solution became brighter when the molarity ratio of nitrate to citric acid was 1:1. The solution was continuously stirred at 70 °C until it was converted into a gel form. Then it was heated at 130 °C for 12 h. The product was ground for 30 min and finally annealed at 500 °C in air for 12 h. X-ray diffraction (XRD) patterns of the samples were obtained at room temperature, with a step of 0.02° , using Bruker D8 ADVANCE X-ray diffractometer with Cu K_{α} radiation ($\lambda = 1.54178$ Å) in the range of $0^{\circ} \le 2\theta \le 100^{\circ}$ at 40 kV. Fourier transform infrared (FTIR) spectra of the samples were recorded at room temperature using a Perkin-Elmer BX2 FTIR spectrometer using KBr pellets as medium. The optical absorbance spectra were taken by using a UV-vis double beam Perkin-Elmer LAMDA 35 spectrophotometer at room temperature in the wavelength range of 250-800 nm. Magnetization of the samples has been studied by utilizing superconducting quantum interference device (SQUID) system (MPMS-XL) of QUANTUM DESIGN with a sample of 0.2 g in the temperature range of 10–300 K. Valence states of the elements have been studied from X-ray photoelectron spectroscopy (XPS) obtained by using the instrument VSW (UK made). The resolution was 0.9 eV. The used X-ray was Al K_{α} and base vacuum was maintained at $10^{-9}\,\text{Torr.}$

3. Results and discussion

3.1. X-ray diffraction

Fig. 1 shows the XRD pattern of $Zn_{0.9}Co_{0.1-x}Ni_xO$ (x=0.0, 0.03, 0.06 and 0.09) samples. The patterns are found to be in good agreement with the standard peak positions of ZnO (JCPDS Card No. 36-1451). These peaks reveal that all the investigated samples are nanocrysalline powder of hexagonal wurtzite structure (space group P6₃mc). The diffraction peak at 43.125° (2 0 0) is attributed to NiO (JCPDS Card No. 78-0643). It begins to appear in sample with x=0.06 (Co=4% and Ni=6%) and grows in intensity with the increasing *x*. Therefore, the formation of NiO may be from unreacted Ni²⁺ ions present in the solution at high doping concentration. This gives the limit of solid solubility of Ni in the ZnO crystal lattice. It has already been found that Ni can dissolve less than 5 at% into ZnO matrix [16]. The relatively higher annealing temperature (500 °C) also enhances the formation of NiO.

Calculation of lattice parameters (Table 1) and indexing of the diffraction peaks of all the samples are done by using the



Fig. 1. X-ray diffraction (XRD) pattern of $Zn_{0.9}Co_{0.1-x}Ni_xO$ (x=0.0, 0.03, 0.06 and 0.09) samples.

Table 1 Lattice parameters, unit cell volume and particle size of the $Zn_{0.9}Co_{0.1-x}Ni_xO(x=0.0, 0.03, 0.06 and 0.09)$ samples.

Samples	<i>a</i> = <i>b</i> (Å)	c (Å)	c/a	Unit cell volume (Å ³)	Size of particle (nm)
x=0.0	3.2495	5.2030	1.6011	47.5792	23.6
x=0.03	3.2490	5.2050	1.6020	47.5828	25.71
x=0.06	3.2493	5.2055	1.6020	47.5874	22.27
x=0.09	3.2490	5.2050	1.6020	47.5828	19.31

PowderX diffraction refinement program. No significant change in the values of lattice parameters 'a' and 'c' is observed with the variation of (Co/Ni) doping as the total concentration of (Co/Ni) is kept at 10%. Furthermore, the values of lattice parameters for all the samples are close to the standard values of ZnO lattice parameters. The result is consistent with the fact that the ionic radii of Co²⁺ (0.72 Å) and Ni²⁺ (0.69 Å) are close to that of Zn²⁺ (0.74 Å). The XRD results indicate that the Co²⁺ and Ni²⁺ ions are incorporated into the ZnO lattice and replace Zn²⁺ sites without changing the wurtzite structure. The size of nanoparticles has been calculated using Debye–Scherer's formula

$$D = 0.9\lambda/\beta\cos\theta$$

(1)

where *D* is the diameter of the nanoparticles, λ is the wavelength of X-ray (1.54178 Å), θ is the Bragg angle and ß is the line broadening at the full width and half maxima (FWHM) on the highest peak of plane (101), which is at ~2 θ =36.27°. The average of nanocrystalline size is found to be 19.31–25.71 nm. The cluster and secondary phases are a concern in any DMS system as a source of magnetism. The NiO can be considered as an extrinsic magnetic source, but it is AFM and no Co metallic cluster or CoO is detected in all the samples within the sensitivity of the present XRD technique.

3.2. Optical absorption spectra

Ultraviolet-visible (UV-vis) optical absorption spectra have been recorded at room temperature in the wavelength range of 250–800 nm as shown in Fig. 2. Redshift in the absorption edge is observed in the samples with the variation of the Co/Ni dopants. The direct band gap energy (E_g) is calculated using the Tauc equation

$$(\alpha hv)^2 = B(hv - E_{\sigma})^{1/2}$$
⁽²⁾

where hv is the photon energy, α is the absorption coefficient and *B* is a constant. The $(\alpha hv)^2$ plotted as a function of hv is displayed in Fig. 3. Values of E_g are obtained by extrapolating the straight line down to $(\alpha hv)^2 = 0$ and are found to vary from 3.22 to 3.28 eV (Table 2). It is well known that the E_g of pure ZnO is 3.35 eV at 300 K [5,6]. Therefore, the absorption edge of Zn_{0.9}Co_{0.1}O (x=0.0) sample shifts towards lower energy ~ 3.28 eV (Redshift). This shows that the Co²⁺ ions have got incorporated into the lattice structure of ZnO. This is interpreted as mainly due to the sp-d exchange interactions between the band electrons and the localized d electrons of the Co²⁺ ions that are substituting Zn²⁺ ions [17].



Fig. 2. Room temperature optical absorption spectra of $Zn_{0.9}Co_{0.1-x}Ni_xO$ (x=0.0, 0.03, 0.06 and 0.09) samples.

The exchange interactions between s–d and p–d orbitals give rise to a negative and a positive correction to the conduction band and valence band edges, respectively, resulting in a decrease in band gap [17,18]. By increasing Ni and decreasing Co dopants, the band gap energy varies and becomes less than that of pure ZnO (Table 2). This reveals that the Ni and Co ions are incorporated into the lattice sites. A direct–indirect transition has been proposed by Rakhshani et al. [19] to explain the band gap narrowing effect. Many groups have suggested that the alloying effect of parent compound with some impurity phases may be responsible for the band gap narrowing [20].

3.3. FTIR spectra

Fourier transform infrared (FTIR) spectra were recorded in the range of 400–4000 cm⁻¹ for all samples. Fig. 4 displays the FTIR spectra for the two extreme (x=0.0 and 0.09) samples. Inset of Fig. 4 shows the enlarged view of spectrum of x=0.9 sample between 400 and 600 cm⁻¹. The distinct absorption band for ZnO appears around 464 cm⁻¹. The position and number of absorption bands not only depend on crystal structure and chemical composition but also on particle morphology [21,22]. Studies concerned with this morphology dependency have shown that in case of spherical ZnO particles, calculated as well as measured spectra show one distinct absorption peak around 464 cm⁻¹ [23]. Reference spectra of ZnO powders often

Table 2

Band gap energy and magnetization parameters of $Zn_{0.9}Co_{0.1-x}Ni_xO$ (x=0.0, 0.03, 0.06 and 0.09) samples.

Samples	Band gap energy (eV)	<i>H_C</i> (emu/g)	M_R (emu/g)	<i>M_s</i> (emu/g)	$M_R/M_S(\%)$
x=0.0 x=0.03 x=0.06 x=0.09	3.28 3.26 3.22 3.25	53.80 70.78 59.79 78.61	$\begin{array}{c} 2.87 \times 10^{-4} \\ 15.7 \times 10^{-4} \\ 3.5 \times 10^{-4} \\ 3.65 \times 10^{-4} \end{array}$	$\begin{array}{c} 14.7\times10^{-3}\\ 14.9\times10^{-3}\\ 1.36\times10^{-3}\\ 8.1\times10^{-3} \end{array}$	1.9 10.5 25.7 4.5



Fig. 3. The $(\alpha h v)^2$ versus. binding energy plots for $Zn_{0.9}Co_{0.1-x}Ni_xO$ samples with x=0.0 (a), 0.03 (b), 0.06 (c) and 0.09 (d). The band gap energy (E_g) is determined by extrapolating the straight line and taking the intersection with x-axis.

demonstrate two absorption maxima at \sim 512 and \sim 406 cm⁻¹ [24]. In the present investigation, FTIR spectra of the samples illustrate the characteristic peaks in the range of 420–620 cm⁻¹ (inset of Fig. 4) and corresponding to the stretching vibration modes of ZnO [25]. The Zn–O stretching mode appears at 425 cm⁻¹, indicating that the transformation from zinc nitrate to zinc oxide is completed in the samples annealed at 500 °C. The bands occurring near 762 and



Fig. 4. FTIR spectra of $Zn_{0.9}Co_{0.1-x}Ni_xO$ (x=0.0 and 0.09) samples in the wave number range of 400–4000 cm⁻¹. The inset shows the absorption peaks for ZnO in the range of 400–600 cm⁻¹.

832 cm⁻¹ are attributed to the vibrations of ZnO–Ni local bonds and defect states respectively. Absorption bands observed in the ranges of 600–680 and 430–470 cm⁻¹ are attributed to the stretching modes of ZnO [26–28] in the tetrahedral and octahedral coordination, respectively. The gradual shift in the absorption frequency with different Co/Ni doping is caused by the difference in the bond lengths that occurs when Co²⁺ and Ni²⁺ ions replace Zn²⁺ ions, and confirm the incorporation of Co and Ni into ZnO lattice structure.

3.4. X-ray photoelectron spectra

The XRD patterns exclude the formation of secondary phases in samples except minor NiO phase at high Ni concentration. However, the nano-clustering of Ni and Co atoms are considered as a source of magnetization. Therefore, XPS study was performed on the sample with x=0.03 ($Zn_{0.9}Co_{0.07}Ni_{0.03}O$). The XPS aims to investigate the oxidation states of ions present in the sample. The peaks of Zn in XPS spectrum are shown in Fig. 5(a). The two peaks are located at 1024.5 and 1047.7 eV, which correspond to the binding energy of core levels $2p_{3/2}$ and $2p_{1/2}$, respectively. The energy difference is 23.2 eV, which coincides with the findings for Zn^{2+} bound to oxygen in the ZnO matrix [29]. The oxygen 1s spectrum shows only a single peak that can be fitted into two Gaussian peaks having different binding energy positions (Fig. 5b). The peak centered at 530.97 eV (the lower binding energy) in the O 1s spectrum is attributed to O^{2-} ions on wurtzite structure of hexagonal ZnO [30]. The peak centered at 532.31 eV (the higher binding energy) is associated with O^{2-} ions in the oxygen deficient regions within the matrix of ZnO [30]. This indicates



Fig. 5. XPS spectra of Zn_{0.9}Co_{0.07}Ni_{0.03}O sample for (a) Zn, (b) O 1s with two Gaussian peaks, (c) Co and (d) Ni.

that there are some oxygen vacancies in the sample [31]. The valence states of cobalt in the system are shown in Fig. 5(c). The Co 2p peaks are located at ~782.36 eV for $2p_{3/2}$ and at ~797.75 eV for $2p_{1/2}$ electrons. Lakshmi et al. [32] have reported the value of difference in binding energy to be ~15.05 eV for pure Co metal and 15.5 eV for Co²⁺ ions. For the present sample, the energy difference is found to be ~15.39 eV which is close to that of Co²⁺. Therefore, we suggest that the Co ions exist in the +2 valence state within the matrix of ZnO. Neither Co cluster metal nor CoO was detected, within the resolution of the technique. XPS spectra of Ni $2p_{3/2}$ and Ni $2p_{1/2}$ in the Zn_{0.9}Co_{0.07}Ni_{0.03}O nanocrystalline powder is displayed in Fig. 5(d). The peak of Ni $2p_{3/2}$ is located at 855.4 eV which is associated with Ni²⁺ ions in the sample [33]. It indicates that the Ni²⁺ ions are substituted for the Zn²⁺ ions in the ZnO lattice.

3.5. Magnetic properties

Fig. 6 illustrates the magnetization versus applied magnetic field (*M*–*H*) curves of $Zn_{0.9}Co_{0.1-x}Ni_xO$ (x=0.0, 0.03, 0.06 and 0.09) samples at room temperature. The inset of Fig. 6 displays the



Fig. 6. *M*-*H* curves for $Zn_{0.9}Co_{0.1-x}Ni_xO$ (*x*=0.0, 0.03, 0.06 and 0.09) samples at 300 K. The inset shows the clear hysteresis as well as H_c and *M*_R for the sample of *x*=0.06. Other samples also show similar behavior.

hysteresis curve for x=0.06 sample. All other samples show similar behavior. The hysteresis loops indicate that all samples have weak RTFM. For the sample of x=0.0 (Zn_{0.9} Co_{0.1}O), the observed H_C is ~53.80 Oe, the remanent magnetization M_R is \sim 2.87 \times 10⁻⁴ emu/g and the saturation magnetization $M_{\rm S}$ is ~ 14.7 × 10⁻³ emu/g at 10 KOe. For $Zn_{0.9}Co_{0.07}Ni_{0.03}O$ (x=0.03) sample, the magnetization increases as compared to x=0 sample and shows very clear hysteresis loop. This can be attributed to the reduction of AFM interaction between Co^{2+} and Co^{2+} ions. The codoping of Ni ions in the samples effectively hampers the formation of metallic clusters, suggesting that it mediates the distribution of Co^{2+} ions in the ZnO host. The samples with x=0.06 and 0.09 show a decrease in magnetization where an appearance of NiO secondary phase is observed (Fig. 1). The bulk NiO is antiferromagnetic with a Neel temperature (T_N) of ~520 K [17] and the nanaocrystalline NiO shows weak ferromagnetic or super-paramagnetic (SPM) behavior at low temperature [18].

Fig. 7a and b illustrates M-T curves for samples of x=0.0 and 0.06, respectively, during zero-field cooling (ZFC) and field cooling (FC) modes in an applied magnetic field of 1000 Oe. The insets demonstrate the inverse magnetic susceptibility (χ^{-1}) plotted as a function of temperature (T). The ZFC and FC curves do not show ferromagnetic transition in the temperature range of 10-300 K. The magnetization increases with the decrease in T and the rapid increase occurs below 60 K. This behavior is similar to paramagnetic one. However, the remanent magnetization at room temperature and the rapid increase of magnetization at low temperature can be considered as ferromagnetic properties. No difference between ZFC and FC in sample of x=0.0 is observed (Fig. 7a), while the sample with x=0.06 (Fig. 7b) displays small disparity between ZFC and FC curves which indicates the presence of antiferromagnetic properties. Inverse magnetic susceptibility (χ^{-1}) is given by

$$\chi^{-1} = (T - \theta)/C \tag{3}$$

where *T* is the absolute temperature, θ is the Curie–Weiss temperature and *C* is the Curie constant. The linear fit of the $(\chi^{-1}-T)$ curves show negative Curie–Weiss temperature ($\theta \sim -62$ and -174 K for x=0.0 and 0.06 respectively). The negative value of θ is usually observed in the case of local atomic antiferromagnetic interaction. However, the magnetization does not become zero and the hysteresis loop shows FM at room temperature.



Fig. 7. *M*–*H* curves for x=0.0 (a) and 0.06 (b) samples in zero-field cooling (ZFC) and field cooling (FC) modes at a magnetic field of 1000 Oe. The insets show inverse of magnetic susceptibility ($1/\chi$ =*H*/*M*) versus temperature from 10 to 300 K.

This may be interpreted as an indication that only minor Co spins are ferromagnetically coupled and the predominant Co spins remain uncoupled or even antiferromagnetically coupled [34]. Effective magnetic moment μ can be calculated from the molar magnetic susceptibility as given by

$$\gamma = N\beta^2 \mu^2 / 3kT \tag{4}$$

where β is the Bohr magneton and *k* is Boltzmann's constant. *N* is the number density of doping ions. Substituting the values of *N*, β and *k*, we may get μ as

$$\mu = 2.827(\chi T)^{1/2} = 2.827 C^{1/2} \mu_{\rm B}$$
(5)

where the Curie constant *C* can be obtained from the slope of χ^{-1} versus. *T* curves using Eq. (3). The calculated value of μ for sample of x=0.0 is found to be 2.47 μ_B which is smaller than the value of spin magnetic moment of Co²⁺ ions (~3.87 μ_B) in tetrahedral symmetry. It confirms that all Co ions do not contribute to the magnetization of the sample. For x=0.06 sample, the value of μ is 2.39 μ_B which is also smaller than the effective magnetic moment of Co²⁺ (~3.87 μ_B) and Ni²⁺ (~2.83 μ_B).

Though the secondary phases are a concern in any DMS system as a source of spurious magnetic signals, the origin of ferromagnetism in the present system cannot be attributed to the formation of secondary phases. The possible secondary phases may be Co metallic cluster, CoO or NiO. But CoO and NiO are antiferromagnetic with small positive susceptibility having $T_N \sim 293$ and ~ 520 K, respectively. The Co metallic cluster can provide the dominant source of the ferromagnetism [35]. However the XRD and XPS data do not support the presence of Co metal in the samples within the sensitivity of XRD and XPS. Therefore, the possibility of ferromagnetism due to Co metallic cluster can be ruled out in the present study.

The weak RTFM cannot be explained by Ruderman-Kittel-Kasuya-Yosida (RKKY) theory [36]. According to this theory, the magnetization is due to exchange interaction between local spinpolarized electrons of Co²⁺ ions and conduction electrons. The interaction leads to the spin-polarization of conduction electrons. Subsequently, the spin-polarized conduction electrons perform an exchange interaction with local spin-polarized electrons of other Co²⁺ ions. Consequently, the long-range exchange interactions lead almost to all the Co^{2+} ions to have same spin direction. The conduction electrons act as media for the interaction among the Co^{2+} ions, where the free carrier is a necessary condition for the appearance of ferromagnetism. But for confirming the existence of free carriers we have studied the resistivity of the samples which is found to be very high ($\sim 10^5 - 10^7 \,\Omega \,\text{cm}$). This indicates to a very low carrier concentration in the present samples. A defect mediated ferromagnetism model based on the bound magnetic polaron (BMP) theory has been predicted theoretically [37,38] and confirmed experimentally [39,40]. For instance, surface defects have been implicated to be essential for the generation of ferromagnetism in DMS oxide [39,41]. In the present study, the oxygen vacancies have been detected by XPS and would likely be generated on the surfaces of the nanoparticles. According to BMP theory, when the concentration of surface defects exceeds the percolation threshold, the surface defects can overlap many dopant ions as well as adjacent defects, inducing a ferromagnetic coupling between dopant spins. Thus, we can speculate that the Co ions at surface of the nanoparticles can be ferromagneticlly coupled and mediated by oxygen vacancies. If the ferromagnetism arises from the surface of Co^{2+} ions, only a few of them may contribute to the ferromagnetism because most of the Co^{2+} ions reside in the core of the nanoparticles. However, due to the insufficiency of oxygen vacancies in the core of the nanoparticles, these Co²⁺ spins are distributed as uncoupled spins or mediated through oxygen ions [34,42]. The enhancement in magnetization by codoping of Ni and Co may be due to Ni-induced acceptor state localized within the gap region, which reduces the acceptor mobility. Oxygen vacancies (V_0) have also been proposed to play a significant role for the origin of ferromagnetism in oxide DMS [38]. An electron locally trapped in V_0 occupies an orbit and overlaps the d shells of Co^{2+} neighbors. This has an important role in the spin orientations of neighboring Co^{2+} ions. Based on the Hund's rule and Pauli's exclusion principle, spin orientations of trapped electrons and neighboring Co^{2+} ions should be parallel in the same direction and the ferromagnetism should be achieved. More oxygen vacancies lead to more $Co^{2+}-V_0$ – Co^{2+} groups, which increases the ferromagnetism in the system [43].

4. Conclusion

Nanoparticles of Zn_{0.9}Co_{0.1-x}Ni_xO (x=0.0, 0.03, 0.06 and 0.09) DMS were synthesized by sol-gel method with annealing temperature of 500 °C. XRD pattern reveal that all investigated samples are nanocrystalline powder of hexagonal wurtzite structure (space group P6₃mc). The average of nanoparticles size is 19.31-25.71 nm. FTIR and UV-vis spectroscopic data show the evidence for the incorporation of Co^{2+} and Ni^{2+} ions into the nonmagnetic host of ZnO lattice without any modification in the structure. The band gap energy decreases with the increase of Ni and decrease of Co dopants concentration. The RTFM has been presented in terms of vacancy in the frame of BPM model, where the Co ions at surface of the nanoparticles can be ferromagnetically coupled and mediated by oxygen vacancies. Because of low carrier concentration in the system, we cannot use the RKKY theory to explain the RTFM. As there is no Co metallic cluster in the present DMS, the cluster as source of ferromagnetism is ruled out.

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