



Effect of Co and Ni codoping on the structural, magnetic, electrical and optical properties of ZnO



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ARTICLE INFO

Article history:

Received 17 March 2015

Received in revised form 19 July 2016

Accepted 24 July 2016

Available online 26 July 2016

Keywords:

Oxides

Magnetic properties

Raman spectroscopy

Crystal structure

ABSTRACT

Co and Ni codoped ZnO-based dilute magnetic semiconductors having a general formula of $\text{Zn}_{0.9}\text{Co}_{0.1-x}\text{Ni}_x\text{O}$ ($x = 0.0, 0.02, 0.04, 0.06, 0.08$ and 0.10) have been prepared using a simple solid-state reaction method. A single-phase hexagonal wurtzite structure, confirmed by X-ray diffraction, has been developed for $\text{Zn}_{0.9}\text{Co}_{0.1-x}\text{Ni}_x\text{O}$ ($x < 0.05$), while minor secondary peaks of NiO were detected in samples having $x = 0.06, 0.08$ and 0.10 . The study of surface morphology revealed grain sizes in the range of 1.41 – 0.71 μm . Raman spectra in the 200 – 800 cm^{-1} range have been studied. The direct band gap energy for all the samples was found to be less than that of pure ZnO. Fourier transform infrared spectroscopy and UV–vis spectroscopy confirmed the incorporation of the Co and Ni ions into a ZnO lattice. Magnetic characterisation performed by vibrating sample magnetometer exhibited room-temperature ferromagnetism. Temperature-dependent electrical resistivity measurements were performed using a four-point probe technique.

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1. Introduction

Doping of magnetic ions into a semiconductor matrix introduces significant changes in magnetic, structural and electrical properties, resulting in the evolution of dilute magnetic semiconductors (DMSs). Electronics, based upon charge and spin degree of freedom, is the main objective of spintronic devices [1]. Among II–VI compounds, ZnO is an attractive semiconductor, due to large band gap (3.35 eV) at room temperature, hardness, chemical stability and suitable piezo-electric properties [2,3]. ZnO-based DMSs are formed by the substitution of cations of the host ZnO with a small amount of transition metals like Fe, Co, Ni and Mn [4]. In oxide-based semiconductors, the origin of ferromagnetism has been a controversial topic [5], hence there is a need to look through systematic structural, magnetic and electrical properties that can help in investigating the origin of ferromagnetism in these materials. It is found that the Curie temperature (T_c) of transition metal doped ZnO can be increased by doping the species, which results in additional carrier concentration [6,7]. Furthermore, in the co-doped Zn(Co–Cu)O, Cu^+ ion

behaves as a superexchange mediator [8]. On the other hand, (Zn, Ni)O and (Zn,Co)O have been investigated as favourable ferromagnetic materials with a high T_c [9].

Another advantage of using ZnO-based DMS materials is that the electrical resistivity of these materials can be tuned through the incorporation of foreign impurities like Co and Ni, which makes ZnO one of the most intriguing electronic materials among all crystalline semiconductors. Co being a shallow level donor impurity introduces energy levels near the valence or conduction band that can be ionised easily using less thermal energy. On the other hand, Ni is a deep-level impurity. It introduces energy levels deep within the forbidden gap of ZnO that act as traps for charge carriers [10]. Hence, the combination of both these impurities introduces fascinating electronic properties in such types of ZnO-based DMS materials, which are quite beneficial for spintronic applications.

In this context, the present work focuses on the codoping of Co/Ni in the host ZnO, in order to investigate its structural, magnetic, optical and electrical properties. The ionic radii of Ni^{2+} and Co^{2+} are comparable to that of Zn^{2+} , hence a comfortable adjustment of the dopant ions at the host sites is expected, resulting in a significant effect on the magnetic, optical and electrical properties without much effect on the structural

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parameters. Hence, a series of samples with composition of $\text{Zn}_{0.9}\text{Co}_{0.1-x}\text{Ni}_x\text{O}$ ($x=0.0, 0.02, 0.04, 0.06, 0.08$ and 0.1) were prepared using a simple solid-state reaction method. The crystal structure was determined using a Bruker D-8 Discover X-ray diffractometer (XRD). Lab Ram HR800 Horiba France was utilised to perform Raman spectroscopy, using a 632.8 nm helium neon laser. Chemical bonding between the dopant and the host species was analysed using Raman spectroscopy and a MIDAC 2000 (USA) Fourier transform infrared spectroscopy (FTIR). A Hitachi (Japan) UV2800 UV–vis spectrophotometer, having a wavelength range of 300–900 nm, was employed to determine the energy band gap of the prepared samples. Temperature-dependent electrical properties were determined by a four-probe technique using Keithley's 6221-2182A, interfaced with LabView. Structural morphology was investigated using a Hitachi S-3400N scanning electron microscope (SEM). Magnetic characterisations were performed using a Lakeshore 7436 vibrating sample magnetometer (VSM).

2. Experimental method

A series of samples having the general formula $\text{Zn}_{0.9}\text{Co}_{0.1-x}\text{Ni}_x\text{O}$ ($x=0.0, 0.02, 0.04, 0.06, 0.08$ and 0.1) was prepared by a solid-state reaction method [11], as shown by the flow chart in Fig. 1, using analytically pure ACS reagents from Sigma-Aldrich, such as ZnO, CoO and NiO. Stoichiometric amounts of these oxides were weighed using a precise digital balance and mixed thoroughly using a ball mill (Pulverisette 23, Fritsch, Germany) for 40 min at 300 rpm to get homogeneous micro-sized particles. These ball-milled powders were then sieved by a mechanical sieve shaker. Ball-milled powders were calcined for 16 h at 1050 °C in a Lindberg USA blue M. BF51524C furnace. The calcined powders were homogenised using an Agate mortar-pestle and then pressed under a pressure of 4 tonnes for 5 min to make pellets with 13 mm diameters using a hydraulic press (Carver, USA). The pellets were sintered at 900 °C for 10 h in a muffle furnace before characterisation. A solid-state reaction method was chosen because it is simple and economic and allows chemical reactions without the presence of solvents.

3. Results and discussion

Fig. 2(a) shows the XRD patterns of $\text{Zn}_{0.9}\text{Co}_{0.1-x}\text{Ni}_x\text{O}$ ($x=0.0, 0.02, 0.04, 0.06, 0.08$ and 0.1) obtained at room temperature using Cu $K\alpha$ radiations with a wavelength of 1.5406 Å. The plots reveal that samples up to $x=0.04$ exhibited the formation of phase pure compositions, as all the peaks present in these patterns were matched perfectly with ICSD code no. 01-075-0576, characteristic of hexagonal wurtzite structure as that of pure ZnO. Hence, it is

inferred that up to 6% Co and 4% Ni ions were successfully incorporated into the host ZnO matrix. However, when the Ni contents were raised to 6% or more, a few impurity peaks related to NiO appeared, as confirmed by ICSD code no. 01-075-0272. The reason behind the appearance of these secondary peaks could be attributed to the excessive amount of Ni^{2+} , resulting in unreacted NiO contents thus limiting the dissolution of Ni in ZnO above 5% [12].

Lattice parameters a and c of the hexagonal structure were evaluated using the procedure described by Cullity by using Eq. (1):

$$\sin^2\theta = \frac{2}{4a^2} \left[\frac{4}{3}(h^2 + hk + k^2) + \frac{l^2}{(c/a)^2} \right] \quad (1)$$

Here λ is the wavelength ($\lambda=0.154$ nm) of Cu $K\alpha$ radiations used for diffraction and hkl are the Miller's indices of the corresponding planes. It was found that both a and c decreased with the increase in Ni concentration, as listed in Table 1 and plotted graphically in Fig. 2(b). The decrease in these parameters could be attributed to the smaller ionic radius of Ni^{2+} (0.69 Å) than that of Co^{2+} (0.745 Å).

The crystallite size was calculated using Scherrer's formula [13], given as follows:

$$\text{Crystallite size} = k\lambda/B\cos\theta \quad (2)$$

where B is full width at half maximum (FWHM), θ is Bragg's angle in radians and $k=0.94$. The average crystallite of all the samples was determined to be in the range of 44.2–44.4 nm.

SEM images revealing the structural morphology of $\text{Zn}_{0.9}\text{Co}_{0.1-x}\text{Ni}_x\text{O}$ ($x=0.0, 0.02, 0.04, 0.06, 0.08$ and 1.0) are shown in Fig. 3. The micrographs reveal a high crystallinity of samples with well-defined grain boundaries. The average grain size was in the 1.41–0.77 μm range as estimated by the line intercept method. It was observed that average grain size decreased as x varied from 0.0 to 1.0 in the series of samples, as listed in Table 1. The large values of grain sizes depict that each grain consists of a number of crystallites, as determined by Scherrer's formula using the data obtained from X-ray diffraction [14,15].

The Raman spectra of all samples were obtained from a standard helium neon laser ($\lambda=514$ nm) in the range of 200–800 cm^{-1} , as shown in Fig. 4, to study the effect of Ni doping in $\text{Zn}_{0.9}\text{Co}_{0.1-x}\text{Ni}_x\text{O}$ DMSs. The vibrational modes present in ZnO systems are given in Eq. (3) [16]:

$$\Gamma_{\text{opt}} = A_1 + 2B_1 + E_1 + 2E_2 \quad (3)$$

In this relation, optical phonons A_1 and E_1 split into A_{1L} and E_{1L} (longitudinal-optical) and A_{1T} and E_{1T} (transverse-optical) modes. E_2 mode has E_{2L} and E_{2H} , i.e., low- and high-frequency phonons [17]. The spectra reveal that all the modes present are associated with the ZnO. The most intense peak E_2 (high) was present at 437 cm^{-1} , while A_1 (TO) was at 380 cm^{-1} and E_2 (high)- E_2 (low) was at 330 cm^{-1} . E_2 (high) is known as the Raman optical active phonon mode that is a characteristic of the wurtzite hexagonal phase, known as the fingerprint of ZnO.

An additional mode is also appeared at 500–600 cm^{-1} which is attributed to Zn(TM)O. It was observed from the spectra that as the concentration of Ni increased from 0 to 0.8, the optical phonon mode present at 460 cm^{-1} , due to the presence of cobalt, gradually lessened in intensity, [18,19]; however, in the last sample, when Ni completely substituted the Co ions in the ZnO matrix, this mode was gone. On the other hand, the intensity of the most prominent peak E_2 in ZnO, whose modes are almost same as those of Ni, was enhanced sharply. This shows that NiO was chosen in order to provoke the migration of interstitial Ni, resulting in an improved crystallinity of Zn(Co)O. However, a broad FWHM of the E_2 (high) mode could be attributed to the presence of CoO, affecting the crystallinity of ZnO. It was attributed to the presence of disorder in

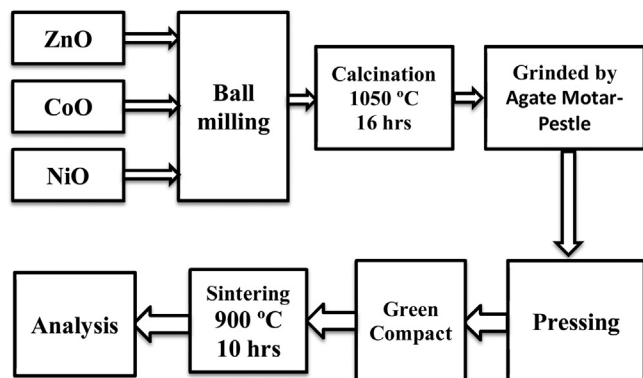


Fig. 1. Flow chart of powder metallurgy route to synthesize Co/Ni co-doped ZnO DMSs.

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