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A Room-Temperature and Microwave Synthesis of M-Doped ZnO (M = Co, Cr, Fe, Mn & Ni)

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A room temperature and microwave method for the preparation M-Doped ZnO, where M = Co, Cr, Fe, Mn & Ni, is described. X-ray diffraction of the synthesized samples shows a single phase ZnO structure without any indication of the dopant. Magnetic studies of the as prepared samples show it to be paramagnetic. However, hydrogenation of particular samples at 573 K for 6 h resulted in transforming the samples to a room temperature ferromagnet.

KEY WORDS: Microwave; ZnO; magnetism.

INTRODUCTION

Development of new applications for zinc oxide (ZnO) has been an integral part of research for the last decade. Current applications for zinc oxide include catalysis, cosmetics, and optical devices [1–3]. Recently, Co, Mn and Ni doped ZnO have been investigated for possible applications as spintronic materials [4–11]. Synthesis of these materials is often accomplished by sputtering, chemical vapor deposition and sol–gel techniques. In most of these methods, the nature of the produced material is amorphous and an additional high-temperature processing step is required in order to obtain crystallinity. However, high temperature processes can lead to significant side-effects such as the formation of multiple phases.

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This paper will focus on the formation and characterization of 5% Mdoped zinc oxide (M = Co, Cr, Fe, Mn and Ni) using room temperature and microwave syntheses. It is significant to note, that microwave irradiation has several advantages over conventional methods including short reaction time, small particle size, narrow size distribution, and high purity [12–21]. The synthesis and magnetic properties of these samples will be discussed.

EXPERIMENTAL

Room-temperature Synthesis

A 1 M solution of zinc nitrate solution (Aldrich 99%) was reacted with a 3 M aqueous solution of NaOH so that the final pH of the solution was 12. The reaction mixture was left overnight and the precipitate allowed to settle. The clear solution was removed and replaced with water, stirred, and left for 3–5 h. This process was repeated until the pH of the solution was 7. Finally, the precipitate was dispersed in ethanol and dried under vacuum. For doping, the appropriate amounts of indicated metal nitrate (specifically $Co(NO_3)_2$, $Cr(NO_3)_3$, $Fe(NO_3)_3$, $Mn(NO_3)_2$ and $Ni(NO_3)_2$) were added to zinc nitrate solution until the concentration of the dopant was 5%. According to the following equations, a zinc hydroxy nitrate complex is first precipitated and then slowly transformed into ZnO, NaNO₃ and water according to the following equations. The NaNO₃ was removed by washing the sample with water.

$$Zn(NO_3)_2 + NaOH \rightarrow Zn(NO_3)(OH) + NaNO_3$$
 (1)

$$Zn(NO_3)(OH) + NaOH \rightarrow ZnO + NaNO_3 + H_2O$$
 (2)

Microwave Synthesis

Synthesis of ZnO was achieved by dissolving approximately 4 g of zinc nitrate (Alfa Aesar) in ethanol. While stirring, 10 ml of 10 N NaOH (Alfa Aesar) was added dropwise. Finally, 2 g of polyethyleneglycol MW ~2000 (Avocado) was added. The resulting solution was then placed in a conventional microwave. The microwave power was set to 33% of 650W and operated in 30 second cycles (on for 10 s off 20 s) for 10 min. The resulting powder was washed with ethanol, distilled water, and acetone and left to dry. M-doped ZnO (M=Co, Cr, Fe, Mn & Ni) was prepared as above, but with the addition of the appropriate amounts of the metal nitrate mixed with the zinc nitrate solution until the concentration of the dopant was 5%.

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Part of the powder was used for magnetic measurements and the remaining used for 3 and 6 h of hydrogenation carried out at 573 K. The hydrogen reduction setup consisted of a tube furnace kept inside a continuously vented hood. The sample, in an open glass boat, was placed inside the furnace. Hydrogen gas was passed over the sample at 573 K with the help of a gas flow control unit.

The X-ray diffraction patterns (XRD) patterns of the powder sample were measured at room temperature with a Rigaku Diffractometer (DMAX-B) and CuK_{α} radiation (λ =1.5418 Å). The samples were mounted on a silicon plate for X-ray measurements. Temperature and magnetic field variations of the magnetization (*M*) of these samples were then measured using a commercial superconducting quantum interference device magnetometer (SQUID). The EMR studies were carried out at frequency f=9.28 GHz using a standard reflection-type spectrometer and a commercial variable temperature cryostat.

RESULTS AND DISCUSSION

Room-temperature Synthesis

Recently, we have developed a simple room temperature synthesis of pure and 10% Co-doped crystalline ZnO nanoparticles by a room temperature sol-gel method [22]. X-ray Fluorescence (XRF) measurements determined that the amount of cobalt doped in ZnO was 10.4%. XRD analysis show an excellent match with zincite without any impurity peaks for Co indicating a perfect doping of Co into the ZnO lattice. Micro Raman analysis reveal that the $2E_2$ modes appearing at 101 cm⁻¹ has been downshifted to 97.4 cm⁻¹ and the peak at 437 cm⁻¹ also down shifted for 10% doped Co spectra when compared to pure ZnO. Moreover, the intensity of the peak at 437 cm^{-1} is significantly reduced and broadened. These observed features are clearly related to the doped Co in the lattice. Magnetic studies of the as-prepared 10% Co/ZnO sample show it to be paramagnetic. The temperature variation of the magnetic susceptibility γ for the as-prepared (10% Co doped ZnO) sample (prior to hydrogenation) was fit to the Curie–Weiss law: $\chi = \chi_0 + C/(T - \theta)$. From the Curie-constant $C = 3.1 \times 10^{-3}$ emu-K/gOe and $C = N\mu^2/3k_B$ (with N being the number $k_{\rm B} = {\rm Boltzmann}$ ions/g. constant and u = magneticof magnetic moment), $\mu = 4.465 \mu_B$ for the Co²⁺ ion is obtained. This magnitude of μ is consistent with the high spin state of Co^{2+} , assuming that Co^{2+} substitutes for the Zn^{2+} . However, hydrogenation of the sample at 573 K for 6 h changes the sample to a room temperature ferromagnet.

Figure 1, specifically 5% Co/ZnO, is representative of the XRD patterns for the as-prepared M-doped samples. It is significant to note that only ZnO is observed (matching with zincite (PDF 36-1451) without any trace of the dopant or its respective oxide. The broad peaks observed in the XRD pattern are indicative of small particles. TEM, as shown in Fig. 2, reveals that the average particle size of the ZnO phase ranges from 20-70 nm. As shown previously, as-prepared 10% Co/ZnO displays paramagnetic behavior. Upon hydrogenation of the sample at 573 K. ferromagnetism is induced at room temperature. It has been reported that oxygen vacancies are essential to provide the exchange coupling between cobalt ions, ultimately leading to intrinsic room temperature ferromagnetism (RTFM) [13]. Hydrogenation was carried out for the 5% M-doped ZnO at 573 K. However, XRD reveals that only cobalt (Fig. 1) and chromium samples show a single phase of ZnO after hydrogenation compared to the XRD of Fe and Mn doped ZnO which show the presence of metallic peaks (Fig. 3 top and bottom respectively). While the peak for



Fig. 1. X-ray diffraction patterns of the as-prepared sample of 5% Co/ZnO (a) and hydrogenated at 573 K for 3 (b) and 6 h (c) prepared by room temperature synthesis matching with the zincite phase (PDF 36–1451).



Fig. 2. TEM micrograph representative of M-doped ZnO. The scale bar is 50 nm.

Fe matches exactly with the reference pattern, the peak for Mn is slightly shifted. However, the most intense peak for Mn (43.0 2 θ) matches the observed peak (~42 2 θ) when compared to those of MnO, Mn₂O₃ and Mn₃O₄. The results of the observed phases are presented in Table I.

Figure 4, specifically 5% Co/ZnO, is representative of the temperature variation of the magnetic susceptibility (χ) for the as-prepared where the solid line is fit to the Curie-Weiss Law. The results for the as-prepared samples and those for the samples that retain their paramagnetic character are reported in Table II. For simplicity, the samples that display additional phases after hydrogenation are not reported (specifically, Fe and Mn doped ZnO prepared via room temperature synthesis and Ni doped ZnO prepared by both methodologies). It is significant to note that the 5% Cr/ZnO sample retains its paramagnetic behavior even after hydrogenation at 573 K for 6 h. The as-prepared sample of 5% Co/ZnO displays paramagnetic behavior, but after hydrogenation for 3 h at 573 K, the sample displays room temperature ferromagnetism as indicated by the observed hysteresis for the M vs H spectra. The remanance (M_r) and coercivity (H_c) data for the hydrogenated samples displaying ferromagnetism are shown in Table III. The temperature variation of the magnetic susceptibility and the M vs Hdata is also indicative of RTFM for the sample hydrogenated for 6 h as shown in (Fig. 5a) and (Fig. 5b).



Fig. 3. X-ray diffraction patterns of the as-prepared sample of 5% Fe/ZnO and 5% Mn/ZnO (a, top and bottom respectively) and hydrogenated at 573 K for 3 h (b). The expected lines for zincite and iron are shown below along with any additional phases observed.

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Sample	As-prepared	Hydrogenated 3 h	Hydrogenated 6 h		
Room temperature synthesis					
Co/ZnO	ZnO	ZnO	ZnO		
Cr/ZnO	ZnO	ZnO	ZnO		
Fe/ZnO	ZnO	ZnO & Fe	ZnO & Fe		
Mn/ZnO	ZnO	ZnO & Mn	ZnO & Mn		
Ni/ZnO	ZnO	ZnO & NiO	ZnO & NiO		
Microwave synthesis					
Co/ZnO	ZnO	ZnO	ZnO		
Cr/ZnO	ZnO	ZnO	ZnO		
Fe/ZnO	ZnO	ZnO	ZnO		
Mn/ZnO	ZnO	ZnO	ZnO		
Ni/ZnO	ZnO	ZnO & NiO	ZnO & NiO		

 Table I. Phases Observed in the XRD Spectra for the as-Prepared and Hydrogenated Samples of 5% M-doped ZnO



Fig. 4. Temperature dependence of the magnetic susceptibility (χ) of the as-prepared 5% Co/ZnO prepared by the room temperature synthesis method. The solid line is fit to the equation shown above.

Microwave Synthesis

Figure 6, specifically 5% Co/ZnO, is also representative of the XRD patterns of as-prepared samples of 5% Cr, Fe, Mn and Ni doped ZnO correspondingly indicating a single phase of ZnO matching with zincite (PDF 36–1451) with no impurity phases of the dopant or their relevant oxides, indicating perfect doping of the metals into the ZnO lattice. It is

Sample	χο	С	θ	
Room temperature synthesis				
As-prepared				
Co/ZnO	1.2×10^{-6}	3.6×10^{-3}	1.6	
Cr/ZnO	1.2×10^{-6}	$2.0 imes 10^{-4}$	2.0	
Hydrogenated 3 h				
Cr/ZnO	1.2×10^{-6}	$2.0 imes 10^{-4}$	2.0	
Hydrogenated 6 h				
Cr/ZnO	2.5×10^{-5}	$2.4 imes 10^{-4}$	1.7	
Microwave synthesis				
As-prepared				
Co/ZnO	1.2×10^{-6}	5.2×10^{-4}	1.4	
Cr/ZnO	$1.4 imes 10^{-6}$	$4.4 imes 10^{-4}$	1.3	
Fe/ZnO	8.3×10^{-4}	3.9×10^{-2}	7.6	
Mn/ZnO	$8.4 imes 10^{-7}$	$7.5 imes 10^{-4}$	6.4	
Hydrogenated 3 h				
Cr/ZnO	9.4×10^{-6}	3.1×10^{-4}	1.2	
Mn/ZnO	5.4×10^{-6}	5.7×10^{-4}	4.5	
Hydrogenated 6 h				
Cr/ZnO	1.4×10^{-5}	3.1×10^{-4}	1.2	
Mn/ZnO	$9.6 imes 10^{-6}$	$6.9 imes 10^{-4}$	2.4	

Table II. Comparison of the Temperature Variation of χ fit the Curie–Weiss Law for the as-Prepared and Hydrogenated Samples

significant to note that XRD indicates that hydrogenation does not affect the composition of the sample, unlike the room-temperature synthesis where only Cr and Co remained doped, except for one case where peaks due to NiO were observed. The results of the XRD analysis indicating the observed phases is also presented in Table I.

The temperature variation of the magnetic susceptibility (χ) for the asprepared samples prepared via the microwave is also represented in Fig. 7 by the 5% Co/ZnO sample. The results of fitting the data fit to the Curie–Weiss Law for the 5% Co, Cr, Mn, Ni and Fe doped ZnO are reported in Table II.

The results of hydrogenating the as-prepared samples can be described as follows: Hydrogenation of 5% Ni/ZnO resulted in the presence of metallic nickel in the XRD pattern as indicated in Table I. However, metallic peaks were not present in the chromium, manganese, cobalt and iron samples after hydrogenation. When hydrogenated for 3 h the chromium and manganese samples still retain Curie–Weiss behavior as shown Table II. The χ vs. *T* measurements for the 3 h hydrogenated samples of cobalt-doped ZnO is shown in Fig. 8a. The absence of a peak in χ for the zero-field-cooled cases, which is a signature of the blocking temperature

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$M_{\rm r}~{ m (emu/g)}$	$H_{\rm c}$ (Oe)
0.26	200
0.47	602
0.10	82
0.18	131
0.37	118
0.11	201
	<i>M</i> _r (emu/g) 0.26 0.47 0.10 0.18 0.37 0.11

Table III.Temperature Variation of the Remanance and the Coercivity Data for 5% Co
and Fe Doped ZnO Hydrogenated for 3 and 6 h at 300 K.

 (T_B) for cobalt, provides assurance that cobalt and iron nanoparticles are not present in our samples. The *M* vs *H* data for this sample indicates a controlled transformation from paramagnetism to room temperature ferromagnetism indicated by the hysteresis loops (shown in Fig. 8b). It is significant to note that the 5% Fe doped ZnO sample also displayed hysteresis after hydrogenation for 3 and 6 h. The remanance (M_r) and coercivity (H_c) data for the hydrogenated Co and Fe doped samples are reported in Table III clearly indicating an increase in ferromagnetism as the time for longer hydrogenation times. However, hydrogenation for 6 h did not alter the paramagnetic behavior observed for the chromium and manganese and continued to display Curie–Weiss behavior (Table II).

One explanation for the observance of metallic peaks for hydrogenated samples of Fe and Mn doped ZnO prepared by room temperature synthesis (that do not appear when the samples are prepared via microwave) can be explained via two different scenarios in which the dopant is incorporated into the zinc oxide lattice as shown in Fig. 9. In both cases the as-prepared samples show only zincite as indicated by XRD. However, it is purposed that hydrogenation of a random distribution of dopant may be different than hydrogenation of a more organized system. Thus, hydrogenation of the organized system may lead to the observance of metallic peaks arising from the dopant due to the close proximity to one another within the lattice. It is also significant to note that Ni doped ZnO prepared by room temperature and microwave syntheses both indicate an organized scenario.

Low temperature (\sim 5 K) EPR derivative spectra of metal (Co, Mn, Fe, Cr, Ni) doped ZnO for both set of samples i.e. RT and MW synthesis have



Fig. 5. Temperature dependence of the magnetic susceptibility (χ) (a) and *M* vs. *H* (b) for 5% Co/ZnO hydrogenated at 573 K for 6 h prepared by the room temperature synthesis method. The inset shows the expanded view.

been taken. For Mn-doped ZnO it is clearly shown the well-resolved hyperfine six-line splitting of EPR line which corresponds to Mn^{2+} ions present in ZnO. Both samples (RT and MW synthesis) give the same EPR pattern. In Co-doped ZnO samples, a broad line at $g \sim 4.3$ is observed at T=10 K which is the characteristic of Co²⁺ ions. The eight-line hyperfine EPR spectra of Co²⁺ is not appearing because of higher cobalt (5%)



Fig. 6. X-ray diffraction patterns of the as-prepared sample of 5% Co/ZnO (a) and hydrogenated at 573 K for 3 (b) and 6 h (c) prepared by microwave synthesis matching with the zincite phase (PDF 36–1451).



Fig. 7. Temperature dependence of the magnetic susceptibility (χ) of the as-prepared 5% Co/ZnO prepared by microwave synthesis. The solid line is fit to the equation shown above.



Fig. 8. Temperature dependence of the magnetic susceptibility (χ) (a) and *M* vs. *H* (b) for 5% Co/ZnO hydrogenated at 573 K for 6 h prepared by microwave synthesis. The inset shows the expanded view.

loading. The interaction between Co^{2+} ions may be the origin of ferromagnetism in this system. In the sample Ni-doped ZnO, a broad line (linewidth $\Delta H = 2500$ Oe) along with a sharp line with g-value g = 2.067 is observed at 5 K. The signature of the sharp line is due to Ni²⁺ and the broad line may be due to NiO nanoparticles. Both the samples give similar results supported by the XRD data. Fe-doped ZnO also gives a broad line



Fig. 9. Two possible scenarios of how the dopant may exist in the lattice.

and along with a indication of a sharp line. The sharp line is due to Fe ions and the broad line may be due to Fe nanoparticles. XRD data confirms this observation. In the Cr-doped ZnO sample a broad and symmetric line with linewidth ΔH =988 Oe and g=2 is observed. This may be due to the presence Cr²⁺.

Thus, the low temperature EPR studies indicate the presence of M^{2+} ions (M=Co, Mn, Fe, Cr, Ni) in ZnO. These ions may be substitutionally incorporated in the interior as well as in the surface region of the ZnO which is confirmed from XRD studies.

CONCLUSION

In conclusion, a straightforward method has been developed for the synthesis of M-doped zinc oxide at room temperature. XRD measurements show the formation of single phase compound without any impurities and the magnetic measurements show that the as-prepared cobalt-doped zinc oxide is paramagnetic. However, hydrogen reduction at 573 K transforms the magnetic nature from paramagnetic to ferromagnetic.

We have also demonstrated a one step synthesis of M doped ZnO nanoparticles via microwave irradiation. To the best of our knowledge this is the first report of a metal being doped into a zinc oxide lattice using microwave irradiation. This method offers extremely short reaction times and produces high purity nanoparticles. The magnetic measurements show

that the as-prepared samples of 5% M doped ZnO are paramagnetic. However, hydrogen reduction at 573 K for the cobalt and iron doped samples transforms the magnetic nature from paramagnetic to ferromagnetic. This method may possibly be extended to synthesize other transition metal doped oxides quickly and efficiently.

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