ISSN : 0974 - 7486 Volume 9 Issue 1

Trade Science Inc.

Materials Science

An Indian Journal

Full Paper

MSAIJ, 9(1), 2013 [24-29]

Magnetic properties and catalytic activity of (Co,Zn)O prepared by self-flash combustion

M.M.Hessien[1,2]

[1]Materials and Corrosion Group, Faculty of Science, Taif University, (SAUDI ARABIA)
[2]Electronic Materials Lab., Advanced Materials Dept., Central Metallurgical Researc and Development Institute (CMRDI), Helwan, Cairo, (EGYPT)
E-mail : hessienmahmoud@yahoo.com

Received: 25th April, 2012; Accepted: 5th October, 2012

ABSTRACT

Spintronics materials, which combine ferromagnetic with semiconductors to take advantage of not only the charge of electrons but their quantum-mechanical 'spin' together, are promising materials. Co-Zn oxide nanoparticles as a diluted magnetic semiconductor (DMS) material is a potential spintronic material and expected to play an important role in magnetic, magneto-optical, and magneto-electric fields. In this study, a self flash combustion method was used to produce Co-Zn oxide nanoparticles. Thermal analysis (TGA and DTA), X-ray diffraction, TEM, and magnetic measurements have been used for characterization of the prepared samples. The influence of the prepared Co-Zn oxide on the degradation of phenol was also studied by using UV/VIS/NIR- spectrophotometer. Results showed that a Co-Zn oxide nanoparticle (77nm) was successfully prepared by a self flash combustion from acetate precursors at low temperature. The values of remnant magnetic flux density (Br), saturation magnetic flux density (Bs) and coercive force (Hc) (measured at 16°C) are 0.03262emu/g, 0.5769emu/g and 83.17Oe respectively. The degradation of phenol containing Co-Zn oxide showed that the concentration of phenol decreased gradually with time and reach to a value near zero at around 67 hours and the degradation of phenol aqueous solution followed first order rate kinetics.

KEYWORDS

(Co,Zn)O;
Spintronics materials;
Diluted magnetic;
DMS;
Phenol;
Catalytic degradation.

INTRODUCTION

Information technology is based on both semiconductor devices making use of the charge of electrons and magnetic materials used for recording applications involving electron spin. For the last two decades, there has been much interest in an innovative technique, now referred to as 'spintronics', which combine ferromagnetic materials with semiconductors to take advantage of not only the charge of electrons but their quantum-mechanical 'spin' together. Diluted magnetic semiconductors (DMS) are therefore extensively studied as potential spintronics materials and expected to play an important role in magnetic, magneto-optical, and magneto-electric fields by realizing new functionality that has not separately existed in magnetic materials or semiconductors[1-4]. Diluted magnetic semiconductors (DMSs), referred to as semiconductor alloys in which magnetic atoms are randomly introduced in the lattice, have attracted much attention as promising materials for spintronics because they have charge and spin degrees of freedom in a single substance[5-6]. The substitution of the cations of III-V or II-VI nonmagnetic semiconductors by magnetic transition-metal ions such as Mn, Fe, and Co allows the existence of charge and spin degree of freedom in a single substance, which leads to a number of magnetic, optical, and magneto-transport phenomena. The development of magnetic semiconductors with practical ordering temperatures could lead to new classes of device and circuits, including spin transistors, and ultradense nonvolatile semiconductors memory[7-12].

Fukumura et al.[4] reported the first successful growth of a ZnO-based DMS by pulsed laser deposition (PLD) technique, namely $Zn_{1-x}Mn_xO$, which was found to exhibit no ferromagnetic ordering. While Jin et al.[13] detected no indication of ferromagnetism in $Zn_{1-x}Co_xO$ films. The ferromagnetic features with a curie temperature as high as 300 K was observed in some of pulsed laser-deposited $Zn_{1-x}Co_xO$ films, although the reproducibility was less than 10% [14]. Prellier et al.[15] report the synthesis of high-quality Co-doped ZnO thin films using the pulsed laser deposition technique on (0001)-Al_2O_3 substrates under an oxidizing atmosphere, using Zn and Co metallic targets. The formed $Zn_{1-x}Co_xO$ films exhibit ferromagnetism with a curie temperature close to room temperature for $x = 0.08$ and at 150K for $x = 0.05$. Dinia et al.[7] used magnetron Co-sputtering to grow $Zn_{0.75}Co_{0.25}$ magnetic semiconductors on SiO_2/Si substrate at 400ú C. Optical absorption measurements have been performed and showed three absorptions bands. Magnetization measurements have been performed at room temperature and shown the presence of the ferromagnetism with a saturation magnetization of about $0.2\mu_B$/Co. Irradiation with He ions at 520°C have been performed on the as-deposited film. For a dose of 6×10^{16} cm^{-2} a huge increase of the magnetic moment up to $0.37\mu_B$/Co has been observed and accompanied with an improvement of the crystalline quality. For higher doses the magnetic moment is strongly reduced down to $0.13\mu_B$/Co. This is attributed to the change in the free carriers density in the ZnO host[7].

The present work studies the preparation of Co-Zn oxide nanoparticles by a novel self flash combustion method. The prepared Co-Zn oxide nanoparticles are investigated for their magnetic properties. On the other hand, catalytic degradation of organic pollutants is one of the most promising green chemistry technology[16-18]. Phenolic compounds are common pollutants that are present in industrial waste-water and hence many studies have been reported on the catalytic degradation of phenols[19-25]. So, the influence of the prepared Co-Zn oxide on the degradation of phenol was studied.

EXPERIMENTAL

Pure Zinc acetate (Zn $(CH_3COO)_2.2H_2O$) and pure cobalt acetate (Co $(CH_3COO)_2.4H_2O$) were used to prepare zinc oxide, cobalt oxide and nanoparticles diluted magnetic materials of zinc – cobalt oxide mixture by a self flash combustion method. For the preparation of zinc – cobalt oxide mixtures, one mole of pure zinc acetate was well mixed in a ball mill with a speed 170 r/m for 6 hours with one mole of cobalt (II) acetate tetrahydrate. The mixture was then heated at 200°C for 16 hours to be sure of complete decomposition. Samples were then calcined in air at 300 and 500°C for 1 hour to obtain zinc oxide, cobalt oxide and zinc – cobalt oxide particles. The different nanosizes were identified by X-Ray diffraction technique using a JSX-6OP JEOL diffractometer. The average crystallite size was calculated from the X-ray diffraction peaks using the following Scherer's as shown below:

$$\mathbf{d = 0.9\lambda/\beta\cos\theta}$$

Where d is the crystallite size, λ is the X-ray wave length, β is half-intensity width of the relevant diffraction and θ is the diffraction angle.

The magnetic properties were investigated by a Vibrating Sample Magnetometer model 9600 while the thermal analysis was performed using MAC-Science model DTA-TGA 2000. FTIR JASCO 410 was used for IR solid phase spectra. In order to measure the catalytic degradation of phenol by the prepared Co-Zn oxide, 1 gm of the sample was added to 10 ppm phenol solution (100 ml) and analyzed using a UV/VIS/

NIR- spectrophotometer (Jasco V 570). During the procedure, the initial absorbance of the phenol in the absence of Co-Zn oxide was measured at 230nm wavelength while the change in the absorbance was measured with the increase of time for the 10 ppm phenol aqueous solution containing 1 gm of Co-Zn oxide.

RESULTS AND DISCUSSION

TGA and DTA curves recorded on heating Zn Ac, Co Ac, and their mixture at 20°C / min in a dynamic atmosphere of air, are shown in Figure 1 and 2 respectively. They indicate that Zn Ac decomposes via two endothermic events occurring at 104 °C (Ia) and 294°C (IIa). Process Ia is an endothermic weight loss (WL) maximized at 104°C and accompanied by a 16.4% WL which is close to that expected (17.1%) for releasing 2 moles of water. Process IIa appears to involve an endothermic weight-invariant reaction maximized at 261°C which is due to melting and another endothermic WL process occurring at 343°C brings a total WL up to 46.46% which is very close to the expected (47%) for decomposition of Zn acetate to ZnO

$\mathbf{(CH_3COO)_2Zn.2H_2O \rightarrow (CH_3COO)_2Zn \rightarrow ZnO + CH_3COCH_3 + CO_2}$

TGA and DTA curves for heating Zn Ac and Co Ac mixture, at 20 °C/min in air indicate that the mixture decomposes via 2 weight loss steps and 3 endothermic processes at 104, 241, and 352 °C. Step Im shows an endothermic process maximized at 104°C and accompanied by a 23% WL which is close to the expected value of 22.9% for releasing 6 moles of H_2O

$\mathbf{(CH_3COO)_2Zn.2H_2O + (CH_3COO)_2Co.4H_2O \rightarrow (CH_3COO)_2Zn + (CH_3COO)_2Co + H_2O}$

Step II appears to involve two endothermic processes. A weight-invariant endothermic step at 241°C which represents a melting of acetate salts and the other is an

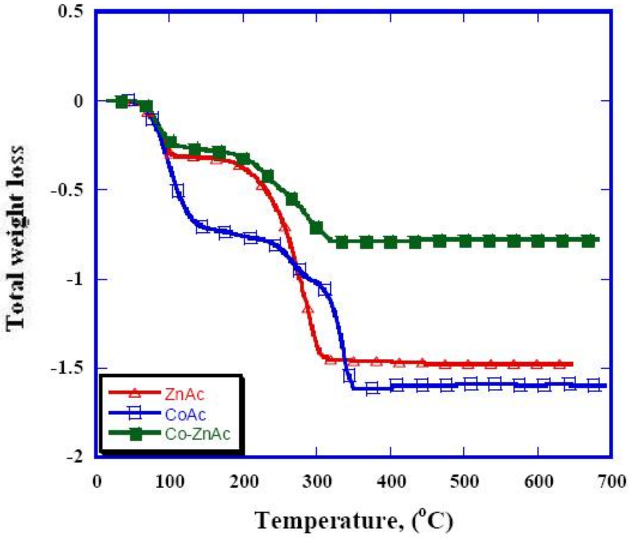

Figure 1 : TGA curves of ZnAc, CoAc and their mixture in dynamic air flow

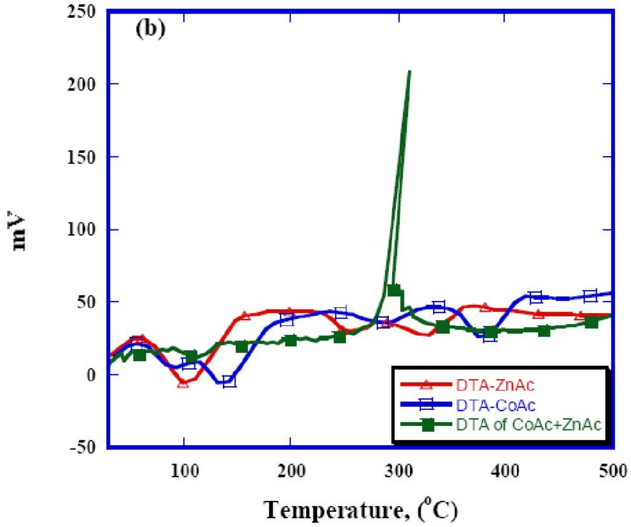

Figure 2 : DTA curves of ZnAc, CoAc and their mixture in dynamic air flow

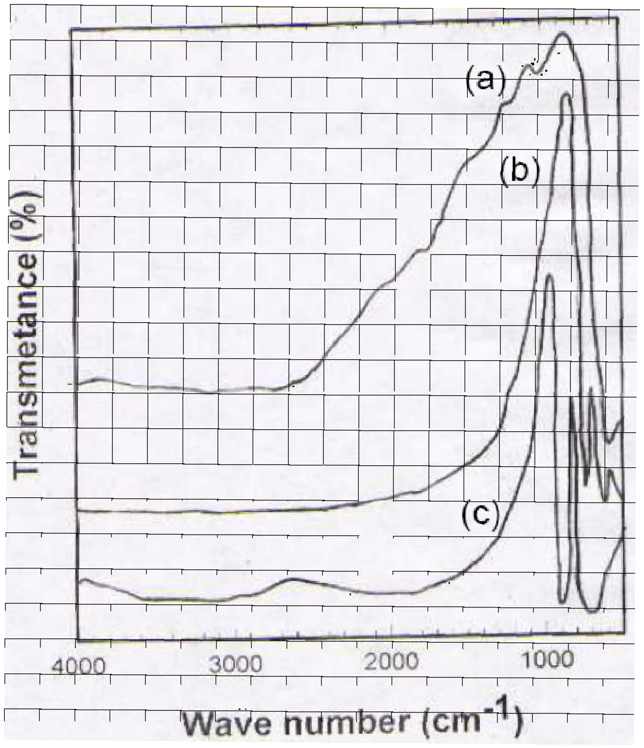

Figure 3 : FTIR spectra for (a) uncalcined Zn acetate and Co acetate mixture, (b) mixture of Co and Zn acetates calcined at 300°C and (c) mixture of Co and Zn acetates calcined at 500°C

endothermic step at 352 °C which indicates total WL up to 45.9% which is close to that expected (47%) for decomposition of acetates to give (Zn, Co)O.

$$(CH_3COO)_2Zn + (CH_3COO)_2Co \rightarrow (Zn, Co)O + CH_3COCH_3 + C_2H_6 + 3CO_2$$

Figure 3(a, b) show IR spectra obtained for the solid phase of uncalcined Zn acetate and Co acetate mixture and a mixture of Co and Zn acetates calcined at 300°C respectively. It displays bands at 1342, 1053, 621 and 482 cm^{-1}, which are assignable to the vibration modes of acetates[26]. The IR spectrum of the solid product of mixture of Co and Zn acetates calcined at 500°C displays bands due to metal oxygen at 1407, 671 and 578 cm^{-1}.

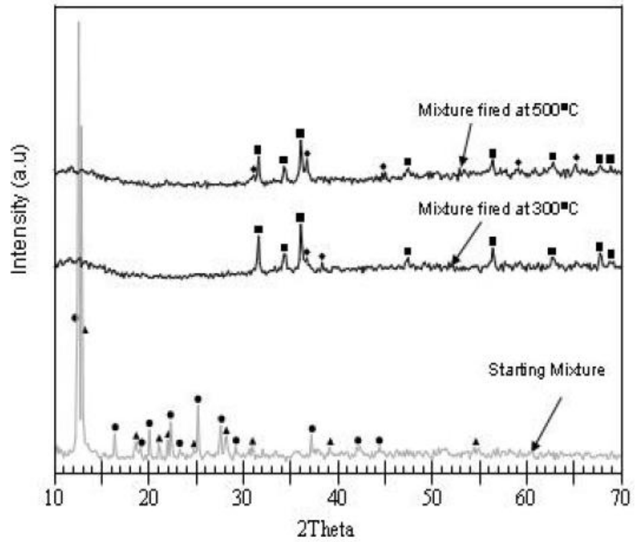

Figure 4 : XRD patterns of starting mixture and combusted products. (● zinc acetate hydrate, ▲ cobalt acetate hydrate, ■zinc oxide and ♦ cobalt oxide)

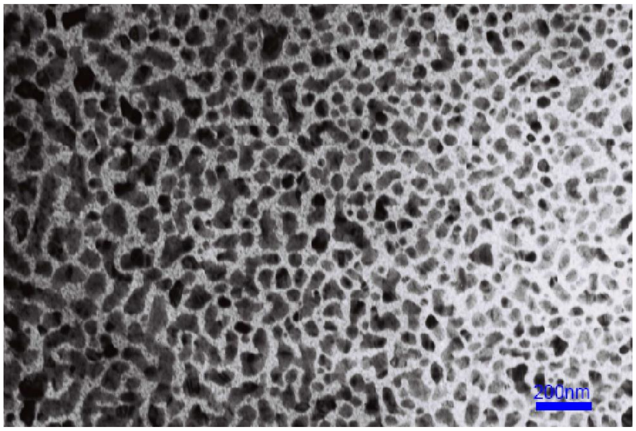

Figure 5 : High-resolution transmission electron microscope (TEM) image of (Zn,Co)O

Figure 4 shows XRD patterns of the starting mixture and the combusted products obtained after firing at 300 and 500°C for 1 hour in air. The patterns of starting mixture give identified peaks corresponding to both zinc and cobalt hydrated acetates. The patterns of fired samples show characteristic peaks for zinc oxide (hexagonal structure) with short peaks for cobalt oxide (Co_3O_4) phase for the sample calcined at 300°C indicating that incomplete formation of (Zn,Co)O at this temperature while the intensity of theses peaks increased for the mix sample calcined at 500°C. This finding is in agreement with the DTA and TG results which showed that decomposition of acetate to give (Zn,Co)O was at 352°C. So, cobalt – zinc oxide mixtures can be clearly obtained by firing the Co-Zn acetate mixture at 500°C.

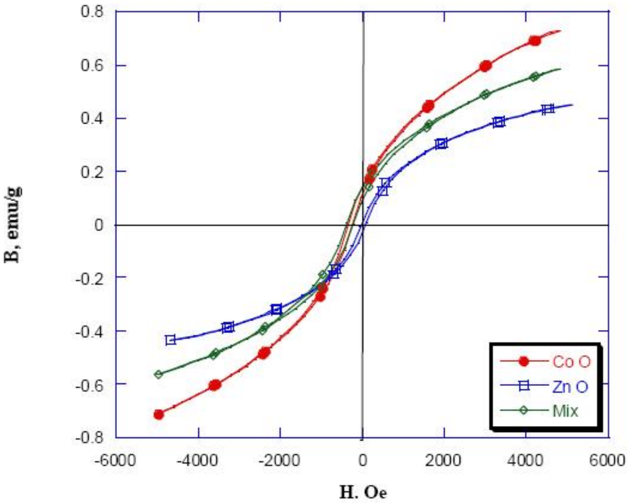

Figure 6 : B-H Hysteresis loop for cobalt oxide, zinc oxide and (Co,Zn)O

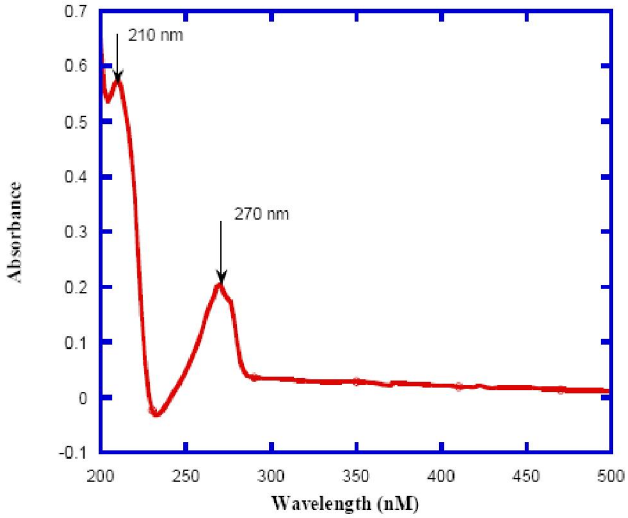

Figure 7 : UV-vis absorption spectrum variation of phenol aqueous solution

The average crystallite size, calculated from the XRD patterns using the Scherer's formula, are 89.3 and 77nm for zinc-cobalt acetate mixtures fired at 300 and 500 °C, respectively. Figure 5 shows the TEM image of the zinc-cobalt oxide prepared by self flash combustion at 500°C from acetate precursor. The image shows homogenous nanoparticles with particle sizes ≈75nm.

TABLE 1: Magnetic properties of fired and unfired samples

	Br (emu/g)	Bs (emu/g)	Hc (Oe)
Zn (Ac) 500ºC	0.01774	0.4462	53.37
Co (Ac) 500ºC	0.02462	0.7259	53.4
Mix heated 500ºC	0.03262	0.5769	83.17

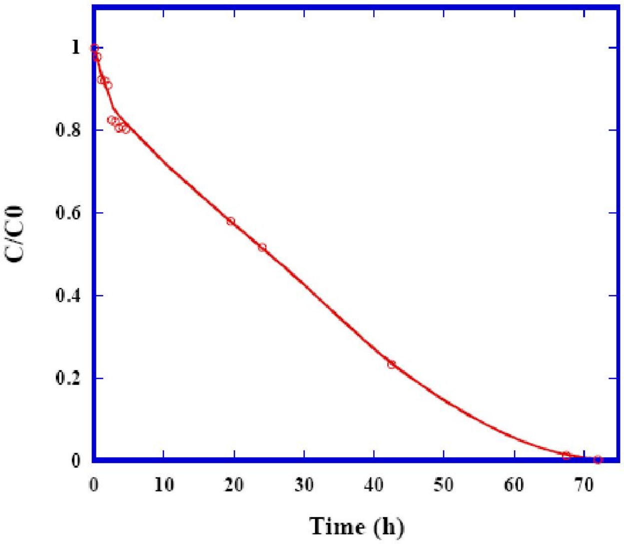

Figure 8 : Normalization concentration profile of phenol during the catalytic degradation by (C0,Zn)O powder

Zn acetate, Co acetate and their equimolar ratio were heated at 500°C for 1 hours. The products were ZnO, CoO and a mixture of (Zn, Co)O with traces of Co_3O_4. The magnetic properties of them were investigated at 16°C using vibrating sample magnetometer at 5 kOe. A ferromagnetic hysterisis loop is shown in Figure 6 and the values of remnant magnetic flux density (Br), saturation magnetic flux density (Bs) and coerecive force (Hc) are summarized in TABLE 1. The B-H hysterisis of Co- doped ZnO showed hysterisis loop of Hc=83.1Oe which is greater than that for pure ZnO and CoO. Bs of the doped sample is estimated to be 0.5769 emu/g which was shown to be greater than corresponding values for ZnO and less than that CoO. The decreases of the Bs of the mixture than that of the CoO can be attributed to contribution of the non-magnetic material (ZnO). It is common in DMS not to recover full magnetization and this usually attributed to antiferromagnetic coupling between neighboring magnetic ions due to super exchange interaction. However, all values are shown to lie in the range of diluted magnetic materials (DMS).

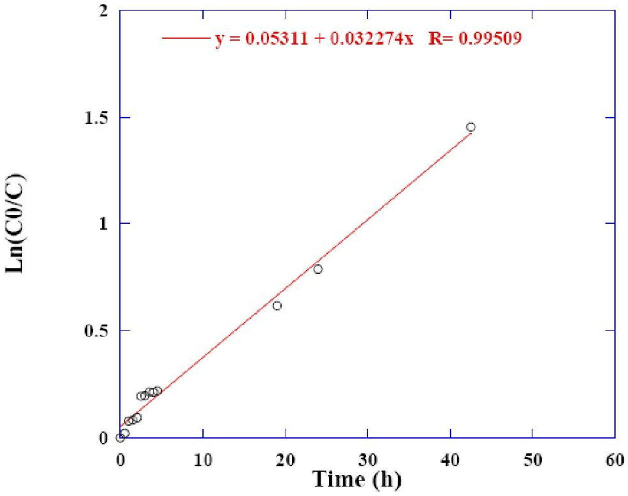

Figure 9 : A plot demonstrating the first order reaction rate character of phenol degradation in the presence of (Co,Zn)O

The degradation of phenol was investigated by using the prepared Co-Zn oxide as a catalyst. The UV-vis absorption spectrum variation of 10 ppm phenol aqueous solution is shown in Figure 7. The aqueous solution of phenol (10 ppm) shows a major absorption band at 210 nm in the absence of (Co,Zn)O. The normalization degradation profiles of phenol containing 1gm of Co-Zn oxide as catalyst is shown in Figure 8, where c is the concentration of the compound at time t and C_0 the initial concentration of the parent compound. The graph shows that the concentration of phenol decreased gradually with time and reach to a value near zero at around 67 hours. More than 20% of the initial concentration of the phenol was decomposed within 2 hours of degradation. Figure 9 is a plot demonstrating the first order reaction rate character of phenol degradation in the presence of (Co,Zn)O. So, the degradation of phenol aqueous solution followed first order rate kinetics. It was reported[27-29] that degradation of phenol depends on the generation of free radicals. Free radicals are generated when phenols react with hydroxyl species or any electron donor adsorbed at the surface of the catalyst. The presence of nanosized (Co,Zn)O powder activate the generation of hydroxyl radicals. The formed reactive hydroxyl radicals are then used to carry out chemical oxidation or to degrade the phenol in waste water treatment. The resultant hydroxyl radicals react with phenol in the ortho-, and some para-, positions to form catechol and hydroquinone, respectively[28]. Further oxidation of the latter compound then occurs to produce benzoquinone, which is hydroxylated/oxidised again and ultimately forms carbon dioxide and water.

CONCLUSION

Co-Zn oxide nanoparticles (77nm) as a diluted magnetic semiconductor (DMS) material was successfully prepared by a novel self flash combustion from acetate precursors at 500°C. From the thermal analysis (TGA, DTA) and IR spectra, the thermal decomposition of CoAc, ZnAc, and the mixture of them were via three endothermic steps. The first step represents releasing of water, the second step represents the melting of acetate salts while the third step represents the decomposition of acetate to give the oxides. Magnetic measurements of Co- doped ZnO showed Coercivity (Hc) 83.1Oe which is greater than that for pure ZnO (53.37 Oe) and CoO (53.4 Oe). Bs of the doped sample is 0.5769 emu/g, which was greater than corresponding values for ZnO and less than that CoO. Co- doped ZnO showed a catalytic effect on the degradation of phenol and the concentration of phenol reach to a value near zero at around 67h. The degradation of phenol aqueous solution followed first order rate kinetics.

REFERANCES

[1] Sang-Wook Lim, Deuk-Kyn Hwang, Tae-Min Myoung; Solid State Communications, **125**, 231 **(2003)**.
[2] U.P.Verma, Sonu Sharma, Nisha Devi, P.S.Bisht, P.Rajaram; J.Magn.Magn.Mater., **323(5)**, 394 **(2011)**.
[3] Ch.Bourouis, A.Meddour; J.Magn.Magn.Mater., **324(6)**, 1040 **(2012)**.
[4] T.Fukumura, Z.Jin, A.Ohtomo, H.Koinuma, M.Kawasaki; Appl.Phys.Lett., **75**, 3366 **(1999)**.
[5] J.Hyun KIM, H.Kim, D.Kim, Y.E.Ihm, W.K.Choo; Physica B., **327**, 304 **(2003)**.
[6] J.K.Furdyna; J.Appl.Phys., **64**, R29 **(1988)**.
[7] A.Dinia, J.P.Ayoub, G.Schmerber, E.Beaurepaire, D.Muller, J.J.Grob; Phys.Lett.A., **333**, 152 **(2004)**.
[8] H.Ohno; J.Magn.Mater., **200**, 110 **(1999)**.
[9] S.A.Wolf, D.D.Awschalom, R.A.Buhrman, J.M.Daughton, S.Inar, M.L.Roukes, A.Y. Chtchelkanova, D.M.Treger; Science, **294**, 1488 **(2001)**.
[10] Y.Matsumoto; Science, **291**, 854 **(2001)**.
[11] K.Ando, H.Saito, Z.Jin, T.Fukumura, M.Kawasaki, Y.Matsumoto, H.Koinuma; J.Appl.Phys., **89**, 7284 **(2001)**.
[12] K.Takamura, F.Matsukura, D.Chiba, H.Hono; Appl.Phys.Lett., **81**, 2590 **(2002)**.
[13] Z.Jin, T.Fukumura, M.Kawasaki, K.Ando, H.Saito, Y.Z.Yoo, M.Murakami, Y.Matsumoto, T.Hasegawa, H.Koinuma; Appl.Phys.Lett., **78**, 3824 **(2001)**.
[14] J.H.Kim, H.Kim, D.Kim, Y.E.Ihm, W.K.Choo; J.Europ.Ceram.Socie., **24**, 1847 **(2004)**.
[15] W.Prellier, A.Fouchet, C.Simon, B.Mercey; Mater.Scie.Engin.B., **109**, 192 **(2004)**.
[16] O.M.Alfano, D.Bahnemann, A.E.Cassano, R.Dillert, R.Goslich; Catal.Today, **58**, 199 **(2000)**.
[17] D.A.Tryk, A.Fujishima, K.Honda; Electrochim. Acta., **45**, 2363 **(2000)**.
[18] D.S.Bhatkhande, V.G.Pangarkar, A.C.M. Beenackers; J.Chem.Technol.Biotechnol., **77**, 102 **(2002)**.
[19] W.A.Zeltner, C.G.Hill, M.A.Anderson; Chemtech, **23**, 21 **(1993)**.
[20] M.Abdullah, K.C.L.Gray, R.W.Mathews; J.Phys. Chem., **94**, 6620 **(1990)**.
[21] M.Trillas, J.Pearl, X.Donenech; J.Chem.Technol. Biotechnol., **67**, 237 **(1996)**.
[22] K.Nagaveni, G.Sivalingam, M.S.Hedge, G.Madras; Environ.Sci.Technol., **38**, 1600 **(2004)**.
[23] M.H.Priya, G.Madras; J.Photochem.Photobiol.A: Chem., **178**, 1 **(2006)**.
[24] K.Okamoto, Y.Yamamoto, H.Tanaka, A.Itaya; Bull. Chem.Soc.Jpn., **58**, 2023 **(1985)**.
[25] D.F.Ollis, E.Pellizzetti, N.Serpone; Environ.Sci. Technol., **25**, 1523 **(1991)**.
[26] D.L.Pavia, G.M.Lampman; Introduction to spectroscopy: Aguide for students of organic chemistry.
[27] A.Santos, P.Yustos, A.Quintanilla, S.Rodriguez, F.Garcia-Ochoal; Appl.Catal.B., **39**, 97 **(2002)**.
[28] D.H.Bremner, A.E.Burgess, D.Houllemare, K.Namkung; Appl.Catal B: Environmental, **63**, 15 **(2006)**.
[29] M.H.Priya, Giridhar Madras; J.Photochem. Photobio.A: Chemistry, **179**, 256 **(2006)**.