Structural and magnetic properties of sol-gel synthesized Co doped ZnO nanocrystals

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We have synthesized Co doped ZnO by Sol gel synthesis technique at varying Co concentration. The synthesis involves formation of metal cation- PEG complex, which is later heated to obtain the desired phase. The TGA-DTA studies were performed onto gel to know about Oxidation temperature of metal complex. The oxidation of metal complex was found to exhibit at ~380^{o}C. The gel was dried at different temperature above the oxidation temperature to obtain powder and was structurally characterized by XRD, SEM and TEM. Gel heated up to 400^{o}C were found to have single phase for all Co concentrations while gel heated above 400^{o}C had shown the phase separation for 20 at% Co concentration having wurtzite ZnO phase and spinel $ZnCo_2O_4$ phase. The c-axis lattice parameter of wurtzite phase showed a monotonic decrease with Co doping and was found to follow Vegards law. SEM studies showed that grains of size 20-30nm were agglomerated in about 150nm particle size. TEM studies showed the crystalline nature of the grains. Compositional analysis performed using EDAX as well as ICPAES technique revealed higher Co content for moderate doping upto 5 at% while for 10 at% the Co content found in the powder were quite small upto 7.3%. Both the techniques showed almost same compositions. The magnetic studies were performed onto sample having 10 at% Co and calcined at 400^{o}C. The powder showed paramagnetic behavior and no sign of ferromagnetism was found in the samples.

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1. Introduction

ZnO is one of the widely studied materials for its number of exciting properties. It is a wide band gap semiconductor material with $E_g \approx 3.37$eV. ZnO has large excitonic binding energy ~ 60m.eV [1], which makes it useful material for room temp UV lasing application [2]. It is used for gas sensing applications [3], surface acoustic wave device [4], transparent coating and solar cell applications [5] and transparent thin film transistors [6]. Recently it has been theoretically predicted that Mn Doped p-type ZnO can exhibit ferromagnetism above room temperature thus making it prospective material for spintronic devices [7]. ZnO is considered as prospect candidate for electronic and photonic devices because of non-toxic nature, easy availability and cheaper processing cost of the material. In the recent years, there has been intense activity to grow nanostructures of ZnO using numerous techniques like vapor phase transport technique [8], thermal decomposition of precursors [9, 10], oxidation of Zn metal [11] or reduction followed by oxidation of ZnS powder [12] at high temperature and inert environment. Catalytic growth of zinc oxide nanowires by vapor transport has been widely used in the past for making ZnO based devices [8]. These methods involve high to moderately high temperature processes for synthesis of nanostructures of ZnO. Aligned array of ZnO nanorods have been synthesized by low temperature solution growth as well as electrodeposition technique [13.14]. Following the theoretical prediction, many researchers have measured magnetic properties of transition metal doped ZnO and found contradictory results explained based on phase separation in solid solution. This paper report the Sol-gel synthesis and magnetic properties of Co doped ZnO Nanocrystals.

2. Experimental details

Nanocrystals of Co doped ZnO were prepared by using Sol-gel technique. The appropriate amounts of 5N pure nitrate of Zn and Co were dissolved in double distilled water to make final conc. 0.03M. An equal amount of ethylene glycol was added to the solution. The resulting solution was stirred for 10-15 min. to ensure homogenous mixing. The solution was heated at 100^{o}c for about one hour to convert solution into gel form with appropriate viscosity. The gel with appropriate viscosity was further heated upto 200^{o}c to convert into powder form.

The converted powder was characterized with TGA-DTA to verify oxidation temperature of metal complex. The obtained metal-complex powder was calcined at different temperature above oxidation temperature as observed from TGA-DTA trace. Nanocrystalline powder of Co doped ZnO after oxidation was characterized with X-ray diffraction (XRD) to identify crystal structure and different emerged phases. The calcined powder was characterized by SEM with EDAX and ICPAES technique to study microstructure and final composition. Magnetic properties of Co doped ZnO were studied with SQUID machine.

3. Results and disscussion

Fig. 1 shows DTA-TGA trace of 5 at% Co doped ZnO powder in air as well as N_2 environment. The DTA-TGA trace for all other compositions was similar. The major weight change in DTA trace upto 200°c is related to evaporation of adsorbed water as well as breakdown of polymer as represented by endothermic and exothermic peak respectively observed in TGA trace taken in both air as well as N_2 environment. There was an observation of an exothermic peak around 400°c in DTA trace in air environment but the same was absent in N_2 environment. This exothermic peak was correlated to the oxidation of metal complex as it was only evident in air environment but was absent in N_2 environment. The obtained powder of metal complex was calcined at different temperatures viz. 400°c, 500°c and 600°c to oxidize the metal complex into Co doped ZnO with different Co concentrations.

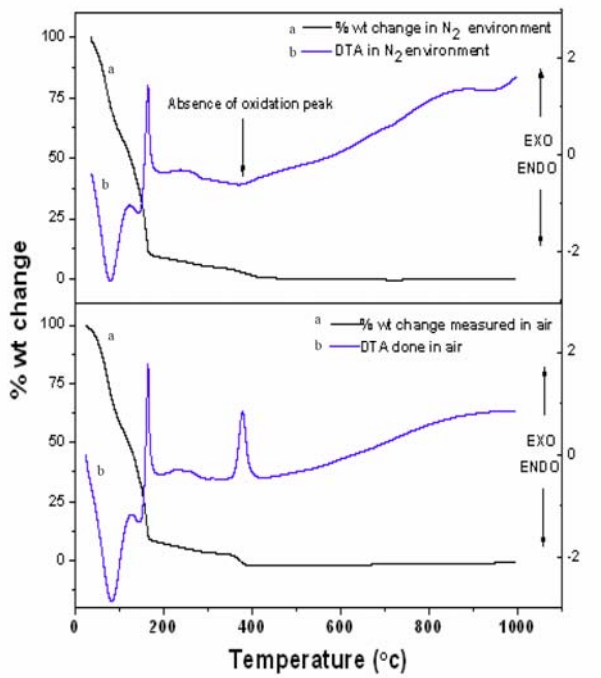

Fig. 1 DTA-TGA of $Zn_{0.95}Co_{0.05}Eg$ complex in air and N_2 environment.

Fig. 2 shows the XRD pattern of 5 at% Co doped ZnO powder obtained by heating at 200°c and calcined at 500°c temperature. Though the powder obtained after heating the gel at 200°c showed ZnO wurtzite crystal structure but low peak intensity reveals poor crystallinity. The increase in peak intensity of calcined powder at 500°c showed an improved crystallinity. The sample with 20 at% Co doped ZnO showed phase separation (spienel $ZnCo_2O_4$ phase along with wurtzite ZnO phase) when calcined at 500°c as shown in figure 3. The Co doping in ZnO matrix was verified with the fact that increase in Co Concentration in sample led to monotonic decrease in c- axis lattice parameter of wurtzite ZnO crystal structure and thus found to obey Vegard's law as shown in inset of Fig. 2.

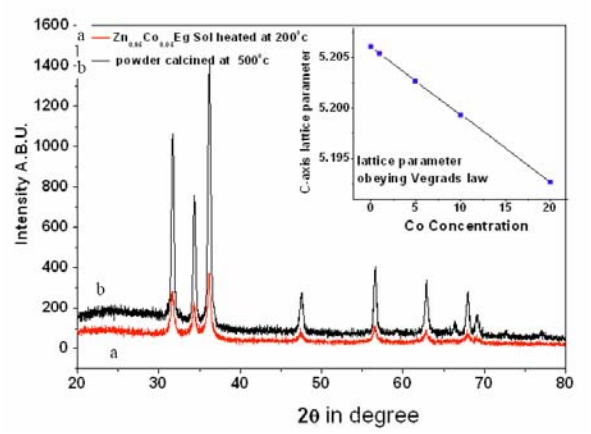

Fig. 2 XRD pattern of $Zn_{0.95}Co_{0.05}O$ obtained by heating at different temperature

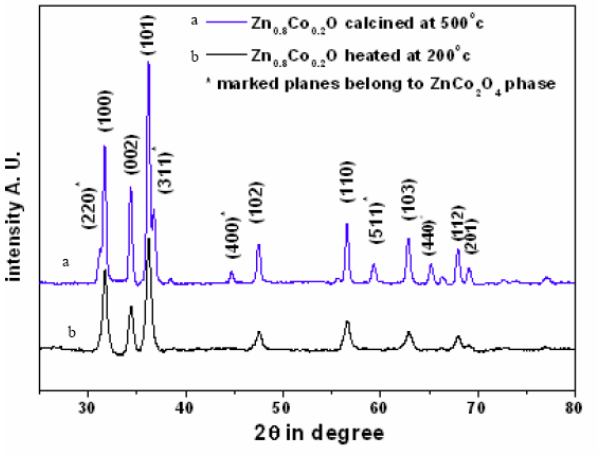

Fig. 3 XRD pattern of $Zn_{0.8}Co_{0.2}O$ heated at 200°c and calcined at 500°c

Fig. 4 shows the SEM image of 5% Co doped ZnO powder. The particle size was found to be 100-150nm with agglomerated grains of av. grain size 25nm. The compositional analysis performed by EDAX technique as well as ICPAES led to similar results as depicted in Table 1.

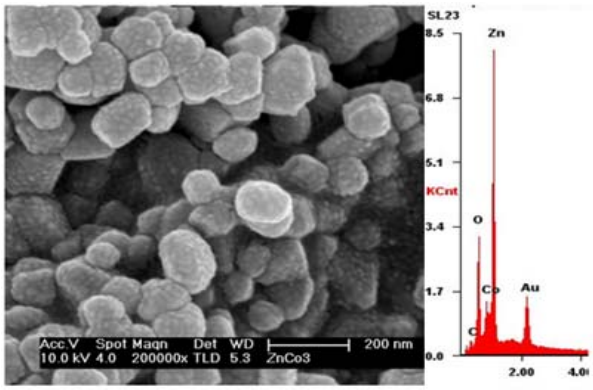

Fig. 4 SEM image of 5% Co doped ZnO powder along with EDAX pattern

Table 1. Table containing composition analysis by EDAX as well as ICPAES

% of Co in ZnO	EDAX	ICPAES
0	0	0
1	1.2	1.1
5	5.6	5.4
10	7.3	7.4
15	12.8	12.6
20	16.5	16.2

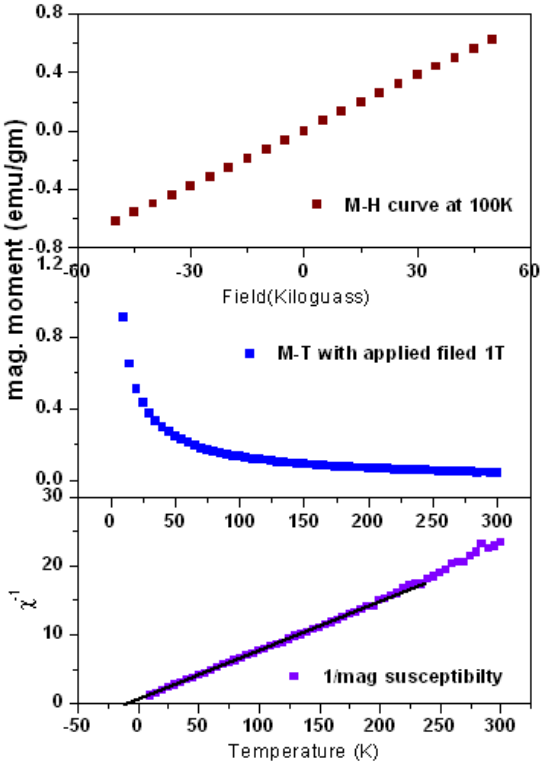

Fig. 5 magnetic moment of $Zn_{0.9}Co_{0.1}O$ obtained by heating at different temperature.

Fig. 5 shows the magnetic moment as a function of applied magnetic field and temperature for 10at% Co doped ZnO powder. There was no hysteresis observed and magnetization was found small and positive revealing the paramagnetic nature of the sample. Magnetic moment decreased with increase in temperature also representing paramagnetic behavior. The M(T) curve revealed the Curie-Weiss paramagnetic behavior that is also evident in $1/\chi(T)$ vs temperature showing typical curie-Weiss linear behavior. Thus magnetic measurement revealed the typical paramagnetic behavior for Sol-gel processed Co doped ZnO powder. There have been contradictory results in magnetic properties of transition metal doped ZnO. Many authors have reported the ferromagnetic behavior in transition metal doped ZnO in thin film [15] and single crystal [16] and there are few reports revealing the absence of ferromagnetism in samples [17]. It has been suggested that the contrast in obtained results might be related to preparation conditions of the sample [18].

4. Conclusions

Powder of Co doped ZnO Nanocrystals were synthesized by Sol-gel technique. The oxidation temperature of metal complex was observed around 400°c. the XRD of annealed samples revealed that metal complex oxidize into ZnO wurtzite phase upto Co concentration 20 at% where another spienel $ZnCo_2O_4$ phase emerged out along with ZnO wurtzite phase. Magnetization measurements revealed the paramagnetic behavior of studied samples.

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