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Synthesis and Magnetic Properties of Cobalt Doped Zinc Oxide Nanoparticles

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Abstract: ***Recent focus of nano-phase research has oriented to the oxide semiconductors that have wide band gap [around 3 eV] and can be doped suitably. The wide band gap leads toa transparent semiconductor that has various applications. Substituting cations in low proportion by atoms with unpaired electrons is expected to give magnetic properties in semiconducting environment. Diluted magnetic semiconductors (DMS), as these are called, can be promising for strong ferromagnetic exchange coupling between localized spins. These are important for potential of producing a well-controlled spin-polarized transport and detection of spin currents. Band structure calculation studies suggested the possible ferromagnetism in case of ZnO host. We synthesize zinc oxide and cobalt doped zinc oxide in powder nanoparticle morphology using a chemical route. The samples are characterized for crystallinity, crystallite sizes and magnetic properties. Nanoparticles exhibit room temperature ferromagnetism.***

Keywords: zinc oxide nanoparticle, cobalt doped zinc oxide nanoparticle, magnetism, chemical route

1. Introduction

Harnessing the charge and spin of electrons in semiconducting environment has initiated word wide research on II-IV type hosts with dilute magnetic impurity. Such materials, known as Diluted magnetic semiconductor (DMS) are expected to play an important role in interdisciplinary materials science and future spintronics because charge and spin degrees of freedom accommodated into single semiconductor, and to explore novel physics and new devices in interdisciplinary materials sciences [1].Giant magnetoresistance and tunnel magnetoresistance have almost commercialized [2- 6] in which spin of electron is their physical basis.

A successful functionality requires obtaining considerable magnetic susceptibility in a resistive environment at temperatures well above room temperature. Though several attempts in III-V semiconductors appear in literature, a high T_c ferromagnetism is yet not found in them. Non- realizing aTc beyond 180 K -190 K in materials like (Ga, Mn)As led experts to turn their focus on wide band gap II-IV hosts. Zinc oxide is such a wide band gap (3.30 eV) and large excitonic binding energy (60 meV) candidate.

It is n-type semiconductor due to oxygen vacancies, and produces bright excitonic emissions in UV region [7-11], has large photo-conductivity, good piezo- and pyro-electric behavior [12], and long spin coherence [13]. In nanosizes, it offers well defined doping and defects that associate high spin states.

Among various transition elements, cobalt doping appeared promising due to abundant electron states, large solubility in host, and the Curie temperature as high as 1400 K[14-16].

2. Experimental Technique

Bulk methods of chemical route do not work for nano size crystallite synthesis. The chemical precursors of analytic research grade zinc acetate, cobalt acetate (for doping) and potassium hydroxide (flux) were procured. Metal acetate precursors and potassium hydroxide were mixed in molar proportion in de-ionized water. The mixture was stirred at 60^0C at hot plate with magnetic stirrer. A homogeneous solution was obtained at the end, and the solution was left for aging. After aging of 25 hours precipitates were separated, and ringed several times with de-ionized water for removing unreacted materials. The precipitate was dried at 100^0C to remove water.

A portion of sample was taken for pre-annealing analysis, and the remaining sample was annealed at 800^0C.

For un-doped sample preparation, the same procedure was undertaken except that doping compound cobalt acetate was not taken.

3. X-Ray Diffraction

Un-annealed and annealed samples of pure zinc oxide and cobalt doped zinc oxide were characterized by X-ray diffraction using Cu-K_α-radiation (X’PertPRO) for investigation of size of crystallites and purity of phases. The spectrum obtained [intensity of diffracted x-rays against angle 2θ] indicated no clustering or secondary phases (fig 1). Some un-reacted cobalt oxide peaks (marked by + in figure 2) are observed however. According to the Debye-Scherrer equation:

$$d = \frac{k\,\lambda}{\beta\cos\theta}$$

where *d* is the size of the crystallites, β is the full-width at half-maximum (HWHM) of a diffraction line located at angle , λ is the x-ray wavelength (1.5418Å for Cu K-alpha x-rays) and *k* is a Scherrer constant (0.9), which depends on the peak breadth, crystallite shape, and crystallite size distribution. The particle size, as crystallite size is often called, ranged from 30 nm to 70 nm.

4. Magnetization

Custom built superconducting quantum interferometer device(SQUID) magnetometer results for a temperature range from 2 K to 200 K under field up to H=0.5 kOe(and for 10 kOe)are tabulated. The magnetization in cobalt doped zinc oxide nanoparticles varies with size and concentration of dopant.

Table 1: Magnetic property of ZnO and ZnO:Co

Sample	*Fraction of Co*	*Morphology*	*Magnetization (memu/g)*
Un-doped	0.00	Powder NP	1.5
1% doped	0.01	„	0.013
5%doped	0.05	„	0.07
10% doped	0.10	„	0.13 (at H= 10 kOe)
15% doped	0.15	„	0.78

5. Discussion

Exhibition of magnetic order in un-doped zinc oxide has several sources. Oxygen vacancy and crystallite size are reported causes [17]. Also, zinc vacancy and interstitials contribute to magnetism[18,19].Defect identification is done by EPR and XPS, and have been used to indicate strong surface effects of nanoparticles to bind OH and H to surface, thus contributing to magnetism[17,20,21]. The same is also indicated by CVD methods used by others [22]. Low temperature annealing [100^0C] of CVD sample is reported to show ferromagnetism but at high temperature [500^0C] gives diamagnetism. Crystallinity is increased at high temperature[22]. Un-doped or non-transition metal doped oxides without d or f-bands also show magnetism [23-25]. It is theoretically important to investigate the origins.Diverse factors like oxygen vacancies,zinc vacancy and interistials ,grain boundaries and surface defects contribute to long range ordering.

Although un-doped and doped zinc oxide both exhibit FM, it is not easy to control various sources of FM in Zn O as compared to ZnO:Co.

6. Conclusion

In this paper we report on the structural, morphological and magnetic properties of synthesized ZnO and Zno:Co nanoparticles in powder morphology, synthesized using cost effective chemical method. The measurements were made using XRD and SQUID. XRD measurements indicated that the synthesized ZnOnano-particles exhibit good crystal structure with no impurities. Therefore, this method is suitable for some important applications of prepared sample such as spin based devices, LEDs, UV photo detectors, sensing and for other optoelectronic devices. Magnetization measurements indicate ferromagnetism in un-doped and cobalt doped zinc oxide nanoparticles obtained in powder morphology. Considerable effort is still necessary in developing a stable and sufficiently strong FM for functional spintronic devices.

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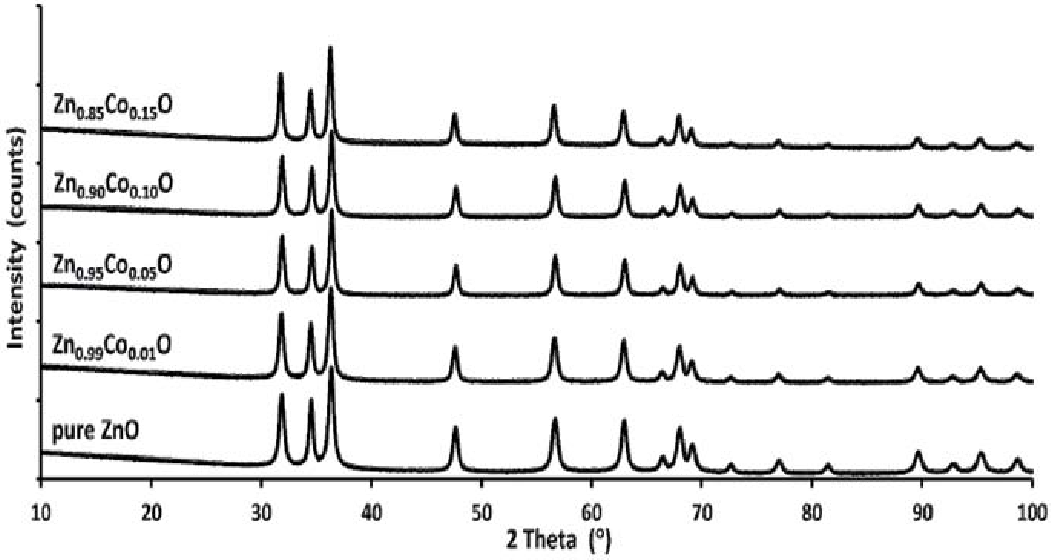

Figure1: XRD pattern of samples before annealing (concentrations as shown)

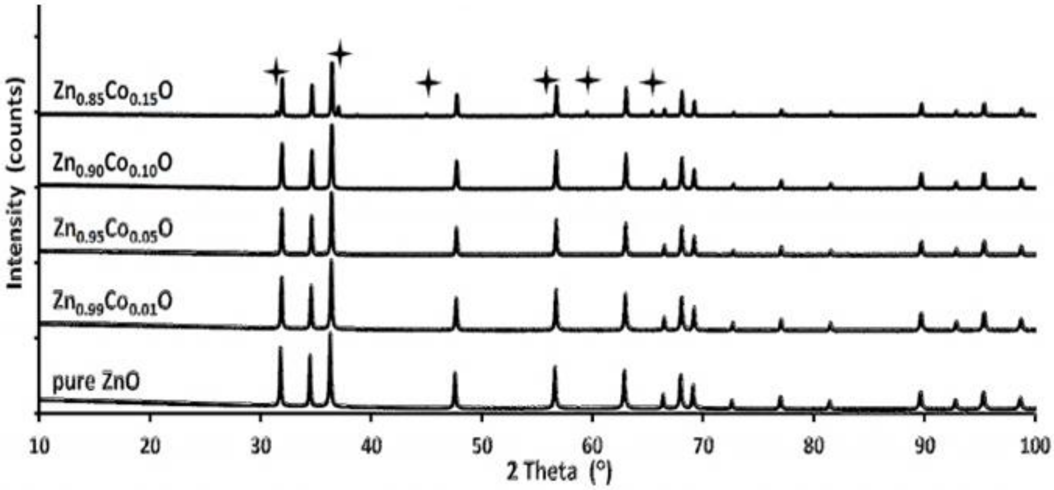

Figure 2: XRD pattern of samples after annealing at 800^0C (concentrations as shown)