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Synthesis and characterization of Mn-doped ZnO diluted magnetic semiconductors

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ABSTRACT

In the present work undoped and Mn doped ZnO nanoparticles (ZnO:Mn), diluted magnetic semiconductors, were successfully synthesized by the sol–gel method at room temperature. The morphology of ZnO nanoparticles constituted by flower-like structures with hexagonal morphologies that changed significantly after the incorporation of Mn. Rietveld refinements results showed that Mn ions are successfully doped into ZnO matrix without altering its wurtzite phase. Meanwhile, Raman spectroscopy analyses confirm the wurtzite structure of undoped ZnO and ZnO:Mn nanoparticles. The lattice parameters increase with increasing Mn content due to the large ionic radius of Mn^{2+} compared to that of Zn^{2+}. Electron spin resonance measurements were performed to gain information about oxidation state and site occupancy of the magnetic Mn ions in the ZnO lattice. Moreover, UV–vis absorption spectra have been utilized to calculate the optical band gap of the undoped ZnO and ZnO:Mn nanoparticles before and after different γ-irradiation doses. The band gap of ZnO:Mn (2%) is 2.62 eV which is noticeably smaller than the 3.26 eV of undoped ZnO. The thermal decomposition properties of the prepared nanoparticle samples were also studied using simultaneous Thermogravimetric analysis in temperature range from 30 to 500 °C.

1. Introduction

Diluted magnetic semiconducting nanomaterials have received much attention because of their combined properties and multiple potential applications such as biomedical, magnetic resonance imaging and telecommunication devices [1,2]. The development of magnetic nanocomposite materials has been the discovery source of unique spectacular new technology. This technology depends on the ability to use electron rotation instead of electron charge to be an alternative to traditional semiconductor technology. Most of diluted magnetic semiconducting studies concentrated on metal oxides, chalcogenide semiconductors and superparamagnetic iron oxide nanoparticles [3–6]. The magnetic properties of these materials are strongly depending on the host material and sample preparation conditions.

ZnO is a hexagonal wurtzite structure semiconductor with wide direct band gap (3.3 eV) and exciton binding energy of ~60 meV at room temperature [7]. ZnO is also an environmentally safe and inexpensive host material that can be doped with different metal ions, including transition metal elements (Cr, Mn, Fe, Ni, Co, etc.) [8–10]. Transition metal doped ZnO nanoparticles were prepared by different methods such as the co-precipitation method [11], wet-chemical method [12], sol–gel [13], radio frequency magnetron sputtering [14] and pulsed laser deposition [15]. Among these methods, sol–gel is attracting increased interests because it offers several advantages such as high chemical homogeneity, low processing temperature, possibility of controlling the size and morphology of particles, simplicity and low cost [16–18]. Up till now Mn-doped ZnO materials are considered as the most promising candidates because it is easier to fabricate than other diluted magnetic oxide materials, widely use in a number of applications like magneto-optic devices and has been found to be ferromagnetic with the highest reported Curie temperature [19]. Generally, diluted magnetic semiconductors materials are an active research area of current global interest and requires further research work.

Herein we report the preparation of Mn doped ZnO nanoparticles via the sol–gel technique using low Mn concentrations (1 and 2 at%). With a view to understand the effect of Mn low concentrations a systematic study was done on the structural, electron spin resonance and optical properties of ZnO. Also, the effects of γ-irradiation on the optical band gap of the prepared samples were investigated.

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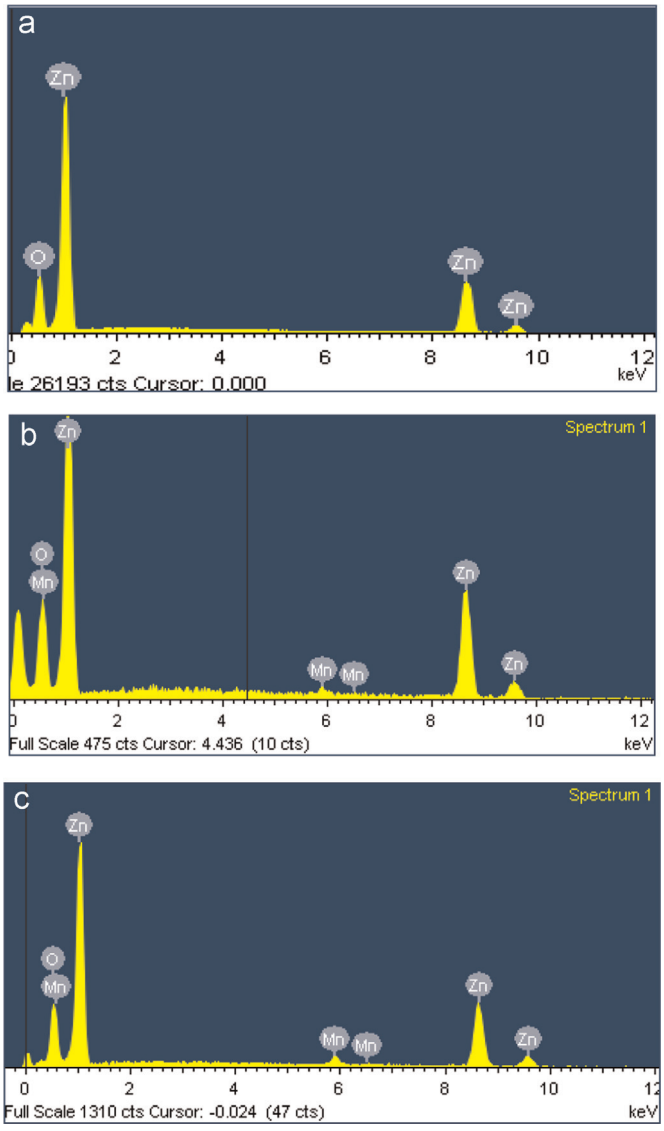

Fig. 1. EDX spectra of the synthesized ZnO:Mn nanoparticles with different Mn doping concentrations: (a) 0%, (b) 1%, and (c) 2%.

2. Experimental

2.1. Materials

Zinc acetate dihydrate ($Zn(CH_3COO)_2{\cdot}2H_2O$, 98.5%) and manganese acetate tetrahydrate ($Mn(CH_3COO)_2{\cdot}4H_2O$, 99.3%) were all purchased from Qualikems, while sodium hydroxide (NaOH, 99.0%) from universal fine chemicals.

2.2. Synthesis of Mn-doped ZnO nanoparticles

In this work, undoped and Mn doped ZnO nanoparticles (1 and 2 at%) were synthesized by the sol–gel method. Specific amounts of $Zn(CH_3COO)_2{\cdot}2H_2O$ and $Mn(CH_3COO)_2{\cdot}4H_2O$ were dissolved in deionized water. This solution was stirred with a magnetic stirrer at room temperature under constant stirring for 60 min until complete dissolution of the precursors. Then, sodium hydroxide NaOH (2 M) was added to the resulting solution slowly drop by drop in order to get pH ≈ 10. The solution was kept for 24 h to complete the gelation and hydrolysis process. The precipitates were slowly crystallized and settled down. To obtain undoped and Mn doped ZnO nanoparticles, the precipitates were centrifuged and washed three times with deionized water and finally by ethanol then dried in air at about 120 °C.

Table 1
EDX composition analysis of the ZnO and ZnO:Mn nanoparticles.

Comp.	Zn (atomic %)	Mn (atomic %)	O (atomic %)
ZnO	45.96	–	54.04
ZnO:Mn (1%)	44.95	1.08	53.97
ZnO:Mn (2%)	45.24	2.04	52.72

2.3. Characterization of Mn-doped ZnO nanoparticles

Elemental analyses and morphology of the undoped and Mn doped ZnO nanoparticles were performed by energy-dispersive X-ray (EDX) spectroscopy using a scanning electron microscope (SEM, Zeiss Leo Supra55).

The crystalline phases of the obtained nanopowders were identified by X-ray diffraction (XRD, Shimadzu XD-6000) operated at 40 keV and 30 mA with Cu k_α radiation of wavelength $\lambda =$ 1.5418 Å. The electron spin resonance (ESR) measurements were