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Optical and magnetic properties of Co-doped ZnO synthesized by magnetic assisted hydrothermal method

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ABSTRACT

Cobalt(Co) doped ZnO nanoparticles were synthesized by a hydrothermal method with a magnetic field pretreatment(in the hydrolysis reaction). The pretreatment time(t) was set as 0 h(no pretreatment), 1 h, 2 h and 4 h. The crystallite structure, the lattice constant have been estimated by X-ray diffraction (XRD) with Rietveld refinement, which shows slight lattice expansion due to Co doping. Scanning electron microscopy (SEM) reveals flower-like microstructure and transmission electron microscopy (TEM) indicates the single crystalline in nature. The defect, the optical and magnetic properties of the four obtained samples were systematically investigated by Raman spectroscopy, photoluminescence (PL) spectra and vibrating sample magnetometer (VSM) respectively. The results show that the pretreatment time of magnetic field has a significant influence on optical and magnetic properties of Co-doped ZnO, and the effective time of magnetic field in the hydrolysis reaction on the magnetic property is between 1 h and 2 h. When $1\ h \leq t \leq 2\ h$, more Co atoms are incorporated into ZnO and the saturation magnetization (M_S) increases by nearly three times, comparing with the sample without pretreatment. Samples of different pretreatment time show changes in the emission band of PL spectra and defect related bands of Raman spectra. The characterization of Raman scattering combined with the analysis of PL spectra suggests that the original of room temperature ferromagnetism(RTFM) may arise from the Co^{2+}–$V_O{}^{+}$–Co^{2+} bound magnetic polaron(BMP).

1. Introduction

Zinc oxide (ZnO) is a transparent semiconductor compound with a direct electronic transition [1–3]. It has a wide band gap of 3.37 eV and large excitonic binding energy of 60 meV at room temperature, which makes it a potential candidate for ultraviolet optoelectronic devices [4–6]. ZnO is a kind of diluted magnetic semiconductor (DMS) that possesses both charge and spin degrees of freedom when small amounts of transition metal atoms (Mn [7–11], Co [12–20], Ni [21–26], Gd [27–29], or Fe [30–34]) are introduced into ZnO, opening up new prospects for applications in spintronic devices. The main challenge in the practical applications of the DMS materials is the attainment of ferromagnetism above room temperature [35], also the mechanism of ferromagnetism is still inconsistent or controversial. Based on its specific applications, numerous techniques have been utilized for the fabrication of ZnO nanostructures including sol-gel method [36,37], vapor phase growth [38], solvothermal method [39], thermal decomposition [40,41], hydrothermal method [42,43]. Among these methods, hydrothermal method is an ideal method for deriving uniform doping DMS because it is simple, convenient and environment-friendly. Nowadays, multiple experimental studies have been trying to induce some new ways in the process of growth to change the morphology, structure and the orientation of crystal to investigate the magnetic, optical and electrical properties of ZnO. For example, a pulsed magnetic field was applied in the hydrothermal process in order to control the morphology and regulate the magnetism of DMS [44,45]. In Chu group, a sealed autoclave with reactant mixture was appended in a 12 T superconducting magnet and maintained at 393 K for 5 h to urge the energies of ferromagnetic spin alignment to decrease to a degree that ferromagnetism might be activated [46]. The external magnetic field was involved in the whole hydrothermal process in these studies. In this letter, Co-doped ZnO nanoparticles were prepared by hydrothermal method. Before the heating process, a 0.4 T constant magnetic field was added in the hydrolysis reaction, the time of imposition of the magnetic field was fixed as different hours. The effect of the magnetic field pretreatment time on the morphologies, optical and magnetic properties of Co-doped ZnO were investigated.

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2. Experiments and characterization

2.1. Experiments

Zinc acetate dihydrate(0.75 g) and cobalt acetate tetrahydrate (0.0265 g, doping concentration of 3%) powders were thoroughly mixed and dissolved in 70 mL mixed solvent of absolute ethanol and deionized water(mixture ratio is 1:1). All of the reagents were analytical grade and were used without any further purification. And 1.75 mL ammonia buffer solution was slowly dropped into the former solution and mixed by a magnetic stirrer. Then the mixed solution was transferred into an autoclave (100 mL), which was placed in a 0.4 T constant magnetic field subsequently. The pretreatment time was set as 0 h (no pretreatment), 1 h, 2 h and 4 h. The hydrothermal process was carried out at 170 °C for 24 h in an oven. Thereafter the products were cooled to room temperature. Finally, the resulting precipitates were washed several times with deionized water and absolute ethanol and dried at 60 °C for 8 h. The four $Zn_{0.97}Co_{0.03}O$ samples obtained were marked by S(t = 0 h), S(t = 1 h), S(t = 2 h) and S(t = 4 h) respectively.

2.2. Characterization

The crystalline phase structure of the samples was characterized by a Bruker D8 ADVANCE X-ray diffractometer using Cu-Kα radiation (1.5418 Å) in the range of $20° \leq 2\theta \leq 80°$. The morphology and microstructure of the samples were observed by SEM and TEM. Raman spectra was measured by a Horiba LabRAM HR800 Raman spectroscope using a 532 nm Nd-YAG laser as the excitation source in the range of 200–1000 cm^{-1}. PL spectra was recorded by a PerkinElmer fluorescence spectrometer with the excitation wavelength of 320 nm. Magnetization studies were performed through the Vibrating Sample Magnetometer from Quantum Design company in the United States.

3. Results and discussion

3.1. Morphological and structural properties

Fig. 1(a)–(d) shows the SEM image of S(t = 0 h), S(t = 1 h), S(t = 2 h) and S(t = 4 h), and the inset of Fig. 1(a) is the magnification image of a random region. The size and distribution of all samples is uniform, which confirms that the hydrothermal method could prepare good quality particles. As seen from the inset of Fig. 1(a), the particles are flower shaped with seven petals and the length of each petal is around 900 nm. Comparing Fig. 1(a)–(d), no significant change in the microstructure can be observed.

Fig. 2 depicts XRD patterns of $Zn_{0.97}Co_{0.03}O$ obtained with different magnetic field time applying in the hydrolysis reaction. To cross-reference, the pure ZnO was prepared by the same reaction conditions. In all cases, only the wurtzite structure of ZnO can be found and indexed as JCPDS card no. 36-1451. Comparing with pure ZnO, there is no structural change and formation of additional phases due to the incorporation of Co in ZnO within the sensitivity of XRD technique, confirming that Co dopants are well substituted in ZnO and doping samples are highly pure and single-phase crystal. The diffraction angle (2θ), full width at half maximum (FWHM), and lattice parameters that given by Rietveld refinement of XRD are illustrated in Table 1. It is observed that peaks shift slightly towards lower diffraction angle due to the small lattice expansion by additional Co atoms. The same results were observed in the reports of the literature [1,47–50]. Lower 2θ value is found in S(t = 2 h) and S(t = 4 h), that is, more Co atoms enter into ZnO with the increase of pretreatment time. Comparing with pure ZnO, the little increase in lattice constant a and c with t could be explained by the lattice distortion [51]. And S(t = 2 h) and S(t = 4 h) have the larger cell volume, the increase of cell volume is due to the lattice expansion. The value of FWHM turns to larger in S(t = 2 h) and S(t = 4 h), which may reveal more defects in S(t = 2 h) and S(t = 4 h). On

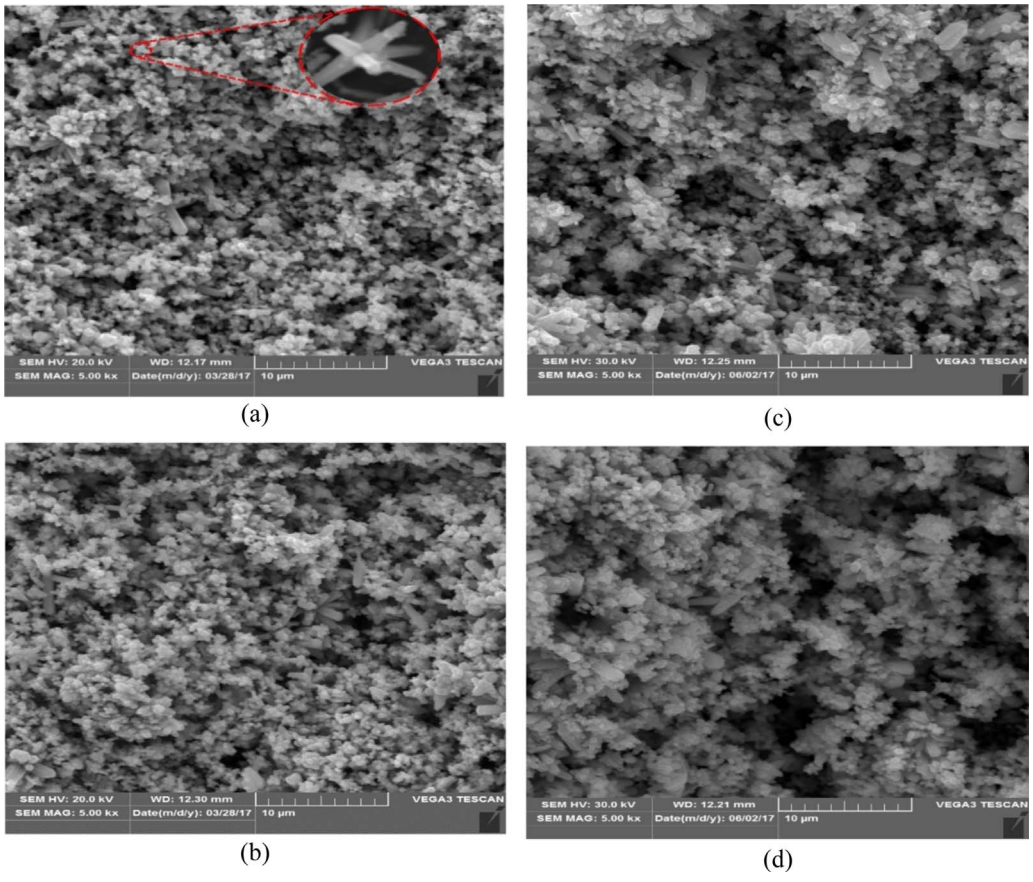

Fig. 1. SEM image of $Zn_{0.97}Co_{0.03}O$ (a) S(t = 0 h), (b) S(t = 1 h), (c) S(t = 2 h), (d) S(t = 4 h).