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Room-temperature ferromagnetic Mn-doped ZnO nanocrystal synthesized by hydrothermal method under high magnetic field

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ABSTRACT

Mn-doped ZnO nanocrystal have been synthesized by the hydrothermal method under a 4 T pulsed magnetic field. X-ray diffraction (XRD) and scanning electron microscopy (SEM) characterizations reveal the samples are nano-columns with a hexagonal wurtzite ZnO structure. Raman measurement indicates that internal stress and structure defects of the samples increase due to the Mn atoms intercalate into the ZnO crystal lattice. Vibrating sample magnetometer (VSM) detection reveals well room-temperature ferromagnetism for our Mn-doping samples. The origin of room-temperature ferromagnetism may arise from the exchange interaction between Mn^{2+} ions and defects in ZnO. Combined with XRD, Raman and VSM measurement, it can also find that high pulsed magnetic field introduces more defects into Mn-doped ZnO samples, thus leads to the enhancement of their saturation magnetization.

1. Introduction

Diluted magnetic semiconductors (DMS) have attracted considerable attention due to their high magnetic ordering curie temperature (T_c) and large spin polarization of charge carriers [1]. DMS, which is usually obtained by doping magnetic ions as impurities into the host semiconductor, can be used for the high-density, high-speed and low-power electronic devices [2,3]. Dietl et al. [4] predicted that 5% Mn-doped ZnO DMS have a higher curie temperature than room temperature. This prediction triggered a worldwide interest in research of the Mn-doped ZnO DMS [5–7]. At present, many methods have been used to prepare Mn-doped ZnO nanocrystal, such as vapors phase growth [8], thermal decomposition [9], seed-mediated [1] and reverse micelle [10]. Compared with those methods, hydrothermal method is simple, economical and convenient. It is an ideal method for synthesizing uniform-doping DMS. In order to control the morphology and regulate the magnetism of DMS, high magnetic field has been applied in the hydrothermal process. It has found that magnetic field can control crystalline orientation and texture [11,12]. In addition, the high magnetic field can also improve distribution as well as control grain boundary and morphology of precipitates [13]. However, as far as we know, few works have been reported about the effect of high magnetic field on the preparation of Mn-doped ZnO nanocrystal. In this paper, a high magnetic field was used when synthesizing Mn-doped ZnO nanocrystal. Its effects on the morphology, structure and magnetic properties of the product were investigated.

2. Experimental

Mn-doped ZnO nanocrystals were synthesized by the hydrothermal method under high magnetic field. A certain amount of manganese acetate (purity 99.9%) were taken at an appropriate ratio and dissolved in 12 ml zinc acetate solution (0.75 mol/L), and then 8 ml ammonia buffer solution (3 mol/L) was added and mixed together. The mixed solution was stirred for 30 min in a surrounding ice-water bath, then placed into an autoclave (25 ml) and maintained at 453 K for 4 h under a 4 T pulsed magnetic field with the frequency of twice per minute. The precipitate obtained was filtered, washed with distilled water and dried at 353 K for 10 h.

The morphologies of as-prepared samples were observed by scanning electron microscopy (SEM, JSM-6700F, JEOL, 15 kV). Energy dispersive spectroscopy (EDS, INCA, Oxford) had been used for determining the elements in nanocrystal. The crystalline structure of the samples had been characterized by X-ray diffraction (XRD, D/max 2550 V, Rigaku, Cu Kα, λ = 0.15406 nm, 4 °C/min). Magnetic measurement had been performed by vibrating sample magnetometer (VSM, 7407, LakeShore). Raman scattering (RS, in-Via plus, Renishaw) had been used for obtaining information about the crystal defect and change of free carriers in the as-prepared samples.

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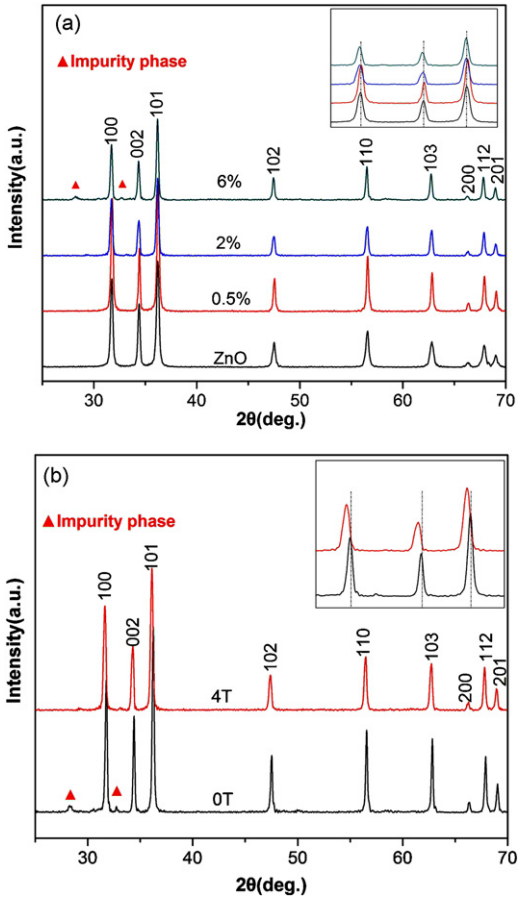

Fig. 1. (a) X-ray diffraction patterns of 0.5%, 2% and 6% Mn-doped ZnO synthesized under 4 T magnetic field. (b) X-ray diffraction patterns of 2% Mn-doped ZnO synthesized under 4 T and no magnetic field. The insets show the details of (1 0 0), (0 0 2) and (1 0 1) diffraction patterns.

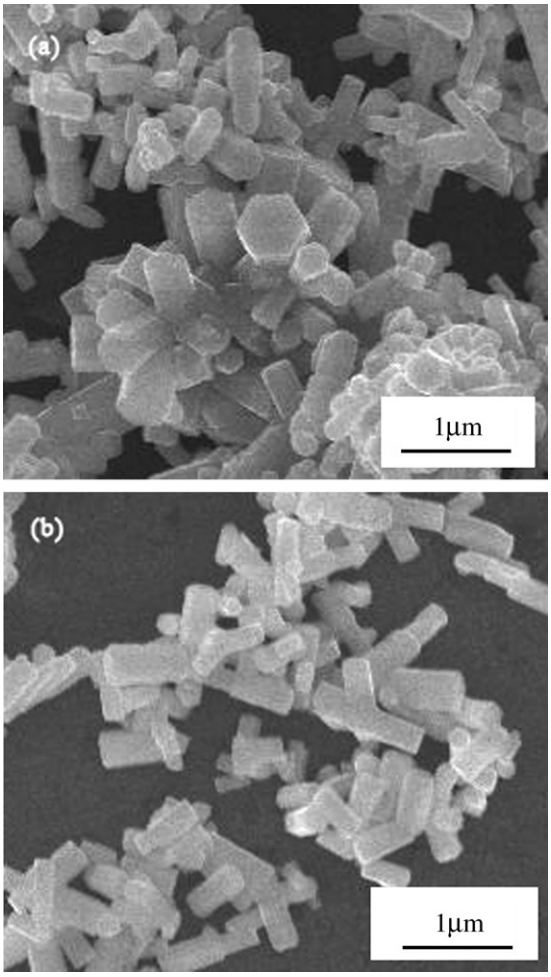

Fig. 3. (a) SEM image of 2% Mn-doped ZnO nanocrystal synthesized under 0 T magnetic field. (b) SEM image of 2% Mn-doped ZnO nanocrystal synthesized under 4 T magnetic field.

3. Results and discussion

Fig. 1(a) shows the X-ray diffraction patterns of the different Mn content samples synthesized under 4 T magnetic field. After indexing, most of the diffraction peaks match those of hexagonal wurtzite ZnO (JCPDS no. 36-1451). From the inset in Fig. 1(a), the diffraction peaks of Mn-doped ZnO shift to small angles which indicate that the lattice constants of Mn-doped ZnO have changed slightly. Here, lattice constants *a* and *c* were determined by using Jade 5.0, as shown in Fig. 2. It can be seen that both lengths of *a*- and *c*-axes expand monotonously with the increase of Mn content. This is because the ionic radius of Mn^{2+} (0.8 Å) is larger than Zn^{2+} (0.74 Å) [14], the more Zn^{2+} were substituted by Mn^{2+} the greater lattice distortion of ZnO would be generated.

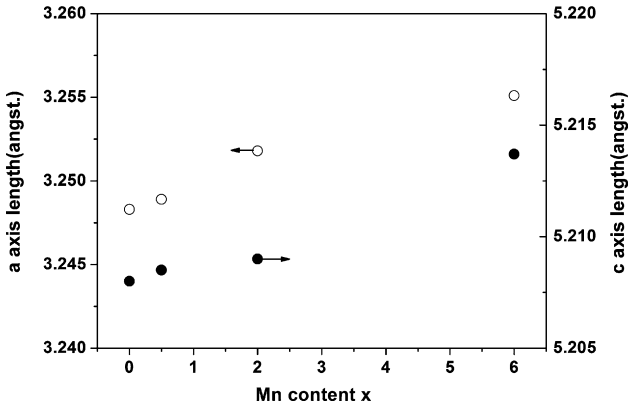

Fig. 2. *a*- and *c*-axes lattice constants as function of Mn content *x* for Mn-doped ZnO.

Besides the diffraction peaks of hexagonal wurtzite ZnO, few additional peaks of impurity are also observed in Fig. 1(a). The diffraction peak intensities of impurity become stronger with the increase of Mn content, indicating that the impurity phase volume fraction increases. EDS analyses (not shown) demonstrate co-existing of Zn, Mn, and O in the as-synthesized samples, no other elements are detected. The additional peaks correspond to $ZnMn_2O_4$ (JCPDS no. 24-1133). Fig. 1(b) shows XRD of the 2% Mn-doped samples synthesized under 4 T and no magnetic field. The diffraction peaks of the sample synthesized under 4 T move to small angles when comparing with those of the sample synthesized under no magnetic field, indicating more Zn^{2+} were substituted by Mn^{2+} under high magnetic field. EDS measurements verify the actual Mn content in these two samples are 1.58% and 1.28% respectively, which also shows that more Mn atoms have been doped into ZnO structure under high magnetic field. At the same time, it can be seen the $ZnMn_2O_4$ impurity phase in the sample prepared under no magnetic field is more obvious than that prepared under 4 T magnetic field, indicating that Mn atoms are easier to form impurity phase under no magnetic field.

Fig. 3 displays the SEM images of the 2% Mn-doped samples synthesized under 0 T and 4 T magnetic field. From the Fig. 3(a), the morphologies of the sample synthesized under no magnetic