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Structure and magnetic properties of Fe-doped ZnO prepared by the sol–gel method

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Abstract

Zn_{0.97}Fe_{0.03}O nanoparticles were synthesized by the sol–gel method. X-ray diffraction (XRD) and transmission electron microscope (TEM) analysis revealed that the samples had pure ZnO wurtzite structure and Fe ions were well incorporated into the ZnO crystal lattice. X-ray photoelectron spectroscopy (XPS) showed that both Fe²⁺ and Fe³⁺ existed in Zn_{0.97}Fe_{0.03}O. The result of x-ray absorption near-edge structure (XANES) further testified that Fe ions took the place of Zn sites in our samples. Magnetic measurements indicated that Zn_{0.97}Fe_{0.03}O was ferromagnetic at room temperature.

1. Introduction

Recent studies show that III–V and II–VI based diluted magnetic semiconductors (DMSs) are promising materials for spintronics applications [1]. It is essential for realizing practical spintronics devices that the DMS systems display ferromagnetism at room temperature. Earlier first-principle electronic structure calculations by Sato *et al* [2, 3] suggested that transition-metal (TM) doped ZnO compounds were ferromagnetic provided that the carriers produced by the TM doping formed a partially filled spin-split impurity band. Dietl *et al* [4] predicted that wide band gap materials such as ZnO should have a high Curie temperature (T_C) with hole doping. In fact, room temperature ferromagnetism (RTFM) has been reported for ZnO–Mn [5] and ZnO–Co [6] systems. In contrast, Yang *et al* [7] believe that the magnetism of Zn_{1-x}Mn_xO is paramagnetic at room temperature. The conflicting results have led to the growing interest in both theoretical [4] and experimental [8] studies on transition-metal (TM) doped ZnO.

Recently, more reports about Fe-doped ZnO diluted magnetic semiconductor have been issued [9–15]. A wide range of contradictory experimental results, debating

the success versus failure of obtaining a T_C above room temperature, have injected much excitement in the doping mechanism and the origin of ferromagnetism in the system. In the present work, Fe-doped ZnO nanoparticles were synthesized by the sol–gel method. The structure and the room temperature magnetic properties of Zn_{0.97}Fe_{0.03}O have been also studied.

2. Experimental details

According to the ferric concentration ($x = 3$ at.%), appropriate proportions of Zn(NO₃)₂·6H₂O (99.9%) and Fe(NO₃)₃·9H₂O (99.9%) high-purity powders were thoroughly mixed and dissolved in water to obtain a homogeneous solution. The mixture was then poured into citric acid [C₆H₈O₇] (99.5%) while stirring. The solution was dried at 80 °C to obtain xerogel and the swelled xerogel was completed at 130 °C. After being ground, the powders were sintered at 600 °C for 10 h under air atmosphere. The reaction mechanism of the decomposing citrate technique has been described previously [16].

Structural characterization of Zn_{0.97}Fe_{0.03}O was performed by XRD on a D/max-2500 copper rotating-anode x-ray diffractometer with Cu K α radiation (40 kV, 200 mA), TEM

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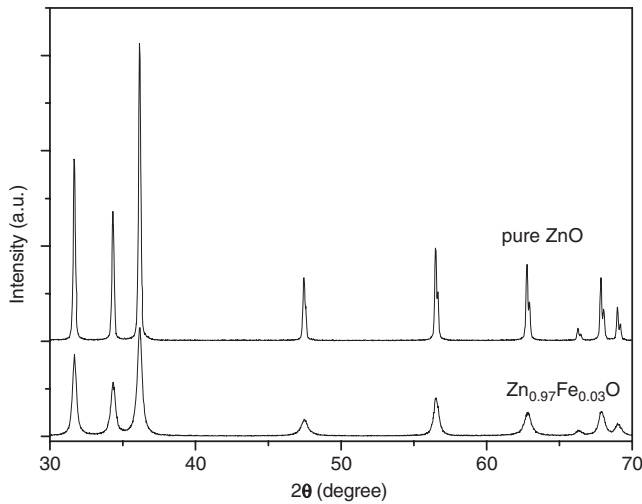


Figure 1. XRD patterns of ZnO and $Zn_{0.97}Fe_{0.03}O$.

(200 keV, JEM-2100HR, Japan) and x-ray photoelectron spectroscopy (XPS) (VG ESCALAB Mark II). The x-ray absorption near-edge structure (XANES) of $Zn_{0.97}Fe_{0.03}O$ was carried out at the XAFS station of the Hefei National Synchrotron Radiation Laboratory. Magnetic hysteresis loops and $M-T$ curves of $Zn_{0.97}Fe_{0.03}O$ were measured by a Lake Shore 7407 vibrating sample magnetometer (VSM).

3. Results and discussion

The XRD patterns for pure ZnO and $Zn_{0.97}Fe_{0.03}O$ are presented in figure 1. The samples had a hexagonal wurtzite structure belonging to the C_{6v}^4 space group ($P63mc$) according to the standard JCPDS card. No diffraction peaks of other impurity phases were found in $Zn_{0.97}Fe_{0.03}O$ and the mean particle sizes of the sample were also estimated to be around 40 nm using the Scherrer formula. From figure 1, it also can be seen that the XRD peaks of $Zn_{0.97}Fe_{0.03}O$ were broadened comparing with the pure ZnO. Two factors contribute to this phenomenon. On one hand, it can be attributed to the smaller particle size of $Zn_{0.97}Fe_{0.03}O$. On the other hand, doping Fe

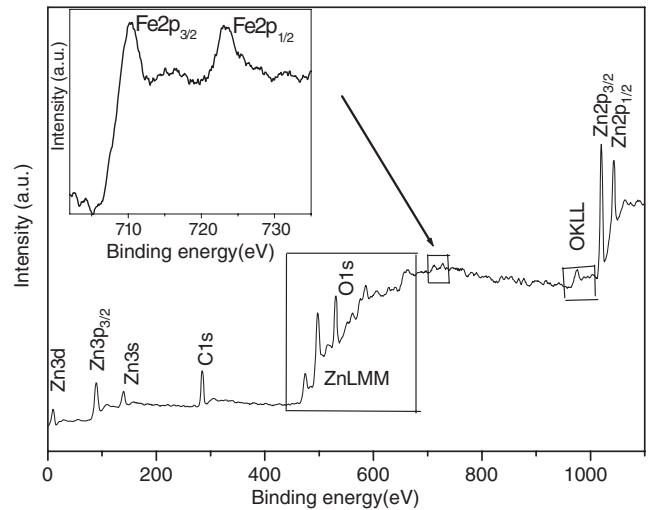


Figure 3. XPS spectrum of $Zn_{0.97}Fe_{0.03}O$ (peak positions are referenced to the adventitious C 1s peak taken to be at 284.6 eV).

into the ZnO crystal lattice can inhibit crystallization of the sample.

The results of TEM characterizations are shown in figures 2(a) and (b). The low-resolution TEM micrograph for $Zn_{0.97}Fe_{0.03}O$ revealed that the average size of the particles was about 40 nm, which was consistent with the calculation results from XRD. So we concluded that the Fe-doped ZnO prepared by the sol-gel method was a nanostructure material. High-resolution TEM micrographs showed that the interplanar distance of fringes was 0.26 nm, which is in good agreement with the (002) plane of wurtzite ZnO. All the nanoparticles in the sample were single crystal and free from major lattice distortions. According to the results of XRD pattern and HRTEM images, we believed that the Fe ions were well incorporated into the crystal lattice of ZnO.

XPS spectra showed the indexed peaks corresponding to C, Fe, O and Zn, calibrated by C 1s (284.6 eV) as shown in figure 3. The peaks at 710.1 and 723.1 eV correspond to the binding energy of Fe $2p_{3/2}$ and Fe $2p_{1/2}$, respectively. The Gaussian fitting results indicated that the $2p_{3/2}$ and $2p_{1/2}$ peaks

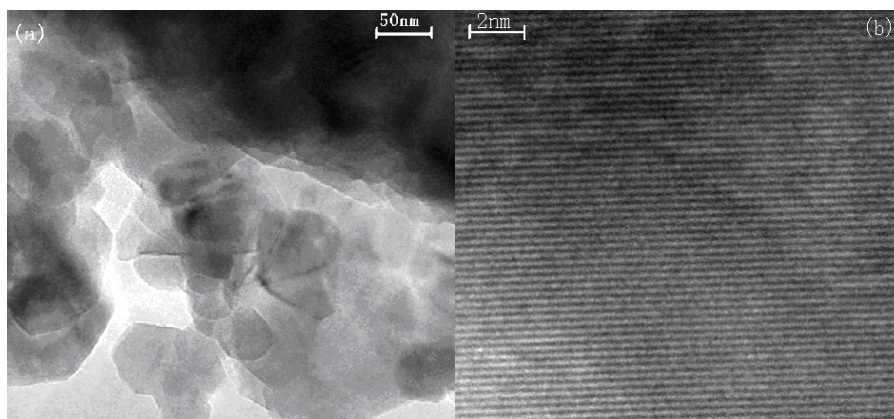


Figure 2. (a) Low-resolution TEM micrograph of $Zn_{0.97}Fe_{0.03}O$ nanoparticles. (b) High-resolution TEM micrograph of $Zn_{0.97}Fe_{0.03}O$ nanoparticles.

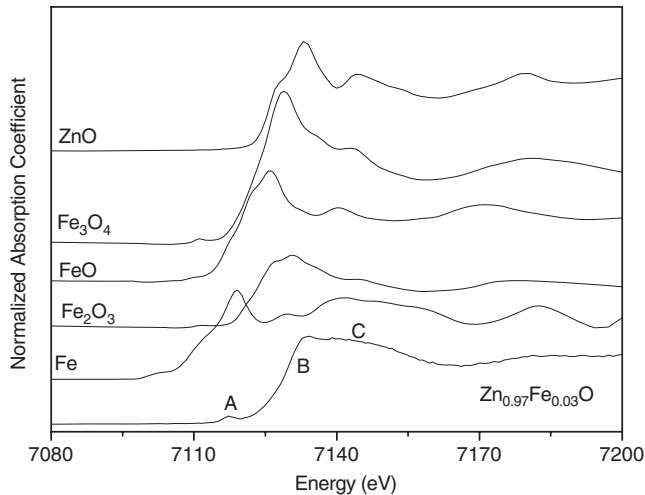


Figure 4. Normalized Fe K-edge XANES spectra of $\text{Zn}_{0.97}\text{Fe}_{0.03}\text{O}$ and reference samples.

for Fe^{2+} are located at 710.3 and 722.3 eV and the $2p_{3/2}$ and $2p_{1/2}$ peaks for Fe^{3+} are located at 710.7 and 724.0 eV [17], respectively. Hence, the valence state of Fe is believed to be major Fe^{2+} and minor Fe^{3+} , the characteristic peak of the zero-valent state of metal clusters or particles was not found. Usually, if Fe is present in the substitutional site in a defect-free ZnO crystal, the valence state of Fe will be +2. However, the XPS results confirmed the existence of uncoupled Fe^{3+} within the sample. In our system, Fe^{3+} ions were present mainly due to the existence of the cation vacancy. A cation vacancy near Fe can promote Fe^{2+} into Fe^{3+} and also mediate the Fe^{2+} - Fe^{2+} exchange interaction. Since the TM doping percentage was slightly on the higher side toward the cationic percolation threshold, Fe^{2+} - Fe^{3+} exchanges, although being fewer in number in comparison to the Fe^{2+} - Fe^{2+} interaction, may also be possible [18]. And the presence of Fe^{3+} in our sample was a possible signature of hole doping induced by Zn vacancies. The atomic ratio of Fe:Zn of this sample is about 0.028, close to the expected nominal composition (0.03).

Figure 4 shows the normalized Fe K-edge XANES spectra of our sample and reference samples. Three main features are identified in the XANES spectrum of $\text{Zn}_{0.97}\text{Fe}_{0.03}\text{O}$ nanoparticles: the small pre-edge peak A, the dominant main peak B, and the shoulder C at the post-edge region. The interpretations of K-edge XANES features for 3d transition-metal oxides are well established [19, 20]. Generally, peak A is interpreted as a quadrupolar electronic transition from 1s to the 3d final states hybridized with 4p character of the absorber; peak B arises from the dominant dipolar transition from 1s to the 4p-related final states; and peak C corresponds to a phase transition.

Comparing the XANES spectra of Fe and Fe oxides with our doping sample, we concluded that there was no Fe metal, FeO or Fe_2O_3 phase in $\text{Zn}_{0.97}\text{Fe}_{0.03}\text{O}$ nanoparticles because there were obvious differences of the pre-edge regions between them and $\text{Zn}_{0.97}\text{Fe}_{0.03}\text{O}$ nanoparticles. However, the XANES spectra of our sample and the Fe_3O_4 reference illustrated similarity, which revealed that the valence states of Fe in

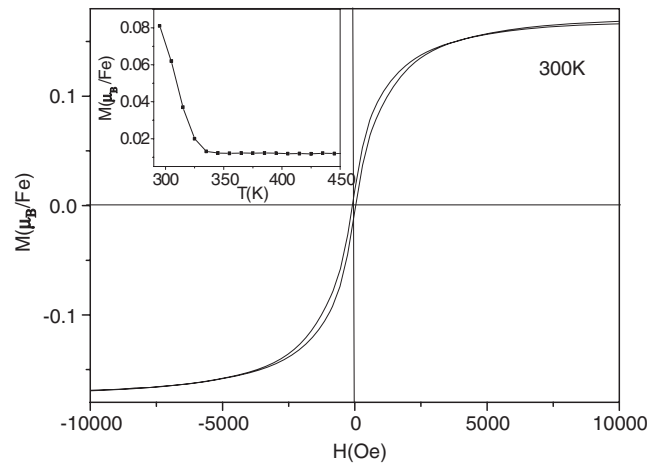


Figure 5. Magnetic hysteresis (M - H) loops of $\text{Zn}_{0.97}\text{Fe}_{0.03}\text{O}$ at room temperature under 10 kOe. The inset shows the temperature dependence of magnetic moment for $\text{Zn}_{0.97}\text{Fe}_{0.03}\text{O}$ under 1 kOe.

the $\text{Zn}_{0.97}\text{Fe}_{0.03}\text{O}$ nanoparticles were Fe^{2+} and Fe^{3+} , which was consistent with the results of the XPS. The XRD results in figure 1 show that there were no Fe_3O_4 in our sample, which indicates Fe atoms dissolved into the ZnO lattice without forming secondary phases. In addition, in order to compare Fe K-edge XANES spectra of Fe-doped ZnO nanoparticles with Zn K-edge XANES spectra of ZnO conveniently, we moved the Zn K-edge XANES spectra to the position of Fe K-edge XANES spectra parallelly. The Fe K-edge features of our sample and Zn K-edge features of ZnO reference were similar, showing that the chemical environment of Fe in the Fe-doped ZnO nanoparticles was almost the same as that of Zn in ZnO. As a result, we believed that Fe ions had substituted Zn ions and occupied the position of Zn in ZnO.

Figure 5 shows the magnetization versus magnetic field (M - H) loops and temperature dependence of magnetic moment (M - T) curve for $\text{Zn}_{0.97}\text{Fe}_{0.03}\text{O}$. The sample showed ferromagnetic ordering at room temperature and possesses a moment of $0.13 \mu_{\text{B}}/\text{Fe}$ atom. The inset in figure 5 shows a temperature dependence of magnetic moment for $\text{Zn}_{0.97}\text{Fe}_{0.03}\text{O}$ under 1 kOe. With increasing temperature, the magnetization moment for $\text{Zn}_{0.97}\text{Fe}_{0.03}\text{O}$ decreased and reached a Curie temperature (T_{C}) below 335 K, which is below the Curie temperature of iron oxide. By comparison with the results of the XRD and XANES spectra, we can further testify that Fe atoms are already dissolved into the ZnO lattice without forming iron oxide. Therefore, the ferromagnetism of the $\text{Zn}_{0.97}\text{Fe}_{0.03}\text{O}$ in this study was an intrinsic property of Fe-doped ZnO.

Recently, there have been many theoretical understandings about the origin of ferromagnetism in zinc-oxide-based dilute magnetic oxide [21, 22]. Based on the XPS analysis, we believe that a hybridization picture of super and double exchange gives the explanation of our observed ferromagnetism. The Zn vacancies also play a role in the stabilization of the RTFM in $\text{Zn}_{0.97}\text{Fe}_{0.03}\text{O}$.

4. Conclusion

In summary, $\text{Zn}_{0.97}\text{Fe}_{0.03}\text{O}$ nanoparticles were synthesized by the sol-gel method and investigated by XRD, TEM, XPS, XANES and VSM. The analysis results revealed that Fe ions in $\text{Zn}_{0.97}\text{Fe}_{0.03}\text{O}$ nanoparticles had Fe^{2+} and Fe^{3+} components and they well substitutionally incorporated into the crystal lattice of ZnO. Magnetic measurements indicated that $\text{Zn}_{0.97}\text{Fe}_{0.03}\text{O}$ was ferromagnetic at room temperature. The analysis also showed that the observed room temperature ferromagnetism was an intrinsic property of Fe-doped ZnO.

Acknowledgments

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