

Research Article

Effect of Cr Content on the Properties of Magnetic Field Processed Cr-Doped ZnO-Diluted Magnetic Semiconductors

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Cr-doped ZnO-diluted magnetic semiconductor (DMS) nanocrystals with various Cr contents were synthesized by hydrothermal method under high magnetic field. The result indicated that both the amount of Cr contents and high magnetic field significantly influenced crystal structure, morphology, and magnetic property of Cr-doped ZnO DMSs. When the Cr contents increased from 1 at% to 5 at%, the morphology of grains sequentially changed from flower-like to rod-like and then to the flake-like form. All the samples remained hexagonal wurtzite structure after Cr ions were doped into the ZnO crystal lattice. The Cr doping led to the increasing amount of defects and even enhanced the magnetic property of the matrix materials. All the Cr-doped ZnO DMSs obtained under high magnetic field exhibited obvious ferromagnetic behavior at room temperature. The results have also shown the successful substitution of the Cr³⁺ ions for the Zn²⁺ ions in the crystal lattice.

1. Introduction

Recently the interest in diluted magnetic semiconductors (DMSs) has significantly increased because of their unique magnetic property and potential applications in many fields [1–6]. Ferromagnetic DMSs with Curie temperatures (T_c) above room temperature are usually obtained by doping magnetic ions into the host semiconductors. Zinc oxide is one of representative semiconductor [7, 8], due to its wide bandgap of 3.37 eV and large exciton energy (60 meV). As a transition metal ion, Cr³⁺ is often used as a dopant for ZnO because of the close ionic radius with Zn²⁺ and the ferromagnetic stability of Cr-doped ZnO DMSs [9, 10].

Currently, many methods have been reported to fabricate ZnO DMSs, such as vapor-phase growth [11], thermal decomposition [12], seed-mediated [13], and reverse micelle [14]. Recently, our group has successfully developed a novel hydrothermal method under high magnetic field to prepare a series of transition metal ions (Cr³⁺, Mn²⁺, Co²⁺) doped ZnO DMSs. According to our previous work, it

revealed that high magnetic field played an important role in introducing ions into ZnO crystal lattice and improving the magnetic properties [15–17]. In the present work, the effect of Cr content on the structure, morphology, and magnetic property of Cr-doped ZnO DMSs prepared by HPMF method was investigated in detail.

2. Experimental

A hydrothermal method with pulsed magnetic field of 4 Tesla (T) was used to synthesize the Cr-doped ZnO DMS materials with different Cr nominal contents (1 at%, 2 at%, 3 at%, 5 at%). The typical synthesis process was as follows. A 12 mL 1.33 M solution of potassium hydroxide was slowly dropped into a solution of 4 mL of 1.00 M zinc acetate. The mixture was stirred at 273 K for 0.5 hours. Then, a desired amount of 0.02 M chromium nitrate solution, which was calculated according to the nominal Cr content, was slowly dropped into the former mixture at 273 K in the ice bath, and followed by stirring for 1 h. The entire mixtures with

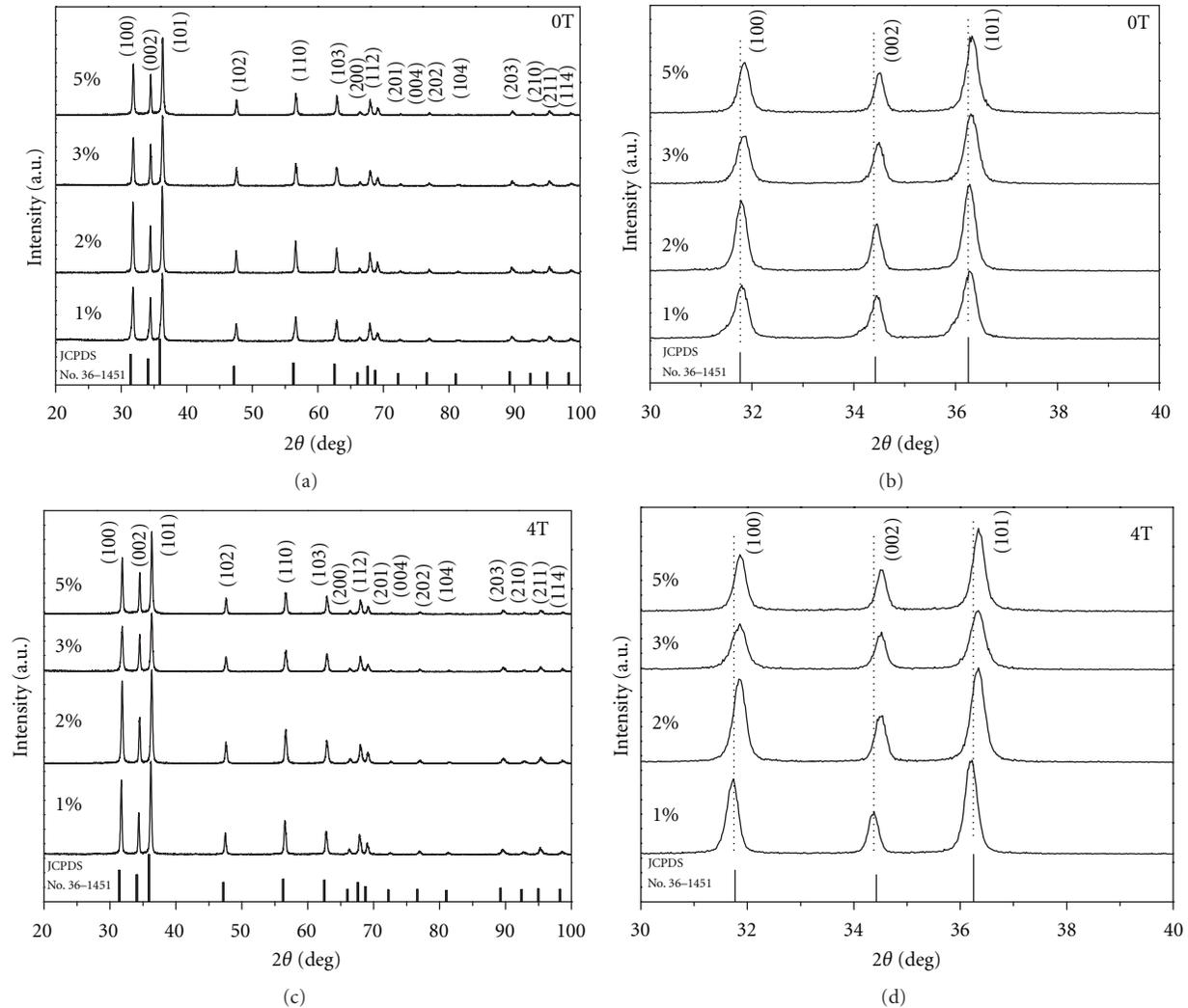


FIGURE 1: XRD patterns of 1%, 2%, 3%, and 5% Cr-doped ZnO synthesized under 0 T ((a), (b)) and 4 T ((c), (d)) magnetic fields.

a certain concentration of chromium nitrate in zinc acetate solution were then transferred into autoclave (25 mL) and maintained at 453 K for 4 h with 4 T pulsed magnetic field (the obtained sample named as 4T-N%) or without pulsed magnetic field (named as 0T-N%), respectively, in which N presents the Cr nominal content. Finally, the precipitated products were washed with distilled water three times and dried at 373 K for 10 h.

The crystal structures of the samples were determined by X-ray diffraction (XRD) equipped with $\text{CuK}\alpha$ radiation ($\lambda = 1.5406 \text{ \AA}$). Field emission scanning electron microscope (FE-SEM, JEOL JSM-6700) was used to observe the morphologies. The Raman scattering spectra of the samples were recorded by a Renishaw InVia Confocal micro-Raman system using the 785 nm line as excitation source. Magnetic property of the samples was measured by vibrating sample magnetometer (VSM, Lakeshore 7407). The valence state of the Cr element was analyzed by X-ray photoelectron spectroscopy (XPS) (Thermo ESCALAB 250).

3. Results and Discussion

Figure 1 shows the XRD patterns of the Cr-doped ZnO DMSs with various Cr contents synthesized with and without 4 T magnetic fields. All the diffraction peaks (Figures 1(a) and 1(c)) are sharp and match well with those of hexagonal wurtzite structure of ZnO (space group: P63mc (186), JCPDS no. 36-145). No Cr, Cr oxides, or any other impurity-phase peaks are observed which reveals that Cr-doped ZnO DMSs maintain a highly pure crystalline wurtzite structure. Comparing the diffraction peaks (100), (002), and (101) of Cr-doped ZnO DMSs (Figures 1(b) and 1(d)), the peaks shift to larger angles with the increase of Cr contents and the highest shift is for sample with 5% Cr nominal content. The reason is due to the smaller ion radius of Cr^{3+} (0.63 \AA) comparing to that of Zn^{2+} (0.74 \AA). The lattice constants of ZnO decrease slightly after Cr ions doped into the crystal lattice which cause the main peaks moving to the higher angles. The higher the content of Cr ions in the ZnO lattice, the farther the peaks move. Furthermore, the diffraction

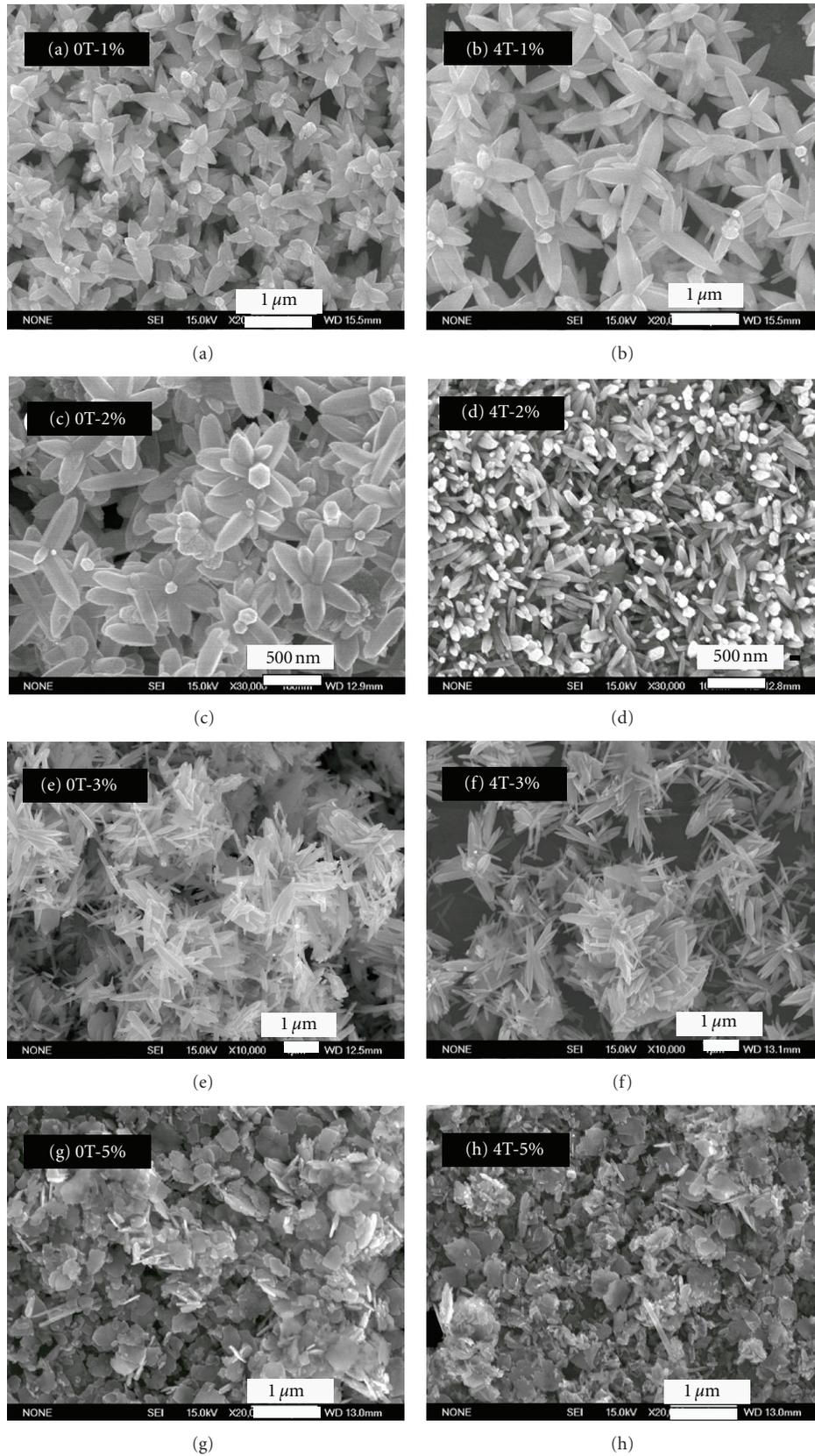


FIGURE 2: SEM images of Cr-doped ZnO with different Cr nominal content synthesized under 0 T ((a), (c), (e), (g)) and 4 T magnetic fields ((b), (d), (f), (h)).

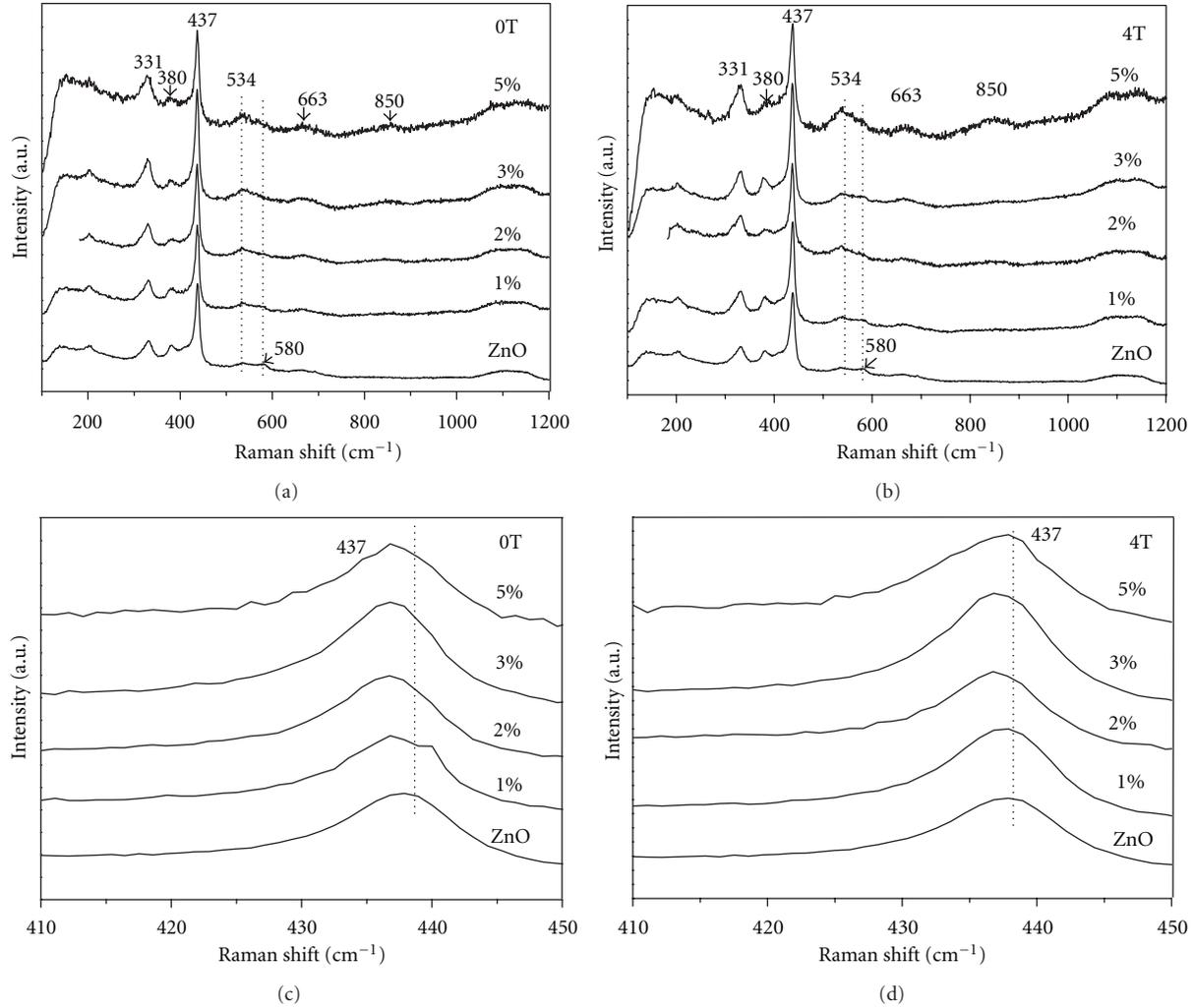


FIGURE 3: Raman spectra of Cr-doped ZnO DMSs with different Cr nominal contents obtained under 0 T ((a), (c)) and 4 T ((b), (d)) magnetic fields, respectively.

peaks (100), (002), and (101) of samples synthesized under 4 T magnetic field move to larger angles comparing with those of the same Cr content samples synthesized without magnetic field, which indicates that, under high magnetic field, larger amount of Cr ions were doped into the ZnO lattice.

Figure 2 shows the SEM images of Cr-doped ZnO with various Cr nominal contents synthesized under 0 T and 4 T magnetic fields. It is observed that with the Cr contents' increase from 1% to 5%, the morphologies of particles change from flower shape to rod shape and eventually to flake shape. For samples with Cr nominal content of 1% (Figures 2(a) and 2(b)), the grains are both flower shape, but the sizes are different, as sizes of the 4T-1% are much smaller than that of 0T-1%. However, for the 2% Cr content samples (Figures 2(c) and 2(d)), both crystalline shapes and sizes are different, the 4T-2% sample appears as fine dense rod shape with rod diameter of 50–100 nm, whereas the 0T-2% sample appears as flower shape with rod diameter of 100–250 nm. Both of

the samples with Cr nominal content of 3% (Figures 2(e) and 2(f)) appear with irregular rod shape with a little difference in particles size. When the Cr nominal content reaches 5% (Figures 2(g) and 2(h)), both samples appear with irregular flake shapes, while the 4T-5% sample shows more small grains than the 0T-5% sample. Clearly, the morphologies of zinc oxides grains are influenced dramatically as the Cr content increased. Concurrently high magnetic field also plays a significant role in the morphologies of Cr-doped ZnO DMSs. Tanaka et al. [18] reported that *c*-axis-oriented ZnO could be fabricated in a rotating sample container under static magnetic field during the hydrothermal doping process. The high pulsed magnetic field essentially provided an external energy and promoted the nucleation and growth of the grains, which finally caused the differentiation of crystal morphology.

All the EDS data (Table 1) verify that the actual incorporated Cr contents are lower than the corresponding Cr nominal contents in the doping process, and increase

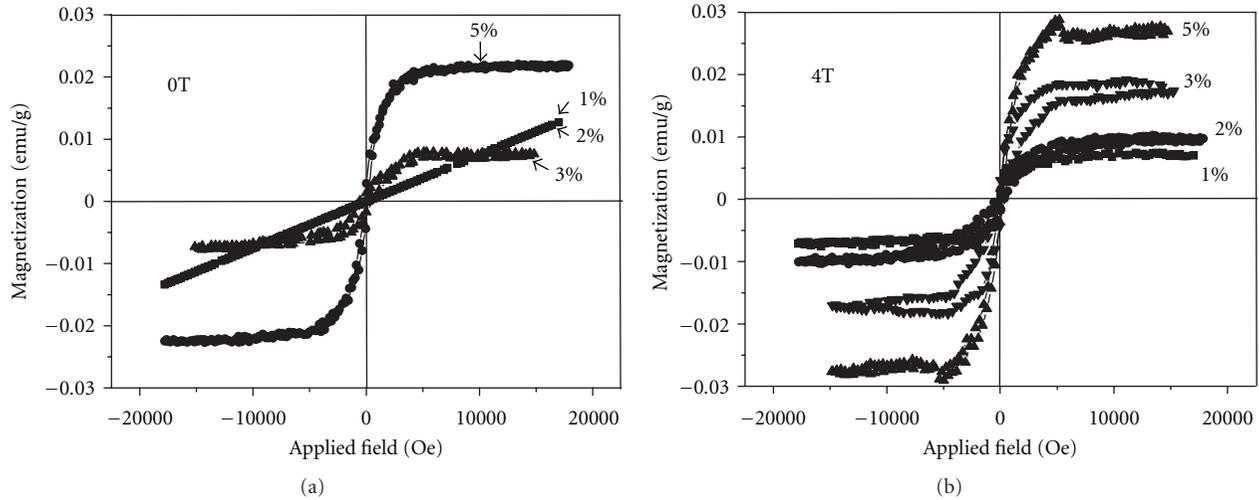


FIGURE 4: Hysteresis loops of Cr-doped ZnO DMSs with different Cr nominal contents synthesized under 0 T (a) and 4 T (b) magnetic fields, respectively.

nominal Cr contents does increase the actual incorporation of Cr. Furthermore, the incorporation of Cr into the ZnO crystal lattice is greater with applying magnetic field than without, which agrees with the results of XRD.

Raman scattering is a versatile technique to characterize the incorporation of Cr ions and the defects in the host lattice. The peak at about 437 cm^{-1} assigned to the E_2 (high) mode of ZnO, which is the characteristic mode of the wurtzite structure and sensitive to internal stress [19]. The peak at 580 cm^{-1} assigned to A_1 (LO) mode, which is sensitive to changes in the free carrier concentration [20]. From Figures 3(a) and 3(b), there is no obvious observed shift at 437 cm^{-1} for all samples. But compared to the pure ZnO, there is a blue shift with the increase of the Cr doping as shown in the magnified Raman shift region as shown in Figures 3(c) and 3(d). These indicate that with the increase of Cr doping, a little structure disorder was occurred and the little blue shift of the peak also illustrates that the lower amount of Cr doping would not change the crystal structure significantly although defects was introduced by Cr doping. Additionally, when Cr ions were doped, the Raman peaks were slightly changed for the 1%, 2%, 3% samples, and comparing to the characteristic peaks of pure ZnO the peak at 580 cm^{-1} gradually disappeared. The gradually disappearance of the 580 cm^{-1} peak is created by the increase of carrier concentration. When Cr ions increased to 5%, the peak at 534 cm^{-1} increased disproportionally and a new peak appeared at 850 cm^{-1} . This new phenomenon is rather unique for the 4T-5% sample only. All these spectroscopic changes probably indicated that the increase of Cr ions incorporation also increases the defect and structures of the ZnO nanocrystals.

Figure 4 shows the magnetic hysteresis (M-H) loops of the Cr-doped ZnO with various Cr nominal contents synthesized under 0 T and 4 T magnetic fields, respectively. It can be seen from Figure 4(a) that 0T-1% and 0T-2% samples show paramagnetic behavior, while 0T-3% and 0T-5%

TABLE 1: EDS parameters and saturation magnetization of Cr-doped ZnO DMSs synthesized with or without high magnetic fields.

Cr nominal content (at%)	Actual Cr content (at%)		Ms (emu/g)	
	0 T	4 T	0 T	4 T
1	0.22	0.35	—	0.0075
2	1.1	1.4	—	0.01
3	2.3	2.4	0.01	0.02
5	3.1	3.7	0.02	0.03

samples show ferromagnetic behavior at room temperature. It had been discussed in our previous work [15] that the weak hybridization effect between Cr ions and defects is the reason which results in paramagnetic behavior of sample 0T-2% at 298 K. From Figure 4(b), all the samples obtained under 4 T magnetic fields manifest room temperature ferromagnetic behavior. The saturation magnetizations (M_s , Table 1) of 1%, 2%, 3%, and 5% sample under pulsed high magnetic field was enhanced compared with 0 T samples, respectively. It is believed that the occurrence of strong electronic coupling between bound polarons and Cr ions forms bound magnetic polarons (BMPs) [3], which is proposed to play an important role in the ferromagnetic origin of Cr-doped ZnO DMSs [21, 22]. Kittilstved et al. [23] suggested defect-bound carriers such that point defects hybridization with magnetic dopants would induce ferromagnetism in transition metal ions doped ZnO. In this study, we have found that, by applying high magnetic field, it can increase the incorporation of Cr ions into the ZnO crystal lattice, and this is shown by the XRD, SEM, and Raman analysis. Since more defects are introduced into the crystal lattice under high magnetic field, the hybridization between defects and Cr dopants should be more efficient, which is probably the cause of room temperature ferromagnetism and the enhancement of saturation magnetization of the Cr-doped ZnO DMSs.

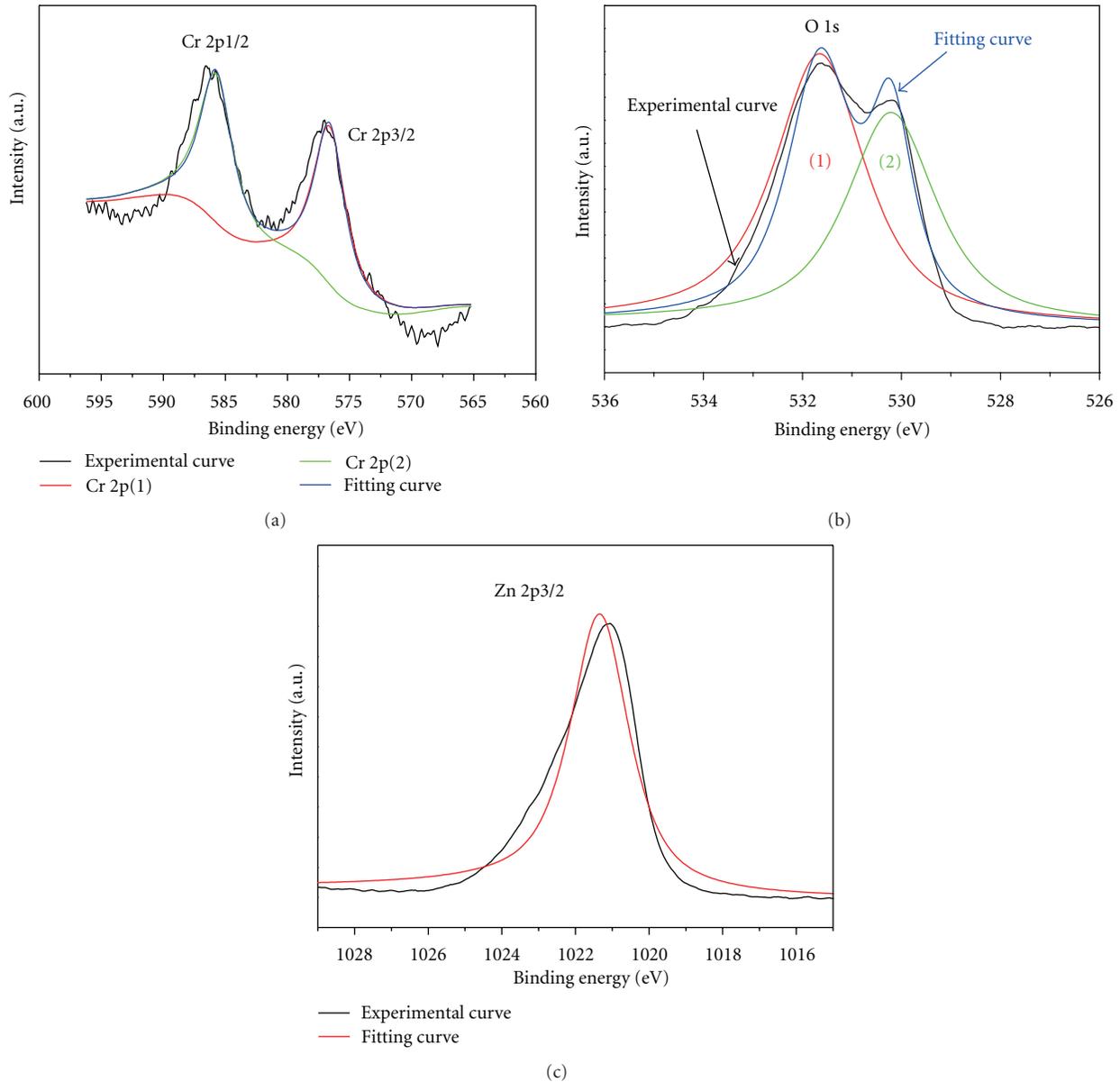


FIGURE 5: XPS spectrum of Cr-doped ZnO nanoparticles.

In order to investigate the chemical state of the host and dopant elements, the XPS studies were undertaken. XPS analysis shows the presence of Zn, Cr, and O elements in Cr-doped ZnO. The overlapped bands were resolved into separated peaks by using XPS PEAK41 software. The Cr 2p_{3/2}, Cr 2p_{1/2}, O 1s, and Zn 2p_{3/2} XPS spectral regions of the Cr-doped ZnO nanoparticle are shown in Figure 5 for 1% Cr-4T sample. Based on the Gauss fitting, the Cr 2p_{3/2} peak position is at 576.6 eV in the Cr-doped ZnO nanoparticle. It is clearly different from 574.2 eV of Cr metal and 576.0 eV of Cr²⁺, but it is quite close to the peak position of Cr 2p_{3/2} (576.7 eV) in Cr₂O₃ [24]. It suggests that the Cr dopants in the ZnO lattice are actually the Cr³⁺ ions.

4. Conclusions

The 1%, 2%, 3%, and 5% Cr-doped ZnO DMSs nanocrystals were synthesized by hydrothermal method under high magnetic field. Both the Cr content and high magnetic field significantly impacted the microstructure and magnetic property of Cr-doped ZnO DMSs. With the increase of Cr contents from 1% to 5%, the morphologies of particles changed from flower shape to rod shape and eventually to flake shape. After the incorporation of Cr, the ZnO DMSs nanocrystals still retained wurtzite crystal structure. The Cr doping caused the increased amount of defects and the enhancement of magnetic property of the materials. All the Cr-doped ZnO DMSs obtained under high magnetic field exhibited ferromagnetic behavior at room temperature. The

Cr ions that incorporated in the ZnO lattice were shown to be the Cr³⁺ cations.

Acknowledgments

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