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Al–Mg co-doping effect on optical and magnetic properties of ZnO nanopowders

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A B S T R A C T

$Zn_{0.97-x}Mg_xAl_{0.03}O$ ($x = 0, 0.01, 0.03$ and 0.05) nanoparticles were prepared by hydrothermal growth, and their optical and magnetic properties were systematically studied by the X-ray diffraction (XRD), the UV-visible spectrophotometer, the infrared spectrometer and the physical properties measurement system (PPMS). These results showed that all the nanopowders had hexagonal wurtzite structures. With increasing the content of Mg, the strength of the (110) intensity peak increased. When Mg atoms were not incorporated into the $Zn_{0.97}Al_{0.03}O$ lattice, the infrared light transmittance was higher than that of other groups of samples. In the UV range, the absorption decreased with the increase of the concentration of Mg. Mg doping weakened the magnetic property of the nanoparticles at room temperature. The zero-field-cooled (ZFC) and field-cooled (FC) magnetization curves were separated with the decrease of temperature due to the pinning effect between the ferromagnetic domain and antiferromagnetic domain.

1. Introduction

Currently, nanostructured Zinc Oxide (ZnO) materials have attracted great interest from scientists due to their remarkable performance in electronics and optics. As a wide bandgap semiconductor material, ZnO has excellent photoelectric properties because of the large exciton binding energy (60 meV) and the wide bandgap (3.37 eV) [1]. Furthermore, dilute magnetic semiconductors (DMSs) have dual characteristics of magnetism and semiconductor at the same time. Hence, ZnO has attracted a great deal of attention due to its excellent functions in information storage and information processing. It is promised to be widely used in the area of memory, magnetic sensors, optical isolator, semiconductor integrated circuits, semiconductor laser and spin quantum computer because of the excellent optical, electrical and magnetic properties [2–4]. Recently, the study of DMSs based on ZnO has focused on the doping of ferromagnetic 3d transition metals and non-magnetic elements. Most of the products, such as Cu doped ZnO [5] and (Al, Cu) co-doped ZnO [6], have been found to be ferromagnetic at room temperature. However, the inner mechanism of DMSs based on ZnO still remains as a research hotspot and difficult issue due to the fact that doping elements in ZnO DMSs tend to form secondary phases, unpaired spin-electrons or defects on their surface. In theory, the interpretation of magnetic properties has been mainly concentrated in two aspects. One is the Ruderman–Kittel–Kasuya–Yosida (RKKY) mechanism in which ferromagnetic exchange function is associated with the concentration of carrier charge. The synthesis of (Al, Ni) co-doped ZnO [7] and (Al, Cu) co-doped ZnO [8] demonstrated that doping of a small amount of Al atoms could increase the carrier charge concentration, which then enhance the ferromagnetic effect. The other is the bound magnetic polarons (BMPs). This model was presented for low concentration of carrier charge and illustrated that the main cause of the bound magnetic moments was associated with structural defects. Du [9] et al. found that doping Mn–ZnO with Li (a P-type dopant) resulted in a high carrier charge concentration, which could enhance the intrinsic magnetic moment of ferromagnetic coupling between Mn^{3+}. Many research groups have made great efforts toward Al doped ZnO or Mg doped ZnO alloys [10–12] and have confirmed that the introduction of Al ions can lead to the presence of lattice defects such as oxygen and zinc vacancies. These vacancies in the cluster form will give rise to the magnetic moment and affect the spin polarization effect of ions around defects. These would affect the magnetism of the samples at room temperature.

In our previous papers [13–15], nano-structure, DMSs, magnetic properties, and magnetocaloric effect have been investigated in Mn–Zn nano-ferrite, Co bulk metallic glass and Co-doped ZnS nanoparticles, and some results have been obtained. In this present study, $Zn_{0.97-x}Mg_xAl_{0.03}O$ ($x = 0, 0.01, 0.03$ and 0.05) nanoparticles were prepared by hydrothermal growth. The performance of the samples with different contents of Mg doping was studied, and

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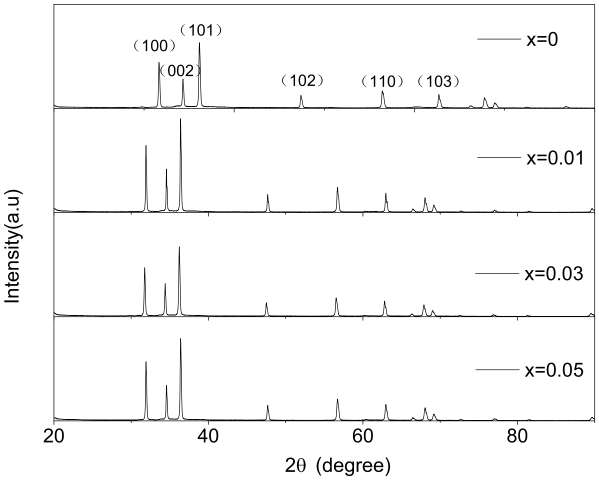

Fig. 1. The XRD patterns of $Zn_{0.97-x}Mg_xAl_{0.03}O$ ($x = 0, 0.01, 0.03$ and 0.05) particles.

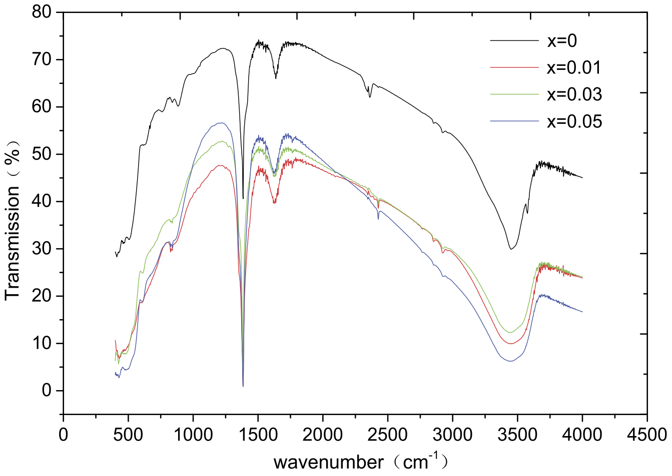

Fig. 2. The infrared spectra of $Zn_{0.97-x}Mg_xAl_{0.03}O$ ($x = 0, 0.01, 0.03$ and 0.05) particles.

Table 1
The refined lattice parameters (a and c) (Å) of $Zn_{0.97-x}Mg_xAl_{0.03}O$ ($x = 0, 0.01, 0.03$ and 0.05).

Systems	Parameters		
	a (Å)	c (Å)	c/a
0%	3.258	5.218	1.601
1%	3.240	5.210	1.608
3%	3.245	5.196	1.601
5%	3.253	5.190	1.595

the structure, optical and magnetic properties were also discussed in detail.

2. Experimental

$Zn_{0.97-x}Mg_xAl_{0.03}O$ ($x = 0, 0.01, 0.03$ and 0.05) nanoparticles were prepared using a hydrothermal method, where 7.437 g of $Zn(NO_3)_2 \cdot 6H_2O$ and 3.504 g of $C_6H_{12}N_4$ were dissolved in 100 ml de-ionized water. Then 0.29 g of $Al(NO_3)_3 \cdot 9H_2O$ and a certain amount of $Mg(NO_3)_2 \cdot 6H_2O$ were added to the above mixed solution. The mixed solution was then stirred for 2 h at room temperature. After this procedure, the precursor solution was injected into the reactor, keeping it at 90 °C for 8 h. After filtering and washing for several times, the precipitate was obtained. Followed by drying at 100 °C for 12 h, the samples were obtained finally.

The structures of the fabricated nanoparticles were characterized by X-ray diffraction (XRD, BRUKER D8 ADVANCE) using Cu $K\alpha$ radiation. The optical properties were characterized by the infrared spectrometer (SHIMADZU FTIR-8400S) and the UV-visible spectrophotometer (SHIMADZU UV-6550). Magnetic measurements were performed by the physical properties measurement system (PPMS/Quantum Design).

3. Results and discussions

3.1. The XRD structural analysis

The XRD patterns of $Zn_{0.97-x}Mg_xAl_{0.03}O$ ($x = 0$, 0.01, 0.03 and 0.05) nanoparticle samples are shown in Fig. 1. All the diffraction peaks can be indexed to the wurtzite structure hexagonal phase (ICDD card No. 36-1451) without any impurity phase. This result means that all of Mg and Al ions were substitutionally or interstitially incorporated into the ZnO lattice without causing an obvious change of ZnO structures around Mg atom inside the $Zn_{0.97}Al_{0.03}O$ lattice below Mg = 0.05. From Fig. 1, we can see that an obvious peak shift toward the small angles occurred when Mg atoms were incorporated into ZnO lattice, and this is due to the small difference between the ionic radii of Mg^{2+} and Zn^{2+} ions ($Zn^{2+} \sim 0.74$ Å, $Mg^{2+} \sim 0.72$ Å). Simultaneously, the lattice parameters c decreases monotonously with increasing the Mg content (shown in Table 1). These results may suggest that most of the Mg atoms were incorporated into the $Zn_{0.97}Al_{0.03}O$ interstitial lattice based on Bragg law. These diffraction peaks were high and sharp which suggested the good crystallinity of all the samples. In this study, the diffraction peak of co-doping with 0.01 Mg was stronger than these of 0.03 and 0.05. The reason lies in that the crystallinity of our samples was lowered when a larger number of Mg atoms were incorporated into the crystal lattice.

3.2. The optical properties

3.2.1. The infrared spectrum analysis

Fig. 2 shows the infrared spectra of $Zn_{0.97-x}Mg_xAl_{0.03}O$ ($x = 0, 0.01, 0.03$ and 0.05) nanoparticles. The infrared spectrum is one kind of molecular vibration spectrum which is related very closely with the molecular real structure and grain size. In the study of ZnO, the application of infrared spectrum becomes very common [16–18]. As can been seen from Fig. 2, all the absorption curves with different Mg contents are similar in shape. When $x = 0$, the strength of infrared transmittance was higher than that of other groups of samples. The absorption peaks are mainly located at 470 cm^{-1}, 1400 cm^{-1}, 1630 cm^{-1} and 3400 cm^{-1}, respectively. The absorption peak near 470 cm^{-1} is the characteristic of zinc oxide absorption peak. The absorption peak near 1400 cm^{-1} is the characteristic of the methyl absorption peak, which may be due to the hexamethylenetetramine which is used to prepare the samples. The size of nanoparticles was very small and thus the organic remnants could not be removed completely after being cleaned using anhydrous ethanol. The absorption peak around 3400 cm^{-1} is attributed to a certain amount of hydroxyl on the surface and the absorption peaks near 1630 cm^{-1} is attributed to the bending vibration of free water.

3.2.2. The UV-vis absorption spectrum analysis

The absorption versus wavelength loops observed for different doping concentrations of Mg are shown in Fig. 3, where all co-doped samples have larger UV light absorption. The absorption shows a slight change with the increase of Mg content. The contents of Mg and Al in the samples are similar and thus Mg atoms have little effect on the band structure [19]. For $x \geqslant 0.03$, the absorption is similar in the UV region. This may be attributed to the