

Structures and Properties of $\text{Zn}_{1-x}\text{Cu}_x\text{O}$ Nanoparticles by Sol-gel Method

LIU Hui-lian^{1,2,3}, YANG Jing-hai^{1,2,3*}, ZHANG Yong-jun³, WANG Ya-xin³ and WEI Mao-bin³

1. Key Laboratory of Excited State Processes, Changchun Institute of Optics, Fine Mechanics and Physics, Chinese Academy of Sciences, Changchun 130033, P. R. China;

2. Graduate School of the Chinese Academy of Sciences, Beijing 100049, P. R. China;

3. Institute of Condensed State Physics, Jilin Normal University, Siping 136000, P. R. China

Abstract Copper-doped ZnO nanoparticles were synthesized by the sol-gel method. The X-ray diffraction(XRD) result shows that $\text{Zn}_{1-x}\text{Cu}_x\text{O}$ ($x = 0.04$) samples are single phase with ZnO-like wurtzite structure, while the secondary phase Cu is observed in a $\text{Zn}_{0.95}\text{Cu}_{0.05}\text{O}$ sample. Magnetic measurements indicate that $\text{Zn}_{1-x}\text{Cu}_x\text{O}$ ($x = 0.04$) samples are ferromagnetic at room temperature. A strong green peak(520 nm) was observed except for UV band peak in photoluminescent(PL) spectrum of $\text{Zn}_{0.98}\text{Cu}_{0.02}\text{O}$.

Keywords Diluted magnetic semiconductor; Sol-gel; Ferromagnetism

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1 Introduction

Diluted magnetic semiconductors(DMSs) are under intense investigation worldwide because of the possibility of manipulating the charge and spin degrees of freedom in a single material. ZnO with wide band gap has been identified as a promising semiconductor material for exhibiting room temperature ferromagnetism(RTFM) when doped with most of the transition metal elements^[1–7]. For example, ferromagnetism was observed in ZnO:Co and ZnO:Mn^[8,9]. However, the origins of RTFM remain controversial: some reports claim that the magnetic signature arises from secondary phase, while others claim that the magnetic property may be caused by the substitution of TM ions into the Zn site^[10]. We chose Cu-doped ZnO as the study object to avoid controversies because the Cu-related secondary phase is antiferromagnetic^[11,12]. In this article, the structures and properties of $\text{Zn}_{1-x}\text{Cu}_x\text{O}$ nanoparticles synthesized by sol-gel method were studied.

2 Experimental

Zn nitrate $[\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$, 99.9%] and appropriate amounts of Cu nitrate $[\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$, 99.9%] were dissolved in citric acid $[\text{C}_6\text{H}_8\text{O}_7$, 99.5%] with stirring. The solution was dried at 80 °C to obtain xerogel.

After the swelled xerogel was completed at 130 °C, a reticular substance was obtained, and then ground to powder in an agate mortar. The powder was sintered at 600 °C under Ar atmosphere for 10 h. The reaction mechanism of decomposing citrate was described previously^[13]. This method allows the mixing of the chemicals at atomic level, thus reducing the possibility of undetectable impurity phase. Additional advantages are the good reproducibility and the simple experimental procedure. The structural properties of $\text{Zn}_{1-x}\text{Cu}_x\text{O}$ nanoparticles were studied by XRD on a D/max-2500 copper rotating-anode X-ray diffractometer with Cu $K\alpha$ radiation(40 kV, 200 mA). The $\text{Zn}_{0.96}\text{Cu}_{0.04}\text{O}$ was determined by XPS(VG ESCALAB Mark II). Magnetic hysteresis loops of $\text{Zn}_{1-x}\text{Cu}_x\text{O}$ ($x = 0.04$) were measured by a Lake Shore 7407 vibrating sample magnetometer with a maximum field of 7.96×10^5 A/m. PL(He-Cd Laser, 325 nm) was used to characterize the optical properties of $\text{Zn}_{1-x}\text{Cu}_x\text{O}$.

3 Results and Discussion

3.1 Structure

The XRD patterns of $\text{Zn}_{1-x}\text{Cu}_x\text{O}$ ($x=0, 0.02, 0.04, 0.05$) are shown in Fig.1. All peaks are perfectly

*Corresponding author. E-mail: jhyang1@jlnu.edu.cn

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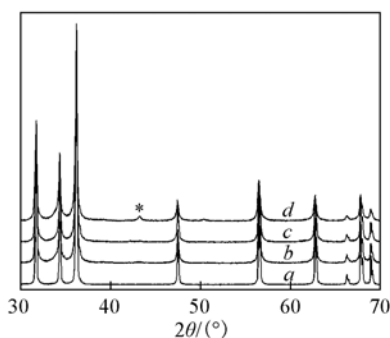


Fig.1 XRD patterns of $\text{Zn}_{1-x}\text{Cu}_x\text{O}$

x : a. 0; b. 0.02; c. 0.04; d. 0.05; * Cu.

indexed and correspond to wurtzite structure ZnO with Cu doped concentration up to 4%(molar fraction). No trace of copper metal, oxides, or any binary zinc copper phases was observed within the sensitivity of XRD. For $\text{Zn}_{1-x}\text{Cu}_x\text{O}$ ($x = 0.04$), with the increase of x , these peaks shift towards lower angles. Calculation shows larger cell parameters of a and c for $\text{Zn}_{1-x}\text{Cu}_x\text{O}$ than the corresponding ones of the undoped sample (Fig.2). For the first four concentrations, the cell parameters increase almost linearly, whereas for the fifth one ($x=0.05$), they decrease, indicating that the limiting composition must be lesser than that. The $\text{Zn}_{0.95}\text{Cu}_{0.05}\text{O}$ shows segregation of a second phase, which is Cu according to the standard JCPDS card. It is well known that the radius of Cu^{2+} ion (radius=0.057 nm) is smaller than that of Zn^{2+} ion (radius=0.074 nm). From the results of the ZnO:Cu films and ZnO:Co powder^[14,15], we can conclude that the reason of increment may be owing to the nonuniform substitution of Cu ions into the Zn sites.

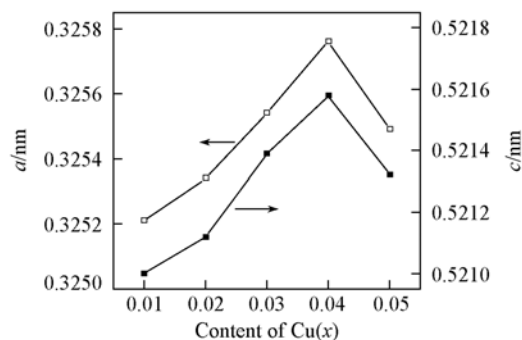


Fig.2 Dependence of the cell parameters a and c on x of $\text{Zn}_{1-x}\text{Cu}_x\text{O}$

3.2 Magnetic Properties

The magnetic properties of $\text{Zn}_{1-x}\text{Cu}_x\text{O}$ ($x=0, 0.01, 0.02, 0.03, 0.04$) were characterized at room temperature on a vibrating sample magnetometer. Fig.3 shows the magnetization hysteresis curves of $\text{Zn}_{1-x}\text{Cu}_x\text{O}$ samples at room temperature; all samples show fer-

romagnetic ordering at room temperature except pure ZnO and with the Cu concentration increasing, the magnetic moment per Cu atom decreases markedly. The atom magnet moments of 1%, 2%, 3%, and 4% Cu doped samples are 0.74, 0.66, 0.40 and 0.19 μ_B/Cu , respectively. The largest moment observed was 0.74 μ_B/Cu atom; this value is larger than the experimental value reported by Herng *et al.*^[16] and lesser than the theoretical value (1.00 μ_B/Cu). The moment per Cu atom can be lesser owing to the nanostructured nature of the material, and weaker interparticle exchange is also responsible for the low magnetic moment. The consistent drop in moment per Cu atom of dopant at a higher Cu concentration can be an increased occurrence of antiferromagnetic coupling between Cu pairs occurring at shorter separation distances, which have been predicted in earlier theoretical studies. Theoretical modeling of the $\text{Zn}_{1-x}\text{Cu}_x\text{O}$ system indicates that the location of the Cu atoms with relation to each other can strongly affect the magnetic properties of the system^[17-19].

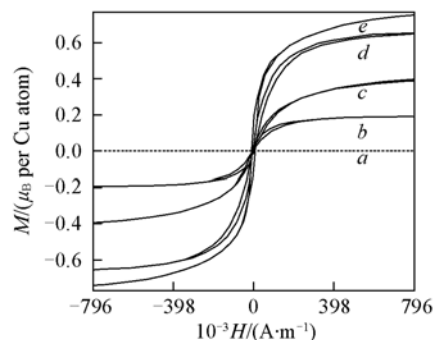


Fig.3 Magnetization hysteresis curves of $\text{Zn}_{1-x}\text{Cu}_x\text{O}$ samples at room temperature

Content of Cu, x : a. 0; b. 0.04; c. 0.03; d. 0.02; e. 0.01.

3.3 Photoluminescence Properties

To study the influence of Cu doping on the luminescence of ZnO, the room temperature photoluminescence (PL) measurements were carried out, and the PL spectra of $\text{Zn}_{1-x}\text{Cu}_x\text{O}$ samples ($x=0, 0.01, 0.02$) are shown in Fig.4.

The unique UV band peaks are observed at 384 and 405 nm individually in the entire photoluminescence spectrum for undoped ZnO and $\text{Zn}_{0.99}\text{Cu}_{0.01}\text{O}$. The UV emission is originated from excitonic recombination^[20,21], corresponding to the near-band-edge (NBE) emission of ZnO. Compared with the PL spectrum of undoped ZnO, the UV emission peak of $\text{Zn}_{0.99}\text{Cu}_{0.01}\text{O}$ exhibits a large redshift; this is attributed to the shift of the optical band gap in these

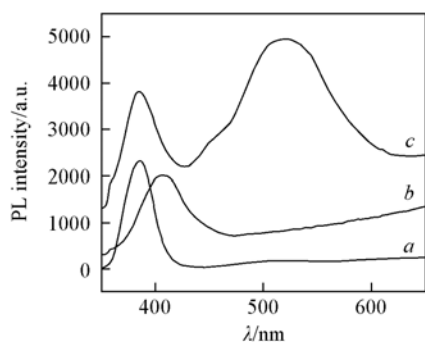


Fig.4 Room temperature PL spectra of $\text{Zn}_{1-x}\text{Cu}_x\text{O}$ samples

a. $x=0$; *b.* $x=0.01$; *c.* $x=0.02$.

samples. A red-shift of the band edge reveals the incorporation of Cu in the lattice sites in $\text{Zn}_{0.99}\text{Cu}_{0.01}\text{O}$. This supports the X-ray results on the incorporation of Cu into the ZnO structure. When doped with 2%(molar fraction) Cu atoms, the sample exhibited NBE emission at about 384 nm and a broad green emission centered at about 520 nm. To explain the green emission in ZnO, various models have been proposed, for example, the emission involved O-vacancy(V_O)^[22–25], interstitial Zn and $\text{O}^{[26]}$, Zn-vacancy(V_Zn)^[27,28], an electronic transition from an interstitial Zn to a Zn-vacancy, and extrinsic impurities such as substitutional Cu^[29]. Theoretical investigations have also been reported, that is, the green emission is owing to intrinsic and extrinsic defects in $\text{ZnO}^{[30]}$. In our article, the green emission in the PL spectrum of $\text{Zn}_{0.98}\text{Cu}_{0.02}\text{O}$ is mainly attributable to the extrinsic impurities when most of the Cu atoms have substituted into the ZnO lattice sites. At the same time, point defects, such as oxygen vacancies or impurities also make a contribution to the green emission.

4 Conclusions

In summary, we have prepared Cu-doped ZnO nanoparticles with the Cu content up to 5%(molar fraction) by the sol-gel method. The results of XRD show that the samples($x=0.04$) are single phase with the ZnO-like wurtzite structure, while a secondary phase Cu was observed in $\text{Zn}_{0.95}\text{Cu}_{0.05}\text{O}$ sample. The magnetization data of samples doped with up to 4% Cu show ferromagnetic ordering at room temperature. The PL spectra of $\text{Zn}_{1-x}\text{Cu}_x\text{O}$ all contain a UV band peak, and a relatively strong green band was obtained

in $\text{Zn}_{0.98}\text{Cu}_{0.02}\text{O}$.

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