

Structure, magnetic, and optical properties in $\text{Zn}_{0.98-x}\text{Cu}_{0.02}\text{Fe}_x\text{O}$ diluted magnetic semiconductors

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Cu-doped and Cu, Fe codoped ZnO diluted magnetic semiconductors (DMSs) powders samples were synthesized by the sol–gel method. The X-ray diffraction (XRD) results showed the $\text{Zn}_{0.985}\text{Cu}_{0.02}\text{O}$ and $\text{Zn}_{0.95}\text{Fe}_{0.03}\text{Cu}_{0.02}\text{O}$ samples were of single phase with the ZnO-like wurtzite structure. Magnetic measurements indicated that room-temperature ferromagnetism of $\text{Zn}_{0.98}\text{Cu}_{0.02}\text{O}$ was intrinsic in nature and the saturation

magnetization of $\text{Zn}_{0.98}\text{Cu}_{0.02}\text{O}$ DMSs increased after Fe doping. Photoluminescence (PL) measurements showed that the intensity of the ultraviolet (UV) emission band and the visible-light emission band of $\text{Zn}_{0.95}\text{Cu}_{0.02}\text{Fe}_{0.03}\text{O}$ samples increased and the UV emission peak exhibited blue shift compared to $\text{Zn}_{0.98}\text{Cu}_{0.02}\text{O}$ samples.

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1 Introduction ZnO-based diluted magnetic semiconductors (DMSs) have been predicted to exhibit ferromagnetic behavior with a Curie temperature (T_C) above room temperature and to have a large saturation magnetization (M_s), which makes them promising candidate materials for the next generation of spintronic devices with magnetism controlled by electricity or optics [1–4]. Room-temperature ferromagnetism in ZnO-based DMSs have been reported by many groups [5–9]. Based on a number of experimental results, researchers found that the carrier concentration in transition-metal-ion doped ZnO DMSs could influence their properties. So, more groups have tried to dope other ions into the ZnO DMSs in order to change the magnetic and optical properties by introducing additional carriers [10–13]. In this work, we report the room-temperature magnetic and optical properties of $\text{Zn}_{0.98}\text{Cu}_{0.02}\text{O}$ and $\text{Zn}_{0.95}\text{Cu}_{0.02}\text{Fe}_{0.03}\text{O}$ powders prepared by the sol–gel method. The effects of Fe on the structure, magnetic, and optical properties of $\text{Zn}_{0.98}\text{Cu}_{0.02}\text{O}$ have been studied in detail.

2 Experimental Appropriate proportions of Zn ($(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ (99.9%), Cu ($(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$ (99.9%), and Fe ($(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ (99.9%) high-purity powders were thoroughly mixed and dissolved into water to get a homogeneous

solution. The mixture was then poured into citric acid [$\text{C}_6\text{H}_8\text{O}_7$] (99.5%) while stirring. The solution was dried at 80 °C to obtain a xerogel. After the swelled xerogel was completed at 130 °C, a reticular substance was obtained, which was then ground to powder in an agate mortar. The powder was sintered at 600 °C for 10 h under an air atmosphere. This method allows mixing of the chemicals at the atomic level, thus reducing the possibility of undetectable impurity phase. $\text{Zn}_{0.98-x}\text{Cu}_{0.02}\text{Fe}_x\text{O}$ powders were obtained after the sol–gel process and sintered. The reaction mechanism of the decomposing citrate technique was described previously [14]. $\text{Zn}_{0.98}\text{Cu}_{0.02}\text{O}$ powder also obtained by the same procedure without the $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ (99.9%) in the solution.

Structural characterization of ZnO and $\text{Zn}_{0.98-x}\text{Cu}_{0.02}\text{Fe}_x\text{O}$ ($x = 0, 0.03$) was performed by X-ray diffraction (XRD) on a D/max-2500 copper rotating-anode X-ray diffractometer with Cu K α radiation (40 kV, 200 mA). Magnetic hysteresis loops of $\text{Zn}_{0.98}\text{Cu}_{0.02}\text{O}$ and $\text{Zn}_{0.95}\text{Cu}_{0.02}\text{Fe}_{0.03}\text{O}$ were measured by a Lake Shore 7407 vibrating sample magnetometer (VSM). The optical properties of samples were obtained by photoluminescence (PL) measurements using HR800 LabRam Infinity spectrophotometer excited by a continuous He–Cd laser with a wavelength of 325 nm at a power of 50 mW.

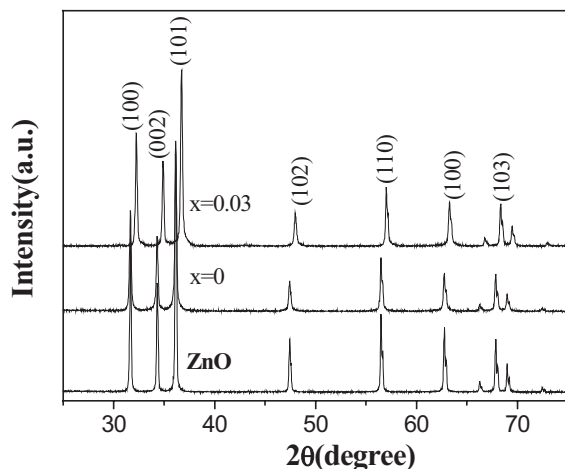


Figure 1 X-ray diffraction (XRD) patterns of ZnO and $\text{Zn}_{0.98-x}\text{Cu}_{0.02}\text{Fe}_x\text{O}$ ($x = 0, 0.03$) at room temperature.

3 Results and discussion Figure 1 shows the XRD patterns of ZnO and $\text{Zn}_{0.98-x}\text{Cu}_{0.02}\text{Fe}_x\text{O}$ ($x = 0, 0.03$). The patterns show a hexagonal wurtzite structure that belongs to the C_{6v}^4 space group (P_6^3mc) according to the standard JCPDS card. No second phase, such as binary zinc-copper or zinc-iron phases, is detected within the sensitivity of XRD. In comparison with undoped ZnO, the XRD diffraction peaks of $\text{Zn}_{0.98}\text{Cu}_{0.02}\text{O}$ are broadened due to the smaller size. The mean grain size of the $\text{Zn}_{0.98}\text{Cu}_{0.02}\text{O}$ is calculated to be ~ 38 nm by the Scherrer formula. However, the crystal lattice has no obvious difference after Cu doping due to the radius of Cu being similar to that of Zn. Compared with $\text{Zn}_{0.98}\text{Cu}_{0.02}\text{O}$, the XRD diffraction peaks of $\text{Zn}_{0.95}\text{Cu}_{0.02}\text{Fe}_{0.03}\text{O}$ shifted to a larger angle. The shift of diffraction peaks may be associated with Fe doping. There are three modes for the Fe doped into the ZnO lattice: Fe ions fill Zn vacancies of ZnO; Fe ions replaced the Zn^{2+} in ZnO as replacement atoms, and Fe ions exist in the ZnO lattice as interstitial atoms. Comparing the Zn ionic radius with that of Fe ion with different valences, we believe that when Fe^{3+} substitutes for Zn^{2+} , the bond length of the Fe–O in samples is less than that of the original Zn–O, the lattice constant would become smaller and lead to the higher-angle shift of the XRD diffraction peaks. Of course, the lattice constants of ZnO will change during the annealing process under high temperature, for our experimental setting the doping process should be the main reason for the change of lattice constant. Therefore, we speculate that Fe^{3+} ions replace the Zn^{2+} in ZnO as replacement atoms in the samples. The mean grain size of the $\text{Zn}_{0.95}\text{Cu}_{0.02}\text{Fe}_{0.03}\text{O}$ estimated was about 40 nm.

In order to study the effect of Fe on the magnetic properties of $\text{Zn}_{0.98}\text{Cu}_{0.02}\text{O}$, the magnetization *versus* magnetic field (M – H) curves of $\text{Zn}_{0.98}\text{Cu}_{0.02}\text{O}$ and $\text{Zn}_{0.95}\text{Cu}_{0.02}\text{Fe}_{0.03}\text{O}$ powders have been measured using a VSM and the results are shown in Fig. 2. The two samples exhibit ferromagnetic ordering at room temperature. The M_s is $0.65 \mu_B/\text{Cu}$ and $0.78 \mu_B/\text{Cu}$ for $\text{Zn}_{0.98}\text{Cu}_{0.02}\text{O}$ and $\text{Zn}_{0.95}\text{Cu}_{0.02}\text{Fe}_{0.03}\text{O}$, which are much lower than that of

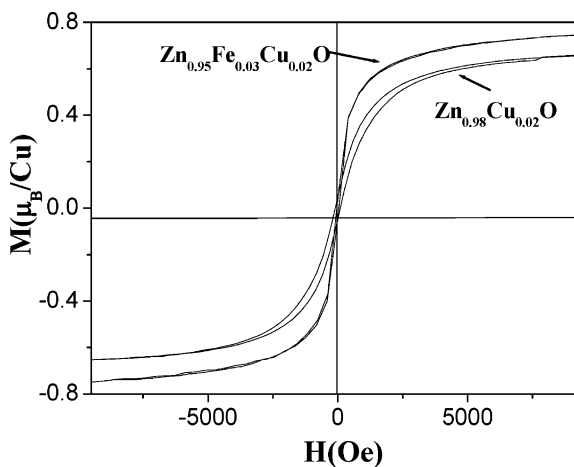


Figure 2 Magnetization *versus* field hysteresis (M – H) loops of $\text{Zn}_{0.98-x}\text{Cu}_{0.02}\text{Fe}_x\text{O}$ ($x = 0, 0.03$) at room temperature.

metallic Fe. In the previous papers [15, 16], we reported that the origin of room temperature ferromagnetism in Cu- and Fe-doped ZnO is the existence of the Cu and Fe element in the ZnO lattice and the Cu and Fe ion substitute into Zn sites. Super- and double exchange give the explanation of our observed ferromagnetism. Several groups [17, 18] have found that the point defects play crucial roles in the FM of ZnO-based DMSs. More detailed work is essential to understand the magnetic behaviors of these materials.

As we observed, the magnetization of $\text{Zn}_{0.95}\text{Cu}_{0.02}\text{Fe}_{0.03}\text{O}$ increases markedly in comparison with that of $\text{Zn}_{0.98}\text{Cu}_{0.02}\text{O}$ powder samples. In other words, the introduction of Fe element can enhance the formation of ferromagnetic order. Most researchers [19–21] believed that Fe doped into ZnO acts as n-type dopant, while Cu in doped samples acts as a p-type dopant, therefore, Fe and Cu play opposite roles in the ZnO system. So, the working mechanism for our samples is n-type carrier-conditioned double-exchange. Because the Fe in doped ZnO is an n-type dopant, the effective electronic carrier concentration is increased after Fe doping, which finally

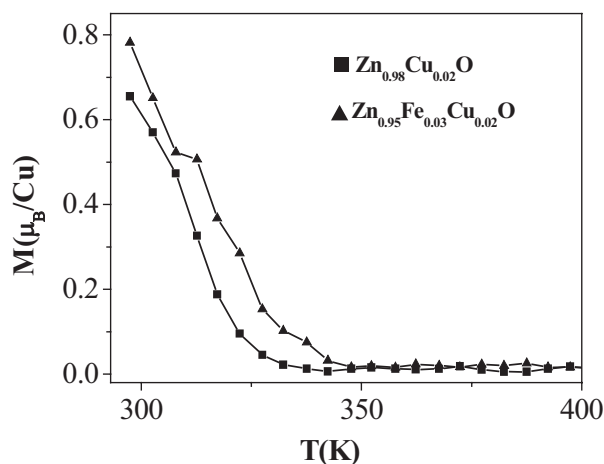


Figure 3 Magnetization *versus* temperature (M – T) loops of $\text{Zn}_{0.98-x}\text{Cu}_{0.02}\text{Fe}_x\text{O}$ ($x = 0, 0.03$) under 1 kOe.

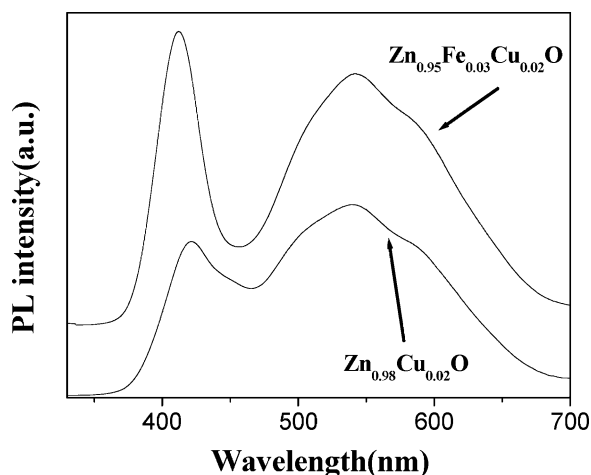


Figure 4 Photoluminescence (PL) spectra of $\text{Zn}_{0.98-x}\text{Cu}_{0.02}\text{Fe}_x\text{O}$ ($x = 0, 0.03$) at room temperature.

enhances ferromagnetic coupling in the system. Figure 3 shows the temperature dependence of magnetic moment for $\text{Zn}_{0.98-x}\text{Cu}_{0.02}\text{Fe}_x\text{O}$ ($x = 0, 0.03$) under 1 kOe. With increased temperature, the magnetization moment for $\text{Zn}_{0.98-x}\text{Cu}_{0.02}\text{Fe}_x\text{O}$ ($x = 0, 0.03$) decreases and reaches the T_C below 335 and 345 K, respectively, which is below the T_C of iron oxide. Both of their T_C are high enough for practical applications at room temperature.

Figure 4 shows the PL spectra of $\text{Zn}_{0.98}\text{Cu}_{0.02}\text{O}$ and $\text{Zn}_{0.95}\text{Cu}_{0.02}\text{Fe}_{0.03}\text{O}$ powders excited by a 325-nm laser at room temperature. The PL spectra of two samples show a strong ultraviolet (UV) emission band and a visible-light emission band. The UV emission is originated from excitonic recombination corresponding to the near-band-edge emission of ZnO [22, 23]. Compared with the PL spectrum of $\text{Zn}_{0.98}\text{Cu}_{0.02}\text{O}$ powders, the peak intensity of UV emission in $\text{Zn}_{0.95}\text{Cu}_{0.02}\text{Fe}_{0.03}\text{O}$ powders enhances and the peak position exhibits a blue shift. The decrease of the nanoradiative defects and decrease of powders size after the Fe doping process could increase UV emission. For Fe-doped $\text{Zn}_{0.98}\text{Cu}_{0.02}\text{O}$ powders, more electrons contributed by iron dopants take up the energy levels located at the bottom of conduction band. When they are excited by the laser of 325 nm, the excitons take up higher-energy levels at the bottom of conduction band. Radioactive recombination of these excitons will lead to a blue shift [24]. In addition, the lattice strain induced by the lattice distance would also lead to some shift in bandgap but may not play a major role in the determination of bandgap due to such small deformation of the lattice distances. From Fig. 4, we observe a relatively strong visible luminescence band in the PL spectrum of $\text{Zn}_{0.95}\text{Cu}_{0.02}\text{Fe}_{0.03}\text{O}$ powders compared to that of the $\text{Zn}_{0.98}\text{Cu}_{0.02}\text{O}$ powders. Visible-light emission intensity is related to the density of intrinsic defects (such as oxygen vacancies or Zn-interstitial-related defects) [24, 25] and the special surface structure [26, 27]. We ascribe the appearance of the strong visible luminescence in $\text{Zn}_{0.95}\text{Cu}_{0.02}\text{Fe}_{0.03}\text{O}$ powders to the destroyed lattice order. When Fe enters into

the $\text{Zn}_{0.98}\text{Cu}_{0.02}\text{O}$ lattice, some new defects, such as oxygen vacancies, Zn interstitials, and so on, are generated in samples, which enhances the visible luminescence.

4 Conclusion In summary, we prepared $\text{Zn}_{0.98}\text{Cu}_{0.02}\text{O}$ and $\text{Zn}_{0.95}\text{Cu}_{0.02}\text{Fe}_{0.03}\text{O}$ powders by the sol-gel method. Structure analyses indicate that both Cu-doped ZnO and Cu, Fe codoped ZnO are wurtzite structure. The magnetization results of $\text{Zn}_{0.98}\text{Cu}_{0.02}\text{O}$ and $\text{Zn}_{0.95}\text{Cu}_{0.02}\text{Fe}_{0.03}\text{O}$ powders show the room-temperature ferromagnetism of the samples in this study is an intrinsic property. The M_s of Cu-doped ZnO increases after Fe doping. The intensity of UV and visible-light emission in $\text{Zn}_{0.95}\text{Cu}_{0.02}\text{Fe}_{0.03}\text{O}$ increase, and the UV emission peak exhibits a blue shift compared to the $\text{Zn}_{0.98}\text{Cu}_{0.02}\text{O}$ sample.

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