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Synthesis and Magnetic Properties of M (Mg, Mn, Ni and Zn) Doped CuO Ceramics

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$M_xCu_{1-x}O$ (M = Mg, Mn, Ni and Zn, x = 0.04) ceramics were synthesized using traditional ceramic product method. Crystal structures of all the samples were studied by X-ray diffraction, from which we can see that all the samples were well crystallized. Field dependences of magnetization and temperature dependences of magnetization were performed on a superconducting quantum interference device (SQUID) at 5 K with the applied of 5 T and in the range from 5 K to 300 K, respectively. Both M-T and M-H results implied the ferromagnetic behaviour of Mn and Mg doped CuO samples. Meanwhile Ni and Zn doped CuO samples still showed antiferromagnetic behaviour with the transition temperature at *ca.* 230 K. The only effects brought by Ni and Zn doping were the increase of magnetization of CuO. Through comparing of the different magnetic behaviours, we discussed the mechanism of ferromagnetism observed in Mn and Mg doped CuO samples.

Key Words: Ceramics, CuO, Ferromagnetism.

INTRODUCTION

Diluted magnetic semiconductors (DMS) are series of materials combining ferromagnetism (FM) and semiconducting for applying the spin of charge carriers as an additional degree of freedom in addition to their charge. Thus a spin-polarized device can be fabricated. Since it has been predicted by Dietl *et al.*[1] of the high temperature ferromagnetism in transition metals doped wide-band-gap semiconductors, much effort has been made to realize ferromagnetism in doped semiconductor oxides, especially for TiO_2 and ZnO[2,3]. Among these semiconducting oxides, CuO is related to high-temperature superconductors, thus it has special interests to study the doping effect in CuO semiconductors both for theoretical and experimental purposes[4-10]. Pure CuO is a *p*-type semiconductor with a band gap of 1.2 ev and shows quasi 1-dimensional, antiferromagnetism below the magnetic transitions temperature of 230 K[11]. We have fabricated Mn doped CuO samples and ferromagnetism was observed in all the samples[4]. Since then, much effort has been devoted to the study of CuO doped with transition metal atoms as diluted magnetic semiconductors. Most of these works were based on Mn doping, including first principle calculation[5], low concentration doping effect[6], size effect[7] and metal-insulator transition effect[5,10] *etc.* Though ferromagnetism was observed in all of the Mn-CuO systems, the origin of ferromagnetism is still a matter of further studies[4-10].

In the present work, four special elements (Mg, Mn, Ni and Zn) are selected as dopants. Manganese can have mixed valences while others usually have a fixed valence of 2+; Mg doesn't have any d electrons while others are 3*d* elements; Zn has a full *d* orbital while *d* orbital of Mn and Ni are partially occupied. Considering all the results together may help us to understand the origin of ferromagnetism in the doped CuO systems and the results of Mg-CuO may provide a new aspect to study diluted magnetic semiconductorss.

EXPERIMENTAL

Four $M_xCu_{1-x}O$ (M = Mg, Mn, Ni and Zn, x = 0.04) samples were fabricated by traditional ceramic production method. In short, CuO, MgO, $MnCO_3$, NiO and ZnO were used as precursor.

General procedure: Appropriate amounts of precursor powders were weighed and mixed to give a nominal doping elements' composition of x = 0.04. Then the mixed powders were pressed into disks with diameter of 10 mm and sintered in the air at 900 ºC for 10 h and naturally cooled down to room temperature.

Detection Method: The crystal structures of the products were characterized by X-Ray diffraction (XRD; PANational x'pert) with CuK_α radiation. Field dependent magnetization was performed on a superconducting quantum interference device (SQUID) at 5 K and temperature dependent magnetization were performed at a magnetic field of 1000 Oe from 5 K to 300 K.

RESULTS AND DISCUSSION

Fig. 1 shows the XRD patterns of the four samples. The patterns illustrate all the products are monoclinic CuO with little amount of impurity phases. Because of the different size of radius between Cu^{2+} and the dopant cations, when the dopants were doped into the lattice of CuO, shift of the corresponding peaks would be observed in the XRD patterns. In present XRD patterns, the corresponding peaks shift clearly (shown in Fig. 1b), which makes us believe that the dopants were doped into the lattice. On the other hand, due to the existence of the second phase, the real doping level is lower. Similar to the previous studies[4,7-9], $CuMn_2O_4$ was observed in Mn doped CuO samples. In Mg, Ni and Zn doped samples the impurities are the corresponding monoxides of the dopants.
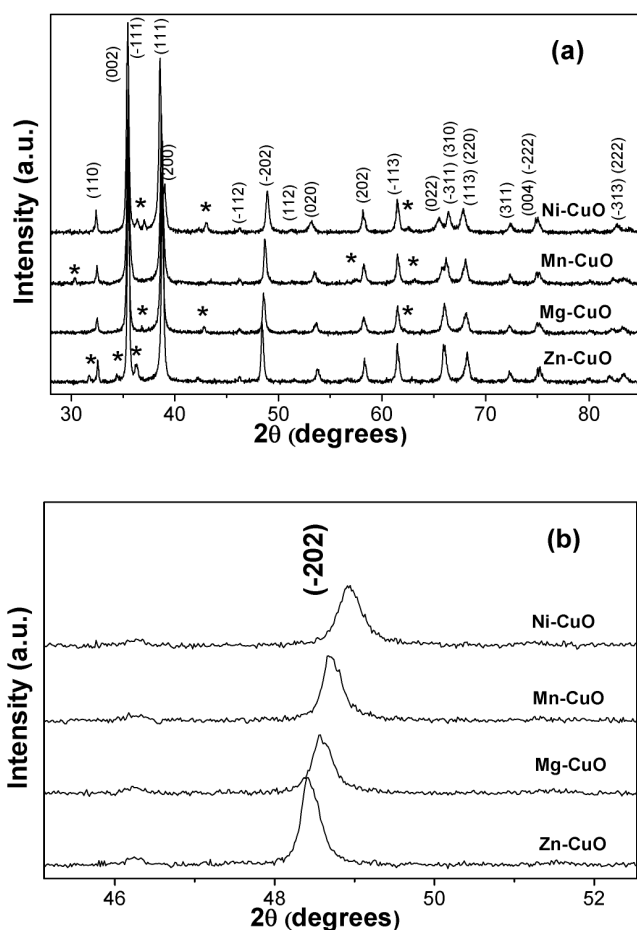

Fig. 1(a) XRD patterns of $M_{0.04}Cu_{0.96}O$ (M = Mg, Mn, Ni and Zn) samples, indexed peaks belong to CuO and those marked by * belong to impurities ($CuMn_2O_4$ for Mn-CuO and the corresponding monoxides of the dopants for other samples) (b) Details of the peak (-202)

Magnetic hysteresis loops were measured at 5 K for all of the four samples with the maximum magnetic field of 5 T. Temperature dependence of magnetization at 1000 Oe was measured in the range from 5 K to 300 K for all of the 4 samples and both in zero-field-cooled (ZFC) and field-cooled (FC) conditions for Mn and Mg doped samples.

The results of zero-field-cooled and field-cooled temperature dependence and field dependence of magnetization of $Mn_{0.04}Cu_{0.96}O$ sample were plotted in Fig. 2. As expected, Mn doped CuO sample shows clear ferromagnetism signature at 5 K (the hysteresis loop are shown in the inset of Fig. 2). The maximum magnetization is about 2.78 emu/g and the coercive field is about 600 Oe, which are consistent with previous results[4,6-9]. A blocking temperature of about 20 K and the Curie temperature of about 80 K are observed, which are also consistent with the literatures[4,6-9]. The large range between blocking temperature and Curie temperature indicates a spin-glass behaviour. This result is similar to that reported in Mn doped CuO nano particles[7]. Considering the very low doping level (< 4 %), finite Mn-CuO clusters, which were ferromagnetism were formed by Mn cation doped into CuO lattice and these clusters can be treated as nanoparticles which may result to the spin-glass behaviour.
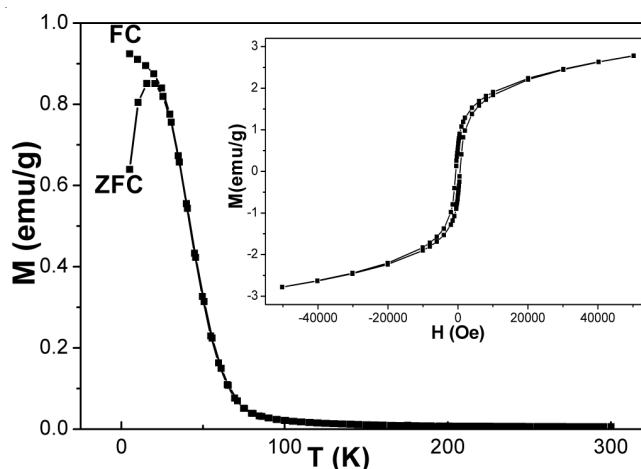

Fig. 2.   Zero-field-cooled (ZFC) and field-cooled (FC) temperature dependence of magnitization of $Mn_{0.04}Cu_{0.96}O$ under 1 K Oe, inset shows its magnetic hysteresis loop at 5 K

Fig. 3 shows the magnetic hysteresis loops of the other three samples measured at 5 K. The straight lines (shown in Fig. 3a) are obtained for Ni and Zn doped CuO samples, while presence of hysteresis is observed in Mg doped sample, which reveals weak ferromagnetism behaviour of the sample at 5 K (Fig. 3b), with a maximum magnetization of *ca.* 0.31 emu/g and a coercivity of about 50 Oe (Fig. 3b). To the best of our knowledge, the ferromagnetism in Mg doped CuO has not been reported in the previous works.
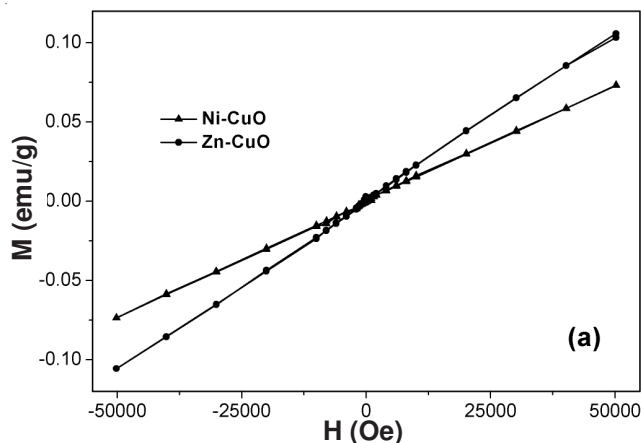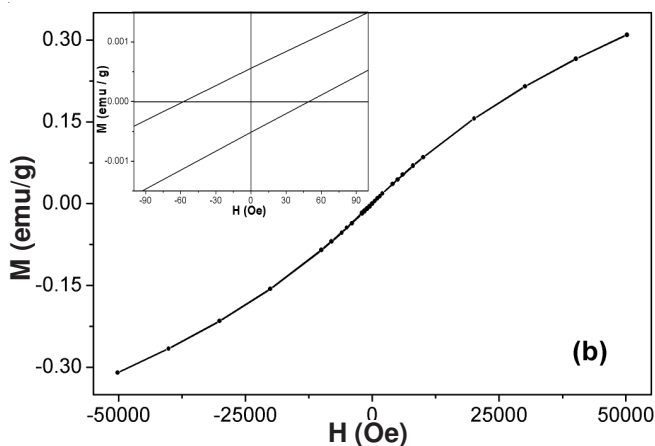
Fig. 3.   Magnetic hysteresis loops of (a) Ni, Zn doped CuO samples at 5 K and (b) Mg doped CuO samples at 5 K, inset is the details in the field range from -90 to 90 Oe to show the coercive field

Inset of Fig. 4 shows the temperature dependent magnetization results of Ni and Zn doped CuO samples. These results combined with the straight M-H lines illustrate that Ni and Zn doped CuO samples are antiferromagnetism below the critical temperature of *ca.* 230 K. The shape of the lines and the critical temperature are both similar to pure CuO[12] and Zn doped CuO samples in the previous works[13]. The only effects of Ni and Zn doping are the enhancement of the magnetization of pure CuO.
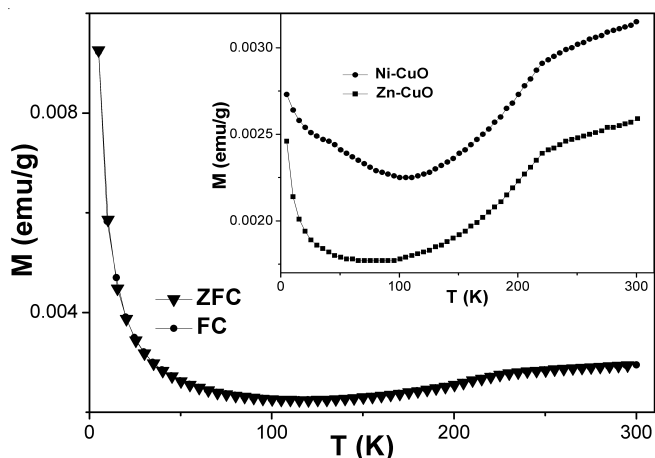

Fig. 4.   Zero-field-cooled (ZFC) and field-cooled (FC) temperature dependance of magnetization of Mg doped CuO samples under a magnetic field of 1000 Oe. Inset is the ZFC temperature dependance of magnetization of Ni and Zn doped CuO samples under the same conditions

Fig. 4 shows the whole temperature dependent magnetization results of Mg doped CuO samples. The magnetization decreases with decreasing temperature from 300 K to 100 K which is the common temperature dependent magnetization of antiferromagnetism materials and the behaviour at *ca.* 230 K similar to Ni and Zn doped samples shows the phase transition of CuO matrix between paramagnetic and antiferromagnetism. As temperature decreases further to 5 K, the rapid increase of magnetization indicates the weak ferromagnetism behaviour, corresponding with the M-H loop (Fig. 3b) of this sample.

To learn the origin of the ferromagnetism in diluted magnetic semiconductors, three mechanisms in the literatures have been considered *i.e.*, the formation of a secondary ferromagnetism phase, substitutional dopants on cation sites and orbital defect state[14].

In the present work, Mn doped CuO sample shows ferromagnetism behaviour at 5 K and its Curie temperature is about 80 K. The only impurity in this sample is $CuMn_2O_4$, which shows antiferromagnetism behaviour[4] below 30 K. This means that the measured ferromagnetism should not come from the formation of the secondary ferromagnetism phase. On the other hand, Mn is 3*d* transition element that are compatible with those of Cu, which is also 3*d* element, which means there are no orbital defects induced by Mn doping. Our results support that the ferromagnetism in Mn doped CuO is induced by Mn substitution on Cu sites. As has been illustrated in the literature, carrier mediated mechanism should be eliminated[6]. Some researchers pointed out that Mn-O-Cu-O-Mn chain should be responsible for the ferromagnetism in Mn-CuO samples. If it is true, Ni and other 3*d* elements doped CuO would also show ferromagnetism behaviour. Actually no ferromagnetism was induced by Ni or Zn doping in CuO neither in the literature[13]. According to this fact, this mechanism should not be resonable. Different from Ni and Zn doped sample, in Mn doped CuO, Mn can have mixed valences and the most possible origin of the ferromagnetism in Mn-CuO is double exchange between Mn ions with different valences. This mechanism was also supported by previous studies[5,7].

Weak ferromagnetism is also observed in Mg-CuO system, which contains none ferromagnetism phases in MgO, CuO or the compounds of Mg-Cu-O. Non-magnetic element induced ferromagnetism has been observed in Al doped $Co-Cu_2O$[15]. They attributed the origin of ferromagnetism to orbital defects which has already been applied to explain the origin of the magnetism in the Mn doped $CdGeP_2$ system[16]. In this work, Ni, Zn and Mg ions have the same fixed valence states (+2), therefore no carriers or holes are brought in by doping. As both are 3*d* elements, Zn and Ni ions have *d* orbitals that are compatible with that of Cu, which means there are no orbital defects brought by 3*d* elements doping and no ferromagnetism are induced by Ni and Zn doping. Meanwhile, the outermost orbits are s and p for Mg ion. So there is no orbital compatibility with the 3*d* element Cu that means there are orbital defects in Mg doped sample; and Mg doped sample shows weak ferromagnetism behaviour. By considering these facts, we attribute the origin of the ferromagnetism in Mg doped CuO to the orbital defect between non-3*d* element Mg and 3*d* element Cu.

Conclusion

In conclusion, to study the origin of ferromagnetism in doped CuO, four different samples $M_xCu_{1-x}O$ (M = Mg, Mn, Ni, Zn, x = 0.04) were fabricated using traditional ceramic production method. At 5 K, clear hysteresis loops were observed in Mn-CuO system (T_c = 80 K) and in Mg-CuO system (T_c = 25 K). In Ni and Zn doped samples, both M-H and M-T measurements showed antiferromagnetism behaviour. Comparing all the results of these four samples, we attribute the origin of ferromagnetism in Mn-CuO system to double exchange and

Mg-CuO system to orbital defects. And non-magnetic elements doping may be another choice to study diluted magnetic semiconductorss.

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