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Structure and magnetic properties of Mn-doped CuO solids①

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Abstract: The CuO doped with 5%－20% Mn(molar fraction) solids were sintered from CuO and MnO_2 powder at high temperature (1 273 K) for 8 h. X-ray diffraction was used to determine the solid crystallinity and to address the formation of secondary phases. It is found that it is difficult to achieve pure $Cu_{1-x}Mn_xO$ phase using standard solid phase reaction. However, sintering under a pressure of 27.7 MPa significantly reduces the undesirable second phase $CuMn_2O_4$, providing a route to achieve pure $Cu_{1-x}Mn_xO$ phase. SQUID magnetometry was employed to characterize the magnetic properties. Mn-doped CuO presents ferromagnetic characteristics below 70 K. Electrical transport properties were measured in a current-perpendicular-to-plane(CPP) geometry using the PPMS, which suggests variable-range hopping mechanism.

Key words: Mn-doped CuO; diluted magnetic semiconductor; solid crystallinity; hopping mechanism

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1 INTRODUCTION

The interests in ferromagnetic semiconductors surged because of their potential applications in spintronics[1] and the discovery of ferromagnetism (FM) Ⅲ-Ⅴ based diluted magnetic semiconductors (DMS's) such as $Ga_{1-x}Mn_xAs$[2]. Ferromagnetic semiconductors promise efficient spin injection and transport, and potential seamless integration with current semiconductor technology[3]. A new class of ferromagnetic semiconductors, for example, Co-doped TiO_2[4] or Fe-doped ZnO[5], changing from a paramagnetic phase to a ferromagnetic phase with decreasing temperature and some of them undergoing an insulator-metal, have created great interest because the fundamental mechanisms remain elusive. Recently, theoretical studies have predicted the existence of room temperature(RT) FM in diluted semiconductors such as ZnO[6] and AlN[7]. Experimentally, RT FM has been reported in diluted FM semiconductors Co-TiO_2[4], Mn-GaN[8], Fe-ZnO[5], and Co-Cu_2O[9].

Pure CuO is an antiferromagnetic (AFM) semiconductor, which has been studied in part due to its relation to high-temperature cuprate superconductivity and colossal magnetoresistance(CMR) materials[10]. Theoretical predictions also suggest that carrier-mediated ferromagnetism should be favored for p-type material[11]. CuO is a p-type, direct wide bandgap oxide semiconductor. The selection of Mn as the transition metal dopant is based on the best available evidence in determining which magnetic impurities are likely to yield ferromagnetism[12-14]. The FM has been reported in the Mn-doped CuO solid, however a second phase ($CuMn_2O_4$) exist in the solid samples[15]. While the ferromagnetism has been observed in this system, the exact origin and the specific transport properties are not clearly understood. In this article, the synthesis and properties of the Mn-doped CuO solids are presented. The details of structure, magnetic and transport properties of Mn-doped CuO solids examined.

2 EXPERIMENTAL

Using the solid phase reaction technique, the author attempted to dope Mn, Mg, Ca, Ti, V, and Fe into CuO. The powders of CuO(99.8%), MnO_2(98%), MgO(98%), CaO(98%), TiO_2(99%), V_2O_5(99%), and Fe_3O_4(98%) served as the starting materials. The doped atomic fractions x in $Cu_{1-x}A_xO$(A= Mn, Mg, Ca, Ti, V, or Fe) were 0.05, 0.10 and 0.15, respectively. Through

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blending and triturating, the powders were pressed as pellet-shaped samples (d = 10 mm), followed by sintering at different temperatures (973 − 1 273 K) for 8 h in air. Another sample, $Cu_{0.85}Mn_{0.15}O$, has been fabricated at 1 223 K for 2 h in air with pressure of 27.7 MPa applied perpendicular to sample surface.

The structure of the Cu-O solids was characterized by scanning electron microscopy (SEM) (Jeol JSM—6335FEG) and X-ray diffractometry (XRD) (Philips 3100 Diffractometer). The magnetic properties of the solids were characterized by superconducting quantum interference device (SQUID) magnetometer (Quantum Design, Inc) in the temperature range of 5 − 300 K. Electrical transport properties was measured in a current-perpendicular-to-plane (CPP) geometry using the Physical Property Measurement System (PPMS) (Quantum Design, Inc, Model 6000).

3 RESULTS AND DISCUSSION

The crystal structure of CuO is monoclinic (C2/c), in which Cu atoms are coordinated to four coplanar oxygen atoms situated at the corners of an almost rectangular parallelogram. With two more distant apical O atoms, a distorted octahedron is formed because of large Jahn-Teller effect. The cell parameters for a natural crystal tenorite are a = 4.462 Å, b = 3.417 Å, c = 5.118 Å, and β = 97°29′. There are two bond angles of Cu-O-Cu: 146° and 99°. Magnetic measurements and neutron diffraction experiments shows that the structure is AFM, with a commensurate propagation vector (1/2, 0, −1/2) below the Néel temperature[16].

The structures of all the doped samples were determined by XRD, the results show that Mn doping in CuO has the best substitution among six metal ions used in this studies. Fig. 1 shows the XRD results for $Cu_{1-x}Mn_xO$ samples. The samples consist of the main phase CuO(C2/c) and a small amount of $CuMn_2O_4$. The presence of $CuMn_2O_4$ increases with the increasing Mn concentration similar to the recent report[15], indicating that the Mn ions in CuO are very easy to be accumulated together. Therefore, it's difficult to form a single phase where Mn substitutes Cu in CuO completely. Interestingly, the $CuMn_2O_4$ phase can be significantly suppressed in $Cu_{0.85}Mn_{0.15}O$, which was fabricated at 1 223 K for 2 h under a pressure of 27.7 MPa (Fig. 2). This provides a route to achieve pure $Cu_{1-x}Mn_xO$.

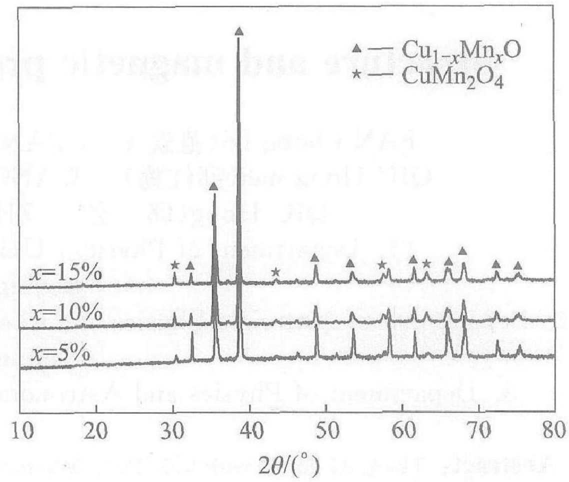

Fig. 1 XRD patterns for $Cu_{1-x}Mn_xO$ samples

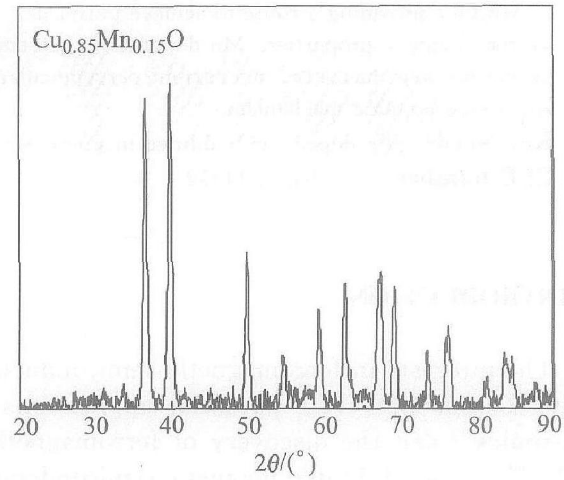

Fig. 2 XRD pattern for $Cu_{0.85}Mn_{0.15}O$ samples
(A pressure of 27.7 MPa is perpendicularly inflicted on surface during process of sintering)

The composition and structure of the Mn-doped samples were further characterized by FE-SEM and EDX. Fig. 3 shows the FE-SEM images of the $Cu_{1-x}Mn_xO$(x = 0, 0.05, 0.10, 0.15) after 8 h sintering in air at 1 273 K. The image the sample with x = 0 shows that the surface of pure CuO sample is composed of some plates of about 5 μm and voids (Fig. 3(a)). The Mn doping samples become more compact, which is particularly true in $Cu_{0.85}Mn_{0.15}O$ sample (Fig. 3(d)). The grain size is less than 1 μm and uniform. The results of EDX show that Mn concentration in the sample is different from the nominal concentration, which might be due to the nonuniform Mn distribution. The results are consistent with the XRD results, which shows that the structure of the samples consists of two phases.

The magnetic properties of the solids were characterized by SQUID magnetometer in the temperature range of 5 − 300 K. The field and temperature dependences on the magnetization of the $Cu_{0.85}Mn_{0.15}O$ sample are shown in Fig. 4. The results suggest that the sample is ferromagnetic below 70 K, consistent to the reported results in Ref. [16], the coercive fields is 1.13×10^5 A/m for x = 0.15 at 5 K. Above 70 K, the sample is in paramagnetic phase. The Mn-doped CuO presents ferromagnetic

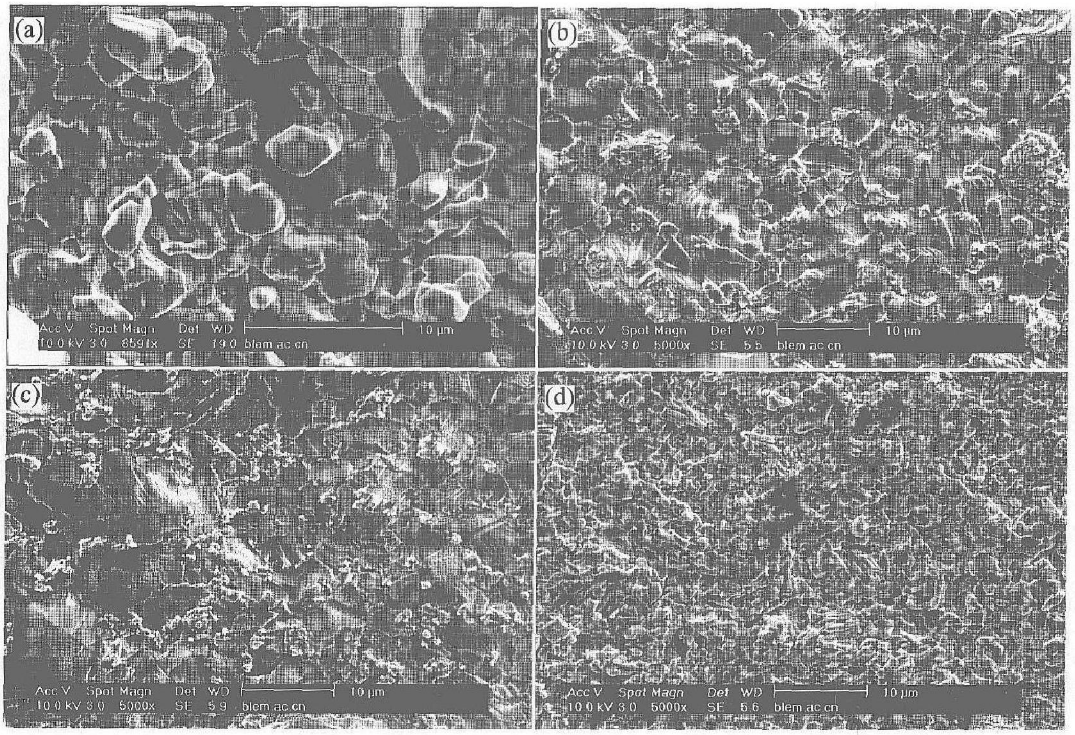

Fig. 3 FE-SEM images of $Cu_{1-x}Mn_xO$
(a) —CuO; (b) —$Cu_{0.95}Mn_{0.05}O$; (c) —$Cu_{0.90}Mn_{0.10}O$; (d) —$Cu_{0.85}Mn_{0.15}O$

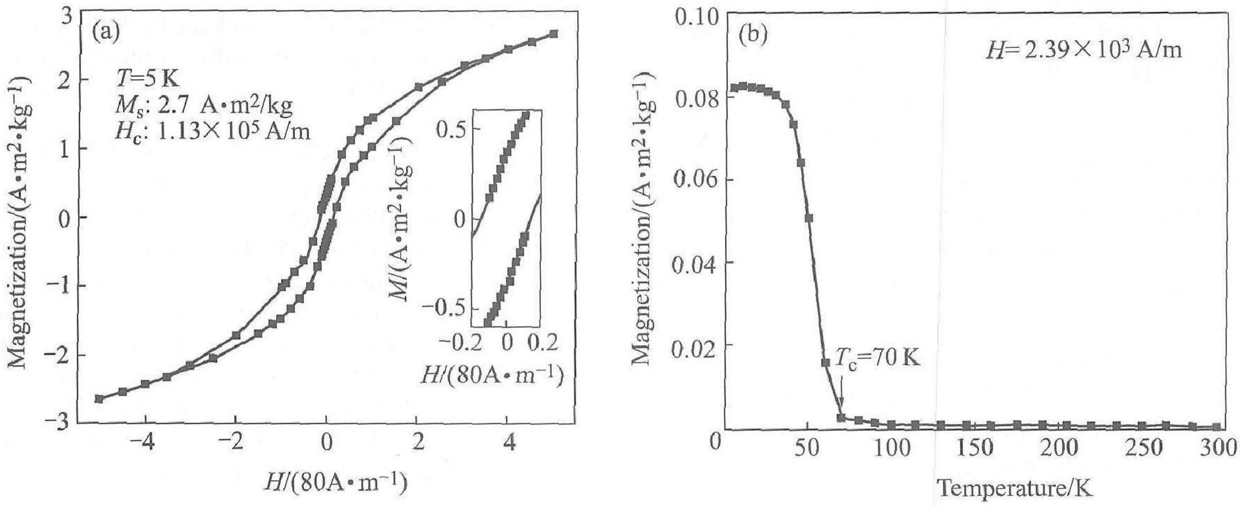

Fig. 4 Magnetization curves of $Cu_{0.85}Mn_{0.15}O$ sample at $T = 5$ K(a) and magnetization of $Cu_{0.85}Mn_{0.15}O$ sample at $H = 2.39 \times 10^3$ A/m(b)

characteristics at low temperatures and the transition occurs at 70 K. The $CuMn_2O_4$ phase shows the canted AFM behavior with the Nèel temperature at about 30 K[15], thus this phase does not contribute to the observed hysteresis(Fig. 4).

The electrical transport properties were carried out in Quantum Design PPMS system. The temperature dependence of the resistance (R) is shown in Fig. 5 and the inset shows the $\ln R$ versus $T^{-1/2}$ curve. The result suggests that the electrical transport is mainly from the variable-range hopping(VRH) of electron in the presence of a Coulomb gap described by Efros and Shklovskii rather than the thermal activation. At about 120 K, the resistance of the sample was above the limitation of our equipment.

The underlined physics of magnetic impurities vs carrier-mediated ferromagnetism is complex, and is a central topic of discussion for other semiconducting oxides that exhibit ferromagnetism, in particular the Co-doped TiO_2 system. Though the Zener double-exchange mechanism[17] has been successfully applied to diluted magnetic semiconductors such as Mn-GaAs[7], this mechanism requires the material has high carrier concentration. However the high resistivity of the $Cu_xMn_{1-x}O$ solids shows that this mechanism is not available. It is certainly fair to say that the origin of ferro-

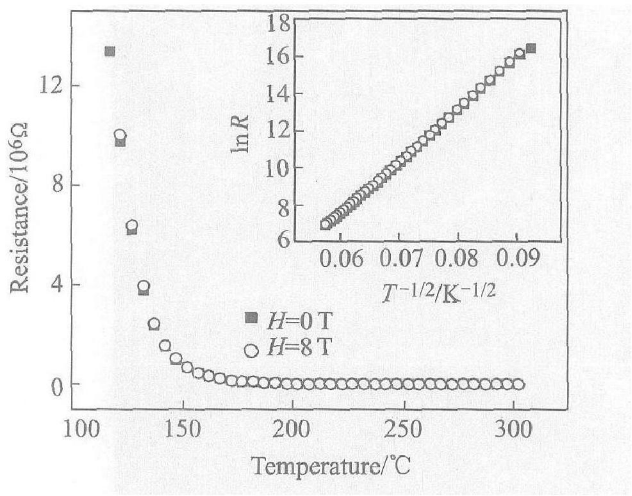

Fig. 5 Resistance as function of temperature for $Cu_{0.20}Mn_{0.80}O$ solids
(Inset plots $\ln R$ as function of $T^{-1/2}$)

maynetism in $Cu_xMn_{1-x}O$ is still not totally understood.

4 CONCLUSIONS

Six metal ions, Mn, Mg, Ca, Ti, V, and Fe, have been doped in CuO, the results of XRD show that Mn-doped CuO has the best substitution. However, a secondary phase, $CuMn_2O_4$, exists in the samples. The results of FE-SEM and EDX indicate that the distribution of Mn ions in CuO is nonuniform. Sintering under a pressure significantly reduces the second phase, which provides a route to achieve pure $Cu_{1-x}Mn_xO$ phase. Ferromagnetic characteristics have been observed in Mn-doped CuO with a Curie temperature at 70 K. The electrical transport of the sample is dominated by the variable-range hopping with strongly electron interactions. The ferromagnetism in $Cu_{1-x}Mn_xO$ is still not clear.

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