Effect of Mn doping on the microstructure and magnetic properties of CuFeO_2 ceramics

Fengjiao YE, Haiyang DAI, Ke PENG, Tao LI, Jing CHEN,
Zhenping CHEN*, Nannan LI

School of Physics and Electronic Engineering, Zhengzhou University of Light Industry, Zhengzhou 450002, China

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Abstract: The effects of Mn doping on the microstructure and magnetic properties of CuFeO_2 systems were studied using X-ray diffraction (XRD), X-ray photoelectron spectroscopy, scanning electron microscopy (SEM), and a physical property measurement method. The microstructure measurements demonstrated that the substitution of Mn for Fe can cause lattice distortion, promote grain growth, and change the valence state of Fe and Mn ions. Ceramic samples with doping content $x = 0.00$ – 0.03 exhibited two successive magnetic transition temperature (T_N) at $T_{N1} \approx 14$ K and $T_{N2} \approx 10$ K. T_N decreased gradually with the Mn^{4+} content, and T_{N2} was not observed in the $x > 0.05$ samples within a temperature range of $T = 5$ – 300 K. Magnetic hysteresis loops revealed that only anti-ferromagnetic behavior occurred in the low-doped samples ($x = 0.00$ – 0.03), and the coexistence of ferromagnetism and anti-ferromagnetism was observed in the high-doped samples ($x = 0.05$ – 0.10). Besides, the $x = 0.10$ sample had a maximum magnetization of 5.98 emu/g. This study provides basic experimental data for investigating the relationship between the microstructure and magnetic properties of CuFeO_2 systems.

Keywords: CuFeO_2 ; ceramics; microstructure; magnetic property

1 Introduction

As a delafossite compound, multiferroic CuFeO_2 (CFO) has a triangular lattice anti-ferromagnetic (TLA) structure composed of two layers of O^{2-} and one layer of Cu^+ along the c axis in crystallography [1,2]. Anti-ferromagnetic interaction between iron ions ($S = 5/2$ and $L = 0$) causes geometric frustration [3,4]. Without an external magnetic field, the magnetic phase of CFO changes from a paramagnetic (PM) phase to a

partially disordered (PD) incommensurate phase at the transition temperature $T_{N1} = 14$ K with a $R\bar{3}m$ space group lattice structure, and then to a four-sublattice (4SL) state at the transition temperature $T_{N2} = 11$ K with a monoclinic $C2/m$ structure. The potential applications, unique magnetic frustrated structures, and physical properties of CFOs have attracted widespread attention. Although in-depth research has been conducted, the magnetic mechanism of CFOs remains elusive [3,5]. As reported in many studies, chemical substitution is an effective method for modifying the crystal structure, exchanging interactions between spins, and affecting the magnetic properties of CFO [6–9]. Elkhoun *et al.* [10] found that

* Corresponding author.
E-mail: czhpj2007@163.com

the partial replacement of Fe^{3+} with Sc^{3+} induced spin dilution and anti-ferromagnetic phase transition in CFO systems, causing a dimensional crossover of low-energy anti-ferromagnetic excitation from three-dimensional (3D) to two-dimensional (2D) anti-ferromagnetic interactions. Seki *et al.* [11] reported that increasing the Al^{3+} doping concentration significantly improved the ferromagnetism, which was ascribed to the arbitrary distribution of Al^{3+} in the ferrite hexahedron adjusting the spin structure of CFO systems. Shi *et al.* [12] reported that Ga^{3+} substitution in Fe^{3+} sites weakened the anti-ferromagnetic interactions in CFO systems, obviously shifting $T_{\text{N}2}$ to lower temperatures and inhibiting the formation of collinear 4SL ground phases at low temperatures.

As a strongly correlated electron system, CFO physical properties are extremely sensitive to strong coupling between electron spins, charges, defects, characteristics, and other microstructures. The substitution of Mn^{4+} for Fe^{3+} in CFO systems requires charge compensation, which will influence the creation of cation vacancies and change the system ion valence state, adjusting the effects on the magnetic ground state. Furthermore, replacing Fe^{3+} with magnetic Mn^{4+} ions generates mixed-valence ions caused by the charge balance, dilution effect, exchange interaction, and spin inhibition, affecting competition among ions with different magnetic moments that can enrich the CFO system's magnetic properties. However, few studies have reported magnetic ions in CFO systems. Thus, we synthesized Mn-doped CFO via solid-state reactions and studied systematically using X-ray diffraction (XRD), scanning electron microscopy (SEM), Raman spectroscopy, and physical property measurement. The interplay between the magnetic properties and microstructure was also studied in detail.

2 Experimental

$\text{CuFe}_{1-x}\text{Mn}_x\text{O}_2$ ($x = 0, 0.01, 0.03, 0.05$, and 0.10) samples were prepared via solid-state reactions using stoichiometric amounts of CuO (purity 99.99%), Fe_2O_3 , and MnO_2 as reagents. The raw powders in the required proportions were mixed according to their stoichiometric ratios and carefully ground to form a mixture that was calcined at 1123 K for 12 h in argon. The mixtures were finely reground and compressed into cylindrical discs of 13 mm in diameter and

1.5 mm in thickness under a hydraulic press with a pressure of 7 MPa and then sintered at 1373 K for 12 h in argon. To prevent monovalent Cu^+ in the CFO system from oxidizing into divalent Cu^{2+} , the calcination and sintering processes were conducted in an argon atmosphere.

The sintered pellets' crystal phases were analyzed via XRD (D8 Advance) with Cu K α radiation. X-ray photoelectron spectroscopy (XPS, ESCALAB250Xi) was used to study the specimens' binding energy and ion valence state. The Raman spectra were studied using Renishaw's Raman systems via spectrometry with a 514 nm Ar laser at room temperature. The fracture morphology was studied via high-resolution SEM (Quanta 250 FEG). The samples' magnetic properties were investigated using a physical property measurement system (PPMS, Quantum Design). The temperature-dependent magnetic susceptibility was tested from 4 to 300 K, and the magnetic hysteresis loops (M – H) at 10 and 13 K were collected using a vibrating sample magnetometer.

3 Results and discussion

3.1 XRD analysis

Figure 1(a) shows the powder XRD of the $\text{CuFe}_{1-x}\text{Mn}_x\text{O}_2$ samples. The doping content $x = 0.00$ – 0.03 phase ceramics have a single hexagonal delafossite structure with a $R\bar{3}m$ space group (CuFeO_2 (PDF#04-007-2807)), and some weak diffraction peaks at approximately 38.85° , 30.15° , and 56.90° corresponding to CuO and MnO_2 impurities are observed in the $x = 0.10$ samples. This demonstrates that a small amount of Mn doping (0.00 – 0.05) in the CFO system forms a single-phase structure, but excess doping ($x = 0.10$) can introduce impurities. The amount of CuO and MnO_2 in the $x = 0.10$ sample indicates that the substitution limitation of Mn^{4+} ions in the CFO is less than 10%. No traces of manganese oxide or manganate can be observed in the $\text{CuFe}_{1-x}\text{Mn}_x\text{O}_2$ samples ($x = 0$ – 0.05), indicating the successful introduction of Mn^{4+} into the CFO lattice. Rietveld refinement of the XRD data was conducted to obtain the samples' accurate lattice information. The Rietveld refinement of $\text{CuFe}_{0.99}\text{Mn}_{0.01}\text{O}_2$ is described in Fig. 1(b). The inset in Fig. 1(a) shows the magnified patterns of the (012) peak. The variations in the samples' peak positions indicate that Mn^{4+} doping induces a significant lattice distortion, which is also

Fig. 1 (a) XRD patterns of the $\text{CuFe}_{1-x}\text{Mn}_x\text{O}_2$ ($x = 0.00$ – 0.10) samples. The inset illustrates the expansion of the main peak (012). (b) Rietveld analysis of $\text{CuFe}_{0.99}\text{Mn}_{0.01}\text{O}_2$.

confirmed by the calculated lattice parameters in Fig. 2. Figure 2 shows the lattice parameters of $\text{CuFe}_{1-x}\text{Mn}_x\text{O}_2$ calculated via PowderX software. The lattice parameters (a and c) slightly decrease with the Mn content from 0 to 0.03, which is attributed to the smaller cation size of Mn^{4+} (0.54 Å) than Fe^{3+} (0.64 Å). In the CFO system, the samples' lattice constants are affected by the amount of Mn^{4+} and stress induced by sintering [13,14]. The lattice parameters of the $x = 0.05$ sample increase abnormally compared with the $x = 0.00$ – 0.03 samples, which may be ascribed to Fe^{2+} (0.76 Å) with a larger ionic radius induced by charge compensation as a competitive advantage. In the $x = 0.10$ sample, the lattice parameters decrease compared with the $x = 0.05$ sample, which may be due to the decrease in the Fe^{2+} concentration (as described in the following XPS results). The main diffraction peaks of the $x = 0.05$ and $x = 0.10$ samples are slightly split, indicating that the delafossite structure of the CFO system with a $R\bar{3}m$ space group may be distorted due to the higher doping

concentration [15–17].

3.2 XPS analysis

XPS was used to study the effect of Mn^{4+} doping on the CFO ceramics' chemical valence. Figure 3 shows the survey spectrum of the undoped sample. To calibrate the binding energy scale, the C 1s level was assumed to be 284.6 eV. The undoped sample's survey spectrum consists of Cu 2p, Fe 2p, C 1s, and O 1s lines.

Figure 4 shows the fitted XPS spectra of the $\text{Fe } 2p_{3/2}$ in the $\text{CuFe}_{1-x}\text{Mn}_x\text{O}_2$ samples. The CFO system's $\text{Fe } 2p_{3/2}$ exhibits an asymmetrically broadband, indicating mixed Fe valence states in the synthesized samples. The $\text{Fe } 2p_{3/2}$ core level for each spectrum can be divided into two peaks. The peaks located at approximately 710.0 and 712.8 eV correspond to Fe^{2+} and Fe^{3+} , respectively [18,19]. The Fe^{2+} content is obtained using the ratio of the Fe^{2+} peak area to the sum of the Fe^{2+} and Fe^{3+} peak areas. Figure 5 shows that the

Fig. 2 Lattice parameters a and c of $\text{CuFe}_{1-x}\text{Mn}_x\text{O}_2$ samples as a function of Mn content x .

Fig. 3 Survey spectrum of the $x = 0$ sample.

Fig. 4 Fe 2p XPS spectra of the $\text{CuFe}_{1-x}\text{Mn}_x\text{O}_2$ samples.

Fig. 5 Amount of Mn^{4+} and Fe^{2+} in the $\text{CuFe}_{1-x}\text{Mn}_x\text{O}_2$ samples.

calculated Fe^{2+} content is approximately 45.62%, 54.45%, 58.92%, 58.52%, and 41.48% for the $x = 0.00, 0.01, 0.03, 0.05$, and 0.10 samples, respectively. This may be ascribed to the decrease in the oxygen vacancy concentration caused by Mn^{4+} doping, indicating that the charge neutralization effect caused by Mn^{4+} doping at the Fe site can induce a different amount of Fe^{2+} ions in the CFO system. A similar phenomenon can be observed in other studies [20]. Compared with the $x = 0.05$ sample, the Fe^{2+} content in the $x = 0.10$ sample decreases, which can be ascribed to the insufficiently reacted Fe_2O_3 inside the CFO system increasing the Fe^{3+} content and then decreasing the Fe^{2+} content.

The measured $\text{Mn } 2p_{3/2}$ spectrum is depicted in Fig. 6. The $\text{Mn } 2p_{3/2}$ peak can also be fitted with two peaks. The two peaks represent the Mn^{3+} (approximately 640.2 eV) and Mn^{4+} (approximately 641.5 eV),

respectively. The Mn^{3+} content can be obtained using the ratio of the Mn^{3+} peak area to the sum of the Mn^{3+} and Mn^{4+} peak areas. The calculated Mn^{3+} concentrations shown in Fig. 6 show for the $x = 0.01, 0.03, 0.05$, and 0.10 samples are 53.7%, 46.7%, 51.2%, and 38.4%, respectively. This indicates that the concentration of Mn^{3+} decreases with the Mn content, which can be ascribed to the charge compensation effect caused by Mn^{4+} doping that induces the charge balance in the CFO system.

3.3 Raman spectroscopy

Figure 7 shows the Raman spectra of the $\text{CuFe}_{1-x}\text{Mn}_x\text{O}_2$ ceramics. The CFO has a $R\bar{3}m$ space group at room temperature and the four atoms in the cell can be characterized with 12 vibration modes ($\Gamma = A_{1g} + E_g + 3A_{2u} + 3E_u$), where A_{1g} and E_g are the vibrations of the Cu–O and Fe–O bonds, respectively [6,10,21]. The samples display two Raman active modes and obey the Horseman selection rule. The peak at approximately 345 cm^{-1} is the E_g mode and the peak at approximately 678 cm^{-1} is the A_{1g} mode. The vibration of the two modes correspond to the edge-shared FeO_6 octahedron and O–Cu–O linear bond, respectively. Mn doping induces changes in the peak intensity and the width of E_g and A_{1g} modes in all of the samples. The intensity of the two modes gradually increases with the amount of Mn^{4+} , which is related to the variations in Fe–O and Mn–O bonding induced by Mn substitution. It means that Mn substitution has an obvious effect on the

Fig. 6 Mn 2p XPS spectra of the $\text{CuFe}_{1-x}\text{Mn}_x\text{O}_2$ samples.

Fig. 7 Raman micrographs of the $\text{CuFe}_{1-x}\text{Mn}_x\text{O}_2$ samples.

CuFeO_2 system's molecular polarizability [10]. The shift in frequency to lower wavenumbers as the amount of Mn^{4+} doping increases indicates the weakening of the Fe–O and Mn–O bonds, which is ascribed to the lattice expansion caused by Mn^{4+} doping (as confirmed by the XRD results). The shift in frequency also indicates that Mn is successfully introduced into the CFO lattice. A broad peak at approximately 470 cm^{-1} is observed in the $x = 0.03\text{--}0.10$ samples, which may be due to the relaxation of the selection rules caused by the Cu vacancies, interstitial oxygen atoms, or tetrahedrally coordinated $\text{Mn}^{4+}/\text{Fe}^{3+}$ at the Cu site [22]. Similar phenomena occurred in other reports on CFO systems [6,20,21]. Therefore, we confirm that this

broad peak is related to defect compensation induced by the charge compensation due to high-valence ion doping.

3.4 SEM

Figure 8 shows the microstructural evolution of the fracture surface morphology in the $\text{CuFe}_{1-x}\text{Mn}_x\text{O}_2$ ($x = 0.00\text{--}0.10$) samples. The undoped sample has a dense structure with indistinct grain boundaries and few pores. As the amount of doping increases, the doped samples' grain sizes increase, the grain boundaries are obvious, and the pore sizes increase. This occurs because the cation vacancies induced by Mn^{4+} doping effectively stimulate the movement of cations, promoting grain growth [23]. Compared with the other samples, the grain of $x = 0.05$ sample adhered, the pore volume increases significantly, and some small crystal grains are attached to the large crystal grains. Further increasing the doping concentration, the $x = 0.10$ sample exhibits the largest grain sizes and good densification. The largest grain size may be also attributed to the Cu-rich phase (CuO) compounds with a lower melting point (1299 K) [24]. The melting point of CFO is 1443 K [25], which can promote grain growth [26,27]. The compact fracture morphology in the $x = 0.10$ sample could be due to the grown grains occupying the voids. To further study the changes in grain sizes, the samples' grain sizes are calculated by

Fig. 8 SEM micrographs of the $\text{CuFe}_{1-x}\text{Mn}_x\text{O}_2$ samples.

considering the most intense diffraction peak in the XRD pattern using Scherrer's equation:

$$D = \frac{K\lambda}{\beta \cos \theta} \quad (1)$$

where D and λ are the crystallite size and wavelength of the incident radiation, respectively; $K = 0.89$; β and θ are the full width at half maximum in radian and diffraction angle, respectively. The samples' grain size is shown in Table 1. Mn^{4+} doping induces an increase in the samples' grain size, consistent with the SEM analysis. The $x = 0.10$ sample with a grain size of 89.998 nm is the largest among the Mn^{4+} -doped samples.

Table 1 Lattice parameters, grain size, and the content of Fe^{2+} and Mn^{3+} for $\text{CuFe}_{1-x}\text{Mn}_x\text{O}_2$ ($x = 0.00–0.10$) samples

Mn content	0	0.01	0.03	0.05	0.10
a (Å)	3.033(5)	3.028(9)	3.024(4)	3.032(1)	3.029(4)
c (Å)	17.146(3)	17.127(4)	17.122(2)	17.163(3)	17.154(8)
D (nm)	78.177(2)	81.202(1)	80.651(4)	81.191(7)	89.998(2)
Fe^{2+} content	45.62%	54.45%	58.92%	58.52%	41.48%
Mn^{3+} content	0	53.7%	46.7%	51.2%	38.4%

3.5 Magnetic properties

Figure 9 presents the plots of the samples' magnetic susceptibility χ and inverse magnetic susceptibility

Fig. 9 Temperature dependence of zero-field-cooling susceptibility of the $\text{CuFe}_{1-x}\text{Mn}_x\text{O}_2$ samples.

$1/\chi$ as a function of the temperature in a range of 5–300 K. The samples' $1/\chi$ – T plots demonstrate a linear relationship at high temperatures, suggesting that the samples have a paramagnetic (PM) state at high temperatures. The $1/\chi$ – T plots show different non-linear behaviors at low temperatures, possibly due to the appearance of different interactions (anti-ferromagnetism, ferromagnetism, or ferrimagnetism) at low temperatures. Compared with Refs. [20,22,28,29], different ion-doped CFO series exhibited similar magnetic characteristics in a measured temperature range of $T = 5$ –300 K. Therefore, the doped ion sizes and magnetic properties do not affect the competition between the anti-magnetic and ferromagnetic behaviors in the paramagnetic state in high-temperature and low-temperature regions. To demonstrate the changes in the magnetic transition temperature (T_N), the samples' χ – T curves within a narrow temperature range of 5–25 K are shown in Fig. 9. In the $x = 0.00$ –0.03 samples, a broad peak corresponding to magnetic transitions from PM to collinear incommensurate spin structures occurs at $T_{N1} \approx 15$ K and then abruptly decreases, which is associated with the transition to a collinear commensurate spin structure at $T_{N2} \approx 11$ K [12]. Figure 10 shows that T_{N1} and T_{N2} decrease as the Mn content increases from 0.00 to 0.10. T_{N2} could not be detected in the $x = 0.05$ –0.10 samples, which agrees with Refs. [6,12]. In the $x = 0.10$ sample, T_{N1} decreases at approximately 9 K. This evolution of T_{N1} and T_{N2} could be caused by structural modulation resulting from Mn doping. In general, changes in T_N are ascribed to three factors: the dilution effect, exchange interactions, and release of spin frustration [28]. First, the decrease in T_N induced by the dilution effect [27]

Fig. 10 Expansion of the samples' χ – T curves in a range of $T = 5$ –25 K.

occurs because the magnetism of Mn^{4+} is lower than that of Fe^{3+} ($\text{Mn}^{4+}(m = 4 \mu_B)$ and $\text{Mn}^{3+}(m = 5 \mu_B)$). Increase in T_{N1} is thought to be related to the increase in exchange interactions and partial release of spin frustration [29]. In the $x = 0.01$ and 0.03 samples, the exchange interactions may have increased because of the lower lattice parameters than in the undoped samples as demonstrated by the XRD results [30]. In the $x = 0.05$ –0.10 samples, T_{N1} shows the same trend as $0.01 \leq x \leq 0.03$. Therefore, the dilution effect has the competitive advantage among the three factors in all of the samples.

To clarify the magnetic characteristics near T_N , the M – H loops of the $\text{CuFe}_{1-x}\text{Mn}_x\text{O}_2$ samples were collected. As shown in Fig. 11, the shape of the samples' M – H curves at 10 and 13 K is similar, demonstrating that the samples display similar magnetic properties. The samples' magnetization is unsaturated under the measured field of 0.5, indicating the presence of multiple magnetic interactions [31]. The $x = 0.00$ –0.03 samples' M – H curves exhibit linear field-dependent magnetization, indicating their anti-ferromagnetic behavior, while the $x = 0.05$ –0.10 samples demonstrate typical and symmetric hysteresis loop characteristics, indicating the presence of weak CFO-based ferromagnetism due to the short-range Fe–O–Fe interactions induced by Mn doping [28,32].

As shown in Fig. 11, the magnetization increases with the amount of Mn in the $\text{CuFe}_{1-x}\text{Mn}_x\text{O}_2$ ($x = 0$ –0.10). The magnetization of $x = 0.10$ sample is 5.98 emu/g, almost five times larger than that of the undoped sample (1.21 emu/g). The magnetic properties of CFO ceramics improved by element doping was previously reported by Refs. [11,32,33]. The structure and area of the M – H loop are closely related to the material's particle size, composition, pore size, and cation distribution [34,35]. CFOs' magnetic properties are sensitive to the strong coupling between electron spin, charge, and lattice [36]. The samples' different magnetization is attributed to competition between the different magnetic moments of Fe^{3+} ($M = 5.9\mu_B$), Fe^{2+} ($M = 5.4\mu_B$), Mn^{4+} ($M = 4\mu_B$), and Mn^{3+} ($M = 5\mu_B$). Therefore, the amount of ions has a significant impact on a system's magnetic properties. As shown in Fig. 4, as the amount of Mn^{4+} doping increases, the amount of Fe^{3+} in the CFO system gradually increases and the amount of Mn^{3+} gradually decreases, and the amount of Fe^{3+} gradually increases, improving the CFO system's magnetic properties. Increasing the amount of Mn^{3+}

Fig. 11 M – H loops of the $\text{CuFe}_{1-x}\text{Mn}_x\text{O}_2$ samples.

inhibits the CFO system's magnetic properties [37,38]. Therefore, in CFO systems, competition occurs between various magnetic moments and ionic magnetism. For example, the $x = 0.10$ sample has a maximum magnetization of 5.3 emu/g, and the amount of Fe^{3+} is greater than in the other samples. Thus, the improvement in magnetization can be elucidated based on the following factors: (1) Increasing the grain size and amount of Mn causes deformation in the magnetic spin structure, improving the CFO's magnetic properties; (2) the charge compensation induced by the substitution of tetravalent Mn by trivalent Fe causes cationic vacancies. The anti-parallel spin ordering in CFOs may be affected by vacancies, improving their magnetic properties; (3) the substitution of Fe by Mn in CFOs can change the bond lengths and angles, changing the inclination angle of FeO_6 octahedron, which modulates the system's magnetic spin and improves the magnetic properties; (4) the greater the Fe^{3+} ion content, the greater the magnetization. Compared with the studies on Ti-doped CFO [32], in cases of the same valence ion substitution, the magnetic structure deformation caused by small-size ion doping, and the competitive effect among ions of different magnetic moments is more significantly conducive to improving the magnetic properties of CFO systems. In conclusion, changes in the microstructures,

grain sizes, charge compensation, and magnetic moments of different ions are important factors affecting the magnetic properties of CFO systems.

4 Conclusions

CFO samples were prepared via solid-state reactions, and the effects of Mn-doped CuFeO_2 on the structures and magnetic properties were investigated. The microstructure results demonstrated that Mn doping caused obvious changes in the lattice parameters and high Mn concentration damaged the single-phase structure in the CFO system. The SEM results showed that the average grain size increased due to Mn doping. The $x = 0.1$ sample had a denser microstructure, larger grains, and more distinct grain boundaries than other samples. The Raman spectroscopy results demonstrated that Mn^{4+} successfully entered the CFO's crystal lattice and Mn substitution affected the variations in Fe–O and Mn–O bonding and had an obvious effect on the deformation of the CuFeO_2 system's molecular polarizability. The magnetic measurements showed that the anti-ferromagnetic T_N gradually decreased as the amount of Mn decreased. However, in the $x = 0.05$ – 0.10 samples, T_{N2} could not be detected within the tested temperature range. The M – H curves

demonstrated that the $x = 0.00$ – 0.03 samples exhibited the highest anti-ferromagnetic behavior, and the $x = 0.05$ – 0.10 samples had weak ferromagnetism. The $x = 0.10$ sample had the highest magnetization compared with other samples. The improvement in ferromagnetism induced by Mn doping can be attributed to the size effects, structural distortion, charge compensation effects, and magnetic moments of the different ions.

Acknowledgements

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