

Magnetism and phase transformation of Cu-Fe composite oxides prepared by the sol-gel route

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Abstract The Cu-Fe composite oxides were prepared by an epoxide assisted sol-gel route. The structural and magnetic properties of Cu-Fe composite oxides calcinated at different temperatures were determined by X-ray diffraction (XRD), Mössbauer spectroscopy measurements, and magnetic measurements. These results indicated that CuFe_2O_4 was only formed as calcination temperature increased to 500 °C, and a crystalline phase transformation from c- CuFe_2O_4 to t- CuFe_2O_4 occurred in elevating calcination temperature above it. All Cu-Fe oxides had ferromagnetic nature, and the significant superparamagnetic behavior was observed in the results of magnetic and Mössbauer spectroscopy measurements.

Keywords Cu-Fe composite oxides · Sol-gel · Phase transformation · CuFe_2O_4 · Mössbauer spectroscopy

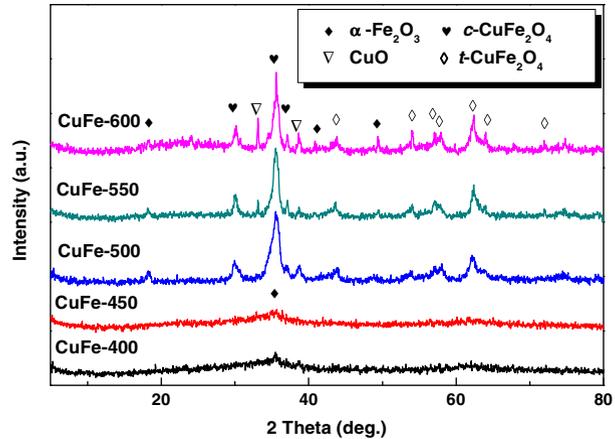
1 Introduction

Ferrites are a group of mixed metal oxides characterized by specific electric and magnetic properties, which have found important applications in a great variety of technical fields. Copper ferrite (CuFe_2O_4), belongs to a subgroup of spinel-type ferrites, has an inverse spinel structure with 8 Cu^{2+} ions on octahedral sites and 16 Fe^{3+} ions, which are equally distributed between both the tetrahedral and octahedral sites of the unit cell [1, 2]. Its preparation method and subsequent treatment play a very important role with regard to the chemical, structural and magnetic properties.

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Fig. 1 The XRD patterns of Cu-Fe composite oxides calcinated at different temperatures



Based on these, Yokoyama et al. [3] observed the changes in the crystal structure of nanosized CuFe₂O₄ obtained by coprecipitation and subsequently annealed, and proved that the copper spinel is cubic phase at temperatures below 300 °C and tetragonal phase over 400 °C. While this structure changes was determined at higher temperature over 500 °C, for which nanosized copper ferrites were prepared by thermal method from the corresponding hydroxide carbonate precursors [4]. This transformation is ascribed to the changed of Cu²⁺ in the B-sublattice. While the Cu²⁺ fraction in the B-sublattice strongly depends on the technologies of synthesis and subsequent temperature treatment. Herein, the aim is investigated the magnetic properties and phase transformation of Cu-Fe composite oxides, which are prepared by an epoxide assisted sol-gel route. The effect of calcination temperature was examined for understanding the formation process of spinel CuFe₂O₄ and transformation of crystalline phase.

2 Experiments

The Cu-Fe composite oxides were synthesized by a sol-gel route [5, 6]. The structure and magnetic properties were determined by X-ray diffraction (XRD) [6], Mössbauer spectroscopy and magnetic measurements. ⁵⁷Fe Mössbauer spectra were recorded at room temperature using a Topologic 500 A spectrometer with a proportional counter. Moving ⁵⁷Co(Rh) in a constant acceleration mode was used as the radioactive source. The magnetization was characterized by a superconducting quantum interference (SQUID, MPMSXL5) magnetometer with a maximum field of 15 kOe at 27 °C.

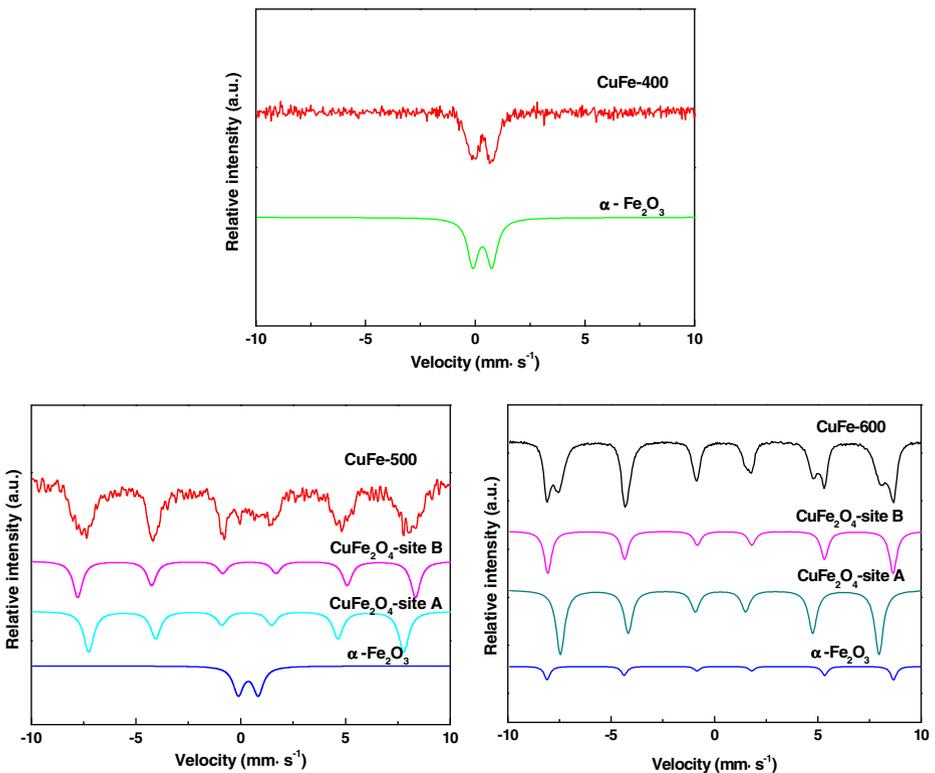
3 Results and discussion

The XRD patterns of Cu-Fe composite oxides calcinated at different temperatures are depicted in Fig. 1. After thermal treatment at 400 °C, only one low broad diffraction peak was observed corresponding to α-Fe₂O₃. As calcination temperature

Table 1 The average particle sizes and molar fraction of ion species for Cu-Fe composite oxides obtained from XRD patterns

Sample	D (nm) ± 2				Molar fraction ^a (%)		
	t-CuFe ₂ O ₄	c-CuFe ₂ O ₄	CuO	α -Fe ₂ O ₃	t-CuFe ₂ O ₄	c-CuFe ₂ O ₄	α -Fe ₂ O ₃
CuFe-400	–	–	–	2	–	–	–
CuFe-450	–	–	–	3	–	–	–
CuFe-500	7	8	10	7	50	38	12
CuFe-550	16	10	20	16	58	33	9
CuFe-600	20	10	24	22	60	31	9

^aMolar fraction of iron species in the mixture of t-CuFe₂O₄, c-CuFe₂O₄ and α -Fe₂O₃

**Fig. 2** Mössbauer spectra of Cu-Fe composite oxides calcinated at different temperatures

increased, good crystalline CuFe₂O₄ phase (major phase, tetragonal CuFe₂O₄ and cubic CuFe₂O₄) and trace amount of CuO and α -Fe₂O₃ were identified in the XRD patterns. The molar fraction of ion species in a (t-CuFe₂O₄)-(c-CuFe₂O₄)-(α -Fe₂O₃) mixture was calculated from XRD patterns as shown in Table 1. It was not hard to found that a transformation process from cubic CuFe₂O₄ phase to tetragonal phase occurred. The similar transformation has been reported by Tsoncheva et al., demonstrated the phase composition of the obtained product strongly depends on the annealing temperature [4]. And a greater degree of crystallinity and crystallite

Table 2 ^{57}Fe Mössbauer parameters of Cu-Fe composite oxides calcinated at different temperatures

Sample	State	IS/mm·s ⁻¹	QS/mm·s ⁻¹	H/T	RI (%)	LW/mm·s ⁻¹
CuFe-400	$\alpha\text{-Fe}_2\text{O}_3$	0.33	0.86	–	100	0.59
CuFe-500	CuFe ₂ O ₄ -Site B	0.35	–0.13	50.0	38.0	0.54
	CuFe ₂ O ₄ -Site A	0.27	–0.03	46.6	46.2	0.58
CuFe-600	$\alpha\text{-Fe}_2\text{O}_3$	0.35	0.95	–	15.8	0.58
	CuFe ₂ O ₄ -Site B	0.39	–0.20	51.8	33.3	0.43
	CuFe ₂ O ₄ -Site A	0.27	–0.03	47.8	58.3	0.49
	$\alpha\text{-Fe}_2\text{O}_3$	0.38	–0.19	52.0	8.4	0.34

Table 3 The magnetic properties of Cu-Fe composite oxides calcinated at different temperatures

Sample	Ms (emu/g)	Mr (emu/g)	Mr/Ms	Hc (Oe)
CuFe-400	15.53	4.81	0.31	431
CuFe-500	17.13	0.99	0.06	70
CuFe-600	20.80	9.54	0.46	828

growth was observed at higher temperature, which was proved by the increased particle sizes in Table 1.

The results of ^{57}Fe Mössbauer spectra are shown in Fig. 2, with the hyperfine interaction parameters summarized in Table 2. As known, the IS value is the most important factor for diagnosing the chemical states of iron [7]. In the case of CuFe-400 sample, the Mössbauer spectra of IS = 0.33 mm·s⁻¹ and QS = 0.86 mm·s⁻¹ are in agreement with these value of $\alpha\text{-Fe}_2\text{O}_3$ in the form of doublet, as reported in Ref. [8]. While for the CuFe-500 sample, the Mössbauer spectrum could be fitted into two partially resolved magnetic sextets arising from Fe³⁺ in tetrahedral (A) and octahedral (B) sites [9], with a doublet of $\alpha\text{-Fe}_2\text{O}_3$. Surprisingly, three sextets were contained in the Mössbauer spectrum of CuFe-600 sample. Wherein, the sextets with RI = 33.3 and 58.3 could be attributed to CuFe₂O₄-Site B, and CuFe₂O₄-Site A, respectively. While the sextet with ^{57}Fe Mössbauer parameters of IS = 0.38 mm·s⁻¹ and QS = –0.19 mm·s⁻¹, which could be attributed to $\alpha\text{-Fe}_2\text{O}_3$ [10]. This change from doublet to sextet is due to the increase of particle size, which could be observed from XRD. Compared with the CuFe-500 sample, the RI ratio of CuFe₂O₄-Site A to Site B in CuFe-600 sample was increased, which was due to the migration of Fe³⁺ ions from B sites to A sites and an increase in the degree of distortion, resulting in the increase of the t-CuFe₂O₄ phase. This is in agreement with the XRD results. Since the Mössbauer parameters of t-CuFe₂O₄ is so close to c-CuFe₂O₄, the fraction of which is not determined. The CuFe-400 and CuFe-500 samples exhibited the superparamagnetic behavior due to the present of doublet in Mössbauer spectrum originating from $\alpha\text{-Fe}_2\text{O}_3$ with small particle size, which was also proved by magnetic measurement in the later.

Magnetic properties of the Cu-Fe nanoparticles were also investigated. The hysteresis loops obtained (not shown) show a normal S-shape type, which is suggestive of a significant content of ferromagnetic materials. For easy discussion, the magnetic properties of Cu-Fe composite oxides are listed in Table 3. The ratio of the remnant to the saturation magnetization (Mr/Ms) decreased at the beginning and then increased as increasing calcinations temperature. It can be further noticed that the Mr/Ms ratio for CuFe-600 is very close to the ideal 0.5 value characteristic of

single-domain non-interacting particles. The large reduction of this ratio in CuFe-400 and CuFe-500 adds evidence to the significant superparamagnetic behavior [9].

Due to α -Fe₂O₃ in CuFe-400 with a low degree of crystallinity and small particle size, it exhibited lower saturation magnetization compared to CuFe-500 sample. Obviously, this was also related to the change of phases. For the CuFe-500 and CuFe-600 samples, the higher saturation magnetization was observed for the later one. One of the reasons is that the larger particle size lead to higher saturation magnetization, which is attributed to surface effects that are the result of finite-size scaling of nanocrystallites [11]. The other is that the saturation moment is increased with increasing the inversion degree due to an increased in tetragonal CuFe₂O₄ phase [9], resulting in the increase of saturation magnetization. Based on these, it is reasonable that the higher saturation magnetization was observed for CuFe-600 sample.

4 Conclusion

The Cu-Fe composite oxides have been synthesized successfully by an epoxide assisted route. With increasing calcination temperature, the significant change of crystalline phases was observed from XRD results. As calcination temperature increased to 500 °C, the spinel CuFe₂O₄ was formed. And a transformation of crystalline phases from cubic to tetragonal CuFe₂O₄ with elevating calcination temperature was determined by XRD and Mössbauer spectroscopy. The magnetic characterization showed that all Cu-Fe composite oxides had ferromagnetic nature and the saturation magnetization values monotonously increased with increasing calcination temperature. Besides, the CuFe-400 and CuFe-500 sample exhibited the significant superparamagnetic behavior, which was proved by Mössbauer spectroscopy as the presentation of doublet.

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References

1. Ristić, M., Hannover, B., Popović, S., Musić, S., Bajraktaraj, N.: Ferritization of copper ions in the Cu-Fe-O system. *Mater. Sci. Eng. B* **77**, 73–82 (2000)
2. Ahmed, Y.M.Z., Hessien, M.M., Rashad, M.M., Ibrahim, I.A.: Nano-crystalline copper ferrites from secondary iron oxide (mill scale). *J. Magn. Magn. Mater.* **321**, 181–187 (2009)
3. Yokoyama, M., Nakamura, A., Sato, T., Haneda, K.: Jahn-Teller effect in ultrafine copper ferrite particles. *J. Magn. Soc. Jpn.* **22**, 243–245 (1998)
4. Tsoncheva, T., Manova, E., Velinov, N., Paneva, D., Popova, M., Kunev, B., Tenchev, K., Mitov, I.: Thermally synthesized nanosized copper ferrites as catalysts for environment protection. *Catal. Commun.* **12**, 105–109 (2010)
5. Ma, Z., Xiao, Z., van Bokhoven, J.A., Liang, C.: A non-alkoxide sol-gel route to highly active and selective Cu-Cr catalysts for glycerol conversion. *J. Mater. Chem.* **20**, 755–760 (2010)
6. Xiao, Z., Ma, Z., Wang, X., Williams, C.T., Liang, C.: Effect of preparative parameters on structure and catalytic performance of Cu-Cr Catalysts in non-alkoxide sol-gel route. *Ind. Eng. Chem. Res.* **50**, 2031–2039 (2011)
7. Murad, E., Cashion, J.: *Mössbauer Spectroscopy of Environmental Materials and Their Industrial Utilization*, p. 19. Kluwer Academic, Boston (1984)

8. Liu, K., Wang, A.Q., Zheng, W.S., Wang, J.H., Huang, Y.Q., Shen, J.Y., Zhang, T.: Quasi in situ ^{57}Fe Mössbauer spectroscopic study: quantitative correlation between Fe^{2+} and H_2 concentration for PROX over Ir-Fe/ SiO_2 catalyst. *J. Phys. Chem. C* **114**, 8533–8541 (2010)
9. Goya G.F., Rechenberg, H.R.: Superparamagnetic transition and local disorder in CuFe_2O_4 nanoparticles. *Nanostruct. Mater.* **10**, 1001–1011 (1998)
10. Manova, E., Tsoncheva, T., Paneva, D., Popova, M., Velinov, N., Kunev, B., Tenchev, K., Mitov, I.: Nanosized copper ferrite materials: mechanochemical synthesis and characterization. *J. Solid State Chem.* **184**, 1153–1158 (2011)
11. Deraz, N.M.: Size and crystallinity-dependent magnetic properties of copper ferrite nanoparticles. *J. Alloys Compd.* **501**, 317–325 (2010)