

# X-ray diffraction and Mössbauer studies of phase transformation in manganese ferrite prepared by combustion synthesis method

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## Abstract

Mixed ferrite  $\text{MnFe}_2\text{O}_4$  has been prepared by combustion synthesis method and subsequent heat treatment. The effects of annealing temperature and quenching conditions on phase compositions of the samples have been investigated by X-ray diffraction and Mössbauer spectroscopy. The results show that the combustion of  $\text{Fe}_2\text{O}_3$ ,  $\text{MnO}_2$  and Fe results in a series of mixtures of new phases, which convert to  $\text{MnFe}_2\text{O}_4$  single spinel phase during subsequent heat treatment at 1200 °C for 2 h and rapid quenching. Moreover, combustion synthesis of  $\text{MnFe}_2\text{O}_4$  can efficiently induce a redistribution of divalent and trivalent ions in the A and B sites.

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**Keywords:** Mn ferrite; Heat treatment; X-ray diffraction; Mössbauer spectroscopy

## 1. Introduction

Spinel ferrites, often exhibit technically important electrical and magnetic properties, are well known for their specialized applications. Manganese ferrite,  $\text{MnFe}_2\text{O}_4$ , has a mixed spinel structure consisting of, divalent ( $\text{Mn}^{2+}$ ) and trivalent ( $\text{Fe}^{3+}$ ) ions occupying both tetrahedral (A) and octahedral (B) sites. The cation distribution in  $\text{MnFe}_2\text{O}_4$  ferrites is given by  $(\text{Mn}^{2+}_{1-\delta}\text{Fe}^{3+}_{\delta})_A[\text{Mn}^{2+}_{\delta}\text{Fe}^{3+}_{2-\delta}]_B\text{O}_4^{2-}$ , where inversion parameter  $\delta$  is 0.2 and indicates the degree of inversion. Recently, it has been demonstrated that combustion synthesis of ferrites can produce metastable phases and such combustion synthesized ferrites possess high sintering activity [1,2]. In this work, an attempt was made to prepare  $\text{MnFe}_2\text{O}_4$  ferrite using combustion synthesis method. The phase transformation during the combustion synthesis of Mn ferrite and subsequent heat treatment was also reported by using XRD and Mössbauer spectra.

## 2. Experimental

The materials used in the experiments were Fe,  $\text{MnO}_2$  powders, with the average particle size of 25, 0.8 and

1  $\mu\text{m}$ , respectively. The purity of the raw materials is more than 99%. The starting materials were weighed according to the required stoichiometric proportion, mixed in ethanol followed by ball-milling for 8 h and then dried in air. The mixture of powders was packed in a quartz container. A tungsten wire was used to initiate the reaction and the experiments were carried out in a water-cooled tube. Within a few seconds, the combustion reaction was completed with the resultant products filling in the container, which were then milled and  $\text{MnFe}_2\text{O}_4$  powders were obtained. The structure of the combustion synthesis (CS) reactor has been reported in a previous paper [3].

To study the influences of annealing temperature and quenching conditions on phase compositions, the as-synthesized samples were annealed at 1100 and 1200 °C for 2 h and subsequently quenched in three different ways: the first batch of the samples was rapidly quenched in air, the second was rapidly quenched in water and the third was slowly quenched in air by switching off the power supply of the furnace. The details of annealing conditions are listed in Table 1.

Phase compositions of the samples were investigated by X-ray diffraction analysis (XRD) (Rigaku D/max-rB). The Mössbauer spectra of the samples were recorded at room temperature using a constant acceleration Mössbauer spectrometer (Oxford MS-500, UK).

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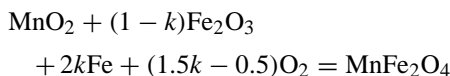
Table 1  
Samples preparation conditions

Sample no.	Heat treatment temperature (°C)	Quenching conditions
S11	1100	Rapid quenching in water
S12	1100	Rapid quenching in air
S13	1100	Slow quenching in air by switching off the power supply of the furnace
S21	1200	Rapid quenching in water
S22	1200	Rapid quenching in air
S23	1200	Slow quenching in air by switching off the power supply of the furnace

### 3. Results and discussions

#### 3.1. XRD analysis of the combustion products

MnFe<sub>2</sub>O<sub>4</sub> powder samples were prepared according to the following reaction:



where  $k$  is the coefficient which controls the exothermicity of the mixture. The larger the  $k$  value, the higher the molar ratio of Fe:Fe<sub>2</sub>O<sub>3</sub> in the reactants should be. The combustion temperature and combustion wave velocity increase with the increase of both  $k$  value and oxygen pressure. Such results are in agreement with earlier work [3].

Phase transformation of all as-synthesized and heat-treated samples are determined by X-ray diffractions. Fig. 1 shows the XRD patterns of as-synthesized samples at different oxygen pressures when  $k$  value is fixed at 0.65. The XRD curves suggest that the samples were not well crystallized, being composed of the spinel crystalline phase and

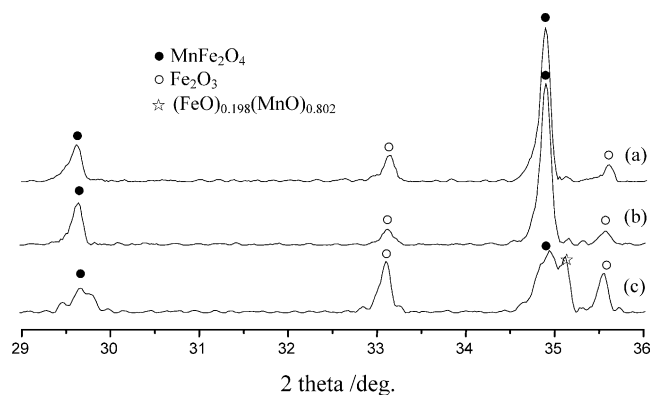
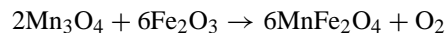
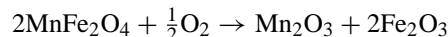


Fig. 2. X-ray diffraction patterns of the samples heat-treated at 1100 °C for 2 h and quenched in different conditions: (a) S11, (b) S12 and (c) S13.

secondary phases. At low oxygen pressure, as shown in Fig. 1(a)–(c), secondary phases, Mn<sub>2</sub>O<sub>3</sub>, Mn<sub>3</sub>O<sub>4</sub> and Fe<sub>2</sub>O<sub>3</sub> were found. As the oxygen pressure is increased, the peak intensities corresponding to Mn<sub>3</sub>O<sub>4</sub> gradually decrease, while those related to Mn<sub>2</sub>O<sub>3</sub> phase have not changed considerably and those related to MnFe<sub>2</sub>O<sub>4</sub> spinel phase increase. This is due to the fact that as the oxygen pressure rises, Mn<sub>3</sub>O<sub>4</sub> gradually changes to MnFe<sub>2</sub>O<sub>4</sub> and disappears completely at 1.4 MPa, which is according to the following reaction:



However, secondary phases, Mn<sub>2</sub>O<sub>3</sub> and Fe<sub>2</sub>O<sub>3</sub> exist in all samples. A possible explanation is that manganese ferrite is unstable when cooling in air, as it starts to decompose according to the following reaction:



The XRD patterns indicate that the spinel phase, which usually forms at high temperatures in conventional

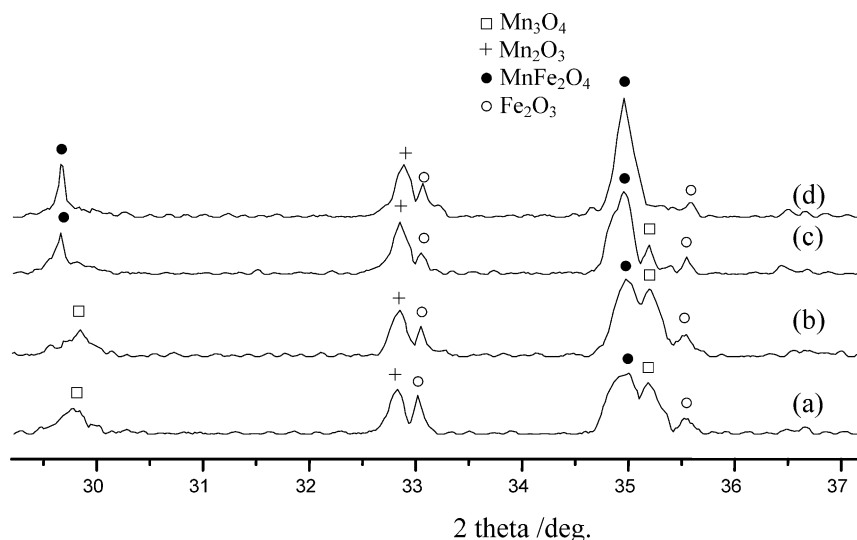


Fig. 1. XRD patterns of the products synthesized under different oxygen pressures ( $k = 0.65$ ): (a)  $p = 0.5$  MPa; (b)  $p = 0.8$  MPa; (c)  $p = 1.2$  MPa; (d)  $p = 1.4$  MPa.

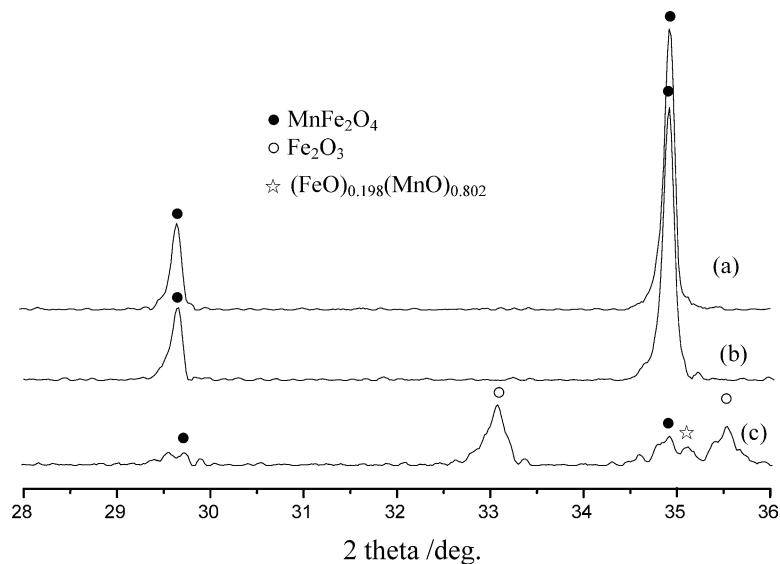


Fig. 3. X-ray diffraction patterns of the samples heat-treated at 1200 °C for 2 h and quenched in different conditions: (a) S21, (b) S22 and (c) S23.

method [4], has partially been formed during combustion synthesis.

Fig. 2 shows XRD patterns of the samples after heat-treated at 1100 °C for 2 h and subsequently quenched in different conditions. The XRD patterns of samples rapidly quenched in water (Fig. 2(a)) are similar to that of rapidly quenched in air (Fig. 2(b)). The phase compositions can be indexed as  $\text{MnFe}_2\text{O}_4$  as major phase and the only secondary phase present is  $\text{Fe}_2\text{O}_3$ . While for the

samples being slowly quenched (Fig. 2(c)), besides peaks of  $\text{MnFe}_2\text{O}_4$  and  $\text{Fe}_2\text{O}_3$  phases, a small peak at 35.2° fitted to  $(\text{FeO})_{0.198}(\text{MnO})_{0.802}$  phase is detected, evidently due to the reaction during annealing. It is obviously that the peaks related to  $\text{Mn}_2\text{O}_3$  disappear after heat treatment.

Fig. 3 shows XRD patterns of the samples after heat treatment at 1200 °C for 2 h and subsequent quenching in different conditions. A comparison of the XRD spectra of samples after annealing at 1200 °C and those of the samples

Table 2  
Mössbauer parameters of as-synthesized sample and heat-treated samples at different conditions

Sample	Assigned subspectrum	IS ( $\text{mm s}^{-1}$ )	QS ( $\text{mm s}^{-1}$ )	Hin KOe	Fe	Absorption area ratio, $s_B/s_A$
S1	$\text{MnFe}_2\text{O}_4$ A	0.29	−0.02	475.1	31.4	1.27
	$\text{MnFe}_2\text{O}_4$ B	0.38	0.01	429.3	40.0	
	$\text{Fe}_2\text{O}_3$	0.38	0.20	511.6	17.0	
	$\text{FeMnO}_3$	0.38	0.91		11.6	
S11	$\text{MnFe}_2\text{O}_4$ A	0.40	−0.08	434.9	41.2	0.77
	$\text{MnFe}_2\text{O}_4$ B	0.40	0.01	408.1	31.8	
	$\text{Fe}_2\text{O}_3$	0.37	0.22	511.4	27.0	
S12	$\text{MnFe}_2\text{O}_4$ A	0.32	−0.06	459.7	28.2	1.93
	$\text{MnFe}_2\text{O}_4$ B	0.40	−0.03	418.1	54.5	
	$\text{Fe}_2\text{O}_3$	0.37	0.22	512.6	17.3	
S13	$\text{MnFe}_2\text{O}_4$ A	0.31	−0.04	460.7	24.0	1.46
	$\text{MnFe}_2\text{O}_4$ B	0.39	−0.02	403.3	35.0	
	$\text{Fe}_2\text{O}_3$	0.37	0.20	511.8	41.0	
S21	$\text{MnFe}_2\text{O}_4$ A	0.38	−0.14	456.5	35.7	1.80
	$\text{MnFe}_2\text{O}_4$ B	0.40	0.01	427.9	64.3	
S22	$\text{MnFe}_2\text{O}_4$ A	0.34	−0.09	461.9	33.1	2.02
	$\text{MnFe}_2\text{O}_4$ B	0.40	−0.04	426.8	66.9	
S23	$\text{MnFe}_2\text{O}_4$ A	0.34	−0.18	435.1	24.0	0.55
	$\text{MnFe}_2\text{O}_4$ B	0.44	0.00	383.1	13.2	
	$\text{Fe}_2\text{O}_3$	0.37	0.17	512.4	62.8	

after annealing at 1100 °C shows that, after heat treatment at 1200 °C and rapid quenching, the peaks corresponding to Fe<sub>2</sub>O<sub>3</sub> completely disappear and the samples have a single spinel structure, as exhibited in Fig. 3(a) and (b). While the XRD spectra of the sample after heat treatment at 1200 °C and slow quenching (Fig. 3(c)) are almost the same as those of treated at 1100 °C (Fig. 2(c)).

### 3.2. Mössbauer spectra of the samples

The room temperature Mössbauer spectra of as-synthesized samples and heat-treated samples are shown in Fig. 4. In Fig. 4(a), the spectrum of as-synthesized sample is fit-

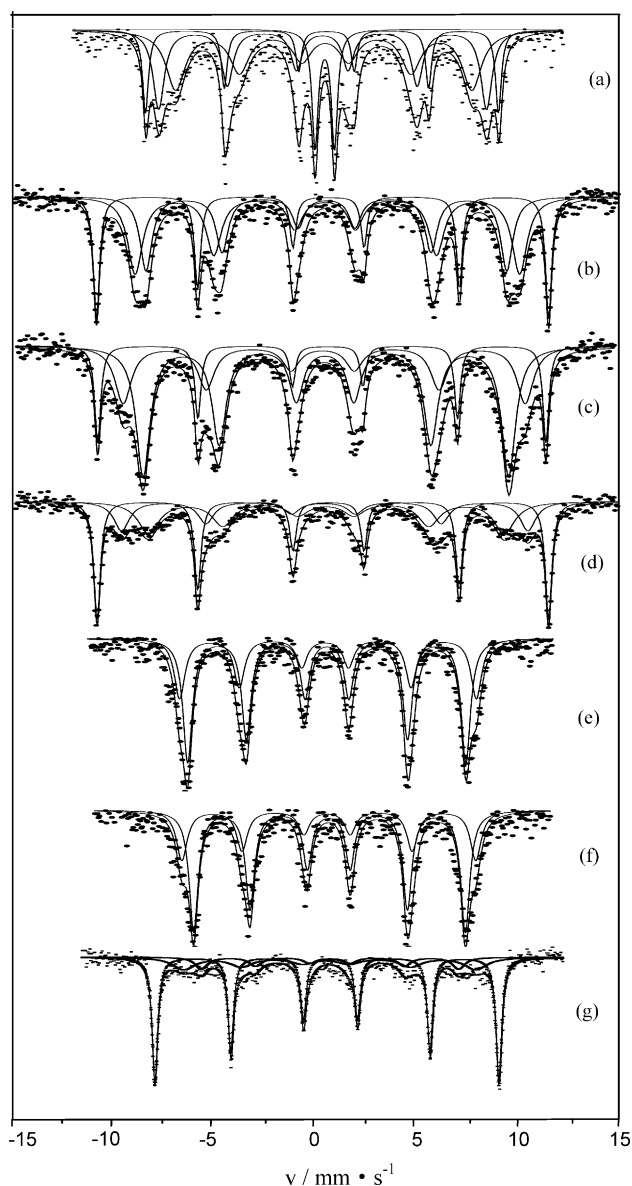


Fig. 4. Mössbauer spectra of as-synthesized samples and heat-treated samples at room temperature: (a) as-synthesized sample, (b) S11, (c) S12, (d) S13, (e) S21, (f) S22 and (g) S23.

ted with three sextets and a large absorption of a doublet with very small magnetically split patterns. Two of the sextets are assigned to the Fe<sup>3+</sup> ions in tetrahedral (A) and octahedral (B) sites of a typical spinel crystal structure. Third sextet is attributed to Fe<sub>2</sub>O<sub>3</sub> and the doublet is attributed to FeMnO<sub>3</sub>. For XRD patterns of the samples, the diffraction peaks corresponding to FeMnO<sub>3</sub> phase are not observed. This can be attributed to the overlap of the peak of Fe<sub>2</sub>O<sub>3</sub> at 33.15° and that of FeMnO<sub>3</sub> at 33.11°. The parameters of Mössbauer spectra are listed in Table 2.

Information on the cation distribution can be obtained from the area ratio of the A and B sites in Mössbauer spectra [5]. The  $s_B/s_A$  area ratio of the two sextets obtained from Table 2 for as-synthesized MnFe<sub>2</sub>O<sub>4</sub> is 1.27, which is significantly smaller than the area ratio of the stoichiometric MnFe<sub>2</sub>O<sub>4</sub>. The changes in the absorption area ratio indicate that Fe<sup>3+</sup> ions concentration of the tetrahedral sites is lower. Since the combustion process proceeds in the oxygen atmosphere, one would therefore expect that the as-synthesized MnFe<sub>2</sub>O<sub>4</sub> contains a considerable amount of Mn(III) and Fe(III). Mn(III) cation would preferentially occupy the octahedral sites in the spinel structure [6], which lead to a larger fraction of Fe(III) on tetrahedral sites and a amount of cation vacancies which mainly distribute in the octahedral sites compared with that in stoichiometric MnFe<sub>2</sub>O<sub>4</sub>. Consequently, the combustion process results in the formation of manganese ferrites characterized by varying cation oxidation and distribution.

Fig. 4(b)–(d) shows the Mössbauer spectra of samples heat-treated at 1100 °C. The spectra are almost the same which all consist of three sextets of the magnetically split pattern. Besides one sextet assigned to Fe<sub>2</sub>O<sub>3</sub>, the other two sextets are attributed to A and B sites of MnFe<sub>2</sub>O<sub>4</sub>, respectively. Compared with the spectrum of as-synthesized MnFe<sub>2</sub>O<sub>4</sub> (Fig. 4(a)), the paramagnetic doublet is not found which indicates that the FeMnO<sub>3</sub> phase disappears after heat treatment.

Analysis of the Mössbauer spectra for the heat-treated samples indicates that the percent of Fe atoms in Fe<sub>2</sub>O<sub>3</sub> is increased compared with that of as-synthesized samples, as shown in Table 1. This is due to the decomposition of MnFe<sub>2</sub>O<sub>4</sub> during annealing.

Fig. 4(e)–(g) shows the Mössbauer spectra of heat-treated samples at 1200 °C. The spectrum of the samples after rapidly quenched in water is fitted with two sextets assigned to A and B sites of MnFe<sub>2</sub>O<sub>4</sub>, as shown in Fig. 4(e). The samples after rapidly quenched in air also exhibit similar Mössbauer spectrum (Fig. 4(f)). This indicates that after heat treatment at 1200 °C and rapidly quenching, magnetic sextet assigned to Fe<sub>2</sub>O<sub>3</sub> disappears. Such result is consistent with that of XRD. However, the Fe<sup>3+</sup> ions fraction on tetrahedral sites is significantly larger (35.7 or 33.1%) than the stoichiometric MnFe<sub>2</sub>O<sub>4</sub> due to preferentially occupation of Mn(III) on octahedral sites. For the Mössbauer

spectrum of the samples after slowly quenching (Fig. 4(g)), the sextet related to  $\text{Fe}_2\text{O}_3$  still exists. The differences in phase compositions for the samples with different heat treatment indicate that the phase formation is dependent of the annealing conditions.

#### 4. Conclusions

We have prepared  $\text{MnFe}_2\text{O}_4$  ferrite powders by combustion synthesis method. It is found that the combustion of  $\text{Fe}_2\text{O}_3$ ,  $\text{MnO}_2$  and Fe results in a series of mixtures of new phases, which convert to  $\text{MnFe}_2\text{O}_4$  single spinel phase during subsequent heat treatment at  $1200^\circ\text{C}$  and rapid quenching. XRD and Mössbauer spectroscopy are used to discuss the phase formation during different preparation stages. The results also show that combustion synthesis of  $\text{MnFe}_2\text{O}_4$  can efficiently induce a redistribution of divalent and trivalent ions in the A and B sites.

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#### References

- [1] P.B. Avakyan, E.L. Nersisyan, M.D. Nersesyan, *Int. J. SHS* 4 (1995) 79–83.
- [2] Y. Li, J.P. Zhao, J.X. Jiang, *Mater. Res. Bull.* 38 (8) (2003) 1393–1399.
- [3] Y. Li, J.P. Zhao, J.C. Han, *Bull. Mater. Sci.* 25 (2002) 263–266.
- [4] A.T. Jenifer, T. Steven, A. Rosen, *Am. Ceram. Soc. Bull.* 74 (4) (1995) 91–94.
- [5] M.H. Mahmoud, H. Hamdeh, A.I. Abdel-Mageed, *Physica B* 291 (2000) 49–53.
- [6] G. Bonsdorf, M.A. Denecke, K. Schäfer, *Solid State Ionics* 101 (1997) 351–357.