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Crystal and microstructure of MnFe$_2$O$_4$ synthesized by ceramic method using manganese ore and iron sand as raw materials

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Abstract. We have succeeded to synthesize the octahedral micro shape of MnFe$_2$O$_4$ through the co-precipitation process followed by a ceramic processing method. At the beginning, the Mn$_3$O$_4$ and Fe$_2$O$_3$ nanoparticles were separately synthesized by the co-precipitation method from the low grade manganese ore and iron sand, respectively. Here, effect of the weight ratio of Fe$_2$O$_3$ and Mn$_3$O$_4$ to the crystal and microstructure of MnFe$_2$O$_4$ were investigated. Four cases of weight ratio i.e. 60:40, 70:30, 80:20, and 90:10 were considered. After mixing and compaction process in the cylindrical mould shape, the samples were sintered at 1000 °C and for 6 hours. XRD data showed that a high quality crystal phase of MnFe$_2$O$_4$ can be obtained for both mass ratio of 60:40 and 70:30, while in the case of 80:20 and 90:10 the MnFe$_2$O$_4$ appear together with impurity of Fe$_2$O$_3$. The particle shapes are almost octahedral in the micrometer size in the range of 1.2 to 1.5 m. The magnetic property shows a soft-magnetic type with a 27.5 emu/g of saturated magnetization. This will be potential for applications as the electrode materials and the magnetic core.

1. Introduction

Manganese ferrite is one of the spinel ferrite which is widely used for various applications, including storage media, absorbing electromagnetic waves, catalysts, and water treatment [1-4]. It has MnFe$_2$O$_4$ structure where the ionic distribution of spinel is often written as (Mn$_{1-x}$Fe$_x$)$_2$[Mn$_x$Fe$_{2-x}$]O$_4$, with the elements in the parentheses and the square brackets lodge in the tetrahedral and the octahedral sites formed by the oxygen ions, respectively [5]. Here, the degree of inversion x is ranging from 0 to 1 [6]. The properties of manganese ferrite can be adjusted depend on the composition, morphology, and size, which are strongly related to the synthesis parameters [7]. Several methods have been developed to synthesize MnFe$_2$O$_4$ nanoparticles, such as solid-phase reactions [8, 9], mechanical ball-milling [10], salvothermal [11], hydrothermal [12], coprecipitation [13], combustion [14], and microemulsion method [15].
Increasing demand on the alternative energy triggers the development of energy storage technologies and efficient energy transformation systems. Manganese ferrite as a low-loss soft magnet has widely used as a magnetic core of high frequency transformers and efficient high power switching. It can also be used as an energy storage material. Then, the production process of manganese ferrite from natural resources becomes an attractive theme of research. For example, MnFe$_2$O$_4$ has been synthesized by co-precipitation method from low grade manganese ore and iron steel making waste [16]. Recently, MnFe$_2$O$_4$ was being synthesized by similar method combining the iron sand and MnCl$_2$·4H$_2$O as Fe and Mn sources, respectively [17].

In this paper we firstly extract separately Fe$_2$O$_3$ and Mn$_3$O$_4$ nanoparticles using the co-precipitation method from iron sand and manganese ore, respectively. Then, the MnFe$_2$O$_4$ was produced by the ceramic method from the mixed fine powder of Fe$_2$O$_3$ and Mn$_3$O$_4$.

2. Experimental sections

2.1 Synthesis of Fe$_2$O$_3$ nanoparticles
The typical procedure can be found in [18]. After separation of iron powders from iron sands and cleaning process from any impurities with distilled water and acetone, respectively, then iron powders were dried in an oven at 60 °C for 24 hours. The 20 gr of iron powder was dissolved in 12 M 50 ml HCl at a constant temperature of ~60 °C and under stirring condition. Then solution was filtered and transferred to the three necks round bottom flask. The precipitating solution, 6M NH$_4$OH, was prepared and added drop-wise to the previous solution. The temperature was kept at ~60 °C. Just after mixing solution, colour changed from light brown to brown as an indicator of the precipitation process was took place. Stirring process was still continued for 6 minutes. The reaction pH was adjusted to be 10 at the final stage. After centrifugation and washing processes, the as-synthesized products were dried at temperature of 60 °C and for 24 hour. Finally, to ensure the formation of /gamma/-Fe$_2$O$_3$, the product was calcined in atmospheric condition for 1 h and at temperature of 500 °C.

2.2 Synthesis of Mn$_3$O$_4$ nanoparticles
The procedure was quite similar to Section 2.1. The manganese ore was firstly grinded to pass through 200 mesh sieve. After cleaning processes, the manganese powder was dried in an oven at 60 °C for 24 hours. A typical 20 g of manganese ore was, then, dissolved in 12 M 50 ml HCl at a constant temperature ~60 °C and under stirring condition. Then the solution was filtered and transferred to the three necks round bottom flask. The precipitating solution, 6M NH$_4$OH, was prepared and added drop wise to the previous solution until the pH reaches ~10. The precipitated solution was centrifuged, washed, and dried for 24 h at temperature of 60 °C. Finally, the as synthesized powder were collected and to be characterized.

2.3 Synthesis of MnFe$_2$O$_4$ micro particles
The homogenous mixture of Fe$_2$O$_3$ and Mn$_3$O$_4$ nanoparticles at different mass ratio i.e. 60:40, 70:30, 80:20, and 90:10 were mounted on the cylindrical shape mould and subsequently pressed. The polyvinyl alcohol was used as an adhesive agent. After a pre-sintering condition at 800 °C for 30 minutes, samples were sintered at temperature of 1000 °C for 8 hours.

2.4 Characterization
The synthesized particles were identified by means of X-ray diffraction (XRD) with a Rigaku Smartlab X-ray diffractometer with Cu Ka radiation ($\lambda = 1.540598$ Å) at a scan rate of 0.017/s. The morphologies of the as-prepared products were characterized by a TESCAN S8000. Magnetic measurements were carried out with vibrating sample magnetometer (VSM) Oxford 1.2H type.
3. Results and Discussions

Mn$_3$O$_4$ and $\gamma$-Fe$_2$O$_3$ nanoparticles were successfully synthesized with high purity which can be seen through the XRD data shown in Figure 1. Figure 1(a) shows that the diffraction peaks matches to the JCPDS card no. 24-0734 belongs to the tetragonal structure of hausmanite (Mn$_3$O$_4$) with the space group of $I41/amd$. The highest peak is found at an angle of 36.15° for the Miller index of (3 1 1). The average crystal diameter was calculated from diffraction plane of (3 1 1) using the well-known Scherrer formula

$$D = \frac{k\lambda}{\beta \cos \theta}$$

(1)

where $\lambda$, $\beta$, and $\theta$ are wavelength, full width half maximum, and diffraction angle of a specific diffraction peak. Here the constant parameter $k$ is 0.89. It gives $D = 34.55$ nm. The cell parameters are $a = 5.7621$ Å and $c = 9.4696$ Å. The SEM image of Mn$_3$O$_4$ is shown in Figure 2(a). The particles tend to cluster in larger sizes.

Figure 1(b) shows the XRD data of the as-synthesized particles from the iron sand which matches to JCPDS card no. 39-1346 namely the maghemite ($\gamma$-Fe$_2$O$_3$) with cubic structure ($a = 8.3515$ Å) and space group of $P4_132$. The highest peak is belonging to diffraction plane of (311). The crystal diameter is 18.31 nm. The SEM image is shown in Figure 2(b). It is clear that the particle size is in the nano scale range.

![Figure 1. XRD spectra of (a) Mn$_3$O$_4$ and (b) $\gamma$-Fe$_2$O$_3$ nanoparticles](image1)

![Figure 2. SEM image of (a) Mn$_3$O$_4$ and (b) $\gamma$-Fe$_2$O$_3$](image2)
Figure 3. XRD peaks of the as-prepared samples after sintering at 1000 °C and 6 h.

Figure 3 shows XRD peaks of samples with different compositions of Mn3O4 and Fe2O3 i.e. 60:40, 70:30, 80:20, and 90:10, respectively. The high purity MnFe2O4 was achieved when the compositions are both 60:40 and 70:30. All the diffraction peaks for both cases can be perfectly indexed to the (2 2 0), (3 1 1), (2 2 2), (4 0 0), (4 2 2), (5 1 1), and (4 4 0) diffraction planes of the MnFe2O4 phase, which were consistent with the standard values in JCPDS card no. 10-0319 as the face-centered cubic structure of jacobsite ferrite. It belongs to a space group of Fd-3m with cell parameter \( a = 8.499 \) Å. It should be noted here that the Fe2O3-Mn3O4 weight ratio of 60:40, 70:30, 80:20, and 90:10 correspond to the molar ratio of Fe2O3-Mn3O4 i.e. 2.2:1, 3.3:1, 5.7:1, and 12.9:1, respectively. The molar ratio for formation of MnFe2O4 is 3:1 according to the following chemical reaction

\[
\frac{1}{3} \text{Mn}_3\text{O}_4 + \text{Fe}_2\text{O}_3 + \frac{1}{6} \text{O}_2 \rightarrow \text{MnFe}_2\text{O}_4
\]

However, when the molar ratio of Fe2O3 exceeds 3, parts of it did not take part in the reaction with Mn3O4 remaining in a stable phase. It shows existence of additional diffraction peaks except MnFe2O4 in Figure 3. Those peaks match to the JCPDS card no 24-0072 or hematite (\( \alpha \)-Fe2O3) and can be indexed to (0 1 2), (1 0 4), (1 1 3), (0 2 4), (1 1 6), and (3 0 0) facets, respectively. The hematite is the stable phase of iron oxide formed at high temperature [19]. If Fe3O4 is exposed to temperature, at the beginning when temperature is ranging from 150 to 650 °C, Fe3O4 change to be \( \gamma \)-Fe2O3 as a meta-stable phase of iron oxide. Then, at higher temperature, a transformation from \( \gamma \)-Fe2O3 to \( \alpha \)-Fe2O3 as the stable phase of iron oxide was took place. The minor diffraction peaks of \( \alpha \)-Fe2O3 were considered as the impurity along with the main product MnFe2O4

Table 1. Summary of calculated parameter from XRD data

| Weight ratio (%) | MnFe2O4 |
|------------------|--------|
| Fe2O3 | Mn3O4 | Purity (%) | Diameter (nm) |
| 60 | 40 | 100.0 | 37.70 |
| 70 | 30 | 100.0 | 39.95 |
| 80 | 20 | 90.2 | 44.41 |
| 90 | 10 | 82.8 | 46.69 |
Figure 4. SEM images and its corresponding particle size distributions for different weight ratio (a,d) 60:40, (b,e) 70:30, and (c,f) 90:10.

The purity level of MnFe$_2$O$_4$ decreases to be 90.2% and 82.8% for the case of weight ratio of 80:20 90:10, respectively. Here, the purity level was calculated from

$$p(\%) = \frac{I_M}{I_M + I_F} \times 100\% \quad (3)$$

where $I_M$ and $I_F$ are total intensity of intended phase and the impurity, respectively. The crystal diameter of MnFe$_2$O$_4$ tends to grow from 37.70 nm to 46.68 nm as the content of Fe$_2$O$_3$ in the sample increases. The diameter of impurity agent, $\alpha$-Fe$_2$O$_3$, has also the tendency to increase from 52.34 nm to 70.03 nm as the abundance of Fe increases from 80% to 90%. It should be noted here that the calculation of crystal size did not take into account the peak broadening and other effects may include in XRD data. All extracted parameters based on the XRD data are listed in Table 1

Figure 4(a-c) shows SEM image of samples with composition of 60:40, 70:30, and 90:10. The non uniform particle distributions are shown in Figure 4(c-e). Particles shapes are the octahedron with non uniform size distribution. In all cases the dominant particle sizes are 1.2-1.5 $\mu$m. Formation of the octahedral shape of MnFe$_2$O$_4$ can be found many reports with different synthesis method [11, 20]. In [11] formation of octahedral shape was attributed to the dosage effect of surfactant (cetyltrimethylammonium bromide or CTAB) on the synthesis process by salvothermal method. Addition of CTAB in the process makes the $\text{--(NCH$_3$)$_3$}$ can be absorbed by the specific (1 0 0) facets which are then stabilized and growing slowly; hence, the growth of other facets will gradually diminish. The octahedral shape becomes a stable phase of MnFe$_2$O$_4$. A rather similar method was in the work of [20]. They use Fe(NO$_3$)$_3$$\cdot$9H$_2$O and MnSO$_4$ in the co-precipitation process and then followed by sintering at 900 – 1200 $^\circ$C. The octahedral shape of pure MnFe$_2$O$_4$ appears at temperature of 1100 $^\circ$C. Formation of octahedral shape was influenced by the presence of anhydrous ethanol. The [Fe(H$_2$O)$_6$]$^+$ molecules were adsorbed by anhydrous ethanol, which can reduce the growth speed of (1 1 1) facets. The growth speed of (1 0 0), (0 1 0) and (0 0 1) facets were equal and the final ratio of (1 0 0) to (1 1 1) was 1.73.
In our work the polyvinyl alcohol was used as an adhesive agent in compaction stage of Mn3O4-Fe2O3 mixture. The –OH functional group in PVA may play an important role in the formation of the octahedral shape. The high concentration of hydroxide can easily absorb onto (1 1 1) planes are then stabilized and grow slowly; hence, the growth of other planes will gradually diminish. Similar phenomena of –OH site can favourite formation of octahedral shape can be found in [4, 21].

Hysteresis shape of magnetization for sample with ratio 70:30 was shown in Figure 5. The insert shows magnified views of the hysteresis loop at low applied fields. The saturated magnetization (\(M_S\)), coercivity field (\(H_C\)) and remanent magnetization (\(M_r\)) are 27.5 emu/g, 135 Oe, and 1.33 emu/g, respectively.

![Hysteresis curve of MnFe2O4](image)

**Figure 5.** Hysteresis curve of MnFe2O4

4. Conclusion
The high purity octahedral micrometer size of MnFe2O4 has been synthesized by ceramic method from manganese ore and iron sand. High purity MnFe2O4 phases are achieved when the weight ratio of Fe2O3 to Mn3O4 is 60:40 and 70:30. Those conditions are in the vicinity of the molar ratio 1:3 as the stoichiometrical condition. The \(\alpha\)-Fe2O3 as a stable phase of Fe2O3 appears as the impurity together with MnFe2O4 with purity level up to 82.8%. The dominant particle size is ranging from 1.2 to 1.5 μm. The magnetic property shows a typical soft magnetic case with the value of saturated magnetization \(~27.5\) emu/g. This research demonstrates utilization of ceramic method to produce manganese ferrite in a regular orthogonal form using the Fe2O3 and Mn3O4 which are synthesized directly from iron sand and low grade manganese as the raw materials.

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