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Short communication

A new method for the identification and quantification of magnetite–maghemite mixture using conventional X-ray diffraction technique

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ABSTRACT

The electrical explosion of Fe wire in air produced nanoparticles containing the binary mixture of magnetite (Fe_3O_4) and maghemite (γ-Fe_2O_3). The phase identification of magnetite and maghemite by the conventional X-ray diffraction method is not a simple matter because both have the same cubic structure and their lattice parameters are almost identical. Here, we propose a convenient method to assess the presence of magnetite–maghemite mixture and to further quantify its phase composition using the conventional peak deconvolution technique. A careful step scan around the high-angle peaks as (5 1 1) and (4 4 0) revealed the clear doublets indicative of the mixture phases. The quantitative analysis of the mixture phase was carried out by constructing a calibration curve using the pure magnetite and maghemite powders commercially available. The correlation coefficients, R^2, for magnetite–maghemite mixture was 0.9941. According to the method, the iron oxide nanoparticles prepared by the wire explosion in this study was calculated to contain 55.8 wt.% maghemite and 44.2 wt.% magnetite. We believe that the proposed method would be a convenient tool for the study of the magnetite–maghemite mixture which otherwise requires highly sophisticated equipments and techniques.

1. Introduction

X-ray diffraction technique has been an indispensable tool for the identification and characterization of various iron oxide phases. Nevertheless, the identification of magnetite ($Fe(II)Fe(III)_2O_4$) and maghemite (γ-$Fe(III)_2O_3$) phases by X-ray diffraction is quite intricate, because both phases possess the same spinel structure and almost identical lattice parameters.

In many previous studies, iron oxide particles have been successfully synthesized through various methods and indexed to maghemite or magnetite based on the fact that its lattice parameter was more close to one of the both phases [1–8]. Nevertheless, more researchers employed various supplementary analytical techniques in order to substantiate the identification of their iron oxides: wet chemical analysis [9–13], Mössbauer spectrometry [10,11,14–20], Raman spectroscopy [16,21,22], Fourier Transform Infrared (FT-IR) spectrophotometry [17,21,23–27], X-ray Photoelectron Spectroscopy (XPS) [16,28,29], Field Emission Transmission Microscopy with Selected Area Diffraction (FE-TEM/SAD) [4,16,18,27,30–36]. It appears that these techniques were very successful for this purpose especially when the sample was a single phase magnetite or maghemite.

Mössbauer spectrometry has been considered to be the most suitable technique, because the magnetite spectra consist of two discrete sextets [10,11,17–20]. Even though Mössbauer spectroscopy can provide most reliable quantitative data, it often suffers from the difficulties in fitting the complicated spectra [17,37]. Furthermore, the differentiation between non-stoichiometric magnetite and magnetite–maghemite mixture was claimed to be almost impossible [38,39]. The quantification of Fe(II) and Fe(III) has been widely attempted by the traditional wet-chemical method, though an extreme care should be practiced to prevent the oxidation of magnetite during the measurement routine [11]. XPS is a surface-sensitive analytical tool providing little information on the bulk properties. For example, the preferential oxidation on the surface of magnetite to maghemite was successfully analyzed using XPS [28,29]. A simple FT-IR has also been adopted for the quantification of iron-oxide mixture phase using a calibration curve with relatively low coefficient of determination of R^2 [25].

As stated above, numerous analytical techniques have been utilized to differentiate the magnetite and maghemite powders produced by various methods. Nevertheless, to the best knowledge of the authors, the quantitative analysis of magnetite–maghemite

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Table 1
Iron oxide powders synthesized by the wire explosion in this study and the commercial powders used to prepare the standard mixture samples of known compositions.

Sample	Maker	Particle size	Lattice parameter (Å)
Iron oxide	This study	33.8 ± 20.6 nm	8.3763 ± 0.006
Magnetite (Fe_3O_4)	Sigma–Aldrich no.310069	1 μm	8.396 (JCPDS 19-629)
Maghemite (γ-Fe_2O_3)	Sigma–Aldrich no. 544884	<50 nm	8.3515 (JCPDS 39-1346)

mixture by the X-ray diffraction method has never been attempted. The iron oxide powders produced by the wire explosion in this study appeared to contain both phases. Therefore, in the course of the study on this subject, we could elaborate a simple way to verify the existence of the magnetite–maghemite mixture and to further quantify their relative compositions. For the quantification of the mixture, a calibration curve was constructed from the standard mixtures of known compositions using the commercial magnetite and maghemite powders.

2. Experimental procedure

2.1. Electrical explosion

The explosion device consists of a high voltage dc power supply, a bank of capacitors, a plasma switch and an explosion chamber. The plasma switch initiates the discharge. The capacitance of the exploding circuit was 3.5 μF and the applied voltage across the 20 mm-long wire was 11.4 kV. Therefore, the stored energy was about 227 J about 80–90% of which was considered to be transferred to the wire. The diameter of Fe wire for the explosion experiment was 0.3 mm. To begin with, the explosion chamber was evacuated and flushed with pure argon gas. The explosion experiment was conducted in a 30-l stainless chamber with the cover plate loosely tightened. The total number of explosions for each condition was about 600. After the explosion, the powders were filtered through a 125 μm sieve to remove some misfired portions. The morphology of the nanopowders were examined by FE-TEM (Field-Emission Transmission Electron Microscope, model JEM-2010F, JEOL Ltd., Japan).

2.2. X-ray diffraction

X-ray diffraction (XRD, D/MAX 2200, Rigaku Corp., Japan) study was conducted with Cu K_α radiation equipped with a graphite monochromator. A continuous scan XRD data were collected at diffraction angles between 20° and 80° operating at 40 mA and 40 kV. The step scan was conducted typically under the following conditions: 2θ range 56–58.5° for (5 1 1) peak and 61–64° for (4 4 0) peak; with the step width 0.01°; counting time of 10 s. The peak deconvolution and lattice parameter measurement were carried out using the MDI Jade 6.5 program furnished with the XRD. The data profiles were fit with a pseudo-Voigt profile function. TEM micrographs were analyzed for particle size measurement using a commercial image processing software (Image-Pro Plus 4.5.1). The particle size distribution was rather broad and the average particle size measured for more than 500 particles was 33.8 ± 20.6 nm.

2.3. Calibration curve

To quantify the binary mixture, the standard mixture samples were prepared by mixing the pure magnetite and maghemite powders commercially available. Table 1 shows the commercial powders used to make the mixture samples along with the powders synthesized in this study. The X-ray diffraction patterns from the magnetite and maghemite matched exactly to JCPDS 19-629 and JCPDS 39-1346, respectively. No other phases were observed. Six reference samples (0 wt.%, 20 wt.%, 40 wt.%, 60 wt.%, 80 wt.%, 100 wt.% maghemite) containing corresponding amounts of magnetite and maghemite powders were mixed as listed in Table 2. All step scan X-ray diffraction experiments were performed at least in triplicate, and the average values were used to construct the calibration curve.

Table 2
The standard mixture samples prepared by mixing the commercial maghemite and magnetite powders.

Samples	Composition
0%	Pure magnetite
20%	20 wt.% maghemite + 80 wt.% magnetite
40%	40 wt.% maghemite + 60 wt.% magnetite
60%	60 wt.% maghemite + 40 wt.% magnetite
80%	80 wt.% maghemite + 20 wt.% magnetite
100%	Pure maghemite

3. Results and discussion

3.1. X-ray diffraction study of the explosion products

Fig. 1 shows the X-ray diffraction pattern of nanoparticles synthesized by the wire explosion in this study. It shows a cubic structure which may be indexed to either magnetite or maghemite. No other peaks from other oxide phases as hematite or wüstite were noticed. As previously stated, the lattice parameters of the magnetite and maghemite phases are very close and difficult to be differentiated unless it is a single phase of well-crystallized structure. In this study, the lattice parameter calculated from the pattern in Fig. 1 was 8.3763 Å (see Table 1) which lies between that of magnetite and maghemite (8.396 Å and 8.3515 Å, see Table 1). Therefore, it was not possible for us to decide whether the reaction product is the magnetite or the maghemite. We supposed that it may be a mixture of both phases.

Supposedly, the maghemite phase is known to exhibit few extra peaks at 23.77° (2 1 0) and 26.10° (2 1 1) which may possibly be used to distinguish it from the magnetite phase. However, in reality, the intensities of these peaks are very weak (5%) for the positive

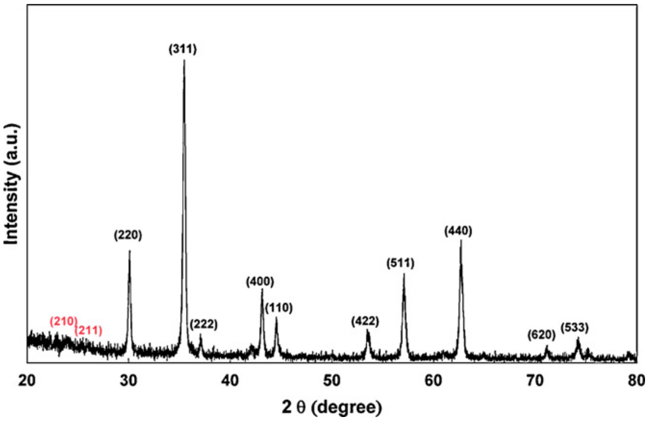

Fig. 1. X-ray diffraction pattern from the iron oxide nanoparticles produced by the explosion of Fe wire in air. Here, the peaks correspond to either magnetite or maghemite phase though the (2 1 0) and (2 1 1) peaks which are the characteristic peaks of the maghemite phase are not obvious.