Local structure examination of mineral-derived Fe$_2$O$_3$ powder by Fe K-edge EXAFS and XANES

H. Husain$^{1,2}$, B. Hariyanto$^1$, M. Sulthonul$^1$, P. Thamatkeng$^3$, S. Pratapa$^{1*}$

$^1$Department of Physics, Faculty of Natural Sciences, Institut Teknologi Sepuluh Nopember (ITS) Jl. Arief Rahman Hakim, Surabaya 60111 Indonesia
$^2$Department of Physics, Faculty of Mathematics and Natural Sciences, Universitas Negeri Makassar (UNM), Jl. A. Pangeran Pettarani, Makassar 90222 Indonesia
$^3$Synchrotron Light Research Institute (Public Organization), Nakhon Ratchasima, Thailand

E-mail: suminar_pratapa@physcs.its.ac.id

Abstract. Fe K-edge XANES (X-ray Absorption Near Edge Structure) and EXAFS (Extended X-ray Absorption Fine Structure) spectra have been used to investigate the local structures of hematite (Fe$_2$O$_3$) powders which were synthesized from local iron stone. The formation of hematite with various calcination temperature (500, 650, 800) °C was observed from XRD data of each powder, and Fe K-edge EXAFS and XANES were performed to sample with calcination temperature 800 °C. The XANES spectra confirmed the oxidation state of the powders. The energy position of the first pre-edge peak at (7113.5 ± 0.5) eV confirm Fe$^{3+}$. The absorption edges of Fe$_2$O$_3$ powders was 7123.41 eV. The first EXAFS data analysis showed that Fe$_2$O$_3$ powder exhibited nearest-neighbor distances $R_{Fe-O} = 1.56449$ Å and $R_{Fe-Fe} = 3.01449$ Å. The XRD lattice parameter values for the sample is in a fair agreement with the nearest-neighbor distances according to the EXAFS data.

Keywords. EXAFS, XANES, oxidation state, local structure, iron stone mineral, and Fe$_2$O$_3$.

1. Introduction

Applications of materials are determined by their characteristics. The characteristics of the materials depend on the internal structure. The internal structure consists of atoms and associates with neighboring atoms in crystals, molecules, and microstructures [1]. There are many tools for material analysis especially for structure studies such as x-ray diffraction (XRD) and x-ray absorption spectroscopy (XAS). XRD is usually used for crystal (phase) study, while XAS is utilized in the so-called “local structure” assessment. XAS can be divided into XANES (x-ray absorption near edge structure) and EXAFS (extended x-ray absorption fine structure). XANES covers the area of the spectrum which dominated by strong photoelectron scattering within a specific absorbing atom, while EXAFS comprises an area of weak photoelectron scattering of about 40 eV above the absorption edge value which can be correlated with neighboring atomic interactions. XANES is used for qualitative analysis, particularly the oxidation state of the absorbing atoms which makes it offers results that x-ray diffraction cannot yield [2]. Meanwhile, EXAFS uses quantitative analysis to obtain local information.

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structure, one being the distance between the nearest atoms. The structural data from EXAFS are believed more accurate than those from XRD [3].

XAS has been used for characterization Fe-based materials, such as BiFeO3, Bi2Fe4O9 and La2−xSrxFeO3 [4–5], with Fe2O3 (hematite) as one of the raw material. Usually, Fe2O3 was obtained from commercial materials. Meanwhile, the natural iron stone mineral has been used as a source of Fe compounds for the synthesis of iron oxide [6] but synthesized Fe2O3 from the mineral need a further investigation because the purity can not be granted only by using XRD measurements. This is because Fe atom tends to absorb Cu radiation [7]. Therefore, XAS was expected to confirm the formation of Fe2O3 from the mineral through the oxidation state and nearest-neighbor distances using XANES and EXAFS data analysis, respectively.

In this paper, we reported the structure characteristic of Fe2O3 which was synthesized from a local iron stone mineral. The characterization includes XRD for phase identification and lattice parameter determination and XANES and EXAFS to analyze the electronic and local structure. In addition, we compared the XANES spectra of our hematite sample and hematite model to investigate the quality of our sample.

2. Materials and methods

The Fe2O3 was synthesized from natural iron stone by using co-precipitation [6]. The synthesis followed several steps. Firstly, an iron stone (6 g) was dissolved in 80 mL HCl by stirring at 70 °C for 1 h. Then, the solution was filtered two times using a filter paper. Next, titration was performed by adding NH4OH in the solutions until pH = 5 was achieved. Then, the solution was washed several times. The precipitate was dried at 110°C using a hot plate for 7 hours. The powders were calcined at 500 °C, 650°C, and 800°C to achieve a pure Fe2O3.

The XRD patterns were collected using X-Ray diffractometer XPert MPD (\(\lambda_{CuK\alpha} = 1.54060 \text{ Å}\)) with step size 0.0170°, and generator set on 40 kV and 30 mA. The patterns were analyzed for phase identification and then subjected to the Rietica software for lattice parameter determination. Fe K-edge XANES and EXAFS spectra were recorded with X-Ray Absorption Spectroscopy (XAS) instrument at beam line 8 SLRI (Synchrotron Light Research Institute), Thailand. Fe K-edge spectra were recorded with 0.2 eV step size in fluorescence mode with silicon drift detector and fixed-exit double crystals X-ray monochromator. XANES and EXAFS spectra were analyzed by using Athena and Artemis software [8]. XANES was used for investigation of oxidation state. Meanwhile, EXAFS was used to determine the local structure parameters, i.e., distance between nearest atoms and average of structure irregularity (\(\sigma^2\)), were determined by fitting of radial structure function between EXAFS data from the sample and the model from Fe K-edge spectrum.

3. Results and discussion

The XRD patterns of the synthesized powders can be seen in Figure 1. The patterns reveal that pure phase of Fe2O3 has been formed (PDF No. 96-210-1169) with the strongest peak at 20 = 33° (Figure 1a, Figure 1b, Figure 1c). It is clear, however, that the quality of the data is rather poor as shown by the low “signal-to-noise” ratio since Fe atom tends to absorb Cu radiation [7]. This may give impact on the quality of the extracted data from the patterns after pattern-fitting analysis, e.g., using the Rietveld method.

Rietveld phase analyses using Rietica software revealed the structure data as shown in Table 1. The fitting between model and observed data (Figure 1) were acceptable as shown by GoF values which were less than 2 %. The quality of the data, however, is fair as shown by the \(R_w\) values which are larger than 15 % As a result of this quality, the lattice parameters of hematite in the samples are also fair. Table 1 shows the lattice parameter and cell volume of the synthesized hematite. The lattice parameters and cell volumes of hematite in all samples were relatively similar, but the sample with relatively large standard deviations. In general, the standard deviation of less than 1/50000 acceptable [9], but in our case, the values are only in the range of 1/10000 and 1/20000. Therefore, the XRD data quality gave a significant impact on the extracted lattice parameter values. Since these values are important for explaining the physical characteristics of the bulk samples, there is a requirement to

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measure them more accurately. The XAS experiment was then expected to provide structural data with better accuracy and also oxidation number of the absorbing atom.

**Figure 1.** XRD patterns (CuKα radiation) of Fe₂O₃ which were synthesized at (a) 500 °C, (b) 650 °C, and (c) 800 °C.

**Table 1.** Lattice parameters of the synthesized hematite from a local iron stone.

| Sample     | GoF | Rwp | Lattice Parameter (Å) | Volume        |
|------------|-----|-----|------------------------|---------------|
| Fe₂O₃ (500 °C) | 1.52 | 5.42 | a=b 4.968079 c 13.569098 | 290.040 ± 0.166 |
| Fe₂O₃ (650 °C) | 1.66 | 5.31 | a=b 4.967348 c 13.563683 | 289.839 ± 0.149 |
| Fe₂O₃ (800 °C) | 1.44 | 4.40 | a=b 4.971446 c 13.572015 | 290.491 ± 0.095 |

Figure 2 shows the XANES plot of the 800 °C Fe₂O₃ powder sample and the Fe₂O₃ standard sample. The pre-edge peak (noted by 1 in Figure 2) for both spectra is ± 7113.5 eV which is consistent with Fe³⁺ [10–13]. The data for the synthesized sample qualitatively support the conclusion about the present of Fe³⁺ with no reduction to Fe²⁺ during the process. Furthermore, the absorption edges (Eₒ) for both powders was 7123.41 eV (noted by line 2 in Figure 2). Eₒ can be interpreted as the required energy to raise the photoelectrons just at the outmost energy band. These two results show that the synthesized powder has the same oxidation number with the standard, confirming that it exhibits Fe₂O₃. We also noted that there was a slightly different value of the second peak (noted by @ and *) between the samples, indicating different absorption energy when the photoelectrons interact with the neighboring atom. Meanwhile, the EXAFS region started at 40 eV above the absorption edge (noted by 3 in Figure 2).

Furthermore, the structure information from the XAS measurement about the nearest-neighbor distances was obtained from EXAFS data analysis by using Artemis software. Figure 3 presents the fitting of radial structure function between the model and the EXAFS data for 800 °C Fe₂O₃ sample. Fitting was made to the first shell distances of Fe-O and Fe-Fe. The fitting was acceptable as evidenced by the low values of the reliability factor σ² refers to the average of structure irregularity caused by thermal vibration [13]. The analysis showed that Fe₂O₃ powder exhibited nearest-neighbor distances Rₑ-O = (1.56449 ± 0.01000) Å and Rₑ-Fe = (3.01449 ± 0.001000) Å. On the other hand, the Rietica-derived lattice parameters and atomic positions gave nearest-neighbor atom between Fe-O and Fe-Fe have been calculating, 1.9195 Å and 2.8582 Å, respectively. We notice here that the EXAFS and XRD nearest-neighbor distances are quite different, therefore, for the assurance of more accurate measurements we need further measurement, for example using Standard Reference Materials (SRM) which have known lattice parameters. Moreover, the values of σ² are 0.00936 and 0.00503 for Fe-O
and Fe-Fe, respectively, explaining that thermal vibration does not significantly raise structure
irregularity.

![Graph](image)

**Figure 2.** Fe K-edge absorption of (A) Fe₂O₃ standard sample, (B) Fe₂O₃ synthesized powder.
Peak Position: @ = 7134.03 eV; * = 7133.20 eV

![Graph](image)

**Figure 3.** Fitting EXAFS Fe₂O₃ sample and model from Fe K-edge spectrum

4. Conclusions
Hematite has been successfully synthesized with various calcination temperature by co-precipitation method from local iron stone. XRD analysis showed the pure hematite for all sample variation, with slightly different lattice parameter values. The XANES and EXAFS experiment was performed for the Fe₂O₃ sample with calcination temperature 800 °C. The pre-edge peak of the spectra confirmed the presence of the only Fe³⁺, in conjunction with hematite and supporting the phase identification results from XRD. The nearest-neighbor distances from The EXAFS data analysis were \( R_{\text{Fe-O}} = 1.56449 \) Å and \( R_{\text{Fe-Fe}} = 3.01449 \) Å. The accuracy of the results, however, requires further investigation.
Acknowledgments

The author (H.H.) would like to thank Indonesian Endowment Fund for Education (LPDP) scholarship to support finance of the author. The authors would like to thank SLRI, Thailand for providing XAS beamtime (Project ID 2618).

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