Synthesis and structural characterization of iron chromite nanoparticles: A preliminary study

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Abstract. In this work, the synthesis of iron chromite nanoparticles was performed employing Indonesian iron sand through the coprecipitation route. The crystal and molecular structures of the prepared iron chromite nanoparticles were characterized by means of XRD and FTIR spectrophotometer. Meanwhile, the elemental mapping and morphology of the samples were evaluated using the SEM-EDX technique. The data analysis results showed that the iron chromite nanoparticles had a spinel cubic structure with the lattice parameters and crystallite size of 8.303 Å and 6.8 nm, respectively. The molecular structure analysis for the FTIR spectrum showed that the Fe and Cr ions placed the tetrahedral and octahedral sites. The average particle size of the iron chromite nanoparticles was 30.4 nm and tended to agglomerate. Interestingly, the elemental mapping indicated that the Fe, Cr, and O atoms distributed homogenously.

1. Introduction
Up to recently, the development of magnetic nanomaterial synthesis in achieving uniform particle sizes has been exclusively studied by experts. Magnetite is one of the most researched iron oxides over the years for certain purposes due to its unique magnetic and transport properties from scientific and technological aspects [1]. Magnetite has been considered a metal transition from a mixture valence compound with a chemical formula Fe$_{3+}$[Fe$_{2+}$Fe$_{3+}$]$_2$O$_4$[2]. Also, tetrahedral site (A) is placed by Fe$^{3+}$ and octahedral site (B) is placed by Fe$^{2+}$ and Fe$^{3+}$ with the same amount so that it produces inverse cubic spinel structure [3]. Based on these formulas, some interesting innovations were developed to improve application performance through the substitution process of various transition metals such as Ni, Mn, Ti, and Cr [4-7]. In relation to this, Fe and Cr atoms have advantages for the development of special applications such as catalysts because Fe and Cr atoms have high stability [6] and are able to offer imperative flexibility in adjusting functional characteristics based on the high level of solubility of different cations in the parent lattice [7].

The selection of Fe and Cr atoms in forming ferrite nanoparticle systems in the form of iron chromite has its own advantages. One of which is multifunctional magnetic properties and optoelectronic characteristics originating from the electronic interactions of adjacent Fe$^{3+}$ and Fe$^{2+}$ ions. Therefore, such material is authentically intriguing to be applied in data storage and energy conversion technology [8]. In metal oxide systems, Cr ions are one of the transition metals that have special characteristics with stable valence ranging from 3+ to 6+ [9]. With the substitution of Cr ions into magnetite to form iron chromite nanoparticles using natural iron sand as the main raw material, it can change the ionic arrangement for specific behavior that is better and more effective and efficient in mass production [10].
Therefore, in this work, it is imperative to carry out a preliminary study related to the crystal structure, molecular structure, particle size distribution, and elemental mapping of iron chromite nanoparticles produced in the form of nanopowder. The importance of this preliminary study is a platform for further application development, especially as one of the materials in the application of harvesting energy systems.

2. Methods
The synthesis of iron chromite nanoparticles was carried out using the coprecipitation method. The main ingredients used as a raw material for synthesis are Indonesian natural iron sand, hydrochloric acid (HCl), chromium (III) chloride hexahydrate (CrCl$_3$•6H$_2$O), ammonium hydroxide (NH$_4$OH), distilled water, and alcohol. The synthesis of iron chromite nanoparticles was begun by reacting 20 g of iron sand powder with 60 mL of HCl for 30 min, then filtered using filter paper. The filtered product was then reacted with 3.484 g of CrCl$_3$•6H$_2$O for 60 min, followed by a titration process using 25 mL NH$_4$OH for 30 min. Brown colored precipitates were washed using distilled water to reach a normal pH and heated at 100 °C until the iron chromite powder was obtained. The crystal structure of the iron chromite powder was characterized using XRD (PANalytical, X’Pert PRO MRD) in the range of 25°–65°, and the data obtained were analyzed using the Rietveld refinement method. The electron density mappings were also calculated using a Fourier transform approach. The iron chromite functional groups were tested by FTIR (IRPrestige-21, Shimadzu) spectrophotometer, while its particle size and distribution of the atoms making up the iron chromite were evaluated using SEM-EDX machine (FEI, Inspect-S50).

3. Results and Discussion
The iron chromite diffraction pattern and its crystal structure are shown in Figure 1. Qualitatively, the diffraction has a similar pattern to magnetite nanoparticles, as reported in previous studies with the highest Bragg peak found at 2θ ≈ 35.7º and the reflection plane (311) [10-12]. This indicates that iron chromite crystallizes in a single phase. On the other hand, the quantitative analysis employing ICSD No. 30860 with F d-3 m space group portrays that the crystal structure of the iron chromite is in the form of a cubic spinel with a lattice parameter of $a = b = c$ which is around 8.303 Å and a particle size of 6.8 nm. The particle size corresponds to the previous studies reporting that the size of iron chromite particles ranged between 6.9 and 10.0 nm [11,12].

In principle, the magnetite structure has a common chemical formula AB$_2$O$_4$, in which A is a divalent metal (Fe$^{2+}$), while B represents a trivalent metal (Fe$^{3+}$). Besides, inverse spinel structure is formulated if all divalent metal ions occupy site B, with half fraction of trivalent metal ions occupy site B, while half of the trivalent metal ions occupy site A [13]. This was also explained experimentally by Scafetta et al. where the substitution of Fe by Cr in magnetite to form iron chromite predicts nonlinear changes in lattice parameters caused by the transition from normal spinel (Fe$^{3+}$ is tetrahedral) to inverse spinel (Fe$^{2+}$ is octahedral) [8]. Furthermore, Nguyen et al. also reported that magnetite doped Cr particles could increase their lattice parameters by increasing Cr composition [5]. Since Cr-doped magnetite has three cation formations, namely Fe$^{2+}$, Fe$^{3+}$, and Cr$^{3+}$, in general, three metal ions are placed randomly at sites B and A so that when Cr replaces Fe in magnetite, Cr can occupy tetrahedral or octahedral sites [7]. As the spinel atomic arrangement model of iron chromite is shown in Figure 1 (right), the spinel atomic arrangement model of iron chromite is shown in Figure 2. The crystal structure model indicates that the tetrahedral and octahedral positions at the magnetite atomic site have successfully been occupied by Cr ion. A similar finding was reported by Taufiq et al. showing that the quite low variation in Cr composition can contribute to the reduction of lattice parameters, cell unit volume, and iron chromite particle size [14]. The reduced particle size of magnetic material in the order of the nanometric scale correlates with the increased stability of magnetic nanoparticles in ferrofluid systems [15].
The electron density maps, showing the distribution of electron density of the iron chromite nanoparticles, using Fourier transform are given in Figure 2. The maps were visualized from the z-axis to provide the symmetrical characteristics of the iron chromite crystal structure. It is clearly noticed that the electron density pattern of the structural model is equivalent to the measured sample. It implied that our sample crystallized in a similar crystallographic pattern with the modeling structure of the iron chromite. A very careful Rietveld fitting was conducted to match all the refinable parameters in the way that the calculated structural model was well fitted with the measured data. The difference of Fourier transform plot between the two electron density maps can also be seen in Figure 2. Lower peaks in the left of the figure represented the presence of electrons, the A site of the iron chromite spinel structure, and the higher peaks corresponded to the B site electronic densities. In addition, negative electron densities were also observed due to the interaction among A-O and B-O bonding to form A-O-B super-
The possible electronic configurations of the iron chromite were Fe: [Ar] 3d⁶ 4s², Cr: [Ar] 3d⁵ 4s¹, and O: [He] 2s² 2p⁴. This on-site Coulombic interaction of the 3d states of the Cr and Fe atoms, unlike the 2p orbital of the O atoms, in the inverse spinel structure dictates the magnetic properties of the iron chromite nanoparticles [17].

![Figure 3. FTIR spectrum of the iron chromite nanoparticles.](image)

![Figure 4. (a) SEM image and elemental mapping of (b) Fe, (c) O, (d) Cr, (e) Fe-Cr-O, and e) particle size distribution of the iron chromite nanoparticles.](image)

The FTIR analysis, as the main reference, was used to study the molecular structure, demonstrating each functional group in iron chromite nanoparticles, as presented in Figure 3. The FTIR spectrum of iron chromite nanoparticles was analyzed in the range of 400–4000 cm⁻¹. The peaks located at a wavenumber of ~3450 cm⁻¹ correspond to the O-H stretching functional group [10]. Nonetheless, the O-H bending functional group is shown at a wavenumber of ~1650 cm⁻¹ [18]. The appearance of O-H bonds indicates that there are water molecules absorbed by iron chromite nanoparticles [19]. Also, the peaks in the wavenumbers of ~2879, ~1500, ~1350, and ~950 cm⁻¹ correspond to the C-H bending functional group [11,14]. Transmission peaks at ~700 and ~418 cm⁻¹ wavenumbers correspond to spectra that have tetrahedral and octahedral oxygen-metal M-O bonds [10]. This range shows the
characteristics of atomic vibrations in the tetrahedral and octahedral positions in the cubic structure [21], which indicates that the Fe and Cr ions divalent and trivalent have placed the tetrahedral and octahedral positions in the sample.

SEM-EDX is used to analyze the morphology, particle size, and distribution of iron chromite nanoparticles atoms. In this section, the results of a particle size analysis of SEM are reported with a magnification of 20,000 times, and the results are shown in Figure 4 (a). Visually, the morphology obtained from iron chromite nanoparticles has been well-crystallized, and the resulting morphology tends to be in the form of agglomerated spheres. Furthermore, Figure 4 (b-e) indicates that the Fe, Cr, and O atoms are evenly distributed in the iron chromite nanoparticles. The average particle size distribution obtained from the fitting data results is 30.4 nm, as shown in the right side in Figure 4 (f).

These results correlate with previous studies portraying that the particle size distribution of the nanomaterial iron chromite ranges from 6–35 nm [22].

4. Conclusion

The synthesis of the iron chromite nanoparticles was successfully carried out by means of the coprecipitation method. Based on the XRD characterization, the crystal structure of the iron chromite is in the form of a cubic spinel with a lattice parameter of 8.303 Å and a particle size of 6.8 nm. In addition, the refinement of the XRD analysis using the Rietveld refinement method also showed that the highest Bragg peak of iron chromite was found in the hkl plane (311) at position 2θ ≈ 35.7º. The electron density mappings showed the formation of the inverse spinel structure of the iron chromite in detail. The molecular structure of iron chromite nanoparticles from FTIR characterization shows the stretching, as well as the bending of O-H functional groups and the presence of oxygen-metal bonds in the tetrahedral and octahedral positions which indicate that the Fe and Cr ions divalent and trivalent successfully occupy these positions. Besides, the analysis of SEM image fitting data confirms that the average size of iron chromite particles is 30.4 nm, with each atom of the dispersion evenly distributed.

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Acknowledgment
This study was funded by PUI research grant (PNBP) from Universitas Negeri Malang.