Structural, Band Gap Energy, and Magnetic Characters of Fe$_{2.9}$Cr$_{0.1}$O$_4$ Nanoparticles for Preparing Ferrofluids

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Abstract: Ferrite nanoparticles have become interesting materials originating from their performances in many applications. In this paper, the preparation metal-doped ferrites in the system of Fe$_{2.9}$Cr$_{0.1}$O$_4$ nanopowders is reported. The Cr$_{0.1}$Fe$_{2.9}$O$_4$ nanopowders were utilized to produce ferrofluids. The Indonesian sand was used as a raw material to prepare the samples using co-precipitation route. The Fe$_{2.9}$Cr$_{0.1}$O$_4$ particles structured in cubic spinel with the particle size and lattice parameter of about 9.4 nm and 8.36 Å, respectively. The band gap energy of the Cr$_{0.1}$Fe$_{2.9}$O$_4$ nanopowders was 2.26 eV. Furthermore, the saturation magnetization of the powder was higher than that of the fluid as the effect of particle size and aggregation.

Keywords: Fe$_{2.9}$Cr$_{0.1}$O$_4$, ferrofluid, nanopowder, aggregation, iron sand.

1. Introduction
In nanoscience and nanotechnology fields, one of the materials that intensively investigated is magnetic nanoparticles, especially associated with their biomedical applications. Recent article based on the Elsevier database reported that number of articles of the magnetic particles associated with their biomedical applications increase significantly in an exponential growth for the last decade [1]. Furthermore, in the form of Fe$_3$O$_4$ ferrofluids, the magnetic nanoparticles have a specific excellent performance regarding their physical, chemical, and biological characters. Ferrofluids can be defined as a stable colloidal suspension containing superparamagnetic magnetic particles with particle size in superparamagnetic dispersed in organic or inorganic liquid carriers [2].

Commonly, organic or inorganic materials can be used as coated or layered agents to prevent aggregations of the Fe$_3$O$_4$ particles in ferrofluids. Based on the structure, Fe$_3$O$_4$ becomes one of the spinel groups with a general chemical formula of AB$_2$O$_4$, where A is the divalent metal (Fe$^{2+}$) and B is the trivalent metal (Fe$^{3+}$). The inverse spinel structure can be formed when all divalent metallic ions place B site, a half of trivalent metallic ions places B site and a remained half of the trivalent metallic ions places A site [3]. Therefore, the inverse spinel of the Fe$_3$O$_4$ particles can be expressed in the formula of Fe$_5^{3+}$O$^{2-}$[Fe$^{2+}$Fe$^{3+}$]$_8$O$_3^{2-}$. Such formula guides us to rearrange easily the structure by incorporating other metallic ions such as Mn, Co, Zn, Cu, Cr, and other to enhance the performances of the particles.

In this experiment, we introduce chromium (Cr) as one of the metallic transitions in the group VI-B having special character due to its stable oxidation. Cr doped Fe$_3$O$_4$ in the system of Fe$_{2.9}$Cr$_{0.1}$O$_4$ nanoparticles have three cation formations such as Fe$^{2+}$, Fe$^{3+}$, and Cr$^{3+}$ that would change the ionic...
The arrangement for a better specific behavior. In general, the three metallic ions will place randomly in B and A sites. Quadro and co-workers identified that the Cr and Fe-based catalysts have been utilized in a long time of period for commercial processes due to their high stability [4]. To be more effective and efficient in mass production, despite the important in introducing Cr ions to incorporate Fe$_3$O$_4$ particles, it is also important to exploit an iron sand from local place in Indonesia as a raw material. Moreover, in this paper, the detailed nanostructure, functional group, band gap energy, and magnetic behaviors of the prepared Fe$_{2.9}$Cr$_{0.1}$O$_4$ in nanopowders and in ferrofluids are also reported.

2. Experimental Method
The main precursor (magnetite powder) was firstly purified from Indonesian sand through mechanical process using a magnetic bar. The magnetite powder was mixed with HCl at room temperature using a magnetic sitter to produce iron chloric solution. The solution was then mixed with CrCl$_3$ solution and following by dropping NH$_4$OH to obtain precipitate. To obtain the powder sample, the precipitate was rinsed by using H$_2$O and following by a calcination process at 100 °C. Meanwhile, to obtain the ferrofluid sample, the precipitate was directly coated by TMAH and dispersed in H$_2$O. The obtained samples was characterized by means of XRF, XRD, VSM, FTIR spectrometer, and UV-Vis spectrometer. The data from all characterizations were finally analysed based on the qualitative and quantitative approaches.

3. Results and Discussion
Before investigating the structure and phase purity of the Fe$_{2.9}$Cr$_{0.1}$O$_4$ particles, the elemental composition was investigated using an XRF machine at room temperature. Based on the data analysis, it was shown that the sample had the elemental content with the Cr:/(Cr + Fe) ratio of 4.1 %. Therefore, to study the detailed crystal structure and phase purity of the Fe$_{2.9}$Cr$_{0.1}$O$_4$ particles, we characterized the sample using an XRD machine at room temperature and its result is shown in Figure 1.

![XRD pattern of the prepared Fe$_{2.9}$Cr$_{0.1}$O$_4$ particles](image)

Based on the qualitative data analysis, the XRD pattern has similar pattern to the patterns of the Fe$_3$O$_4$ and Mn-doped Fe$_3$O$_4$ nanoparticles as reported in the literature [5]. It means that the prepared
Fe$_{2.9}$Cr$_{0.1}$O$_{4}$ particles from iron sand crystallize in a mono phase. Further quantitative data analysis of the XRD pattern presented that the Fe$_{2.9}$Cr$_{0.1}$O$_{4}$ particles has a spinel structure with the particle size of about 9.4 nm. The XRD pattern presents the crystal structure in the space group of $F \bar{d}$-3 $m$ $Z$ in the absence of other phases. Using a Rietveld analysis by performing ICSD No. 29129, it was resulted that the lattice parameters of $a = b = c$ were of approximately 8.396 Å. Nguyen et al. reported that the Cr-doped Fe$_{3}$O$_{4}$ particles increase the lattice parameters of the system by increasing Cr composition [6]. Additionally, their work presented that the shape and morphology of the magnetic nanoparticles are still in spherical shapes with agglomeration. In order to investigate the structural behavior, the functional group of the sample was investigated using a FTIR spectrometer and its result is presented in Figure 2.

![Figure 2. FTIR spectrum of the prepared Fe$_{2.9}$Cr$_{0.1}$O$_{4}$ nanoparticles](image)

The FTIR spectrum in the wavenumber range of 4000 - 400 cm$^{-1}$ exhibits several transmission peaks at $\approx$3400, $\approx$1620, $\approx$1400, $\approx$580, and $\approx$410 cm$^{-1}$. The transmission peaks at wavenumber of 3400 and 1620 cm$^{-1}$ are resulted from stretching and bending functional groups of O-H [7,8]. Furthermore, the peaks at wavenumber of $\approx$1400, $\approx$580, and $\approx$410 cm$^{-1}$ are resulted from the functional groups of M-$\text{O}$ (metal-oxygen). It means that the divalent and trivalent ions of Fe and Cr were successfully occupied the tetrahedral and octahedral positions.

After investigating the structure of the Fe$_{2.9}$Cr$_{0.1}$O$_{4}$ nanoparticles, it is followed by investigation of the magnetic behaviors of the samples. The magnetic characters were performed using $M$-$H$ experiment at ambient temperature as presented in Figure 3-4. In the $M$-$H$ experiment, the external magnetic field was varied from -1 T to 1 T. From Figure 3-4, it is easy to be known that all hysteresis curves have $S$ patterns indicating all samples exhibit as superparamagnetic materials. Theoretically, the superparamagnetic state of the samples can be calculated or fitted using a Langevin function [3], as written in Equation 1.

$$\frac{M}{M_s} = \coth(\frac{\mu H}{k_B T}) - \frac{1}{\frac{\mu H}{k_B T}}$$ (1)
Where respective $M$ and $M_S$ are the magnetization and saturation magnetization, $\mu$ and $H$ are the magnetic moment and magnetic field, $T$ is the temperature, and $k_B$ is the Boltzmann constant.

![Figure 3. M-H curve of the prepared Fe$_{2.9}$Cr$_{0.1}$O$_4$ nanopowders](image3.png)

![Figure 4. M-H curve of the prepared Fe$_{2.9}$Cr$_{0.1}$O$_4$ ferrofluids](image4.png)

Regarding Figure 3-4, the Langevin function is fitted well the experimental data both for the samples in fluids and in powders. The $M_S$ of the Fe$_{2.9}$Cr$_{0.1}$O$_4$ nanopowders has a value, which is higher than that of the ferrofluids. The phenomenon is predicted as the effect of the particles size and its clustering. In general, the secondary particle size and clustering of the magnetic nanoparticles in powders has higher than that of the ferrofluids. Physically, in the fluids, the secondary and clustering are affected by the presence of the coated magnetic particles using TMAH dispersing in H$_2$O [9]. In this situation, the building block of the magnetic nanopowders subjected to their primary particles is similar to the building block of the ferrofluids. As superparamagnetic material, the particle size of the Fe$_{2.9}$Cr$_{0.1}$O$_4$ both in the
powders and in fluids should be smaller than a Weiss domain of the corresponding particles in bulk forms [10].

In this work, another fundamental character of the prepared Fe$_{2.9}$Cr$_{0.1}$O$_4$ nanoparticles was investigated using UV-Vis spectrometer and its result is presented in Figure 5. Such experiment was performed to study the optical band gap energy ($E_g$) of the sample. The $E_g$ of the prepared Fe$_{2.9}$Cr$_{0.1}$O$_4$ nanoparticles was determined by plotting the absorption coefficient ($\alpha h \nu$)$^2$ and photon energy ($h \nu$) using Tauc’s equation as shown in Equation 2 [11]. Based on the fitting analysis, the $E_g$ of the prepared Fe$_{2.9}$Cr$_{0.1}$O$_4$ nanoparticles was about 2.26 eV indicating that the value is in the range of the semiconductor character [12].

\[
(\alpha h \nu)^2 = B(h \nu - E_g)
\]  
(2)

Where $B$ is the constant.

![Figure 5. Band gap energy of the prepared Fe$_{2.9}$Cr$_{0.1}$O$_4$ nanoparticles](image)

Based on the above discussion regarding band gap energy, the Fe$_{2.9}$Cr$_{0.1}$O$_4$ ferrofluids from Indonesian sand open potential applications such as for magnetic sensor based on magneto-optics. In our previous work, the Fe$_3$O$_4$ ferrofluids from Indonesian sand prepared by coprecipitation method had excellent performance related to optical character polarization angle of the fluids under external magnetic field [13]. Moreover, the ferrofluids performed a good response in a linear relation originating from the relation of the intensity obtained by photodetector and the external magnetic field varying from zero to 140 mT. Therefore, it is necessary to develop further research by employing the the Fe$_{2.9}$Cr$_{0.1}$O$_4$ ferrofluids resulted in this work for magnetic sensor.

4. Conclusion
The Fe$_{2.9}$Cr$_{0.1}$O$_4$ nanoparticles formed in spinel structure in nanometric scale of about 9.4 nm. The Fe-O, Cr-O, and H-O bonds dominated the functional groups of the Fe$_{2.9}$Cr$_{0.1}$O$_4$ nanoparticles. The samples had a superparamagnetic characteristics associating with $S$ shape of the $M$-$H$ curves. The Fe$_{2.9}$Cr$_{0.1}$O$_4$ nanopowders has $M_s$ value higher than that of the ferrofluids predicted as the effect of particles size and clustering of the magnetic particles. Moreover, the $E_g$ of the Fe$_{2.9}$Cr$_{0.1}$O$_4$ nanoparticles was about 2.26 eV presenting a semiconductor material.
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5. References

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