Structural and Morphological Properties of Undoped and Manganese Doped Hematite Nanoparticles Prepared by Ball Milling Method

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Abstract. Hematite nanoparticles of undoped and manganese doped were synthesized from natural sand of Logas District Kuansing Regency Riau Province by ball milling method. Structural and morphological properties of these compounds were studied using X-Ray Diffractometer (XRD) and Scanning electron microscope (SEM) respectively. Crystalline structure, lattice parameters, morphologies of the synthesized compounds were studied and the results are discussed. X-ray diffraction (XRD) confirmed the presence of a hematite (α-Fe₂O₃) phase. Average crystallite size based on flections (1 0 4) for undoped and manganese doped magnetic iron oxide particles are 39.2 nm and 38.2 respectively. The intensity of (1 0 4) reflection is stronger for magnetic iron oxide synthesized for 60 hours than that of 2 step (60+60) hours ball milling. This indicates the product grown along (1 0 4) direction. The average crystallite size decreases when magnetic iron oxide is doped with 10% Mn as confirmed by SEM images.

1. Introduction
Magnetic iron oxide nanoparticles are a new class of materials when prepared in nanoscale size, they exhibit superparamagnetic behaviour. Among these iron oxides, hematite (α-Fe₂O₃) has been extensively studied due to its wide technological applications including enhanced catalytic activity[1], water treatment[2], magnetic data storage[3], magnetic resonance imaging[4], and drug delivery target[5]. Today a number of methods are used to prepare iron oxide nanoparticles such physical, chemical and biological methods[6]. In physical methods, one of the well-known methods is ball milling[7, 8, 9, 10]. This method is simple, efficient, high yield and low cost compared to other methods. For example, previous researchers [11, 12] have used stainless ball as milling ball to produce hematite powders and iron balls to produce magnetite. Their findings revealed that the iron balls as milling ball determined the formation of hematite as a milling product. Previous researchers [13, 14, 15, 16, 17] have used ball milling method to produce magnetic iron oxide nanoparticles. In order to produce iron oxide particles (Fe₂O₃), the researcher [13, 14] used ball milling method. Moreover, other researchers[15] used high-energy ball milling to prepare 10 nm α- Fe₂O₃ nanoparticles directly from crude α- Fe₂O₃ by, and found that the surface anisotropy constant of α- Fe₂O₃ nanoparticles is higher than bulk material produced by this method. Moreover, magnetic properties, phase and morphology of the obtained particles are depended on time, speed and types of milled balls[17]. One of the most
important parameters for controlling the magnetic properties of magnetic iron oxide nanoparticles is the size of the particles. However, development of a simple, reliable, and low cost methodology to synthesize magnetic iron oxide nanoparticles with controllable size and size distribution remains a challenging task for researchers.

According to previous researchers[18], when transition metal elements doped into nanoparticles, they will alter the structural properties of that nanoparticles. Moreover, doping methodology and selection of doped transition ions influence the properties of magnetic iron oxide nanoparticles. In this paper, we have investigated the structural morphological properties of undoped and manganese doped magnetic iron oxide particles of natural sand from Logas, Kuansing District, Riau Province using ball-milling method.

2. Experimental Method
Natural sand samples were collected from Logas, Kuansing Regency, and Riau Province. Iron sand separator was employed for removal of the non magnetic particles prior to ball milling process. The product of iron sand separator was milled using ball milling for 120 hours. The magnetic and nonmagnetic particles were separated using neodymium iron boron magnet (NdFeB). Finally, the product of ball milling was milled together with manganese as a dopant with manganese composition of 5, 10 15 and 20 % for 20 hours in order to obtain a fine powder. Structural and magnetic phases of the synthesized compound before and after manganese doped hematite nanoparticles were studied using X-Ray Diffractometer (XRD) technique equipped with Cu K\textalpha\ radiation of \(\lambda=0.15406\) nm. The morphology compound were studied using scanning electron microscope (SEM).

3. Results and Discussion

3.1. Elemental composition of the samples
Elemental composition of natural sand before and after ball milling process was determined using X-ray fluorescence spectroscopy (XRF). This composition is presented in Table 1 below.

| Type of Composition | Before Milling Percentage of Composition (%) | Type of Composition | After Milling Percentage of Composition (%) |
|--------------------|---------------------------------------------|--------------------|---------------------------------------------|
| Si                 | 92.264                                      | Si                 | 11.854                                      |
| Ti                 | 0.423                                       | Ti                 | 29.141                                      |
| Al                 | 3.676                                       | Al                 | 1.906                                       |
| Fe                 | 0.371                                       | Fe                 | 51.533                                      |
| Others             | 6.942                                       | Others             | 7.472                                       |

Table 1 shows that the elemental composition of Natural sand of Logas District. This composition was affected by milling process. It shows that the Fe contents were increased very significantly after milling 120 hours. Some other compounds for examples Si and Al were decreased, however, the other such as Fe and Ti was increased. This indicates that natural sand grains break into smaller parts so that the non-magnetic and magnetic grains were separated during milling process. Moreover, it is clear that Fe and Ti elements cannot be separated until 120 hours milling process suggesting that Fe and Ti were exist in the form of compound of FeTiO\textsubscript{3} as indicates in X-ray diffraction patterns (Fig.1).

3.2. X-Ray Diffraction (XRD) Analysis
Magnetic phases for undoped and manganese doped magnetic iron oxide particles were obtained using X-Ray Diffractometer that available in Indonesian Science Institute (LIPI) that produced x-ray radiation with wavelength of 0.15406 nm. In this measurement, the diffraction angle was selected in interval of 10° to 90° with the step of 0.01°. X-ray diffraction patterns were obtained by applying high
voltage source that is around 40 kV and 30 mA. X-ray diffraction patterns of an undoped and manganese doped magnetic iron oxide particles are shown in Figure 1a and 1b.

![X-ray diffraction patterns](image)

**Figure 1.** X-ray diffraction patterns for (a) undoped hematite nanoparticles and (b) 10% manganese doped hematite nanoparticles. The inset pattern shows the standard peaks of Fe₂O₃ crystal structure[19]

Figure 1 shows two XRD patterns for undoped and manganese doped magnetic iron oxide particles. It can be easily found that the diffraction peaks on undoped magnetic iron oxide particles at 2θ value of 23.96°, 32.79°, 35.38°, 40.49°, 49.01°, 53.42°, 61.83°, and 63.42° were completely matched the reflections of (012), (104), (110), (113), (024), (116), (018) and (214) respectively indicates the magnetic iron oxide particles are in good agreement with the diffractions peaks of the Fe₂O₃ (JCPDS no. 33-0664)[19]. The narrow and sharp peaks showed that the particles are crystallized. It can be seen from Fig. 1b that shift in most peak positions, to slightly higher angles, are observed for manganese doped magnetic iron oxide particles (Fe₂O₃). This shift of peak positions to lower angles such as 32.75°, 35.35°, 40.44°, and 48.95° is being thought due to smaller ionic radii of manganese as compared with those of iron. These peak positions are correspond to d-spacing
or inter planar distances of 2.732, 2.5369, 2.2284, and 1.8590 respectively. Therefore, small radii of manganese ion leads to decrease in d-spacing unit cell of crystal structure result small shifts the peak positions to higher angles after being doped with manganese ions. Moreover, peaks corresponding to MnO₂ or Mn₃O₄ could not be observed in diffraction pattern of XRD suggesting that the Mn is incorporated into the ferrite structure rather than precipitating as a manganese oxide on the surface of the iron oxide[20]. Some other diffraction peaks from other crystalline forms such as silicon (Si) and titanium (Ti) were detected, which demonstrates that these magnetic iron oxide particles (α-Fe₂O₃) samples are not high purity.

The intensity of (1 0 4) reflection is stronger for undoped magnetic iron oxide than that of doped manganese ions. This indicates the undoped magnetic iron oxide grown along (1 0 4) direction. Average crystallite size is calculated using Scherrer’s formula D = kλ/ β cos θ, where D is the size of the crystalline, k is the Scherrer’s constant (k=0.9), λ is the wavelength of the X-ray used, β is the (FWHM) intensity and θ is the position of the peak. Average crystallite size is determined for flections (1 0 4) for undoped and manganese doped magnetic iron oxide particles are 39.2 nm and 38.2 nm respectively. The average crystallite size decreases when magnetic iron oxide is doped with 10% Mn.

3.3. Scanning Electron Microscopy (SEM) Study
The scanning electron microscopy (SEM) images of 120 hours and 120 hours 10 % and 20 % manganese doped milled samples with 1000-x magnification are shown in Fig. 2. This analysis was carried out in order to investigate the shape and size of the synthesized hematite nanoparticles.

Figure 2. Scanning electron microscope images for magnetic iron oxide particles milled for (a) 120 hours (b) 120 hours milling 10% manganese doped and (c) 120 hours Milling 20 % manganese doped
In the first step of milling, after 120 hours milling time, the natural sand from Logas undergo fragmentation due to momentum transfer among milling balls and natural sand as shown in Fig. 2(a). Particles size of a synthesized magnetic iron oxide with a milling time of 90 hours was roughly estimated in the range from 20 to 200 μm with irregular form. It can be noticed that particle size distribution is larger. The particles size for the synthesized 10 % and 20 % manganese doped iron oxide particles for milling time of 120 hour is in the range from 0.5 to 50 μm. Moreover, the particles size distribution is relatively narrower compared to that for 120 hours milling time as indicates in Fig. 2(a). From Fig. 2(a), (b) and (c) it can be estimated that the average particles size decreases with increasing manganese concentration. Magnetic iron oxide particles synthesised for 120 hours doped with 20% manganese ions shows particle agglomeration.

4. Conclusion

From all the findings in this work, it can be concluded that undoped and manganese-doped hematite (α-Fe₂O₃) nanoparticles have been prepared using ball milling method. XRD results indicated the formation of phase pure hematite in undoped and manganese doped hematite nanoparticles. XRD peaks corresponding to manganese oxide or metal manganese could not be observed in diffraction pattern suggesting manganese ions were highly dispersed in the Fe₂O₃ lattice and both Mn and Fe have almost similar ionic size. Some other diffraction peaks from other crystalline forms such as silicon (Si) and titanium (Ti) were clearly observed, which suggest that these hematite nanoparticles (α-Fe₂O₃) samples are not high purity. The SEM image shows that hematite nanoparticles consist of irregular shapes and different sizes. For manganese doped hematite nanoparticles, the morphology of the particles changes to particle agglomeration.

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