Synthesis of Iron sand into Nano Mn-Ferrite

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ABSTRACT

Magnetic material, Mn-Ferrite, was prepared from iron sand using precipitation and sol-gel methods. The methods were applied to produce a homogenous and nanosized powder. The precipitation process was taken place at room temperature. MnO_2 and Fe_3O_4 were dissolved with HCl solution to obtained $MnCl_2$, $FeCl_2$ and $FeCl_3$ and the resulted solution were mixed. NH_4OH and NaOH solutions were added into mixed solution to produce precipitated material. At the heating temperature of 70°C, 59% of $(Mn,Fe)_2O_3$ was obtained with its particle size around 1-10 nm. By applying sol-gel method, the iron sand was processed into iron (III) nitrate using nitric acid. Then Iron (III) nitrate was mixed with manganese (II) nitrate in the EG solvent and heated for 2 hours in 100°C until gel was formed. To get the powder, the gel was dried at 150°C for 2 hours and then continued into 350 -700°C for 2 hours. The XRD characterization shows that the powder produced from 350°C heating contain 100% of $(Mn,Fe)_3O_4$ with spinel cubic structure. At the heating treatment of 700°C, the compound was changed into $(Mn,Fe)_2O_3$ and $MnFeO_3$. By applying Scherrer method, it was known that the average particle size was 1 nm and homogenous. The XRF characterization of the material resulted by both of the methods indicates that there were impurity elements such as Ti, Mo, Zn, Ca, Cu and Ni exist in the sample, since the study was used row material of iron sand.

| Iron Sand | Mn-Ferrite | Precipitation | Sol-gel |

1. INTRODUCTION

Indonesia is blessed with an abandon of iron sands as iron oxide sources. As a valuable materials, generally iron sand can be found in the sea shores and beaches along Indian Ocean, from western part of Sumatra up to some islands in eastern part of Indonesia, such as in Bali, Sumbawa as well as Lombok. In Central Java, iron sand can be found in almost all beaches of southern part and in some locations of northern part, such as around the mountain of Muria [1,2].

The existence of this mineral material influences scientists of some field of study to conduct research concerning this material. Geophysical study of this material, for instance, tries to explore and to explain the mechanism of its formation, resources, etc. Physical study of iron sand is mainly used to explain its physical properties. Those studies will be resulting weighty information, which in turn can be considered in deciding its strategy of iron sand processing to become a more valuable product.

Previous study indicated that iron sand contained iron oxides such as magnetite (Fe_3O_4), maghemite (γ-Fe_2O_3) and hematite (α-Fe_2O_3) [3], the basic materials of ferrite which were considered as very most essential component in the manufacture of magnets. Considering its benefit, several researchers have studied and utilized Indonesian iron sand into ferrite magnet, and some of the studies mainly explored appropriate method of producing hard magnetic materials

[4,5,6], but left the production of soft magnetic into further study.

Mn ferrite has a great influence in the development of soft magnetic materials because of their high initial magnetic permeability, saturation magnetization, electrical resistivity and low power losses [7]. This material is widely used in various applications such as microwave devices, computer memory chips, digital storage media, transformer cores, rod antennas as well as the application of telecommunication and electronics engineering [8].

Current researchs about nanoparticle were conducted to get high performance of materials [9]. Synthesis of Mn ferrite nanoparticles has been conducted by various methods which will yield the structure and properties of materials of different ones.

This study utilized two methods of sof magnetic production, they were precipitation and sol-gel methods. Both methods have several advantages such as producing high purity, homogeneity, small particle size, requring efficient energy, and as the reaction did not need any container, it might increase the purity of the product [9].

By comparing the two methods, this study was aimed to get best method to produce high purity and nano-sized Mn-Ferrite.

2. EXPERIMENTAL

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2.1 Material of Iron Sand

Based on the previous studies, it has been known that the dominant magnetic material of iron sands is magnetite (Fe_3O_4) and it is associated with other gauge minerals, both magnetic and non-magnetic. The gauge minerals associated in the iron sand but they are evenly distributed. There is difference of detail characteristic of iron sand from several locations [2].

Magnetite grains were extracted and purified from iron sand obtained from a disclosed location in the north coast of Java, Indonesia. The extraction used both manual and mechanical means and the purification applied grounding and sieving. This method of purification produced 99% pure magnetite powders were about [10]. Those powders were then used in this study.

2.2 Precipitation Procedure

Two main precursors were utilized to prepare Mn ferrites within precipitation method, they were $MnCl_2$ and $FeCl_3$. Both of them were obtained from MnO_2 and Fe_3O_4 which were produced by manual extraction of iron sands that were dissolved in 36% HCl in equal weight and stirred approximately for 15 minutes. The reaction equation was:

$MnO_2+4HCl➡MnCl_2+2H_2O+Cl_2$

$Fe_3O_4+8HCl➡FeCl_2+2FeCl_3+4H_2O$

After the reaction completed, the two precursors were separated from impurities using filter papers. $MnCl_2$ solution and iron salts solution, in concentration ratio of 1:1, were then mixed together. 21% NaOH and 21% NH_4OH solutions were added into the final mixture in concentration ratio of 1:2 respectively. After reacting for about 5 minutes, black precipitated material was obtained.

The precipitated material was separated from impurities solution and it was washed using aquades for many times. This process produces mud precipitated material that was bowled to obtain half dry precipitated materials. After that heating process was administered utilizing microwave in temperature of 70°C for 20 minutes to get material powder [11].

2.3 Synthesis using Sol-gel method

Both iron(III) nitrate and manganese(II) nitrate were obtained from iron sand, by synthesizing magnetite (Fe_3O_4) and manganese dioxide MnO_2, which were extracted fron iron sand with nitric acid. Iron nitrate ($Fe(NO_3)_3·xH_2O$) 0,2 mol and manganese nitrate ($Mn(NO_3)_2·xH_2O$) 0,1 mol were used as a precursor. Both of precursors were mixed and added 100 ml of ethylene glycol as a solvent. The concentration ratio between NO_3- : EG was 1: 1. The solution was stirred for 2 hours in a temperature of 100°C to obtain a homogeneous and transparent sol then cooled to reach room temperature and ethanol was added while stirring to get gel

form. Ethanol addition was aimed to increase the solubility of the sol [7]. Gel was heated at a temperature of 150°C for 2 hours to form the nano-particle. Dried gel particles were placed on a special plate then heated at a temperature of 350-700°C for 2 hours.

The powders produced by both methods were characterized by X-ray Diffraction to determine the structure and the purity produced Mn-ferrite. X-ray fluorescent was applied to explore the elements in the produced materials.

3. RESULTS & DISCUSSION

3.1 Mn-Ferrite using precipitation method

The XRD patterns of the samples were used to determine the spinal structure of Mn ferrite by comparing with the ICDD (International Centre Diffraction Data) data. Figure 1.a shows XRD the pattern of Mn ferrite synthesized by adding NH_4OH. Some peaks informed Mn ferrite peaks, (JCPDS PDF# 10-0319), they were peaks at (111), (222), (400), (422), (511) and (444). However, the intensity of the peaks was small.

Meanwhile, Fig. 1.b shows XRD pattern of Mn ferrite synthesized by adding NaOH. There were no peaks that described Mn ferrite peaks. From XRD pattern of both samples, it could be considered that sample 1 (Fig.1.a) contained Mn ferrite and sample 2 (Fig. 1.b) did not.

The quantitative analysis revealed that sample 1 contained 59% Mn ferrite and 41% $αFe_3O_4$; however they were not completely pure in spinal-cubic structure, since the precipitation process was conducted at room temperature. Further study which conducts the process in higher temperature should be conducted to find out best temperature for the process resulting higher percentage of Mn ferrite. On the other hand, sample 2 only contained 10% MnO_2, 55% Fe_3O_4, 35% Fe_2O_3 hence; Mn ferrite has not obtained yet.
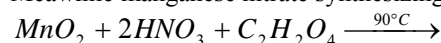
XRF result of precipitated powder sample shows that there were many impurities in the powder. It is possibly because the material used in experiment was raw material iron sands Iron sand can be consider as secondary rock, which was formed from igneous rock Table 1 shows types of impurities in precipitated samples..
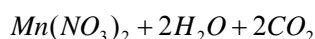
3.2 Mn-Ferrite produced using sol-gel method

Iron(III) nitrate and manganese(II) nitrate were obtained by synthesizing basic material with nitric acid, using oxalic acid as a catalyst. The synthesizing of iron nitrate follows this chemical process:

$$2Fe_3O_4 + 24HNO_3 + 2C_2H_2O_4 \xrightarrow{90°C}$$
$$6Fe(NO_3)_3 + 3Fe(NO_3)_2 + 14H_2O + 4CO_2$$
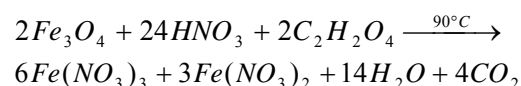
Meawhile manganese nitrate synthesizing reaction is:
$$MnO_2 + 2HNO_3 + C_2H_2O_4 \xrightarrow{90°C}$$

$$Mn(NO_3)_2 + 2H_2O + 2CO_2$$

The reaction product of iron nitrate formed golden brown solution which is comprised of compound $6Fe(NO_3)_3$ and $Fe(NO_3)_2$. The brown colour is caused from ion Fe^{3+} whereas the yellow from ion Fe^{2+}. Product solution is more brown colour show that ion Fe^{3+} more dominant than ion Fe^{2+}. If the solution letting settle then formed a white crystalline *anhydrate ferrous nitrate* which is a solid form of iron oxide. Iron nitrate crystals are highly reactive and easily oxidized. While the synthesis reaction of manganese oxide and nitrate acid solution formed a ligth red manganese nitrate $Mn(NO_3)_2$. It's very easily to be precipitate (crystalization).

Mn ferrite powders obtained by sol gel method. Percusor solution of iron nitrate and manganese nitrate dissolved in ethylene glycol (EG). Base on the oxidation reaction principle of ethylene glycol and NO^{-3} ions into

glyoxylate dyanion combination complex formed a heteropolynuclear $Fe_2Mn(OH)_4(C_2H_2O_4)H_2O$. While NO gases and HNO_3 will be lost during the process of sol-gel.

The graph in figure 2 indicates prominent peaks at an angle 2θ 30.2231°, 35.6027°, 43.3097°, 53.7787°, 57.2675°, 62.9088°, and 74.3963°. The peaks were related to the phase of formed compound. Identified peaks indicate that the compound is $(Fe,Mn)_3O_4$. By XRD quantitative analysis it is known that the compound is fully $(Fe,Mn)_3O_4$, it is close to appropriate data of ICDD PDF39-1346. Using integrated software in XRD system it can be identified that the compounds is cubic of $(Fe,Mn)_3O_4$ with space group FD-3m (No. 227). $(Fe,Mn)_3O_4$ is a special Mn ferrite spinel which there Mn^{2+} are substituted in to spinel. Spinel $(Fe,Mn)_3O_4$ consist of $FeFe_2O_4$ or $MnFe_2O_4$. Both are ferrimagnetic materials.

Table 1. The existence impurities in the powder of precipitated material

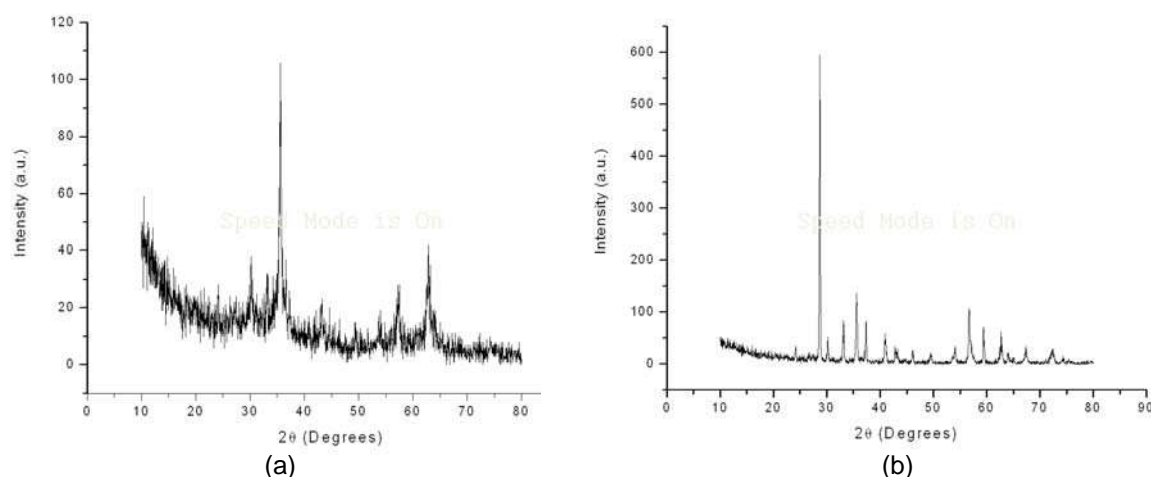| Element	Concentration / Percent (%)	Element	Concentration / Percent (%)
Ti	5.05	Cr	0.30
Si	2.10	P	0.27
Al	1.90	Re	0.20
Bi	0.73	Ca	0.19
Eu	0.66	Zn	0.09
V	0.48	Ni	0.004
Rb	0.45	Yb	0.003

Fig. 1 XRD Pattern of the precipitated material (a) using NH_4OH and (b) using NaOH
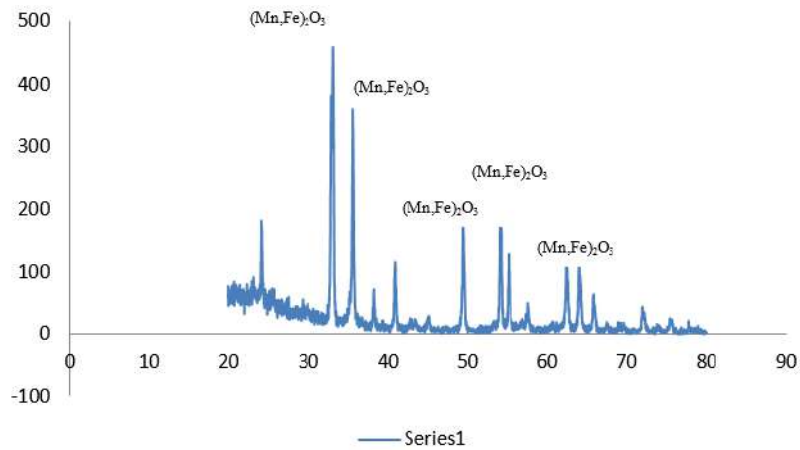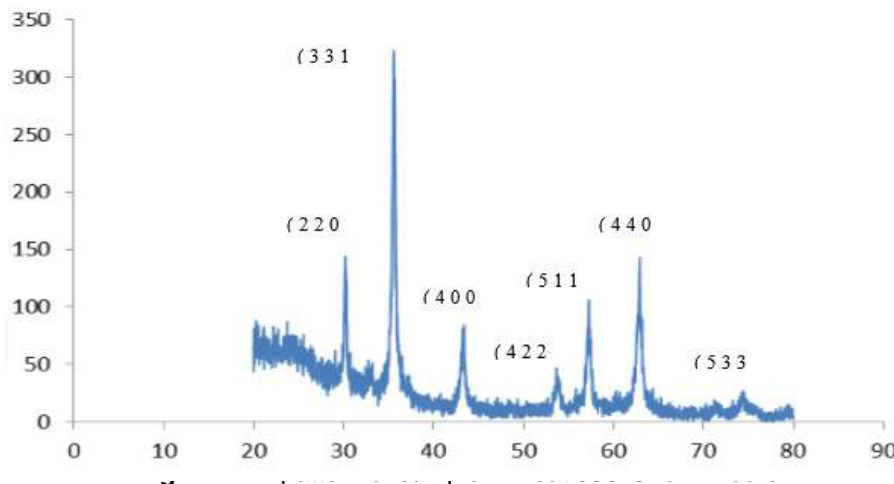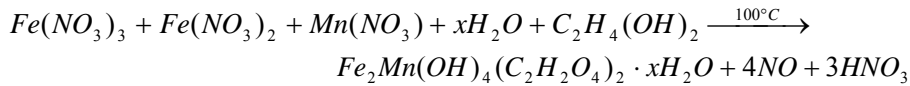
In the spinel $(Fe,Mn)_3O_4$, divalent ions Fe^{2+} dan Mn^{2+} arrange the octahedral lattice dan trivalent ions Fe^{3+} are tetrahedral ones. Magnetic ions will be paired where the sub lattice A dan B are antipararel. Each sub lattice has one ion Fe^{2+} in sub lattice B and ion Fe^{3+} in sub lattice A. There is unbalanced antiparalel couple because of a magnetic

moment pair thus generated by ion Fe^{2+}. So the material is ferrimagnetic.

In the compoud of $MnFe_2O_4$, the presence of ions Mn^{2+} repalced the ions Fe^{2+} in the Fe_3O_4 lattice. It is related to the activation energy that is kinetic [temperature] reaction. Activation energy for the formation of ferrite is not the same for several metals. The activation energy associated with the

temperature required for the formation of ferrite between 20°C -100°C in sol gel method. Activation energy of manganese is at temperature of 100°C [12,13]. There is $FeFe_2O_4$ compounds because percusor used are $Fe(NO_3)_3$ and $Fe(NO_3)_2$. Ion Fe^{3+} from $Fe(NO_3)_3$ tends to be Fe_2O_3 whereas ion Fe^{2+} from $Fe(NO_3)_2$ tends to be FeO.

$$Fe(NO_3)_3 + Fe(NO_3)_2 + Mn(NO_3) + xH_2O + C_2H_4(OH)_2 \xrightarrow{100°C}$$
$$Fe_2Mn(OH)_4(C_2H_2O_4)_2 \cdot xH_2O + 4NO + 3HNO_3$$

XRD pattern of sample 2 shows that it's peaks is different from sample 1. There is a phase trasformation from magnetite in sample 1 change into hematite phase in the heating of 700°C. The oxidation of magnetit Fe_3O_4 will be change in to maghemit γ-Fe_2O_3 or hematit α-

Fe_2O_3. It will not occure at a lower temperature because the hematite formed in the outer layer of grains of magnetite coating will protect it from further oxidation[8]. The advent of hematite confirmed by XRD spectra where peaks are formed at an angle which is the main peak of

hematite. The angles are 33,17°, 35,64°, 49,50°, 54,11°, 62,48° dan 64,04°. It's shown at figure 2.

The analysis results show that formed 70.46 % of $(Mn,Fe)_2O_3$ compound having space group R-3 (No. 167) is formed. It has a trigonal structure and 29.54 % of cubic $MnFeO_3$ with space group I a-3 (No. 206). The advent of $(Mn,Fe)_2O_3$ and $MnFeO_3$ are caused by the oxidation and reduction process during heating. This reaction can occur depending on the oxygen partial pressure and heating temperature heating [3]. Ferrite formation must occur at a lower pressure than the pressure of the oxygen in the air, so it is quite heated at low temperatures. If the high temperature is given, so as the partial pressure of oxygen in the air is higher then the decomposition of ferrite.

$$(Mn,Fe)_3O_4 + [O_2] \rightarrow (Mn,Fe)_2O_3 + MnFeO_3$$
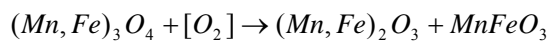
With the Scherrer method, particles size can be known by the formula

$$d = \frac{0,94\lambda}{\beta \cos\theta}$$

where λ is wave length of used Xray, β is full width half maximum (FWHM) and θ is bragg angle. The data is taken from XRD spectrum data. From the calculations yield an average particle size is 1 nm.

The results of XRF sample 1 shows a rasio of the composition of Fe and Mn are 58,0 % and 32,9 %. Likewise rasio of the composition sample 2 Fe and Mn are 59,3 % banding 33,3 %. This composition is suitable for the formation of Mn ferrite $(MnFe_2O_4)$ that Fe and Mn rasio are 2:1. As for the other metals that arise include Ti, Mo, Zn, Ca, Cu and Ni are impurity of the iron sand. Extraction of natural iron sand is not really pure Fe_3O_4. Homogeneity of the elemental composition of the compound seen in the sample are almost the same. This shows the sol gel method gives good homogenity.

Based on the result of the characterization, it can be stated that Mn-Ferrite produced using precipitation and sol-gel methods has different properties relatively. Mn-Ferrite produced by sol-gel method has grain nano-size, purity and homogenity better than those produced by precipitation.

4.   CONCLUSION

Mn ferrite can be synthesized from iron sand by applying precipitation and sol gel methods. However, the later produced higher purity and nano sized of Mn-ferrite than the former method. XRD characterization result indicates that temperature of heating affects the crystal structure in both methods. In Sol gel method, heating process of 350°C is effective to produce Mn ferrite powders having 100% cubic inverse spinel structure. Whereas at 700°C the phase is phase trasformed into trigonal $(Mn,Fe)_2O_3$ and cubic $MnFeO_3$ which composition 70,46% and 29,54%. By Scherrer method, the average of particle size is 1 nanometer. From the characterization results obtained XRF elemental composition information in a sample consisting of elements Fe, Mn and elements which are impurities such as Ti, Mo, Zn, Ca, Cu and Ni were scattered evenly between the two samples indicates equitable homogeneity.

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