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To cite this article: S Bahtiar *et al* 2017 *IOP Conf. Ser.: Mater. Sci. Eng.* **202** 012052

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Synthesis, Investigation on Structural and Magnetic Behaviors of Spinel M-Ferrite [M = Fe; Zn; Mn] Nanoparticles from Iron Sand

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Abstract. Spinel M-ferrite [M = Fe; Zn; Mn] nanoparticles were prepared from iron sand using a coprecipitation-sonochemical approach. The purified Fe₃O₄ from iron sand, ZnCl₂ and MnCl₂·4H₂O, HCl, and NH₄OH were used as raw materials. X-Ray Diffractometer (XRD), Fourier Transform Infra-Red (FTIR) spectroscopy, Transmission Electron Microscopy (TEM), and Vibration Sample Magnetometer (VSM) were employed to characterize the crystal structure, functional groups, particle size, morphology, and magnetic behavior of the prepared samples, respectively. From the XRD data analysis, M-ferrite particles exhibited a single phase in spinel structure. Furthermore, the M-ferrite particle increased their lattice parameter and crystal volume tracking the metallic-ionic radii of M. The particle size of the M-ferrites particles varied with M, whereas the biggest and lowest were for Zn and Mn, respectively. Based on the magnetization curve, the M-ferrite nanoparticles tended to perform a superparamagnetic behavior and their saturation magnetization as a function of their M ion and particle size.

Keywords: M-ferrite [M = Fe; Zn; Mn], nanoparticle, coprecipitation, sonochemical, structure, magnetization

1. Introduction

In the past few decades, the interest of spinel ferrite particles preparation especially in nanometric size has been reinforced by many nanoscience and nanotechnology experts due to the numerous potential applications of the nanostructured ferrites [1]. M-ferrite or MFe₂O₄ particles in the spinel structure, where M is the metallic ions such as Fe, Zn, Mn, Ni, Co, and others, become a group of functional materials that have created interest due to their physical and chemical behaviors. Therefore, various preparation approaches have been intensively performed by many researchers to achieve the spinel M-ferrite nanoparticles in different sizes and morphologies. Moreover, in order to fabricate the spinel M-



ferrite nanoparticles in a mass production, the preparation method has also been developed by finding alternative precursors as raw materials from natural resources that are abundantly available in the world. One of the natural resources that can potentially be utilized as raw materials is iron sand.

Several papers reported that the M-spinel ferrite nanoparticles in the forms of nanopowders, films, magnetic fluids, and magnetic gels were prepared from iron sand through a simple coprecipitation method by varying several physical and chemical parameter processes [2–8]. The coprecipitation method was successfully developed for preparing the M-spinel ferrite nanoparticles in several sizes and morphologies in relatively simple, quick, and inexpensive ways. However, the phenomenon of the magnetic nanoparticle agglomeration has not been overcome yet. Therefore, it is necessary to find and or develop a method for overcoming the problem. One way that can be conducted is by combining the coprecipitation method with the sonochemical route. The main reason of such combination is due to the performance of the acoustic cavitation in producing high temperature and pressure in the liquid [9].

In this paper, we report the successful combination method of coprecipitation and sonochemical approaches in the fabrication of M-ferrite [M = Fe; Zn; and Mn] nanoparticles from the natural resource of Indonesia. The M-ferrite nanoparticles for M = Fe, Zn, and Mn were selected regarding their performances that can be potentially applied in several fields such as for drug delivery vehicles and MRI contrast agents [10], for the detection of pathogenic bacteria [11], as anode materials for lithium-ion batteries [12], and so forth. Furthermore, the structural, morphological, and magnetic behaviors of the prepared M-ferrite nanoparticles are also discussed.

2. Experimental Method

2.1 Materials

In this experiment, the materials used in preparing M-ferrite nanoparticles were iron sand from East Java Indonesia, zinc chloride (ZnCl₂), manganese (II) chloride tetrahydrate (MnCl₂·4H₂O), ammonium hydroxide (NH₄OH), hydrochloric acid (HCl), and distilled water.

2.2 Preparation

M-ferrite [M = Fe; Mn; Zn] nanoparticles were prepared by a combination of coprecipitation-sonochemical methods. The iron sand was utilized to obtain magnetite powder. The magnetite was then dissolved in the hydrochloric acid for 20 minutes to form a solution containing Fe²⁺ and Fe³⁺ salts. The formation mechanism of the iron salts is presented in the following equation [13].



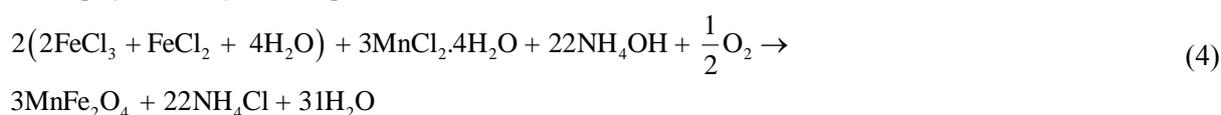
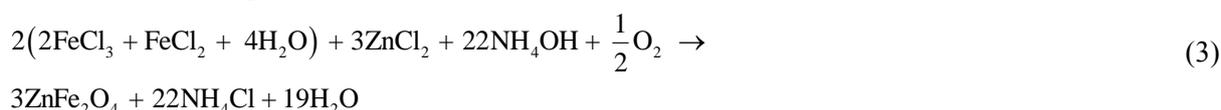
The product of reaction (1) was then dropped wisely with the ammonium hydroxide to form magnetite nanoparticles. Meanwhile, the product was mixed with ZnCl₂ and MnCl₂·4H₂O before adding the ammonium hydroxide to form Zn-ferrite and Mn-ferrite, respectively. These processes were combined with the sonochemical method using an ultrasonic bath at a frequency of 40 kHz. All of the operations were kept at the ambient temperature. In order to obtain the M-ferrite particles in nanopowders, the process was continued by the washing process for several times and followed by drying process at 100 °C.

2.3 Characterizations

All prepared samples were characterized by using XRD (X-ray Diffractometer) to investigate their phase purity, crystallite size, and crystal structure. Meanwhile, the FTIR (Fourier Transform Infra-Red) spectroscopy was employed to study the functional groups of the samples. Furthermore, the TEM (Transmission Electron Microscopy) was also used to determine the morphology and particle size of the samples. Finally, the magnetic behavior of the samples was investigated by means of VSM (Vibration Sample Magnetometer). All characterization processes were kept at ambient temperature.

3. Results and Discussion

The chemical formation of the prepared spinel M-ferrite particles can be expressed by the following equations.



The iron salts containing Fe^{2+} and Fe^{3+} ions resulted from one stage reaction of the purified iron sand with HCl were directly wisely dropped by NH_4OH to form Fe_3O_4 particle according to reaction (2). The ZnCl_2 and $\text{MnCl}_2 \cdot 4\text{H}_2\text{O}$ were also mixed with the iron salts and then followed by dropping NH_4OH carefully to form ZnFe_2O_4 and MnFe_2O_4 particles. The NH_4Cl and H_2O as unwanted products were cleaned or removed through washing and drying processes to obtain the spinel M-ferrite particles in a single phase. In order to investigate the success of the synthesis process, the details of the phase purity, crystal structure, and crystallite size were discussed in the following section.

Figure 1 shows the X-ray diffraction patterns of the M-ferrite particles prepared by using a combined coprecipitation-sonochemical route. Based on the picture, it is clear that all samples have similar diffraction patterns which correspond to the similar phase. All diffraction patterns have Miller indexes (hkl) on the planes (220), (311), (400), (422), and (511) representing the diffraction patterns of ferrites. The qualitative analysis of the XRD data showed that all samples construct a single phase without any impurities. The Zn-ferrite particle has the sharpest peak indicating that it has the largest particle size, while the Mn-ferrite particle has the opposite one. Furthermore, the quantitative analysis of the XRD data pointed out that the refinement model represented by the solid line fits well the data represented by a circle. The detailed results of the fitness are tabulated in Table 1. From the table, the lattice parameter values are 0.837, 0.839, and 0.842 nm for iron, zinc, and manganese ferrites, respectively. In accordance with the results of this work, Syue *et al.* reported that the manganese ferrite nanoparticle prepared from commercial precursors by combustion method has the largest lattice parameters than that of zinc ferrite nanoparticle [14]. Logically, the increasing lattice parameters are originated from the contribution of the ionic radii of the M-ions, where the Mn^{2+} has larger ionic radii ($\sim 0.82 \text{ \AA}$) than that of Zn^{2+} ($\sim 0.74 \text{ \AA}$), and Fe^{2+} ($\sim 0.78 \text{ \AA}$). These metallic ions were distributed randomly in the spinel crystal structure, both in the octahedral and tetrahedral positions.

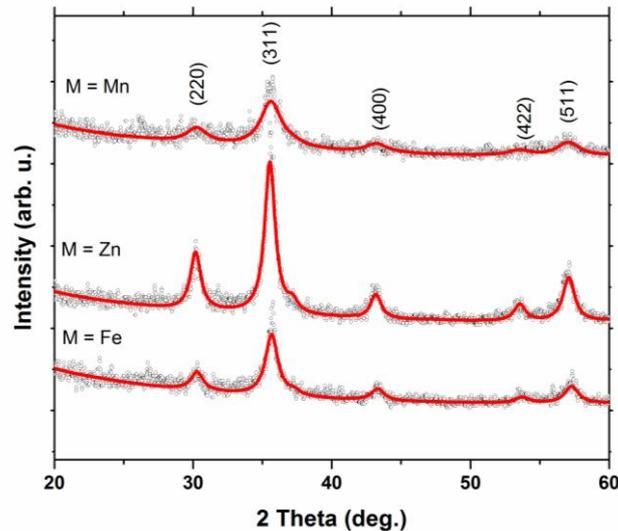


Figure 1. XRD patterns of the M-ferrites [M = Fe; Zn; Mn] from iron sand

The crystallite size (D) of the prepared samples was determined by using Debye-Scherrer's formula (5).

$$D = \frac{K\lambda}{B_0 \cos \theta} \quad (5)$$

Where K is constant, B_0 is the full width at half maximum, and θ is the diffraction angle. From the calculation, as shown in Table 1, the samples have the crystallite in nanometric size ranging from about 5.1 to 8.7 nm. Remarkably, the crystallite size of the M-ferrite particles in this work was smaller than that of M-ferrites produced by a combustion method [1]. Therefore, it can be concluded that the combined method of sonochemical and coprecipitation approaches in this work was able to prepare the M-ferrite particles from natural iron sand in a single phase in a nanometric size.

Table 1. Results of Rietveld refinement of the M-ferrites [M = Fe; Zn; Mn] XRD patterns

Sample	M = Fe	M = Zn	M = Mn
Lattice parameter (nm)	0.837	0.839	0.842
GoF	0.6	0.6	0.6
R_p	14.0	14.7	14.3
R_{wp}	19.8	19.1	19.7
D (nm)	8.7	10.3	5.1

The particle size of the prepared samples was also confirmed by the TEM characterizations as presented in Figure 2. Based on the figure, it can be seen that both of $FeFe_2O_4$ and $ZnFe_2O_4$ have an

average particle size below 100 nm. The TEM images show that the magnetic nanoparticles tended to form spherical-particle agglomerations. Quantitatively, the ZnFe_2O_4 average particle size corresponded to the XRD data analysis more than that of FeFe_2O_4 . Further analysis in studying the functional groups of the prepared samples will be discussed in the following section.

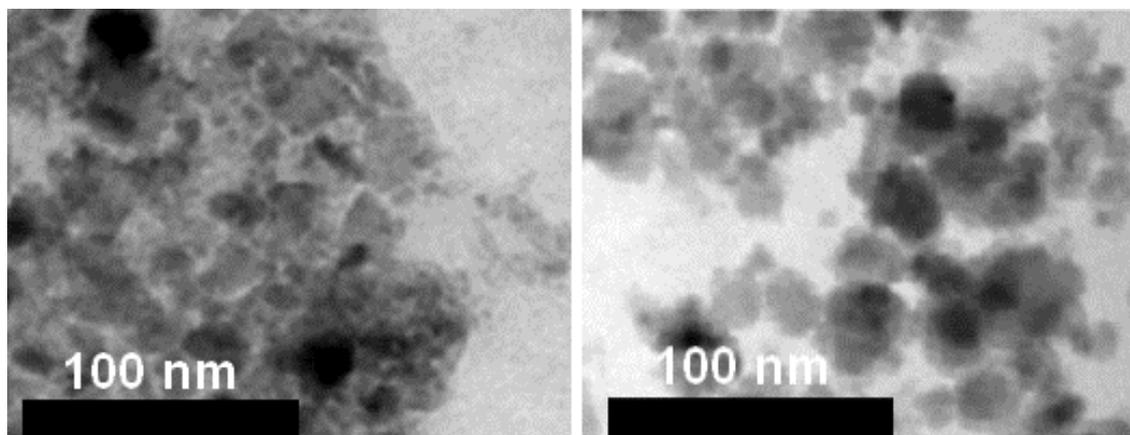


Figure 2. TEM images of the M-ferrites from iron sand (the left picture for M = Fe and the right one for M = Zn)

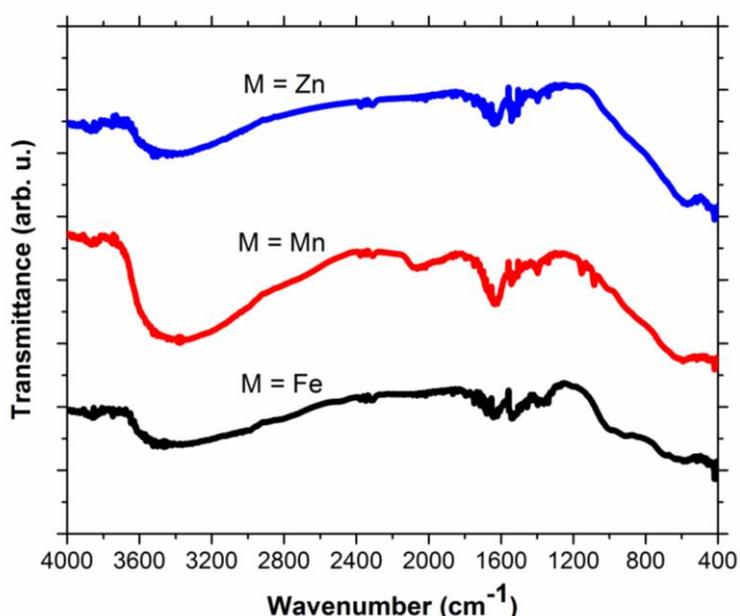


Figure 3. FTIR spectra of the M-ferrites [M = Fe; Zn; Mn] from iron sand

Figure 3 presents the FTIR spectra of the prepared M-ferrite nanoparticles in the electromagnetic waves ranging from 4000 to 400 cm^{-1} . Based on the quantitative analysis, there are several peaks of about 420-590, 1640, and 3420 cm^{-1} . The OH group of waters absorbed in the samples can be represented at the wavenumber of around 3420 cm^{-1} . Furthermore, the vibration of Metal-O bonds both in the octahedral and tetrahedral sites are described by the peaks in the range of 420 – 590 cm^{-1} . These results are in good agreement with the FTIR data of the ferrite systems that have a general spectrum at the frequency of about 400-600 cm^{-1} [15]. Additionally, another group pointed out that the vibration at around 1640 cm^{-1} was contributed by the O-H bending [16]. Therefore, these spectra

became alternative evidence that the M-ferrite nanoparticles were successfully prepared from iron sand using a coprecipitation-sonochemical approach.

The magnetic properties of the M-ferrite [M = Fe; Zn; Mn] nanoparticles are presented in Figure 4. The figure represents the magnetization (M - H) curve by varying the external magnetic field from -1 to 1 T. Qualitatively, all of the samples have an S-shaped hysteresis curve indicating that the prepared M-ferrite nanoparticles performed a superparamagnetic behavior. However, in order to ensure that the prepared samples in this work present a superparamagnetic character, it is still necessary to conduct further research by FC-ZFC experiment. Further quantitative analysis showed that the saturation magnetization (M_s) values of the M-ferrite nanoparticles for M = e, Zn, and Mn are of about 42.1, 29.8, and 17.4 emu/g, respectively. Based on the theoretical calculation, because Mn^{2+} has a higher magnetic moment ($5 \mu_B$) than that of Fe^{2+} ($4 \mu_B$) and Zn^{2+} ($0 \mu_B$), the Mn-ferrite particle should have the largest net magnetic moment among the others [17]. However, based on the experimental results, the Mn-ferrite particle has the smallest saturation magnetization among the others. These phenomena can be explained by the effect of the particle size of the M-ferrite nanoparticles where the Mn-ferrite particle has the smallest size according to the XRD data analysis. Another work reported that the magnetization saturation of ferrite nanoparticles decreased along with the reducing particle size [18]. Furthermore, Taufiq *et al.* reported that the magnetic properties of the ferrite nanoparticles, as well as their magnetization saturation and blocking temperature, are contributed not only by the metallic ions compositions, but also by the primary and secondary particles, cluster, and fractal dimension [3]. Therefore, the magnetization saturation of the M-ferrite particles in this experiment is contributed not only by the type of M ions but also by the particle size. For final remark, after successfully fabricating the M-ferrite nanoparticles from iron sand via the combined methods, it is also essential to conduct a further experiment by utilizing these ferrites for advanced applications as well as for sensors, for antibacterial systems, and as radar absorbing materials.

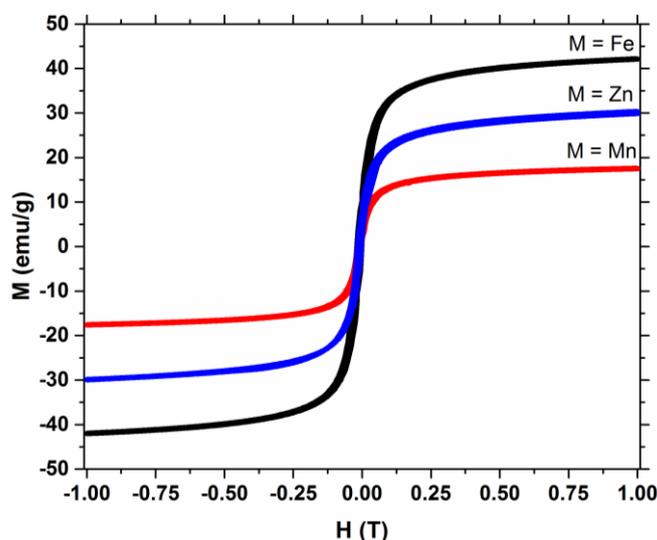


Figure 4. Magnetization curves of the M-Ferrites [M = Fe; Zn; Mn] from iron sand

4. Conclusion

The iron sand was utilized as a raw precursor to prepare the spinel M-ferrite [M = Fe; Zn; Mn] nanoparticles via a combined coprecipitation-sonochemical approach. In this work, all prepared samples formed a single phase with the spinel cubic structure. The M-ferrite particles formed in nanometric size and tended to agglomerate. The lattice parameter of the M-ferrite nanoparticles varied

with M types with the largest value for M = Mn originated from the Mn²⁺ ionic radii. The saturation magnetization value of the M-ferrite nanoparticles was contributed by the M ion and particle size.

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Acknowledgements

The authors appreciate Kemenristekdikti, Republic of Indonesia, in supporting “research grand” for AT 2016-2017.