

Synthesis and Characterization of $Zn_xMn_{1-x}Fe_2O_4$ Nanoparticles by a Reverse Micelle Process

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ABSTRACT

The preparation of $Zn_xMn_{1-x}Fe_2O_4$ nanoparticles in an Igepal CO-520-cyclohexane water reverse micelle solution has been studied. The transmission electron microscopy and X-ray diffraction pattern analyses revealed the resulting particles to be $Zn_xMn_{1-x}Fe_2O_4$. The average size and distribution of the synthesized particles calcined at 500°C for 5 h were in the range of 10 to 20 nm and broad, respectively. The phase of the synthesized particles was crystalline, the magnetic behavior of the synthesized particles was ferromagnetic. The effect of the synthesis parameters, such as the molar ratio of water to surfactant and calcination temperature, is discussed.

Key words : $Zn_xMn_{1-x}Fe_2O_4$ nanoparticles, Reverse micelle process

1. Introduction

Ferrites are important magnetic materials, and are widely used in many electronic and magnetic applications, such as in transformers, choke coils, high frequency applications, data storage, noise filters and recording heads, due to their high magnetic permeabilities and low magnetic losses. Recently, the magnetic carrier technology (MCT) was developed using a magnetic bead coated with bioactive materials to selective extraction of biological components or to deliver medicine to the intended body parts.¹⁾ The magnetic properties of the nanosized ferrites are entirely different from those of their bulk counterparts, such as the superparamagnetic behavior and associated properties. Nanosized ferrites with a uniform particle size and a narrow size distribution are desirable for a variety of applications including targeted drug delivery, ferrofluids, medical imaging, other biomedical applications, magnetic data storage, etc.²⁻⁶⁾ With the rapid development of electronic applications focusing on miniaturization, lightweight applications, integration, and multifunctionality, the demand for MnZn ferrites, which are applied as core materials for transformers in switching mode power supplies (SMPS) and DC/DC converters, are increasing. This development requires MnZn ferrites to maintain a low power loss (P_{CV}), high initial permeability (μ_i), large magnetic induction (Bs) and high electrical resistivity (ρ).⁷⁾ The present studies on this ferrite system focus on the production of nanosized materials at very low temperatures, so that the nanosized material

produced can be sintered at relatively lower temperatures; compared with the high temperatures required for materials synthesized by the conventional ceramic method. Using low temperatures makes it easier to obtain better dielectric properties, high performance parameters, and improved magnetic and related properties,^{8,9)} for such materials. Better sinterability at low temperatures is desired in terms of saving energy as well as minimizing the zinc loss that occurs during high temperature sintering. The Mn-Zn ferrite is a mixed spinel in which the tetrahedral (A) sites are occupied by Zn^{2+} and Fe^{3+} ions, and the octahedral (B) sites are occupied by Mn^{2+} and Fe^{3+} ions in the spinel formula AB_2O_4 . The distribution of the different ions in the tetrahedral and octahedral sites is different when the ferrite is synthesized at low temperatures and when the particles are nanosized.¹⁰⁾ Unusual magnetic behaviors and improved properties can be expected after processing these nanosized materials. Many different methods of producing nanosized ferrite powders are described in the literature such as, hydrothermal processing, glycol-thermal processing, Sol-Gel processing and ion exchange resin manufacture methods.¹¹⁻¹⁴⁾ Compared with other methods, the reverse micelle method is one of the most promising wet chemistry syntheses. This method provides a favorable microenvironment to control the chemical reaction. Thus, in this method, the reaction rate can be easily controlled, compared with other methods, and a narrow size distribution of nanoparticles was obtained.¹⁵⁾ Reverse micelle solutions are transparent, isotropic, thermodynamically stable water-in-oil microemulsions in which the aqueous phase is dispersed as nanosized droplets surrounded by a monolayer of molecules in the continuous polar organic phase.¹⁶⁾ The surfactant stabilized water pools provide a microenvironment for the preparation of ultrafine particles by exchanging their contents via the

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fusionredispersion process and by preventing the excess aggregation of particles.^{17,18)} Therefore, the particles obtained in such a medium are very fine and monodispersed. The objective of this study is to prepare the nanosized $Zn_xMn_{1-x}Fe_2O_4$ powders with superparamagnetic property by reverse micelle method and to investigate the effects of the processing conditions on the formation, morphology and phase of the powders.

2. Experimental procedures

$Zn_xMn_{1-x}Fe_2O_4$ precursors were precipitated from cyclohexane (Sigma-Aldrich, HPLC grades), poly(oxyethylene) nonylphenyl ether (Aldrich Chemical Co. LTD), generally known as Igepal CO 520 (Aldrich Chemical, 98% used without further purification), and aqueous solutions of 1.4M $Fe(NO_3)_3 \cdot 9H_2O$, 1.4M $Zn(NO_3)_2 \cdot 6H_2O$ and 1.4M $Mn(NO_3)_2 \cdot 6H_2O$ (Aldrich Chemical, 99.9%). A microemulsion with a total volume of 100 ml was prepared at ambient temperature in a 250 ml vial with rapid stirring. The microemulsions were comprised of 20.05 g of Igepal CO 520, 50 ml of cyclohexane, 3.25–6.5 ml of 10^{-1} M mixed aqueous solution ($X=0.4$), deionized water and 0.75–1.5 ml of NH_4OH . The average size of the synthesized powders was controlled by the $R=[water]/[surfactant]$ ratio. The microemulsion was mixed rapidly, and then equilibrated for 5 min. The reverse micelles were prepared from a nonionic surfactant Igepal CO-520. The microemulsion was then centrifuged to extract the particles, which were subsequently washed with ethanol to remove any residual surfactant and water. After drying at $80^\circ C$ for 12 h and calcinations at $500^\circ C$ for 5 h in air due to the excess temperature, MnO_2 could be observed. The structure, size, and morphology of the resulting particles were examined using a transmission electron microscopy (TEM). The recovered powders were analyzed for phase composition using X-ray diffraction and the magnetic properties of the powder were measured with vibrating sample magnetometer (VSM) at 298 K.

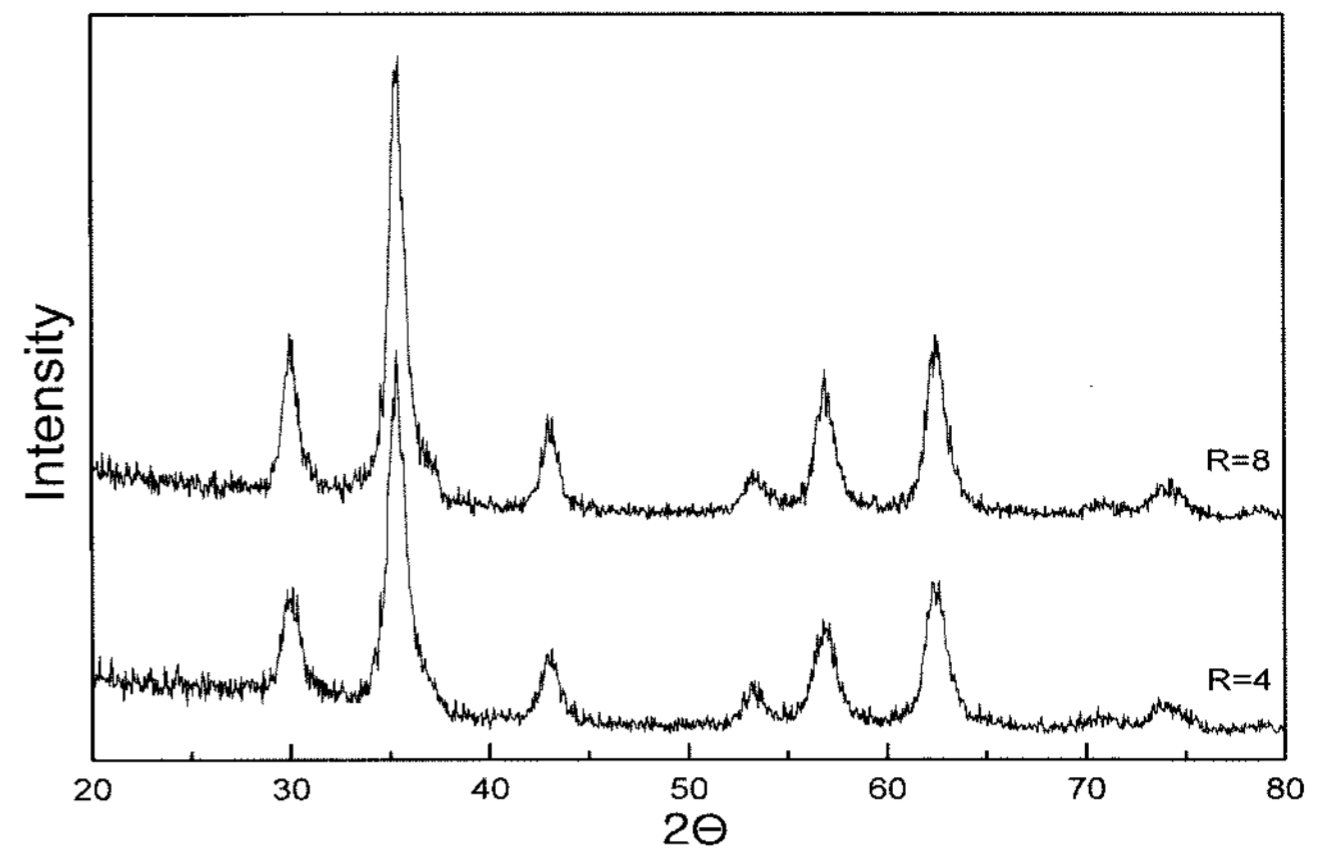


Fig. 1. X-ray diffraction patterns of the synthesized $Zn_xMn_{1-x}Fe_2O_4$ powder calcinations at $500^\circ C$ for 5 h as a function of R (water/surfactant molar ratio), $x=0.4$.

3. Results and discussion

Ternary systems of Cyclohexane/Igepal CO 520/water offer certain advantages: they are spheroidal and monodisperse aggregates where water is readily solubilized in the polar core, forming a 'water pool' that is characterized by the ratio of water to surfactant concentration. Another important property of reverse micelles its dynamic character; the water pools can exchange contents through a collision process. The aggregation and self-assembly of the oil/surfactant/water species is complex, and very little is known about the cluster growth and final nanostructure as a function of the synthesis conditions. The molar ratio of water to surfactant can determine the size of the microemulsion water core.¹⁹⁾ Therefore, the diameter of the nanoparticles in the microemulsion can be controlled through the water/surfactant molar ratio(R) and Zn molar ratio($X=0.4$) at an aqueous solution value. In the present study, $x=0.4$ was chosen because the magnetic moment decreased as the concentration increased to $x=0.5$ due to lattice perfection,

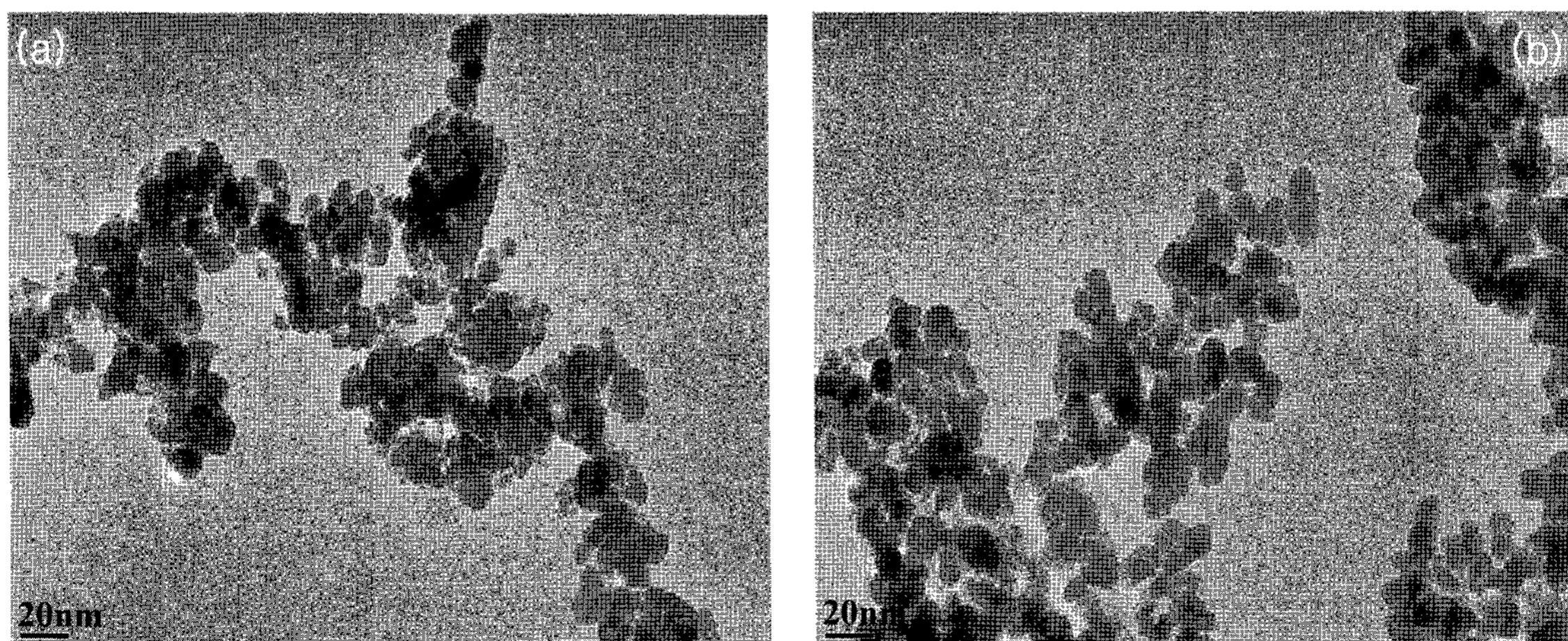


Fig. 2. TEM micrographs of the synthesized $Zn_xMn_{1-x}Fe_2O_4$ nanoparticles calcined at $500^\circ C$ for 5 h by a reverse micelle process: (a) $R=4$ and (b) $R=8$ ($x=0.4$).

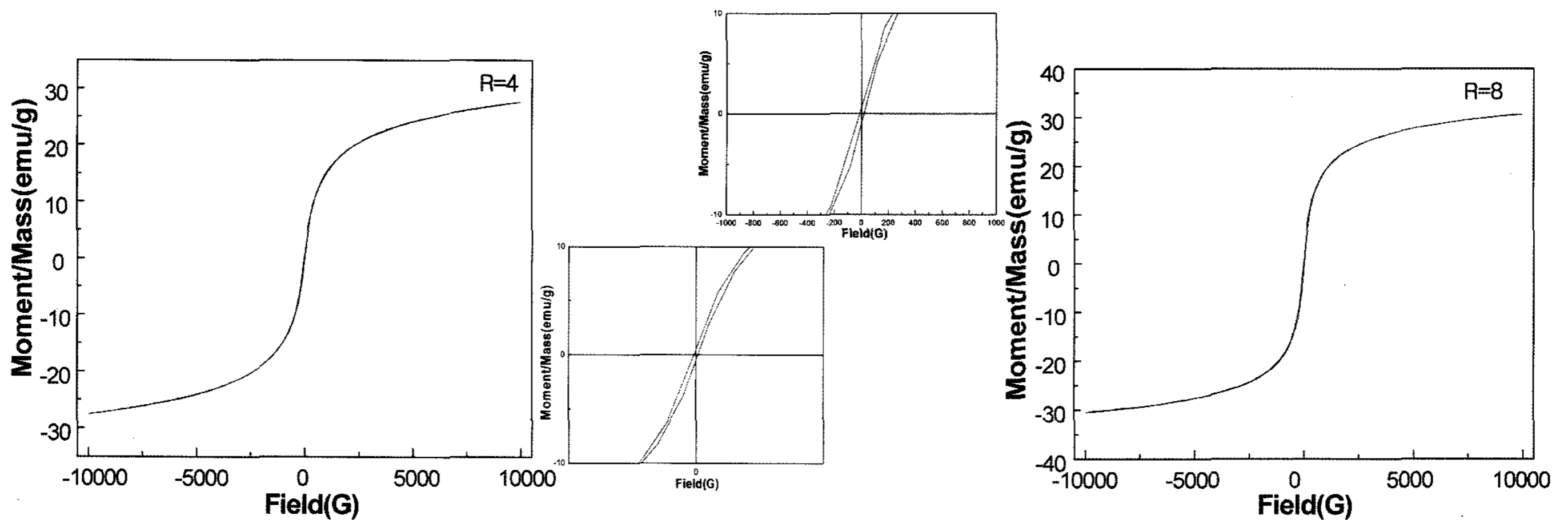


Fig. 3. Magnetic properties of the synthesized $Zn_xMn_{1-x}Fe_2O_4$ powder calcinations at $500^\circ C$ for 5 h as a function of R (water/surfactant molar ratio) $x=0.4$.

which is caused by an increased number of Zn ions on the A site. As result of this as the interaction increases with the spin of the B site due to the magnetic moment of the A site being weak, the magnetic moment is decreased resulting in the semi-balance ingredient being grown.²⁰⁾ Fig. 1 shows the XRD patterns of the synthesized $Zn_xMn_{1-x}Fe_2O_4$ nanoparticles with calcinations at $500^\circ C$ for 5 h as a function of R ($x=4$). The nanocrystalline $Zn_xMn_{1-x}Fe_2O_4$ ferrites have a spinel-type FCC structure. It is clearly seen that with an increasing R, all XRD peaks become sharper; this is an indication of the increase in the particle size. The variation of the particle size, as a function of R(water/surfactant molar ratio), is shown in Fig. 2. which shows the transmission electron microscopy of the synthesized $Zn_xMn_{1-x}Fe_2O_4$ particles. It has been shown that the average size of the synthesized powder are approximately 10–20 nm and the synthesized $Zn_xMn_{1-x}Fe_2O_4$ particle size and distribution increased from 4 to 8 with increased R. Fig. 3 shows the magnetic properties of the $Zn_xMn_{1-x}Fe_2O_4$ particles as a function of R. From the VSM analysis, it can be seen that the synthesized nanosized crystalline powder exhibits superparamagnetic properties. It is also clearly seen that the magnetic moment increased with an increased R (4 to 8), and the saturation magnetization of the synthesized $Zn_xMn_{1-x}Fe_2O_4$ powders were below 30 (emu/g). It also possible that the magnetic nanoparticles could be applicable for drug delivery as nanoparticulate magnetic carriers.

4. Conclusion

Nanosized $Zn_xMn_{1-x}Fe_2O_4$ powders were prepared using the reverse micelle process. The water/surfactant molar ratio at an aqueous solution value influenced the average size and distribution of the synthesized particles. The average size and size distribution of the synthesized particles were approximately 10–20 nm and broad, respectively. The reverse micelle synthesis of the $Zn_xMn_{1-x}Fe_2O_4$ powders yields a nanosized crystalline powder exhibiting superpara-

magnetic character. The saturation magnetization of synthesized the $Zn_xMn_{1-x}Fe_2O_4$ powders was below 30 (emu/g). It is possible for the synthesized powder to be used as magnetic nanoparticles for drug delivery using a nanoparticulate magnetic carrier. If the water/surfactant molar ratio and the mixture ratio of the aqueous solutions (Zn concentration) are carefully controlled, it is possible to control the average size, crystalline phase, and magnetic property of the synthesized powders.

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