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FABRICATION AND MAGNETIC PROPERTIES OF $\text{Mn}_{1-x}\text{Zn}_x\text{Fe}_2\text{O}_4$ ($0 \leq x \leq 0.8$) NANOPARTICLES

PHAM HOAI LINH, TRAN DANG THANH, DO HUNG MANH,
NGUYEN CHI THUAN, LE VAN HONG, AND NGUYEN XUAN PHUC

*Institute of Materials Science, VAST
18 Hoang Quoc Viet, Hanoi Vietnam*

Abstract. *In this paper, we report results on the fabrication and magnetic properties of spinel ferrite $\text{Mn}_{1-x}\text{Zn}_x\text{Fe}_2\text{O}_4$ ($0 \leq x \leq 0.8$) nanoparticles. The nanoparticles were synthesized by a co-precipitation method. The effects of substituting Zn for Mn on the magnetic properties and particles size were focused. It was found that the phase-formation temperature is 90°C and the average particle size decreases from 40 nm to 10 nm when increased Zn concentration from zero to 0.8. The Curie temperature T_C strongly decreases from 585 K ($x = 0$) to 320 K ($x = 0.8$) concomitantly with a decrease of the saturation magnetization M_S . With a T_C of 320 K and M_S of 17 emu/g, the $x=0.8$ sample could be a promising candidate for some biomedical applications.*

I. INTRODUCTION

In recent years, spinel ferrite nanoparticles have attracted great interests of researchers because of their promising application in several fields such as ferrofluid technology, information storage system, medical diagnostics, etc. Among spinel ferrite materials, $\text{Mn}_{1-x}\text{Zn}_x\text{Fe}_2\text{O}_4$ (MnZn ferrite) has the structure and magnetic properties that strongly depends on the ratio of Mn^{2+} to Zn^{2+} . $\text{Mn}_{1-x}\text{Zn}_x\text{Fe}_2\text{O}_4$ has a mixed spinel structure, in which Mn^{2+} , Zn^{2+} , and Fe^{3+} cations are distributed in tetrahedral and octahedral sites. In most cases, the quantity of Mn^{2+} ions predominate over Zn^{2+} ions in crystal and Mn^{2+} ions occupy most the octahedral sites that produce the inverse spinel structure. Conversely, Zn^{2+} ions predominate over Mn^{2+} ions and prefer to hold the tetrahedral position which results in a normal spinel structure [1]. Due to these special structures, MnZn ferrite particles with some of properties such as high permeability, high saturation magnetization, low core loss that have been intensively investigated for various applications such as transformer [2], electromagnetic interference [3], asymmetric digital subscriber line [4]. In addition, $\text{Mn}_{1-x}\text{Zn}_x\text{Fe}_2\text{O}_4$ nanoparticles, with stable magnetization and low Curie temperature, have the promising capability for biomedical applications and cancer treatments [5].

$\text{Mn}_{1-x}\text{Zn}_x\text{Fe}_2\text{O}_4$ nanoparticles can be prepared using various preparation techniques such as high-energy ball milling [6], micro-emulsion [7], hydro-thermal [8], co-precipitation [9], sol-gel [10], etc. However, the co-precipitation method allows preparing particles of small size and high surface reactivity, yielding an ability to effectively adsorb ions and surfactants, necessary for the formation of stable colloidal suspension (ferrofluid). Based

on this reason, we chose the co-precipitation method to synthesize $\text{Mn}_{1-x}\text{Zn}_x\text{Fe}_2\text{O}_4$ ($x = 0-0.8$) nanoparticles. Aiming to the application of the magnetic heating effect, we focus on studying the effect of Zn^{2+} substitution on the structure and magnetic properties of $\text{Mn}_{1-x}\text{Zn}_x\text{Fe}_2\text{O}_4$ nanoparticles.

II. EXPERIMENT

$\text{Mn}_{1-x}\text{Zn}_x\text{Fe}_2\text{O}_4$ ($x = 0 - 0.8$) fine particles were prepared by the chemical co-precipitation method. Aqueous solution of FeCl_3 , MnCl_2 , and ZnCl_2 in their respective stoichiometry were mixed and kept at 90°C . The molar ratio of Mn^{2+} and Zn^{2+} ions to Fe^{3+} ions of 0.5 was nominally taken for different Zn^{2+} substitution concentrations. The mixed solution was then boiled together with a solution of NaOH for 2 hours. The precipitation and formation of nanoferrites took place by a conversion of the metal salts into hydroxides and that, in turn, immediately transformed into ferrites. During the reactions, magnetic-stirring speed was kept at 1000 round/min. After that, obtained nanoparticles were separated and washed several times with distilled water and then with acetone. Finally, the products were dried at 60°C for 2 hours.

The structural and morphological examinations were carried out by using an x-ray diffractometer D5000 of SEMIEN and a field-emission scanning electron microscope S4800 of Hitachi Company (FESEM). Magnetic properties were measured by a vibrating sample magnetometer (VSM).

III. RESULT AND DISCUSSION

Fig. 1 shows the XRD patterns for the $\text{Mn}_{1-x}\text{Zn}_x\text{Fe}_2\text{O}_4$ samples. It is clear that all the samples are single phase of a spinel structure without any diffraction peaks corresponding to any additional phase. A systematic shift and widening of the peaks give a clear evidence for the substitution effect of Zn for Mn in the crystal structure and also the decrease of particle size with increasing Zn content.

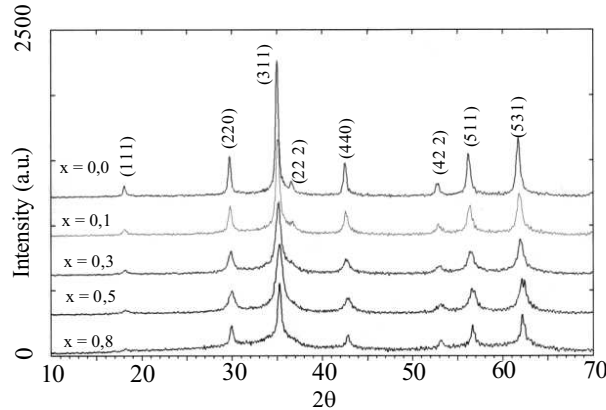


Fig. 1. XRD patterns for the $\text{Mn}_{1-x}\text{Zn}_x\text{Fe}_2\text{O}_4$ samples

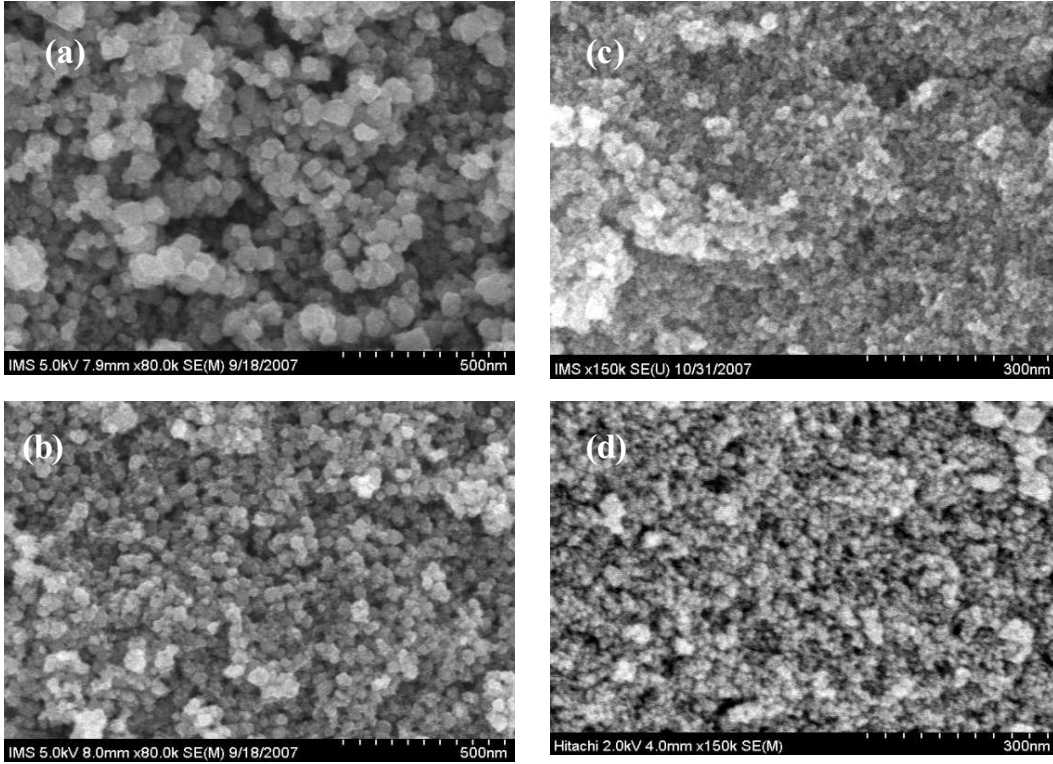


Fig. 2. The FESEM images of the samples (a) $x = 0$, (b) $x = 0.1$, (c) $x = 0.5$, (d) $x = 0.8$

The FESEM images shown in Fig. 2 indicate that average size of the $\text{Mn}_{1-x}\text{Zn}_x\text{Fe}_2\text{O}_4$ particles decreases from 40 nm to 10 nm as the Zn^{2+} content increases from $x = 0$ to $x = 0.8$. This result can be explained as following: since the diameter of Mn^{2+} ion (0.93 \AA) is larger than that of Zn^{2+} (0.74 \AA), the substitution of Zn^{2+} for Mn^{2+} ions in the octahedral sites causes a lattice distortion and slows down the crystallization process. In addition increasing the presence of Zn^{2+} ions in the crystal lattice would lead to an increase of the surface tension of particles and therefore hinders their growth. This result is generally in agreement with the XRD patterns, except for the sample of $x = 0.8$ where the spectral peaks are quite narrow but the obtained particle size by FESEM images is smallest. We suppose that it is unclear result and needs to study in details in the future.

Fig. 3 shows the magnetization curves measured at 300 K for all the samples. While the bulk Mn ferrite exhibits a M_S of 80 emu/g, the nanoparticles of the same composition have $M_S = 53$ emu/g. There are many factors that contribute in reducing the M_S of nanoparticles such as the existence of a dead surface spin-disordered layer forming

a core-shell structure, the paramagnetism effect of small particles, the disordered cation distribution, and distribution of particle size, etc. [13].

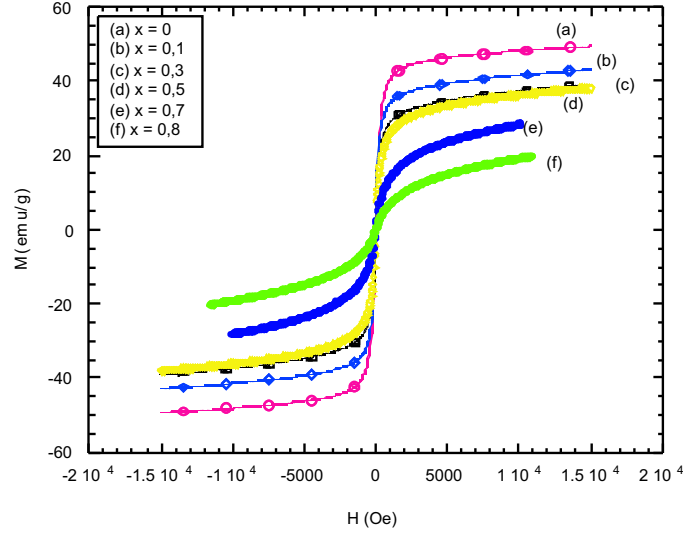


Fig. 3. Magnetization curves at 300K of the samples $Mn_{1-x}Zn_xFe_2O_4$ ($x = 0 \div 0.8$)

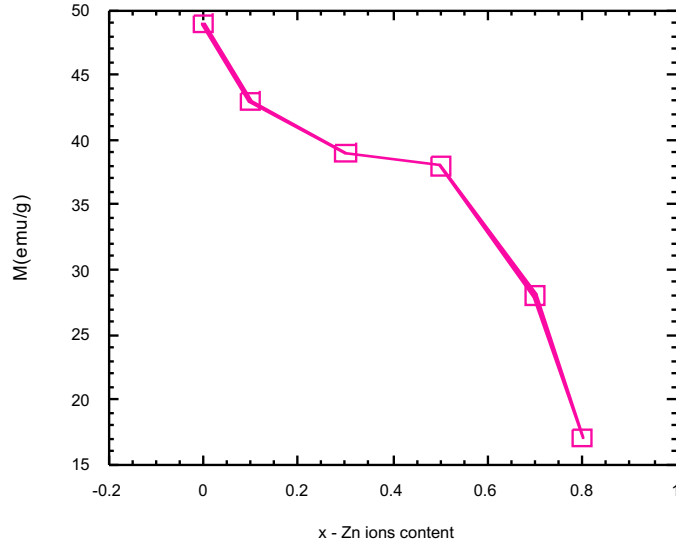


Fig. 4. The dependence of the saturation magnetization on x of the $Mn_{1-x}Zn_xFe_2O_4$

The measured results also show that the saturation magnetization is highest for the $x = 0$ sample with $M_S = 49$ emu/g and decreases to 17 emu/g with increasing Zn^{2+} concentration to $x = 0.8$. This result is in agreement with the results in Ref. 13, where

Rath *et. al.* reported that M_S of the $Mn_{1-x}Zn_xFe_2O_4$ nanoparticles reduces from 50 emu/g to 20 emu/g with increasing Zn^{2+} concentration from $x = 0$ to $x = 1$.

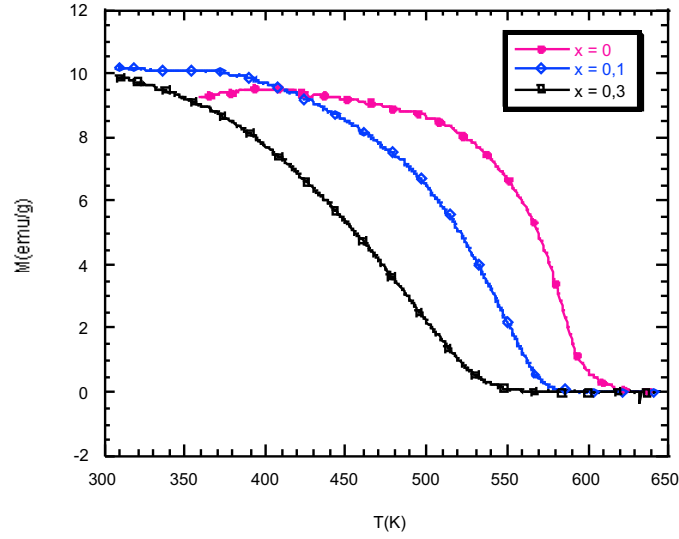


Fig. 5. $M(T)$ of the $Mn_{1-x}Zn_xFe_2O_4$ samples ($x = 0, x = 0.1, x = 0.3$)

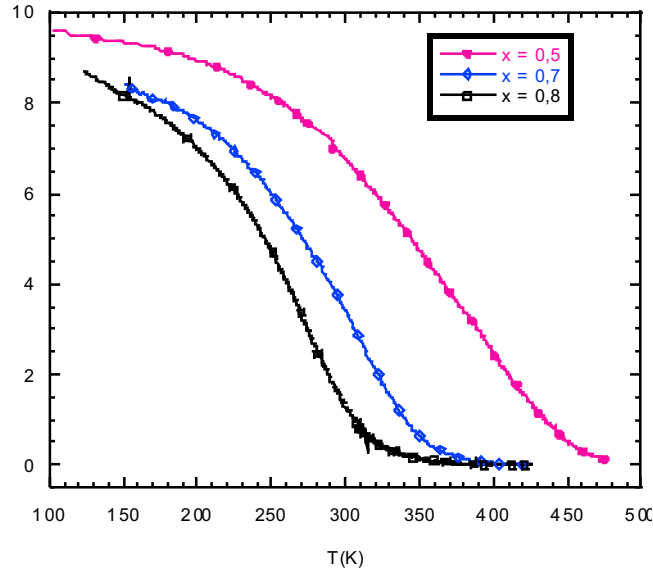


Fig. 6. $M(T)$ of the $Mn_{1-x}Zn_xFe_2O_4$ samples ($x = 0.5, x = 0.7, x = 0.8$)

The Curie temperature estimated from the temperature-dependent magnetization $M(T)$ curves displayed in figures 5 and 6 for the $Mn_{1-x}Zn_xFe_2O_4$ samples measured at

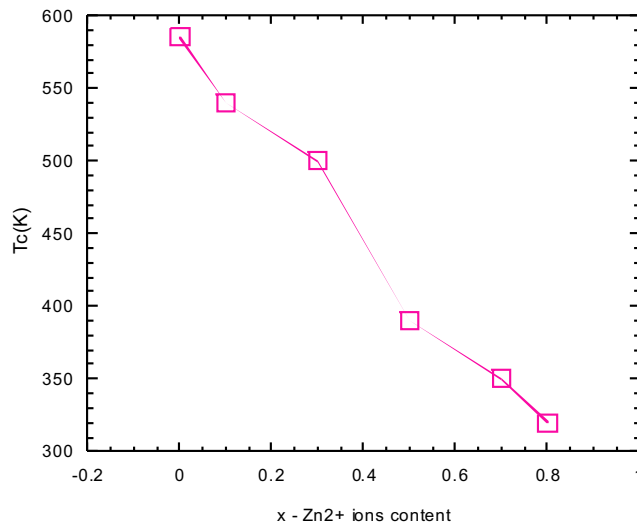


Fig. 7. Curie temperature T_C versus x of the $Mn_{1-x}Zn_xFe_2O_4$

100 Oe exhibits a strong decrease with increasing Zn^{2+} concentration. The substitution of Mn^{2+} by nonmagnetic Zn^{2+} ions, which has a preferential A-site occupancy, not only dilutes the magnetic sublattices but also causes a reduction of the super-exchange interaction between A-site and B-site, resulting in the decrease in T_C . Other factors which contribute to the decrease in T_C may be due to the paramagnetism effect of small particles. Comparing with the Curie temperature of the bulk ($T_C = 585$ K) [14], we find that T_C of nanoparticles is lower. However, for $x = 0$ with particle size of about 40 nm, T_C of the nanoparticle system is very close to that of the bulk sample. Hence, it is plausible that T_C is not affected by the size effect for MnZn ferrite nanoparticles having diameters greater than 40 nm. Remarkably, with $T_C = 320$ K and a rather high saturation magnetization $M_S = 17$ emu/g, the $Mn_{0.2}Zn_{0.8}Fe_2O_4$ nanoparticles are suitable for the magnetic heating technique used in cancer treatments.

IV. CONCLUSION

Single-phase spinel ferrite $Mn_{1-x}Zn_xFe_2O_4$ nanoparticles with the average size from 10 to 40 nm were successfully synthesized by co-precipitation processes. The obtained results show that the magnetic properties of material were strongly influenced by the substitution of Zn^{2+} for Mn^{2+} ions. The saturation magnetization decreases from 49 emu/g to 17 emu/g and the Curie temperature decreases from 585 K to 320 K with increasing Zn^{2+} concentration from $x = 0$ to $x = 0.8$. This result would open a promising route for synthesizing the magnetic nanoparticles used in biomedical applications.

V. ACKNOWLEDGMENTS

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