

Composition and Magnetic Properties of Zinc Ferrite Nanoparticles Prepared by the Co-Precipitation Method at Different Temperatures

R. Raeisi Shahraki*, S.A. Seyyed Ebrahimi** and M. Ebrahimi***

Center of Excellence for Magnetic Materials, School of Metallurgy and Materials,
Faculty of Engineering, University of Tehran, Tehran, P. O. Box: 11155-4563, Iran

*Reisi.r@ut.ac.ir, **saseyyed@ut.ac.ir, ***ebrahimi_m@ut.ac.ir

ABSTRACT

In this work, Superparamagnetic single phase zinc ferrite nanoparticles have been prepared by coprecipitation method at 40, 60 and 80 °C without any subsequent calcination process and the effect of the reaction temperature on the composition, structural and magnetic properties of these particles have been studied. The formation of nanoparticles with different composition, microstructure, crystallite size and magnetic properties were investigated using X-ray diffractometer, field emission scanning electron microscope, Transmission electron microscope, and Vibrating sample magnetometer. The XRD patterns proved that the nanoparticles were single phase cubic spinel $ZnFe_2O_4$ with crystallite size below 10 nm. The magnetization curves presented an “S” shape hysteresis loop showing that the nanocrystalline zinc ferrites had superparamagnetic behavior. The effect of increasing reaction temperature on the magnetic properties showed that the saturation magnetization of the powders decreased with increasing the reaction temperature.

Keywords: zinc ferrite, co-precipitation, superparamagnetic, nanoparticles, magnetic properties

1 INTRODUCTION

In the past decade, semiconductor nanoparticles have been greatly interested because of their special structure, unique physical and chemical properties with various applications including electronic devices and optical devices. Spinel zinc ferrite is a p-type semiconductor with band gap 1.9 eV which has a lot of applications like magnetic materials, gas sensors, catalysts, photocatalysts, hot-gas desulfurization and absorbent materials because of its unique properties such as chemical and thermal stability. It is also well-known that the zinc ferrite has particle size dependent physical properties, especially the magnetic properties [1,2]. Bulk $ZnFe_2O_4$ has a normal spinel structure with the Zn^{2+} ions without magnetic moment in the tetrahedral sites, which makes it antiferromagnetic. However, it has been demonstrated that the both crystallite size and synthesis method can affect the magnetic properties of nanocrystalline zinc ferrite [3]. For example, the redistribution of iron and zinc cations into octahedral and

tetrahedral sites resulted in ferrimagnetic behaviour in zinc ferrite nanoparticles [4].

Several methods such as ball milling, sol-gel, coprecipitation, hydrothermal auto-combustion, reverse micelle and ultrasonic cavitation [5,6] have been used to synthesize zinc ferrite nanoparticles. In most of the above methods, they require subsequent calcination which results in particle agglomeration and crystal growth. However, the co-precipitation is well-known method to synthesis the ferrite nanoparticles at low temperatures and often without post-calcination at high temperatures. It is demonstrated that the precipitation temperature can affect the structural and physical properties of ferrite nanoparticles.

In this work, we have synthesized zinc ferrite nanoparticles via co-precipitation technique and investigated the effects of precipitation temperature on the structural and magnetic properties.

2 EXPERIMENTAL PROCEDURE

Iron (III) chloride hexahydrate ($FeCl_3 \cdot 6H_2O$), zinc (II) chloride ($ZnCl_2$), sodium hydroxide (NaOH) and acetone were analytical grade.

Zinc ferrite nanoparticles were synthesized by chemical coprecipitation method. In this procedure, 100 mL mixed aqueous solutions prepared by dissolving required weights of iron and zinc chloride with the molar ratio of Fe to Zn as 2:1, in distilled water. 50 mL aqueous solution of 1.5 M NaOH was used as the precipitating agent. Metal chloride and NaOH solutions were added drop wise from two separate burettes into a reaction vessel containing 100 mL of distilled water under magnetic stirring for obtaining uniform particle size distribution. After aging for 2h, the resultant precipitates were collected and centrifuged at 6000 rpm and then washed with distilled water and acetone for several times and finally dried in air.

In order to investigate the dependence of structural, optical and magnetic properties of zinc ferrite on the coprecipitation temperature, the reaction vessel was heated up to the desired temperature (40 - 80°C).

The purity and crystal structure of the precipitated particles was characterized by a Philips Xpert powder x-ray diffractometer with monochromatic Cu-K α radiation ($\lambda = 1.5405 \text{ \AA}$) operating at 40 kV and 30 mA at a rate of 2 degree/min. The X-ray diffraction (XRD) patterns were obtained in the 2θ range of 20-80°.

The average crystallite size and the lattice parameter of the samples were calculated by applying X-ray line broadening of (311) peak using Scherrer's formula:

$$D = (0.9 \lambda) / (\beta \cos \theta) \quad (1)$$

where D is mean crystallite size, λ is wavelength of radiated X-ray (in Å), θ is corresponded Bragg diffraction angle (in radian) and β is full width at half maximum (in radian) after correction for instrumental error.

The morphology and microstructure of the particles were observed by a Hitachi S-4160 field emission scanning electron microscope (FESEM) at 30 KV and Philips CM200 transmission electron microscope (TEM) at 200 KV. Selected area electron diffraction (SAED) pattern and energy dispersive spectrum (EDS) were also taken on TEM. A vibrating sample magnetometer (Meghnatis Daghigh kavir Kashan Co., Iran) was employed to measure magnetic properties of the samples at room temperature.

3 RESULTS AND DISCUSSION

Figure 1 shows XRD patterns of the samples synthesized at various precipitation temperatures. The XRD results indicate that the all samples prepared at low temperatures (40-80 °C) are single phase $ZnFe_2O_4$ and all diffraction peaks can be indexed to cubic spinel structure of zinc ferrite (JCPDS NO. 22-1012). The diffraction peaks become narrower and stronger with increasing of precipitation temperature from 40 °C to 80 °C, indicating an increase of crystallinity and crystallite size.

Dependence of the calculated lattice parameter and the crystallite size on the precipitation temperature is shown in Figure 2. The crystallite size of the samples is in the range of 7-10 nm which increases with the precipitation temperature, due to the rapid diffusion of cations at high temperatures. The measured lattice parameter of the samples are larger than that of the normal spinel structure of zinc ferrite ($a=8.4412 \text{ \AA}$).

The FESEM photographs of the samples synthesized at different temperatures are shown in Figure 3. As can be seen, the fine particles are agglomerated and form clusters in the all samples and particles size increases with increasing reaction temperature.

The TEM image, SAED pattern and EDAX spectrum of zinc ferrite nanoparticles precipitated at 40 °C are presented in Figure 4. It can be seen that the $ZnFe_2O_4$ nanoparticles are monodisperse and spherical with the average particle size of 7 nm. Furthermore, the ring SAED patterns are related to the diffraction of the single phase zinc ferrite with nanocrystalline structure, which is consistent with XRD results. The presence of only Zn, Fe and O elements in the EDAX spectrum indicates that the high purity nanoparticles are formed, without residual side products. The carbon and copper peaks in the EDAX spectrum are related to the TEM substrate.

Figure 5 shows the magnetization curves of $ZnFe_2O_4$ nanoparticles synthesized at different precipitation temperatures. The samples exhibit linear magnetization

with zero coercivity indicating that the zinc ferrite nanoparticles are superparamagnetic. Furthermore, the samples can not be fully saturated at 10 kOe [7].

The magnetization increase with decreasing of the precipitation temperature from 80 to 40 °C, which is related to the decreasing of the crystallite size. The increase in the magnetization with decreasing the crystallite size is due to the increase in cation inversion coefficient and hence the strength of superexchange interaction between Fe^{3+} ions in tetrahedral and octahedral sites [8].

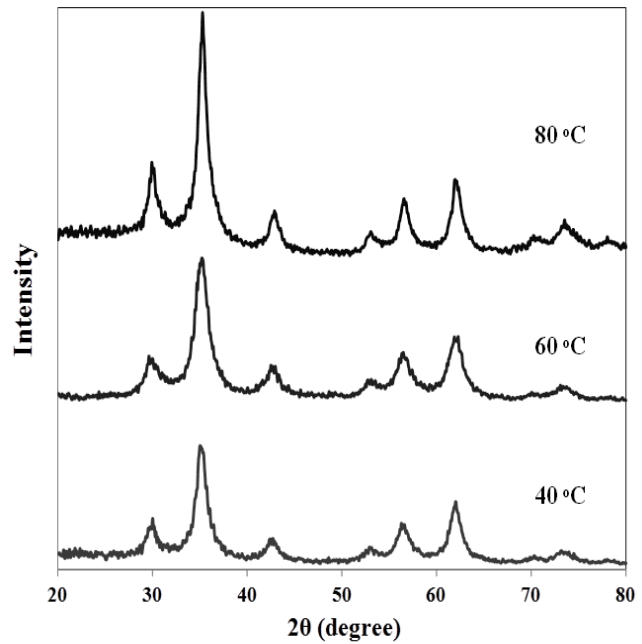


Figure 1: XRD patterns for the precipitates synthesized at different temperatures.

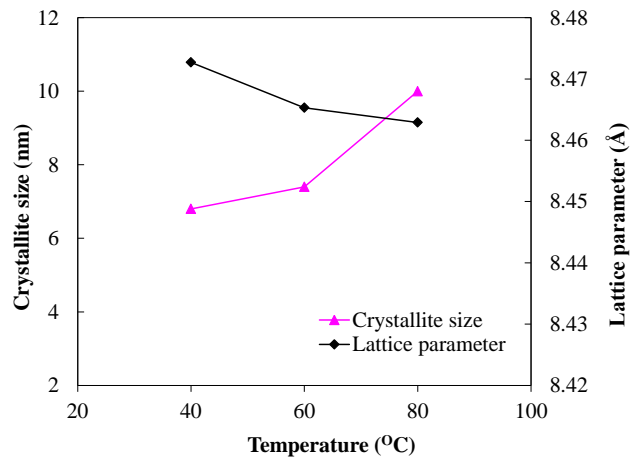


Figure 2: Dependence of crystallite size and lattice parameter on the precipitation temperature.

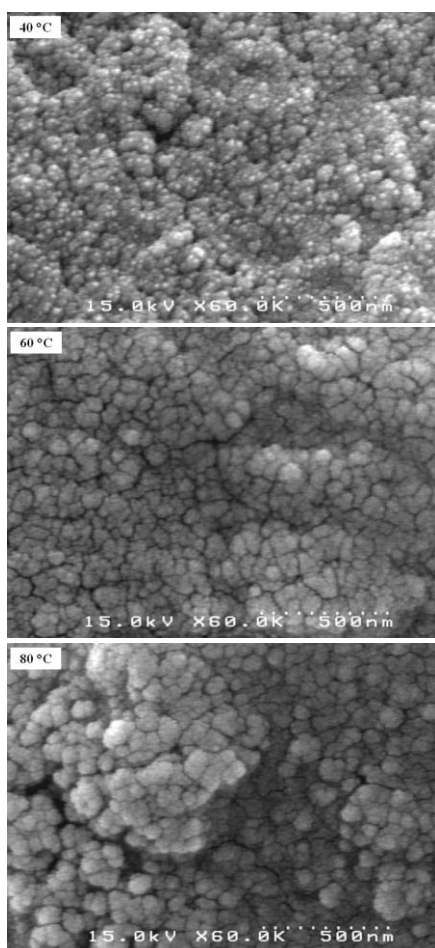


Figure 3: FESEM images of ZnFe_2O_4 synthesized at 40, 60 and 80 °C.

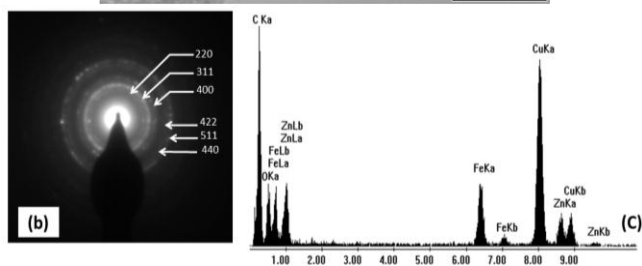
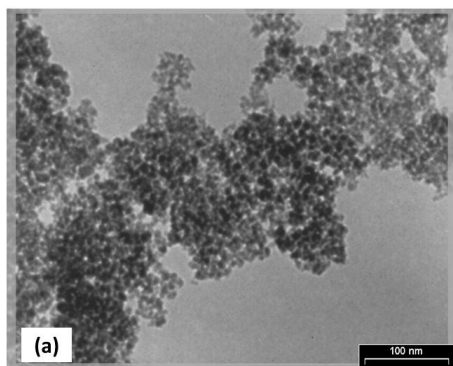


Figure 4: (a) TEM image of ZnFe_2O_4 nanoparticles (b) SAED pattern and (c) EDAX of zinc ferrite synthesized at 40 °C.

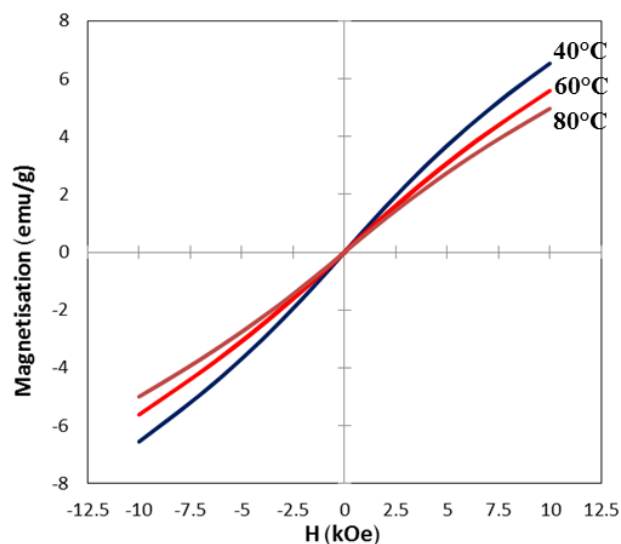


Figure 5: Room temperature hysteresis loops of ZnFe_2O_4 as a function of magnetic field.

4 CONCLUSION

Nanocrystalline zinc ferrite powders were synthesized by coprecipitation method using metal chlorides as precursors. The influence of the reaction temperature on the formation and magnetic properties of zinc ferrite nanocrystalline powders was investigated. The XRD patterns revealed that the nanoparticles were single phase zinc ferrite nanoparticles. The effect of increasing reaction temperature on the magnetic properties revealed that the saturation magnetization of the powders decreased with increasing the reaction temperature due to the decrease in cation inversion coefficient.

REFERENCES

- [1] A. Pradeep, P. Priyadharsini, G. Chandrasekaran, *Journal of Alloys and Compounds*, 509, 3917–3923 2011.
- [2] B. D. Cullity, C. D. Graham, *Introduction to magnetic material*, John Wiley & Sons, Inc., Hoboken, New Jersey, 2009.
- [3] M.R. Anantharaman, S. Jagatheesan, K.A. Malini, *Journal of Magnetism and Magnetic Materials* 189, 83–88(1998).
- [4] Na-oki Ikenaga, Yousuku Ohgaito, Hiroaki Matsushima, Toshimitsu Suzuki, *Fuel* 83, 661–669, 2004.
- [5] R. Sharma, C. J. Chen, *J Nanopart Res* 11:671–689, 2009.
- [6] Animesh Kundu, C. Upadhyay, H.C. Verma, *Physics Letters A* 311, 410–415, 2003.
- [7] G.A. El-Shobaky, A.M. Turky, N.Y. Mostafa, S.K. Mohamed, *Journal of Alloys and Compounds* 493, 415–422, 2010.
- [8] A. L. Patterson, *Physical Review* 56, 10, 1939.