

A Simple and Effective Synthesis of Nanosized ZnFe₂O₄ Particles

AVNISH KUMAR ARORA^{1*}, RITU¹ and PANKAJ KUMAR²

¹Department of Chemistry, Maharishi Markendeshwer University, Mullana-133 203, India

²Department of Chemistry, University of Petroleum and Energy Studies, Dehradun-248 007, India

*Corresponding author: Fax: +91 1731304111; E-mail: aroradcy@gmail.com

(Received: 10 September 2012;

Accepted: 24 June 2013)

AJC-13691

Nanosized spinel zinc ferrite (ZnFe₂O₄) has been synthesized by precipitation method and characterized by using XRD, TEM and magnetic measurements techniques. XRD studies show that zinc ferrite was formed as spinel ZnFe₂O₄. Magnetic measurements showed that ZnFe₂O₄ is super paramagnetic in nature at room temperature and hence can be used in magnetic devices. TEM images of as synthesized ZnFe₂O₄ show that the size of particles of ZnFe₂O₄ varied from 10-30 nm which is in good agreement of the theoretically predicted size of nanomaterials. This method is convenient, easy and effective in comparison to the known methods of the synthesis of ZnFe₂O₄ nanomaterials like ultrasonic radiation, sol-gel approach, Fe implantation, thermal decomposition of metal-surfactant complexes, colloid mill, mechanical milling.

Key Words: Nanaomaterial, TEM, Zinc ferrite, XRD analysis.

INTRODUCTION

Spinel ferrites are magnetic materials and have wide applications in magnetic devices and switching devices¹⁻³. Zinc ferrite (ZnFe₂O₄) is of interest as it has wide applications in not only to basic research in magnetism, but also has great potential in technological application, such as magnetic materials⁴⁻¹⁰, gas sensors¹¹, catalysts¹², photocatalysts¹³ and absorbent materials¹⁴⁻¹⁸. Different methods have been reported for the synthesis of ZnFe₂O₄. The zinc-doped maghemite nanoparticles were prepared using ultrasonic radiation¹⁹. Zn/Fe oxide composite nanoparticles were synthesized by basic hydrolysis of Fe²⁺ and Zn²⁺ ions in aqueous continuous phase containing gelatin. The obtained composite nanoparticles were composed of iron oxide, zinc oxide and zinc ferrite phases²⁰. The antibacterial activity of these nanoparticles was tested against *Staphylococcus aureus* and *Escherichia coli*. Ordered ZnFe₂O₄ nanotube arrays with the average outer diameter of 100 nm were prepared in porous anodic aluminum oxide template using an improved sol-gel approach²¹. Crystallographically oriented magnetic ZnFe₂O₄ nanoparticles have been synthesized by Fe implantation into ZnO and their super paramagnetic behaviour has been studied²². Mixed oxide ZnO-Fe₂O₃ has been synthesized by improved sol gel synthesis and their photocatalytic behaviour has been studied by photocatalytic degradation of potassium cyanide in aqueous dissolution. Ferromagnetic zinc ferrite nanocrystals at ambient temperature were synthesized *via* the thermal decomposition of metal-

surfactant complexes²³. Nanometer-sized zinc ferrite particles capped with a layer of surfactant has been synthesized²⁴. The effect of the surfactant capping on the grain growth of the zinc ferrite nanoparticles was also investigated. The surfactant capping effectively inhibited grain growth and it was observed that the zinc ferrite nanoparticles with a capping layer could readily be dispersed in some organic media due to their surface modification. Nanostructured semiconductor thin films of Zn-Fe₂O₃ modified with underlying layer of Fe-TiO₂ have been synthesized and studied as photoelectrode in photoelectrochemical (PEC) cell for generation of hydrogen through water splitting²⁵. Zinc ferrite (ZnFe₂O₄) photocatalysts with different crystallite sizes have been prepared using the colloid mill and hydrothermal technique and have been applied to photodecompose acid orange II azodye molecule under UV irradiation²⁶. Co_(1-x)Zn_xFe₂O₄ and Mn_(1-x)Zn_xFe₂O₄ (x = 0.1-0.5) nanoparticles are prepared by chemical co-precipitation method and their applications for the synthesis of ferrofluids have been discussed²⁷. Nanostructured zinc ferrite has been prepared by mechanical milling and change in magnetic behaviour with change in size has been discussed²⁸. In the present manuscript, synthesis of ZnFe₂O₄ nanoparticles has been reported by simple aqueous precipitation method. This method involves a simple, low cost and one step process for synthesis of ZnFe₂O₄ nanoparticles as compared to other methods of synthesis like ultrasonic radiation, sol-gel approach, thermal decomposition of metal-surfactant complexes, colloid

mill, mechanical milling *etc.* The obtained particles of ZnFe_2O_4 have size from 10-30 nm. The synthesized nanoparticles were characterized by XRD, magnetic susceptibility and TEM.

EXPERIMENTAL

All chemicals used in the experiment are analytic reagent grade. Ferric nitrate $\text{Fe}(\text{NO}_3)_3$, $\text{Zn}(\text{NO}_3)_2$ and liquor ammonia were purchased from Merck, India. Deionized water was used throughout the experiment.

Synthesis of ZnFe_2O_4 : $\text{Fe}(\text{NO}_3)_3$ and $\text{Zn}(\text{NO}_3)_2$ were taken in equal mass ratio and were dissolved in 500 mL of water. Aqueous ammonia (2 M) was added drop wise with constant stirring until the pH of the solution reached 10. The precipitates thus obtained were filtered by Buckner funnel and washed several times with distilled water. The precipitates were dried in oven at 70 °C for 24 h and were calcined at 500 °C in a muffle furnace for 5 h. Obtained material was ground and sieved through 100 mesh size sieve.

An X-ray measurement was carried out using X-ray diffractometer system Philips PW 11/90, with nickel filtered $\text{CuK}\alpha$ ($\lambda = 1.5405 \text{ \AA}$).

The crystalline size of zinc ferrite was calculated using Scherrer equation.

$$t = \frac{K\lambda}{B\cos\theta}$$

where t is the average crystallite size of the phase under investigation, K is the Scherrer constant (0.89), λ is the wave length of X-ray beam used, B is the full-width half maximum (FWHM) of diffraction (in radians) and θ is the Bragg's angle.

Transmission electron micrograph (TEM) were recorded on Hitachi H7500. The samples were dispersed in ethanol and then treated ultrasonically in order to disperse to individual particles over a gold grid.

The magnetic properties of the solid was measured at room temperature using a vibrating sample magnetometer model 155.

RESULTS AND DISCUSSION

X-Ray studies: X-Ray diffraction of synthesized ZnFe_2O_4 is shown in Fig. 1. X-Ray diffraction pattern of pure ZnFe_2O_4 indicated that zinc ferrite is present in the form of ZnFe_2O_4 (Fig. 1). In X-ray diffraction, some prominent peaks were considered and corresponding d -values were compared with the standard *i.e.*, JCPDS file No. 82-1049 (Table-1). X-Ray diffraction shows that metal oxide is pure ZnFe_2O_4 having spinel structure. Thickness of the crystals has been calculated using Scherrer's formula and it also supports the TEM observations.

TEM studies: TEM studies were carried to find out exact particle size of synthesized ZnFe_2O_4 . Fig. 2 shows the TEM image of the synthesized ZnFe_2O_4 nanoparticles. It shows that the size of the obtained nanoparticles is in the range of 10-30 nm. Most of the particles are in the range of 20-30 nm. TEM images indicate that ZnFe_2O_4 samples were all spherical particles with uniform grain size distribution.

Magnetic measurements: The magnetic measurement of ZnFe_2O_4 was carried out at room temperature and it has been observed that ZnFe_2O_4 shows super paramagnetic

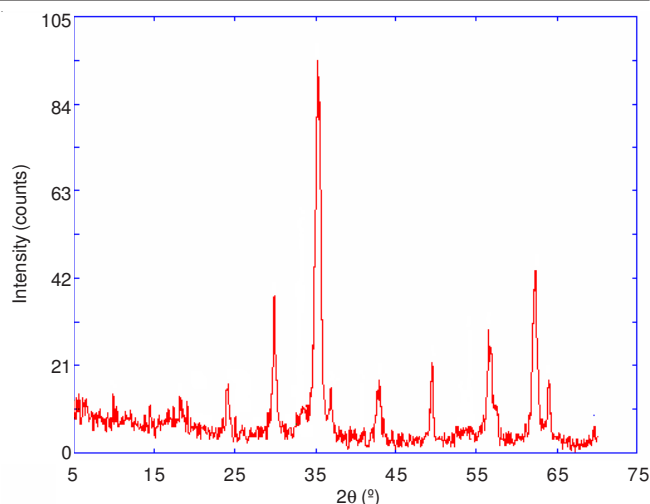


Fig. 1. XRD spectra of zinc ferrite

TABLE-1
X-RAY DIFFRACTION DATA FOR ZnFe_2O_4

S. No.	$d = \lambda/2 \sin \theta$ (Observed)	$d = \lambda/2 \sin \theta$ (Reported)	$I/I_0 \times 100$ % (Observed)	$I/I_0 \times 100$ % (Reported)
1	2.98857	2.98800	40	35
2	2.54627	2.54611	100	100
3	2.43412	2.43857	16	5
4	2.10861	2.11170	18	16
5	1.72381	1.72342	14	7
6	1.62691	1.62478	30	30
7	1.48866	1.49278	46	30
8	1.35144	1.33522	8	2

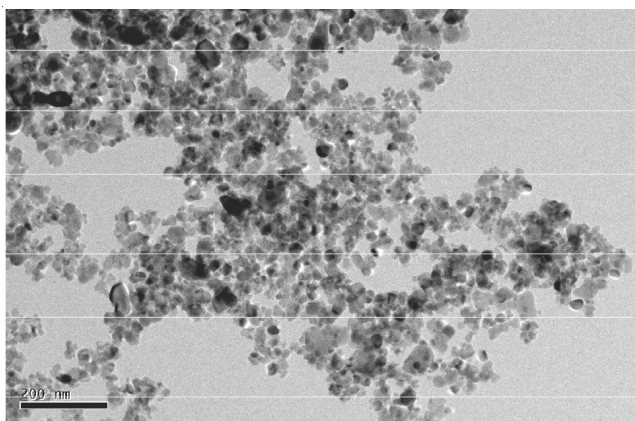
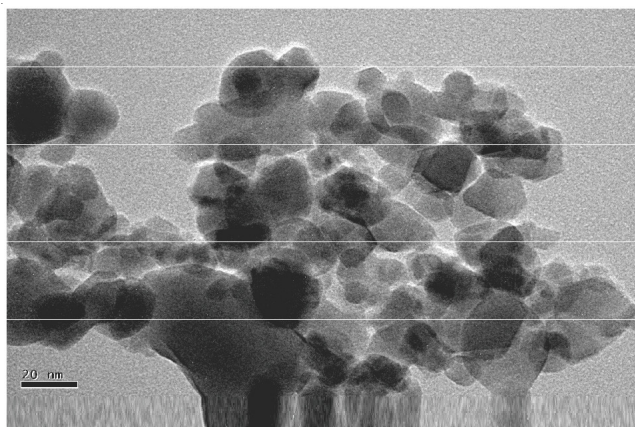


Fig. 2. TEM images of zinc ferrite particles

TABLE-2
REPORTED VALUE OF SATURATION MAGNETIZATION IN LITERATURE

Ms (emu/g)	Temp (°C)	Size	Synthesis method	Ref. Number
50	300	10-30	Precipitation	This work
38	60	4	Hydrothermal method	29
25	5	12	Ultrasound-assisted emulsion	30
53.9	5	14.8	Polyol method	31
70	3	3.7	Oil-in-water micelles	32
61.87	80	300	Hydrothermal in ammonia solution	33
11.9	2	32	Self-propagating combustion	34
37	4.2	47	Ball milling	35
22	5	8.1	Supercritical sol-gel + drying at 513 K	36
38	4.2	5-20	Hydrothermal in supercritical methanol	37
20.7	4.2	36	Ball milling	38
40.3	4.2	50	Ball milling + calcinations at 773 K	38
10	300	11	Ball milling	39
58	5	9	Ball milling	40
46.9	4.2	55	Co-precipitation at 373 K	41
26.4	5	29	Co-precipitation at 373 K + calcination	41
65.4	10	9.8	Thermal decomposition	42
56.6	300	–	Thin film pulsed lased deposition	43

behaviour at room temperature (300 K) with saturation magnetization (Ms) value 50 (Fig. 3). Previously reported values of magnetization for zinc ferrite nanoparticles prepared by various methods has been reported in Table-2. The value of magnetization ranging from 12-88 emu g⁻¹ shows that magnetization strongly depends on the synthesis method used²⁹⁻⁴³. This magnetization value at room temperature is good and comparable with methods of synthesis as thermal decomposition method (magnetization value 42 at 300 K and magnetization value 65.4 emu g⁻¹ at 10 K), ball milling (magnetization value 20.7 in at 4.2 K) and other co-precipitation routes which shows a maximum magnetization 46.9 at 4.2 K (Table-2).

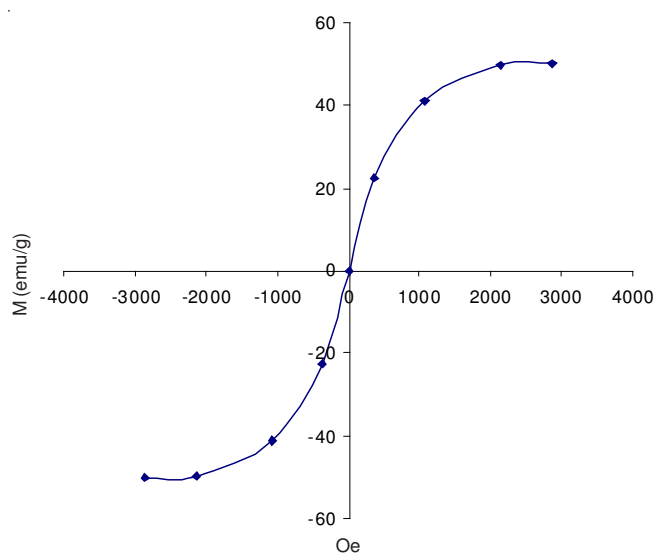


Fig. 3. Magnetic measurement of synthesized zinc ferrite particles

Conclusion

ZnFe₂O₄ nanoparticles with spinel structure are synthesized successfully by aqueous precipitation method. From TEM study it is found that particles are having average size of 10-30 nm. Magnetic measurements show that ZnFe₂O₄ is super paramagnetic in nature having saturation magnetization value 50 emu/g. This method is advantageous over existing

methods of synthesis of nanoparticles because other methods require specialized instrumentation, highly skilled labour, expensive materials and methods. Therefore, the proposed precipitation method is very promising, easy and cheap and may have extensive applications.

REFERENCES

1. M. Tsutaoka, T. Ueshima, T. Tokunaga, Nakamura and K. Hatakeyama, *J. Appl. Phys.*, **78**, 3983 (1995).
2. T. Nakamura, T. Tsutaoka and K. Hatakeyama, *J. Magnet. Magnet. Mater.*, **138**, 319 (1994).
3. R. Chantrell and G.K. Wo, *The Magnetic Properties of Fine Particles in Applied Magnetism*, Kluwer Academic Publishers, Dordrecht, The Netherlands, p. 113 (1994).
4. H. Ehrhardt, S.J. Campbell and M. Hofmann, *Scripta Mater.*, **48**, 1141 (2003).
5. S. Bid and S.K. Pradhan, *Mater. Chem. Phys.*, **82**, 27 (2003).
6. A. Kundu, C. Upadhyay and H.C. Verma, *Phys. Lett. A*, **311**, 410 (2003).
7. A.T. Pathan, M.R. Bhandare, B.K. Chougule and A.M. Shaikh, *Asian J. Chem.*, **24**, 5695 (2012).
8. F. Grasset and N. Labhsetwar, *Langmuir*, **18**, 8209 (2002).
9. H. Deng, X. Li, Q. Peng, X. Wang, J. Chen and Y. Li, *Angew. Chem. Int. Ed.*, **44**, 2782 (2005).
10. M.H. Sousa, F.A. Tourinho, J. Depeyrot, G.J. Da Silva and M.C. Lara, *J. Phys. Chem. B*, **105**, 1168 (2001).
11. X. Niu and W. Du, *Sens. Actuators B*, **99**, 405 (2004).
12. Y. Li, W. Chen, Y.Y. Chen, H.Y. Xu and L. Xu, *Asian J. Chem.*, **24**, 3959 (2012).
13. J.C. Qiu and G.M. Wang, *Mater. Sci. Eng. B*, **112**, 1 (2004).
14. M. Kobayashi, H. Shirai and M. Nunokawa, *Ind. Eng. Chem. Res.*, **41**, 2903 (2002).
15. M. Kobayashi, H. Shirai and M. Nunokawa, *Energy Fuels*, **16**, 1378 (2002).
16. M. Pineda, J.M. Palacios, E. García, C. Cilleruelo and J.V. Ibarra, *Fuel*, **76**, 567 (1997).
17. N.O. Ikenaga, Y. Ohgaito, H. Matsushima and T. Suzuki, *Fuel*, **83**, 661 (2004).
18. F. Tomás-Alonso and J. Latasa, *Fuel Processing Technol.*, **86**, 191 (2004).
19. M. Drogenik, M. Kristl, D. Makovec, Z. Jaglicic and D. Hanzel, *Mater. Manuf. Processes*, **23**, 603 (2008).
20. T. Gordon, B. Perlstein, B. Houbara, I. Felner, E. Banin and M. Shlomo, *Colloid. Surf. A*, **374**, 1 (2011).
21. Y. Xu, Y. Liang, L. Jiang, H. Wu, H. Zhao and D. Xue, *J. Nanomater.*, **2011**, 525967 (2011).
22. P. Feng, G. Ying, C. Feng-Feng, F. Tao and Y. Shu-De, *Chin. Phys. B*, **20**, 127501 (2011).
23. C. Yao, Q. Zeng, G.F. Goya, T. Torres, J. Liu, H. Wu, M. Ge, Y. Zeng, Y. Wang and J.Z. Jiang, *J. Phys Chem. C*, **111**, 12274 (2007).

24. Y. Zhihao and Z. Lide, *Mater. Res. Bull.*, **33**, 1587 (1998).
25. P. Sharma, P. Kumar, D. Deva, R. Shrivastav, S. Dass and R. Vibha, *Int. J. Hydrogen Energy*, **35**, 10883 (2010).
26. G. Fan, Z. Gu, L. Yang and F. Li, *Chem. Eng. J.*, **155**, 534 (2009).
27. R. Arulmurugan, B. Jeyadevan, G. Vaidyanathan and S. Sendhilnathan, *J. Magnet. Magnet. Mater.*, **288**, 470 (2005).
28. H. Ehrhardt, S.J. Campbell and M. Hofmann, *Scripta Mater.*, **48**, 1141 (2003).
29. C. Upadhyay, H.C. Verma, V. Sathe and A.V. Pimpale, *J. Magnet. Magnet. Mater.*, **312**, 271 (2007).
30. M. Sivakumar, T. Takami, Y and B. Iida, *J. Phys. Chem.*, **110**, 15234 (2006).
31. A. Ammar, N. Jouini, F. Fievet, Z. Beji, L. Smiri, P. Moline, M. Danot and J.M. Greneche, *J. Phys.: Condens. Matter*, **18**, 9055 (2006).
32. J.F. Hocheplid, P. Bonville and M.P. Pileni, *J. Phys. Chem. B*, **104**, 905 (2000).
33. S.H. Yu, T. Fujino and M. Yoshimura, *J. Magnet. Magnet. Mater.*, **256**, 420 (2003).
34. H. Xue, Z.H. Li, X.X. Wang and X.Z. Fu, *Mater. Lett.*, **61**, 347 (2007).
35. G.F. Goya and H.R. Rechenberg, *J. Magnet. Magnet. Mater.*, **203**, 141 (1999).
36. H.H. Hamdeh, J.C. Ho, S.A. Oliver, R.J. Willey, G. Oliveri and G. Busca, *J. Appl. Phys.*, **81**, 1851 (1997).
37. C.R. Bluncson, G.K. Thompson and B.J. Evans, *Hyperfine Interact.*, **90**, 353 (1994).
38. G.F. Goya, H.R. Rechenberg, M. Chen and W.B. Yelon, *J. Appl. Phys.*, **87**, 8005 (2000).
39. C.N. Chinnasamy, A. Narayanasamy, N. Ponpandian, K. Chattopadhyay, H. Guerault and J.M. Greneche, *J. Phys.: Condens. Matter*, **12**, 7795 (2000).
40. F.J. Burghart, W. Potzel, G.M. Kalvius, E. Schreier, G. Grosse, D. Noakes, A. Martin and M.K. Krausse, *Physica B*, **289-290**, 286 (2000).
41. T. Kamiyama, K. Haneda, T. Sato, S. Ikeda and H. Asano, *Solid State Commun.*, **81**, 563 (1992).
42. C. Yao, Q. Zeng, G.F. Goya, T. Torres, J. Liu, H. Wu, Z. Yuewu, M. Ge, Y. Wang and J.Z. Jiang, *J. Phys. Chem. C*, **111**, 12274 (2007).
43. N. Wakiya, K. Muraoka, T. Kiguchi, N. Mizutani and K. Shinozaki, *J. Magnet. Magnet. Mater.*, **310**, 2546 (2007).