



Influence of Temperature in the Synthesis of Fe₃O₄ Magnetic Nanoparticles and their Properties

KEYWORDS

Temperature, magnetite, Iron oxide, X-rd

Dr. K.Balamurugan

Assistant Professor, Department of Physics, Annamalai University, Tamil Nadu, India-608002

M. Anbarasu

Department of Physics, Annamalai University, Tamil Nadu, India-608002

ABSTRACT Magnetic nanoparticle of Fe₃O₄ has been fabricated through chemical co-precipitation method by using 1,6 hexamethylenediamine as a reductant, the influence of different reaction temperatures were analyzed. Their structure, morphology and thermal properties were characterized by x-ray powder diffraction (XRD), Scanning electron microscopy (SEM)-Energy dispersive spectrometer (EDS) and thermo gravimetric analysis (TGA). Furthermore, magnetic properties of the products were studied by vibrating sample magnetometer (VSM). It was found that the as-prepared nanoparticles, the reaction temperature had effect on the phase formation of the product particles. The Fe₃O₄ nanoparticles were formed at 40°C. But, when the temperature range was increase to 60 and 80°C, the product of iron oxides α-Fe₂O₃ phase was formed.

Introduction

Magnetite (Fe₃O₄) is a kind of mixed iron oxide (FeO. Fe₂O₃) with an inverse spinel crystal structure. In this structure, half of the Fe³⁺ ions are tetrahedral coordinated while the other half of the Fe³⁺ ions and all of the Fe²⁺ ions are octahedrally coordinated. Each octahedral site has six nearest neighbor O²⁻ ions arranged on the corners of an octahedron; meanwhile, each tetrahedral site has four nearest neighbor O²⁻ ions arranged on the corners of a tetrahedron [1]. It has exhibited unique electrical and magnetic properties based on the transfer of electron between Fe²⁺ and Fe³⁺ ions in the octahedral that are different from those of the bulk materials due to their small size and fundamental changes in the coordination, symmetry and confinement [2]. The potential application in magnetic recording media [3], sensors [4], and especially in biomedical fields [5-8]. Therefore, the synthesis of magnetic nanoparticles has been long pursued for their extensive scientific and technological interest. Fe₃O₄ nanoparticles can be synthesized in a number of ways: the sol-gel [9], sonochemistry [10] colloidal method [11], non aqueous route [12, 13] pyrolysis reaction [14], co-precipitation of an aqueous solution of ferrous and ferric ions by a base [15,16] etc.

Here, in order to present a more comprehensive and systematic study for preparing Fe₃O₄ nanoparticles, we discussed the influences of the reaction temperature on the phase formation of the product of iron oxides nanoparticles.

Experimental

All the reagents were of analytical grade and purchased sigma Aldrich and without further purification.

In a typical 0.03M FeCl₃ and 0.017 FeCl₂ were dissolved in 100ml double distilled water. Then 50ml of 0.25M 1, 6 hexanediamine was slowly added into the FeCl₃ and FeCl₂ solution under the magnetic stirring the magnetic stirrer aging time for 3 hours. In during the synthesis temperature range was varied as room temperature (37°C), 40, 60 and 80°C as named as T₁, T₂, T₃ and T₄ respectively.

Results and discussion

X-Ray diffraction

XRD measurement was conducted to identify the phase

formation of product nanoparticles by chemical co-precipitation method. Fig.1 the XRD pattern of sample T₁, T₂, T₃ and T₄ revealed that the Fe₃O₄ phase was identified from sample T₁ and T₂, all of the peaks were matching standard file of Fe₃O₄ (JCPDS#19-029). While four peaks positioned at 2θ = 30.13°, 35.48°, 43.12° and 62.81° can be assigned to the (220), (311), (400) and (440) planes, respectively, which indicates the cubic spinel crystal structure of pure Fe₃O₄. Fig.1 shows the XRD pattern of sample T₃ and T₄ revealed that, the hematite (α-Fe₂O₃) phase was identified with standard file of α-Fe₂O₃ (JCPDS#1309-1) expect two peaks positioned at 2θ = 36.01° and 46.98° which are (310) and (330) planes moreover, the average crystallite size can be estimated by X-ray diffraction pattern, using the scherrer's equation [17].

$$\beta = K\lambda/d\cos\theta \quad \dots\dots\dots (1)$$

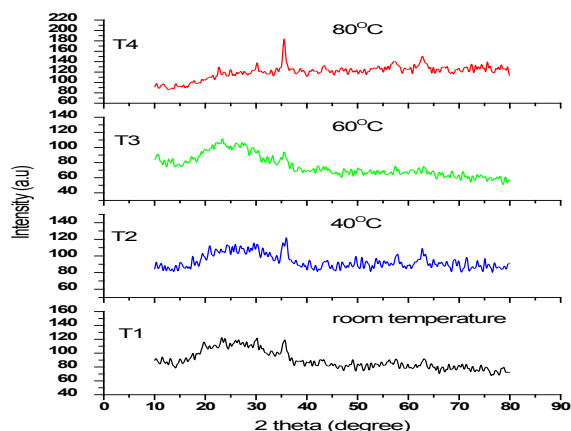


Fig.1. X-ray diffraction pattern of samples T₁, T₂, T₃ and T₄

Where, β is the peak width at half of maximum intensity, K is the shape factor, λ is the X-ray diffraction wavelength (λ = 0.154nm), d is the average crystallite size and θ is the bragg angle in degree, it should be noted that the shape factor K is rotated with several factors, indicating the moller index of the reflection plane and the shape of the crystal, is namely 0.89[18]. The result were listed in Table.1.

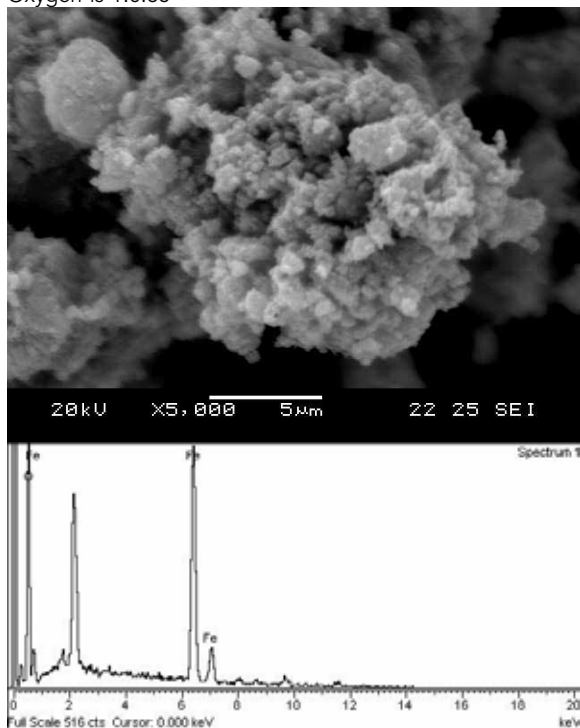
Table :1.

List of the temperature, 20, chemical phase and particle sizes of the samples.

S.no	Samples names	Temperature (°C)	2θ (°)	Chemical Phase	Particle Sizes(nm)
1.	T ₁	37	35.60	Fe ₃ O ₄	8.56
2.	T ₂	40	35.20	Fe ₃ O ₄	14
3.	T ₃	60	36.01	α-Fe ₂ O ₃	8.26
4.	T ₄	80	36.00	α-Fe ₂ O ₃	278

Scanning electron microscope-Energy dispersive X-Ray (SEM-EDX) studies of magnetite (Fe₃O₄) nanoparticles

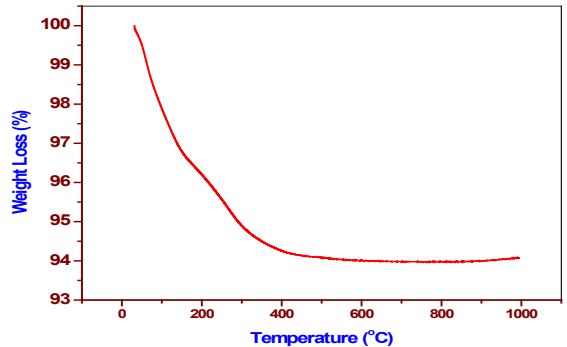
Scanning electron microscopy is a convenient method for studying the surface morphology of the nano materials. Fig.2 shows the SEM micrographs of the Fe₃O₄ nano particles at room temperature with 10K magnification using the equipment JSM 5610. Fig.2 indicates the particles are non-uniform in size and shape. No characteristic morphology is observed. This might be due to agglomeration of nano-structures. Moreover Elemental composition of the Fe₃O₄ nanoparticles was analyzed by EDX in SEM. The EDX spectrum of the sample T₂ reveals that the prepared sample contains only Fe and O elements which indicate the prepared nanoparticles have been found to be of high purity by EDX measurement. The atomic ratio of the component is listed in inside Fig. 2 (b). The atomic ratio of Iron and Oxygen is 1:0.65

**Fig. 2. SEM image (a)-EDX spectrum (b) of samples T₂**

Thermal properties of Magnetite (Fe₃O₄) nanoparticles

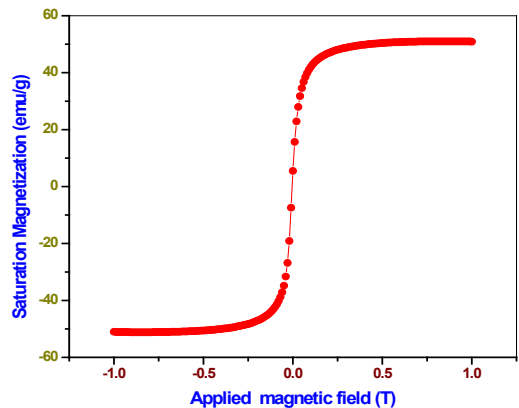
Fig. 3 show the thermo gravimetric analysis (TGA) of Fe₃O₄ nanoparticles of sample T₂. The decomposition process consists of three regions. They are at 50-150°C, 150-480°C and 420-780°C, owing to the initial breakdown of the complex and spontaneous combustion. The first weight loss region obtained from 50-150°C is 3.6% from the sample, which indicates the evaporation of absorbed

water with the liberation of H₂O and CO₂. The second weight loss region observed between 150-480°C is 3.2% from the sample is ascribed to dehydration of OH group in the spinel structure of Fe₃O₄ that lead to degradation of the systems involving both inter molecular transfer reaction, the oxidation of complexes and formation of semi organic carbon metal/metal oxide [19]. The third weight loss region in the temperature range of 420-780°C is 2.06% is believed to be due to the formation of corresponding metal oxide and the spinel phase. Above 780°C, there is no weight loss. From this study, it was clearly seen that the TGA curve is steady, demonstrating the absolute volatility of water and organic compound, in the composites.

**Fig .3. Thermo gravimetric analysis (TGA) of sample T₁**

Magnetic properties of Magnetite (Fe₃O₄) nanoparticles

Fig.4 shows the hysteresis loop plot for the sample T₂ (40°C). It has been found from the loop that the coercivity is almost zero and the saturation magnetization value is 56 emu/g which is a characteristic of super paramagnetism [20]. It has been reported that Ms of 7-22 emu/g is adoptable for biomedical application [21]. Therefore, the level of Saturation Magnetization (Ms) achieved for this sample is sufficient for biomedical applications.

**Fig.4. Magnetization curves of sample T₂**

Conclusion

The method of synthesis of Fe₃O₄ nanoparticles by chemical co-precipitation method was investigated with a focus on the influence of temperature on the formation of Fe₃O₄ nanoparticles. The presence of α-Fe₂O₃ or Fe₃O₄ was confirmed by XRD study. From this results sample T₂ was chosen for further analysis, due to the presence of Fe₃O₄ phase. Morphology and chemical composition was carried out by SEM with EDX. The thermal properties was analyzed by TGA for the sample T₂ moreover the magnetic properties of the sample T₂ was studied by VSM, from the graph the coercivity is almost

zero and the saturation magnetization value is 56 emu/g, this indicates the sample T_2 having superparamagnetic behaviour. There the sample T_2 with M_s value is suitable for biomedical application.

REFERENCE

- [1] R.C.O'Handley, *Modern Magnetic Materials: Principles and Applications*, John Wiley & Sons, New York, 2000, p. 126-132 [2] D.L. Leslie-Pelecky, R.D. Rieke. Magnetic properties of nanostructured materials. *Chem. Mater.* 8 (1996) 1770-1783. [3] S.H. Sun, C.B. Murray, D. Weller, L. Folks, A. Moser. Monodisperse FePt nanoparticles and ferromagnetic FePt nanocrystal superlattices *Science* 287 (2000) 1989-1992. [4] H. Zeng, J. Li, Z.L. Wang, J.P. Liu, S. Sun. Exchange-coupled nanocomposite magnets by nanoparticle self-assembly nanocomposite magnets by nanoparticle self-assembly. *Nature*, 420 (2002) 395-398. [5] M. Benz, A.M. Van der Kraan, R.J. Prins. Mg-Fe hydroxalcite as a catalyst for the reduction of aromatic nitro compounds with hydrazine hydrate *J. Appl. Catal. A* 172 (1998) 149-154. [6] U. Hafeli, W. Schutt, J. Teller, M. Zborowski, Scientific and Clinical Applications of Magnetic Carriers, Plenum Press, New York, 1997. [7] H. Gu, K. Xu, C. Xu, B. Xu. Bioconjugation of poly(ethylene glycol) methacrylate-coated iron oxide magnetic nanoparticles for magnetic capture of target proteins. *Chem. Commun.* 17(2006) | 941-956. [8] S. Mornet, S. Vasseur, F. Grasset, E. Duguet. Carboxyl group | (-CO 2 H) functionalized ferrimagnetic iron oxide nanoparticles for potential bio-applications. *J. Mater. Chem.* 14 (2004) 2161-2167. [9] J.W. Choi, C.H. Ahn, S. Bhansali, H.T. Henderson, Sens. Actuators. A new magnetic bead-based, filterless bio-separator with planar electromagnet surfaces for integrated bio-detection systems *BChem.* 68 (2000) 34-42. [10] J.H. Wu, S.P. Ko, H.L. Liu, S.S. Kim, J.S. Ju, Y.K. Kim. | Sub 5 nm magnetite nanoparticles: Synthesis, microstructure, and magnetic properties. *Mater. Lett.* 61 (2007) 3124-3129. [11] T. Fried, G. Shemer, G. Markovich. Ordered Two-Dimensional Arrays of Ferrite Nanoparticles *Adv. Mater.* 13 (2001) 1158-1161 [12] J. Xu, H.B. Yang, W.Y. Fu, K. Du, Y.M. Sui, J.J. Chen, Y. Zeng, M.H. Li, G.T. Zou. Preparation and magnetic properties of magnetite nanoparticles by sol-gel method. *J. Magn. Magn. Mater.* 309 (2007) 307. [13] R. Vija ya Kumar, Y. Koltypin, Y.S. Cohen, Yair Cohen, D. Aurbach, O. Palchik, I. Felner, A. Gedanken. Preparation of amorphous embedded in polyvinyl alcohol using ultrasound radiation *J. Mater. Chem.* 10 (2000) 1125-129. [14] I. Martínez-Mera, M.E. Espinosa-Pesqueira, R. Pérez-Hernández. Synthesis of magnetite (Fe₃O₄) nanoparticles without surfactants at room temperature. *J. Arenas-Alatorre, Mater. Lett.* 61 (2007) 4447-4451. [15] N. Pinna, S. Grancharov, P. Beato, P. Bonville, M. Antonietti, M. Niederberger. Magnetite nanocrystals: Nonaqueous synthesis, characterization, and solubility *Chem. Mater.* 17 (2005) 3044-3049. [16] Z. Li, H. Chen, H. Bao, M.Y. Gao. Aqueous dispersion of monodisperse magnetic iron oxide *Chem. Mater.* 16 (2004) 1391-1393. [17] W.S. Chiu, S. Radiman, M.H. Abdullah, P.S. Khiew, N.M. Huang, R. Abd-Shukor. One pot synthesis of monodisperse Fe₃O₄ nanocrystals by pyrolysis reaction of organometallic compound *Mater. Chem. Phys.* 106 (2007) 231-235. [18] W. S. Lu, Y. H. Shen, A.J. Xie, W. Q. Zhang. Green synthesis and characterization of superparamagnetic Fe₃O₄ nanoparticles *Journal of Magnetism and Magnetic Materials* 322 (2010) 1828-1833. [19] D.K. Kim, M. Mikhaylova, Y. Zhang, M. Muhammed. Size-Controlled Synthesis of Fe₃O₄ Magnetic Nanoparticles in the Layers of Montmorillonite *Chemistry of materials* 15 (2003) 1617-1627. [20] P. Sivakumara, R. Ramesh, A. Ramanand S. Ponnusamy, C. Muthamizhchelvan. Synthesis, studies and growth mechanism of ferromagnetic NiFe₂O₄ nanosheet. *Mat. Rese. Bulle.* 46(2011) 204-2207. [21] P. Deb., A. Basumallick, S. Das, (2007) "Controlled of monodispersed superparamagnetic nickel ferrite nanoparticles". *b solid state communications* 142,702-705 [22] N.A. Brusentov, V.V. Gogosov, T. N. Brusentov, A.V. Sergeev, N.Y. Jurchenko, A.A. Kuznetsov, O.A. Kuznetsov, L.I. Shumakov. Evaluation of ferromagnetic fluids and suspensions for the site-specific radiofrequency-induced hyperthermia of MX11 sarcoma cells in vitro *Journal of Magnetism and Magnetic Materials* 225 (2001) 113-117. |