SYNTHESIS OF FERRITE NANOPARTICLES THROUGH AQUEOUS PROCESS FOR BIOMEDICAL APPLICATIONS

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SUMMARY - The magnetic properties of materials deteriorate when the particle size reaches the superparamagnetic limit and hence it is important to have an appropriate particle size depending on the end use. In this paper we describe the synthesis of manganese zinc ferrite through aqueous process. Oxidation method has been employed through acqueous process to achieve large particles with high magnetization at low temperatures compared to other chemical methods. The synthesis conditions have been optimized to maximize the magnetization by increasing the particle size above the superparamagnetic threshold. The optimum concentration of the oxidant required for ferrite synthesis has been found to be 0.08 M of KNO_3 for 0.5 M NaOH. The results show that the largest particle size that could be achieved using the oxidation method is 80 nm and the magnetization is 49 Am^2/kg.

1. INTRODUCTION

Ferrite nanoparticles find important applications in high frequency devices, information storage, heat transfer devices, drug delivery systems and medical diagnostics. Nanosize particles of ferrites can be prepared by using various synthesis techniques namely ball-milling, citrate precursor method, hydrothermal synthesis, coprecipitation and oxidation methods. Mangenese zinc ferrites are useful for ferrofluid and biomedical applications due to low Curie temperature and high magnetization-temperature gradient. The magnetization value depends on the particle size as smaller particle size leads to superparamagnetism and decreases the magnetization.

In order to increase the magnetization the particle size has to be increased. Synthesis of ferrites through ball milling results in agglomerated particles and other methods like hydrothermal method involve high temperatures. Coprecipitation method results in smaller particle size and hence the magnetization value is low since the particle sizes are of the order of 10-20 nanometer and their magnetic properties are also influenced by parameters like cation distribution "Jeyadevan et al (2000)". Oxidation method can be used to synthesise nanoparticles of bigger sizes compared to the coprecipitation technique. However, the largest particle size obtainable with the oxidation method also varies according to the synthesis conditions used. In this paper we describe the synthesis of Mn-Zn ferrite through oxidation method involving low temperature synthesis in an aqueous medium and its magnetic properties with respect to particle size.

2. MATERIALS AND METHODS

Mn-$ZnFe_2O_4$ was synthesized using analytical grade reagents of $Fe_2SO_4.7H_2O$, $MnCl_2.4H_2O$, $ZnSO_4.H_2O$ and adopting the oxidation method. The ratio of Mn^{2+} to Zn^{2+} ions was fixed as 2 for all the experiments. NaOH was used for precipitation and KNO_3 was used as the oxidant. All the chemicals were of purity greater than 99% (Wako). Oxidation method can be used to synthesize larger particles by oxidising the hydoroxide precipitate with an oxidant to convert the ferrous ions to ferric and form the ferrite phase at lower temperatures. Fe, Mn and Zn salts were dissolved separately in water (0.5 L) and allowed to react with NaOH dissolved in the same amount of water. The resulting precipitate was purged with N_2 before heating to prevent atmospheric oxidation. The metal hydroxide precipitate with a pH between 12-13 was oxidized with various amounts of KNO_3 in a water bath at 90 ^oC with constant mechanical stirring. The duration of the reaction was 2 h. The phases produced were analyzed using X-ray diffraction (XRD). The average grain size was determined using the Scherrer formula. The morphology of the particles was examined using Scanning Electron Microscopy (SEM). The magnetic properties were measured using a Vibrating Sample Magnetometer (VSM).

The basic reaction mechanism of ferrite formation in the simple case of $FeO.Fe_2O_3$ (magnetite) is as follows:

(a) Fe(II) hydrolysis:

$Fe^{2+} + H_2O \rightarrow FeOH^+ + H^+$

(b) Fe(II) oxidation:

$2FeOH^{+} + 1/2\ O_2 + H_2O \rightarrow 2\ Fe(OH)_2^{+}$

(c) Precipitaion of partially oxidized intermediate:

$(2-x)Fe(OH)_2^{+} + (1+x)Fe(OH)^{+} + xSO_4^{2-} + (3-2x)OH^{-} \rightarrow (Fe^{3+})_{2-x}(Fe^{2+})_{1+x}(SO_4^{2-})_x(OH^{-})_{8-3x}$

(d) Additional Fe(II) oxidation at constant pH:

$2[(Fe^{3+})_{2-x}(Fe^{2+})_{1+x}(SO_4^{2-})_x(OH^{-})_{8-3x}] + x/2\ O_2 + 5xH_2O \rightarrow 2\ [(Fe^{3+})_{2-x}(Fe^{2+})(OH^{-})_8] + 2xH_2SO_4$

(e) De-hydration and magnetite formation:

$[(Fe^{3+})_{2-x}(Fe^{2+})(OH^{-})_8] \rightarrow FeO.Fe_2O_3 + 4H_2O$

From these reactions, it is seen that the ferrite phase formation occurs by hydrolysis and subsequent dehydration. A similar reaction mechanism takes place in the synthesis of Mn-Zn ferrite also. The ferrite phase formation also depends on the temperature and duration of the reaction. In the case of Mn-Zn ferrites, the temperature of 90 ^{o}C and the duration of 2 h were sufficient for the reaction to complete.

Metal salts of 0.17 M are allowed to react with 0.5 M of NaOH. The resulting metal hydroxide precipitate was heated with various moles of KNO_3. The KNO_3 mole values used were 0.05 M, 0.07 M, 0.08 M, 0.09 M, 0.15 M and 0.20 M.

3. RESULTS AND DISCUSSION

Fig.1 shows the XRD of the Mn-$ZnFe_2O_4$ sample with (a) 0.08 M (b) 0.09 M and (c) 0.20 M. The XRD showed the formation of pure spinel phase with increasing moles of KNO_3. The average grain size was found to be in the range of 23-27 nm upto 0.09 M KNO_3 and thereafter decreased to

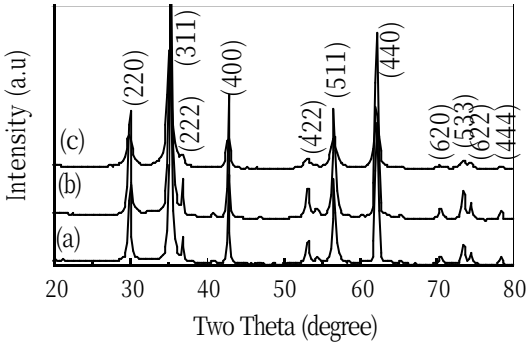

Fig.1. The XRD of the Mn-$ZnFe_2O_4$ sample with KNO_3 of (a) 0.08 M, (b) 0.09 M and (c) 0.20 M.

12 nm for the 0.20 M KNO_3 sample. For the lowest concentration of KNO_3 a small amount of hydroxide impurity peak is observed. Fig.2 shows the SEM photographs of the 0.09 M KNO_3 added sample. It is seen from the SEM results that the average particle size is 80 nm for the samples synthesized with less than 0.09 M of KNO_3 and

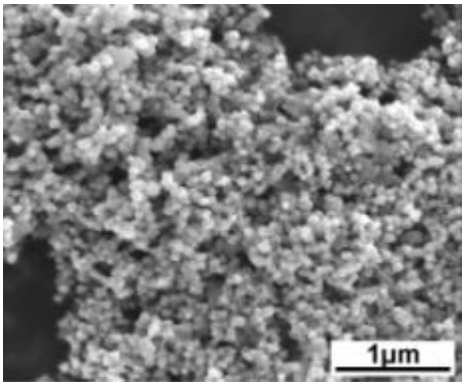

Fig.2. The SEM photograph of the Mn-$ZnFe_2O_4$ synthesized with 0.09 M KNO_3.

the average particle size decreased to less than 20 nm when the KNO_3 was 0.20 M. Fig.3 shows the saturation magnetization as a function of KNO_3 concentration. It is seen that the saturation magnetization is maximum with 49 Am^2/kg for the 0.08 M sample whereas it decreases to 39 Am^2/kg for the 0.20 M of KNO_3 due to reduction of particle size. The Mn-Zn ferrite particles synthesized using coprecipitation method have

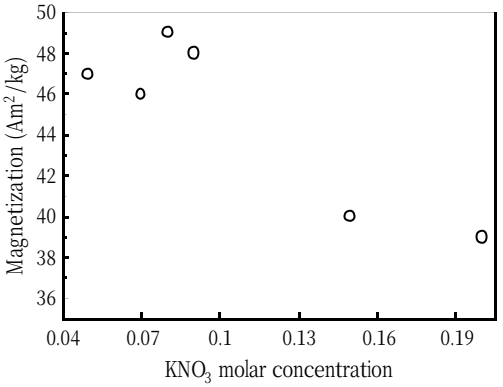

Fig.3. The saturation magnetization of the Mn-$ZnFe_2O_4$ as a function of KNO_3 concentration.

given a magnetization value of 37 Am^2/kg for 9 nm particles as reported by "Jeyadevan *et al* (2003)" whereas with the oxidation method we are able to synthesise 80 nm nanoparticles with a magnetization of 49 Am^2/kg.

4. CONCLUSIONS

Mn-Zn ferrite has been prepared by the oxidation method. The spinel phase formation depends upon the concentration of the oxidant used and the optimum amount of KNO_3 required for the maximum particle size is found to be 0.08 M for a fixed molar concentration of metal salts. The largest magnetization obtained is 49 Am^2/kg for a particle size of 80 nm.

5. ACKNOWLEDGEMENTS

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6. REFERENCES

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