Interacting or non-interacting nanoparticles of (Mn$_{1-x}$Zn$_x$)$_{0.5}$Co$_{0.5}$Fe$_2$O$_4$(x= 0 -1) ferrite synthesized by reverse micelle

A Ghasemi$^{1,2,*}$, S E Shirsath$^3$, A P Júnior$^4$, X Liu$^1$ and A Morisako$^1$

$^1$Spin Device Technology Center, Faculty of Engineering, Shinshu University, Nagano, Japan
$^2$Department of Materials Engineering, Malek Ashtar University of technology, Shahin Shahr, Isfahan, Iran
$^3$Department of Physics, Dr. Babasaheb Ambedkar Marathwada University, Aurangabad, India
$^4$Centro de Ciências Exatas, Departamento de Física, Universidade Estadual de Maringá, Brazil

*E-mail: ali13912001@yahoo.com

Abstract. (Mn$_{1-x}$Zn$_x$)$_{0.5}$Co$_{0.5}$Fe$_2$O$_4$ (x= 0 – 1) ferrite nanoparticles were prepared using reverse micelle process. X-ray diffraction patterns demonstrated that single phase spinel ferrites are obtained. Vibrating sample magnetometer (VSM) was employed to probe magnetic properties of samples. The compositional dependence of blocking temperature was measured using superconducting Quantum Interference Device (SQUID). Magnetic dynamics of the samples was studied by the measurement of AC magnetic susceptibility versus temperature at different frequencies. The phenomenological Néel – Brown and Vogel – Fulcher models were employed to distinguish between the interacting or non-interacting system. Results exhibited that there is strong interaction between fine particles.

1. Introduction

Reverse micelles are water-in-oil microemulsions in which molar ratio of constitutive components and pH control the size of water pools and resultant particles. There are several literatures about the synthesizing of Ni-Zn and Mn-Zn ferrite with reverse micelle method [1-5].

In the recent years, we have focused our studies on the preparation and magnetic characteristics of ferrite nanoparticles [6-10]. (Mn$_{1-x}$Zn$_x$)$_{0.5}$Co$_{0.5}$Fe$_2$O$_4$ has a verity of promising technological applications in high-density recording devices, high frequency devices and microwave-linked applications. The magnetic character of the particles depends crucially on size, shape, purity and magnetic stability of these nanoparticles. The particles should be single domain, of pure phase, suitable coercivity, moderate magnetization and stable blocking effects. From the application point of view, in recording technologies the superparamagnetic blocking temperature of the particles should be well above the room temperature in order to have a stable data recorded in these nanoparticles. In biomedical applications, the nanoparticles are used as drug carriers to the areas of the body where conventional drug delivery systems may not work. For this purpose the nanoparticles used should be magnetically in superparamagnetic unblocked state with relatively low blocking temperature and coercivity. So it is very important to tailor various magnetic properties in these materials according to their requirements. To the best of our knowledge no studies on the preparation of this ferrite via reverse micelle method have been reported.
With this view in mind, current interest is to make $(\text{Mn}_{1-x}\text{Zn}_x)_{0.5}\text{Co}_{0.5}\text{Fe}_2\text{O}_4$ ferrite nanoparticles using reverse micelle technique at a low temperature.

2. Materials and methods

$(\text{Mn}_{1-x}\text{Zn}_x)_{0.5}\text{Co}_{0.5}\text{Fe}_2\text{O}_4$ nanoparticles were prepared by a reverse micelle process. In the preparation of ferrites, two microemulsions were synthesized. The first, using a metal solution and the second one, using ammonium hydroxide. Stock solutions of 0.5 M sodium dioctylsulfosuccinate (AOT) were prepared in isooctane. A metal solution was synthesized using $\text{FeCl}_2$, $\text{ZnCl}_2$, $\text{CoCl}_2\cdot6\text{H}_2\text{O}$ and $\text{MnCl}_2$ dissolved in 8 ml of water and 66 ml of AOT- isoctane. The second microemulsion was prepared by mixing 2 ml of ammonia, 2 ml of water and 66 ml of AOT- isoctane. The second microemulsion was then added to the first one and stirred for one hour at room temperature. After rapid magnetic stirring, methanol was used to extract the surfactant and organic solvent. The colloidal precipitate was sedimented by centrifuging and washing with methanol and water. To obtain spinel ferrite in the final product, the pH must be carefully controlled. The pH was adjusted to 10.3 in this experiment. The synthesis temperature was kept 200 °C.

X-ray powder diffraction was performed on the nanoparticles using a Phillips X-ray diffractometer employing Cu $K\alpha$ radiation from a sealed tube (50 kV, 30 mA) source. The vibrating sample magnetometer was employed to investigate the variation of magnetization with magnetic field. The temperature dependence of the magnetic susceptibility of nanoparticles was studied under an applied field of 115 Oe at different temperature ranges using Lake Shore magnetic susceptometer model 7000. Magnetization versus temperature variation in the range of 100-300 K was measured with a superconducting Quantum Interference Device (SQUID). In this case, after the ZFC process, a field of 115 Oe was applied.

3. Results and Discussions

3.1. Structural and magnetic analysis

The XRD patterns of samples in figure 1 revealed that in all samples, by substituting Mn with Zn, no extra peak corresponding to any secondary phases were identified. Based on the XRD results, it seems that zinc cations could be re-arranged in the spinel structure of Mn ferrite. It is reasonable to conclude from the patterns that the spinel phases can be formed in all the specimens without the existence of any secondary phases at relatively low temperature.

![Figure 1. XRD patterns of nanoparticles synthesized by reverse micelle.](image)

Table 1 reflects the values of coercivity and saturation magnetization of samples prepared by reverse micelle. Interestingly, it has been revealed that the coercivity and remanence are almost zero for all samples. The samples were not saturated even at magnetic field of 10 kOe, which reflects the characteristic of superparamagnetism. The value of saturation magnetization obtained by fitting the high field data to the function $M=M_s(1-\alpha/H)$, where $M$ and $M_s$ are magnetization and saturation magnetization.
respectively, $\alpha$ is the fitting parameter and $H$ is the applied field, appear in Table 1.

Table 1. Magnetic parameters of nanoparticles of spinel $(\text{Mn}_{1-x}\text{Zn}_x)_{0.5}\text{Co}_{0.5}\text{Fe}_2\text{O}_4$ ferrite obtained at room temperature

| $x$ | $H_c$ (Oe) | Ms (emu/g) |
|-----|------------|------------|
| 0   | 0.02       | 47         |
| 0.2 | 0.05       | 43         |
| 0.4 | 0.03       | 38         |
| 0.6 | 0.02       | 36         |
| 0.8 | 0.06       | 32         |
| 1   | 0.04       | 23         |

3.2. Interacting or non-interacting nanoparticles?

Figure 2 illustrates the temperature dependence of magnetization obtained with an applied field of 115 Oe after zero-field cooling (ZFC) from 300 to 100 K for sample synthesized by reverse micelle method. The ZFC curves indicate that the prepared nanoparticles exhibit crystallite size distribution. There is a maximum in the ZFC curve which indicates the value of blocking temperature. It is observed that addition of zinc gives a decrease in the blocking temperature. This can be attributed to the particle size. Actually, with increasing zinc, the particle size decreases and consequently blocking temperature was decreased. To study the magnetic dynamic behavior of the nanoparticles, we measured the AC magnetic susceptibility of prepared ferrite nanoparticle versus temperature at different frequencies. Figure 3 reflects the temperature dependence of real and imaginary parts of AC magnetic susceptibility of sample with $x=1$ at different frequencies in the range of 111-1000 Hz and at an AC magnetic field of 115 Oe. In figure 3, $\chi'' (T)$ shows a peak near 225 K which is frequency dependent and shifted to a higher temperature with increasing frequency. This characteristic maximum is the signature of blocking/freezing process of the superparamagnetic/spin glass systems [11-15]. Since the nanoparticles and consequently their easy axes are randomly orientated, overall susceptibility is reduced with decreasing temperature as figure 3 shows.

It was found that the blocking temperature increases almost linearly with a decrease in Zn concentration in the reverse micelle synthesized samples. Based on the TEM observation, with an increase in Zn content the size of particles decreases. Consequently, it is reasonable to have the mentioned trend in blocking temperature versus zinc content.

The interacting or non-interacting behavior of the fine powders was evaluated by Neé–Brown (non-interacting model) and Vogel-Fulcher (interacting law). According to Neé–Brown model, the blocking temperature measured at a given working frequency, is related to the considered frequency as

$$\ln \frac{1}{2\pi} = \ln \tau_0 + \frac{KV}{kT_B}$$ (1)

$T_B$ can be obtained by assuming that at the maximum of the out-of-phase component of the susceptibility, the relaxation time matches the working frequency. Attempt time is calculated from the curves and it is found that it spreads between $\tau_0 = 10^{-23}$ to $10^{-21}$ s. These values, however, are unphysical, being several orders of magnitude lower than the typical value found in the literature for a non-interacting assembly of superparamagnetic nanoparticles ($10^{-8} - 10^{-11}$ s) [11]. This suggests that the Neél–Brown model is not appropriate to describe the dynamic behavior of our system. In this case, deviations from the model can be ascribed to the presence of strong interactions. The interaction between nanoparticles affected the blocking/freezing temperature by modifying the potential barrier. By increasing the strength of interaction, $T_B$ shifts to higher temperatures. For interacting magnetic nanoparticles, the frequency dependence of $T_B$ is given by the Vogel-Fulcher law [11]

$$\ln 1/2\pi = \ln \tau_0 + E_a/k(T-T_0)$$ (2)

here $E_a$ is the energy of barrier, $T_0$ is an effective temperature which reveals the existence of the interaction between nanoparticles and $T$ is the characteristic temperature indicating the onset of the blocking process.

We tried to fit the experimental data of susceptibility for our samples, using Eq. (2). It was found that the
values of attempt time were spread between $3.8 \times 10^{-9}$ to $2.3 \times 10^{-10}$ s. The good agreement between the experimental data and Vogel-Fulcher model confirms the existence of interactions between nanoparticles.

4. Conclusions

Fine particles single phase of $(\text{Mn}_{1-x}\text{Zn}_x)_{0.5}\text{Co}_{0.5}\text{Fe}_2\text{O}_4$ were prepared by reverse micelle method. The value of blocking temperature has straightforward relation with particle size. Temperature dependence of real and imaginary parts of effective magnetic susceptibility was measured. Fitting the experimental data of susceptibility with Néel-Brown model gives unphysical high values for relaxation time and indicates that there are strong interactions between nanoparticles of ferrite. The good agreement between the experimental data and Vogel-Fulcher model confirms the existence of strong interactions between nanoparticles.

Acknowledgements

This work was supported in part by Research (B) from JSPS and Grant-in-Aid for Scientific Research Tokobetsu Kenkyuuiin Shorei-hi.

References

[1] Thakur S, Latyal S C and Singh M 2009 J. Magn. Magn. Mater. 321 1
[2] Uskokovic V, Drofenik M and Ban I 2004 J. Magn. Magn. Mater. 284 294
[3] Shultz M D, Allsbrook M J and Carpenter E E 2007 J. Appl. Phys. 101 09M518
[4] Morrison S A, Cahill C L, Carpenter E E, Calvin S, Swaminathan R, McHenry M E and Harris V G 2004 J. Appl. Phys. 95 6392
[5] Morrison S A, Cahill C L, Carpenrer E E, Calvin S and Harris, V G 2003 J. Appl. Phys. 93 7489
[6] Ghasemi A, Šepelák V, Liu X X and Morisako A J. Appl. Phys. accepted for publication.
[7] Ghasemi A, Šepelák V, Liu X X and Morisako A J. Appl. Phys. accepted for publication.
[8] Ghasemi A, Šepelák V, Liu X X and Morisako A 2009 IEEE Trans. Magn. 45 2456
[9] Ghasemi A, Liu X X and Morisako A 2009 IEEE Trans. Magn. 45 4420
[10] Ghasemi A and Morisako A 2008 *J. Magn. Magn. Mater.* **320** 1167
[11] Dormann J L, Fiorani D and Tronc D 1999 *J. Magn. Magn. Mater.* **202** 251
[12] Jönsson P E 2004 *Adv. Chem. Phys.* **128** 191
[13] Suzuki M, Fullem S I and Suzuki I S 2009 *Phys. Rev. B* **79**, 024418
[14] Parker D, Dupuis V, Ladieu F, Bouchaud J P, Dubois E, Perzynski R and Vincent E 2008 *Phys. Rev. B* **77**, 104428
[15] Vasseur S, Duguet E, Portier J, Goglio G, Mornet S, Hadová E, Knížek K, Maryško M, Veverka P and Pollert E 2006 *J. Magn. Magn. Mater.* **302** 315