Magnetic properties of Co$_{1-x}$Ni$_{x/2}$Sr$_{x/2}$Fe$_2$O$_4$ (x = 0–1) ferrite nanoparticles synthesized by self-assembling media of reverse micelles

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Abstract. Co$_{1-x}$Ni$_{x/2}$Sr$_{x/2}$Fe$_2$O ferrite nanoparticles were prepared using reverse micelle process. Mean particle size of pure ferrite nanoparticles is approximately 9 nm as determined by transmission electron microscopy (TEM). The heating thermograms of samples confirmed that there are no hydroxides in the ferrites fabricated via reverse micelles. Vibrating sample magnetometer (VSM) was employed to probe magnetic properties of nanosized. It was found that with increasing the amount of Ni and Sr in nanosized ferrites, the saturation magnetization decreases. 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 interacting or non-interacting system. Results show that there is strong interaction between fine particles.

Introduction

Soft ferrite nanoparticles have been fabricated by different processing including sol-gel process, mechanical alloying, thermolysis, shock waves synthesis, electro-deposition, severe plastic deformation consolidation, hydrothermal processing, hydrolysis method, sonochemical decomposition and co-precipitation [1-10]. These methods are able to produce fine particles; however control of size distribution is arbitrary. In most of the mentioned technique, the particle size is varied by changing post-annealing temperature. It is well known that although the size of particles changes according to the sintering temperature, however the distribution of cations in the crystallographic sites (octahedral and tetrahedral) is also varied by temperature. Therefore, when sintering process is used to
control the particle size, the correlation between particle size and magnetic characteristics is not possible, due to the re-distribution of cations which is another important variable. In order to correlate size of particle with magnetic properties, it is essential to employ a synthesis technique that allows for preparation of nanoparticles at relatively low temperature. Precipitation in reverse micelles is a very promising technique to prepare nanoparticle in the narrow distribution size and at low temperature. In this process self-assembling media of reverse micelles leads to synthesis nanoparticles of ferrite. Briefly, 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 [11-15]. In the recent years, we have focused our studies on the preparation and magnetic characteristics of ferrites [16-20]. In the present research, Co\textsubscript{1-x}Ni\textsubscript{x/2}Sr\textsubscript{x/2}Fe\textsubscript{2}O\textsubscript{4} ferrite has cubic spinel structure and is widely used in many electronic devices because of high electrical resistivity, hard mechanical properties, high Curie temperature and environmental stability. To the best of our knowledge no studies on the preparation of this ferrite via reverse micelle are report. With this view in mind, current interest is to make Co\textsubscript{1-x}Ni\textsubscript{x/2}Sr\textsubscript{x/2}Fe\textsubscript{2}O\textsubscript{4} ferrite nanoparticles using reverse micelle technique at low temperature. The structural and magnetic characteristics were evaluated by employing XRD, TEM, TGA, VSM, and AC susceptometer. We experimentally analyze magnetic susceptibility behavior of prepared samples and interpret our experimental results using Néel – Brown and Vogel – Fulcher laws.

Experiments

Co\textsubscript{1-x}Ni\textsubscript{x/2}Sr\textsubscript{x/2}Fe\textsubscript{2}O\textsubscript{4} ferrite nanoparticles were synthesized by reverse micelle process at 100 ºC. X-ray powder diffraction was performed on the nanoparticles using a Phillips x-ray diffractometer employing Cu Kα radiation from a sealed tube (50 kV, 30 mA) source. A JEOL 2010 model TEM was employed to characterize the morphologies and particle size distribution of the prepared samples. The nanoparticles were suspended in methanol and agitated in an ultrasonic bath. The TEM samples were prepared by placing a few drops of this suspension on a copper grid.

TGA and DTA measurements were performed in air up to 500 ºC, with heating and cooling rate of 5 ºC/min. The vibrating sample magnetometer was employed to investigate the variation of magnetization with magnetic field at room temperature. The temperature dependence of the magnetic susceptibility of nanoparticles was studied under an applied field of 115 Oe in the temperature range of 100 – 300 K by magnetic susceptometer.

Results and Discussion

Structural and magnetic properties

The XRD patterns of samples in Fig. 1 revealed that in all samples, by substituting Ni and Sr with Co, no extra peak corresponding to any secondary phases were identified. Based on the XRD results, it seems that substituted cations could be rearranged in the spinel structure of cobalt ferrite. It is reasonable to conclude from the patterns that the spinel phases can be formed in the all specimens without existence of any secondary phases at relatively low temperature.

The heating thermograms of sample x=1 prepared by reverse micelle is presented in Fig. 2. In the TGA graph of sample fabricated by reverse micelle 3 % of samples evaporated while heating to 500 ºC. This reduction in mass is related to the evaporation of water and partly due to the oxidized remaining surfactant. Normally the heating analysis of ferrite nanoparticles exhibit one or more exothermic peaks in the temperature range of 200-350 ºC. The mentioned peaks are attributed to the amorphous-to-crystalline phase transition and oxidation of remaining surfactant molecules. It is worthy to note that the absence of exothermic peaks in the graphs clarifying that the sample prepared at 100 ºC has no secondary hydroxide phases, while in another synthesizing method the existence of sharp weight-loss peak in the TGA curve demonstrate that the intermediate hydroxides are present in the sample.
It was found from the VSM loops (not shown here) that the coercivity and remanence are almost zero for all samples. The samples were not saturated even at magnetic field of 20 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.

It was found that with an increase in Ni and Sr content from $x=0$ to $x=1$, the values of saturation magnetization decline from 40 to 23 emu/g. The variation of magnetization of synthesized ferrite nanoparticles prepared by reverse micelle indicated that up to a specific magnetic field, the magnetic moments of core align with applied field. Beyond that field, any increase in the magnetic field has an effect on the shell of the particles and therefore the slope in the increasing of magnetization slows down. The lower values of saturation magnetization of nanocrystalline ferrites prepared by reverse micelle compared to the bulk ferrites is attributed to the surface effects which leads to the non-collinearity of the magnetic moments on their surface and can be explained in terms of core-shell model of nanoparticles in which the core contains ferrimagnetically aligned spin and the surface or interface with a certain degree of spin canting. The disordering in the shell is caused due to local chemical disorder, broken exchange bonds and different local symmetry for those atoms near the surface [21]. Some researchers report that this partially disordered layer gives rise to a spin canting due to the imbalance of ferromagnetic sublattice [22, 23]. However, other authors claimed that the spin canting involves the whole particle and is not restricted to the surface layer [24]. The vacancies or modified cation distribution weakens the super-exchange paths and therefore causes the spin canting in the core of ferrite nanoparticles. It must be noted that if the surfactant molecules from reverse micelle method are absorbed on the surface of nanoparticles and the electrons can no longer participate in the super-exchange interaction, then the pinning of spin occurs [25].
Table 1. Saturation of magnetization of synthesized samples.

| x   | 0   | 0.2 | 0.4 | 0.6 | 0.8 | 1   |
|-----|-----|-----|-----|-----|-----|-----|
| $M_s$ (emu/g) (nanoparticles) | 40  | 36  | 30  | 27  | 25  | 23  |
| $M_s$ (emu/g) (bulk)         | 72  | 65  | 59  | 51  | 46  | 40  |

Interacting or non-interacting nanoparticles

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 $x=1$ at different frequencies in the range of 111-1000 Hz and at an AC magnetic field of 115 Oe. In Fig. 3 the real parts of effective magnetic susceptibility has a peak value. This characteristic maximum is the signature of blocking/freezing process of the superparamagnetic/spin glass systems [26-30]. The blocking temperature is the threshold point of thermal activation. Above blocking temperature magnetocrystalline anisotropy is overcome by thermal activation and the magnetization direction of each nanoparticle simply follows the applied field direction. Consequently, the nanoparticles show paramagnetic properties. Below the blocking temperature, thermal activation is no longer able to overcome the magnetocrystalline anisotropy of the nanoparticles. As a consequence, the magnetization direction of each nanoparticle rotates from the field direction back to its own easy axis without any movement of the nanoparticle. Since the nanoparticles and consequently their easy axes are randomly orientated, overall susceptibility is reduced with decreasing temperature as Fig. 3 shows. It was found that the blocking temperature increases almost linearly with an increase in Ni and Sr concentration in synthesized samples. The main reason is attributed to the size of nanoparticles. It is well known that blocking temperature has linear proportional to the volume of particles and anisotropy constant. It was found that with an increase in Ni and Sr content the size of particles increases. Consequently, it is reasonable to have the mentioned trend in blocking temperature versus substitutions content.

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

$$\ln \frac{1}{2\pi v} = \ln \tau_0 + \frac{K_V}{k T_B}$$

$T_B$ 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 $\tau_0 = 10^{-25}$ to $10^{-23}$ 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) [26]. 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 [26]

$$\ln \frac{1}{2\pi\nu} = \ln \tau_0 + \frac{E_a}{k(T-T_0)}$$  \hspace{1cm} (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 $4.2 \times 10^{-9}$ to $5.1 \times 10^{-10}$ s. The good agreement between the experimental data and Vogel-Fulcher model confirms the existence of strong interactions between nanoparticles.

![Real parts of effective magnetic susceptibility](image)

Figure 3. Thermal variation of real parts of effective magnetic susceptibility of synthesized samples.

Conclusions

Fine particles single phase of spinel phase are prepared by reverse micelle method. The value of calculated saturation magnetization for fine particles is much lower than that of large particles. This behavior can be explained by core-shell model. 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 Neél-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.

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