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Synthesis and characterization of nano silver ferrite composite

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ABSTRACT

We report the synthesis of nano sized silver ferrite composite having the empirical formula $AgFeO_2$ by a co-precipitation method. The resulting powders are thin platelets, transparent and a rich ruby red in color in transmission. The X-ray diffraction (XRD) powder data consisted of only nine reflections, and the analysis showed the unit cell to be rhombohedral. The powders showed extensive XRD line broadening and the sizes of the crystals are calculated to be in the range 4–36.5 nm. The morphology of the silver ferrite composite studied using scanning electron microscope showed nano sized particles. The particle size is found to increase with increase in annealing temperature. The magnetic behavior, measured using a vibrating sample magnetometer, indicated a change from paramagnetic to ferromagnetic with increase in particle size.

1. Introduction

Magnetic particles of the nanometer scale size are of interest due to their technological applications and unique magnetic properties which differ considerably from the bulk materials. Magnetic particles with sizes less than the critical size become single domain in contrast with the usual multi-domain structure of the bulk magnetic materials exhibiting unique phenomena such as superparamagnetism [1].

Semiconductor technologies are developing magnetic random access memories (MRAMS) where non-volatile magnetic dots are used for storage in place of storage capacitors of a traditional semiconductor. The storage media relating to today's commercial magnetic hard disks involve typical grain sizes of 10–20 nm at approximately 10^3 grains/bit with a recording density of 1 G bit/in^2. The grains segregate randomly and introduce statistical noise into the read-out signal due to the variation in grain size coercivity and domain structure. Superparamagnetic behavior of grain size is the primary requirement for reducing these fluctuations and to improve the magnetic storage density and the superparamagnetic limit imposes a minimum particle size of 10 nm [2]. Magnetic nanoparticle systems exhibiting superparamagnetic behavior display little or no remanence and coercivity while keeping a very high saturation magnetization and have potential applications in biomedicine [3,4], magnetic drug delivery, cell-sorting systems [5,6] and in magnetic refrigeration technology [7,8]. These applications require biocompatible magnetic nanomaterials. Both silver and ferrites meet these requirements but are not yet synthesized in the nanoform. However the formation of bulk silver ferrite was reported by Croft et al. [9]. For the first time we report here the synthesis, characterization and magnetic studies of nano silver ferrite composite.

2. Experimental

2.1. Materials

All the chemicals used in this study are of analytical reagent grade. Silver nitrate, ferric nitrate, and sodium hydroxide procured from M/s. Merck and BDH [Analar] have been used as received.

2.2. Synthesis of nano silver ferrite composite

In a typical synthesis process, a mixture of 0.05 M silver nitrate and 0.05 M ferric nitrate solutions in double distilled and de-ionized water was stirred for 4 h at 27 °C, and then heated to 70 °C for 1 h. 0.4 M (25 ml) solution of sodium hydroxide was prepared and slowly added to the above solution by monitoring the pH of the solution. The reactants were constantly stirred by a magnetic stirrer until a pH level of 11–12 was reached [14] [15]. The stirring was further continued for 6 h for aging. The resulting ruby-brown precipitate was collected by filtration and washed with de-ionized

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water for several times and then dried. The resulting powders are found to be of rich ruby red color. These powders were annealed at 400, 700 and 900 °C and subjected to XRD studies to characterize the structure and determine the grain size.

2.3. Instrumentation

X-ray diffraction pattern of the composite was recorded using a Philips 1011 X-ray diffractometer (operating with 40 KV and 45 mA) with Cu Kα (1.5406 Å) radiation. A Philips field effect (model XL 30) scanning electron microscope (SEM) with energy-dispersive spectrometer (EDS) working at 30 kV was used to examine the surface morphology and elemental composition of the powders. The magnetization measurements of the samples were carried out at room temperature using a Lakeshore-7400 vibrating sample magnetometer (VSM) with the applied magnetic field in the range of −15 to 15 kG.

3. Results and discussion

The XRD pattern (Fig. 1) of powders annealed at 400, 700 and 900 °C clearly showed the formation of the nano silver ferrites. The sizes of the silver ferrite particles calculated using the Scherer formula at different annealed temperatures were found to range between 4.5 and 36.5 nm as shown in Table 1. Notice from Table 1 that the size of the nanoparticles increases with increase in annealing temperature. The analysis of XRD pattern with nine reflections (curve labeled as (a) in Fig. 1 and inset) revealed the unit cell present in the crystal structure of the silver ferrites to be rhombohedral. The SEM images of these nano silver ferrites annealed at 400 and 700 °C are shown in Figs. 2 and 3. SEM images clearly show that surface morphology of the silver ferrites is quite different with annealing temperature and the size of the particles increases with increase in annealing temperature and consistent with data obtained from XRD analysis. Further it is also observed that nano sized silver ferrite composite crystals are stable at 400 °C. At higher temperatures the composition is not a single phase and the phase $AgFeO_2$ decomposes irreversibly above 400 °C with loss of oxygen to yield both metallic silver and Fe_2O_3 or silver doped ferrites.

$$2Ag_2Fe_2O_4 \overset{700^0C}{\rightarrow} 4Ag + 2Fe_2O_3 + O_2$$

The size of the particles is observed to increase linearly with annealing temperature, while annealing generally decreases the lattice defects and strains. However it could also increase the average size of the nanoparticles [8]. The nano silver ferrite powders are observed to be rich ruby red colored thin platelets. Microscopic and SEM observation of the platelets revealed that some of them are six sided though the true symmetry is rhombohedral [9] as characterized by XRD.

The magnetic properties of these nanoparticles are analyzed using a vibrating sample magnetometer (VSM). The VSM analyses of the nano silver ferrite samples annealed at different temperatures are shown in Fig. 4. The VSM data of silver ferrite composite annealed at 400 °C show that the sample is paramagnetic in nature. The magnetic remanence (M_R=0.0023 emu/g) is found to be very small (inset of Fig. 4) and shows high magnetic moment, M_S=1.10 emu/g, at an applied field of 15 kG. On the other hand, silver ferrite composite annealed at 700 and 900 °C showed ferromagnetic character (Fig. 4) with M_R=0.035 emu/g, M_S=0.3833 emu/g and M_R=0.069 emu/g, M_S=0.3046 emu/g at 15 kG applied magnetic field. The parameters deduced from VSM analysis of the samples are given in Table 1. It can be seen

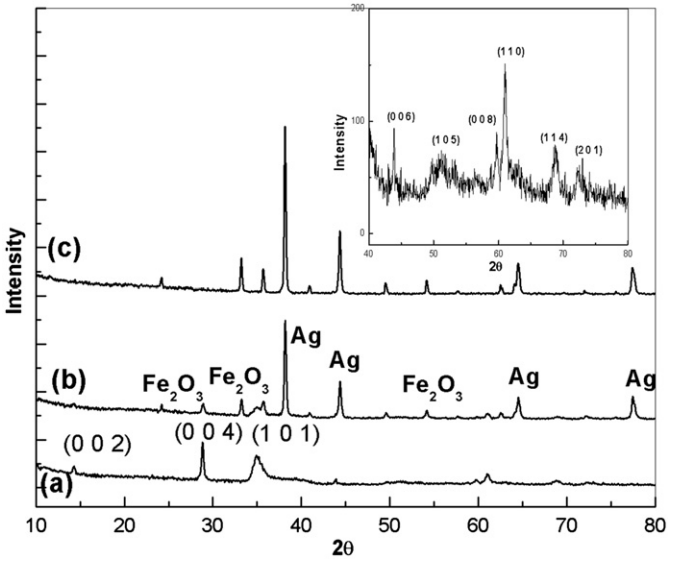

Fig. 1. The XRDs of nano silver ferrite composite annealed at 400 °C (a), 700 °C (b) and 900 °C (c). Sizes of the nano composite are 4.5 nm (400 °C), 32 nm (700 °C) and 36.5 nm (900 °C).

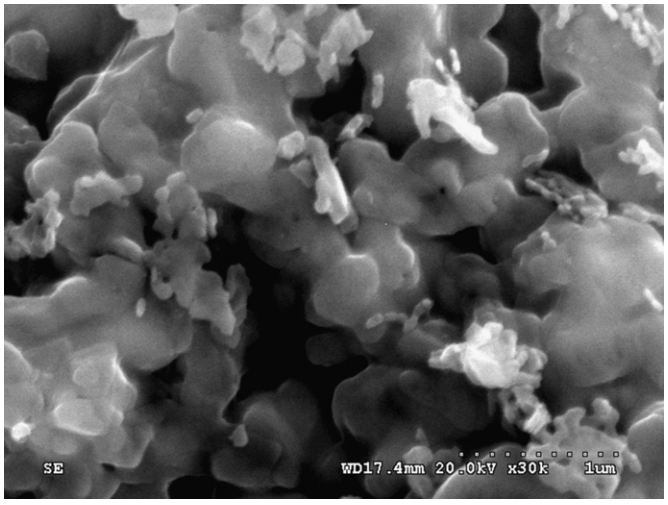

Fig. 2. SEM image of nano silver ferrite composite annealed at 400 °C.

Table 1
Various magnetic parameters of nano silver ferrite composite at different annealing temperatures.

Annealing temperature (°C)	Particle size (nm)	Saturation magnetization, M_S (emu/g) at 15 kG	Remanent magnetization, M_R (emu/g)	Coercivity, H_C (kG)	Magnetic nature
400	4.5	high	0.002	0.002	Paramagnetic
700	32	0.383	0.035	0.548	Ferromagnetic
900	36.5	0.305	0.069	0.785	Ferromagnetic

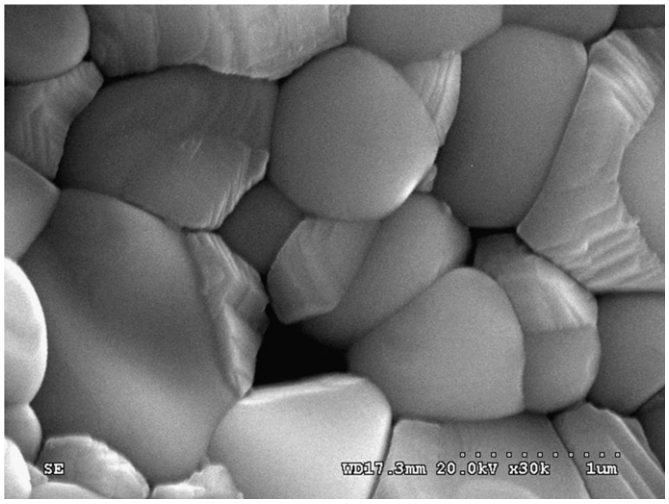

Fig. 3. SEM image of nano silver ferrite composite annealed at 700 °C.

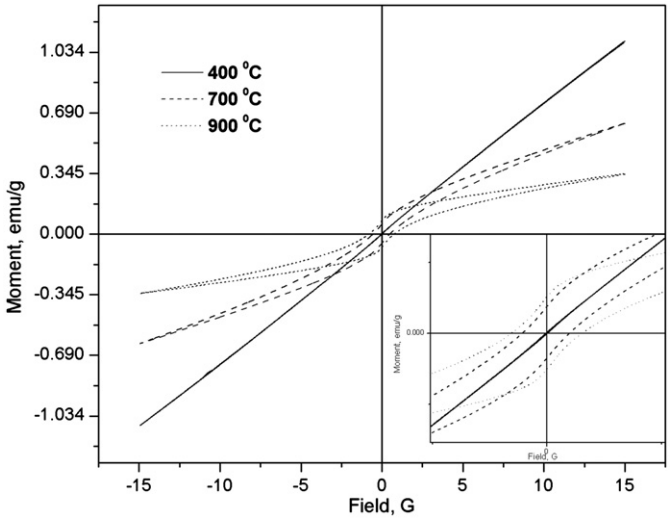

Fig. 4. The VSM data of nano silver ferrite composite annealed at 400, 700 and 500 °C.

from Table 1 that the coercivity of the samples increases with increase in annealed temperature when particles are nano sized.

The very large coercivity and low saturation magnetization observed at 900 °C is consistent with a pronounced growth of magnetic anisotropy inhibiting the alignment of the moment in an applied magnetic field. The remanence ratios at these temperatures indicated the same feature, increasing from 0.0345 to 0.069 emu/g at room temperature (Table 1). The value of remanence ratio of 0.5007 is very close to the expected value of 0.5 for a system of non-interacting single domain particles with uniaxial anisotropy [10] even though the silver ferrite composite has a rhombohedral structure. The existence of an effective uniaxial anisotropy in magnetic nanoparticles is attributed to surface effects [11]. Vibrating sample magnetometer data indicate that as the particle size increases with annealing temperature the paramagnetic nature of the composite changes to ferromagnetic. Hence, it is expected that in between annealing temperatures of 400 and 700 °C the nanopowder could be in superparamagnetic state. The coercivity of the nanoparticles is also studied as a function of particle size at room temperature (300 K) [12] and is shown in Fig. 5. The linear fit to the data shows that the coercivity increases steeply with increase in size.

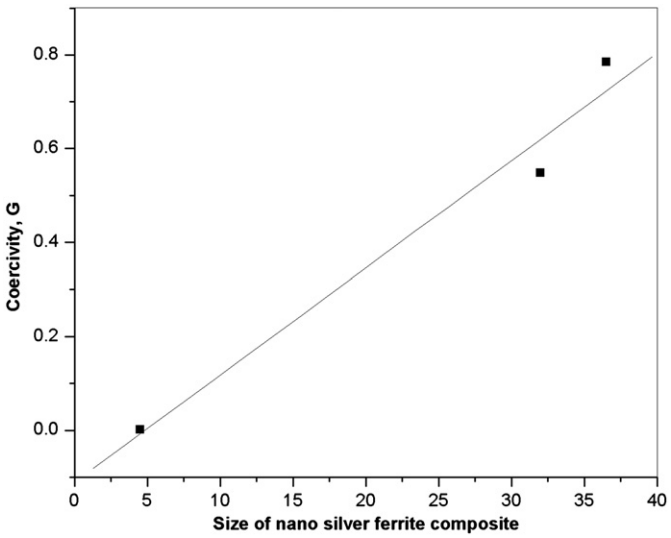

Fig. 5. The variation in coercivity with size of nano silver ferrite composite.

The magnetization of different sized nanoparticles as a function of annealing temperature is shown in Fig. 4. The magnetic nature not only depends on the variation of the particle size but also depends on doping levels of Ag. Doping decreases the strength of the exchange interactions, and leads to the decrease in the value of the saturation of magnetization with increase in particle size [13]. The saturation value of the magnetization for smaller particles is found to be significantly less than that of the bulk and approaches the bulk value with increase in particle size. The smaller value of M_S in smaller particles is attributed to the greater fraction of surface spins and leads to a superparamagnetic state and a smaller value of net magnetic moment.

4. Conclusions

For the first time, we have successfully prepared single phase materials of the AgFeO system. We conclude that the single phase is not stable at above 400 °C .The onset of ferromagnetic order in samples annealed at 700 and 900 °C suggests the decomposition of the phase. The particle size of $AgFeO_2$ annealed at 400 °C is quiet small (4 nm).The simplicity and feasibility of making nano $AgFeO_2$ by our method seems very promising.

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