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Characterization and Magnetic Properties of Nickel Ferrite Nanoparticles Prepared by Ball Milling Technique

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Nickel ferrite nanoparicles with various grain sizes are synthesized using annealing treatment followed by ball milling of its bulk component materials. Commercially available nickel and iron oxide powders are first mixed, and then annealed at 1100°C in an oxygen environment furnace and for 3 h. The samples are then milled for different times in an SPEX mill. X-ray diffraction pattern indicates that in this stage the sample is single phase. The average grain size is estimated by scanning electron microscopy (SEM) and x-ray diffraction techniques. Magnetic behavior of the sample at room temperature is studied using a superconducting quantum interference device (SQUID). The Curie temperature of the powders is measured by an LCR–meter unit. The x-ray diffraction patterns clearly indicate that increasing the milling time leads to a decrease in the grain size and consequently leads to a decrease in the saturation magnetization as well as the Curie temperatures. This result is attributed to the spin-glass-like surface layer on the nanocrystalline nickel ferrite with a ferrimagnetically aligned core.

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There is a growing interest in magnetic ferrite nanoparticles because of their wide applications in permanent magnets, magnetic drug delivery, microwave devices and high density information strong technology.[1−4] Spinel ferrites have the general molecular formula $(A^{2+})[B_2^{3+}]\ O_4^{2-}$, where A^{2+} and B^{3+} are the divalent and trivalent cation respectively, occupying tetrahedral (A) and octahedral (B) interstitial positions of an fcc lattice formed by O^{2-} ions. Nickel ferrite, $NiFe_2O_4$, is an inverse spinel in which the tetrahedral sites (A) are occupied by Fe^{2+} and Ni^{2+} ions.[2] This material is largely used in electric and electronic devices as well as in the catalysis.[5] In the present study we investigate the synthesis of the nanocrystalline $NiFe_2O_4$ powders by ball milling, fallowed by annealing the powders at moderate temperatures (400–800°C). Curie temperature, as a function of powder grain size, and the other magnetic properties of the samples, i.e. saturation magnetization and hysteresis (M-H) loops, has been investigated.

Nickel ferrite was first synthesized in nanocrystalline form by the conventional ceramic method. In order to make nickel ferrite ($NiFe_2O_4$), both nickel oxide (Ni_2O_3) and iron oxide (Fe_2O_3) were mixed at a molar ratio of 1:2 followed by annealing the mixture in an oxygen environment furnace at 1100°C for 3 h. There would exist the chemical reaction

$$2Ni_2O_3 + 4Fe_2O_3 \rightarrow 4NiFe_2O_4 + O_2. \qquad (1)$$

The produced nickel ferrite with various grain sizes then was milled in a steel cylinder of a SPEX high energy shaker mill. The mill cylinder was loaded with 10 g of $NiFe_2O_4$ (with the purity of 99.95 at%) and 30 g steel balls. The mill was then operated to shake at the frequency of approximately 1200 Hz. In order to keep the ratio of balls to loaded mass constant at 3 : 1 for all the samples, the mill cylinder was cleaned and loaded with exactly 10 g of material for each milling trial. Milling time has been varied between 1 and 10 h. The milled samples (especially one which milled for 10 h) were annealed at the temperatures varying between 400 and 800°C.

In order to investigate the formation of different phases in the milled and annealed nickel ferrite powders, the structure of the samples was studied using x-ray diffraction technique. The Curie temperature of the samples was also measured by an LCR–meter unit. Magnetic properties and magnetization measurements were performed using a superconducting quantum interference device (SQUID) magnetometer to study the samples' hysteresis ($M - H$) loops.

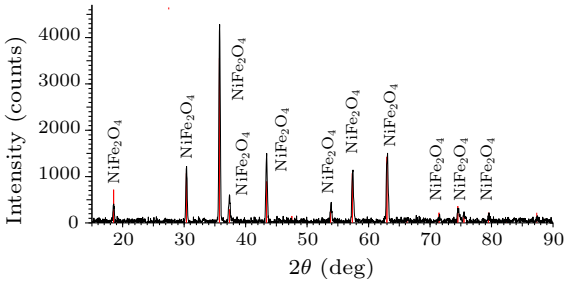

Fig. 1. X-ray diffraction pattern of a $NiFe_2O_4$ powder sample, prepared by the conventional ceramic method.

The x-ray diffraction pattern (XRD) of the bulk $NiFe_2O_4$ prepared by the conventional ceramic method is shown in Fig. 1. The diffraction pattern of as obtained sample confirms the spinel phase.[6] The

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SEM image of a similar sample, as shown in Fig. 2, illustrates the general morphology of the $NiFe_2O_4$. The octahedron faces are apparently distinguishable. The size distribution of the octahedrons ranges from 300 to 350 nm.

The x-ray pattern of the sample milled for various times is shown in Fig. 3. The diffraction peaks of the milled samples are broadened, which can be the result of grain size reduction as well as the atomic level strain introduced during the milling process.[2] After 8 h ball milling, the sample is not still single phase, and some new picks appear in the x-ray pattern. In order to omit the undesired picks and to repeat recovery $NiFe_2O_4$ phase, the sample was then milled for 10 h annealed in the various temperatures.

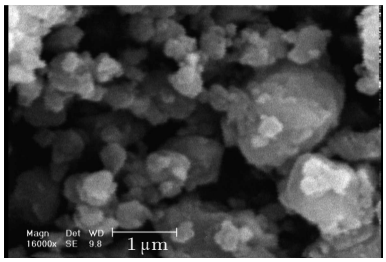

Fig. 2. Scanning electron microscopy image of a $NiFe_2O_4$ powder sample prepared by the conventional ceramic method.

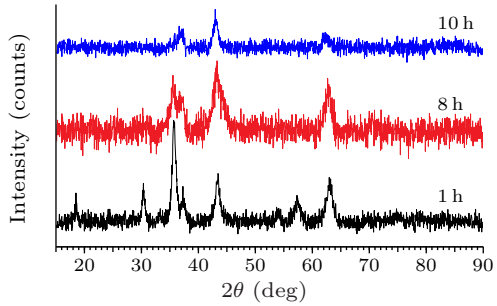

Fig. 3. X-ray diffraction pattern of the $NiFe_2O_4$ powder after milling for 1, 8 and 10 h, respectively.

The x-ray pattern of the sample milled for 10 h followed by annealing for 5 h in the various temperatures is shown in Fig. 4. With the increasing annealing temperature, the diffraction peaks become narrower and sharper, suggesting the increase in particle size and crystallinity.

The average crystallite size has been evaluated from the full width at half maximum of the reflection (311) peak in the XRD pattern, using the Debye–Scherrer formula[7]

$$t = \frac{0.9\lambda}{\beta \cos\theta}, \tag{2}$$

where t is the crystallite size, β is the full width of the diffraction line at half of the maximum intensity measured in radians, λ is x-ray wavelength (Cu $K\alpha 1$ radiation, 0.154 nm) and θ is the Bragg angle.

The average crystallite sizes are estimated by Debye–Scherrer formula for the samples milled for 10 h and annealed at 400, 500 and 800°C for 5 h. The results indicate that the crystalline sizes increase with the annealing temperature and reach the values of 10, 12 and 31 nm, respectively. The reason why the grain sizes increase dramatically at annealing temperature of 800°C might be due to the dominance of the activation energy during the grain growth process.

The lattice parameters for different prepared samples are calculated using the formula[7]

$$a = \frac{\lambda\sqrt{h^2 + k^2 + l^2}}{2\sin\theta}, \tag{3}$$

where λ is the x-ray wavelength, θ is the Bragg angle, h, k and l are the miller indices, and a is the lattice parameter. The calculated values for lattice parameter and densities are about 8.33 ± 0.01 Å and 5.36 ± 0.02 g·cm^{-3}, respectively. No significant change in the lattice parameter sizes was observed for the samples annealed at different temperatures and even for non-annealed sample. The small differences may well be within the experimental error, because Fe^{3+} ions and Ni^{2+} ions are attributed to homogeneity in spinel structure and there is a strong electrostatic force between ions so that the ball milling process can not destroy it.

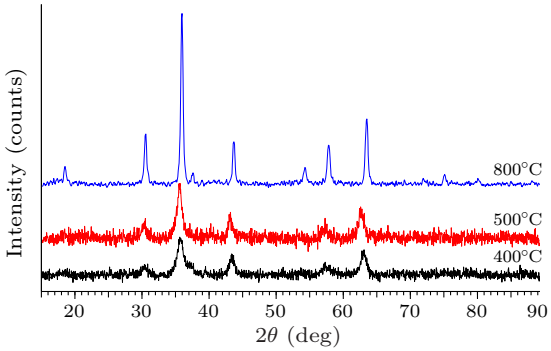

Fig. 4. X-ray diffraction pattern of a $NiFe_2O_4$ milled sample for 10 h at different temperatures.

Table 1. Lattice parameters and densities for the $NiFe_2O_4$ samples at different temperatures.

Temperature (°C)	Lattice parameter (Å)	Density (g·cm^{-3})
Bulk	8.33	5.38
400°C	8.33	5.35
500°C	8.32	5.36
800°C	8.33	5.37

X-ray density d_x was calculated using the following formula[8]

$$d_x = \frac{8M}{Na^3}, \tag{4}$$

where M, N and a are the molecular weight, Avogadro's number and lattice parameter, respectively. The d_x values are also tabulated in Table 1. The fact that the x-ray densities increase with the annealing

temperature may be attributed to the result of porosity reduction during the annealing process.

The inductance of a closed packed coil (solenoid) woven around a material with the magnetic permeability of μ is calculated using the equation[9]

$$L = \frac{\mu N^2 A}{l}, \tag{5}$$

where l and A are the sample length and cross section respectively, N is the number of coils and μ is the magnetic permeability. The magnetization M of a specific core material located inside the coil is then calculated using the following equation[9]

$$M = \frac{H(\mu - 1)}{4\pi}, \tag{6}$$

where H is the magnetic field produced by the coil. Since the magnetization is proportional to the coil inductance ($M \propto L$), as the magnetization changes with temperature the inductance also changes. Therefore the Curie temperature can be indicated from the variation of the coil inductance versus temperature.

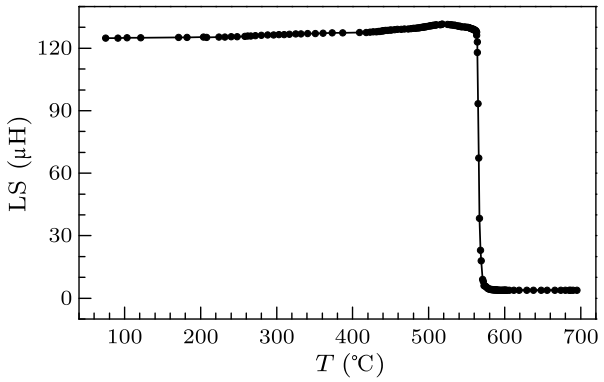

Fig. 5. Inductance versus temperature for the bulk $NiFe_2O_4$. Curie temperature is measured to be about 570°C.

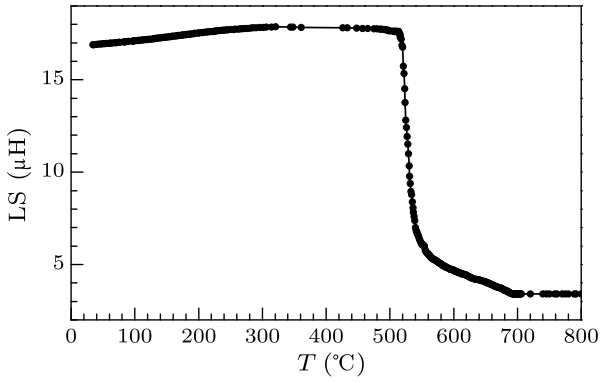

Fig. 6. Inductance versus temperature for a nanocrystalline $NiFe_2O_4$ sample. Curie temperature is measured to be 517°C.

The Curie temperature measurements for both the bulk and nanocrystalline nickel ferrites has been performed using an LCR meter. The results are shown in Figs. 5 and 6, respectively. As can be seen from the figures, the Curie temperature value for the nanocrystalline sample is found to be 517°C, much smaller than that measured for the bulk sample (570°C).

The decrease in T_C as the particle size decreases might be explained on the basis of the molecular field of ferrimagnetism theory.[10] According to this theory, as the temperature is raised, magnetization decreases monotonically until it becomes zero at a temperature known as the Curie temperature. The smaller the magnetic particle size, the lower the saturation magnetization, hence the lower the Curie temperature. In our samples the saturation magnetization for the nanocrystalline $NiFe_2O_4$ is found to be significantly smaller than that measured for bulk $NiFe_2O_4$ materials, resulting in the nanoscale size of the milled $NiFe_2O_4$ samples.

In order to investigate the magnetic properties of nanocrystalline nickel ferrite in an accurate manor, the variation of magnetization as a function of applied magnetic field at room temperature is studied using an SQUID magnetometer. The result is presented in Fig. 7.

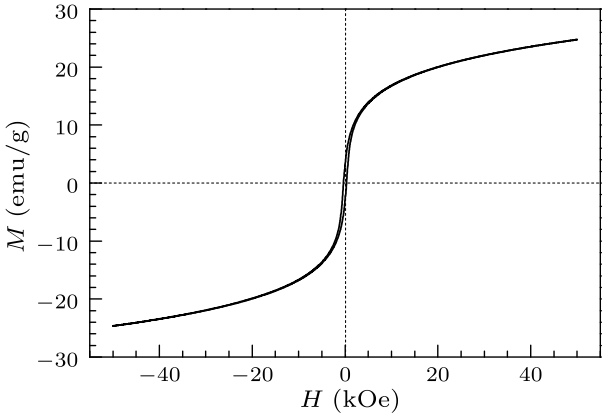

Fig. 7. Hysteresis loop (magnetization as a function of applied magnetic field) for a typical nanocrystalline nickel ferrite sample.

This sample exhibits nearly zero remanence and zero coercivity suggesting a superparamagnetic behavior for nanocrystalline nickel ferrite. The saturation magnetization for the nanocrystalline $NiFe_2O_4$ at 300 k is measured to be 24 emu/g. This value is significantly lower than 55 emu/g, which was reported for the multidomain bulk $NiFe_2O_4$.[11] The small value of saturation magnetization (compared to that measured for the multidomain bulk $NiFe_2O_4$) has recently been explained in terms of the core shell morphology of the nanoparticles consisting of ferrimagnetically aligned core spins, and spin-glass-like surface layer. This model is illustrated in Fig. 8. The spin glass shell leads to decrease of the number of aligned magnetic moment in the entire particles. As can be seen in Fig. 8, if the magnetization of spin glass shell drops to

zero, then we can adopt the equation[12]

$$M_S = M_{SO}(1 - 2t/D)^3, \tag{7}$$

where M_S is the saturation magnetization of the powder sample, M_{SO} is the saturation magnetization of the bulk sample, t is thickness of shell, and D is the grains average diameter.

If this surface layer is absent, the magnetization of the particles will have a saturation value, increasing with applied magnetic field up to a particular magnetic field, and the core magnetic moments would be aligned in the applied field. Nanoparticles which have a large surface to volume ratio exhibit enhanced spin disorder relative to that for the large (in micron size) particles when they are measured in the same applied magnetic field and temperature.[1] The surface layer magnetic moment anomalies might be due to broken exchange bonds, high anisotropy layer on the surface, or a loss of the long-rang order in the surface layer. These effects are more intense in the case of ferrites because of the super exchange interactions through the oxygen ions. The presence of another atom (ion) in the form of impurity or absence of the oxygen ions at the surface leads to the breakage of the super exchange bonds between the magnetic cations inducing a large surface spin disorder.[13] The super-exchange interaction depends on the bond angles and the bond lengths, which would obviously be different at the surface due to termination of the bonds.[14]

Nanocrystalline nickel ferrite was synthesized using the mechanical alloying method. The nanocrystallie grain sizes were estimated to be about 10–31 nm (depends on the heating treatment); using the XRD technique and the SEM study. The nanocrystalline nickel ferrite exhibits a Curie temperature of 517°C, well below the measured one for the bulk nickel ferrite (570°C). The decrease in saturation magnetization of magnetic nanocrystalline compared to the bulk ferrite can be explained in terms of two-component nanoparticle system consisting of a spin-glass-like surface layer and a ferrimagnetically aligned core. Magnetic properties of a selected sample were studied using an SQUID magnetometer. This sample exhibits nearly zero remanence and zero coercivity, suggesting a superparamagnetic behavior for nanocrystalline nickel ferrite.

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