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Low temperature ferromagnetic properties, magnetic field induced spin order and random spin freezing effect in $Ni_{1.5}Fe_{1.5}O_4$ ferrite; prepared at different pH values and annealing temperatures

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ABSTRACT

We present the low temperature magnetic properties in $Ni_{1.5}Fe_{1.5}O_4$ ferrite as the function of pH at which the material was prepared by chemical route and post annealing temperature. The material is a ferri/ferromagnet, but showed magnetic blocking and random spin freezing process on lowering the measurement temperature down to 5 K. The sample prepared at pH ~12 and annealed at 800 °C showed a sharp magnetization peak at 105 K; the superparamagnetic blocking temperature of the particles. The magnetization peak remained incomplete within measurement temperature up to 350 K for rest of the samples, although peak temperature was brought down by increasing applied dc magnetic field. The fitting of temperature dependence of coercivity data according to Kneller's law suggested random orientation of ferromagnetic particles. The fitting of saturation magnetization according to Bloch's law provided the exponent that largely deviated from 3/2, a typical value for long ranged ferromagnet. An abrupt increase of saturation magnetization below 50 K suggested the active role of frozen surface spins in low temperature magnetic properties. AC susceptibility data elucidated the low temperature spin freezing dynamics and exhibited the characters of cluster spin glass in the samples depending on pH value and annealing temperature.

1. Introduction

Spinel ferrites, having general formula of MFe_2O_4 (M = divalent metal ion, e.g. Ni, Co, Cu, etc.), remained as one of the most attractive magnetic oxides due to a rich class of magnetic and electronic properties. The interest for Nickel ferrite ($NiFe_2O_4$) stems from the fact that it is a soft ferri/ferromagnet with reasonably high magnetization. The magnetic properties of $NiFe_2O_4$ are determined primarily by the superexchange interactions between Ni and Fe ions in tetrahedral (A) and octahedral (B) sites of cubic spinel lattice structure [1,2]. Without elemental substitution effect, the long-ranged ferrimagnetic spin order in $NiFe_2O_4$ can also be perturbed in nanocrystalline form by surface effects (spin disorder, anisotropy, and exchange interactions) and exchange of Ni and Fe ions among the A and B sites. This increases multifunctionalities in nanocrystalline form of soft ferromagnetic ferrites and make them suitable for applications in the field of power electronics (transformer core), recording media, microwave devices, and medical treatment (hyperthermia, ferrofluid) [3–5]. The tuning of ferromagnetic parameters (coercivity, saturation magnetization, magnetic blocking, and ferromagnetic squareness) in a wide temperature scale is important for applying the magnetic material. Hence, it is necessary to understand the basic mechanisms that control the tuning of ferromagnetic parameters in magnetic materials.

From literature reports, it is understood that the nature of surface spin structure, magnetic frustration and inter-particle interactions determine the low temperature magnetic properties of nanoparticles in the form of superparamagnetic blocking, spin glass, and exchange bias effect [6–9]. The reduction of magnetization, higher coercivity, and surface spin disorder in nanoparticles of $NiFe_2O_4$ are remarkably different from that in micron-sized particles [2,10]. Core-shell spin structure has been modeled to explain the magnetic reduction in $NiFe_2O_4$ nanoparticles [1,11], where spins in the core are ferrimagnetically aligned as in bulk and shell forms a disordered spin structure that controls the magnetic reduction and exhibition of spin glass and superparamagnetic feature. The exchange of Ni and Fe ions among A and B sites and surface spin canting were identified as other factors that determine magnetic reduction and spin glass feature in $NiFe_2O_4$ nanoparticles [1,9]. Lee et al. [12] considered the intermediate spin layer

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between core and shell for the magnetic field induced shift of blocking temperature. It is a great challenge to distinguish the blocking of core spins from the freezing of surface spins [6]. Kodama et al. [11] attributed the spin glass like feature in $NiFe_2O_4$ nanoparticles due to freezing of frustrated surface spins. In NiO nanoparticles, Winkler et al. [13] proposed that antiferromagnetic core of NiO was blocked at higher temperature and disordered surface spins showed spin glass like freezing at low temperature. Recent studies have shown that blocking/freezing phenomena and ferromagnetic properties in nanoparticles remarkably depend on the variation of synthesis conditions (pH value, annealing temperature, annealing atmosphere, etc) of chemical routed ferrite samples [9,10,14].

We reported the room temperature magnetic properties of $Ni_{1.5}Fe_{1.5}O_4$ ferrite [15] with the variation pH value and annealing temperature. The as-prepared material was annealed in the temperature range 500–1000 °C [16]. Using dielectric spectroscopy study [17], we observed a transformation in electrical charge dynamics from low temperature semiconductor state to high temperature semiconductor state with an intermediate metal like state in the samples. The metal like state was understood as an effect of the crossover of localized hopping of electronic charge (electrons) at low measurement temperatures to thermally activated long range hopping at higher temperatures. In this work, we report the electronic spin dynamics in $Ni_{1.5}Fe_{1.5}O_4$ samples under magnetic field for measurement temperature down to 5 K. Our objective is to study the effects of the variation of pH value during chemical reaction and post annealing temperature on low temperature magnetic phenomena (blocking/freezing of electronic spin moment) and tuning of ferromagnetic parameters in $Ni_{1.5}Fe_{1.5}O_4$ ferrite.

2. Experimental

2.1. Sample preparation

Details of the material preparation and characterization were reported earlier [15–17]. The samples were prepared by chemical reaction of the stoichiometric amount of $Ni(NO_3)_2{\cdot}6H_2O$ and $Fe(NO_3)_3{\cdot}9H_2O$ salts in solution at 80 °C by maintaining pH at 6, 8, and 12. Finally, the chemical routed (as-prepared) material was made into pellets and annealed at selected temperatures. The X-ray diffraction pattern (CuK_α lines with $\lambda = 1.5406$ Å) and Raman spectra were used to confirm the formation of single phased cubic spinel structure. The material chemically reacted at pH value 8–12 formed single phase upon annealing the as-prepared material in air. The sample prepared at pH 6 formed a minor amount of α-Fe_2O_3 when annealed in air. However, the sample when annealed under vacuum ($\sim 10^{-5}$ mbar) formed single-phased cubic spinel structure with space group Fd3m. The samples are labeled as NFpHX_Y, where X is pH and Y is annealing temperature in degree centigrade. The structural information (lattice parameter and grain size) for some of the single-phased samples used in this work is indicated in Fig. 1 for information to readers. The roles of pH value and annealing temperature of the samples on the variation of grain size and lattice parameter were described in details in the earlier work [16].

2.2. Measurement

Magnetic properties of the samples were studied using physical properties measurement system (PPMS-EC2, Quantum Design, USA). The temperature dependent dc magnetization (M) was measured using zero field cooling (ZFC) and field cooling (FC) modes. In ZFC mode, the sample was cooled from higher temperature (320 K) without applying external magnetic field down to the lowest measurement temperature (5 K). Then, magnetic measurement started in the presence of set magnetic field (say, 100 Oe) and MZFC(T) data were recorded during the increase of temperature (T) from 5 K to 300 K/320 K. In FC mode, the sample was cooled under set magnetic field from 320 K to low temperature (5 K) and MFC(T) data were recorded without changing the magnetic field during the increase of temperature up to 320 K. The magnetic field (H) dependence of dc magnetization (M(H)) was measured by zero field cooling the sample from 320 K to the measurement temperature, which was set in the range 5–300 K. The ac susceptibility (real: χ' and imaginary: χ'' components) data were recorded in the temperature range 10 K–340 K by applying ac magnetic field (amplitude 1 Oe with frequencies in the range 37 Hz–10 kHz).

3. Results and discussion

3.1. Temperature dependent magnetization

Fig. 1 shows the temperature dependence of MZFC and MFC curves at dc field of 100 Oe for the samples, chemically synthesized at pH values 6 (Fig. 1(a–d)), 8 (Fig. 1(e–g)), 12 (Fig. 1(h–i)) and annealed at different temperatures. The samples, prepared at pH 6 and 8, exhibited the characters of ferro/ferrimagnetic nanoparticles with splitting between MFC(T) and MZFC(T) curves below 320 K, where MZFC(T) curve decreased and MFC(T) curve increased on decreasing the measurement temperature down to 5 K. The MZFC (T) curves of these samples indicated a broad maximum or incomplete maximum within the measurement temperature limit 320 K. However, magnetic gap between MZFC and MFC curves at lower temperature decreases and the peak appears to be shifted to higher temperature on increasing the annealing temperature (and increase of grain size) of the samples. The magnetization of the samples prepared at pH 6 is found higher than the samples prepared at pH 8 and 12. An additional magnetic shoulder is clearly appeared at low temperature (below 30 K) for the samples prepared at pH 6 and annealed at higher temperature (800–1000 °C). The origin of low temperature magnetic feature will be discussed using the ac susceptibility data. A different type of magnetic feature is observed for the samples prepared at pH 12 and annealed at 800 °C (grain size ~6 nm). This sample exhibited a well defined superparamagnetic blocking temperature (T_B) at about 105 K, and splitting between MZFC and MFC curves below the blocking temperature (Fig. 1(h)). On increasing the annealing temperature to 1000 °C, the sample prepared at pH 12 was not able to achieve the blocking temperature within 300 K (Fig. 1(i)). This is the effect of increasing grain size (6 nm–29 nm) in the material. From physics point of view, the FC curve is in quasi-equilibrium state due to local ordering of spins or cluster of spins during field cooling process while the ZFC curve is in non-equilibrium blocking state when relaxation time (τ) of the spins or cluster of spins is greater than the magnetic measurement time ($\tau_m \sim 10^2$ s). Since MZFC(T) curves exhibited a broad maximum or incomplete maximum, it is difficult to exactly determine the blocking temperature for most of the samples. A broad peak indicates a distribution of blocking temperature (T_B), which can be related to distribution of magnetic anisotropy constant (K) and grain volume (V) by the relation $k_BT_B \sim 25$ KV [18]. In such case, the temperature derivative of MZFC(T) curve ($\frac{dMZFC}{dT}$) was fitted with Gaussian shape to get the information of the distribution of relaxation time or anisotropy barrier of the magnetic particles below T_B [19]. The average blocking temperature was estimated from the intercept of $\frac{dM_{ZFC}}{dT}$ vs. T curves on temperature axis where $\frac{dMZFC}{dT} = 0$. The fit parameters, like peak position (inflection point of M_{ZFC} (T) curves below T_B), full width at half maximum (FWHM) of the peak, and peak height)