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Re-creation of single phase, and improvement of magnetic property of $CoFe_2O_4$ nanoparticles versus heat treatment

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ABSTRACT

Our studies on the crystal characterization and magnetic property of $CoFe_2O_4$ nanoparticles (NPs) point out their instability in a specific temperature range. While as-prepared NPs exhibit single phase in a cubic spinel structure, annealing at temperatures T=673–1273 K leads to the development of an impurity phase of Fe_2O_3. Interestingly, annealing at higher temperatures re-creates the single phase of NPs. This strongly influences their magnetic property. The magnetic inhomogeneity and/or multiple phase exist in as-prepared NPs and in those annealed below 1273 K, better magnetic property is found in the samples with annealing temperature (T_{an}) higher than 1273 K. Ferromagnetic-paramagnetic phase transition temperatures of these samples are located around 815–850 K, and are less dependent on T_{an}. At room temperature, their saturation magnetization is located in the range of 41–55 emu/g, while the coercivity can be changed from 600 to ~3200 Oe. These results are related to microstructures, structural phases, and exchange interactions between Fe and Co ions situated in the *A* and *B* sites of the spinel structure, which are modified by heat treatment.

1. Introduction

Spinel-ferrite oxides are ferrimagnetic compounds with the general chemical formula PQ_2O_4, where P and Q are divalent and trivalent ions, respectively. The spinel structure has two different interstitial positions of the cations. The first position is the tetrahedral (or *A*) site, where a cation is surrounded by four oxygen ions located at the corners of a tetrahedron. The second one is the octahedral (or *B*) site, where a cation is surrounded by six oxygen ions located at the vertices of an octahedron. A normal spinel is defined where eight divalent P cations occupy the *A* site, and the sixteen trivalent Q cations occupy the *B* site. If the *B* site is half occupied by divalent and half by trivalent ions, and the *A* site is occupied by trivalent ions, the structure is defined as inverse spinel [1]. Normal, inverse, and/or mixed spinels can be constituted under different fabrication and processing conditions. This leads to many intriguing optical, electrical, and magnetic properties, such as their multiferroicity, geometric frustration, charge-ordering transition, and magnetoresistance [2–8].

Among spinel-ferrite oxides, cobalt ferrite ($CoFe_2O_4$) has attracted much interest, because it has a high ferromagnetic-paramagnetic (FM–PM) transition temperature [9] and wealth of magnetic and electronic properties (such as large coercivity, moderate magnetization, photomagnetism, magnetostriction, wear resistance, and electrical insulation), and shows many applications in electronic devices, ferrofluids, magnetic delivery microwave devices, and high density information storage [10].

Normally, $CoFe_2O_4$ prefers an inverse arrangement of atoms (inverse spinel), independently of the valence of Co ions. This means that Co and Fe cations are attributed to both sites. The chemical formula is thus described as $(Co_{1-x}Fe_x)[Co_xFe_{2-x}]O_4$, where the round and square brackets refer to the *A* and *B* sites, respectively. The valences of Co and Fe in these compounds are usually 2+ and 3+, respectively [11–13], resulting in super-exchange interactions of (Co_A^{2+}, Fe_A^{3+})-(Fe_B^{3+}, Co_B^{2+}) pairs. In some cases, Co^{3+} ions are also present, and occupy the *B* site [10]. The various distributions of these cations over the *A* and *B* sites leads to different magnetic properties.

$CoFe_2O_4$ materials are easily prepared by many physical and chemical methods, such as the solid-state reaction [6,11], combustion reaction [10,11], double-microemulsion [11], co-precipitation [12], aqueous solution [13,14], sol-gel [15,16], spin-coating [17], and nanocasting strategy [18]. Accordingly, the structural characterization and magnetic properties of fabricated samples are very different [12,13,18]. For nanoparticles (NPs) synthesized by chemical methods,

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as-prepared $CoFe_2O_4$ products usually have low crystal quality, and consequently poor magnetic properties [7]. Heat treatment at high temperatures is thus necessary to improve their crystal structure and magnetic properties. To address this issue, we have prepared $CoFe_2O_4$ NPs and studied the changes in their particle size, structural characterization, and magnetic properties. Our study points out that both crystal quality and magnetic properties of the samples annealed above 1273 K are remarkably improved, compared with lower-temperature processed samples.

2. Experimental details

$CoFe_2O_4$ NPs were prepared by a hydrothermal method. Cobalt(II) acetate tetrahydrate, $Co(CH_3COO)_2{\cdot}4H_2O$, iron(II) chloride tetrahydrate, $FeCl_2{\cdot}4H_2O$, with purity above 98% (purchased from Daejung Chemicals & Metals Co. Ltd) were used as initial chemicals. The 0.1 M solution of the chemicals with stoichiometric amounts was well mixed in de-ionized water under constant stirring at room temperature for 2 h to achieve a uniform solution. This solution, together with ammonium hydroxide, NH_4OH (ACS reagent, 28–30% solution), was then poured into a glass cup, and additionally stirred for 30 min. The obtained homogeneous solution was poured into a stainless steel autoclave with a Teflon liner, sealed up, and maintained at 180 °C for 24 h for chemical reactions. After the synthesis, NPs were filtered, washed several times using de-ionized water and ethanol, and then dried at 120 °C for 5 h. Thermogravimetric analyses (TGA) of these as-prepared NPs (denoted as the sample with annealing temperature T_{an}=393 K) were carried out in the Ar ambient, with temperature increments of 3 K/min. They were also divided into small parts, and annealed in the Ar ambient for 4 h at different temperatures (T_{an}) of 673, 873, 1073, 1273, 1473 and 1573 K. The morphology and particle sizes of the samples obtained after heat treatment were checked by field-emission scanning electron microscopy (FE-SEM, Hitachi S-4800) equipped with an energy-dispersive X-ray spectrometer (EDX, Horiba), and the crystal structure determined by X-ray diffractometry (Rigaku, MiniFlex) equipped with a Cu-K_α radiation source (λ=1.54056 Å). Raman scattering (RS) spectra were acquired by XPLORA-Plus Horiba micro-Raman spectrometry working with an Ar ion laser (λ=532 nm). Magnetic properties at temperatures T=300–900 K were studied by using a vibrating sample magnetometer (LakeShore - Model 7404, LakeShore Cryotronics), where the samples were put in a helium medium.

3. Results and discussion

First, we carried out gravimetric analyses of the as-prepared $CoFe_2O_4$ NPs versus changing temperature. Fig. 1 shows TGA data in the temperature range T=373–1273 K (100–1000 °C). With increasing T from 373 to ~880 K, the weight of NPs gradually decreased. In this region, the total weight loss is about 3%, which is mainly caused by the evaporation of water and the decomposition of organic compounds persisting in NPs after fabrication. At higher temperatures (T=880–1273 K), the change in weight loss is less than 0.2%, as seen in the inset of Fig. 1. The formation and disappearance of an impurity phase Fe_2O_3, as confirmed below, could lead to this phenomenon.

Heat treatment influences not only the weight loss of NPs, but also their morphology and size. Fig. 2 shows SEM imagery of four typical samples with T_{an}=397, 673, 1073, and 1573 K. The results revealed the samples were composed of NPs in cluster. The annealing enhances the size of NPs, and leads to aggregation of NPs into larger clusters. Based on the particle-size distribution, the insets of Fig. 2, we estimated the average particle size (D) of NPs, which ranges from 25 to ~980 nm, as shown in Table 1. Notice that the D value of the T_{an}=673 K sample is about 7% smaller than that of T_{an}=393 K. This is due to the weight loss of NPs caused by heat treatment.

In Fig. 3, it shows room-temperature XRD patterns of all fabricated $CoFe_2O_4$ samples. The structural analyses with Miller-indexed peaks reveal the as-prepared sample (T_{an}=393 K) exhibits single phase in cubic-spinel structure, belonging to the $Fd\bar{3}m$ space group. However, the T_{an} increase from 673 to 1273 K leads to the development of anomalous XRD peaks, denoted in Fig. 3 by asterisks. These additional peaks are associated with an impurity phase of Fe_2O_3. Interestingly, Fe_2O_3 crystals are dissolved at temperatures $T_{an}{\geq}1473$ K to form a well-crystallized $CoFe_2O_4$ spinel phase. Such results prove that the crystal quality of Co ferrite NPs prepared by chemical routes are unstable in the T_{an} region of 673–1473 K, though as-prepared NPs are single phase in the cubic structure, and the annealing at temperatures $T_{an}{\geq}1473$ K is necessary to improve and re-create their single-phase structure. Based on the Miller-indexed XRD peaks, we also determined the average lattice parameter (a) and cell volume (V) of cubic $CoFe_2O_4$ NPs versus T_{an}. As shown in Table 1, a and V values for T_{an}=393 K sample are 8.389 Å and 590.379 Å^3 and tend to decrease gradually to about 8.367 Å and 585.746 Å^3 for the T_{an}=1573 K sample, respectively. The average crystallite size (d) of NPs in the samples obtained from the Scherrer equation, $d=0.9\lambda/\beta\cos\theta$ [19], where β is the full-width-at-half-maximum of diffraction angle θ, changes from 25.6 to 60.8 nm. Table 1 shows that similar to the variation tendency of D, d also increases with increasing T_{an}.

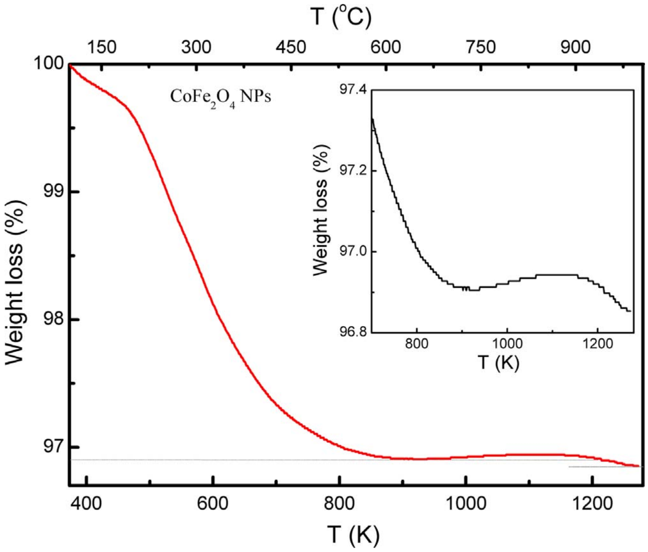

Fig. 1. TGA data in the temperature range T=373–1273 K of $CoFe_2O_4$ NPs recorded in an Ar ambient. The inset is an enlarged view of TGA data at temperatures $T > 700$ °C.

An alternative assessment of the structure of NPs versus heat treatment is that based on RS spectroscopy. For this measurement, we used 532 nm wavelength (with laser power of ~0.25 mW) to focus on the NP samples, and recorded Raman shifts in the range of 150–1000 cm^{-1}. According to the group theory for spinel-structured oxides, optical phonons at the Γ point of the Brillouin zone consist of the modes: $\Gamma = A_{1g}+E_g+T_{1g}+3T_{2g}+2A_{2u}+2E_u+4T_{1u}+2T_{2u}$ [20]. While $A_{1g}+E_g+3T_{2g}$ are five first-order active Raman modes, the T_{1u} modes are infrared-active. The modes above 600 cm^{-1} are associated with the motion of oxygen atoms in tetrahedral AO_4, and those at lower frequencies are characteristic of the octahedral BO_6 sites [20,21]. Fig. 4 shows that the RS spectrum for the T_{an}=393 K sample shows phonon modes peaking at about 197, 298, 455 and 677 cm^{-1}, which are assigned to $T_{1g}(3)$, E_g, $T_{1g}(2)$ and $A_{1g}(1)$, respectively [11]. These modes with stronger intensity shift towards higher wavenumbers of about 202, 301, 468 and 686 cm^{-1} for the samples T_{an}=673–1573 K. Out of the assigned modes, the RS spectra of these samples also show two other modes peaking at ~568 and 607 cm^{-1} (belonging to $CoFe_2O_4$ NPs), associated with $T_{1g}(1)$ and $A_{1g}(2)$, respectively [11]. Notice that the peak position and the appearance of modes in Co ferrites depend on many factors, such as particle sizes, laser power, and dopants [11,22].