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Magnetic properties of nanoparticles of cobalt chromite

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ABSTRACT

Magnetic properties of cobalt chromite nanoparticles of size 8–12 nm synthesized through conventional coprecipitation route are reported. Magnetization versus temperature measurement plot reveals a transition from paramagnetic to superparamagnetic (SPM) phase in contrast with the transition from paramagnetic to long-range ferrimagnetic phase at Curie temperature, T_c, reported in bulk. The blocking temperature, T_b, of SPM phase is found to be 50–60 K. On cooling in the presence of 10 kOe field these nanoparticles show an enhancement in coercivity and shifting of loop at 10 K, which is absent at 50 K. While the later observation supports the blocking temperature of the SPM phase, the former one is attributed to a disordered spin configuration at the surfaces and the distribution of nanoparticle sizes.

1. Introduction

Chromite, cubic normal spinel compounds have recently attracted much attention as multiferroic materials [1]. Cobalt chromite ($CoCr_2O_4$), one of the spinel family, is ferrimagnetic in nature in which magnetic Co^{2+} ions occupy A site and magnetic Cr^{3+} ions occupy B site [2]. The strong interactions among chromium ions in chromite control the magnetic order [3–5]. The antiferromagnetic alignment between A and B sites is completely destroyed and system exhibits a screw ordering. This is otherwise named as ferrimagnetic spiral wherein the spins lie on the conical surfaces. The magnetic order is mostly studied in bulk and single crystals. Menyuk et al. [6] studied the magnetic ordering through neutron diffraction and magnetic measurements of bulk samples and have shown that below T_c, magnetic ordering consists of a ferrimagnetic component and a spiral component. The ferrimagnetic component exhibits long range order at all temperatures below T_c while the spiral component exhibits a short range order. Tomiyasu et al. [7] revisited the spiral ordering by neutron scattering and magnetic measurements in $CoCr_2O_4$ single crystals and report a simultaneous formation of long range order of ferrimagnetic component and a short range order of the spiral component at lowest temperature phase. In addition to the magnetic order investigated by Menyuk et al. [6] in polycrystalline sample, a dielectric anomaly below spiral magnetic order has been observed in polycrystalline sample [8] as well as in single crystals [1,9]. The spiral component induces the electric polarization and also a spontaneous magnetization for which it is said to be as multiferroic. Due to lack of studies on nanoparticles of cobalt chromite, we have synthesized these particles in nanometer range by conventional coprecipitation route and studied the magnetic properties of these materials by varying temperature and magnetic field. We observed a transition from paramagnetic to superparamagnetic (SPM) phase at T_c instead of a transition from paramagnetic to ferrimagnetic phase. These nanoparticles exhibit an exchange bias phenomena below T_b.

2. Experimental methods

2.1. Synthesis of cobalt chromite powder

Conventional coprecipitation technique was used to synthesize cobalt chromite powders. We have used cobalt nitrate hexahydrate, $Co(NO_3)_2 \cdot 6H_2O$ (molecular weight 291.03 g, 99%), chromium nitrate nonahydrate, $Cr\ (No_3)_3 \cdot 9H_2O$ (molecular weight 400.15 g, 98%) and ammonia solution (30% by weight) to synthesize cobalt chromite. Acetone of analytical grade was used for drying the precipitate. Stock solutions of cobalt nitrate (0.5 M), chromium nitrate (0.5 M) and ammonia solution (1.5 M) were prepared in 500 ml volumetric flasks separately by dissolving appropriate amount of $Co(NO_3)_2 \cdot 6H_2O$, $Cr(NO_3)_3 \cdot 9H_2O$ and NH_3 (about 30%) in double distilled water respectively. From the stock solution, desired quantity of cobalt nitrate was taken in a 1000 ml beaker. Desired quantity of chromium nitrate solution was added slowly to the cobalt nitrate solution under continuous stirring. The mixed solution was further stirred at room temperature

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for 2 h. Further, aqueous ammonia solution (1.5 M) was added dropwise to the mixed solution till the pH of 8.9 was attained. The hydroxide precipitate was filtered, washed several times with distilled water till the filtrate attains a pH value of about 7. Finally the hydroxide precipitate was washed with acetone and was dried in an oven at 120 °C for 16 h to get the desired oxide. The dried oxide was calcined at 600 °C for 4 h to get well crystalline phase.

2.2. Characterization of cobalt chromite powder

The calcined powders were characterized by X-ray Diffraction (XRD) using an 18 kW rotating anode (Cu K_α) based Rigaku powder Diffractometer operating in the Bragg–Brentano geometry and fitted with a graphite monochromator in the diffracted beam. Field emission scanning electron microscopy (FESEM, ZEISS: SUPRA 40) at 5 kV is used for structural characterization of $CoCr_2O_4$ nanoparticles. We measured the temperature and field dependent dc magnetization using Vibrating Sample Magnetometer insert of Physical Properties Measurement System (PPMS-VSM) of Quantum Design operating between 2 to 350 K. For frequency dependent ac susceptibility measurements SQUID magnetometer (Quantum Design) is used. We measured specific heat as a function of temperature using the heat capacity insert of PPMS (Quantum Design) for 8 mg pressed powder rectangular bar.

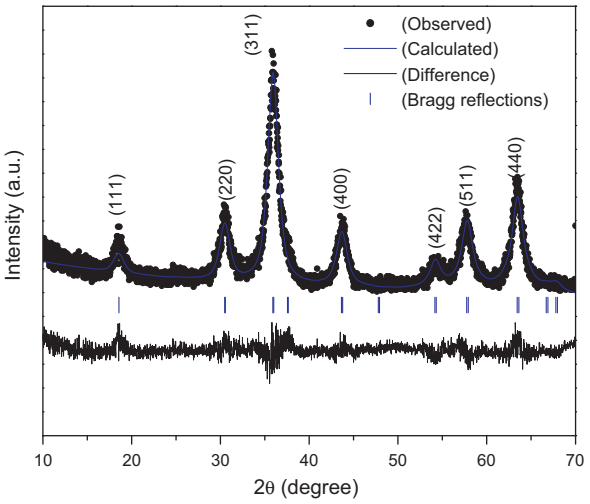

Fig. 1. X-ray diffraction spectrum of calcined $CoCr_2O_4$ nanoparticles synthesized at pH 8.9 and fitted using Fullprof program with Fd3m space group. The observed pattern, calculated data after Le-Bail analysis and the difference pattern between observed and calculated one are shown as dots, continuous line and as bottom line, respectively.

3. Results and discussion

Fig. 1 depicts the XRD pattern of $CoCr_2O_4$ calcined at 600 °C. The pattern is fitted using Fullprof program with Fd3m space group. The observed pattern, calculated data after Le-Bail analysis and the difference pattern between observed and calculated one are shown as dots, continuous line and as bottom line, respectively. The tick marks above the difference plot show the positions of the Bragg peaks. The well defined peaks corresponding to miller indices (1 1 1), (2 2 0), (3 1 1), (4 0 0), (4 2 2), (5 1 1) and (4 4 0) are ascribed to cubic phase of $CoCr_2O_4$ (JCPDS file no:780711). No peaks other than $CoCr_2O_4$ have been observed. The lattice parameter is found to be 8.310 Å, which is in agreement with the bulk value (8.334 Å). The mean crystallite diameter along (3 1 1) calculated using the Scherrer formula after correcting the instrumental broadening is found to be ~8 nm. Field emission scanning electron micrograph is shown in Fig. 2. The particles are mostly agglomerated and majority of particles are in 8–12 nm range as observed from particle size distribution histogram shown as inset of Fig. 2. Crystallite size is in good agreement with the particle size measured from FESEM.

Fig. 3a shows magnetization as a function of temperature under zero field cooling (ZFC) and field cooling (FC) condition

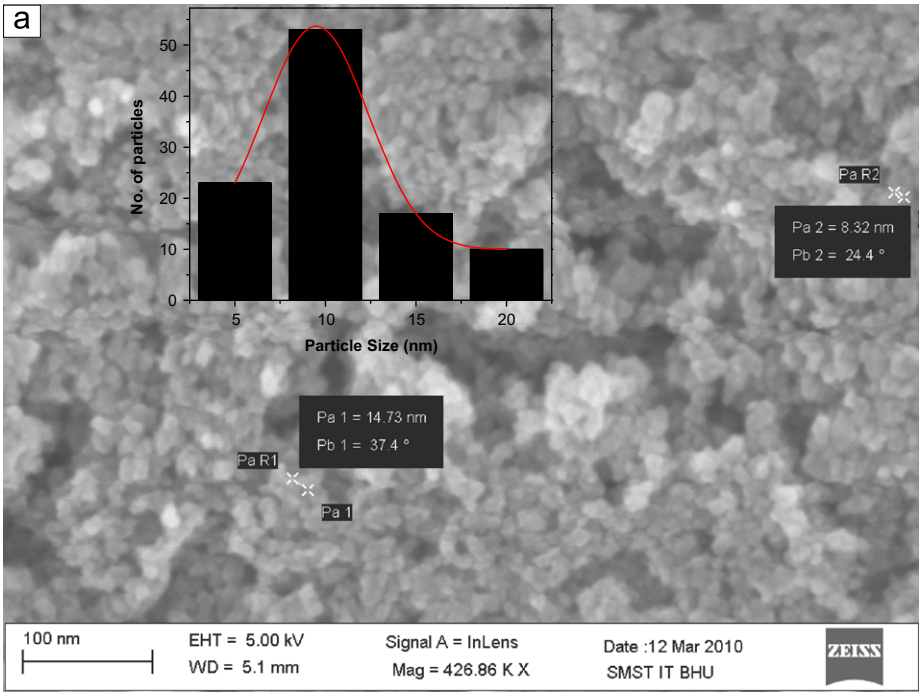

Fig. 2. Field Emission Scanning Electron Micrograph of $CoCr_2O_4$ nanoparticles calcined at 600 °C and inset shows the particle size distribution histogram.