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Full Length Article

Annealing temperature induced phase evolution and exchange bias properties of Fe/CoO nanocomposites

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ABSTRACT

Nanocomposites of Fe/CoO (10 at. wt.% of α-Fe) have been prepared successfully by high energy ball-milling process. The effect of annealing temperature on the structural and magnetic properties of the sample has been studied by annealing the sample at different temperatures (200/400/600/800 °C) for one hour. X-ray diffraction measurements show the formation of composite phase in nano regime and evolution of cobalt ferrite phase at higher annealing temperatures. Mossbauer studies show the formation of one sextet and one doublet pattern for the sample at room temperature. But with annealing at higher temperatures (400 °C & above) evolution of another sextet pattern is observed corresponding to the Fe atoms occupying different sites. The most interesting phenomena have been observed while recording magnetization measurements as a vertical shift (M_{Shift}) in the M-H loop with enhancement in saturation magnetization and coercivity is observed. The exchange bias (H_{EX}) increases at lower annealing temperatures (200/400 °C) but vanishes at higher annealing temperatures (600/800 °C). Upon annealing, FM alpha Fe and AFM CoO forms a ferrimagnetic Co-Ferrite, which lacks the FM-AFM interface required for exchange bias.

1. Introduction

Magnetism at nano scale is interesting and challenging [1]. This is the reason why nanomagnetism is the thrust research area for scientists and engineers in developing materials of high applicability. Limiting size of magnetic domains in a nanoscopic material presents distinctly novel properties which needs to be tailored for its fruitful applications [1]. Magnetically ordered ferromagnetic (FM) and anitiferromagneic (AFM) materials from this class receive substantial importance due to their incredible technological applications in high density recording media, medicine, spin valves, permanent magnets, sensors, domain stabilizer etc [2–6]. In a combined system where we assemble a FM and AFM material and look from the interface the phenomenon seems to be more delightful. If the size of the FM material is small enough below the critical length, stable magnetic orientation vanishes [7]. The magnetic anisotropic energy decreases with decrease in particle size and becomes insufficient to hold the magnetic moment along a fix direction below a critical size of the particle. At this stage, the anisotropy energy is of the order of thermal energy which triggers the magnetic moments to flip randomly losing its stable magnetic order [8]. This is called superparamagnetism (SPM) and the magnetic ordering in a SPM particle can be restored by coupling it with an antiferromagnet (AFM) material [9]. Coupling of a FM material with an AFM material may lead to exchange anisotropy which may results to interesting physical phenomena such as exchange bias (EB), memory effect, super-spin-glass etc at the interface [5,10,11]. The EB effect is an old phenomenon and was first discovered in 1956 by Meiklejohn and Bean in Co/CoO core–shell nanoparticles cooled in a static magnetic field by observing a shift of the magnetic hysteresis loop along the field axis [12,13]. To understand this complex phenomenology many studies have been made on numerous different morphologies at artificial interfaces namely, layered structures [5,14,15], core–shell nanostructures [16] or irregular metal and metal oxide nanostructures [17–19] and FM nanoparticles embedded in an AFM matrix [9,20–22]. Co-existing FM/AFM nanocomposite system comprising transition metals also show significant EB effect [9,20,23–26]. However, realization of EB effect in materials at room temperature and its high temperature sustainability remains unanswered due lack of understanding of the microscopic coupling in the above conditions. To move a step forward in this direction we initiated a study on a similar system (Fe/CoO nanocomposite). Both

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α-Fe and CoO are technologically suitable materials among which CoO has high magnetocrystalline anisotropy ($K = 2 \times 10^5$ erg/cm^3 at 4.2 K) with Neel temperature close to the room temperature ($T_N = 291$ K) [27]. The high magnetocrystalline anisotropy of CoO is useful for the observation of exchange bias and the Neel temperature around room temperature makes easy for the experiment. Significant applications in fabrication of storage devices with novel properties have also been observed in nanocrystalline Fe [28]. So a study on the EB properties of Fe/CoO nanocomposites at different annealing temperatures to infer about the high temperature stability of this and similar kind of materials for compatibility in CMOS environment is worthy and conducted.

2. Experimental method

2.1. Synthesis mechanism

Fe/CoO nanocomposites were prepared by high energy planetary ball-mill (Fritsch Pulverisette 7) method. The milling was carried out by using an 80 cm^3 stainless-steel vial charged with 10 mm diameter stainless steel balls. Closed milling condition was maintained in argon atmosphere with milling at 300 rpm for 30 h keeping ball to powder mass ratio 10:1. For the synthesis, precursor materials of high purity such as analytical grade powders of Fe (99.998%) and CoO (99.9%) were used. The composite was prepared by taking 10 at. wt% of Fe and 90 at. wt% of CoO in the above condition without any additives (dry milling) [29]. Subsequently, the powders were annealed at different temperatures such as 200, 400, 600, 800 °C for one hour in vacuum. Consequently, the samples were named according to their annealing temperature for example FC0 and FC2 represent samples un-annealed and annealed at 200 °C respectively.

2.2. Characterization techniques

XRD measurements of the samples were carried out using a Bruker D8 advance diffractometer with Cu-Kα radiation (λ = 0.15496 nm) in the Bragg-Brentano geometry in 20°–80° range of 2θ. Microstuctural analysis of the products was performed by a high-resolution transmission electron microscope (TEM) (JEOL 2100) operating at 200 kV. The hyperfine magnetic measurements were carried out by ^{57}Fe Mossbauer spectroscopy (1024 channels) in transmission geometry at room temperature. The source for this purpose was taken as ^{57}Co (25 mCi) in Rh matrix moving in constant acceleration mode. The spectrometer was calibrated using a high purity standard iron foil of 12 mm thickness and the spectra were fitted by using LGFIT 2 program. DC magnetization studies were carried out by using a SQUID magnetometer (Quantum Design, MPMS XL 7).

3. Results and discussion

3.1. Structural analysis

The XRD spectra of Fe/CoO nanocomposites annealed at different temperatures are depicted in Fig. 1. The patterns for all the samples show the presence of well defined Bragg peaks which tell about the high crystalline nature of the samples. The diffraction peaks of the samples were compared with standard database (JCPDS No. 05-0696 & JCPDS No. 48-1719) and indexed accordingly. The result shows that for sample FC0 (Fe/CoO nanocomposite without annealing) pure nanocomposite phases of α-Fe and CoO have been formed. The average crystallite size has been calculated using Scherrer's equation and it found to be 12 nm for the sample FC0. Annealing the sample with 200 °C (FC2), we observed no

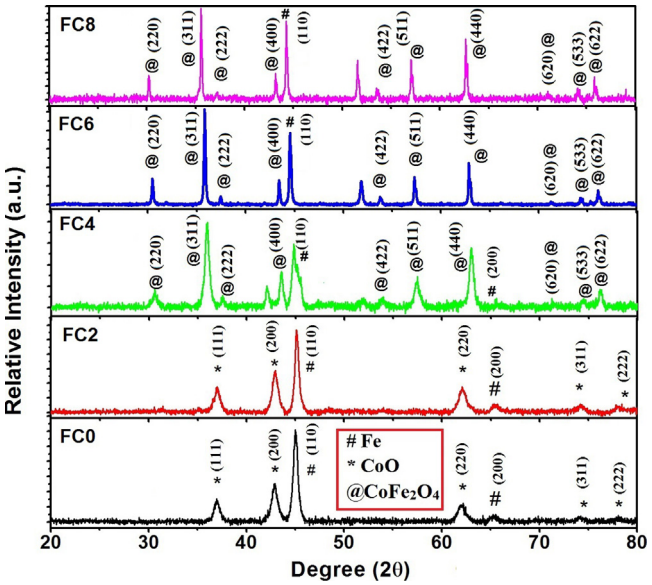

Fig. 1. X-ray diffraction patterns of Fe/CoO nanocomposites annealed at different temperatures.

change in the diffractogram as the number of peaks and their positions remained the same. But, an increase in average crystallite size to 14 nm is observed. With increasing annealing temperatures (400/600/800 °C), new diffraction peaks were observed in the XRD pattern which have been ascribed to $CoFe_2O_4$ (JCPDS No-22-1086) [30]. So, higher annealing temperature leads to the evolution of new ferrite phase along with increase in particle size. The particle size is found to be 15, 37 and 58 nm for the samples FC4, FC6 and FC8 for sample annealed at 400, 600 and 800 °C respectively. The annealing temperature dependence of average crystallite size has been illustrated in Fig. 5. Upon annealing the average crystallite size remains almost constant until 400 °C, and above that it increases linearly. It has been well documented that annealing improves crystallinity in materials which has been observed in our case [31]. Microstuctural analysis of sample FC0 has been done and the TEM images have been illustrated in Fig. 2. It shows the existence of monodispersed nanoparticles of dimension around 10 nm which is in line with our XRD data. The sample is found to be polycrystalline as evidenced from the selected area electron diffraction (SAED) pattern. The composite phases have been identified by calculating the 'd' values from the ring patterns. The corresponding crystal planes are labeled as (111)-(*d*-2.4 Å), (200) (2.1 Å), (220) (d-1.5 Å) planes of α-Fe and (110)-(d-2.06 Å), (200)-(d-1.46 Å) planes of CoO. So the formation of pure phase composite has been confirmed from TEM measurements.

3.2. Hyperfine study

^{57}Fe Mössbauer spectroscopy is an excellent tool to investigate the hyperfine properties of materials having Fe content as it is very sensitive to the different ionic states and their contents. Accordingly we did the measurements for all the samples and the obtained room temperature Mossbauer spectra have been depicted in Fig. 3. The spectra have been fitted with lorentzian line shape and the hyperfine parameters are tabulated in Table 1. The spectra of samples at lower annealing temperature (FC0 & FC2) show the presence of a sextet and a doublet pattern in the spectra. The value of hyperfine field ($H_{int} \sim 33$ T) and zero isomer shift of the sextet in these two samples confirm the phase of FM α-Fe [8,9,20]. The sextet corresponds to the α-Fe particles in blocked state and the doublet arises due to the α-Fe particles undergoing superparamagnetic (SPM)

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