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Structural phase change in $Co_{2.25}Fe_{0.75}O_4$ spinel oxide by vacuum annealing and role of coexisting CoO phase on magnetic properties

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ABSTRACT

The spinel oxide $Co_{2.25}Fe_{0.75}O_4$ has been prepared by co-precipitation route. The as prepared material has been annealed at 800 °C under vacuum. Properties of the samples annealed under vacuum have been compared with the sample annealed in air. Synchrotron X-ray diffraction, Raman spectroscopy and X-ray absorption near edge structure spectroscopy have been used for structural phase characterization. The cubic spinel structure in air annealed sample has been splitted into Co and Fe rich phases. The Co rich spinel phase has transformed into Cobalt monoxide (CoO) after vacuum annealing. This has resulted an increase of Fe:Co ratio in the Fe rich spinel phase. Raman spectra indicated a transformation of the distribution of Co and Fe ions from normal spinel like structure for the sample annealed in air to mixed spinel structure for the samples annealed under vacuum. The existence tetravalent Fe^{4+} ion has been confirmed in all the samples and it is new information for Co doped spinel ferrite system. All the samples exhibited ferrimagnetic behavior and exchange bias effect. The focus point is that vacuum annealing has been used as an effective route of material processing to control the structural phase and also, enhancement of magnetic properties in Co rich ferrite.

1. Introduction

The derivatives of Co rich ferrite ($Co_xFe_{3-x}O_4$) with ferrimagnetic properties are highly promising to design advanced magnetic materials for electro-magnetic and micro-wave devices [1–4]. The basic requirements for applied magnetic materials are moderate spontaneous magnetization, tuneable coercivity and high squareness [5,6]. The spinel ferrites belong to a special class of oxides with formula unit AB_2O_4 [5], where tetrahedral (A) and octahedral (B) sites are occupied by metal ions and oxygen (O) ions occupy the fcc positions of the lattice structure. The superexchange interactions J(A-O-B), J(B—O—B) and J(A-O-A) between magnetic ions in *A* and *B* sites control ferrimagnetic properties. In a collinear spins arrangement, the antiferromagnetic exchange interactions between the magnetic moments in *A* and *B* sites (sublattices) form, in principle, a ferrimagnetic spin structure. But, net magnetic moment per formula unit is either along *B* or *A* sublattice direction and the magnetic features are resembled to a typical ferromagnet. Hence, the term ferromagnet instead of ferrimagnet has also been used in literature to describe magnetic properties of ferrites. The ferro/ferrimagnetic parameters (magnetization, coercivity, squareness and blocking of magnetic domains) have been controlled by varying Co content and distribution of cations in spinel ferrite structure by adopting suitable materials processing techniques [7–10]. The distribution of magnetic ions among *B* and *A* sites has played an important role for magnetic properties in spinel structure. This is explained from the fact that Co_3O_4 is an antiferromagnet with Neel temperature ~35 K and Fe_3O_4 is a ferrimagnet with Neel temperature ~850 K. In the normal spinel structure of Co_3O_4 (distribution of ions: $(Co^{2+})_A[Co_2^{3+}]_BO_4$) all the divalent Co^{2+} ions occupy *A* sites and in the inverse spinel structure of Fe_3O_4 (distribution of ions: $(Fe^{3+})_A[Fe^{3+}Fe^{2+}]_BO_4$) the trivalent Fe^{3+} ions fully occupy *A* sites. In the intermediate compositions ($Co_xFe_{3-x}O_4$ with $1 \leq x \leq 3$) of Fe_3O_4 and Co_3O_4, mixed spinel structure appears in the compound and one expects a substantial change in structure (coexistence of Co^{2+} and Fe^{3+} ions in A sites), and magnetic properties [11–13].

The ratio of Fe and Co atoms in spinel structure and coexistence of secondary phases have played a crucial role in determining the

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magnetic properties of $Co_xFe_{3-x}O_4$ system [9,14]. Although reports on magnetic order and exchange coupling in Co-rich ferrites are available in literature [15,16], but the role of secondary phase on magnetic properties is not well understood [12,13,17,18]. The present work has been taken as a case study to demonstrate the role of secondary phases in $Co_{2.25}Fe_{0.75}O_4$ spinel oxide. The magnetic properties of this composition have been discussed in previous work [19] by annealing the chemical routed (as-prepared) material at different temperatures up to 1000 °C in air. The notable feature was that cubic spinel structure of the compound split into Co rich and Fe rich phases for annealing temperature below 900 °C in air. The as-prepared material after annealing at 800 °C for 4 h in air has been denoted as CoFe8A4 and this bi-phased sample has exhibited maximum coercivity. We have taken another pellet of the as-prepared material for annealing under vacuum. The Co rich phase of spinel structure, as noted in air annealed CoFe8A4 sample, has transformed into antiferromagnetic CoO phase by vacuum annealing. We demonstrate the properties of the samples annealed in vacuum and compare with the properties of the sample CoFe8A4, used as the reference sample for the present work. Though few reports [7] are available on structural phase transformation of Co-rich ferrite by vacuum annealing, but detailed magnetic properties are not studied. We show that structural phase transformation by vacuum annealing has affected the ferrimagnetic properties. From application point of view, the tuning of ferrimagnetic properties without changing elemental composition of a material, known as self-composite [3], is desirable for the development of advanced magnetic materials and understanding the mechanism in magnetic composites.

2. Experimental

2.1. Sample preparation and characterization

The spinel oxide composition $Co_{2.25}Fe_{0.75}O_4$ has been prepared by co-precipitation of Co and Fe nitrates in highly alkaline medium. Details of the sample preparation and characterization have been demonstrated in earlier work [19]. We briefly discuss the procedures for reference purposes. Stoichiometric amounts of metal nitrates ($Co(NO_3)_2.6H_2O$, $Fe(NO_3)_3.9H_2O$ with purity > 99.999%) have been dissolved in distilled water. The NaOH solution with initial pH ~13 has been used as the precipitating agent and added drop wise in the nitrates solution until the pH reached to ~11. Then chemical reaction of the solution has been carried out at 80 °C for 2 h. The resultant product has been allowed to cool down to room temperature and settled at the bottom of the beaker, which has been used to contain the solutions. The product has been washed several times with distilled water and dried at 100 °C. The obtained black powder has been heated at 200 °C for 2 h and ground to get a fine powder. The pellet form (diameter 13 mm and thickness ~ 1 mm) has been annealed at 800 °C in air and under vacuum separately for 4 h. The vacuum annealing of the same pellet has been extended up to 16 h. The air annealed sample has been denoted as CoFe8A4, as referred in work [19]. The samples annealed under vacuum (AUVs) for time 4, 8, 12, and 16 h have been denoted as CoFe8V4, CoFe8V8, CoFe8V12 and CoFe8V16, respectively. The rate of heating and cooling during annealing process has been maintained @ 10 °C/min.

Crystal structure of the samples has been characterized at room temperature. The Synchrotron X-ray powder diffraction (SXRD) and X-ray absorption near edge structure spectroscopy (XANES) have been performed on the angle dispersive X-ray diffraction beam line (BL-12) at Indus-2 synchrotron source, India. The beam line consists of a Si (111) based double crystal monochromator and two experimental stations, viz., a six circle diffractometer (Huber 5020) with a scintillation point detector and an image plate (Mar 345dtb) area detector. Photon energy and the sample to detector distance for SXRD have been calibrated using SXRD pattern of LaB_6 NIST standard using X-ray wave length 0.7765 Å. XANES measurements have been carried out in fluorescence mode. Sample absorptions around Co K-edge (7.709 keV) and Fe K-edge (7.112 keV) have been measured by an energy dispersive detector (Vortex-EX). Photon energies below and above of the Co and Fe K-edges have been resolved using a Si (111) double crystal monochromator. Energy resolution ($\Delta E/E$) has been estimated to be 1.5×10^{-4} around the Co and Fe K-edges. Raman microscopy (Reni Shaw, UK) with 488 nm LASER has been used to record Raman spectra of the samples. LASER power has been optimised to 3 mW on the sample surface for acquisition time 30 s. Magnetic properties have been studied using a vibrating sample magnetometer (Cryogenics, UK) in the temperature range 4 K–300 K and field range ± 70 kOe.

3. Results and discussion

3.1. Structure

3.1.1. Synchrotron X-ray diffraction (SXRD)

Fig. 1 compares the SXRD patterns of the samples annealed under vacuum (AUVs) with the SXRD pattern of the CoFe8A4 sample (annealed in air). All the SXRD patterns have been analyzed using Rietveld profile fitting. SXRD profile of CoFe8A4 sample shows coexistence of two cubic spinel phases (space group Fd3m). The spinel phase component appearing at lower 2θ side of the peak position is attributed to Fe-rich phase and that at higher 2θ side is attributed to Co-rich phase. These phase components have been defined from the facts that Co rich phase had more Co atoms and the Fe rich phase had more Fe atoms than that expected for normal composition of the compound after annealing the as prepared material at 900 °C in air [19]. The SXRD profile fit gives the lattice parameter ~8.3260(3) Å and 8.1510(4) Å for Fe rich phase and Co rich phase, respectively. The average intensity ratio of the prominent (311, 440, 511) peaks is ~22% and 78% for Fe rich and Co rich components, respectively. There is a major change in the intensity ratio of the Fe rich and Co rich phases for the AUVs. The peak intensity for Cobalt monoxide (CoO: cubic structure with space group Pm3m) appeared at the expense of the peak intensity of Co-rich spinel phase. The important point is that CoO as secondary phase has been formed at relatively low temperature under vacuum annealing in comparison to the higher temperatures (≥950 °C) generally noted by air annealing of Co rich ferrite and Co_3O_4 [11,12,19,20]. The segregation of the major fraction of Co rich spinel phase into CoO leads to a change in the peak intensity ratio of Fe rich phase and Co rich phase to 83% and 17% of the total spinel phase component (excluding CoO peak intensity) in CoFeV84 sample. Finally, Co rich spinel phase has fully converted into CoO in the present ferrite sample by increasing the annealing has time under vacuum to 8, 12 and 16 h. We understand that the absence of sufficient oxygen gas in vacuum has forced to convert the Co-rich spinel phase component into CoO phase and this process is completed after long annealing time under vacuum. Since Fe rich spinel phase and CoO phase belong to different crystal structure, their intensity ratio will not give to the phase percentage in the material. However, Fe rich spinel phase and CoO phase are nearly stabilized at higher annealing time (8 h and 16 h). The lattice constant of Fe rich spinel phase (8.3782–8.4024 Å) and CoO (4.2630–4.2689 Å) has slightly increased with increase of annealing time under vacuum. The increase of lattice constant in spinel phase component in the AUVs is consistent to the increase of Fe:Co ratio in spinel structure [4,13,22]. We estimated grain size of the samples using Debye–Scherer formula. The prominent SXRD peaks