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Effect of Mn substitution on the cation distribution and temperature dependence of magnetic anisotropy constant in $Co_{1-x}Mn_xFe_2O_4$ ($0.0 \leq x \leq 0.4$) ferrites

M. Atif[a,b,*], R. Sato Turtelli[b], R. Grössinger[b], M. Siddique[c], M. Nadeem[d]

[a]Department of Physics, Air University, PAF Complex E-9, Islamabad, Pakistan
[b]Institute of Solid State Physics, Technical University of Vienna, A-1040 Vienna, Austria
[c]Physics Division, PINSTECH, PO Nilore, Islamabad, Pakistan
[d]Electronic and Magnetic Materials Group, PD, PINSTECH, PO Nilore, Islamabad, Pakistan

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Abstract

The effect of Mn substitution on temperature dependent magnetic properties of Mn substituted cobalt ferrite, i.e., $Co_{1-x}Mn_xFe_2O_4$ ($x=0.0$–0.4), prepared by a ceramic method has been investigated. X-ray diffraction (XRD) analysis reveals that all samples posses a single phase cubic spinel structure. The lattice constant determined from XRD increases with Mn substitution whereas the bulk density of the samples decreases. Mössbauer results reveal that Co, Fe and Mn ions are distributed over the tetrahedral (A) and octahedral (B) sites for the prepared samples. Hysteresis loops yield a saturation magnetization (M_s) and coercive field (H_c) that vary significantly with temperature and Mn content (x). The temperature dependence of the magnetization obtained for $\mu_o H=5$ T presents a maximum at 175 K which is also dependent on the value of x. The high field regimes of the hysteresis loops are modeled using the Law of Approach to Saturation (LAS) to determine the first-order cubic anisotropy coefficient (K_1). It has been found that the anisotropy of these materials increases significantly with decreasing temperature. However, below 175 K, the shape of the anisotropy energy function changes significantly causing a first-order magnetization process (FOMP) at higher fields, which also prevents the magnetization to saturate even under a maximum applied field of 5 T. In general, the anisotropy coefficient decreases with increasing Mn substitution at a given temperature, which could be explained in terms of the site occupancy of the Mn^{2+} substituent in the cubic spinel lattice.

Keywords: A. Milling; B. Spectroscopy; C. Magnetic properties; D. Ferrites

1. Introduction

Cobalt ferrite, $CoFe_2O_4$, is a well-known hard magnetic material, which has been extensively studied due to their interesting properties such as high cubic magnetocrystalline anisotropy, high coercivity, good electrical insulation, high chemical stability, significant mechanical hardness and moderate saturation magnetization at room temperature [1–3]. However, the increasing interest in cobalt ferrite and cobalt ferrite based materials is mainly due to their strong magnetoelastic effects and their potential usefulness in developing robust magnetoelastic stress sensors and energy efficient actuators [4,5]. Cobalt ferrite has a partially inverse spinel structure in which both sites, i.e. tetrahedral (A) and octahedral (B) sites, contain a fraction of Co^{2+} and Fe^{3+} cations; however it is generally accepted that a large fraction of Co^{2+} ions are on the B-site and the remaining are on the A-site, which depends on the production methods as well as on the heat treatment procedure [6–8]. Also, it is well known that the magnetic properties of cobalt ferrite depend on the concentration of Co^{2+} at B-site of the spinel structure. Therefore any changes in the site occupancy of Co^{2+} cation and/or deviation of targeted composition from stoichiometry ($CoFe_2O_4$) caused by cation

*Corresponding author at: Department of Physics, Air University, PAF Complex E-9, Islamabad, Pakistan. Tel.: +92 51 9262557 480; fax: +92 51 9260158.
E-mail addresses: matif_80@yahoo.com, atififp@gmail.com (M. Atif).

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substitution or heat treatment will affect the physical properties of cobalt ferrite including the temperature dependence of magnetic properties and magnetomechanical hysteresis [9–11].

Recently, the temperature dependence of the magnetic anisotropy of a series of mixed ferrites $CoM_xFe_{2-x}O_4$ (M=Mn, Cr, Ga and Al) has been investigated [12–15] and it was found that substituting M for Fe in cobalt ferrite allows adjustment of the Curie temperature (T_c) of the material, thereby influencing the temperature dependence of its stress sensitivity and magnetomechanical response of these materials. It has been shown that manganese substituted cobalt ferrites, i.e. $CoMn_xFe_{2-x}O_4$, are excellent candidates for stress sensors due to a large magnetomechanical effect and high sensitivity to stress. This is because weakening of the exchange coupling results in a decrease of the magnetocrystalline anisotropy which also results in a steeper response of strain to applied magnetic field [16]. From the studies on the magnetic and magnetostrictive properties of Mn substituted cobalt ferrites [16–18], it has been found that substitution of Mn enhances the saturation magnetization as well as the magnetostrictive properties of the cobalt ferrite; when Mn is substituted by Co in the B-site as compared to the displacement of Co from the B- to A-sites when Mn is substituted by Fe in the Co–Mn ferrite ($0.0 \leq x \leq 0.4$) system. This is because; the high magnetocrystalline anisotropy of the cobalt ferrite is due to the Co at B-site. However, it has been reported in our recent study [19] that the direct substitution of Mn for Co in the cobalt ferrite, i.e., $Co_{1-x}Mn_xFe_2O_4$, showed a comparatively higher magnetostriction and strain derivative at relatively low magnetic fields for a peculiar composition, which depicts the importance of Mn substitution for Co in tuning the magnetoelastic response of cobalt ferrite [20]. Since, the temperature dependence of the magnetoelastic properties is strongly dependent on the magnetostriction and magnetic anisotropy, as well as coercivity, permeability, and chemical composition of the material. Therefore, it would be interesting to study the effect of substitution of Mn for Co instead of Fe in $CoFe_2O_4$ on the temperature dependent magnetic anisotropy and coercive field for the Mn substituted cobalt ferrites (i.e. $Co_{1-x}Mn_xFe_2O_4$). In the present work, we report a systematic study on the crystal structure and magnetocrystalline anisotropy at various temperatures (i.e. 10–400 K) of Mn substituted cobalt ferrites $Co_{1-x}Mn_xFe_2O_4$ for $0.0 \leq x \leq 0.4$ prepared under optimum synthesis conditions [9].

2. Experimental

A series of manganese substituted cobalt ferrite samples with compositions of $Co_{1-x}Mn_xFe_2O_4$ ($x=0.0$, 0.2, 0.4) were prepared by ball milling technique. The process involved mixing of Fe_2O_3, Co_3O_4 and MnO_2 powders in their stoichiometric amounts and then ball milled by using Spex 8000 high-energy vibratory mill for 8 h, followed by calcinations at 900 °C for 12 h. To have better homogeneity in the samples, the powders were re-milled with intermediate annealing at 1000 °C for 12 h and then the powders were pressed under a hydrostatic pressure of 167 MPa. Finally the pressed pellets were sintered at 1350 °C for 24 h and were subsequently furnace cooled to room temperature.

XRD patterns (obtained from the pellet surfaces) were recorded by means of an Xpert Philips diffractometer (Goniometer Philips PW3050/60) using $CuK_{\alpha 1,2}$ radiation in a Bragg Brentano geometry and a X'Celerator detector. The X-ray generator Philips PW 3040/60 worked at a power of 40 kV and 40 mA, and the goniometer was equipped with a graphite monochromator. Diffraction patterns were recorded in the angular range 15–90° with a scan step size of 0.02°. Collected data were refined using the Rietveld package TOPAS (Bruker AXS Topas V 2.1) based on the fundamental parameter approach, with diffractometer parameters and wavelength settings adjusted using a LaB6 standard. The sintered pellets of all samples were properly ground for collecting room temperature Fe^{57} Mössbauer spectra. Co^{57} (Rh-matrix) source was used in transmission mode. α-Fe foil was used for the Mössbauer spectrometer calibration. Data were analyzed using the MOS-90 computer program by assuming all peaks as Lorentzian in shape. For the magnetic characterization, temperature dependent hysteresis loop measurements applying a maximum magnetic field of 5 T (1 T≈796 kA/m) were performed using a vibrating sample magnetometer (PPMS-VSM) from Quantum Design Inc.

3. Result and discussion

3.1. Structural analysis

Fig. 1 illustrates the XRD pattern of the Mn substituted cobalt ferrite sample with $x=0.4$ (i.e., $Co_{0.6}Mn_{0.4}Fe_2O_4$). All samples present similar XRD patterns, as shown in Fig. 1. XRD analysis followed by a Rietveld refinement based on the fundamental parameter approach shows that all peaks in Fig. 1

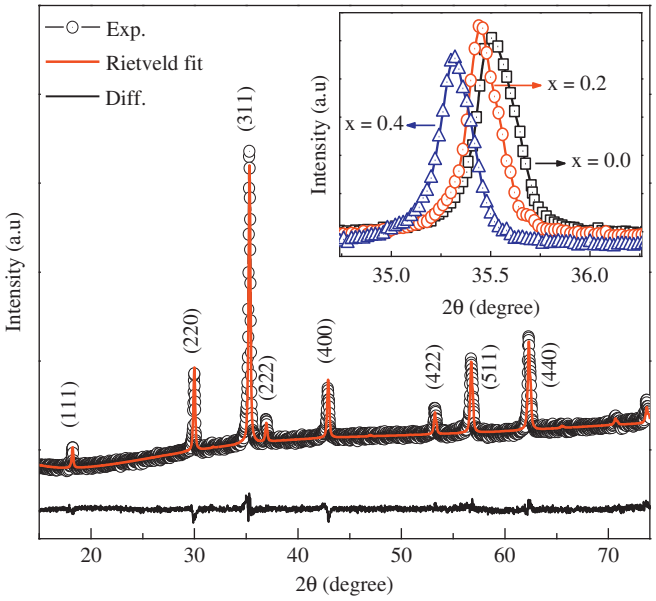

Fig. 1. X-ray diffraction patterns (experimental and Rietveld refinement) of $Co_{0.6}Mn_{0.4}Fe_2O_4$ sample sintered at 1350 °C for 24 h. Inset shows the enlarged (311) XRD peaks for $Co_{1-x}Mn_xFe_2O_4$ samples.