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Effect of manganese substitution on magnetoimpedance and magnetostriction of cobalt ferrites

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ABSTRACT

Influence of manganese substitution on the magnetoimpedance ratio and magnetostrictive constant of cobalt ferrite samples has been studied in the present investigation. Magnetoimpedance was found to vary with manganese content and frequency under the action of applied axial magnetic field. Maximum value of magnetoimpedance ratio was obtained for the composition $Co_{1.1}Mn_{0.1}Fe_{1.8}O_4$ at a low frequency of 10^2 Hz. In order to understand magnetoimpedance behavior of the samples Cole–Cole plot of Mn substituted cobalt ferrites was studied. It was also noted that magnetostrictive constant under applied dc magnetic field changes with manganese content. The magnetic field required for maximum magnetostriction decreases with substitution of cobalt by manganese in $Co_{1.2-x}Mn_xFe_{1.8}O_4$. The strain sensitivity ratio $d\lambda/dH$ was maximum for $Co_{1.1}Mn_{0.1}Fe_{1.8}O_4$, whereas value of magnetostriction was maximum for $CoMn_{0.2}Fe_{1.8}O_4$ sample.

1. Introduction

Magnetic ceramic materials mainly comprising ferric oxide (Fe_2O_3) are called ferrites. For the past about 60 years they have been considered highly important industrial materials because of their sensitivity to the magnetic field. It is found that both the impedance and the geometrical dimensions of ferrites are influenced by the applied magnetic field. The variation of impedance induced by applied magnetic field is known as magnetoimpedance. A large magnetoimpedance is called giant magnetoimpedance (GMI). The variation of geometrical dimensions of magnetic material under the influence of an external magnetic field is called magnetostriction. On account of these features ferrites became a potential candidate for their use in magnetic sensors, magneto-mechanical stress and torque sensors. Magnetoimpedance sensors are used for measuring magnetic fields, currents and stress. Magnetomechanical sensors use magnetostrictive materials in sensors and actuators [1].

The inverse spinel structured cobalt ferrites ($CoFe_2O_4$) represent a well known and important class of iron oxide materials. The O^{2-} ions form FCC close packing with half the Fe^{3+} ions on the tetrahedral sites (A sites) and the rest together with Co^{2+} ions occupy octahedral interstitial sites (B sites). These two antiparallel sub lattices, which are coupled by superexchange interactions through the O^{2-} ions form a ferrimagnetic structure. Most of the magnetic properties of $CoFe_2O_4$ ferrite strongly depend on size and shape of constituent nanoparticles.

Cobalt ferrites have been extensively studied owing to their magnetoimpedance and magnetostrictive properties. In addition cobalt ferrite has high electromagnetic performance, excellent chemical stability, mechanical hardness and high cubic magneto-crystalline anisotropy. These properties make it a promising candidate for many applications in commercial electronics such as audio and video tapes, high-density digital recording media, and magnetic fluids, magnetic sensors and actuators [2–4]. Manganese substituted cobalt ferrites are promising materials for use in magnetic stress sensors, non contact torque sensing and embedded stress sensing applications due to large magnetomechanical effect and high sensitivity to stress. The substitution of manganese or gallium for iron can decrease the Curie temperature and consequently the temperature of magnetomechanical effect [5–9].

$CoFe_2O_4$ is known to be a hard magnetic spinel ferrite and hence anisotropic material. Therefore, the external magnetic field required to achieve the saturation magnetization is of the order of 10^4 G. It is reported that deviation from stoichiometric composition leads to change in magnetic and magnetostrictive properties of cobalt ferrite [10]. Further, in order to reduce the magnetic anisotropic nature of the samples an attempt has been made to substitute Co by Mn. It is expected to observe reduction in magnetic anisotropy which would lead to weakening of super-exchange interactions and hence decrease in external magnetic field required for obtaining the saturation magnetization.

The impedance of a certain class of magnetic materials depends on the applied dc field. The giant MI effect is demonstrated to arise

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from a combination of skin effect and a strong field dependence of circumferential magnetic permeability associated with circular domain wall movements. Both real and imaginary components of complex impedance contribute to the GMI [9]. To observe the GMI effect it is necessary to deal with a material of large permeability which in addition can be suitably modified by a dc field. In general GMI is expected to be observed in ultrasoft magnetic materials with as large electrical conductivity as possible. However, most of the soft magnetic materials are metallic alloys which may lose the magnetic properties to a large extent on oxidation. Based on the magnetostrictive properties of the manganese substituted cobalt ferrites a new class of stress sensors could be developed [11]. Therefore, in order to explore the possibility of using the oxide based magnetic system for magnetoimpedance and magnetostrictive applications, it is essential to carry out investigations for understanding of these properties. Since GMI changes as a function of external dc magnetic field or applied ac or dc currents, it is possible to design GMI based sensors that can measure either magnetic fields or ac/dc currents. GMI is also sensitive to applied stress and this provides a new opportunity for developing stress sensors.

In the present study we have examined the microstructures of the samples using a Scanning Electron Microscope (SEM). The spinel structure and the presence of residual phases were checked by X-ray diffraction (XRD) analysis. By adjusting the manganese content and the sintering process, the material properties could be varied for use in magnetomechanical stress sensors. We have investigated the influence of the manganese substitution on the magnetoimpedance and magnetostriction of ferrite samples with compositions of $Co_{1.2-x}Mn_xFe_{1.8}O_4$ where $x=0.0$, 0.1 and 0.2.

2. Theoretical background

2.1. Magnetoimpedance

When a magnetic material is subjected to a external magnetic field its complex impedance changes which is known as magnetoimpedance. Both the components, real as well as imaginary parts of the complex impedance change as a function of external magnetic field and the change also depends on the frequency of ac used for the measurement of impedance. The real component varies on account of change in skin depth (δ_m) and the imaginary component due to change in inductance (L). For a cylindrical sample the contribution from inductance is proportional to circumferential permeability (μ_r).

The inductance L of the conductor is given by

$$L = 0.175\mu_r \ell / 2\pi \quad (1)$$

where μ_r is circumferential permeability and ℓ is the length of the conductor.

The skin depth is given by

$$\delta_m = \frac{c}{(4\pi^2 f \sigma \mu_r)^{1/2}} \quad (2)$$

where c is the speed of light, f the frequency of ac imposed and σ is the conductivity of the material. Similarly, the resistance R of a cylindrical conductor is given as

$$R = \rho\ell / 2\pi(a - \delta_m)\delta_m \quad (3)$$

where ρ is the resistivity of the material, ℓ the length of the conductor and a is the radius of cylindrical conductor.

It is observed that different phenomena occur in different frequency regimes; hence the frequency range of our investigation is divided into two frequency regimes for convenience. First low frequency regime from $\sim 10^2$ to $\sim 10^4$ Hz and the second intermediate frequency regime from $\sim 10^4$ to $\sim 10^6$ Hz. In low frequency regime the skin effect is insignificant and the change in impedance of a cylindrical sample is mainly due to contribution of inductance which is proportional to circumferential permeability. In intermediate frequency regime magnetoimpedance occurs mainly from the variation of skin depth due to strong change in effective magnetic permeability caused by the applied magnetic field. Magnetoimpedance is proportional to circumferential permeability [9,12]. Magnetoimpedance is expressed in terms of GMI ratio defined by

$$\Delta Z/Z(\%) = 100 \times \Delta Z/Z, \quad (4)$$

where ΔZ is the change in impedance due to the application of the external magnetic field and Z is the impedance the conductor.

2.2. Magnetostriction

Under the action of a magnetic field on a magnetic crystal the magnetic moments of domains get aligned in the direction of applied magnetic field. Change in the direction of magnetic moment from easy to hard direction leads to a redistribution of the electrons. The redistribution causes a change in atomic spacing of the crystal resulting into change in its dimensions. However, according to domain theory, macroscopically the effect may be attributed to two distinct processes. The first process is dominated by the migration of domain walls within the material in response to weak external magnetic fields. Second is the rotation of the domains under the application of strong magnetic fields. These two mechanisms allow the material to change the domain orientation which in turn causes a dimensional change. Since the deformation is isochoric there is an opposite dimensional change in the orthogonal directions. Although there may be many mechanisms to the reorientation of the domains, the basic idea remains that the movement and the rotation of the magnetic domains cause a physical change of the length in the material [9,12,13].

3. Experimental

Preparation of Material: Hydroxide Co-precipitation Method was employed for the preparation of material. In this method initial ingredients viz. cobalt acetate $[(CHCOO)_2Co]$, ferric nitrate $[Fe(NO_3)_3]$ and manganese acetate $[(CHCOO)_2Mn]$ all from LOBA Chemi were dissolved separately in double distilled water in the required molar proportion and then mixed together. The clear solution so obtained was co-precipitated with NaOH solution at constant temperature of 80 °C. The precipitate was filtered several times using warm double distilled water in order to remove sodium complex formed during co-precipitation reaction. The wet precipitate was dried at 100 °C in order to remove water content and convert hydroxides into oxides. Powder so obtained was pelletized and sintered at 1200 °C for 12 h in air atmosphere. Synthesis steps followed are shown in the flowchart given in Fig. 1. A series of manganese doped cobalt ferrite samples with composition of $Co_{1.2-x}Mn_xFe_{1.8}O_4$ where $x=0.0$, 0.1 and 0.2 were prepared. The samples were named: $Co_{1.2}Fe_{1.8}O_4$ as Sample A, $Co_{1.1}Mn_{0.1}Fe_{1.8}O_4$ as Sample B and $CoMn_{0.2}Fe_{1.8}O_4$ as Sample C.

In order to confirm single phase formation of the materials X-ray diffractograms were recorded using an X-ray diffractometer (Model Bruker D8 Advance). The SEM micrographs were recorded using scanning electron microscope (model JEOL JSM 6360). The impedance measurements were carried out in the frequency range of 10^2–10^6 Hz at room temperature using precision LCR meter (Model HIOKI 3532-50 LCR Hi tester) for all the samples under investigation. For measurement of magnetoimpedance, impedance (Z), real and imaginary parts of Z were recorded under the applied axial magnetic field in the range of 0–10.5 kG at room temperature. Magnetostriction measurements were carried out on ferrite samples using wide range strain indicator (Vishay measurements