Evidence of domain wall pinning in aluminum substituted cobalt ferrites

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ABSTRACT

In the present work spinel structured cobalt ferrites with aluminum substitution having composition $CoAl_xFe_{2-x}O_4$ ($x=0.0$, 0.1, 0.2 and 0.3) have been synthesized using chemical co-precipitation method. Their microstructural, magnetic, magnetostriction and magnetoimpedance properties have been investigated. The piezomagnetic coefficient ($d\lambda/dH$) obtained from magnetostriction data is found to enhance with 0.1 Al substitutions in place of iron which decreases with further increase of Al content. It is noticed that 0.3 Al substitutions in place of Fe introduces domain wall pinning as evidenced from magnetostriction, magnetoimpedance and dc magnetization data. It is noted that ferrites so prepared using a simple procedure are magnetostrictive in good measure and with the addition of very small amount of non-magnetic aluminum their magnetostriction has shown saturation at relatively low magnetic fields. Such magnetostrictive ferrites find their applications in magnetic sensors and actuators.

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1. Introduction

Spinel structured ferrites form a large family of magnetic materials with a general formula MFe_2O_4, where M stands for a divalent metal ion like Mn^{2+}, Fe^{2+}, Co^{2+}, Ni^{2+}, Cu^{2+} or Zn^{2+} etc. They find applications in modern industries e.g. electronics, automobile and space industries etc. Cobalt ferrite ($CoFe_2O_4$) has an inverse spinel structure where oxygen ions are arranged in FCC lattice which gives rise to 64 tetrahedral interstitial A sites and 32 octahedral B sites. Out of these 8 tetrahedral sites and 16 octahedral sites are occupied by divalent ions. Eight Fe^{3+} ions occupy the tetrahedral A sites and another eight together with Co^{2+} ions occupy the octahedral B sites. It is a ferrimagnetic material with a Curie temperature (T_C) of around 793 K. Most ferrites acquire their remarkable properties during their synthesis and heat treatment thereafter. These properties also depend upon stoichiometry and substitution of cations.

Although saturation magnetization of ferrites is less than that of ferromagnetic alloys, they have many advantages such as their suitability for high frequency applications owing to their high resistivity, lower price, greater thermal and corrosion resistance etc. [1]. Recently cobalt ferrites have been extensively investigated because of their electrical, magnetic and magnetostrictive properties [2]. Ferrites have been used in many applications including magnetic recording media, magnetic fluids, magnetically guided drug delivery, sensors and actuators etc.

When a magnetic material is subjected to external magnetic field, its dimensions change. If the dimension parallel to magnetic field elongates the material contracts in the transverse directions. Similarly if the dimension parallel to magnetic field contracts the material elongates in the transverse directions. This is called *magnetostriction (MS)*. The process is isochoric and change in dimensions is such that the volume of the material practically remains constant. Quantitatively MS is the fractional change in the geometrical dimension of a magnetic material with the application of a magnetic field [3]. Impedance of a magnetic material also varies under the action of a magnetic field, this is called *magnetoimpedance (MI)* [4]. MI is defined as the ratio of change in impedance of a material under the action of an applied magnetic field to the original impedance expressed as percentage. Recently cobalt ferrite has attracted considerable attention due to its large magnetocrystalline anisotropy, high coercivity, moderate saturation magnetization, large magnetostrictive coefficient, chemical stability and superior mechanical properties. It is also known that substitution of small amounts of non magnetic elements e.g. Al or Zn in place of magnetic elements in the crystal lattice of spinel ferrites and control of synthesis parameters which decide the spatial distributions of its constituents greatly influence their magnetic, magnetomechanical and magnetoimpedance properties. These attractive properties make cobalt ferrites a good candidate for various applications in designing advanced sensors and actuators [5–15]. The whole process of preparation is therefore closely monitored to produce ferrites of desired characteristics. In the present work we have synthesized aluminum substituted cobalt ferrites $CoAl_xFe_{2-x}O_4$ ($x=0.0$, 0.1, 0.2 and 0.3) by chemical co-

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precipitation method. The prepared powders were compacted and converted into pellets. These were then thermally treated before characterization in terms of their morphological, microstructural, magnetic, magnetostrictive and magnetoimpedance properties.

2. Experimental

2.1. Synthesis of spinel ferrites

Chemical co-precipitation method was employed for preparation of the aluminum substituted cobalt ferrites. The flow chart shown in Fig. 1 gives steps involved in the synthesis of aluminum substituted spinel ferrite system. Aluminum nitrate, cobalt acetate and ferric nitrate from LOBA Chemi were used as initial ingredients. These were weighed in required molar proportion to obtain $CoAl_xFe_{2-x}O_4$ ($x=0.0, 0.1, 0.2$ and 0.3) as a final composition and dissolved separately in double distilled water. The three solutions were then mixed together. The clear solutions so obtained were poured into 3 M NaOH solution at 80 °C with constant stirring to obtain precipitate of initial ingredients. The precipitate was then filtered and washed thoroughly with distilled water until pH of filtrate became 7. It was then dried overnight in an oven at 100 °C which eventually converted it into a black powder of aluminum substituted cobalt ferrite. The powders were then calcined at 700 °C for 10 h. Thereafter powders were mixed with 2% solution of polyvinyl alcohol (PVA) as a binder and shaped into disc like pellets (diameter: 10 mm and thickness: 2–3 mm) under a pressure of 7 MPa. The pellets were finally sintered at 1200 °C for 12 h. Four compositions were prepared and named as follows: $CoFe_2O_4$ as Sample A, $CoAl_{0.1}Fe_{1.9}O_4$ as Sample B, $CoAl_{0.2}Fe_{1.8}O_4$ as Sample C and $CoAl_{0.3}Fe_{1.7}O_4$ as Sample D.

2.2. Characterization

Surface morphology of the samples was investigated using Scanning Electron Microscope (JEOL Model JSM 6360A). X-ray diffraction measurements were carried out using Bruker D8 Advance X-ray machine having $CuK\alpha$ radiations over the 2θ range from 20° to 80°. Vibrational spectra of the samples were recorded using JASCO FTIR 6100 spectrometer which was used to determine infrared absorption peaks. The force constant (k) was calculated using the formula $k=4\pi^2c^2\mu\nu^2$, where c is the speed of light, μ the reduced mass and ν is the wave number of absorption band.

Fig. 1. Flow chart used for chemical co-precipitation procedure to synthesize aluminum substituted cobalt ferrite.

Mossbauer spectroscopy was employed to estimate the Fe^{3+} cations occupying A and B sites. The gamma-ray absorption spectra were recorded using ^{57}Co radioactive source with its present activity of 30 mCi. The spectrometer is equipped with Wissel Velocity Drive. The spectrum was analyzed with Win-NORMS Program. By fitting the sextets it was possible to estimate the relative distribution of Fe^{3+} cations on A and B sites in the cubic spinel lattice. Vibrating Sample Magnetometer (VSM) Lakeshore Model 7307 was employed to record magnetic properties as a function of external magnetic field. Magnetostriction measurements were carried out using P3 Strain Recorder from Vishay Measurements. A 120 Ω strain gauge was glued on the surface of disc shape pellets and magnetic field ranging from 0 to 4500 G was applied in various configurations for the measurement of magnetostriction $\lambda_{11},\ \lambda_{12}$ and λ_{13} as given below:

λ_{11}: Magnetic field parallel to the length of the strain gauge,

λ_{12}: Magnetic field parallel to the breadth of the strain gauge

and λ_{13}: Magnetic field perpendicular to the plain of the strain gauge. Specially designed sample holders were employed to hold the samples firmly in place [15,16]. Magnetoimpedance measurements were carried out using HIOKI LCR HiTESTOR 3532 model in the frequency range of 10^2–5×10^6 Hz. The test current was passed along the axis of the pellets [17]. All measurements were carried out at room temperature.

3. Results and discussion

3.1. Micro-structural analysis

Fig. 2 depicts the SEM micrographs of Sample A, B, C and D at the magnification of x10,000. It is seen from the Fig. 2 that the grains are polygonal in nature for all the samples. With increase in Al content grain size is found to increase. It is interesting to note that the grains for Samples A, B and C show faceted structure, which is common feature of these samples. However, such feature is rarely seen in case of Sample D, rather it comprises more plate like morphology. The grain size is seen to be in the range of 1–5 μm for all the samples.

Fig. 3 shows X-ray diffraction (XRD) patterns of all the four samples under investigation. An examination of XRD pattern confirms formation of single spinel cubic phase. The diffraction lines observed at 30.1°, 35.5°, 43.1°, 53.5°, 57° and 62.6° were indexed as (220), (311), (422),(400), (511), and (440) respectively by comparing with JCPDS Card No: 03-0864. XRD data was used to calculate lattice constant and X-ray density. The X-ray density was calculated from the formula $d_x=8\ M/N_A\ a^3$, where M is the gram-mole of the ferrite, N_A the Avogadro number (6.022×10^{23} mol^{-1}) and 'a' is the lattice constant. Similarly crystallite size (t) was estimated using Scherrer formula $t=0.9\lambda/\beta\cos\theta$, where λ is the wavelength of x-ray used, β is the full width at half maximum and θ is the Bragg angle. The results obtained from XRD data are summarized in Table 1.

Lattice constant is found to be steadily decreasing with aluminum content up to Al content of 0.2 which can be attributed to smaller size of the Al^{3+} ions. Looking at the decreasing trend of lattice parameter with increasing Al content one would expect the lattice parameter of 8.36 Å for Sample D, however it was found to be 8.33 Å. X-ray density data also followed similar trend up to Sample C, however in case of Sample D density was found to be increased in contrast to expected decreased density. The unusual observation in case of Sample D may be associated with the change in magnetic structure of the sample. The crystallite size for thes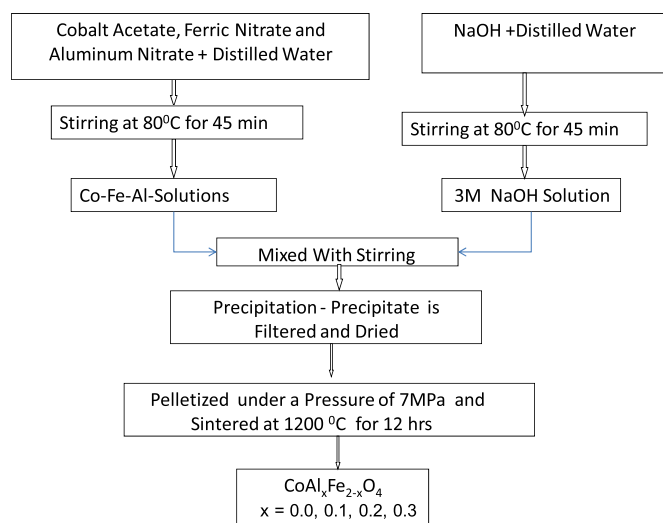e samples was found to be in the range of 55–73.5 nm.