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Magnetic, magnetostrictive, and AC impedance properties of manganese substituted cobalt ferrites

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Abstract

In this study, we investigated the effects of substituting Mn^{3+} for some Fe^{3+} in spinel lattice on the structure, magnetic properties, magnetostriction behavior, and AC impedance characteristics of cobalt ferrites. The manganese substituted cobalt ferrites (Co–Mn ferrites), $CoMn_xFe_{2-x}O_4$, with x varied from 0 to 0.3 in 0.1 increments, were prepared by solid-state reaction. XRD examination confirmed that all sintered Co-based ferrites had a single-phase spinel structure. The average grain size, obtained from SEM micrographs, increased from 8.2 μm to 12.5 μm as the Mn content (x) increased from 0 to 0.3. Both the Curie temperature and coercivity of Co-based ferrites decreased with greater amounts of Mn, while the maximum magnetization (at $H=6$ kOe) of Mn-substituted cobalt ferrites was larger than that of the pure Co-ferrite. Magnetostrictive properties revealed that the pure Co-ferrite had the largest saturation magnetostriction (λ_S), about -167 ppm, and the $CoMn_{0.2}Fe_{1.8}O_4$ sample exhibited the highest strain sensitivity ($|d\lambda_\perp/dH|_m$) of 2.23×10^{-9} $A^{-1}m$ among all as-prepared Co-based ferrites. In addition, AC impedance spectra analysis revealed that the real part (Z') of the complex impedance of Co–Mn ferrites was lower than that of pure Co-ferrite in the low frequency region, and the Co-based ferrites exhibited semiconductor-like behavior.

Keywords: A. Powders: solid state reaction; C. Magnetic properties; D. Ferrites; D. Spinels; E. Functional applications

1. Introduction

Spinel type cobalt ferrite ($CoFe_2O_4$) has been extensively studied and utilized because it has good electromagnetic properties, high magnetocrystalline anisotropy, excellent chemical stability, good mechanical properties, and excellent corrosion resistance, with the added benefit of easy processability [1,2]. In addition, it exhibits a large magnetomechanical effect or high strain sensitivity, which offers prospects for magnetic sensor and/or actuator applications [3]. Cobalt ferrite is a suitable magnetic material for those purposes. However, it is necessary and desirable to enhance the sensitivity of the magnetostrictive strain to an applied magnetic field (i.e., the strain derivative) and decrease the magnetomechanical hysteresis, which would improve the linear response of a future magnetostrictive sensing device [4,5].

The magnetic, magnetostrictive, and electrical properties of the spinel type ferrites are in general affected by the preparation method, microstructure changes, chemical composition, and other factors. Substituting cations for cobalt ferrites appear to hold the promise of modifying their magnetostriction amplitude and enhancing strain sensitivity, as well as providing the possibility of extending the applications of magnetostrictive smart materials [6]. Previous reports have shown that substitution of cations (e.g., Al, Cr, Mn, Zn, Ga, and Ge) for some Fe ions in Co-ferrites could be used to adjust the Curie temperature and reduce the magnetomechanical hysteresis, while enhancing the strain sensitivity and maintaining a sufficient amplitude of magnetostriction [7,8].

It has been demonstrated that Mn is an excellent candidate because substituting Mn^{3+} for Fe^{3+} enhances the strain derivative of Co-based ferrites and reduces the magnetic anisotropic nature, which could minimize magnetomechanical hysteresis [8,9].

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Furthermore, alternating current (AC) impedance spectroscopy is a good scientific tool for understanding the electrical characteristics of ferrites. In this study, we report the effects of substituting Mn for Fe on the structural, magnetic, and magnetostrictive properties, and AC impedance characterization of sintered Co-based ferrites.

2. Experimental

A series of Mn-substituted cobalt ferrites with compositions of $CoMn_xFe_{2-x}O_4$ (where x is 0–0.3) were prepared by solid-state reaction route from high purity powders of Fe_2O_3, Co_3O_4 and MnO_2. Each mixture of oxide powder in stoichiometric amounts was calcined at 1000 °C for 4 h to form the pure spinel phase ferrite powder. The as-calcined powder was re-milled, mixed, pressed into disk-shaped green compacts (5 mm thick and 20 mm diameter) and then sintered at 1350 °C for 4 h under air atmosphere. After the sintering procedure, the Co-based ferrite samples were cooled at a rate of 90 °C/h to room temperature.

The crystal structures of sintered pure Co and Co–Mn ferrites were examined with an X-ray diffractometer (XRD) with CuKα1 radiation. Microstructures of the fractured surfaces of Co-based ferrites were observed with a scanning electron microscope (SEM). The average grain size of each sintered ferrite sample was determined by the mean linear intercept, which was determined from the corresponding SEM image. Each magnetization-magnetic field (*M–H*) hysteresis loop of the ferrite samples was measured using a vibrating sample magnetometer (VSM) at room temperature. The Curie temperature was obtained from a magnetic thermal gravimetric (MTG) scan, up to 750 °C, with a heating rate of 10 °C/min. A rectangular prism having a length of 15 mm, a width of 5 mm, and a height of 1.5 mm was cut from the sintered disk-shaped ferrite sample for magnetostriction measurement. Magnetostriction measurements were performed with linear strain gauges attached to the surface of the rectangular ferrite slab under applied field strengths of ± 6000 Oe. The impedance measurements were carried out in the frequency range of 2.5 kHz–1 MHz at 100 °C using a precision LCR meter.

3. Results and discussion

Fig. 1 shows the XRD patterns of sintered Mn-substituted cobalt (Co–Mn) ferrites. The indexed diffraction peaks were consistent with the standard JCPDS data of cobalt iron oxide (Card no. 22-1086), revealing a cubic spinel crystal structure. No other diffraction signals were detected due to the residual starting materials and formation of the second phase. In addition, we found that the average value of the full width at half maximum (FWHM) from three major diffraction peaks, (311), (511), and (440), of Co–Mn ferrites were narrower than that of pure cobalt ferrite. This implies that the Mn substitution changed the crystallite size.

In order to understand the microstructure changes and evaluate the average grain size of Mn-substituted cobalt ferrites, fractured surface micrographs of the sintered ferrite samples were acquired with a scanning electron microscope. Fig. 2 displays the SEM micrographs of the fractured surfaces for four ferrite samples. The SEM images reveal that the Co-based ferrites had a grain structure of uniformly sized, polygonal grains and underwent microstructure changes with the degree of Mn substitution. Inside the $x=0$ and $x=0.1$ sintered samples, a small amount of micro-pores remained inside (Fig. 2(a) and (b)). The $x=0.2$ sintered samples exhibited a rather homogenous and dense microstructure (Fig. 2(c)), while the $x=0.3$ sintered samples composed of larger grains (Fig. 2(d)) than the $x=0$ and $x=0.1$ sintered samples. The optimum microstructure was observed for $x=0.2$ in $CoMn_xFe_{2-x}O_4$. The calculated average grain sizes from SEM images, given in Table 1, showed that the average grain size increased from 8.2 μm to 12.5 μm as the Mn content increased from $x=0$ to $x=0.3$. Such results imply that Mn substitution could enhance the grain growth rate. Similar changes in microstructure with increasing the amounts of Mn content were reported by Caltun et al. [10].

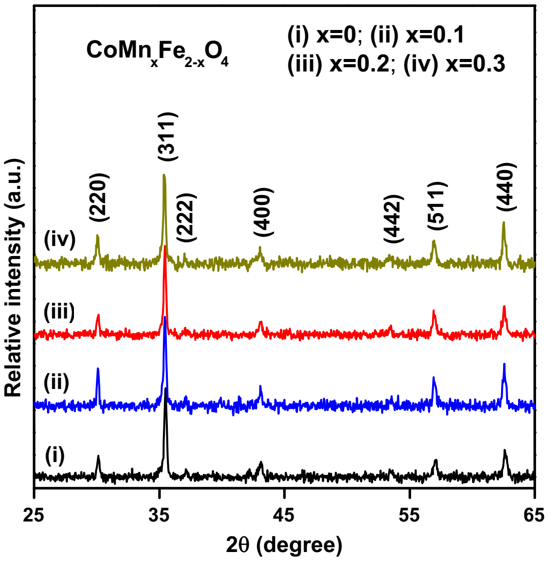

Fig. 1. XRD patterns of Mn-substituted cobalt (Co–Mn) ferrites.

Fig. 3 shows the magnetic field dependence of magnetization (*M–H* curve) for Co–Mn ferrites measured at room temperature. The maximum magnetization (M_m) and coercivity (H_c) values, and the Curie temperature (T_c) are summarized in Table 1. The maximum magnetization first increased with Mn substitution up to $x=0.2$ and then decreased with larger values of x. In the present study, the M_m for the $x=0.2$ sample was 82.5 emu/g, which is close to a previously reported saturation magnetization value ($\sim$82.0 emu/g) for pure Co-ferrite [1]. Caltun et al. suggested that variation of the saturation magnetization depends on the cation distribution in a spinel lattice [10]. In addition, the magnitude of coercivity was found to decrease from 121.7 Oe for $x=0$ to 42.3 Oe for $x=0.3$ (Table 1). The decrease in coercivity is probably associated with the reduction in magnetic anisotropy with increasing Mn content in Co-based ferrites [1]. It is well known that the pure Co-ferrite has high magnetocrystalline anisotropy due to the Co^{2+} ions at the octahedral (B) sites [5]. Krieble et al. investigated the structure changes of Mn-substituted cobalt ferrites by Mössbauer spectroscopy and demonstrated that Mn^{3+} ions occupy the octahedral (B) sites and displace Co^{2+} ions from the octahedral (B) sites to the tetrahedral (A) sites in the