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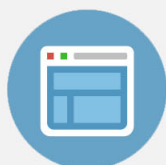
Effect of deviation from stoichiometric composition on structural and magnetic properties of cobalt ferrite, $Co_xFe_{3-x}O_4$ (x = 0.2 to 1.0)

I. C. Nlebedim,[1,a)] J. E. Snyder,[2] A. J. Moses,[2] and D. C. Jiles[3]

[1]*Ames Laboratory, U.S. Department of Energy, Iowa State University, Ames, Iowa 50011, USA*
[2]*Wolfson Centre for Magnetics, School of Engineering, Cardiff University, Cardiff CF24 3AA, United Kingdom*
[3]*Electrical and Computer Engineering Department, Iowa State University, Ames, Iowa 50011, USA*

The effects of deviation from stoichiometric composition on the structural and magnetic properties of cobalt ferrite, $Co_xFe_{3-x}O_4$ (x = 0.2 to 1.0), are presented. Both $CoFe_2O_4$ and Fe_3O_4 have a spinel crystal structure, and it might be expected that intermediate compositions would have the same structure. However, results show that synthesis via the ceramic method leads to the development of a secondary α-Fe_2O_3 phase. Both structural and magnetic properties are altered depending on the concentration of the α-Fe_2O_3 phase. Saturation magnetization is at a maximum for the stoichiometric composition (i.e., x = 1.0) and thereafter decreases with x. In attempts to achieve the properties required for application, the ceramic method offers the ability to selectively adjust the concentrations of both $CoFe_2O_4$ and α-Fe_2O_3 phases. © *2012 American Institute of Physics*. [doi:10.1063/1.3670982]

I. INTRODUCTION

Cobalt ferrite (Co-ferrite) and its derivatives have been studied for magnetoelastic stress sensors and actuators,[1] as a component of multiferroic nanocomposites,[2] and for drug/gene delivery purposes.[3] The samples studied here were $Co_xFe_{3-x}O_4$ (x = 0.2, 0.7, 0.8, and 1.0). Because Co-ferrite prepared via the traditional ceramic approach can deviate from the stoichiometric composition ($CoFe_2O_4$), it is important to understand the range over which the structure is still single phase and how deviation from stoichiometry affects structural and magnetic properties. This research describes the effect of the Co/Fe ratio on the formation of single phase Co-ferrite and the responses of structural and magnetic properties to changes in this ratio.

II. EXPERIMENTAL DETAILS

Fe_3O_4 and Co_3O_4 powders were mixed in their appropriate ratios, calcined twice at 1000 °C, and sintered at 1350 °C in air for 24 h. The crystal structures were determined using x-ray diffractometry (XRD). The microstructures and compositions were studied via scanning electron microscopy (SEM) and energy dispersive x-ray spectroscopy (EDX), respectively. The magnetic properties were measured in a SQUID magnetometer with a magnetic field of up to H = 50 kOe.

III. RESULTS AND DISCUSSION

In Fig. 1, the SEM micrographs for the samples with x = 0.2 and 0.7 show two phases. Although the sample with x = 0.8 appears to have a uniform microstructure, it has a low concentration of the secondary phase (see Fig. 2(a) and subsequent discussion). The sample with x = 1.0 shows a uniform microstructure, indicative of a single phase. In Table I, only the compositions of Co and Fe are shown, because the EDX technique is not sufficiently sensitive to oxygen. The samples with x = 0.8 and 1.0 were slightly richer in Co than targeted. In the two phase samples, specific
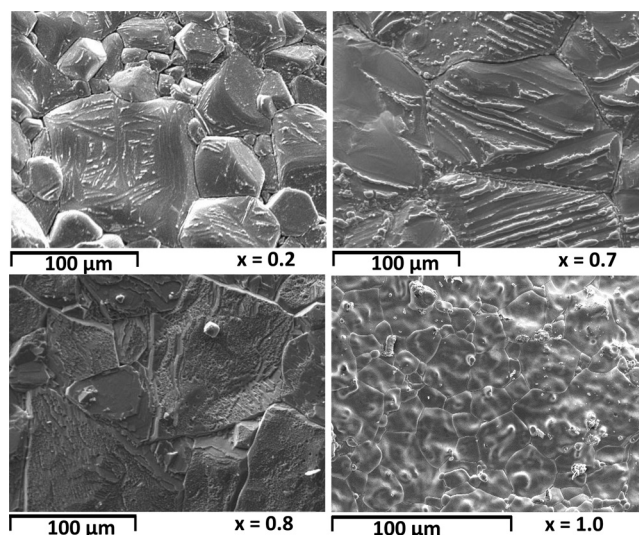
FIG. 1. SEM micrographs of the $Co_xFe_{3-x}O_4$ samples.

a)Author to whom correspondence should be addressed. Electronic mail: nlebedim@iastate.edu.
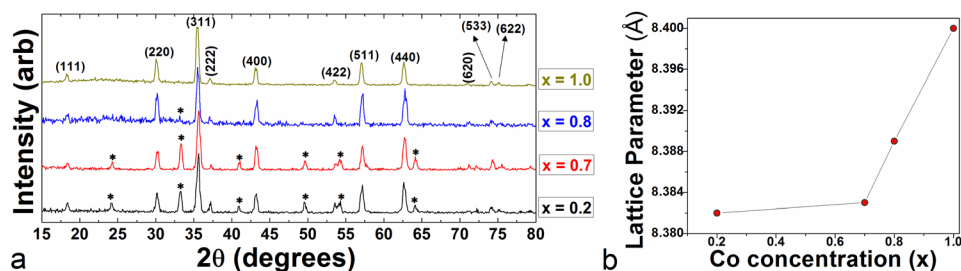
FIG. 2. (Color online) (a) X-ray diffraction pattern of the $Co_xFe_{3-x}O_4$ samples. Peaks marked with * correspond to an α-Fe_2O_3 pattern. (b) Dependence of lattice parameter of the spinel phase on the Co concentration.

compositions were not obtained for each phase because the spatial extents of the phases were too fine to be independently resolved via EDX.

The XRD pattern in Fig. 2(a) shows that the sample with x = 1.0 has only spinel phase peaks. Additional peaks (labeled with *), corresponding to peaks in the α-Fe_2O_3 pattern,[4] were observed at x = 0.2, 0.7, and 0.8. However, only a very small amount of α-Fe_2O_3 seems to be present in the x = 0.8 sample. The similarities in the structure of Fe_3O_4 and Co_3O_4, and in the properties of Fe and Co, would lead one to expect that $Co_xFe_{3-x}O_4$ would be single spinel phase for all $0 \leq x \leq 1$, but this study shows results to the contrary. A previous study on $Co_xFe_{3-x}O_4$ (x = 0.0 to 1.0) (Ref. 5) reported only spinel peaks. However, the samples for that study were produced via the co-precipitation method, whereas those for this study were made using the traditional ceramic approach.

Because the reactivity of Fe_3O_4 depends on surface area,[6] and because the reacting volume of Co_3O_4 is smaller than that of Fe_3O_4, it seems likely that both reactants, in their appropriate proportions, formed $CoFe_2O_4$ and that the excess Fe_3O_4 was oxidized to α-Fe_2O_3. For x = 0.2, Eq. (1) shows the reactions forming $CoFe_2O_4$ and α-Fe_2O_3. If calcined in oxygen, Fe_3O_4 initially forms γ-Fe_2O_3 at about 180 °C, and that changes to α-Fe_2O_3 at about 350 °C.[7] As Fe_3O_4 and Co_3O_4 were calcined twice at 1000 °C and sintered at 1350 °C, it seems likely that the excess Fe_3O_4 was oxidized to α-Fe_2O_3. A similar explanation should apply to the samples with x = 0.7 and 0.8 (Eqs. (2) and (3), respectively). Equations (1)–(3) show that the concentration of α-Fe_2O_3 should decrease with the Co content; thus only the strongest peak in α-Fe_2O_3 ($\sim 2\theta = 33.1°$) was seen at x = 0.8. Although the equations show the primary phase as $CoFe_2O_4$, the measurements in this research cannot completely exclude the presence of other spinel phases. As a result, the primary phase will hereinafter be referred to as the spinel phase. The lattice parameter of the spinel phase shown in Fig. 2(b)

increased with Co content. The changes in the lattice parameter of the spinel phase might be due to the crystal lattice of the α-Fe_2O_3 phase that is present in the two-phase samples.

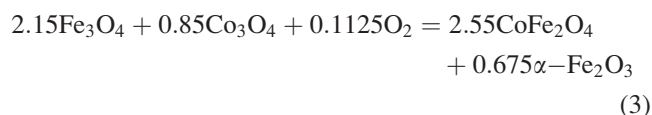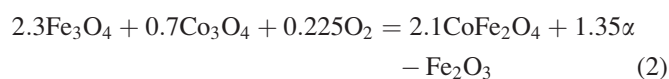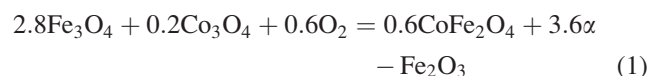$$2.8Fe_3O_4 + 0.2Co_3O_4 + 0.6O_2 = 0.6CoFe_2O_4 + 3.6\alpha - Fe_2O_3 \quad (1)$$

$$2.3Fe_3O_4 + 0.7Co_3O_4 + 0.225O_2 = 2.1CoFe_2O_4 + 1.35\alpha - Fe_2O_3 \quad (2)$$

$$2.15Fe_3O_4 + 0.85Co_3O_4 + 0.1125O_2 = 2.55CoFe_2O_4 + 0.675\alpha - Fe_2O_3 \quad (3)$$

Fig. 3(a) shows the M-H curves, and the inset shows that the saturation magnetization (M_s) increased with x. Although α-Fe_2O_3 is a weakly ferromagnetic material above its Morin temperature of 260 K, its net moment is very small compared to that of the ferrimagnetic spinel phase. Depending on the processing, the magnetization of α-Fe_2O_3 at H = 12.5 kOe is less than 1 emu/g.[8] At a similar magnetic field, spinel $CoFe_2O_4$ (x = 1), for example, has magnetization of $\sim$80 emu/g. In a ferrimagnetic spinel/α-Fe_2O_3 composite system, a higher α-Fe_2O_3 content would be expected to lower the net magnetization, whereas a higher spinel content would increase it. This agrees with the observations here. In Fig. 3(b), the higher coercive field in the samples with a higher concentration of α-Fe_2O_3 could be due to exchange coupling between the two phases or domain wall pinning during magnetization as a result of the two-phase structure.

From these results, it is seen that when Co-ferrite prepared via the ceramic method deviates from stoichiometry, EDX might still show the overall targeted cation ratio expected from a single phase material, even though the secondary α-Fe_2O_3 phase might be present in a fine microstructure. The presence of the secondary phase will alter the magnetic properties of the material relative to those of the single phase material, even though the composition as determined by EDX is the same. When a ferrimagnetic spinel/α-Fe_2O_3 composite is desired, the ceramic method offers the ability to adjust the relative amounts of each phase by adjusting the overall Co content. For example, exchange coupling in bilayers of α-Fe_2O_3 and $CoFe_2O_4$ has been studied for spin-valve sensor development.[9]

TABLE I. Targeted and EDX compositions of the $Co_xFe_{3-x}O_4$ samples.

Target composition (x = Co)	EDX composition	
	Fe	Co
x = 0.20	2.80	0.20
x = 0.70	2.30	0.70
x = 0.80	2.15	0.85
x = 1.0	1.98	1.02

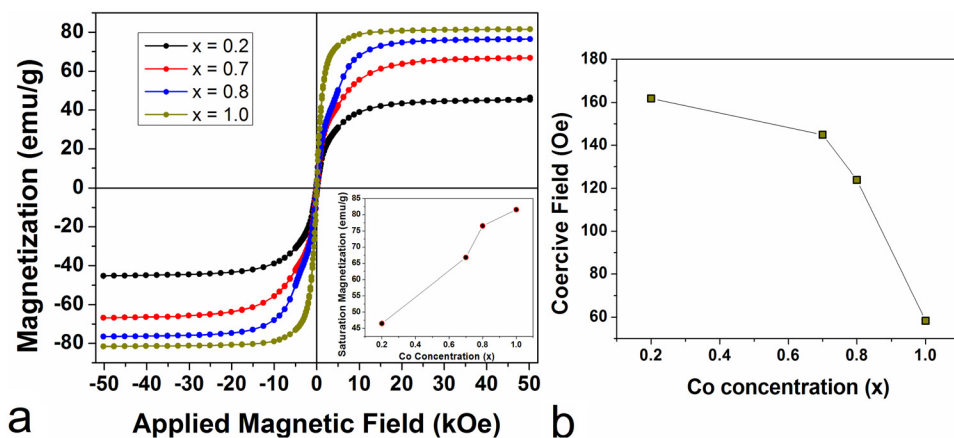FIG. 3. (Color online) (a) Variation of the magnetization with applied field for the $Co_xFe_{3-x}O_4$ samples. Inset shows the variation of the saturation magnetization with the Co concentration. (b) Variation of the coercive field with x.

IV. CONCLUSIONS

In $Co_xFe_{3-x}O_4$ samples prepared via the ceramic method, at $x = 0.2$, 0.7, and 0.8, deviation from stoichiometry ($CoFe_2O_4$) results in a secondary α-Fe_2O_3 phase with a different crystal structure. The α-Fe_2O_3 phase, which was not observed at the stoichiometric composition ($x = 1.0$), changes the microstructure and thereby alters the magnetic properties of the samples.

ACKNOWLEDGMENTS

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