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Effect of deviation from stoichiometric composition on structural and magnetic properties of cobalt ferrite, Co$_x$Fe$_{3-x}$O$_4$ (x = 0.2 to 1.0)

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The effects of deviation from stoichiometric composition on the structural and magnetic properties of cobalt ferrite, Co$_x$Fe$_{3-x}$O$_4$ (x = 0.2 to 1.0), are presented. Both CoFe$_2$O$_4$ and Fe$_3$O$_4$ 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 $\alpha$-Fe$_2$O$_3$ phase. Both structural and magnetic properties are altered depending on the concentration of the $\alpha$-Fe$_2$O$_3$ 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$_2$O$_4$ and $\alpha$-Fe$_2$O$_3$ 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, as a component of multiferroic nanocomposites, and for drug/gene delivery purposes. The samples studied here were Co$_x$Fe$_{3-x}$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$_2$O$_4$), 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$_3$O$_4$ and Co$_3$O$_4$ 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
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 \( \alpha\)-Fe\(_2\)O\(_3\) pattern,\(^4\) were observed at \( x = 0.2, 0.7, \) and 0.8. However, only a very small amount of \( \alpha\)-Fe\(_2\)O\(_3\) seems to be present in the \( x = 0.8 \) sample. The similarities in the structure of Fe\(_3\)O\(_4\) and Co\(_3\)O\(_4\), and in the properties of Fe and Co, would lead one to expect that Co\(_x\)Fe\(_{3-x}\)O\(_4\) would be a single spinel phase for all \( 0 \leq x \leq 1 \), but this study shows results to the contrary. A previous study on Co\(_x\)Fe\(_3\)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\(_3\)O\(_4\) depends on surface area,\(^6\) and because the reacting volume of Co\(_3\)O\(_4\) is smaller than that of Fe\(_3\)O\(_4\), it seems likely that both reactants, in their appropriate proportions, formed CoFe\(_2\)O\(_4\), and that the excess Fe\(_3\)O\(_4\) was oxidized to \( \alpha\)-Fe\(_2\)O\(_3\). For \( x = 0.2 \), Eq. (1) shows the reactions forming CoFe\(_2\)O\(_4\) and \( \alpha\)-Fe\(_2\)O\(_3\). If calcined in oxygen, Fe\(_3\)O\(_4\) initially forms \( \gamma\)-Fe\(_2\)O\(_3\) at about 180 °C, and that changes to \( \alpha\)-Fe\(_2\)O\(_3\) at about 350 °C.\(^7\) As Fe\(_3\)O\(_4\) and Co\(_3\)O\(_4\) were calcined twice at 1000 °C and sintered at 1350 °C, it seems likely that the excess Fe\(_3\)O\(_4\) was oxidized to \( \alpha\)-Fe\(_2\)O\(_3\). 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 \( \alpha\)-Fe\(_2\)O\(_3\) should decrease with the Co content; thus only the strongest peak in \( \alpha\)-Fe\(_2\)O\(_3\) \( (\sim 2\theta = 33.1^\circ) \) was seen at \( x = 0.8 \). Although the equations show the primary phase as CoFe\(_2\)O\(_4\), the measurements in this research cannot completely exclude the presence of other spinel phases. As a result, the primary phase will hereafter be referred to as the spinel phase. The lattice parameter of the spinel phase shown in Fig. 2(b)

\[
\begin{align*}
2.8\text{Fe}_3\text{O}_4 + 0.2\text{Co}_3\text{O}_4 + 0.6\text{O}_2 &= 0.6\text{CoFe}_2\text{O}_4 + 3.6z \\
-\text{Fe}_2\text{O}_3 \\
2.3\text{Fe}_3\text{O}_4 + 0.7\text{Co}_3\text{O}_4 + 0.225\text{O}_2 &= 2.1\text{CoFe}_2\text{O}_4 + 1.35z \\
-\text{Fe}_2\text{O}_3 \\
2.15\text{Fe}_3\text{O}_4 + 0.85\text{Co}_3\text{O}_4 + 0.1125\text{O}_2 &= 2.55\text{CoFe}_2\text{O}_4 + 0.675z -\text{Fe}_2\text{O}_3
\end{align*}
\]

increased with Co content. The changes in the lattice parameter of the spinel phase might be due to the crystal lattice of the \( \alpha\)-Fe\(_2\)O\(_3\) phase that is present in the two-phase samples.

**Table I. Targeted and EDX compositions of the Co\(_x\)Fe\(_{3-x}\)O\(_4\) samples.**

<table>
<thead>
<tr>
<th>Target composition ((x = \text{Co}))</th>
<th>EDX composition</th>
</tr>
</thead>
<tbody>
<tr>
<td>( x = 0.20 )</td>
<td>2.80 0.20</td>
</tr>
<tr>
<td>( x = 0.70 )</td>
<td>2.30 0.70</td>
</tr>
<tr>
<td>( x = 0.80 )</td>
<td>2.15 0.85</td>
</tr>
<tr>
<td>( x = 1.0 )</td>
<td>1.98 1.02</td>
</tr>
</tbody>
</table>

Fig. 3(a) shows the M-H curves, and the inset shows that the saturation magnetization \((M_s)\) increased with \( x \). Although \( \alpha\)-Fe\(_2\)O\(_3\) 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 \( \alpha\)-Fe\(_2\)O\(_3\) at \( H = 12.5 \) kOe is less than 1 emu/g.\(^8\) At a similar magnetic field, spinel CoFe\(_2\)O\(_4\) \( (x = 1) \), for example, has magnetization of \( \sim 80 \) emu/g. In a ferrimagnetic spinel/\( \alpha\)-Fe\(_2\)O\(_3\) composite system, a higher \( \alpha\)-Fe\(_2\)O\(_3\) 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 \( \alpha\)-Fe\(_2\)O\(_3\) 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 \( \alpha\)-Fe\(_2\)O\(_3\) 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/\( \alpha\)-Fe\(_2\)O\(_3\) 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 \( \alpha\)-Fe\(_2\)O\(_3\) and CoFe\(_2\)O\(_4\) has been studied for spin-valve sensor development.\(^9\)
IV. CONCLUSIONS

In Co$_x$Fe$_{3-x}$O$_4$ samples prepared via the ceramic method, at $x = 0.2$, 0.7, and 0.8, deviation from stoichiometry (CoFe$_2$O$_4$) results in a secondary $\alpha$-Fe$_2$O$_3$ phase with a different crystal structure. The $\alpha$-Fe$_2$O$_3$ phase, which was not observed at the stoichiometric composition ($x = 1.0$), changes the microstructure and thereby alters the magnetic properties of the samples.

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4Patterns were compared with others from the International Centre for Diffraction Data (ICDD 00-001-1053).