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Structural, magnetic, and magnetoelastic properties of magnesium substituted cobalt ferrite

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Structural, magnetic, and magnetoelastic properties of magnesium substituted cobalt ferrite
I. C. Nlebedim, R. L. Hadimani, R. Prozorov, and D. C. Jiles

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Magnetic and magnetoelastic properties of Ga-substituted cobalt ferrite
Structural, magnetic, and magnetoelastic properties of magnesium substituted cobalt ferrite

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The effects of substituting Mg on the structural, magnetic, and magnetostrictive properties of cobalt ferrite have been investigated. Comparable values of lattice parameter were obtained for the Mg-substituted samples. Saturation magnetization continuously decreased with increase in Mg concentration. Peak-to-peak magnetostriction amplitude and strain sensitivity had a similar dependence on Mg concentration. © 2013 American Institute of Physics. [http://dx.doi.org/10.1063/1.4798822]

INTRODUCTION

Cobalt ferrite (Co-ferrite) based magnetostrictive materials have been increasingly studied due to their high strain sensitivity. One approach to enhancing their strain sensitivity is by cation substitution into the spinel crystal lattice. Assuming that all Fe2+ in Fe3O4 is replaced by Co2+ to form Co-ferrite, CoFe2O4 can then be written as (Co2+xFe3−x)A-sites [Co3+xFe2−x]B-sites O4−2, x is a measure of the degree of inversion, which, for Co-ferrite can range from 0.67 to 0.96 (Refs. 1 and 2) resulting in most of the Co2+ cations occupying the B-sites. The crystal lattice of the spinel (MgAl2O4), from which Co-ferrite derives its crystal structure, contains the cations, Al3+ and Mg2+, with Al3+ preferring the B-sites and Mg2+ the A-sites. We have previously investigated the effects of substituting Al3+ for Fe3+ on the magnetostrictive properties of Co-ferrite.5,6 It was found that Al-substitution resulted in the best combination of magnetostriction amplitude and sensitivity compared to other studies on cation substituted cobalt ferrite.3 In this study, we present the effect of changing the concentration of Mg, substituted for Fe, on the structural, magnetic, and magnetostrictive properties of Co-ferrite.

EXPERIMENTAL DETAILS

Samples were prepared using Fe2O3, Co3O4, and MgO powders 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 by x-ray diffractometry (XRD). The microstructures and compositions were studied by scanning electron microscopy (SEM) and energy dispersive x-ray spectroscopy (EDX), respectively. A SQUID magnetometer was used to measure the magnetic properties. Magnetostriction was measured with foil strain gauges attached to the surface of the samples.

RESULTS AND DISCUSSION

Uniform contrasts in backscattered electron micrographs are indicative of single phase. Although the contrasts of the backscattered electron micrographs in Fig. 1 are uniform, the XRD patterns in Fig. 2 show that, in addition to the spinel phase, samples x = 0.15 to 0.3 have a secondary phase corresponding to (Mg1−xCo)xO.6 The compositions of the samples obtained by EDX are compared to the target compositions in Table I. Samples with x = 0.15 to 0.3 are cobalt deficient and samples with x = 0.20 to 0.3 are slightly magnesium deficient. Nevertheless, the compositions obtained were close to the target compositions. Table I also shows the lattice parameters of the samples. The lattice parameters of the Mg-substituted samples, x = 0.05 to 0.3, are all comparable and slightly less than that of the un-substituted sample, x = 0. This is also seen in the XRD patterns. The pattern of x = 0 is shifted to the lower 2θ region compared to the rest, indicating higher lattice parameter. For x = 0.05 to 0.3, there was no observable shift, indicating no change in the values of the lattice parameters.

Fig. 3(a) shows that the magnetization of the samples decreased with Mg content, x. The inset shows that the saturation magnetization appears to decrease almost linearly with Mg concentration. Due to antiparallel coupling between the A-sites and B-sites in spinel structured materials, the net magnetization (M) is given by M = ∑MB−sites − ∑MA−sites. Although in the spinel (MgAl2O4), Mg2+ has a stronger preference for the A-sites than Al3+, in ferrites, it has a stronger preference for the B-sites than Fe3+ and Co2+.7,8 If, therefore, non-magnetic Mg substitutes into the B-sites for magnetic Fe, then ∑MB−sites and consequently, M = ∑MB−sites − ∑MA−sites, would decrease, provided that ∑MA−sites remains the same or increases by any other mechanism such as displacement of Co or Fe from the B-sites into the A-sites. This should result in continuous decrease in magnetization with increasing Mg concentration as observed in this study. It is noteworthy that a similar trend was observed when Al was substituted for Fe3+.3 Al has a stronger preference for the B-sites than Mg2+, Co2+, and Fe3+.8

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The similarity in the variation of peak-to-peak magnetostriction amplitude (Fig. 3(a)) and strain sensitivity (Fig. 3(b)) with Mg concentration indicates that a similar mechanism is responsible for the variation of both. In previous studies on cation substituted cobalt ferrites, strain sensitivity often increased at low cation contents but decreased at higher contents. It is known that the magnetocrystalline anisotropy and magnetoelastic properties of Co-ferrite (CoO\ce{Fe}_2\ce{O}_4) compared with magnetite (FeO\ce{Fe}_2\ce{O}_4) are mainly due to Co^{2+} in the B-sites of the spinel crystal lattice. In this study, the strong preference of the Mg^{2+} for the B-sites may have resulted in some of the Co^{2+} being displaced into the A-sites. This would result in the super-exchange interaction due to non-magnetic Mg (Mg-O-Fe) being weaker than that due to the magnetic cations, Co-O-Fe and Fe-O-Fe. Consequently, magnetostrictive properties (and magnetocrystalline anisotropy) would decrease. Moreover, the displacement of Co from the B-sites will weaken the effect of spin-orbit coupling (arising from the unquenched orbital angular momentum of Co^{2+}) that contributes to magnetocrystalline anisotropy. That will also affect the magnetostrictive properties which depend on anisotropy. Also, doping of Mg into Co-ferrite affects the crystalline field energy. This in turn affects magnetocrystalline anisotropy and the magnetostrictive properties.\textsuperscript{9,10}

It is seen from Fig. 3(b) that, unlike the magnetization, the magnetostrictive properties do not decrease monotonically with Mg concentration. A possible reason may be the

<table>
<thead>
<tr>
<th>Target composition ($x = \text{Mg}$)</th>
<th>EDX composition (Fe, Co, Mg)</th>
<th>Lattice parameter (Å)</th>
</tr>
</thead>
<tbody>
<tr>
<td>$x = 0$</td>
<td>1.98 1.02 0</td>
<td>8.41</td>
</tr>
<tr>
<td>$x = 0.05$</td>
<td>1.95 1.05 0.05</td>
<td>8.38</td>
</tr>
<tr>
<td>$x = 0.10$</td>
<td>1.91 1.09 0.09</td>
<td>8.38</td>
</tr>
<tr>
<td>$x = 0.15$</td>
<td>1.89 0.96 0.15</td>
<td>8.37</td>
</tr>
<tr>
<td>$x = 0.20$</td>
<td>1.89 0.93 0.18</td>
<td>8.37</td>
</tr>
<tr>
<td>$x = 0.25$</td>
<td>1.85 0.93 0.22</td>
<td>8.38</td>
</tr>
<tr>
<td>$x = 0.30$</td>
<td>1.82 0.92 0.26</td>
<td>8.38</td>
</tr>
</tbody>
</table>
changes of the sites into which Mg substitutes, the rate of substitution into the sites, and displacement of Fe and Co due to the substitution. Although Mg has a strong preference for the B-sites, it is likely that at higher concentrations, Mg would start to substitute into the A-sites.

CONCLUSIONS

Mg substitution for Fe in cobalt ferrite has been shown to have strong effects on both magnetic and magnetostrictive properties. This has been shown to be due to Mg\(^{2+}\) having a stronger preference for the B-sites than Fe\(^{3+}\) and Co\(^{2+}\) and therefore displacing these cations from the B-sites. It is indicated that a similar mechanism is responsible for the variations in magnetostriction amplitude and strain sensitivity, which may be why both properties varied in a similar way. A further investigation will be undertaken to understand the observed variation in magnetostrictive properties with respect to the variation in magnetocrystalline anisotropy. The result of this should be useful in tailoring these properties for a variety of applications.

ACKNOWLEDGMENTS

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6Patterns were compared with International Centre for Diffraction Data, PDF#-04-002-2875 (n.d.).