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S. H. Song
Iowa State University

Chester C.H. Lo
Iowa State University, clo@iastate.edu

S. J. Lee
Iowa State University

S. T. Aldini
Iowa State University

J. E. Snyder
Cardiff University

See next page for additional authors
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Authors

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Magnetic and magnetoelastic properties of Ga-substituted cobalt ferrite

S. H. Song
Materials and Engineering Physics Program, Ames Laboratory, U.S. Department of Energy, Iowa State University, Ames, Iowa 50011 Department of Materials Science and Engineering, Iowa State University, Ames, Iowa 50011

C. C. H. Lo and S. J. Lee
Center for Nondestructive Evaluation, Iowa State University, Ames, Iowa 50011

S. T. Aldini
Materials and Engineering Physics Program, Ames Laboratory, U.S. Department of Energy, Iowa State University, Ames, Iowa 50011

J. E. Snyder and D. C. Jiles
Wolfson Centre for Magnetics, Cardiff University, Cardiff CF24 3AA, United Kingdom

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Magnetic and magnetoelastic properties of a series of Ga-substituted cobalt ferrites, CoGaFe_{2-x}O_4 (x=0.0–0.8), have been investigated. The Curie temperature T_C and hysteresis properties were found to vary with gallium content (x), which indicates that exchange and anisotropy energies changed as a result of substitution of Ga for Fe. The maximum magnitude of magnetostriction decreased monotonically with increasing gallium content over the range x=0.0–0.8. The rate of change of magnetostriction with applied magnetic field (dH/dH) showed a maximum value of 3.2×10^{-9} A^{-1} m for x=0.2. This is the highest value among recently reported cobalt ferrite based materials. It was found that the dependence of magnetic and magnetoelastic properties on the amount of substituent (x) was different for Mn, Cr, and Ga. This is considered to be due to the differences in cation site occupancy preferences of the elements within the spinel crystal structure: Mn^{3+} and Cr^{3+} prefer the octahedral (B) sites, whereas Ga^{3+} prefers the tetrahedral (A) sites. © 2007 American Institute of Physics. [DOI: 10.1063/1.2712941]

I. INTRODUCTION

Cobalt ferrite based composites have high magnetostriction \( \lambda \) and high sensitivity \( dB/d\sigma \) of magnetic induction to applied stress and are chemically. These factors make these materials attractive for use in magnetoelastic sensors. However, to enable practical applications a family of materials is needed, in which the magnetoelastic response, magnetic properties, and their temperature dependences can be tailored by a well defined “control variable” such as chemical composition. Substituted cations can occupy tetrahedral or octahedral sites in the spinel structure. Mn^{3+} and Cr^{3+} are reported to prefer the octahedral sites. A series of Mn- and Cr-substituted cobalt ferrite CoMnFe_{2–x}O_4 and CoCrFe_{2–x}O_4 (where x=0.0–0.8) was recently studied to investigate the effect of change in chemical composition and crystallographic site occupancy on the magnetic and magnetoelastic properties. Promising results were obtained, showing that Curie temperature and magnetic anisotropy could be decreased, and \( d\lambda/dH \) increased without causing much loss of magnetostriction. Mössbauer spectroscopy investigations confirmed that the Mn^{3+} ions and the Cr^{3+} ions substitute preferentially into the octahedral sites in cobalt ferrite. In the present study, a family of Ga-substituted cobalt ferrite CoGa_{2–x}Fe_xO_4 samples has been investigated. Ga^{3+} is known to prefer the tetrahedral sites, therefore the results were expected to be different from those of Mn- and Cr-substituted cobalt ferrites.

II. EXPERIMENTAL METHODS

A series of polycrystalline Ga-substituted cobalt ferrite samples with compositions of CoGa_{Fe_{2–x}O_4} (where x =0.0–0.8) was prepared by standard powder ceramic techniques using Fe_{2}O_{3}, Ga_2O_3, and Co_3O_4 powders as precursors. Samples were calcined twice, sintered at 1350 °C for 24 h, and were subsequently furnace cooled to room temperature. The final compositions of the sintered samples were found to be close to the target composition, as shown in Table I. All the samples had a cubic spinel structure which was investigated. Ga^{3+} is known to prefer the tetrahedral sites, therefore the results were expected to be different from those of Mn- and Cr-substituted cobalt ferrites.

TABLE I. Target compositions of a series of Ga-substituted cobalt ferrite samples and the final compositions determined by energy-dispersive x-ray spectroscopy (EDX) in a SEM.

<table>
<thead>
<tr>
<th>Target composition</th>
<th>Fe</th>
<th>Co</th>
<th>Ga</th>
</tr>
</thead>
<tbody>
<tr>
<td>CoFe_{2}O_4</td>
<td>2.05</td>
<td>0.95</td>
<td></td>
</tr>
<tr>
<td>CoGa_{0.2}Fe_{1.4}O_4</td>
<td>1.81</td>
<td>1.00</td>
<td>0.19</td>
</tr>
<tr>
<td>CoGa_{0.4}Fe_{1.6}O_4</td>
<td>1.55</td>
<td>1.04</td>
<td>0.41</td>
</tr>
<tr>
<td>CoGa_{0.6}Fe_{1.8}O_4</td>
<td>1.33</td>
<td>0.98</td>
<td>0.69</td>
</tr>
<tr>
<td>CoGa_{0.8}Fe_{2.0}O_4</td>
<td>1.15</td>
<td>1.04</td>
<td>0.81</td>
</tr>
</tbody>
</table>

Electronic mail: song73@iastate.edu
was confirmed using x-ray powder diffraction. Scanning electron microscopy (SEM) investigations showed that all the sintered samples had a homogeneous microstructure with similar grain sizes of the order of 10 μm. Magnetization (M) versus temperature (T) under a field of 7.96 kA/m (100 Oe) and magnetization (M) versus applied magnetic field (H) at ambient temperature (nominally 300 K) were measured using a vibrating sample magnetometer (VSM). The Curie temperature \( T_C \) was determined from the \( M \) vs \( T \) curve by linear extrapolation from the region of maximum slope down to the temperature axis. Magnetostriiction as a function of applied field (\( \lambda \) vs \( H \)) was measured at room temperature using the strain gauge method.

### III. RESULTS AND DISCUSSIONS

The temperature dependent magnetizations of Ga substituted cobalt ferrite samples, \( \text{CoGa}_{x}\text{Fe}_{2-x}\text{O}_4 \), are shown in Fig. 1(a). From the \( M \) vs \( T \) curves, it was evident that the Curie temperature \( T_C \) was reduced by substitution of Ga for Fe. This is considered to be due principally to reduction in the \( A-B \) site exchange interaction caused by Ga substitution. A similar effect has been observed when substituting Mn or Cr for Fe in cobalt ferrite.\(^{5,6} \) \( T_C \) decreases at a greater rate with Ga substitution than with Mn or Cr substitution [Fig. 1(b)]. This can perhaps be understood because the tetrahedral sites have a higher number of next nearest neighbor cations, to which they are superexchange coupled, than the octahedral sites have. Thus the change in interaction energy caused by substitution at the tetrahedral sites may be expected to be larger than at the octahedral sites for the same amount of substitution.

Figure 2 shows the variation in \( M \) vs \( H \) and coercive field (\( H_C \)) with gallium content. Compared with \( M \) vs \( H \) of pure cobalt ferrite, those of Ga-substituted cobalt ferrites show softer magnetic behavior (lower \( H_C \)) as the gallium content increases from \( x=0.2 \) to 0.8. This is believed to be due to the reduction in anisotropy energy caused by Ga substitution. Anisotropy energy decreases as a function of \( T/T_C \) faster than magnetization does. This has been both measured\(^{13} \) and modeled theoretically\(^{14} \) for single-crystal cobalt ferrite. Likewise, we have observed this experimentally for Mn-substituted and Cr-substituted cobalt ferrites.\(^{7,8} \) So with \( T_C \) decreasing as a function of \( x \) even more strongly with Ga substitution than it does for Cr or Mn substitution, the anisotropy energy at 300 K is expected to decrease, even more than for Cr or Mn substitution for the same value of \( x \).

Gallium substitution was found to have a strong effect...
on magnetostriction. As shown in Fig. 3, the magnitude of magnetostriction decreased with increasing Ga content for \( x \) up to 0.8. The magnetostriction for low values of \( x \) (\( x=0.0, 0.2, \) and 0.4) was found to change slope as the field was increased, starting with a negative slope \( d\lambda/dH \) at low fields but changing to a positive slope at high fields. This is indicative of different signs for the two cubic magnetostriction coefficients. For \( x=0.6 \) and \( x=0.8 \) the signs of the slope changed, so that it was positive at low fields, while at high fields the slope changed to negative. The simplest explanation for this is that the addition of Ga changed the sign of the anisotropy coefficient so that the magnetic easy axes changed from those with a negative magnetostriction to those with a positive magnetostriction. This would account for the low field slope change in from negative to positive. However, as the sign of the slope \( d\lambda/dH \) still changed at high fields, this indicates that the magnetic hard axes had magnetostriction coefficients with different signs from the easy axes. It is worth mentioning that substituting small amounts of Ga for Fe (e.g., CoGa\(_{x}\)Fe\(_{2-x}\)O\(_4\)) increased the magnitude of maximum strain derivative \( (d\lambda/dH)_{\text{max}} \) as shown in Fig. 4(a), while the magnitude of magnetostriction decreased monotonically with Ga content. Similar behavior has been observed in recent studies of Mn- and Cr-substituted cobalt ferrites Co\(_{3-x}\)Mn\(_x\)Fe\(_{2-x}\)O\(_4\) and Co\(_{3-x}\)Cr\(_x\)Fe\(_{2-x}\)O\(_4\) \( (x=0.0–0.8) \) in which the largest values of \( (d\lambda/dH)_{\text{max}} \) for Mn- and Cr-substituted cobalt ferrites were reported to be \( 2.5 \times 10^{-6} \) \( \text{A}^{-1} \) \( \text{m} \) (at \( x=0.2 \) for Mn) and \( 2.0 \times 10^{-9} \) \( \text{A}^{-1} \) \( \text{m} \) (at \( x=0.4 \) for Cr), respectively. For Cr-substituted cobalt ferrite, the magnitude of \( (d\lambda/dH)_{\text{max}} \) for \( x=0.2 \) Cr sample was \( 1.5 \times 10^{-9} \) \( \text{A}^{-1} \) \( \text{m} \). Compared with Mn- and Cr-substituted cobalt ferrite, Ga-substituted cobalt ferrite shows much higher magnitude of \( (d\lambda/dH)_{\text{max}} \) (\( 3.2 \times 10^{-9} \) \( \text{A}^{-1} \) \( \text{m} \) even at a much lower applied field of \( H=15 \) kA/m [Fig. 4(b)]. The magnitude of \( d\lambda/dH \) is expected to depend inversely on anisotropy energy (steeper \( d\lambda/dH \) for lower anisotropy, when it is easier to change the direction of magnetization).

For reversible processes under small applied field and stress, there is a thermodynamic relationship which relates \( (d\lambda/dH)_{\text{p}} \) to the stress sensitivity of induction \( (dB/dH)_{\text{p}} \). The strain derivative can therefore be used as a predictor of the stress sensitivity of magnetic induction to stress or torque when selecting materials for stress or torque sensor applications.

IV. CONCLUSIONS

Substitution of Ga for Fe was found to decrease the Curie temperature at a greater rate than Mn or Cr substitution, which is consistent with the suggestion that Ga\(^3+\) ions prefer the tetrahedral sites whereas Mn\(^{3+}\) and Cr\(^{3+}\) prefer the octahedral sites. The maximum magnitude of magnetostriction \( \lambda_{\text{max}} \) decreased at about the same rate as was observed with Cr substitution; however, the strain derivative \( (d\lambda/dH)_{\text{max}} \) of \( 3.2 \times 10^{-9} \) \( \text{A}^{-1} \) \( \text{m} \) for \( x=0.2 \) Ga sample was greater than for any of the Mn- or Cr-substituted samples. This enhanced \( (d\lambda/dH)_{\text{max}} \) implies high stress sensitivity, which suggests that adjusting Ga content substituted into cobalt ferrite can be a promising route for controlling critical magnetic properties of the material for practical stress sensor applications.

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