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Magneto-optic properties of $CoFe_{2-x}Ga_xO_4$

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Research on cobalt ferrite based composites has increased recently due to their potential applications such as noncontact magnetoelastic stress or torque sensors and erasable magneto-optic recording media. We report a study of the polar Kerr rotation spectra for $CoFe_{2-x}Ga_xO_4$ (with $x=0.4$ and $x=0.8$). Each of the spectra consists of two peaks of negative Kerr rotation in the measured photon energy range of 1.5–3.0 eV. For $x=0.4$, one peak occured at 1.8 eV and the other at 2.25 eV. For $x=0.8$, the first peak shifted to a higher energy of about 1.9 eV, while the second peak remained at 2.25 eV. The origin of the peaks in the polar Kerr spectra and the observed shift of peak position resulting from Ga substitution can be explained by the intervalence charge-transfer transition, in which an electron from a metallic cation is transferred to a neighboring cation through an optical excitation. © *2007 American Institute of Physics*. [DOI: 10.1063/1.2693953]

I. INTRODUCTION

Cobalt ferrite $CoFe_2O_4$, which has a spinel crystal structure, shows interesting physical properties such as high sensitivity of magnetization to applied stress, excellent chemical stability, and a large magneto-optic effect.[1–4] There are two types of sublattice sites in the spinel structure, the tetrahedral (*A* sites) and the octahedral (*B* sites), and the different types of metallic ions are distributed according to the formula $Fe_A[CoFe]_BO_4$.[5] The Co^{2+} and Fe^{3+} cation distributions can be described as $(Fe^{3+})_A[Co^{2+}Fe^{3+}]_BO_4$. The magnetic properties or magneto-optic properties, including the exchange interactions, of these ferrites have been found to be dependent on how the cations are distributed among the two sublattices.[6–8]

Recently, cobalt ferrite composites[9] and their Mn-substituted modifications[10] have been actively investigated as part of the development of materials for highly sensitive noncontact stress and torque sensors. It was observed that the substitution of Mn for Fe led to the reduction of both the Curie temperature and the magnetostriction with increasing Mn content. This result indicates that it is possible to adjust the temperature dependence of magnetic properties and magnetomechanical hysteresis by systematic variation of the chemical composition.

Research into the magneto-optic properties of cobalt ferrites and their modifications based on chemical substitution has also been undertaken because of their potential application to magneto-optic recording media. Martens *et al.*[11] studied the magneto-optic properties of cobalt ferrite single crystals. They observed that the extrema (maxima and minima) of the polar Kerr rotation spectrum are located at photon energies of 1.8, 2.1, 3.5, 3.9, and ~5 eV. They concluded that the origin of these is most likely due to charge transfer transitions and crystal field transitions of Co^{2+} on the tetrahedral sites in the spinel structure. Kim *et al.*[2] studied magneto-optic transitions in $CoFe_2O_4$ and $NiFe_2O_4$ samples prepared as films on glass substrates by the sol-gel method. They observed peaks at 2.0 and 2.2 eV in the polar Kerr rotation spectrum. They attributed the peak at 2.0 eV as due to the crystal field transition from the $3d^7$ configuration of the Co^{2+} ions at the tetrahedral sites; and the peak at 2.2 eV as due to the $[Co^{2+}]t_{2g} \rightarrow [Fe^{3+}]t_{2g}$ intervalence charge transfer (IVCT) transitions. In an IVCT transitions, an electron in a cation is transferred to a neighboring cation through an optical excitation.[12]

Peeters and Martens[13] studied the polar Kerr rotations of $CoFe_{2-x}Al_xO_4$ and $Co_xFe_{3-x}O_4$. They have shown that the magneto-optic effects below 2 eV are contributed by the crystal field transitions of Co^{2+} (T_d) and by charge transfer transitions of Co^{2+} to Fe^{3+} on the octahedral sites. Recently Zhou *et al.*[4] investigated the doping effects of Al^{3+} on the magneto-optic Kerr effects in nanocrystalline $CoFe_{2-x}Al_xO_4$ thin films deposited on a silicon substrate. They found that the substitution of Fe^{3+} in $CoFe_2O_4$ by Al^{3+} caused the creation of additional peaks in the spectrum that were associated

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with crystal field transition, and also a shift of the Kerr rotation peak that was associated with an IVCT transition.

Magneto-optic Kerr spectra for iron containing spinels and garnets have similar transition structures for photon energies greater than 3 eV,[14–16] and therefore studies have focused on the polar Kerr rotation spectra below 3 eV.[3,13] In the present work, we studied the polar Kerr rotations for gallium substituted cobalt ferrite samples, $CoFe_{2-x}Ga_xO_4$ with $x=0.4$ and $x=0.8$. The samples were prepared by standard powder ceramic techniques, and the photon energy range of the magneto-optic polar Kerr spectra was measured between 1.5 and 3.0 eV with increments of 0.05 eV.

II. EXPERIMENTAL DETAILS

Polycrystalline bulk cobalt ferrite samples with compositions of $CoFe_{2-x}Ga_xO_4$ ($x=0.4$ and $x=0.8$) were prepared by standard powder ceramic techniques[9] using Fe_2O_3, Ga_2O_3, and Ga_3O_4 powder as precursors. Samples were calcined twice, sintered at 1350 °C for 24 h, and subsequently furnace cooled to room temperature. The final compositions of the sintered samples were found to be close to the target composition.

The crystal structures of the samples were determined using x-ray powder diffractometry. Scanning electron microscopy (SEM) was used to examine the microstructures. The surfaces of the polycrystalline cobalt ferrite samples were prepared for the optical measurements by polishing with abrasives, the final grade being a paste of 0.3 μm diameter alumina. Magneto-optic measurements were performed with a polar configuration setup using a 75 W Xe short-arc lamp light source with a photoelastic modulator (PEM).[17]

In the polar Kerr effect, the near-normal incident, linearly polarized light becomes elliptically polarized light after it is reflected. The major axis of the reflected light is rotated from the polarization axis of the incident light. The angle of rotation is known as the Kerr angle or Kerr rotation. In this experiment, the angle of incidence was kept below 4°. A magnetic field of 5 kG was applied at room temperature perpendicular to the sample surface.

III. RESULTS AND DISCUSSION

X-ray diffraction measurements showed that the polycrystalline cobalt ferrite samples with compositions of $CoFe_{2-x}Ga_xO_4$ ($x=0.4$ and $x=0.8$) have a single phase spinel crystal, as shown in Fig. 1. No extra crystalline phases or peaks related to CoO and Fe_2O_3 were observed. All the sintered samples were found to have a homogeneous microstructure with similar grain sizes of the order of 10 μm. An example is given in Fig. 2, which shows the SEM image of the $CoFe_{1.2}Ga_{0.8}O_4$ sample.

The measured polar Kerr rotation spectra for $CoFe_{2-x}Ga_xO_4$ ($x=0.4$ and $x=0.8$) samples are shown in Fig. 3. Each consists of two peaks of negative Kerr rotation. For $x=0.4$, one peak occurred at 1.8 eV and the other was at 2.25 eV. For $x=0.8$, the first peak shifted to a higher energy of about 1.9 eV, while the second peak remained at 2.25 eV. Similar peaks at 1.8 and 2.1 eV appeared in the polar Kerr

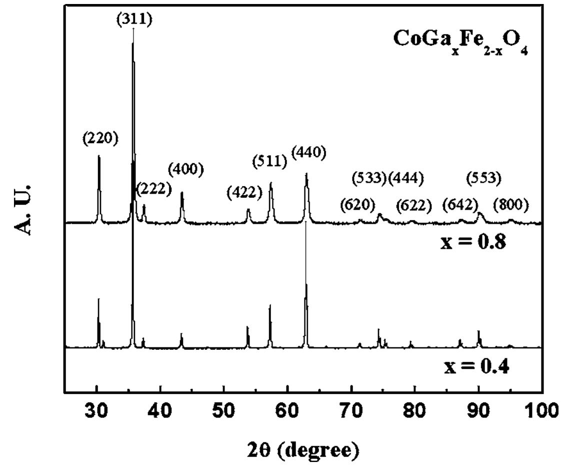

FIG. 1. X-ray diffraction data for polycrystalline cobalt ferrite samples with compositions of $CoFe_{2-x}Ga_xO_4$ ($x=0.4$ and $x=0.8$).

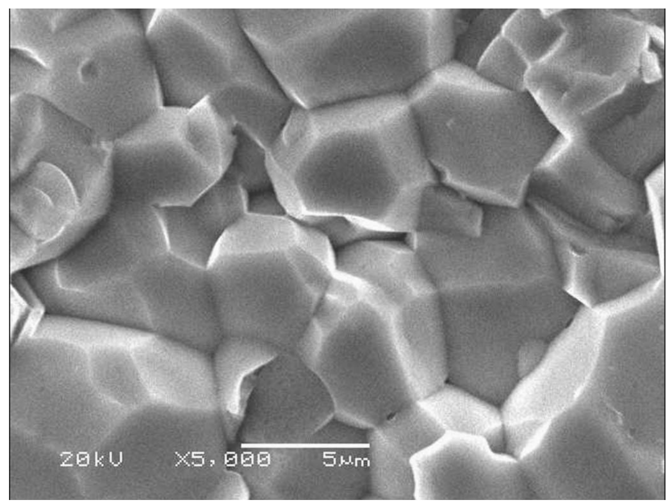

FIG. 2. SEM image showing a homogeneous, equiaxed microstructure of the $CoFe_{2-x}Ga_xO_4$ with $x=0.8$.

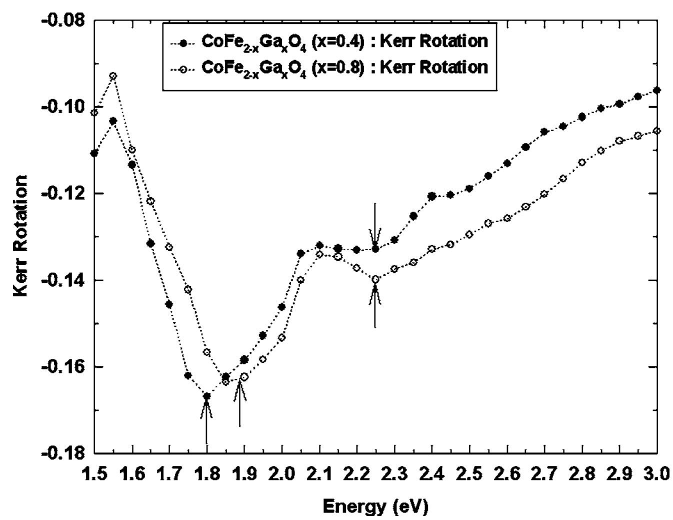

FIG. 3. Magneto-optic Kerr rotation spectra for $CoFe_{2-x}Ga_xO_4$ ($x=0.4$ and $x=0.8$) samples.

rotation spectrum of cobalt ferrite single crystal.[11] The origin of these peaks was not clear, but both Co^{2+} charge transfer transitions and crystal field transitions of Co^{2+} were assumed to contribute to these peaks.

Zhou *et al.*[3] introduced the molecular orbital theory of IVCT transitions to interpret the correlation between structures and IVCT transitions. The theory indicated that doping with the relatively large ions could lead to the increase of the distance between Co^{2+} and Fe^{3+} ions at the octahedral sites, and this caused the energy gap of the IVCT transitions to be reduced. Alternatively when the doping ions are relatively small, the energy gap of IVCT transitions increases. As the radius of the Ga^{3+} ions [r_{VI}=0.062 nm (Ref. 18)] is small compared with that of Fe^{3+} ions [r_{VI}=0.0645 nm with high spin state (Ref. 18)], the energy gap of IVCT transitions would increase with increased Ga^{3+} ion content. The peak position at 1.8 eV shifted to 1.9 eV as the doping concentration of $CoFe_{2-x}Ga_xO_4$ increased from x=0.4 to 0.8, as expected from the molecular orbital theory of IVCT transitions. However, for the peak position of 2.25 eV no noticeable shift was observed as doping level increased.

IV. SUMMARY AND CONCLUSIONS

The magneto-optic spectra and, in particular, the polar Kerr rotations of Ga substituted cobalt ferrites have been investigated for $CoFe_{2-x}Ga_xO_4$ with x=0.4 and x=0.8. A peak appeared at 1.8 eV in the Kerr rotation spectrum of $CoFe_{2-x}Ga_xO_4$ with x=0.4 and this shifted to 1.9 eV for the $CoFe_{2-x}Ga_xO_4$ composition with x=0.8. This shift can be explained by the molecular orbital theory of IVCT transitions, which predicts that the smaller radius of Ga^{3+} ions substituting for Fe^{3+} ions in $CoFe_{2-x}Ga_xO_4$ increases the energy gap of IVCT transitions. This observation was correct for the lower energy peak but was not clear for the higher energy peak at 2.25 eV. It was observed from the experiment that the control of Kerr rotation of Ga substituted cobalt ferrites is possible by adjusting the Ga content.

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