Effects of Cr Doping on Magnetic Properties of Inverse Spinel CoFe$_2$O$_4$ Thin Films

Kwang Joo Kim[*], Hee Kyung Kim, Young Ran Park, and Jae Yun Park[1]

Department of Physics, Konkuk University, Seoul 143-701, Korea
[1]*Department of Materials Science and Engineering, University of Incheon, Incheon 402-749, Korea*

Variation of magnetic properties through Cr substitution for Co in inverse-spinel CoFe$_2$O$_4$ has been investigated by vibrating-sample magnetometry (VSM) and conversion electron Mössbauer spectroscopy (CEMS). Cr$_x$Co$_{1-x}$Fe$_2$O$_4$ samples were prepared as thin films by a sol-gel method. The lattice constant of the Cr$_x$Co$_{1-x}$Fe$_2$O$_4$ samples was found to remain unchanged, explainable in terms of a reduction of tetrahedral Fe^{3+} ion to Fe^{2+} due to substitution of Cr^{3+} ion into octahedral Co^{2+} site. The existence of the tetrahedral Fe^{2+} ions in Cr$_x$Co$_{1-x}$Fe$_2$O$_4$ was confirmed by CEMS analysis. Room-temperature magnetic hysteresis curves for the Cr$_x$Co$_{1-x}$Fe$_2$O$_4$ films measured by VSM revealed that the saturation magnetization (M$_S$) increases by Cr doping. The M$_S$ is maximized when x = 0.1 and decreases for higher x but is still bigger than that of CoFe$_2$O$_4$. The increase of M$_S$ can be explained partly by the reduction of the tetrahedral Fe^{3+} ion to Fe^{2+}.

Key words : spinel, cobalt ferrite, substitution, magnetization, Mössbauer

1. Introduction

Transition-metal (TM) oxides have been found to play an important role in technological applications such as magnetic and optical materials, semiconductors, catalysts, protective coatings, etc. A large number of such TM oxides crystallize in the spinel structure and most of their characteristic properties have been found to depend on the oxidation states of the constituent TM ions. The spinel structure of the oxides with the cationic tetrahedral (A) and octahedral (B) sites of the general formula AB$_2$O$_4$ is responsible for a variety of physical and chemical properties achievable through accommodation of different cations, among the A and B sites, sometimes in more than one oxidation state. Such multi-valence is possible due to the partially-filled nature of TM 3d orbitals.

CoFe$_2$O$_4$ is known as an inverse spinel, exhibiting ferrimagnetism with Curie temperature 793 K [1] and applicable for high-density magnetic and magneto-optic recording media. The octahedral Co^{2+}(d^7) ions in CoFe$_2$O$_4$ are in the high-spin state and the tetrahedral and the octahedral Fe^{3+}(d^5) ions are in the high-spin state with the spin directions antiparallel to each other.

In the present work, effects of Cr substitution for Co on the structural and magnetic properties of CoFe$_2$O$_4$ have been investigated. Spinel compounds Cr$_x$Co$_{1-x}$Fe$_2$O$_4$ were prepared as thin films by a sol-gel method and probed by x-ray diffraction (XRD), vibrating sample magnetometry (VSM), and conversion electron Mössbauer spectroscopy (CEMS) in comparison with CoFe$_2$O$_4$. The cationic preference among the tetrahedral and octahedral sites tends to affect the ionic arrangement and subsequent materials properties of the compound [2-4]. The present experimental data are used to predict the valence of TM ions in Cr$_x$Co$_{1-x}$Fe$_2$O$_4$ and their influence on the structural and magnetic properties of the compounds.

2. Experimental

Cr$_x$Co$_{1-x}$Fe$_2$O$_4$ films were deposited on Si(100) substrates with thickness of about 1 μm by a sol-gel method. The precursor solution for the present sol-gel deposition was prepared by dissolving Co(CH$_3$CO$_2$)$_2$·4H$_2$O, Fe(NO$_3$)$_3$·9H$_2$O, and Cr(NO$_3$)$_3$·9H$_2$O powders together in 2-methoxyethanol at 70°C. The substrate was spin-coated by the precursor solution at 4000 rpm for 20 sec and then heated at 260°C for 5 min after each deposition in order to remove the organic substance. This process was repeated until desired film thickness was attained. Post-annealing of the precursor films was performed in vacuum at 700°C for 4 hr to obtain the present Cr$_x$Co$_{1-x}$Fe$_2$O$_4$.

*Corresponding author: Tel: +82-2-450-3085,
Fax: +82-2-3436-5361, e-mail: kjkim@konkuk.ac.kr

The elemental composition of the films was determined by energy-dispersive x-ray spectroscopy. The crystalline structure of the samples was monitored by XRD measurements in θ-2θ geometry using Cu Kα radiation. The magnetic properties of the samples were examined with Lake-Shore 7300 vibrating sample magnetometer at room temperature. The site preference and ionic valence of Fe ions in the compound was explored by CEMS at room temperature with a ^{57}Co source in a rhodium matrix.

3. Results and Discussion

XRD spectra of a number of the present $Cr_xCo_{1-x}Fe_2O_4$ films are compared to that of $CoFe_2O_4$ in Fig. 1. It is seen that the lattice structure remains cubic up to $x = 0.5$ and the lattice constant changes little by the Cr substitution. The estimated lattice constant of the compound using the (440) peak position is 8.370, 8.374, 8.369, and 8.370 Å for $x = 0$, 0.1, 0.2, and 0.5, respectively. When the Cr content $x = 0.1$, a trace of Cr_2O_5 crystallites is detected as marked by * in Fig. 1. At higher x, such second phase is seen to disappear. That is, formation of $Cr_xCo_{1-x}Fe_2O_4$ alloy is more difficult at low Cr content.

It is known that Cr tends to take an ionic valence of +3 and to occupy the octahedral sites of the spinel structure [5]. When a Cr^{3+} ion substitutes an octahedral Co^{2+} site in $CoFe_2O_4$, charge unbalance between the two ionic species can be compensated through a reduction of a Fe^{3+} ion into Fe^{2+}. The ionic radii of octahedral Cr^{3+} and Co^{2+} ions are
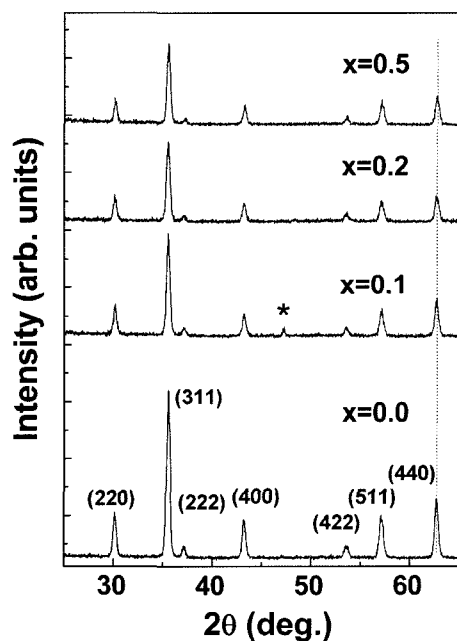
0.775 and 0.885 Å [6], respectively. Despite such difference the lattice constant of $Cr_xCo_{1-x}Fe_2O_4$ is seen to hardly decrease compared to that of $CoFe_2O_4$.

Figure 2 shows the result of CEMS measurements on the $CoFe_2O_4$ films at room temperature compared to that of $CoFe_2O_4$. Significant change in the CEMS spectrum is observed by Cr doping. The CEMS spectra of the $Cr_xCo_{1-x}Fe_2O_4$ films are well fitted by three six-line patterns representing octahedral Fe^{3+} (dotted line), tetrahedral Fe^{3+} (dashed line), and tetrahedral Fe^{2+} (dot-dashed line), while that of $CoFe_2O_4$ has only two, octahedral Fe^{3+} and tetrahedral Fe^{3+}. The isomer shifts for the octahedral Fe^{3+}, tetrahedral Fe^{3+}, and tetrahedral Fe^{2+} ions for $Cr_xCo_{1-x}Fe_2O_4$ ($x = 0.5$) are estimated to be 0.21, 0.42, and 0.63 mm/s, respectively. The trace of tetrahedral Fe^{2+} ions suggests that when a number of Cr^{3+} ions substitute the octahedral Co^{2+} sites, same number of tetrahedral Fe^{3+} ions reduce to Fe^{2+}, thus, satisfying the charge neutrality condition.

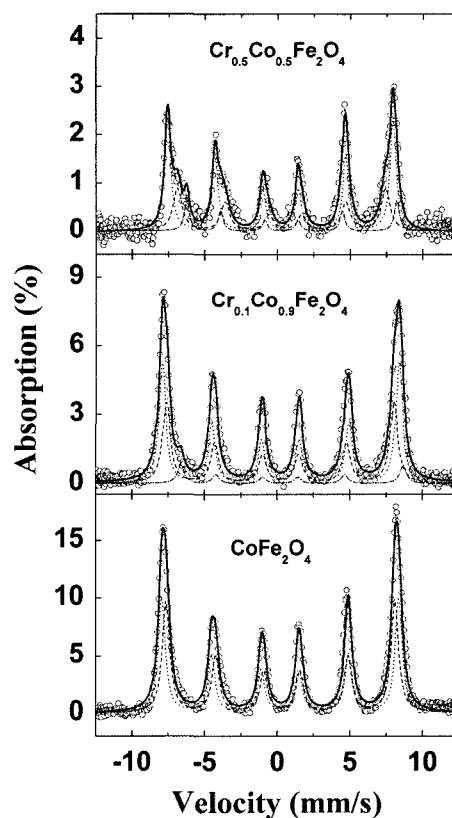The ionic radii of tetrahedral Fe^{3+} and Fe^{2+} ions are 0.63

Fig. 1. XRD spectra of $Cr_xCo_{1-x}Fe_2O_4$ thin films compared to $CoFe_2O_4$.

Fig. 2. CEMS spectra measured at room temperature for $Cr_xCo_{1-x}Fe_2O_4$ films compared to that of $CoFe_2O_4$ film. Dotted, dashed, and dot-dashed lines represent octahedral Fe^{3+}, tetrahedral Fe^{3+}, and tetrahedral Fe^{2+}, respectively. Open circles and solid line represent the experimental data and the fitting result, respectively.
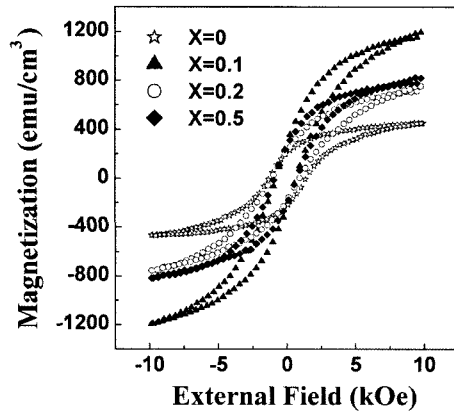
Fig. 3. VSM measurement data on $Cr_xCo_{1-x}Fe_2O_4$ films at room temperature.

and 0.77 Å [6], respectively. Therefore, the increase of the ionic radius of Fe ion by the reduction ($Fe^{3+} \rightarrow Fe^{2+}$) is likely to compensate the decrease through Cr^{3+} substitution of Co^{2+}, thus maintaining the lattice constant close to that of $CoFe_2O_4$ as shown in Fig. 1. For the case of Cr^{3+} substitution of octahedral Fe^{3+} ($Cr_xCoFe_{2-x}O_4$) [7], the lattice constant was found to decrease slightly, explainable in terms of slight difference between the ionic radius of octahedral Cr^{3+} and Fe^{3+}, 0.775 and 0.785 Å [6], respectively.

Figure 3 exhibits the magnetic hysteresis curves of the samples measured by VSM at room temperature. It is seen that the hysteresis loop for the x = 0.1 sample does not saturate up to the external field of 10 kOe. As the Cr composition increases, the saturation magnetization (M_S)
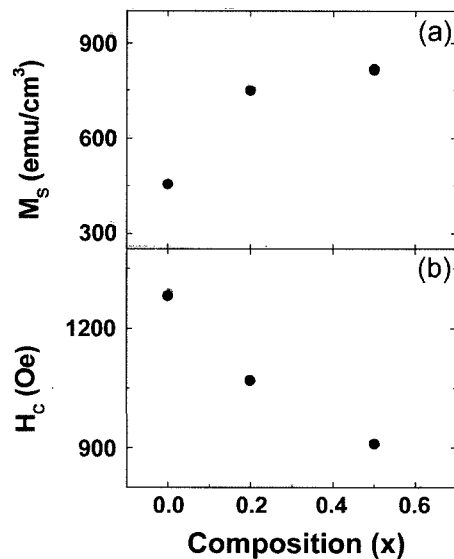

Fig. 4. Saturation magnetization (M_S) (a) and coercive field (H_C) (b) for $Cr_xCo_{1-x}Fe_2O_4$ films at room temperature.

is seen to gradually increase from that of $CoFe_2O_4$ as shown in Fig. 4(a). On the other hand, the coercivity (H_C) decreases with increasing Cr composition as shown in Fig. 4(b). The decrease of H_C is attributed to the decrease of the octahedral Co^{2+} density as x increases [8]. On the other hand, for the case of $Cr_xCoFe_{2-x}O_4$, the M_S was found to gradually decrease with increasing Cr substitution [7].

When $Cr^{3+}(d^3)$ ion replaces the octahedral $Co^{2+}(d^7)$ ion, the spin magnetic moments of them are the same, 3 μ_B. Also, the subsequent reduction of the tetrahedral $Fe^{3+}(d^5)$ to $Fe^{2+}(d^6)$ in $Cr_xCo_{1-x}Fe_2O_4$ is expected to cause an increase of x μ_B per formula unit. Thus, the increase of M_S of the $Cr_xCo_{1-x}Fe_2O_4$ films compared to that of $CoFe_2O_4$ can be partly explained in terms of the reduction $Fe^{3+} \rightarrow Fe^{2+}$ at the tetrahedral sites by the cost of Cr^{3+} substitution of the octahedral Co^{2+}. The decrease of M_S in $Cr_xCoFe_{2-x}O_4$ [7] can also be explained primarily by comparing the spin magnetic moment of Cr^{3+} (3 μ_B) and Fe^{3+} (5 μ_B).

4. Conclusions

Despite an imbalance in ionic valence between octahedral Co^{2+} and Cr^{3+}, $Cr_xCo_{1-x}Fe_2O_4$ thin films could be prepared by a sol-gel method. Formation of stable $Cr_xCo_{1-x}Fe_2O_4$ compounds is possible via a reduction of tetrahedral Fe^{3+} ion into Fe^{2+}. CEMS data revealed the existence of the tetrahedral Fe^{2+} ions. The lattice structure of the $Cr_xCo_{1-x}Fe_2O_4$ films remains cubic with negligible change of the lattice constant. The invariance of the lattice constant of $Cr_xCo_{1-x}Fe_2O_4$ can be explained in terms of the $Fe^{3+} \rightarrow Fe^{2+}$ reduction. The increase of M_S by the Cr substitution can also be partly explained by the reduction of Fe ion.

Acknowledgments

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