

## Effects of Cr Doping on Magnetic Properties of Inverse Spinel $\text{CoFe}_2\text{O}_4$ Thin Films

Kwang Joo Kim\*, Hee Kyung Kim, Young Ran Park, and Jae Yun Park<sup>1</sup>

*Department of Physics, Konkuk University, Seoul 143-701, Korea*

*<sup>1</sup>Department of Materials Science and Engineering, University of Incheon, Incheon 402-749, Korea*

(Received 8 December 2005)

Variation of magnetic properties through Cr substitution for Co in inverse-spinel  $\text{CoFe}_2\text{O}_4$  has been investigated by vibrating-sample magnetometry (VSM) and conversion electron Mössbauer spectroscopy (CEMS).  $\text{Cr}_x\text{Co}_{1-x}\text{Fe}_2\text{O}_4$  samples were prepared as thin films by a sol-gel method. The lattice constant of the  $\text{Cr}_x\text{Co}_{1-x}\text{Fe}_2\text{O}_4$  samples was found to remain unchanged, explainable in terms of a reduction of tetrahedral  $\text{Fe}^{3+}$  ion to  $\text{Fe}^{2+}$  due to substitution of  $\text{Cr}^{3+}$  ion into octahedral  $\text{Co}^{2+}$  site. The existence of the tetrahedral  $\text{Fe}^{2+}$  ions in  $\text{Cr}_x\text{Co}_{1-x}\text{Fe}_2\text{O}_4$  was confirmed by CEMS analysis. Room-temperature magnetic hysteresis curves for the  $\text{Cr}_x\text{Co}_{1-x}\text{Fe}_2\text{O}_4$  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  $\text{CoFe}_2\text{O}_4$ . The increase of  $M_S$  can be explained partly by the reduction of the tetrahedral  $\text{Fe}^{3+}$  ion to  $\text{Fe}^{2+}$ .

**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  $\text{AB}_2\text{O}_4$  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.

$\text{CoFe}_2\text{O}_4$  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  $\text{Co}^{2+}(\text{d}^7)$  ions in  $\text{CoFe}_2\text{O}_4$  are in the high-spin state and the tetrahedral and the octahedral  $\text{Fe}^{3+}(\text{d}^5)$  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  $\text{CoFe}_2\text{O}_4$  have been investigated. Spinel compounds  $\text{Cr}_x\text{Co}_{1-x}\text{Fe}_2\text{O}_4$  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  $\text{CoFe}_2\text{O}_4$ . 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  $\text{Cr}_x\text{Co}_{1-x}\text{Fe}_2\text{O}_4$  and their influence on the structural and magnetic properties of the compounds.

### 2. Experimental

$\text{Cr}_x\text{Co}_{1-x}\text{Fe}_2\text{O}_4$  films were deposited on Si(100) substrates with thickness of about 1  $\mu\text{m}$  by a sol-gel method. The precursor solution for the present sol-gel deposition was prepared by dissolving  $\text{Co}(\text{CH}_3\text{CO}_2)_2 \cdot 4\text{H}_2\text{O}$ ,  $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ , and  $\text{Cr}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$  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  $\text{Cr}_x\text{Co}_{1-x}\text{Fe}_2\text{O}_4$ .

\*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  $\theta$ - $2\theta$  geometry using Cu  $K\alpha$  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  $^{57}\text{Co}$  source in a rhodium matrix.

### 3. Results and Discussion

XRD spectra of a number of the present  $\text{Cr}_x\text{Co}_{1-x}\text{Fe}_2\text{O}_4$  films are compared to that of  $\text{CoFe}_2\text{O}_4$  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  $\text{Cr}_2\text{O}_3$  crystallites is detected as marked by \* in Fig. 1. At higher  $x,$  such second phase is seen to disappear. That is, formation of  $\text{Cr}_x\text{Co}_{1-x}\text{Fe}_2\text{O}_4$  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  $\text{Cr}^{3+}$  ion substitutes an octahedral  $\text{Co}^{2+}$  site in  $\text{CoFe}_2\text{O}_4,$  charge unbalance between the two ionic species can be compensated through a reduction of a  $\text{Fe}^{3+}$  ion into  $\text{Fe}^{2+}$ . The ionic radii of octahedral  $\text{Cr}^{3+}$  and  $\text{Co}^{2+}$  ions are

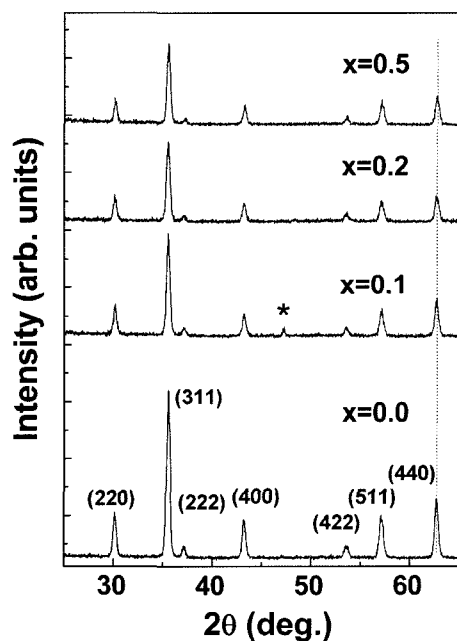


Fig. 1. XRD spectra of  $\text{Cr}_x\text{Co}_{1-x}\text{Fe}_2\text{O}_4$  thin films compared to  $\text{CoFe}_2\text{O}_4$ .

0.775 and 0.885 Å [6], respectively. Despite such difference the lattice constant of  $\text{Cr}_x\text{Co}_{1-x}\text{Fe}_2\text{O}_4$  is seen to hardly decrease compared to that of  $\text{CoFe}_2\text{O}_4$ .

Figure 2 shows the result of CEMS measurements on the  $\text{CoFe}_2\text{O}_4$  films at room temperature compared to that of  $\text{CoFe}_2\text{O}_4$ . Significant change in the CEMS spectrum is observed by Cr doping. The CEMS spectra of the  $\text{Cr}_x\text{Co}_{1-x}\text{Fe}_2\text{O}_4$  films are well fitted by three six-line patterns representing octahedral  $\text{Fe}^{3+}$  (dotted line), tetrahedral  $\text{Fe}^{3+}$  (dashed line), and tetrahedral  $\text{Fe}^{2+}$  (dot-dashed line), while that of  $\text{CoFe}_2\text{O}_4$  has only two, octahedral  $\text{Fe}^{3+}$  and tetrahedral  $\text{Fe}^{3+}$ . The isomer shifts for the octahedral  $\text{Fe}^{3+}$ , tetrahedral  $\text{Fe}^{3+}$ , and tetrahedral  $\text{Fe}^{2+}$  ions for  $\text{Cr}_x\text{Co}_{1-x}\text{Fe}_2\text{O}_4$  ( $x = 0.5$ ) are estimated to be 0.21, 0.42, and 0.63 mm/s, respectively. The trace of tetrahedral  $\text{Fe}^{2+}$  ions suggests that when a number of  $\text{Cr}^{3+}$  ions substitute the octahedral  $\text{Co}^{2+}$  sites, same number of tetrahedral  $\text{Fe}^{3+}$  ions reduce to  $\text{Fe}^{2+}$ , thus, satisfying the charge neutrality condition.

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

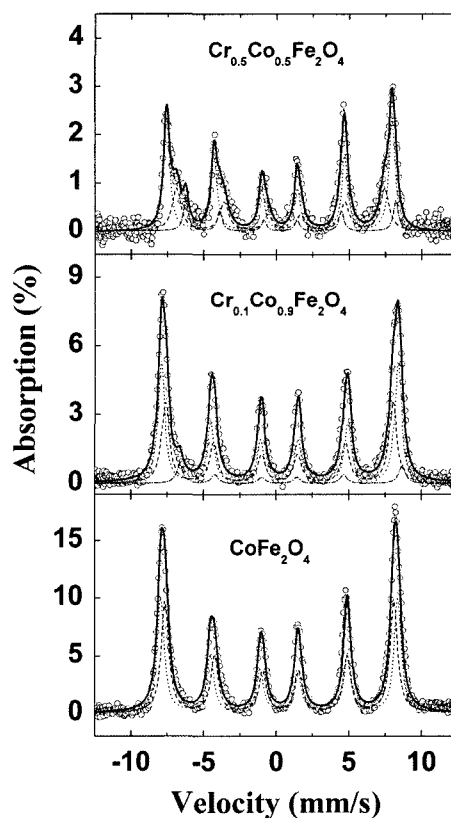


Fig. 2. CEMS spectra measured at room temperature for  $\text{Cr}_x\text{Co}_{1-x}\text{Fe}_2\text{O}_4$  films compared to that of  $\text{CoFe}_2\text{O}_4$  film. Dotted, dashed, and dot-dashed lines represent octahedral  $\text{Fe}^{3+}$ , tetrahedral  $\text{Fe}^{3+}$ , and tetrahedral  $\text{Fe}^{2+}$ , respectively. Open circles and solid line represent the experimental data and the fitting result, respectively.

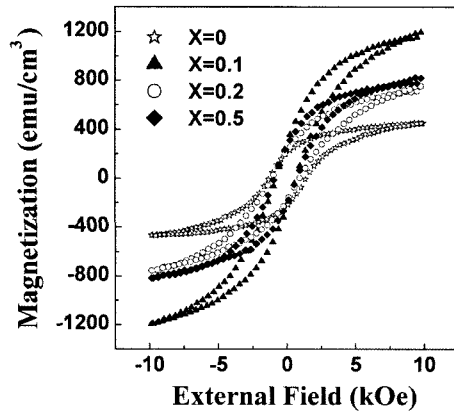


Fig. 3. VSM measurement data on  $\text{Cr}_x\text{Co}_{1-x}\text{Fe}_2\text{O}_4$  films at room temperature.

and  $0.77 \text{ \AA}$  [6], respectively. Therefore, the increase of the ionic radius of Fe ion by the reduction ( $\text{Fe}^{3+} \rightarrow \text{Fe}^{2+}$ ) is likely to compensate the decrease through  $\text{Cr}^{3+}$  substitution of  $\text{Co}^{2+}$ , thus maintaining the lattice constant close to that of  $\text{CoFe}_2\text{O}_4$  as shown in Fig. 1. For the case of  $\text{Cr}^{3+}$  substitution of octahedral  $\text{Fe}^{3+}$  ( $\text{Cr}_x\text{CoFe}_{2-x}\text{O}_4$ ) [7], the lattice constant was found to decrease slightly, explainable in terms of slight difference between the ionic radius of octahedral  $\text{Cr}^{3+}$  and  $\text{Fe}^{3+}$ ,  $0.775$  and  $0.785 \text{ \AA}$  [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  $10 \text{ kOe}$ . As the Cr composition increases, the saturation magnetization ( $M_s$ )

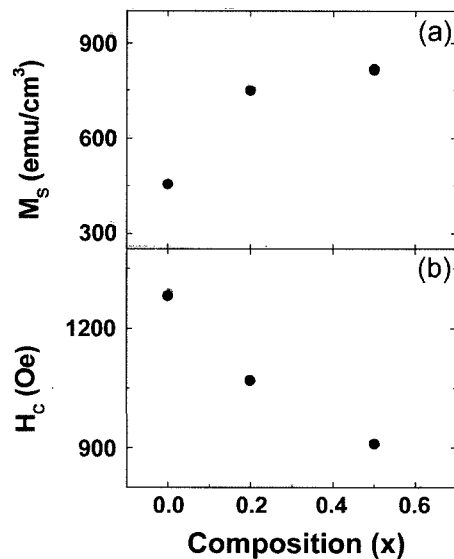


Fig. 4. Saturation magnetization ( $M_s$ ) (a) and coercive field ( $H_c$ ) (b) for  $\text{Cr}_x\text{Co}_{1-x}\text{Fe}_2\text{O}_4$  films at room temperature.

is seen to gradually increase from that of  $\text{CoFe}_2\text{O}_4$  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  $\text{Co}^{2+}$  density as  $x$  increases [8]. On the other hand, for the case of  $\text{Cr}_x\text{CoFe}_{2-x}\text{O}_4$ , the  $M_s$  was found to gradually decrease with increasing Cr substitution [7].

When  $\text{Cr}^{3+}(\text{d}^3)$  ion replaces the octahedral  $\text{Co}^{2+}(\text{d}^7)$  ion, the spin magnetic moments of them are the same,  $3 \mu_B$ . Also, the subsequent reduction of the tetrahedral  $\text{Fe}^{3+}(\text{d}^5)$  to  $\text{Fe}^{2+}(\text{d}^6)$  in  $\text{Cr}_x\text{Co}_{1-x}\text{Fe}_2\text{O}_4$  is expected to cause an increase of  $x \mu_B$  per formula unit. Thus, the increase of  $M_s$  of the  $\text{Cr}_x\text{Co}_{1-x}\text{Fe}_2\text{O}_4$  films compared to that of  $\text{CoFe}_2\text{O}_4$  can be partly explained in terms of the reduction  $\text{Fe}^{3+} \rightarrow \text{Fe}^{2+}$  at the tetrahedral sites by the cost of  $\text{Cr}^{3+}$  substitution of the octahedral  $\text{Co}^{2+}$ . The decrease of  $M_s$  in  $\text{Cr}_x\text{CoFe}_{2-x}\text{O}_4$  [7] can also be explained primarily by comparing the spin magnetic moment of  $\text{Cr}^{3+}$  ( $3 \mu_B$ ) and  $\text{Fe}^{3+}$  ( $5 \mu_B$ ).

#### 4. Conclusions

Despite an imbalance in ionic valence between octahedral  $\text{Co}^{2+}$  and  $\text{Cr}^{3+}$ ,  $\text{Cr}_x\text{Co}_{1-x}\text{Fe}_2\text{O}_4$  thin films could be prepared by a sol-gel method. Formation of stable  $\text{Cr}_x\text{Co}_{1-x}\text{Fe}_2\text{O}_4$  compounds is possible via a reduction of tetrahedral  $\text{Fe}^{3+}$  ion into  $\text{Fe}^{2+}$ . CEMS data revealed the existence of the tetrahedral  $\text{Fe}^{2+}$  ions. The lattice structure of the  $\text{Cr}_x\text{Co}_{1-x}\text{Fe}_2\text{O}_4$  films remains cubic with negligible change of the lattice constant. The invariance of the lattice constant of  $\text{Cr}_x\text{Co}_{1-x}\text{Fe}_2\text{O}_4$  can be explained in terms of the  $\text{Fe}^{3+} \rightarrow \text{Fe}^{2+}$  reduction. The increase of  $M_s$  by the Cr substitution can also be partly explained by the reduction of Fe ion.

#### Acknowledgments

This work was supported by the financial support of Konkuk University made in the program year of 2005.

#### References

- [1] L. Bouet, P. Tailhades, and A. Rousset, *J. Magn. Mater.* **153**, 389 (1996).
- [2] W. F. J. Fontijn, P. J. van der Zaag, M. A. C. Devillers, V. A. M. Brabers, and R. Metselaar, *Phys. Rev. B* **56**, 5432 (1997).
- [3] P. C. Kuo, Y. D. Yao, J. H. Huang, S. C. Shen, and J. H. Jou, *J. Appl. Phys.* **81**, 5621 (1997).
- [4] K. J. Kim, H. K. Kim, Y. R. Park, G. Y. Ahn, C. S. Kim, and J. Y. Park, *IEEE Trans. Mag.* **41**, 3478 (2005).

- [5] C. D. Spencer and D. Schroerer, *Phys. Rev. B* **9**, 3658 (1974).
- [6] R. D. Shannon, *Acta Crystallogr., Sect. A* **32**, 751 (1976).
- [7] K. P. Chae, H. J. Lee, J. G. Lee, S. H. Lee, and Y. B. Lee, *J. Kor. Magn. Soc.* **10**, 74 (2000).
- [8] B. Zhou, Y.-W. Zhang, C.-S. Liao, F.-X. Cheng, C.-H. Yan, L.-Y. Chen, and S.-Y. Wang, *Appl. Phys. Lett.* **79**, 1849 (2001).