

Structural, Magnetic, and Optical Studies on Normal to Inverse Spinel Phase Transition in $\text{Fe}_x\text{Co}_{3-x}\text{O}_4$ Thin Films

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(Received 22 February 2005, in final form 28 March 2005)

Phase transition from normal- to inverse-spinel structure has been observed for $\text{Fe}_x\text{Co}_{3-x}\text{O}_4$ thin films as the Fe composition (x) increases from 0 to 2. The samples were fabricated as thin films by sol-gel method on Si(100) substrates. X-ray diffraction measurements revealed a coexistence of two phases, normal and inverse spinel, for $0.76 \leq x \leq 0.93$. The normal-spinel phase is dominant for $x \leq 0.55$ while the inverse-spinel phase for $x \geq 1.22$. The cubic lattice constant of the inverse-spinel phase is larger than that of the normal-spinel phase. For both phases the lattice constant increases with increasing x . X-ray photoelectron spectroscopy measurements revealed that both Fe^{2+} and Fe^{3+} ions exist with similar strength in the $x=0.93$ sample. Conversion electron Mössbauer spectra measured on the same sample showed that Fe^{2+} ions prefer the octahedral Co^{3+} sites, indicating the formation of the inverse-spinel phase. Analysis on the measured optical absorption spectra for the samples by spectroscopic ellipsometry indicates the dominance of the normal spinel phase for low x in which Fe^{3+} ions tend to substitute the octahedral sites.

Key words : spinel, crystal structure, optical absorption, magnetic hysteresis, Mössbauer spectroscopy

I. Introduction

Spinel oxides containing transition-metal elements have been under a great deal of attention over decades due to their interesting structural, electronic, and magnetic properties, useful for various technological applications. Co_3O_4 is known as a normal-spinel compound exhibiting antiferromagnetism below 40 K [1]. It has been found that the octahedral Co^{3+} ions in the compound have a d^6 configuration of low-spin state with zero magnetic moment, while the tetrahedral Co^{2+} ions have a d^7 configuration of high-spin state [2].

In the present work, the evolution of structural, magnetic, and optical properties of spinel $\text{Fe}_x\text{Co}_{3-x}\text{O}_4$ thin films have been investigated as Fe is added from $x=0$ to 2. The experimental results on the samples are interpreted in terms of the change of electronic structure of the $\text{Fe}_x\text{Co}_{3-x}\text{O}_4$ alloy system through the substitution of tetrahedral and

octahedral sites by Fe^{3+} or Fe^{2+} ions. Phase transition from normal to inverse spinel structure was observed and the related mechanism is discussed.

II. Experimental

$\text{Fe}_x\text{Co}_{3-x}\text{O}_4$ films were deposited on Si(100) substrates with thickness of about $1 \mu\text{m}$ by a sol-gel method. The precursor solution was prepared by dissolving $\text{Co}(\text{CH}_3\text{CO}_2)_2 \cdot 4\text{H}_2\text{O}$ and $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ powders together in 2-methoxyethanol at 70°C .

The substrate was spin-coated by the precursor solution at 3,000 rpm for 20 sec and then heated at 260°C for 5 min after each deposition. This process was repeated for increasing the film thickness. Annealing of the precursor films at 800°C for 4 hr is found to improve the crystalline quality and surface flatness of the resultant $\text{Fe}_x\text{Co}_{3-x}\text{O}_4$ films. The Fe composition of the film was determined by energy-dispersive x-ray spectroscopy.

The crystalline structure of the samples was monitored

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by X-ray diffraction (XRD) measurements employing Cu K_{α} radiation. X-ray photoelectron spectroscopy (XPS) measurements were performed in order to estimate the amount of Fe^{2+} and Fe^{3+} ions in the films. Dielectric functions of the $Fe_xCo_{3-x}O_4$ films were measured by spectroscopic ellipsometry (SE) in the visible-ultraviolet range. Analysis of the optical transitions in the dielectric function can be useful for figuring out the distribution of the Fe ions among the tetrahedral and octahedral sites of the spinel compound. The site preference of the Fe^{2+} and Fe^{3+} ions was also explored by conversion electron Mössbauer spectroscopy (CEMS).

III. Results and Discussion

By XRD measurements the $Fe_xCo_{3-x}O_4$ films are found to consist of polycrystalline grains as in Co_3O_4 . Figure 1 exhibits the angular variation of the strongest XRD (311) peak of the $Fe_xCo_{3-x}O_4$ samples. It is seen that the spinel structure is maintained with gradual increase of the cubic lattice constant with x , likely to follow Vegard's law. Also, the XRD spectra clearly show that two phases coexist for $0.76 \leq x \leq 0.93$. The films are single-phased in the other ranges of x . These two phases are interpreted as due to the coexistence of crystallites with normal- and inverse-spinel structures in the film.

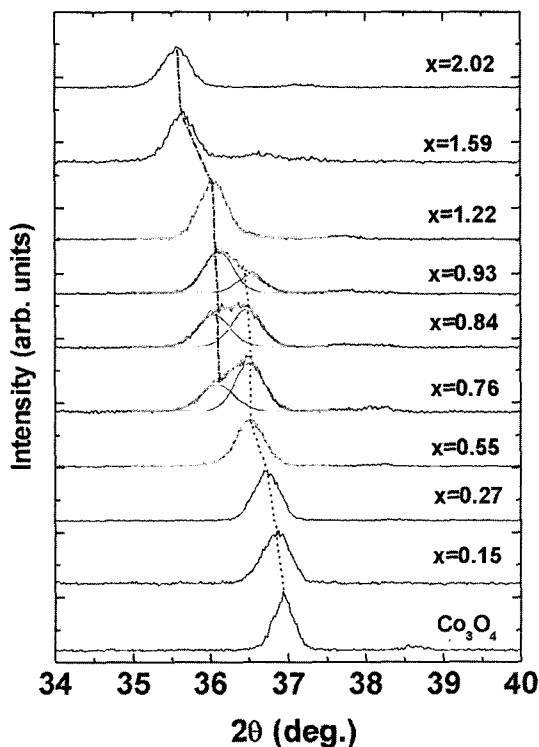


Fig. 1. Evolution of XRD (311) peak of $Fe_xCo_{3-x}O_4$ films.

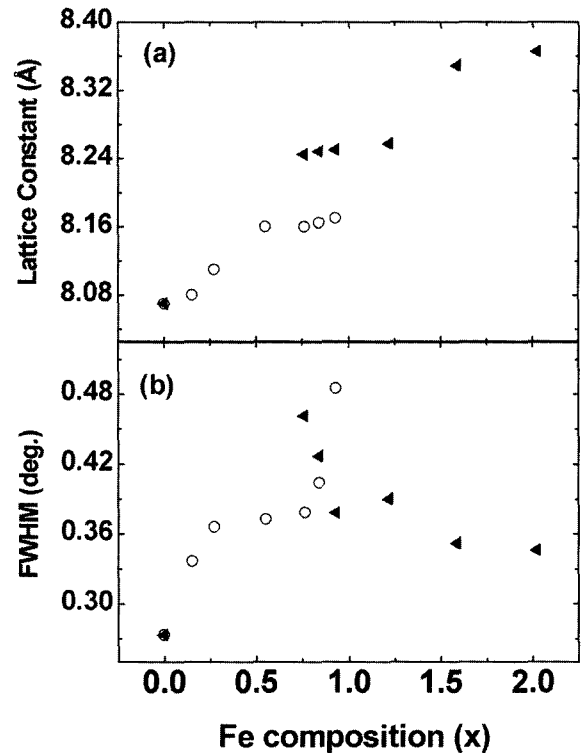


Fig. 2. Variation of the lattice constant (a) calculated using the (311) peak position and the full-width at half-maximum (b) of the peak.

Figure 2 exhibits the variation of the lattice constant (a) calculated using the (311) peak position and the full-width at half-maximum (b) of the peak. For low x (≤ 0.55), the gradual increase of the lattice constant with x was observed and can be interpreted in terms of the substitution of the octahedral Co^{3+} sites by Fe^{3+} ions. The ionic radius of the octahedral Co^{3+} ion in its low-spin state is estimated to be 0.665 \AA [3]. When Fe^{3+} ion substitutes the octahedral site, its ionic radius is estimated to be 0.785 \AA in its high-spin state [3]. Thus, the initial increase of the lattice constant of the present $Fe_xCo_{3-x}O_4$ samples can be interpreted in terms of the substitution of the octahedral Co^{3+} sites by Fe^{3+} ions, maintaining the normal-spinel structure of Co_3O_4 for low x .

On the other hand, the ionic radius of high-spin Fe^{2+} at the octahedral site is 0.92 \AA , larger than that of the high-spin Fe^{3+} . Thus, the phase with the larger lattice constant for $x \geq 0.76$ is attributed to the Fe^{2+} substitution for Co^{3+} , i.e., the inverse-spinel formation. Also, the lattice constants of both the normal- and the inverse-spinel phase change little with x in the $0.76 \leq x \leq 0.93$ region compared to the other regions. The inverse-spinel phase is seen to be dominant for $x \geq 1.22$. It is also noted that a large increase of lattice constant was observed between $x=1.22$ and

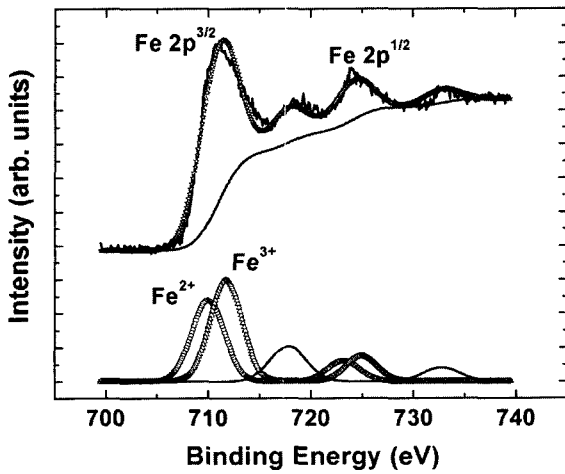


Fig. 3. Result of XPS measurement and line-shape analysis on the Fe 2p core-level spectrum of $\text{Fe}_x\text{Co}_{3-x}\text{O}_4$ ($x=0.93$) film.

1.59. As shown in Fig. 3, curve-fitting analysis on XPS data of $x=0.93$ sample indicates the existence of both Fe^{2+} and Fe^{3+} ions. This result is consistent with the XRD spectrum of the $x=0.93$ sample. The 2p-electron binding-energy difference between the Fe^{2+} and Fe^{3+} ions is estimated to be 1.7 eV.

Figure 4 shows the result of CEMS measurement on the $x=0.93$ film taken at room temperature. The least-squares fitting analysis on the spectrum indicates that Fe^{3+} ions occupy both the tetrahedral and the octahedral sites while Fe^{2+} ions occupy the octahedral sites only. It is consistent with the results of XRD and XPS analyses. CEMS analysis also indicates that the ratio $\text{Fe}^{2+}/\text{Fe}^{3+}$ of octahedral site preference is 0.16 while Fe^{3+} ions occupy both the octahedral and the tetrahedral sites equally.

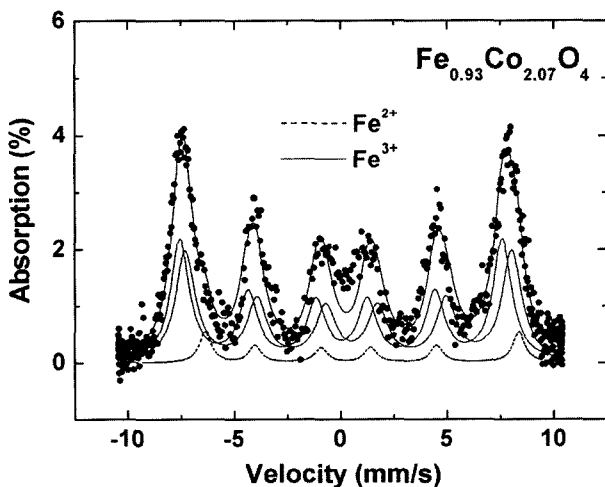


Fig. 4. CEMS spectra of $\text{Fe}_x\text{Co}_{3-x}\text{O}_4$ ($x=0.93$) film measured at room temperature.

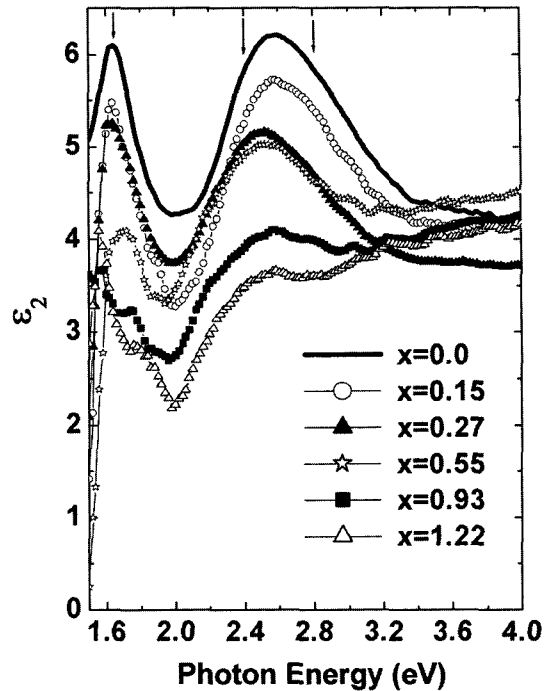


Fig. 5. Imaginary part of measured dielectric functions of $\text{Fe}_x\text{Co}_{3-x}\text{O}_4$ films by SE.

Figure 5 exhibits the imaginary parts of the dielectric functions of the $\text{Fe}_x\text{Co}_{3-x}\text{O}_4$ samples measured by SE at room temperature. The observed strong absorption structures of Co_3O_4 have been interpreted in terms of charge-transfer (CT) transitions between different ionic sites at about 1.65, 2.4, and 2.8 eV as marked by arrows in Fig. 5. As the Fe composition increases, the strength of the 1.65- and 2.8-eV transitions is seen to decrease faster than that of the 2.4-eV transition.

The 1.65-eV absorption structure has been assigned to a d-d CT transition from the $d(t_{2g})$ states of the octahedral Co^{3+} ion to the $d(t_2)$ states of the tetrahedral Co^{2+} ion, $t_{2g}(\text{Co}^{3+}) \rightarrow t_2(\text{Co}^{2+})$, constituting the Mott-Hubbard gap of Co_3O_4 [4]. The absorption structures at the higher energies are interpreted as involving the $p(\text{O}^{2-})$ states located below the $t_{2g}(\text{Co}^{3+})$ states of Co_3O_4 . Thus, the 2.4- and 2.8-eV absorptions are assigned to p-d CT transitions, $p(\text{O}^{2-}) \rightarrow t_2(\text{Co}^{2+})$ and $p(\text{O}^{2-}) \rightarrow e_g(\text{Co}^{3+})$, respectively [5].

Both the 1.65- and 2.8-eV transitions involve the d states of the octahedral Co^{3+} ion. Thus, the reduction of the 1.65- and 2.8-eV transition strength is attributed to the reduction of the Co^{3+} density through the occupation of the octahedral sites by Fe^{3+} ions. The ionic valence of the substituting Fe ions needs to be +3 for ensuring the charge neutrality of the alloy. Thus, the $\text{Fe}_x\text{Co}_{3-x}\text{O}_4$ alloys maintain the normal-spinel structure for low x . This result is consistent with the XRD data.

For $x=0.93$ and above, the 2.4-eV transition also suffers from a reduction of its strength, indicating that the tetrahedral (Co^{2+}) sites are occupied by Fe ions. In the inverse-spinel phase, the tetrahedral sites are expected to be occupied by Fe^{3+} ions and the same amount of Fe^{2+} ions are expected to occupy the octahedral (Co^{3+}) sites in order to maintain the charge neutrality.

IV. Conclusion

As the Fe composition increases from 0 to 2 in $\text{Fe}_x\text{Co}_{3-x}\text{O}_4$, the crystal structure of the alloy system goes through a phase transition from normal to inverse spinel structure. The two phases are found to coexist in the $0.76 \leq x \leq 0.93$ range by XRD. The normal-spinel phase is dominant for $x \leq 0.55$ while the inverse-spinel phase for $x \geq 1.22$. Result of optical absorption measurements supports the dominance of the normal-spinel phase at low x . XPS measurements indicate the coexistence of Fe^{3+} and Fe^{2+} ions for $x=0.93$. Conversion electron Mössbauer spectra for the same

sample show that Fe^{3+} ions occupy both the tetrahedral and the octahedral sites while Fe^{2+} ions occupy only the octahedral sites. The remarkable change of the lattice constant for $x \geq 0.76$ is attributed to the site preference of the Fe^{2+} and Fe^{3+} ions.

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