Journal of Materials Synthesis and Processing, Vol. 9, No. 3, May 2001 (© 2001)

From Magnetite to Cobalt Ferrite

Monica Sorescu,[1,5] A. Grabias,[1,2] D. Tarabasanu-Mihaila,[3] and L. Diamandescu[3,4]

We synthesized $Fe_{3-x}Co_xO_4$ ($x = 0-1$) using the hydrothermal method in order to demonstrate the compositional modulation of magnetite to cobalt ferrite. Our Mössbauer spectroscopy results provided direct evidence for the presence of the Co substitution in the B sublattice, which was found to be accompanied by a systematic increase of the hyperfine magnetic field at these sites. The mechanism we propose relies on the substitution of Fe^{2+} by Co^{2+} in the B sublattice and is supported by the observed dependence of the populations of the (A) and (B) sites on content x of cobalt substitution. The X-ray diffraction (XRD) determinations demonstrated a linear increase in the lattice parameter when going from magnetite to cobalt ferrite. For the particular value $x = 0.1$, we report that the two sublattices of magnetite become equally populated with Fe. For this particular value of the cobalt content, we obtained a thin film sample by laser ablation deposition and characterized its properties by XRD and conversion electron Mössbauer spectroscopy (CEMS).

KEY WORDS: Magnetite; cobalt ferrite; chemical synthesis; Mössbauer spectroscopy.

1. INTRODUCTION

Magnetite (Fe_3O_4) is an oxide with the inverse spinel structure, which has one Fe^{3+} ion on the tetrahedral (A) site and two Fe ions, with a total valence of 5+, on the octahedral (B) site [1, 2]. Although the syntheses and transformations of various iron oxides and oxyhydroxides, such as hematite, maghemite, and goethite have been studied in detail [3–11], not much is known about the formation of synthetic magnetites and the incorporation of impurity elements into them.

In the present paper, we report the preparation of cobalt-doped magnetite by the hydrothermal method, in order to investigate the effect of cobalt substitution on the hyperfine magnetic fields and site populations in the magnetite structure. The lattice constants were determined for magnetite and cobalt ferrite, as well as all intermediates. Bulk versus thin film magnetic properties were studied on a thin film of cobalt-doped magnetite obtained by laser ablation deposition.

2. EXPERIMENTAL

$Fe_{3-x}Co_xO_4$ ($x = 0 - 1$) was prepared using the method of coprecipitation of the iron and cobalt hydroxides from sulfate solutions, mediated by sodium hydroxide in conditions controlled by concentration and pH (7.5). The reactive mixture was treated hydrothermally at 400°C for 30 min. Substituent concentrations in the resulting samples were determined using atomic absorption spectroscopy.

Room-temperature transmission Mössbauer spectra were recorded using a constant acceleration spectrometer and a ^{57}Co (Rh) source. The spectra were analyzed considering two sextets, corresponding to the tetrahedral (A) and octahedral (B) magnetic sublattices present in the samples. Least-squares fitting was performed using the NORMOS-SITE program and all variables of the fit were free. All Mössbauer spectra were fit with exactly the same set of initial parameters and the optimization results were clearly superior to those obtained with other fitting models: one sextet plus one or two field distributions.

[1] Duquesne University, Physics Department, Bayer Center for Natural and Environmental Sciences, Pittsburgh, Pennsylvania 15282-0321.
[2] Institute of Electronic Materials Technology, Wolczynska 133, 01-919 Warszawa, Poland.
[3] Institute of Atomic Physics, R-76900 Bucharest-Magurele, Romania.
[4] Universita "Ca Foscari," Dipartimento Di Chimica Fisica, Calle Larga S. Marta 2137, 30123 Venezia, Italy.
[5] To whom all correspondence should be addressed. e-mail: sorescu@duq.edu

1064-7562/01/0500-0119/0 © 2001 Plenum Publishing Corporation

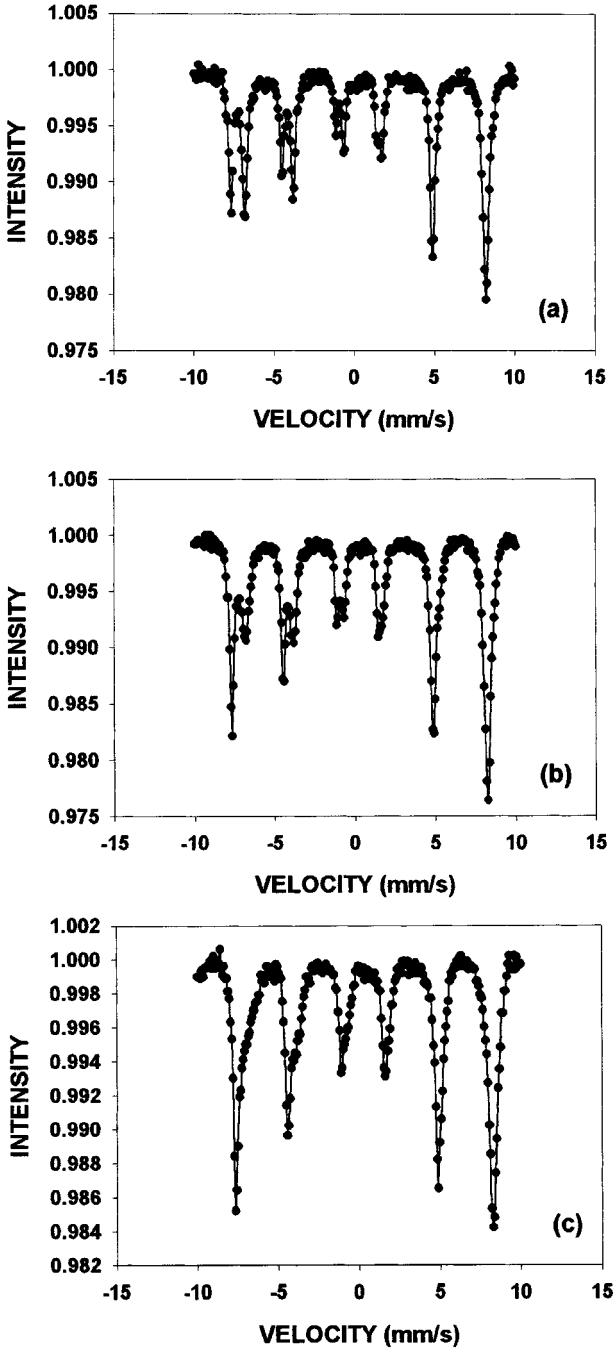

Fig. 1. Room-temperature transmission Mössbauer spectra of $Fe_{3-x}Co_xO_4$: (a) $x = 0$; (b) $x = 0.5$; (c) $x = 1$.

For $x = 0.1$, a thin film of cobalt-doped magnetite was obtained on sapphire substrate using laser ablation deposition of a target resulting from pressed and sintered powder. Our Lambda Physik COMPEX pulsed excimer laser with $\lambda = 248$ nm, pulse width of 8 ns and repetition rate of 10 Hz was used for ablation. The thin film was characterized using CEMS with a flowing He-CH_4 electron counter. The backscattered electrons into 2π solid angle were recorded, so that behavior of surface layers ~100 nm thick could be detailed.

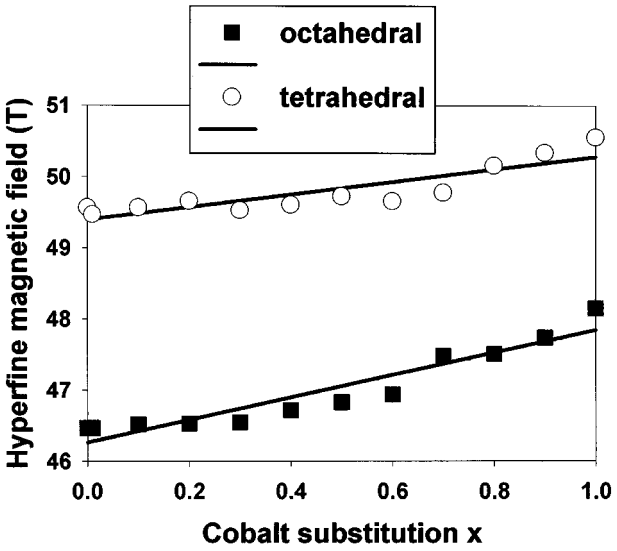

Fig. 2. Dependence of the hyperfine magnetic field of the tetrahedral and octahedral sites of magnetite on the content x of cobalt substitution. The errors are considered within the size of the data markers.

Both powder and thin film samples were characterized by XRD. XRD patterns were obtained with a Rigaku powder diffractometer using CuK_α radiation ($\lambda = 1.5406$) in the range 15–100° Bragg angle (2θ). The lattice constants of all intermediates between magnetite and cobalt ferrite were determined with four exact decimals.

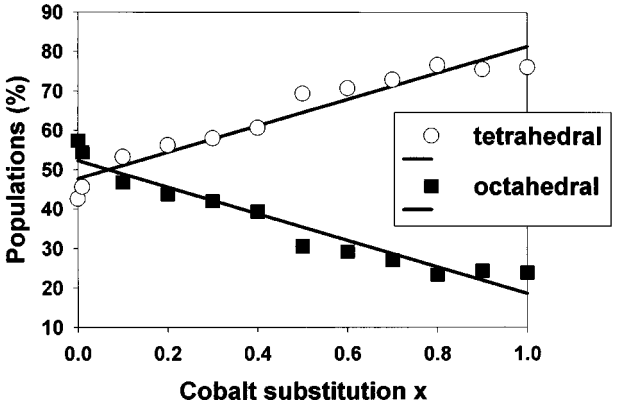

Fig. 3. Dependence of the populations of the tetrahedral and octahedral sites on the amount x of cobalt substitution. The errors are considered within the size of the data markers.

3. RESULTS AND DISCUSSION

Selected transmission Mössbauer spectra are displayed in Fig. 1a–c, corresponding to a cobalt content $x = 0$, 0.5, and 1, respectively. It can be seen that increasing the amount of x of cobalt substitution dramatically affects the B sublattice of magnetite, changing the shape of all transmission Mössbauer spectra. This demonstrates that Co ions exhibit a clear preference for the octahedral sites.

In order to quantify this effect, we extracted from these spectra the values of the hyperfine magnetic fields of the tetrahedral and octahedral sites and plotted them as functions of the amount x of cobalt substitution. Thus, it can be inferred from Fig. 2 that the hyperfine magnetic

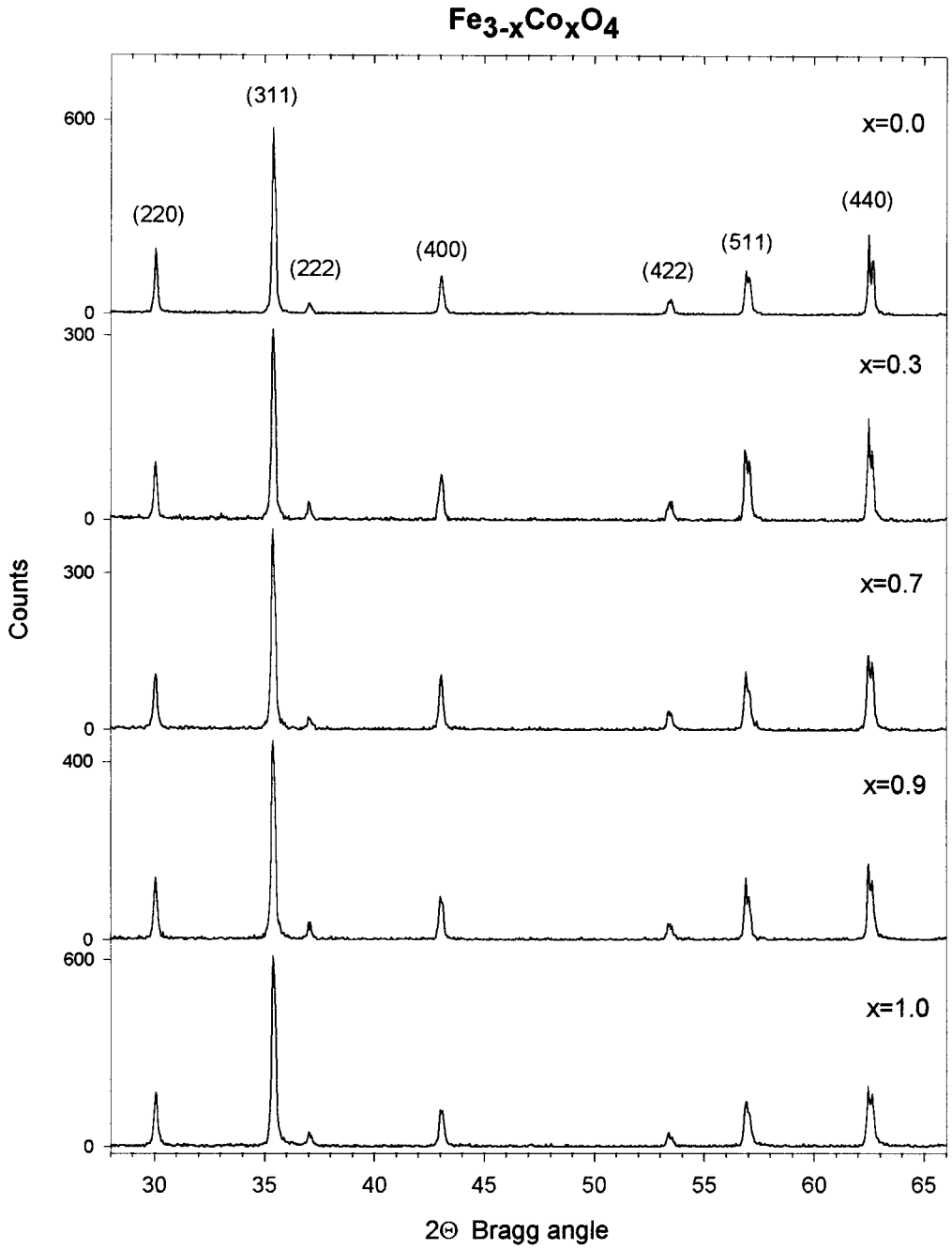

Fig. 4. XRD patterns of cobalt-doped magnetites, from magnetite to cobalt ferrite.

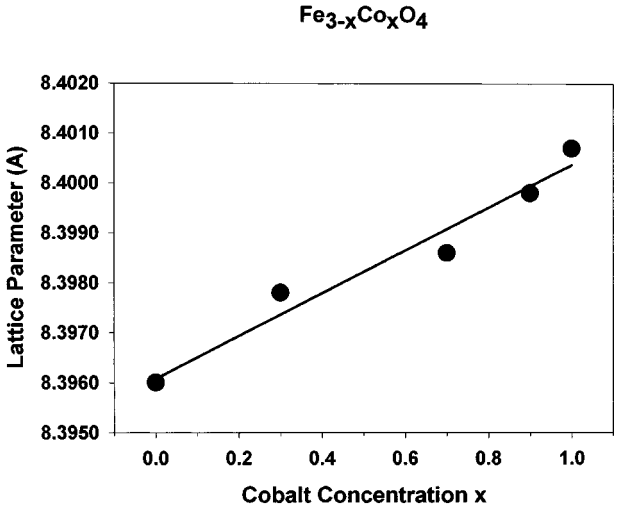

Fig. 5. Dependence of the lattice constants of the cobalt-doped magnetites on the amount of cobalt concentration.

field of the tetrahedral sites is essentially not altered by the cobalt ions. This result is consistent with the fact that the cobalt impurities are not present at tetrahedral sites. In contradistinction to this, the hyperfine magnetic field of the octahedral sublattice increases steadily as a function of cobalt concentration. This result demonstrates that the presence of cobalt at octahedral iron sites increases the values of the hyperfine magnetic fields at these positions. This behavior is similar to that observed in FeCoBSi metallic glass, which was found to exhibit an increased value of the hyperfine magnetic field at the iron sites, induced by the presence of cobalt atoms [12].

The mechanism by which Co^{2+} substitutes for Fe^{2+} in the B sublattice is supported by the concentration dependence of the populations of the tetrahedral and octahedral sites, derived from the areal ratios of the two sublattices in the Mössbauer spectra. In connection with Fig. 2, Fig. 3 provides direct evidence of this phenomenon: the population of the octahedral sites linearly decreases with increasing cobalt content, due to cobalt substituting iron. The population of the tetrahedral sites increases correspondingly.

It may be noted in Fig. 3 that there is a certain value of the cobalt concentration ($x = 0.1$) for which the tetrahedral and the octahedral sublattices become equally populated. However, this result is influenced both by the number of cobalt ions and by the number of specific sites available in each sublattice.

Consequently, the main effects of the cobalt substitutions on the magnetite structure evidenced directly by our Mössbauer study are a linear increase in the hyperfine magnetic field and linear decrease in the population of the octahedral sublattice as functions of substituent concentration.

Figure 4 shows the XRD patterns of magnetite, several cobalt-doped magnetites, and cobalt ferrite. They are all similar and the last ten peaks at the highest Bragg angles were used to determine the lattice constants. An accuracy of four exact decimals was obtained. Figure 5 plots the lattice constants as function of the cobalt amount x and demonstrates that the lattice parameters increase linearly with increasing the cobalt concentration.

For the exact amount of cobalt substituent $x = 0.1$, an ablation target was prepared from the thermally sintered and mechanically pressed powder. This target was used to obtained a thin film of cobalt-doped magnetite by laser ablation deposition. Figure 6 shows the XRD pattern of the film on sapphire substrate and Figure 7 displays the CEMS spectrum of this film. This spectrum could also be resolved by considering two sextets, corresponding to the tetrahedral (A) and octahedral (B) magnetic sublattices characteristic to the magnetite structure. The refined values of the hyperfine magnetic fields were 47.8 and 44.1 *T*, respectively. The populations of the (A) and (B) magnetic sublattices were 48.6 and 51.4%, respectively. If we now look at the values plotted in Fig. 3 for the dependence of the populations on the cobalt content, we see that a value of $x = 0.1$ corresponds best. On the one hand, this result demonstrates that a congruent transfer of composition and stoichiometry exists between target and substrate material and, on the other hand, it confirms the accuracy of the populations plot.

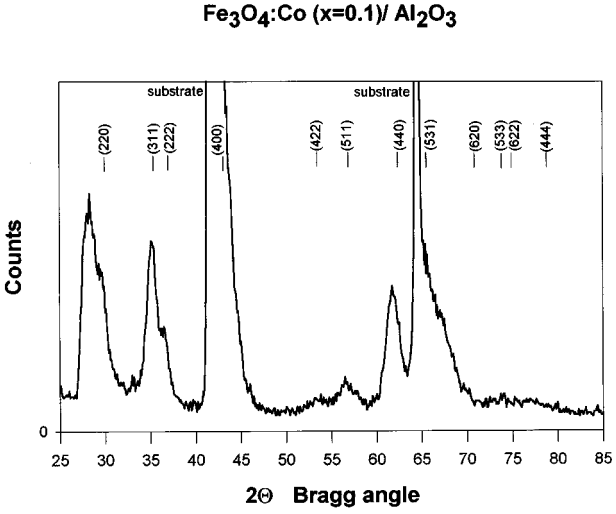

Fig. 6. XRD pattern of a cobalt-doped magnetite thin film ($x = 0.1$) deposited by laser ablation on a sapphire substrate. The markers show the peak positions for pure magnetite.

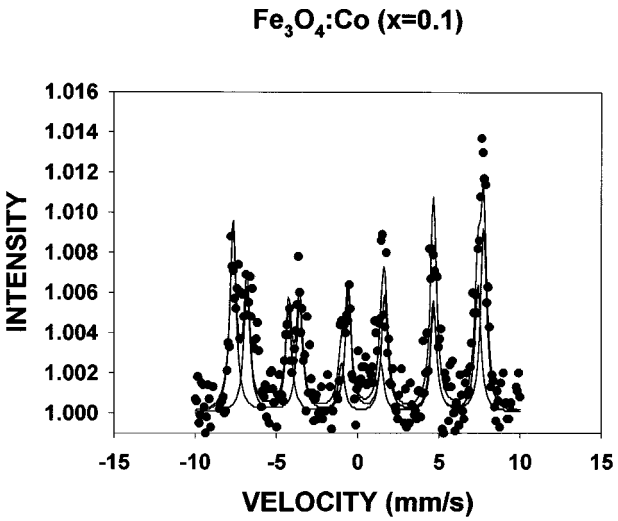

Fig. 7. CEMS spectrum of the cobalt-doped magnetite thin film ($x = 0.1$).

4. CONCLUSIONS

Samples with modulated composition between magnetite and cobalt ferrite, $Fe_{3-x}Co_xO_4$ ($x = 0 - 1$) were prepared by the hydrothermal method. The dependences of the hyperfine fields and populations on the content x of cobalt substitution were derived from Mössbauer spectra. A linear increase in the hyperfine magnetic field and a linear decrease in the population of the octahedral sublattice as functions of substituent concentration were evidenced. A linear increase in the lattice constant from $x = 0$ to $x = 1$ was demonstrated by XRD. For $x = 0.1$ the two sublattices have equal Fe populations. The thin film obtained under these conditions by laser ablation deposition has site populations in agreement with the plot previously derived.

ACKNOWLEDGMENT

This work was supported by the National Science Foundation under Grant DMR-9800753.

REFERENCES

1. M. Sorescu, *J. Mater. Sci. Lett.* **17,** 1059 (1998).
2. A. Okamura, S. Nakamura, M. Tanaka, and K. Siratori, *J. Phys. Soc. Jpn.* **64,** 3484 (1995).
3. M. Sorescu, D. Tarabasanu-Mihaila, and L. Diamandescu, *Appl. Phys. Lett.* **72,** 2047 (1998).
4. P. S. Sidhu, R. J. Gilkes, and A. M. Posner, *J. Inorg. Nucl. Chem.* **40,** 429 (1978).
5. H. N. Ok, L. S. Pan, and B. J. Evans, *Phys. Rev. B* **17,** 85 (1978).
6. U. Schwertmann and E. Murad, *Clays Clay Miner.* **38,** 196 (1990).
7. R. M. Persoons, E. DeGrave, and R. E. Vandenberghe, *Hyperfine Interact.* **54,** 655 (1990).
8. P. H. Hsu, *Soil Sci.* **23,** 17 (1972).
9. P. A. Dickof, P. J. Schurer, and A. H. Morrish, *Phys. Rev. B* **22,** 115 (1980).
10. S. Morup, M. B. Madsen, J. Franck, J. Villadsen, and C. J. W. Koch, *J. Magn. Magn. Mater.* **40,** 163 (1983).
11. A. K. Giri, C. DeJulian, and J. M. Gonzales, *J. Appl. Phys.* **76,** 6573 (1994).
12. M. Sorescu and E. T. Knobbe, *Phys. Rev. B* **52,** 16086 (1995).