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Structural and magnetic properties of Ti^{4+}/Co^{2+} co-substituted cobalt ferrite

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Abstract

The variations in the structural magnetic properties of cobalt ferrite due to $\text{Ti}^{4+}/\text{Co}^{2+}$ co-substitution for 2Fe^{3+} are presented. The non-linear relation in the variation of the lattice parameter agrees with a previous study on cation distribution, which showed that the rate of substitution of cations into the A-sites and B-sites varies with Ti-concentration. Such variation in the rate of substitution into the cation sites was also observed in the magnetization, coercive field, and susceptibility data. The coercive field and differential susceptibility are inversely related. Although the coercive field of the Ti-substituted cobalt ferrite generally decreased compared to the un-substituted cobalt ferrite, magnetic susceptibility was higher at higher Ti-concentrations.

Keywords

Ames Laboratory, Coercive force, Ferrites, Cobalt, Carbon dioxide, Magnetic susceptibilities

Disciplines

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Comments

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Structural and magnetic properties of Ti⁴⁺/Co²⁺ co-substituted cobalt ferrite

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Structural and magnetic properties of $\text{Ti}^{4+}/\text{Co}^{2+}$ co-substituted cobalt ferrite

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The variations in the structural magnetic properties of cobalt ferrite due to $\text{Ti}^{4+}/\text{Co}^{2+}$ co-substitution for 2Fe^{3+} are presented. The non-linear relation in the variation of the lattice parameter agrees with a previous study on cation distribution, which showed that the rate of substitution of cations into the A-sites and B-sites varies with Ti-concentration. Such variation in the rate of substitution into the cation sites was also observed in the magnetization, coercive field, and susceptibility data. The coercive field and differential susceptibility are inversely related. Although the coercive field of the Ti-substituted cobalt ferrite generally decreased compared to the un-substituted cobalt ferrite, magnetic susceptibility was higher at higher Ti-concentrations.

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I. INTRODUCTION

Oxides such as spinel ferrites are chemically and thermally stable and, as a result, are suitable for application in harsh environments. Among the spinel ferrites, cobalt ferrite is further distinguished by its high magnetostriction and magnetocrystalline anisotropy making it a candidate material for magnetomechanical device development. Cobalt ferrite is also more suitable for high frequency magnetostrictive applications compared to other magnetostrictive materials based on intermetallic elements. Cation substitution into cobalt ferrite provides the possibility to expand the applications of the material. Various cation substitutions have been investigated by different researchers. Cation substitution provides multiple degrees of freedom to adjust the magnetic properties of materials based on cobalt ferrite to suit an application of interest. Such degrees of freedom include choice of cation site to substitute into, choice of substitution for either Fe or Co or even both, and the ability to control the site occupation of the substituted cation by heat treatment. Consequently, it is possible to systematically adjust the properties of the material for an application. Copper, zinc, chromium, and nickel have been substituted for cobalt and investigated for biomedical and antibacterial applications.^{1,2}

The present study investigates the role of co-substitution of Ti^{4+} and Co^{2+} for 2Fe^{3+} in tailoring the structural and magnetic properties of cobalt ferrite. Samples studied were of the composition $\text{Co}_{1+x}\text{Ti}_x\text{Fe}_{2-2x}\text{O}_4$ ($x = 0, 0.05, 0.1, 0.2, 0.4, \text{ and } 0.5$).

II. EXPERIMENTAL DETAILS

Fe_3O_4 , Co_3O_4 , and TiO_2 were mixed in appropriate ratios, calcined twice at 1000°C to ensure complete solid state reaction and sintered at 1350°C . Calcinations and sintering were done in air for 24 h. Backscattered electron

images were obtained using a scanning electron microscope (SEM) equipped with an x-ray analyzer for energy dispersive x-ray spectroscopy (EDX) to study the microstructure and compositions. X-ray diffractometry was used to study the crystal structure of the samples. Magnetic properties were measured using a vibrating sample magnetometer (VSM) with applied magnetic field up to $\sim 2390\text{ kA/m}$ ($\mu_0 H = 3\text{ T}$). Maximum differential susceptibility ($\chi' = \frac{dM}{dH}$) was obtained by differentiating the initial magnetization data measured at magnetic field increment of $\sim 4\text{ kA/m}$.

III. RESULTS AND DISCUSSION

The x-ray diffraction patterns of the samples (Fig. 1) show that they are single spinel phase with no observable second phase. In a previous study, a secondary TiFe_2O_5 phase was formed at all concentrations of Ti ($x = 0-0.3$).³ It may at first seem that the inability to make single phase samples in that study could be related to the fact that tetravalent Ti^{4+} was substituted for trivalent Fe^{3+} . However, the observation in that study that the sample $x = 0$ also showed the TiFe_2O_5 phase may suggest that the impurity phase was part of the starting oxide materials.

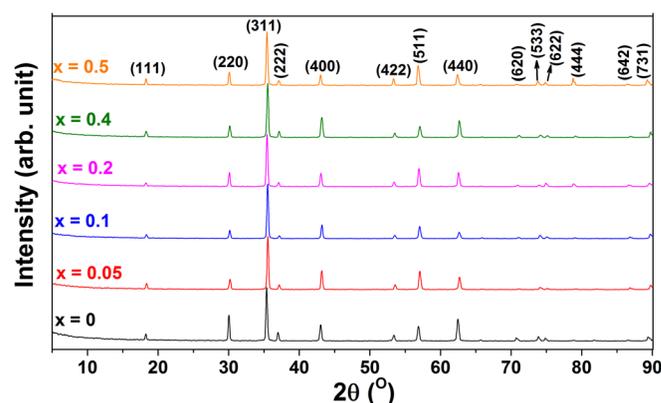


FIG. 1. X-ray diffraction patterns of the $\text{Ti}^{4+}/\text{Co}^{2+}$ co-substituted cobalt ferrite. All peaks are consistent with spinel crystal structure.

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TABLE I. Targeted compositions and composition obtained from EDX analyses of the samples.

Target composition ($x = \text{Ti}$)	EDX composition			Lattice parameter (\AA)
	Fe	Co	Ti	
0	1.99	1.01	0	8.40
0.05	1.89	1.05	0.06	8.37
0.10	1.8	1.09	0.11	8.38
0.2	1.60	1.20	0.20	8.39
0.4	1.22	1.38	0.4	8.38
0.5	1.01	1.50	0.49	8.40

In the present study, high purity oxides were used. In addition, to take care of the valance differences, Co^{2+} and Ti^{4+} were co-substituted for 2Fe^{3+} . The compositions obtained by EDX are very close to the targeted compositions as shown in Table I. The variation in the lattice parameter also shown in Table I deviates from Vegard's law, which may indicate that Ti^{4+} substitutes at varying rates into the cation sites as its concentration increases. As could be seen in the backscattered electron micrographs in Fig. 2, all the samples had uniform contrast which is indicative of single phase materials.

Fig. 3 shows that $\text{Ti}^{4+}/\text{Co}^{2+}$ co-substitution for 2Fe^{3+} resulted in a decrease in magnetization. The inset shows that the saturation magnetization decreased as well. The observed decrease in saturation magnetization is likely due to the site preference of the substituted cations with respect to Fe^{3+} . In ferrites containing either Ti^{4+} or Co^{2+} , both cations are known to have stronger preferences for the octahedral sites than Fe^{3+} which is distributed equally between the tetrahedral (A-sites) and octahedral sites (B-sites).^{4,5} The strong negative superexchange interaction between both cation sites results in the sites being antiferromagnetically coupled such that the net magnetic moment (m) is given by $m = \sum m_{\text{B-sites}} - \sum m_{\text{A-sites}}$. While Ti^{4+} is non-magnetic, the magnetic moment of Co^{2+} ($3 \mu_{\text{B}}$) is less than that of Fe^{3+} ($5 \mu_{\text{B}}$). Therefore, co-substitution of Ti^{4+} and Co^{2+} into the B-sites decreased

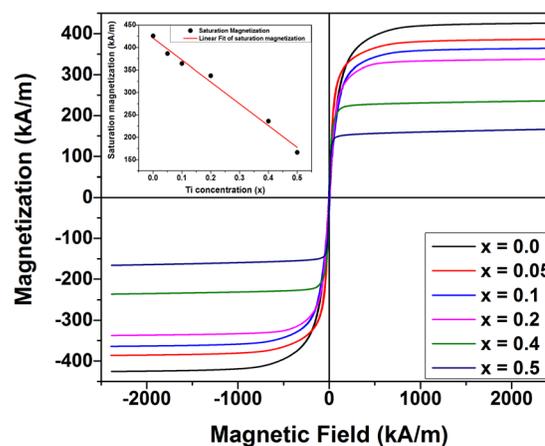


FIG. 3. Magnetization plots of the Ti-substituted cobalt ferrite samples. Saturation magnetization decreased almost linearly and at a faster rate in the high Ti-concentration region.

the contribution of the B-sites cations to the net magnetic moment thus resulting in the observed decrease in magnetization and saturation magnetization. A similar result was obtained in a study³ in which only Ti^{4+} was substituted for Fe^{3+} . In another study,⁴ it was shown that for $\text{Ti}_x\text{Fe}_{2-x}\text{O}_4$, at Ti-concentration (x) in the range $0 \leq x \leq 0.2$, Fe^{3+} , Fe^{2+} , and Ti^{4+} co-occupy the B-sites but the concentration of Fe^{3+} decreased faster in the range $0.2 \leq x \leq 0.8$ such that beyond $x = 0.8$, only Fe^{2+} and Ti^{4+} were on the B-sites. $\text{Ti}_x\text{Fe}_{2-x}\text{O}_4$ can be described as Ti-substituted FeOFe_2O_3 , while the system reported in this work can be considered as Ti-substituted CoOFe_2O_3 . Since Co^{2+} and Fe^{2+} have similar cation site preference, comparable ionic radii, and magnetic moment, one would expect the cation distribution in the system studied here to be similar to that of Ti-substituted FeOFe_2O_3 studied in the previous work.⁴ This would then suggest that the rate of change of magnetization with Ti-concentration (x) would be more drastic in the range $0.2 < x \leq 0.8$ compared to the range $0 \leq x \leq 0.2$. This is in agreement with the observation in Fig. 3. It appears that this behavior, in which properties vary depending on the regions

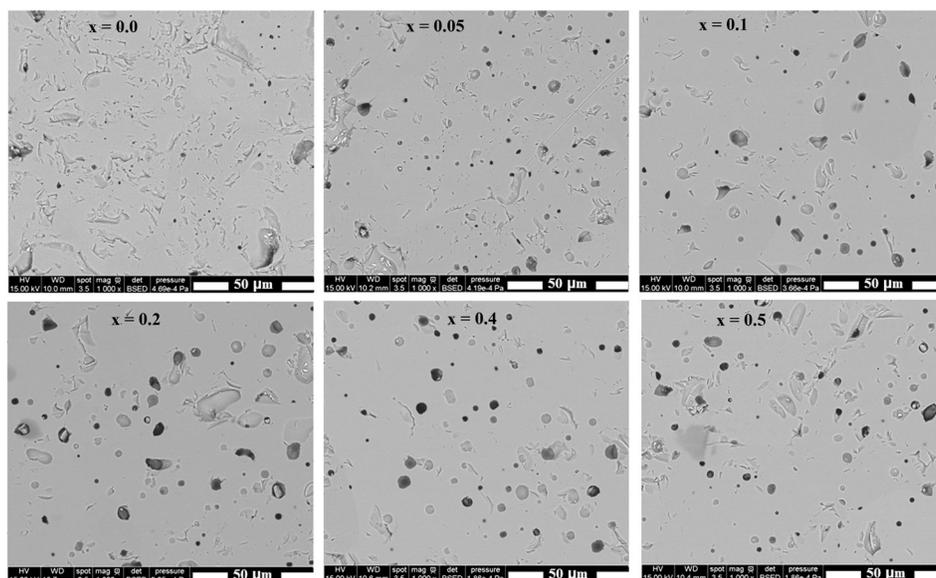


FIG. 2. Backscattered electron micrographs showing uniform contrast which is indicative of single phase samples.

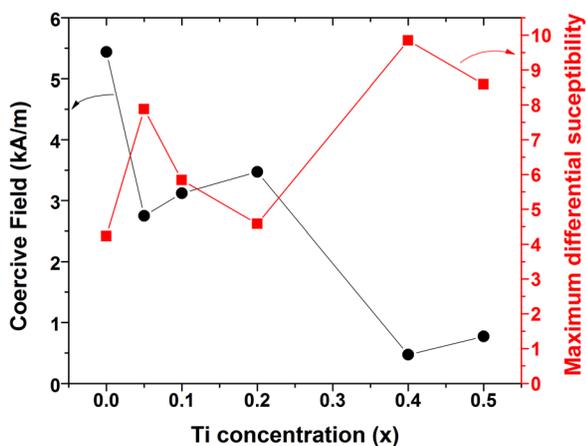


FIG. 4. Variation in coercive field (black circles) and maximum differential susceptibility (red squares) as a function of Ti-concentration (x) in cobalt ferrite.

of Ti-concentration, is particle size dependent. In a study in which the samples were nanoparticles of $\text{Co}_{1+x}\text{Ti}_x\text{Fe}_{2-2x}\text{O}_4$, a different trend was reported.⁶

The variation of coercive field (black circles) and differential susceptibility (red squares) are shown in Fig. 4. Compared to the un-substituted sample, coercive field decreased, which is a consequence of weakened A-B superexchange interaction with Ti-substitution. Such weakening results in lower magnetocrystalline anisotropy, and hence lower coercivity.

The effect of co-substitution of $\text{Ti}^{4+}/\text{Co}^{2+}$ on magnetocrystalline anisotropy will be investigated in a future study. It is interesting to observe that the trend in the variation of coercivity, like the variation in magnetization, can also be divided into two regions. Coercivity is higher in the region $0 < x \leq 0.2$ than $0.2 < x \leq 0.5$. Nevertheless, within each region, while magnetization decreased, coercivity increased. There is also a correlation between the coercivity and the differential susceptibility ($\chi' = \frac{dM}{dH}$); both are inversely related

(Fig. 4). This agrees with the expectation that materials with high susceptibility have lower coercivity, while materials with low susceptibility have higher coercivity. Such has been previously observed in Zn-substituted cobalt ferrite.⁷

IV. CONCLUSIONS

The effect of $\text{Ti}^{4+}/\text{Co}^{2+}$ co-substitution for 2Fe^{3+} in cobalt ferrite has been investigated. The lattice parameters did not follow Vegard's law indicative of variations in the rate at which the cations are substituted into the tetrahedral and octahedral sites. The saturation magnetization, coercivity, and magnetic susceptibility all varied in a pattern that agrees with cation distribution in a similar material previously reported. The coercivity varied inversely with the maximum differential susceptibility of the samples.

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