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Temperature dependence of magnetic properties of heat treated cobalt ferrite

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This study demonstrates the effectiveness of heat treatment in optimizing the magnetic properties of cobalt ferrite, compared to other methods such as cation substitution. It also shows how the magnetic properties of the heat treated cobalt ferrite vary under different temperature conditions. Saturation magnetization increased more due to heat treatment than due to Zn-substitution; a cation substitution that is known to result in high saturation magnetization in ferrites. A remarkable observation is that the increase in the saturation magnetization due to heat treatment was not at the expense of Curie temperature as was often reported for cation substituted materials. The observed variations in the magnetic properties were explained on the basis of cation redistribution arising as a result of the heat treatment. © 2014 AIP Publishing LLC. [http://dx.doi.org/10.1063/1.4862300]

I. INTRODUCTION

Distribution of cations between the tetrahedral and octahedral sites of the crystal lattice of cobalt ferrite and its derivatives is key to controlling the magnetic and magnetostrictive properties. The partially inverse spinel structure of the materials results in a cation distribution in which more cobalt ions (Co2+) occupy the octahedral sites giving rise to the distinctive properties of cobalt ferrite compared to other spinel ferrites. For example, photomagnetism in nanoparticles of cobalt ferrite have been related to this type of cation distribution.1 Its higher magnetocrystalline anisotropy and stronger magnetomechanical effects compared to other spinel ferrites are due to the orbital angular momentum of Co2+ not being completely quenched by the crystalline field. Consequently, Co2+ on the octahedral sites of the crystal lattice contributes an orbital moment, comparable to the spin moment, resulting in strong spin-orbit coupling which is responsible for the characteristic properties of cobalt ferrite.

In order to optimize the properties of cobalt ferrite for applications, one can take advantage of the ability to influence the site preference of the cations by heat treatment or chemical substitution. This can result in cation redistribution which can be systematically controlled. For heat treatment, such control can be realized by tailoring the heat treatment parameters such as temperature, holding time at a particular temperature and the rate of heating/cooling. For cation substitution it can be achieved by controlling the rate at which cations are substituted or by selecting cations with particular site preferences. Both heat treatment and cation substitution can also affect the oxygen stoichiometry which in turn affects the exchange interaction since the cations are indirectly coupled through the oxygen anions in the crystal lattice. Although there have been extensive investigations on improving the properties of cobalt ferrite based materials by cation substitutions,2–7 there has not been a commensurate improvement of the materials after chemical substitution or heat treatment. If, and how temperature variations affect the properties of chemically modified cobalt ferrite11–13 but the authors are unaware of such studies for heat treated cobalt ferrite. In the present study, the changes in the magnetic properties of cobalt ferrite due to heat treatment and the effects of temperatures variation on the heat treated samples are presented. The results obtained are compared to those of chemically substituted cobalt ferrite, especially Zn-substitution which is known to be effective in increasing the saturation magnetization.14 These were similar to the observation in the present study for heat treated samples.

II. EXPERIMENTAL DETAILS

Samples were prepared by the traditional ceramic processing technique. Oxides of Fe3O4 and Co3O4 were mixed in appropriate ratios, calcined twice for 24 h at 1273 K in air furnace and sintered for 24 h at 1623 K. Samples were then separated into six sets. Five sets were annealed at 873 K, 1073 K, 1273 K, 1473 K, and 1673 K. The samples were held at the annealing temperatures for 24 h and afterwards quenched in water to room temperature. To ensure comparable quenching rates, samples of similar dimensions were used. They were also quenched in water of equal volume. In this article, these five sets are denoted after the temperature at which they were annealed before being quenched to room temperature. The sixth set was slowly cooled in air furnace and is denoted “Air cooled” in this study. Samples were of single spinel phase with composition Co1.02Fe1.98O4 and...
lattice parameter \(8.37 \pm 0.02\,\text{Å}\). There was no observable secondary phase. Magnetization as a function of applied magnetic field was studied using a SQUID magnetometer up to a maximum applied magnetic field of 4 MA/m. Magnetization as a function of temperature was also studied with SQUID magnetometer from 400 K to 10 K. The Curie transition temperature was determined at the point of inflection from magnetic moment vs. temperature measurement under an applied field of 7.95 kA/m and up to 873 K using a vibrating sample magnetometer (VSM). The effect of heat treatment on the structural properties of the sample at ambient conditions has been previously reported.\(^\text{10}\)

III. RESULTS AND DISCUSSION

In Fig. 1, the first quadrant of the magnetic hysteresis loops of the samples are plotted. Saturation magnetization increases from 440 kA/m to 470 kA/m with heat treatment temperature as can be seen in Fig. 2 which compares the saturation magnetization of the heat treated samples to those of Zn-substituted cobalt ferrite.\(^\text{14}\) The mechanism by which heat treatment results in the increase in saturation magnetization is cation redistribution arising due to increased ionic mobility at elevated temperatures. It has been shown that annealing and quenching of cobalt ferrite results in the increased occupancy of Fe\(^{3+}\) on the octahedral sites. This corresponds to lower concentration of Co\(^{2+}\) ions on the octahedral sites. Since the net magnetic moment \((m)\) is given by \(m = \sum m_{\text{Octahedral}} - \sum m_{\text{Tetrahedral}}\) and because the magnetic moment of Fe\(^{3+}\) ions is greater than that of Co\(^{2+}\) ions, such redistribution in which more Fe\(^{3+}\) ions are on the octahedral sites results in the increase in magnetization. For Zn-substitution, the mechanism involves reducing the magnetization of the tetrahedral sites (i.e., \(\sum m_{\text{Tetrahedral}}\)), which also leads to increase in magnetization. Zn-substitution can also result in the increase in magnetization by cation redistribution, similar to the mechanism described for heat treatment. The difference in cation redistribution due to heat treatment and Zn-substitution lies in the cation being displaced; specifically, Co\(^{2+}\) or Fe\(^{3+}\). Of the cations in Zn-substituted cobalt ferrite (Co\(^{2+}\), Zn\(^{2+}\), and Fe\(^{3+}\)), Co\(^{2+}\) has the strongest preference for the octahedral sites while Zn\(^{2+}\) has the strongest preference for the tetrahedral sites.\(^\text{16}\) Thus, with the substitution of Zn\(^{2+}\), it is more likely that Co\(^{2+}\) be preferentially displaced out of the tetrahedral sites into the octahedral sites. Such a change results in an increase in the magnetic moment contributed by the octahedral sites cations to the magnetic moment. Consequently for the heat treatment, it is Fe\(^{3+}\) with higher magnetic moment (5 \(\mu_B\)) that is displaced into the octahedral sites but for Zn-substitution, it is Co\(^{2+}\) (3 \(\mu_B\)) that is displaced. Thus, heat treatment results in higher saturation magnetization than Zn-substitution.

Fig. 3 shows the variation of saturation magnetization as a function of temperature measured from 400 K to 10 K at \(H = 4\,\text{MA/m}\). The observed trend is consistent with previous observations for materials based on cobalt ferrite in which saturation magnetization initially increased monotonically with decreasing temperature (hereinafter called regime 1), reaches a maximum (regime 2) and then decreases (regime 3) (these regimes are illustrated for cation substitution in Fig. 4. The regimes shown for low cation concentration is similar to those in Fig. 3.)

This trend in materials based on cobalt ferrite has been explained on the basis of the competition between the thermal energy and the magnetocrystalline anisotropy energy in response to the applied magnetic field.\(^\text{14}\) As temperature decreased from 400 K, the applied magnetic field increasingly became more effective in aligning the magnetic moments in its direction. This results in increased saturation magnetization as seen in regime 1. Further decrease in temperature led to regime 2 where the effect of lower thermal

![FIG. 1. First quadrant of the magnetic hysteresis loops of the samples. Magnetization at any given field increased with heat treatment temperature.](image1)

![FIG. 2. Comparison of the variation in saturation magnetization of the heat treated samples with those of the Zn-substituted samples.](image2)
energy in increasing the magnetization, and the effect of magneto-{

crystalline anisotropy in decreasing it, results in a peak in saturation {

magnetization. In regime 3, the anisotropy energy became dominant as {

temperature is further decreased. As a result the anisotropy field {

resulted the effectiveness of the applied magnetic field in aligning the {

magnetic moments, thereby causing the observed saturation magnetization to be less. {

Magnetocrystalline anisotropy has been shown to increase with decreasing {

temperature for cobalt ferrite.17 It can be seen that the rate at which the saturation magnetization decreased in regime 3 is less at higher heat treatment temperatures. This suggests that magneto-crmalline anisotropy decreases with heat treatment temperature as well. The first cubic magnetocrystalline anisotropy coefficient was determined by the Law of Approach at 300 K. This showed a decreasing trend as heat treatment temperature increased.10 {

The trends observed at lower and higher heat treatment temperatures are comparable to those observed in cation substitutions at lower and higher cation concentrations, respectively.14,18 The effect of cation substitution in reducing the magnetocrystalline anisotropy is stronger at higher concentrations of substituted cations.18,19 This enables the applied magnetic field to have a greater effect in increasing the magnetization at higher concentrations. Consequently, the regimes observed depend on the concentration of the substituted cation as illustrated in Figure 4. At low concentrations, all three regimes are observed. At intermediate cation concentrations, magneto-crystalline anisotropy decreases which results in only regimes 1 and 2 being observed. At higher concentrations there is further decrease in magneto-crystalline anisotropy such that only regime 1 is observed. As expected, this effect depends on the type of cation being substituted. For Al17 substitution (CoAlxFe2−xO4),18 the stage in which only regime 1 is observed is not reached even up to x = 0.5 but for (Co1+xGe2−xO4), that stage is reached at x = 0.4. In general, cation substitution appears to have a stronger effect on magneto-crystalline anisotropy than does heat treatment as deducible by comparing17 with studies on cation substituted cobalt ferrite.5,11,12,14 Figure 5 shows the temperature at which the saturation magnetization reached a maximum (regime 2) plotted against the heat treatment temperature. A decreasing trend with heat treatment temperature was observed. Consequently, higher heat treatment temperature results in regime 3 starting at a lower temperature. Figure 6 shows that the Curie temperature of all the heat treated and air-cooled samples are comparable with values ~763 K. Air cooled cobalt ferrite can have Curie temperature in the range 713 K to 793 K.15,20 Quenching heat treatment on these samples did not result in observable changes in Curie temperature. In comparison, it is readily seen in Fig. 7 that substituting cations such as Zn, Cr, Al, Ga, Mn, and Ge into cobalt ferrite has very strong effect on the Curie temperature. Consider Zn-substituted cobalt ferrite for example, the saturation magnetization for the sample at x = 0.17 is comparable to that of the sample heat treated at 873 K but the Curie temperature is about ~185 K lower. It is interesting that compared to the

FIG. 3. Variation of the saturation magnetization measured at 4 MA/m against the measurement temperatures. The observed trends are typical of materials based on cobalt ferrite. Saturation magnetization increases with decreasing temperature and reached a maximum (solid symbols). Afterwards, it decreases with decreasing temperature (open symbols). Regimes 1 and 2 are plotted with solid symbols while regime 3 is plotted with open symbols.

FIG. 4. Schematic representation of regimes for non-magnetic cation substitution studies.

FIG. 5. Comparison of the temperatures at which the saturation magnetization peaked for the heat treated samples.
The dependence of the magnetic properties of heat treated cobalt ferrite on temperature variations has been presented in this study. Results have been compared with those of cation substituted cobalt ferrite. Heat treatment results in an increase in saturation magnetization while retaining high Curie temperature. This is useful for high temperature applications. Cation substitution, to decrease anisotropy, on the other hand results in significant reduction in the Curie temperature. The differences in the effects of heat treatment and the effects of cation substitution have been explained on the basis of the cation redistribution and site preferences.

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