Magnetic behavior of nanocrystalline MnCo$_2$O$_4$ spinels

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Abstract

A series of powders with different particle sizes of the spinel MnCo$_2$O$_4$ was synthesized by the Pechini method. The resulting precursor was calcined between 400 and 900 °C and characterized by thermogravimetric analyses (TGA), X-ray diffraction (XRD), scanning electron microscopy (SEM) and magnetization measurements. TGA analysis showed a loss of mass in the region from 200 to 650 °C and stability after this. XRD patterns showed an increase of the crystallite size with calcination temperature. Magnetization measurements on the sample calcined at 900 °C showed an unusual behavior of the hysteresis curve and irreversibility of the magnetization with field cooled (FC) and zero field cooled (ZFC) procedures. An evolution of this behavior was observed with increasing crystallite size.

Keywords: Ferrimagnet; Magnetization; Magnetic domains; Nanoparticles; Spin glass

1. Introduction

Spinel mixed oxides with general formula AB$_2$O$_4$ can be considered strategic materials due to their electronic, magnetic, optical and catalytic properties among others [1–8]. These materials contain both rare earth elements and 3d transition metals or only 3d transition metals [9]. The production of high-performance ceramics which display such properties has driven forward the elaboration of new powder synthesis routes. AB$_2$O$_4$ (A and B are 3d transition metals) can be produced using a number of methods including conventional ceramic powder technology, sol–gel processing, powder co-precipitation, and nitrate decomposition [10,11]. Recently, the spinel of the MnCo$_2$O$_4$ series was studied to be used as fuel cell electrodes and for its unusual magnetic hysteresis behavior [4]. Spinel-like nanostructured manganese cobaltate, MnCo$_2$O$_4$ has been extensively studied in the last few years due to their potential for a variety of applications. They essentially depict attractive electronic, magnetic, and catalytic properties. MnCo$_2$O$_4$ is a typical spinel oxide that has been extensively investigated as a case study among spinels containing Mn$^{3+}$–Mn$^{4+}$ [12].

An unusual behavior of the magnetic hysteresis has been observed by Joy and Date [4]. Normal hysteresis behavior was observed down to 130 K, whereas below this temperature, the initial magnetization curve lies outside the main loop. This unusual behavior of the magnetic hysteresis of MnCo$_2$O$_4$, at low temperatures, was associated with irreversible domain wall movements. In this work measurements of magnetic hysteresis and magnetization as a function of the temperature were carried out on MnCo$_2$O$_4$ samples calcined at 700, 800 and 900 °C. An evolution of the magnetic properties is studied with increasing crystallite size.

2. Experimental

MnCo$_2$O$_4$ spinel was synthesized by the Pechini method using a polymeric precursor. The process is based on the
chelation of metallic cations by citric acid in an aqueous solution followed by the addition of ethylene glycol. Manganese citrate and cobalt citrate were used to prepare a polymeric resin. The resulting precursor was calcined between 400 and 900°C and characterized by X-ray diffraction (XRD) and magnetization measurements. The thermal decomposition of the precursor resin was investigated by thermogravimetric analysis (TGA) carried out in a PerkinElmer TGA7 system under flowing nitrogen (50 cm³ min⁻¹). The material was heated up to 900°C at a constant rate of 5°C min⁻¹. The XRD patterns were obtained in a Shimadzu 6000 apparatus using CuKα radiation. Scanning electron micrographs were obtained using a JEOL-JSM scanning electron microscope. The angular range from 5° to 75° was investigated. Magnetization measurements were carried out using a vibrating sample magnetometer (VSM) operating with applied magnetic fields up to 1.5 T.

3. Results and discussion

The TGA analysis revealed that organic matter was continuously burned out from about 300°C up to 700°C (Fig. 1). XRD patterns as a function of the calcination temperature are shown in Fig. 2. The XRD pattern corresponding to the material calcinated above 400°C confirmed the presence of only crystalline phases. Peaks corresponding to a spinel structure could be observed at 2θ = 30.06°, 35.45° and 43.64°. The pattern of the samples heat-treated above 400°C also revealed the formation of MnCo₂O₄ with spinel structure. Increasing the calcination temperature, increased intensity and narrowed Bragg peaks. This behavior suggests an increase of the crystallite size with increasing the calcination temperature. Furthermore, the pattern of the sample heat-treated at 400°C showed broader Bragg peaks at the same positions, indicating the formation of a nanocrystalline material. Rietveld analysis of the XRD patterns for all calcined samples essentially shows single phases corresponding to the expected MnCo₂O₄ spinel with cubic crystal structure and space group Fd3m. Structural and microstructural parameters are shown in Table 1. Both crystallite size and lattice parameter increase with increasing the calcination temperature. The sample calcined at 900°C consisted of bulk-sized particles whereas samples calcined at lower temperatures contained nanometric crystallites.

![Fig. 1. Thermogravimetric analysis (TGA) curve of polymerized resin.](image1)

![Fig. 2. X-ray diffractograms of samples calcined at 400, 700, 800 and 900°C.](image2)

![Fig. 3. SEM micrographs of the samples calcined at 700, 800 and 900°C.](image3)

![Fig. 4. Initial magnetization and magnetic hysteresis curves of the sample calcined at 900°C, recorded at 120 K.](image4)

<table>
<thead>
<tr>
<th>Calcination temperature (°C)</th>
<th>Lattice parameter a (Å)</th>
<th>Average crystallite size (nm)</th>
<th>Goodness of fit</th>
</tr>
</thead>
<tbody>
<tr>
<td>400</td>
<td>8.162 (9)</td>
<td>6.2</td>
<td>0.79</td>
</tr>
<tr>
<td>700</td>
<td>8.298 (1)</td>
<td>51.5</td>
<td>0.86</td>
</tr>
<tr>
<td>800</td>
<td>8.302 (1)</td>
<td>55.4</td>
<td>0.82</td>
</tr>
<tr>
<td>900</td>
<td>8.307 (1)</td>
<td>204.0</td>
<td>0.91</td>
</tr>
</tbody>
</table>
domain wall motion at low fields. The virgin curve lies outside the hysteresis loop above $H_c$ as reported by Joy and Date [4].

The curves for initial magnetization and magnetic hysteresis of the samples calcined at 700 and 800 °C, recorded at 120 K, are shown in Fig. 5. The unusual behavior discussed above was not observed in those samples. The virgin curve lies completely inside the hysteresis loop, in a behavior similar to that observed by Joy and Date [4] at higher temperatures.

The temperature dependence of field-cooled ($M_{FC}$) and zero-field-cooled ($M_{ZFC}$) magnetizations of the samples calcined at 700, 800 and 900 °C, measured at 200 Oe, are

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**Fig. 4.** Hysteresis curve for sample calcined at 900 °C measured at 120 K.

**Fig. 5.** Hysteresis curves for samples calcined at (a) 700 °C and (b) 800 °C measured at 120 K.
In all curves, $M_{FC}$ continuously decreased with increasing temperature indicating the relatively large magnetic anisotropy of the samples. The Curie temperatures obtained were 174.8, 178.9 and 184.5 K, respectively. The thermal irreversibility of magnetization was observed between $M_{FC}$ and $M_{ZFC}$ below Curie temperature. The $M_{ZFC}$ curves show peaks at $T_p = 169.3, 169.2$ and $169.4$ K for samples calcined at 700, 800 and 900 °C, respectively. The overall shape of the $M_{ZFC}$ curve was similar for all samples showing peaks ($T_p$) at practically the same temperature, which become enlarged with increasing calcination temperature. For the sample calcined at 700 °C, $T_p$ decreased with increasing magnetic field, as shown in Fig. 7. $T_p$ decreased from 172 to 160 K when the applied field increased from 50 to 400 Oe. These results showed that the samples studied presented spin glass like behavior.

The results obtained from samples with different crystallite sizes confirmed the assumption that the unusual behavior of the hysteresis is due to irreversible domain wall movements [4]. The hysteresis curve of the sample calcined at 900 °C showed an unusual behavior with the initial magnetization curve outside the main loop. However, samples calcined at 700 and 800 °C depicted normal hysteresis behavior. The virgin curve for these samples lied completely inside the hysteresis loop. This behavior can be attributed to an increase of the mean size of nanocrystallites with increasing the calcination temperature. The samples calcined at 700 and 800 °C presented normal hysteresis behavior, because their crystallite sizes are of the same order of magnitude as the critical diameter $d_{cr}$, where the particle is considered to be single-domain.

In the spherical particle model [13], $d_{cr}$ can be calculated by

$$d_{cr} = \frac{9\varepsilon_p}{2\pi M_s^2},$$

where $\varepsilon_p$ is the surface energy of the domain wall and $M_s$ is the spontaneous magnetization. $\varepsilon_p$ can be expressed as a function of $T_c$ (Curie temperature), $K_1$, the magnetocrystalline anisotropy constant, and $a$, the lattice constant, as follows

$$\varepsilon_p = \left(\frac{2k_B T_c K_1}{a}\right)^{1/2},$$

where $k_B$ is the Boltzmann constant. Herein, with $K_1 = 5.55 \times 10^4$ erg/cm$^3$, $T_c = 185$ K, $M_s = 830$ G and $a = 8.29 \times 10^{-8}$ cm, the following values can be calculated for MnCo$_2$O$_4$ spinel, $\varepsilon_p = 0.19$ erg/cm$^2$ and $d_{cr} = 39$ nm. Comparing the value obtained for $d_{cr}$ with $D_m$ (Table 1) one concludes that the nanocrystallites of the samples calcined at 700 and 800 °C have an incipient structure of magnetic domains. Thus, only the sample calcined at 900 °C depicted multi-domain structure and therefore the possibility to capture the domain wall. The other samples contained pseudo single-domain particles, where the magnetization mechanism is dominated by curling and coherent rotation without domain wall movement.

4. Conclusions

Measurements of magnetic hysteresis and magnetization as a function of temperature were carried out on MnCo$_2$O$_4$ samples calcined at 700, 800 and 900 °C. An unusual behavior of the magnetic hysteresis was observed in the sample calcined at 900 °C. Normal hysteresis behavior was observed for samples calcined at 700 and 800 °C.
unusual behavior of the magnetic hysteresis of the sample calcined at 900 °C was associated with irreversible domain wall movements. This behavior was not observed in samples calcined at 700 or 800 °C because the crystallites have an incipient structure of magnetic domains.

Acknowledgements

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References