1. Introduction

Cobalt ferrite (CoFe$_2$O$_4$) belongs to the inverse spinel ferrites where Co$^{2+}$ ions occupy the octahedral sites of lattice structure and half of the Fe$^{3+}$ cations occupy octahedral sites and the other half stay at the tetrahedral sites of a fcc lattice formed by the oxygen ions [1]. It is a well-known hard magnetic material with moderate magnetization, high coercivity, high Curie temperature and large magnetostrictive coefficient [2,3]. Beside these characteristics, high physical and chemical stability of cobalt ferrite make it technologically attractive for audio and videotape recording and instrumentation with volume (V). Superparamagnetism is caused by the thermal energy (T) being less than the energy barrier (E$\alpha$ = K$_{eff}$V), spin inversion occurs, and there is no inversion of the spins. Furthermore, E$\alpha$ increases as nanoparticles size increases due to its proportionality with volume (V). Superparamagnetism is caused by the transition of the spin blocking state to superparamagnetic state and therefore, highly dependent on the size distribution of the particles. That is the reason we encounter a broad range dispersion in the reported values of blocking temperature (T$_B$) of nanoparticles.
of a particular material, and most of the magnetic nanoparticles cannot be in superparamagnetic regime above certain size [12].

In general, for superparamagnetic particles, below blocking temperature \( T_B \), magnetic susceptibility during ZFC is low as the particles are not in thermal equilibrium and the magnetization is due to the change in orientation of the magnetic dipoles along the axes of easier magnetization. As the temperature is increased, the smaller particles become superparamagnetic, and they align in the direction of the applied field, increasing the net magnetization of the sample. On the other hand, in magnetic susceptibility during FC, the blocking state is frozen, orienting along the easy axis, and as consequence, magnetization is higher than in ZFC. When ZFC susceptibilities are almost the same or slightly larger than those of FC in some temperature range, it is attributed to the strong interactions or large magnetostriction [13,14].

In this paper we report an unusual behavior in the ZFC-FC curves of \( \text{CoFe}_2\text{O}_4 \) nanoparticles, where the magnetic susceptibility values of ZFC curves are larger than those of FC in the whole range of measured temperatures under weak applied magnetic field. The behavior reverses for the applied magnetic field above a certain value.

2. Materials and methods

2.1. Synthesis of \( \text{CoFe}_2\text{O}_4 \) nanoparticles

\( \text{CoFe}_2\text{O}_4 \) nanoparticles were prepared by co-precipitation following the procedure reported by Duong et al. [15]. Stoichiometric amounts of cobalt nitrate hexahydrate \( \text{Co(NO}_3\text{)}_2\cdot 6\text{H}_2\text{O} \) and iron nitrate nonahydrate \( \text{Fe(NO}_3\text{)}_3\cdot 9\text{H}_2\text{O} \) were weighted and dissolved in deionized water. The mixture was heated to 70 °C and then a sodium hydroxide solution (NaOH 2.05 M) was added to it slowly under continuous mechanical stirring at 1000 rpm. The mixture was left in an isotherm (70 °C) for one hour. After cooling to room temperature, the precipitate was decanted and washed with deionized water until the pH reached to 7. Finally, the sample was dried at 80 °C for several hours and afterwards calcined in air at 500 °C for 1 h, to obtain it in powder form.

2.2. Characterization of the ceramic

The phase identification of the sample was performed by powder X-ray diffraction (XRD) using a PANalytical X-ray Empyrean diffractometer with Cu-K\(_\alpha\) radiation (\( \lambda = 1.5406 \) Å) at 45 kV and 40 mA. Particle size and morphology were analyzed using a Jeol JSM-7800F field emission scanning electron microscope and a Jeol JEM-2010F high resolution transmission electron microscope (HRTEM). Magnetic measurements of the ceramic were performed in a Dynacool-9 physical properties measurement system (PPMS) of Quantum Design, with VSM (vibrating sample magnetometer) option. For magnetic characterization, the magnetization vs. magnetic field hysteresis curves of the powder sample were recorded between 1.8 and 378 K, under applied magnetic field up to 3.0 T. The field cooling (FC) and zero field cooling (ZFC) curves of the sample were recorded under 0.01, 0.05, 0.1, 0.15, 0.5 and 1.0 T applied field, in the temperature range 20–375 K.

3. Results and discussion

Fig. 1 shows the XRD pattern of the powder sample synthesized by co-precipitation technique and annealed at 500 °C. Revealed diffraction peaks are consistent with the reported data for spinel ferrite \( \text{CoFe}_2\text{O}_4 \) (PDF cards # 22–1086). Absence of additional peaks associated to any other phases or impurities indicates the phase purity of the sample. The positive slope in the background is product of the X-ray fluorescence of the sample when Cu radiation impinge Co and Fe.

Typical morphology of \( \text{CoFe}_2\text{O}_4 \) powder sample after annealing at 500 °C is presented in Fig. 2. As can be seen from the micrographs, the sample consists of agglomerated and dispersed semi-spherical particles of 8–35 nm sizes with average size (c.a.) 22 nm. As mention above, superparamagnetic transition has a high dependence on particle size. So, a broad size distribution of the nanoparticles implies a broad range of \( T_B \) values. As some of our nanoparticles are within the reported size range (<12 nm), a multidomain to single domain transition for the \( \text{CoFe}_2\text{O}_4 \) nanoparticles is expected at temperatures slightly above the room temperature [16,17].
The morphology and crystallinity of the synthesized cobalt ferrite were studied further through TEM analysis. Typical TEM and HRTEM images of the sample are presented in Fig. 3. The average particle size estimated from TEM images was 21.7 nm, very close to the average size value obtained from SEM analysis. A typical HRTEM micrograph of the sample is shown in Fig. 3b. Crystallographic characteristics of the synthesized nanoparticles were identified by measuring the interplanar spacing, $d$, using the software digital micrograph 3.7.0. Fig. 3b presents CoFe$_2$O$_4$ particles with orientations along (4 0 0), (2 2 0) and (1 1 1) crystalline planes.

Fig. 4 depicts the magnetization (M) vs applied field (H) curves of the sample up to 3 T at different temperatures in an interval of 1.8–378 K. The saturation magnetization ($M_S$) is around 60 (emu/g) for low temperatures and 52 (emu/g) for room temperature and above. The coercive field ($H_C$) is strongly influence by temperature change (Fig. 4 inset). The coercivity decrease with temperature is due the increase of thermal energy that favors the orientation of magnetic dipoles along the applied field [18]. Above room temperature, the sample still shows paramagnetism with weak coercive filed, but not superparamagnetism, probably due to the broad dispersion of particle size and agglomeration. Room temperature value are in good agreement with other reports [7,19].

The ZFC and FC magnetization curves of the cobalt ferrite sample measured in between 20 and 350 K under 0.01, 0.05, 0.1, 0.15, 0.5 and 1.0 T applied magnetic field are presented in Fig. 5. In general, for higher applied fields, all the FC magnetization curves remains almost independent over the whole range of temperatures with a slightly negative slope at high temperatures due to the spin orientation along the applied field. However below 100 K, the FC magnetization tends to saturate. On the other hand, a very unusual behavior was observed on decreasing the applied magnetic field to 0.05 T or lower. The ZFC curves of the sample revealed higher magnetization than its FC curves. We observed such magnetic behavior previously [20] in the solid solution Co$_{1-x}$Ni$_x$Fe$_2$O$_4$ which is less significative when Ni content is increased and finally curves start to flipped out (i.e. the FC curve is over the ZFC curve) at $x = 0.8$. Other workers have also observed such behavior (higher magnetization during ZFC than during FC) in La$_{0.275}$Pr$_{0.35}$Ca$_{0.375}$MnO$_3$ [13], (LaNd)CaMnO manganites [21], silica-coated akaganeite nanorods [22], S-doped graphene [23], Sm-doped TiO$_2$ nanorods [24] in a
certain range of temperature where the ZFC curves have higher magnetization than FC curves, but not for cobalt ferrite. As mentioned above, this behavior has been associated to the high magnetostriction [13] or strong interactions between the particles [25]. In a magnetostrictive material when a magnetic field is applied on the ferromagnetic crystal, the domain walls shift and domains move, causing a change in the dimensions of the material due to the magnetocristalline anisotropy. In other words, the material tends to arrange its structure in a way that the easy axis is aligned along the applied field direction. Different from the mentioned reports, in this work the large magnetostriction is present in the whole range of measured temperatures. When the applied field is decreased to 0.05 T, at lower temperatures, the ZFC and FC curves get merged. Moreover, for 0.01 T applied field, the curves flip-out (ZFC magnetization higher than FC magnetization) for the whole range of measured temperature.

As can be seen from Fig. 5, for higher applied fields (0.15, 0.5 and 1.0 T), the divergence between the FC-ZFC curves increases with applied field, especially at lower temperatures. On the other hand, the maximum position of ZFC increases on lowering the applied field up to 0.1 T (Table 1).

As mentioned above, the dispersion in particle size and agglomeration of some particles (as observed by FESEM and TEM micrographs), which increase the interaction between the particles, provoke the weak coercive field without achieving superparamagnetic state. Due to the same reasons, the maximum of ZFC are not sharp or well defined and cannot be designated as blocking temperature.

Table 1 shows how the maximum of ZFC curves changes as function of applied field. At higher applied magnetic fields the energy required for spin inversion is lower. However, at lower applied magnetic fields, the effect of magnetostriction is prominent, which not only causes a reversal of FZC-FC magnetization, but also reduces the ZFC maximum.

Several authors have synthesized and characterized CoFe$_2$O$_4$ using ZFC-FC magnetization curves [6,26–29]. Most of them obtained different magnetic features depending on the synthesis method, the morphology and particle size. The results not only emphasize the importance of continuing exploration of magnetic behaviors of multiferoic nanoparticles such as CoFe$_2$O$_4$, but also the choice of their synthesis method for desired applications.

4. Conclusion

CoFe$_2$O$_4$ nanoparticles were synthesized by co-precipitation technique. The ceramic showed an unusually large magnetostriction in the whole range of measured temperatures (20–375 K) that can be overcome by increasing the applied magnetic field. The large magnetostriction in a broad range of temperatures can be very useful when a mechanical coupling is required in multiferoic composite systems.

**Acknowledgements**

The work was financially supported by the SEP (Grant # SEP-DGAPA/103.5/16/10420), CONACyT (Grants # INF-2011-1-1163153, and INF-2014-02-23053), Mexico. The authors acknowledge Dr. Ma. Eunice De Anda Reyes for her technical support in performing magnetic measurements of the nanostructures.

**Appendix A. Supplementary data**

Supplementary data associated with this article can be found, in the online version, at https://doi.org/10.1016/j.jmmm.2018.03.074.

**References**