Co-ferrite – A material with interesting magnetic properties

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Abstract. The development of Co-ferrite nanocrystals, and bulk materials for magnetostrictive applications is reviewed. This includes magnetic and structural properties and also processing conditions which are of special importance to increase the magnetostriction as well as to achieve very fine Co-ferrite nanocrystals. The magnetic properties of a single crystal, where a field induced phase transition was found, are also presented.

1. Introduction

Over the past few years, there has been an increasing interest in Co-ferrites as magnetic nanocrystals (as ferro-fluids, magnetic drug delivery, high density information storage etc [1-3]) and magnetostrictive material (as for actuator and sensor applications [4,5]). This interest is due to bulk Co-ferrite exhibiting remarkable properties such as high saturation magnetization, high coercivity, high anisotropy with good mechanical hardness, chemical stability and high magnetostriction [4-9]. Additionally, it is inexpensive and easy to produce. Conventional piezo-ceramics, such as PZT and PMN, and rare-earth based magnetostrictives, such as Terfenol-D, offer large strain values, but have limited mechanical robustness, therefore requires an operation under compressive loading. In contrast, the good mechanical properties of Co-ferrites and the ability to induce anisotropy through stress and field annealing [8,9], enables Co-ferrite to operate in the tensile regime without losing magnetic performance. Although the saturation magnetostriction of cobalt ferrite is lower than that of Terfenol, the slope of the magnetostriction or strain derivative (dλ/dH) which determines the stress sensitivity of a material is higher. Magnetostription values of about 400 ppm can be achieved in polycrystalline ferrite at room temperature under the right processing conditions [9].

Cobalt ferrite is a non-metallic ferromagnetic oxide, which exhibits the highest magnetostriction among all 3d-element based spinel oxides. Its magneto-elastic properties rise mainly due to the presence of Co²⁺-ions in the spinel lattice, which are due to its orbital contribution responsible for the large magnetostriction. The value of the achievable magnetostriction depends strongly on the exact stoichiometry as well as on the production methods [10]. An improvement of magnetic properties of polycrystalline Co-ferrite can be obtained by heat treatment, high compaction pressure and magnetic annealing besides adequate production process of the powders [7-10].

This article reviews the development of the nanocrystalline and bulk polycrystalline cobalt ferrites including structural and magnetic properties (such as magnetization, coercive field, magnetostriction). Additionally the importance of different processing conditions on the improvement of magnetic properties of Co-ferrite as well as on nanocrystalisation is shown. In order to investigate the magnetic properties without grain or grain boundary effects single crystals are ideal to come to a fundamental
understanding of all kind of magnetic properties. Therefore also magnetostriction and magnetization measurements of a Co_{0.8}Fe_{2.2}O_{4} single crystal are presented.

2. Co-ferrite

Ferrites based on Fe_{3}O_{4} crystallize in the spinel structure with the general formula Fe^{2+}Fe^{3+}O_{4}^{2-} which allow a large variety of substitution possibilities on the Fe site. When Fe^{2+} ions are substituted by Co^{2+} ions, we obtain a Co-ferrite. For adjusting the magnetic properties for various applications, the cations can be substituted by other elements such as Zn, Mn, etc which go to preferential sites (tetrahedral (site-A) or octahedral (site-B), see figure 1) according to their oxidation state as well as their ionic radius. The unit cell consists of eight tetrahedral places and 16 octahedral sites.

![Figure 1. The crystal model of the unit cell for spinel ferrite structure and relative position of the nearest neighbour atoms of the tetrahedral and the octahedral sites](image)

According to the distribution of cations on A and B sites, the spinel Co-ferrites are classified into two categories:

- Inverse spinel ferrites: the eight Co^{2+} filling half of the available octahedral sites, and Fe^{3+} ions are distributed randomly over the available tetrahedral and octahedral sites.
- Mixed spinel ferrites: the A- and B- sites are occupied by the both Co^{2+} and Fe^{3+} ions.

The occupancy of one type of divalent cations in the tetrahedral site is called degree of inversion, \(i\). For the CoFe_{2}O_{4} ferrite can be written as: \((Co_{1-i}Fe_{i})[Co_{i}Fe_{2-i}]O_{4}\), where the round brackets indicate the tetrahedral and the square brackets indicate the octahedral sites. Thus we have for the inverse spinel \(i = 1\) and for the mixed spinel: \(0 < i < 1\). As the tetrahedral site is crystallographically smaller than the octahedral, generally the smaller ion usually tends to go on that site.

Magnetically, it is well known that CoFe_{2}O_{4} is a ferrimagnetic material. The magnetic moments of cations in the A- and B-sites are aligned antiparallel with respect to one another yielding a total moment of spins with ferrimagnetic ordering. In the inversed ferrites, half of Fe^{3+} with magnetic moment \(5\mu_{B}\) is placed in A-sites and another half in B-sites. Their moments are mutually compensated and the net moment of ferrite is due to the moment of \(3\mu_{B}\) of Co^{2+} in the B-site. The general formula of the net magnetic moment per formula unit of spinel ferrite as a function of inversion degree may be written as: \(\mu = \mu_{B\text{-sites}} + \mu_{A\text{-sites}} = \{3i+5(2-i)-(5i+3-3i)\}(\mu_{B}) = (7 - 4i)(\mu_{B})\), where \(\mu\) is the net moment of the material, \(\mu_{B\text{-sites}}\) and \(\mu_{A\text{-sites}}\) are moments of cations in B and A-sites, respectively. Thus, the cation distribution affects the magnetic properties of the cobalt ferrite.

3. Nanocrystalline Co-ferrites

Many methods have been developed to prepare nanocrystalline CoFe_{2}O_{4}, namely: co-precipitation [11], combustion [12], micro-emulsion [13], ion exchange [14], sol-gel [7,15], modified oxalate
method [16], forced hydrolysis [17,18]. We could obtain very fine particles by means of modified oxalate method [16] and the forced hydrolysis method [18]. The later, it seems to be one of the best methods to obtain very fine nanocrystalline CoFe₂O₄, since it allows to prepare nano-particles with an equiaxial shape and narrow size distribution exhibiting high saturation magnetization and coercivity at low temperatures [17,18]. Using this method, nanocrystals of Co₁₋ₓZnₓFe₂O₄ (x = 0, 0.2, 0.4) with average particle size of 3 nm could be produced [18] (see figure 2, for example for x = 0.2 sample). Obviously these particles are superparamagnetic at high temperatures as can be seen, for example in susceptibility measurements shown in figure 3. This figure shows also the effect of Zn substitution on the blocking temperature, which changes with Zn content. Additionally, the saturation magnetization, Mₛ, increases and the coercive field, H_c, decreases with Zn [18]. Detailed investigations of the magnetic and structural properties were also made on annealed samples [19,20].

![Figure 2. TEM image of Co₀.₈Zn₀.₂Fe₂O₄ sample [18].](image)

![Figure 3. Susceptibility as function of the temperature measured on the Co₁₋ₓZnₓFe₂O₄ samples with x = 0, 0.2 and 0.4 [18].](image)

For the nanocrystalline CoFe₂O₄ prepared by modified oxalate method a larger average particles size (8 nm) and also a broad distribution of particles size were obtained [16]. The hysteresis loops measured with applied field up to 9 T at different temperatures are presented in figure 4. The blocking temperature of this material is around room temperature, RT.

**4. Magnetic properties of single crystalline Co₀.₈Fe₂.₂O₄**

We investigate the magnetostriction and magnetization of a cobalt ferrite (Co₀.₈Fe₂.₂O₄) single crystal prepared by a flux method [21], as a function of the temperature applying a magnetic field along the three different crystallographic axis: [100], [110] and [111]. Magnetostriction is an intrinsic property of all kind of magnetically ordered materials. Due to the magnetic exchange, the materials change its shape when a magnetic field is applied. Magnetostriction is based on the coupling of the magnetic moment to the lattice, therefore the orbital moment of the atoms must be considered. In a single crystal, the magnetostriction is a tensor property which depends on the crystal structure and symmetry of the lattice.
Figure 4. Hysteresis loops of nanocrystalline CoFe$_2$O$_4$ measured at 4.2 K $\leq$ T $\leq$ 400K. The insert shows $M/M_{Sat(90kOe)}$ vs. $H/T$ which curve is typical of Langevin function that describes a superparamagnetic material.

Figure 5. Normalized to $M_s$(100) magnetization of Co$_{0.8}$Fe$_{2.2}$O$_4$ measured at 10 K with field $//_{\text{to}}$ the [100], [110] and [111] axis. $\alpha$ is the angle between the applied field and M [21]

Figure 6. Magnetostriction measurements of Co$_{0.8}$Fe$_{2.2}$O$_4$ at 4.2 K and the field applied $//_{\text{to}}$ the [100] and [111] axis [21].

Figure 5 shows the applied field, $H$, dependence of the normalized magnetization, $M$, measured at 10 K with a $H$ along the three principal axis, and figure 6 shows the magnetostriction, $\lambda$, as function of $H$ measured with field along the crystallographic axis [100] and [111], at 4.2 K. The $M$ and the $\lambda$ measurements revealed that the [100] axis is the easy axis of magnetization of Co-ferrite over the whole temperature range reaching $M_s$ for an applied field $\mu_0H < 1$ T. The other two axis are magnetically hard, which at 9 T are far away from saturation, as shown in figure 5.

We observed unusual behavior in the magnetic hard axis [111] of the single crystal which manifests in a jump of the $M$ and $\lambda$ curves at a critical field. This jump is visible at $T < 150$ K for both $M$ and $\lambda$ curves. The jump in $\lambda$ was observed first time by us [21], while the jump in $M$ curve was already observed by Guillot et al [22] in Co$_{0.8}$Fe$_{1.96}$O$_4$. For this jump was attributed to a spin-flip phenomenon. However we could prove that the jump in the $M(H)$ curve can be explained as an
Figure 7. Magnetization vs. applied field along [111] axis measured at different temperatures on Co$_{0.8}$Fe$_{2.2}$O$_4$.

Figure 8. Temperature dependence of $M_s$ and $H_c$ measured on a Co$_{0.8}$Fe$_{2.2}$O$_4$ single crystal, applying the field along the [100] axis.

anisotropy driven transition [21], which is known as first order magnetization process (FOMP). This transition is caused by a rotation of the magnetization vector jumping over an energy barrier. Magnetization as function of the applied field along the [111] axis measured at different $T$ in Co$_{0.8}$Fe$_{2.2}$O$_4$ is shown in the figure 7. As can be seen the field where the FOMP occurs, $H_t$, depends on the temperature. It is worth to mention that $H_t$, at a certain temperature is very sensitive to direction deviations of the applied field with respect to the [111] axis. Composition fluctuations are also important.

The decrease of the saturation magnetization and coercive field with temperature measured for the magnetic easy axis of Co$_{0.8}$Fe$_{2.2}$O$_4$ is shown in figure 8. Due to high anisotropy in the [111] axis, at low temperatures the sample was not magnetically saturated up to 9 T (see figure 7). Although saturation magnetization values are comparable to those of polycrystalline Co-ferrites, the coercive fields of single crystal are much smaller than those measured on nanocrystalline (at low temperatures) and polycrystalline materials, because in a single crystal the influence of grain size and grain boundaries don’t exist.

5. Polycrystalline Co-ferrite

As was mentioned in the nanocrystalline section, there are many methods to prepare nanocrystalline Co-ferrite. Generally bulk polycrystalline Co-ferrites are obtained annealing as-cast produced nanocrystalline materials at a convenient temperature and annealing time. Among the preparation methods cited in section 3, for economical reasons the sol-gel and ball-milling method are most common. These methods allow an easy and cheap production process delivering large quantities.

The magnetic properties of polycrystalline Co-ferrite depend strongly on the processing conditions [7-10]. The heat treatment of the samples changes significantly the micro-structural and magnetic properties. Structurally, the grains increase, becoming more homogeneous with increasing annealing temperature, $T_a$, for a certain time or annealing time, $t_a$, at certain temperature. With annealing, due to the increasing of grain size, the magnetization and magnetostriction increase and the coercive field decreases. However, these properties become insensitive for larger grains (see figure 9) [7]. From XANES and XES measurements it was evidenced that all investigated samples in [7] exhibit only Co$^{2+}$ and Fe$^{3+}$ cations (no Co$^{3+}$ and Fe$^{2+}$ions) and adequate Fe-spin states. Additionally, we found that the concentration of Co$^{2+}$ cations in B-sites is larger in BM sample than in SG sample. Therefore the inversion degree in BM sample is higher than that of the SG sample resulting in lower saturation.
magnetization (see figure 9). These results showed thus the dependence of the cations distributions on
the production method.

**Figure 9.** Grain size dependence of the magnetostriction, saturation magnetization and coercive field measured on samples produced by modified sol-gel and ball-milling methods.

**Figure 10.** $H_c, M$ at 5 T and $\lambda$ vs. $P$: BFA are the data from the samples annealed at 1350 °C for 24 h after the application of $P$, while AFA are data obtained from the samples BFA field annealed at 300 °C for 3 h.

**Figure 11.** Magnetization curves obtained for the BFA and AFA samples pressed at 199 MPa. In the AFA sample, $M$ was measured along the magnetic easy and hard axis.

**Figure 12.** Measurements of the longitudinal, transverse and perpendicular (tri-dimensional) magnetostriction, performed on the BFA and AFA samples pressed at 167 MPa.
An improvement of magnetostriction of polycrystalline cobalt ferrite can be obtained by magnetic annealing due to the effect of induced uniaxial anisotropy [8,9]. Nlebedim et al. [8] investigated the influence of powder compaction pressure (87 MPa ≤ P ≤ 127 MPa) and annealing conditions on the magnetostriction of CoFe₂O₄ and found the highest magnetostriction value of 200 ppm for a sample pressed at 127 MPa and annealed at 1350 °C for 24 h. Later we investigated the influence of compaction pressure on magnetostriction also for higher values of P, i.e., for 87 MPa ≤ P ≤ 278 MPa. We found an optimum compaction hydrostatic pressure at around 160 MPa where a maximum magnetostriction of about 400 ppm in the pressure dependence of the magnetostriction curve was found (see figure 10). This high λ value was achieved when the sample was pressed and annealed at 1350 °C for 24 h and afterward again submitted to a heat treatment at 300 °C for 3 h, but in high magnetic field of 10 T [9]. This field annealing process causes an induced uniaxial anisotropy (see figure 11), which results in a reduction of the coercivity (in the easy axis) as well as a dramatic increase of λ up to 400 ppm along the hard axis (see figure 12). However, the microstructure and the saturation magnetization were not varied with field annealing. In the coercive field as a function of the compaction pressure (see figure 10) and magnetic anisotropy show also maxima values [9]. At this optimum pressure the saturation magnetization takes a minimum value (figure 10). Thus the change in magnetic properties is due to the occurrence of a redistribution of Co and Fe cations between A- and B- sites with pressure once a change in microstructure with P was not observed. These results show that the population of Co²⁺ cations in octahedral environment is a deciding factor for magnetic and magnetostrictive properties The M, Hc and λ vs. P behaviors are similar to those found before magnetic annealing (figure 10) showing once that the controlling factor is the distribution of cations.

The final specification of the magnetic and magnetostrictive properties of the cobalt ferrites is not only determined by the basic composition, but also by structural characteristic, induced uniaxial anisotropy and cations distributions influenced by the route of ferrite production.

6. Polycrystalline Co₁₋ₓMnxFe₂O₄ (x = 0-0.4)
In chapter 3 the effect of Zn substitution on nanocrystalline Co-ferrite was shown. Beside many other possible substitutions of elements, always Mn is interesting to investigate. As was described in [23] the substitution of Mn causes an increase of the lattice constant, however the magnetic properties such as Ms, Hc, the Curie temperature and also the magnetostriction decrease with Mn substitution. Figure 12 shows the magnetostriction measured on polycrystalline Co₁₋ₓMnxFe₂O₄ (x = 0-0.4) at room temperature. It is obvious that with Mn substitution the magnetostriction decreases, because this is accompanied with a decreasing magnetocrystalline anisotropy which causes a reduced coercivity [23].

Figure 12. Measurements of the longitudinal and perpendicular magnetostriction, performed on Co₁₋ₓMnxFe₂O₄ (x = 0-0.4)
7. Conclusion
The magnetic properties of polycrystalline Co-ferrite depend strongly on the production process (chemical routes etc., pressure). The annealing process (temperature and time) influence additionally the distribution of the Co\(^{2+}\) cations but also the microstructure (grain size). Powder compaction hydrostatic pressure and field annealing cause a significant increase of the magnetostriction, which is due to a reordering of the Co\(^{2+}\) ions. Single crystalline Co-ferrite exhibits a FOMP transitions which is also visible in the \(\lambda\) times \(H\) curve. Substitutions of Co by other elements such as Zn or Mn cause generally a magnetic softening of the material.

8. References
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