

A Study of Magnetic Moment Studies of Magnetostriction on CoFe_2O_4

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Abstract - The magnetic and electrical properties of ferrites are sensitive to the changes in their chemical composition as well as microstructure, which are greatly influenced by the manufacturing process. For example, controlling the grain size has a larger impact on the magnetic permeability and power loss in the case of Mn-Zn and Ni-Zn ferrites. Different processing parameters such as use of external additives during sintering, heating rate, cooling rate, sintering time and sintering atmosphere, affect the performance of these materials. It is known that the sintering behavior of the ferrite is considerably affected by the particle size of the starting powders. The particle size in the starting powders can be reduced to sub-micron or Nanosized levels by using ball milling technique or by employing different low temperature methods of syntheses. The sintering behavior of powders containing sub-micron or nanoparticles is different as compared to their bulk counterparts. Nanosized ferrite particles have more sinterability due to their fine particle nature as well as the high surface to volume ratio. The sintered products derived from Nanocrystalline ferrite powders exhibit improved magnetic permeability which depends on the microstructure, density, porosity, grain size, etc., as compared to the materials sintered from the bulk counterparts. Magnetostriction studies on ferrimagnetic spinels have been initiated in the 1950s. Domenicali has studied the magnetostriction of magnetite in order to study the crystallographic transitions at low temperature. Bickford et al. have analyzed the magnetostriction behavior of magnetite and cobalt substituted magnetite, and showed that polycrystalline cobalt containing magnetite exhibits very high strains. The magnetostriction constants of single crystals of $M\text{Fe}_2\text{O}_4$, where M stands for Mn, Fe, Co, Ni, and Zn in various proportions, have been determined by Bozorth using the method of strain gages.

Keywords - Magnetic Moment, Magnetostriction, electrical properties, Mn-Zn and Ni-Zn ferrites, Nanosized levels

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INTRODUCTION

In the 1950s, ferrimagnetic spinels were first studied for their magnetostriction properties. Bickford et al. examined magnetostriction behavior of magnetite and cobalt substituted magnetite and found that polycrystalline cobalt containing magnetite exhibits extremely high strains, which is why Domenicali investigated magnetostriction of magnetite to study crystallographic transitions at low temperature. Bozorth used strain gages to determine the magnetostriction constants of single crystals of $M\text{Fe}_2\text{O}_4$, which stand for Mn, Fe and Co in varying proportions. Spinel ferrites' magnetostriction constants were studied in relation to their material anisotropy, crystal symmetry, and magnetic annealing. Cobalt ferrite, one of the spinel ferrites, exhibits an extremely high magnetostrictive strain value. Studies of cobalt ferrite-based magnetostrictive materials have recently sparked interest, in part because of the materials' potential for use in stress sensing applications. The magnetostrictive properties of conventionally prepared

bulk cobalt ferrite have been extensively studied, but the impact of various processing parameters such as processing conditions, microstructure, and sintering aids on the magnetostrictive behavior of cobalt ferrite still needs to be better comprehended and investigated. There is no information on the relationship between sintering conditions, microstructure, and magnetostriction in any of the reported work on polycrystalline cobalt ferrite magnetostriction research. It is also not known how sintering temperature affects the magnetostrictive characteristics of cobalt ferrite in a systematic way. Due to the high saturation magnetization, high coercivity, and significant anisotropy of nanosized cobalt ferrite based materials, they are now being studied for high-density information storage and magneto-optical systems. There are a variety of low temperature wet chemical methods for producing cobalt ferrite besides the traditional ceramic method of synthesis and the ball milling process, which give sub-micron-sized particles, such as coprecipitation, solgel, micro emulsion [29-31], oxalic acid

precursors, urea precursors, combustion synthesis, complexometric, hydrothermal and redox processes. When it comes to cobalt ferrite sintered using powders generated in the Nanocrystalline form, no studies have been done yet. These investigations are expected to aid in the optimization of processing parameters for the development of cobalt ferrite-based magnetostrictive materials. Cobalt ferrite's magnetic and magnetostrictive properties will be studied as a result of this research.

PRELIMINARY STUDIES ON $\text{Co}_x\text{Fe}_{3-x}\text{O}_4$

It has been found that the maximum magnetostriction of polycrystalline samples of CoFe_3O_4 for $x > 1$ decreases with decreasing Co concentration. For compositions close to $x = 1$, a maximum magnetostriction value of 110 ppm is recorded. Various compositions with a greater Co content are generated in the present work in order to better understand the influence of Co on the magnetostriction in the series CoFe_3O_4 and to identify the compositions with the highest magnetostriction values possible. In order to narrow down the possible compositions for further investigation, these studies are carried out. Ceramic synthesis was used to create the CoFe_3O_4 series of compositions ($x = 0, 1, 1, 1, 1.2$, and 1.3). Iron oxide and cobalt carbonate were used as starting materials in a small-scale (15 gram batch) synthesis. Acetone was used as a mixing medium in an agate mortar to combine these raw components. Heat treatments were carried out at 1000°C for 12 h, 1000°C for another 12 h, and 1100°C for another 48 h, with an intermediate grinding after 24 h.

1 Powder XRD Analysis

Powder X-ray diffraction was used to determine the purity of the various mixtures. Figure 1 depicts the XRD patterns for the compositions with $x = 1.0, 1.1$, and 1.2 in Figure 1. The simulated pattern CoFe_2O_4 in the figure is compared with the XRD patterns of the samples. Each sample shows a spinel-like phase, indicating the desired compositions have been formed. When the concentration of Co is increased, the cubic lattice parameter is found to decrease somewhat. Different compositions of the $\text{Co}_x\text{Fe}_{3-x}\text{O}_4$ series made by conventional ceramic and low-temperature techniques have shown similar decreases in the lattice parameter.

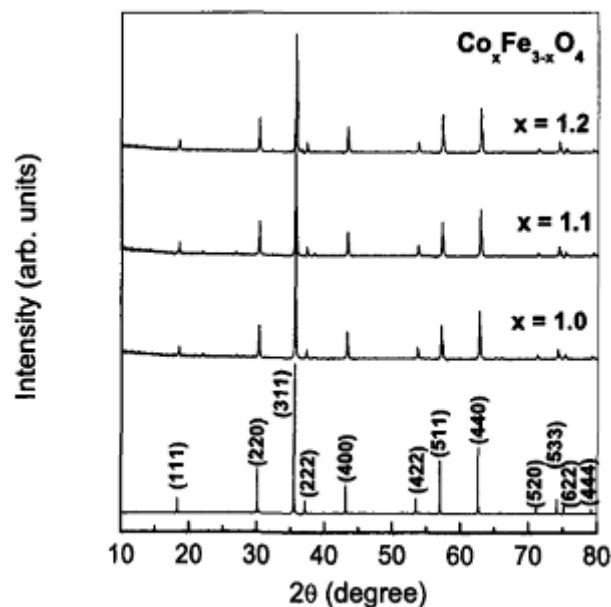


Figure 1: Powder X-ray diffraction patterns for the samples in the $\text{Co}_x\text{Fe}_{3-x}\text{O}_4$ series. The simulated pattern is shown and indexed for comparison

2 TMA Analysis

Compressed powders are investigated using a thermal mechanical analyzer for their sintering behavior. The samples were prepared as thin discs and heated to a maximum temperature of 1350°C at a continuous rate of $10^\circ\text{C}/\text{min}$. Figure 2 displays a comparison of the sintering trajectories for three distinct materials. The sintering behavior of all three compositions is nearly comparable. An effective sintering process begins above 1000°C and doesn't finish until the maximum studied temperature of 1350°C is reached. These pellets were then sintered at 1100°C for 8 hours to study the microstructure and magnetostrictive properties of the final powders. It was determined that the sintered pellets had a density of around 85% of the composition's X-ray density. Figure 5 is a SEM image of CoFe_2O_4 sintered at 1100°C and shows a microstructure with extremely tiny grains and a very porous structure. Sintering at 1100°C for 8 hours shows that the material hasn't been adequately sintered.

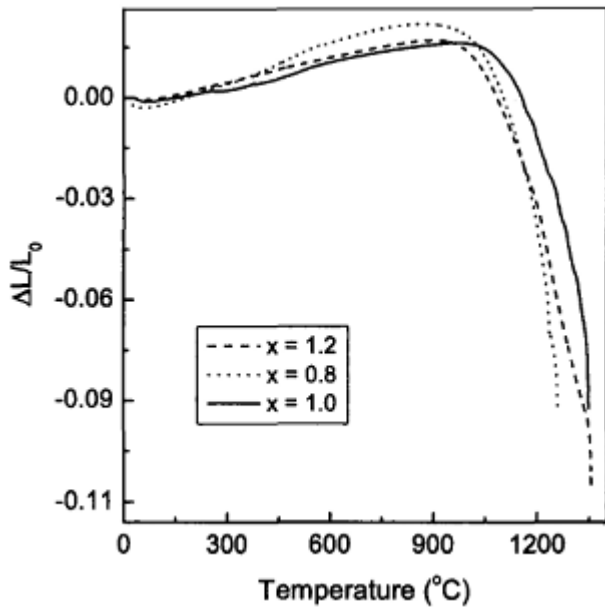


Figure 2: Sintering behavior for the samples in the $\text{Co}_x\text{Fe}_{3-x}\text{O}_4$ series.

3 Magnetic Measurements

At room temperature, figure 3 shows the field dependence of magnetization up to a maximum magnetic field of 15 kOe, which is indicated in the figure. Cobalt ferrite at room temperature is found to have a maximum magnetization of roughly 84.5 emu/g for the composition with $x = 1.0$, which is consistent with the values published for bulk cobalt ferrite at room temperature. The saturation magnetization decreases as the cobalt content increases. because Co^{2+} (3 μ_B) has a lower magnetic moment, the saturation magnetization is projected to be lower than that of Fe^{3+} (5 μ_B) - Similar to the coercivity, the anisotropy of these compositions increases as the concentration of Co^{2+} ions increases, which is explained by an increase in the number of ions.

4 Magnetostriction Studies

Different compositions are illustrated in figure 3.4, with the highest magnetic field strength of 6.0kOe recorded for each. Results are negative because they were taken with respect to the applied magnetic field (A_y). When measured perpendicularly ($A_{j\perp}$), small and positive values were found. The magnetostriction reaches its maximum at 1.0 x 1.2, as illustrated in the image. Compositions with 10 x 1.2 show the highest strain, at about 110 ppm. When comparing our results to those of previous studies on CoFe_2O_4 (225 ppm), we found lower magnetostriction values, which we attribute to the different processing conditions used for the two compositions. Sintered at 1100°C for 8 hours, the powders in this case are substantially more porous. A greater sintering temperature is needed to produce a material with a high compact density, according to the TMA analysis. Recent studies show that cobalt ferrite may be sintered at temperatures as high as 1450°C. Consequently, the samples were sintered at a

temperature of 1450°C for additional magnetostriction investigations.

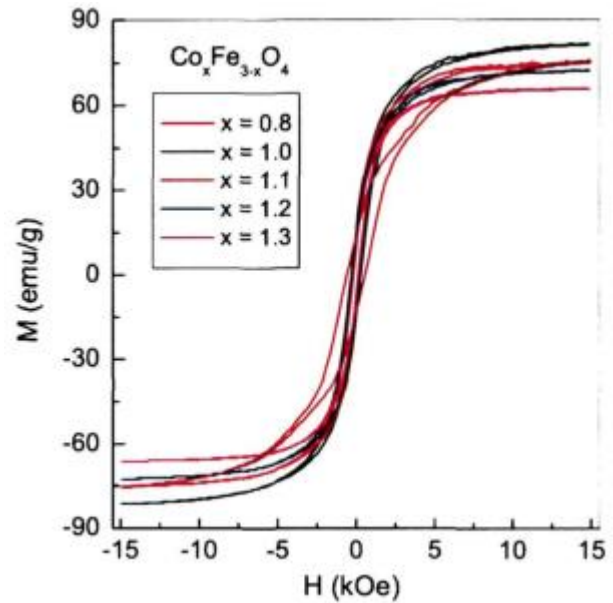


Figure 3: Room temperature magnetization curves for the samples in the $\text{Co}_x\text{Fe}_{3-x}\text{O}_4$ series

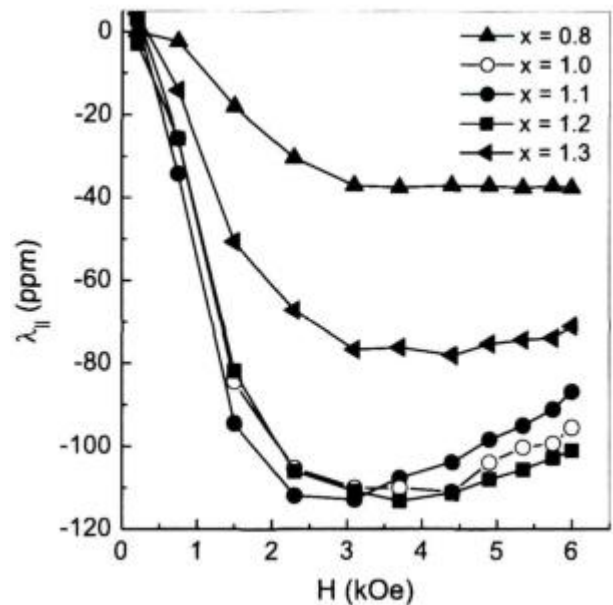


Figure 4: Magnetostriction measured in the direction parallel to the applied field for different compositions in the $\text{Co}_x\text{Fe}_{3-x}\text{O}_4$ series.

STUDIES ON CoFe_2O_4

CoFe_3O_4 series exhibits maximal magnetostrictive stresses between 1.0 x and 1.12 in preliminary investigations. Sintering at higher temperatures may be necessary to properly sinter samples, hence McCallum et al. reported that the composition with $x=1.0$ was sintered for 10 minutes at 1450°C. This

material's magnetic and magnetostrictive characteristics are also investigated in depth.

1 Microstructural Analysis

Figure 5 compares the SEM images of CoFe_2O_4 sintered at 1100°C for 8 h and 1450°C for 10 minutes, which were used in the initial research. The compact sintered at 1100°C is shown in micrograph (A), whereas the sintered at 1450°C is shown in micrograph (B). These images clearly illustrate that the material sintered at 1450°C has a dense microstructure compared to the compact sintered at 1100°C for 8h. Despite the porous nature, there is little evidence of grain development in micrograph (A). After sintering at 1450°C , the sintered density is over 90% of the theoretical density, compared to just 85% for the material sintered at 1100°C . Cobalt ferrite must be sintered at temperatures greater than 1400°C , according to a recent report on the subject.

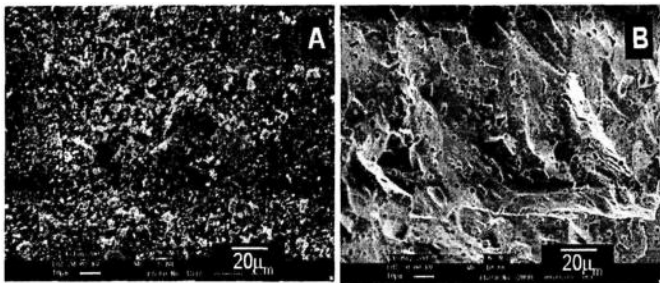


Figure 5: Comparison of the SEM photographs for the composition CoFe_2O_4 sintered at 1100°C for 8 hours (A) and 1450°C for 10 minutes (B).

2 Magnetic Measurements

Figure 6 depicts the field-dependent magnetization of the powder and the sample sintered at 1450°C at room temperature. When compared to the powder sample, the sintered sample has a slightly higher magnetization and a smaller coercive field. The temperature-dependent magnetization of the sintered sample is shown in the inset of the image, which was recorded in a magnetic field of 50 Oe. Cobalt ferrite has been reported to have a Curie temperature of 520°C , which is consistent with our results.

3 Magnetostriction Studies

Figure 7 shows the CoFe_2O_4 sample sintered at 1450°C 's room temperature magnetostriction curve. At room temperature, the measurement is performed with a maximum magnetic field strength of 10 kOe. The applied magnetic field was tested in both parallel ($A_{||}$) and perpendicular (A_{\perp}) directions. CoFe_2O_4 samples sintered at 1100°C for 8 hours show improved magnetostriction in the parallel direction ($A_{||}$) to the maximum value of 140 ppm, as shown in the figure. As a result, the sintering temperature of 1450°C was maintained for future studies on Nanosized cobalt ferrite.

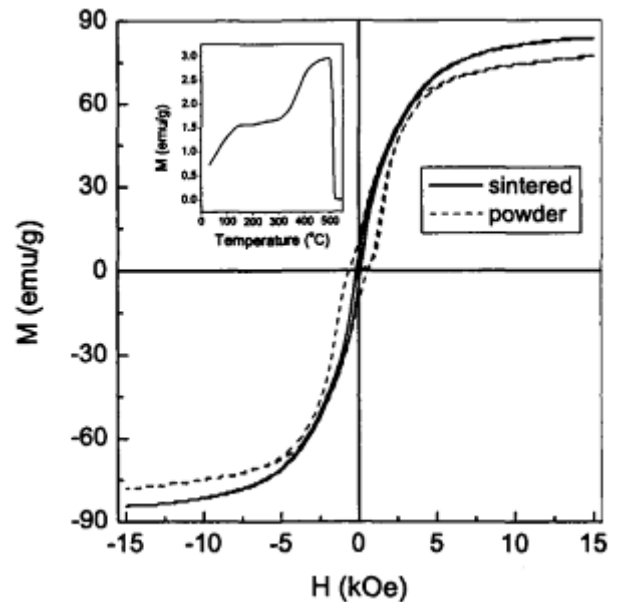


Figure 6: Field dependence of magnetization for the powder and sintered cobalt ferrite. The inset shows the M-T curve recorded for the sintered sample

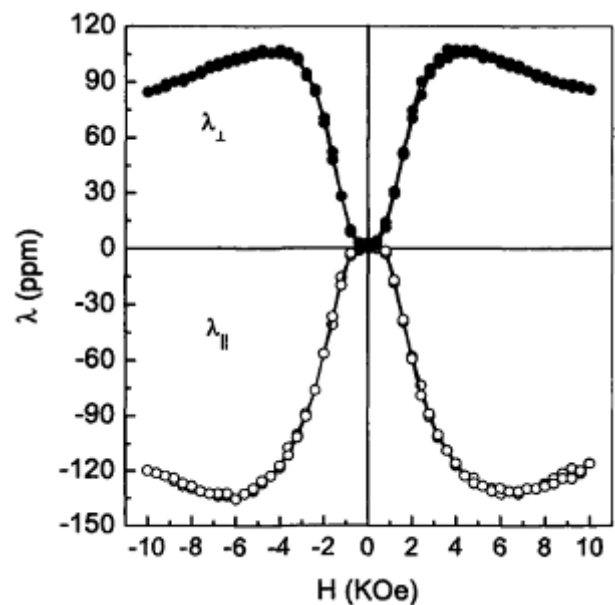


Figure 7: Magnetostriction curves of CoFe_2O_4 sintered at 1450°C for 10 minutes, measured in the parallel and perpendicular directions

STUDIES ON NANOSIZED CoFe_2O_4

When ferrites are manufactured in the Nanocrystalline form, their magnetic characteristics are substantially altered in comparison to their bulk counterparts. Sintering behavior of nanoparticles is likely to be different from that of bulk materials, as well. Many ways exist for synthesizing cobalt ferrite in the Nanoscale form, as was indicated at the beginning of this chapter. Because of their higher permeability and loss factor, sintered goods made from Nanocrystalline powders are well-known. However, little attention has been paid to the

influence of particle size on the magnetostrictive properties of the ferrites, which is a problem. Cobalt ferrite sintered from Nanocrystalline powders is manufactured using three alternative low-temperature methods to compare its magnetic and magnetostrictive properties. Once these results are in, they're compared to the sintered material obtained from traditional ceramic powders.

1 Synthesis

The nanoparticles were synthesized using the procedures listed below. Three low temperature synthesis methods were used, including the coprecipitation method (CPP), the citrate precursor route (CIT), and the glycine nitrate combustion route (GNP). The synthesis was carried out using the following methods. Every chemical utilized in the manufacture of cobalt ferrite by the various procedures was AR grade.

Autocombustion Method

Here, the glycine-nitrate process (GNP) is employed to synthesize metal oxides using metal nitrates as the oxidant, and glycine as the fuel. The metal nitrates of iron and cobalt, $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ and $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$, were dispersed in distilled water in stoichiometric amounts to make cobalt ferrite. The metal-to-glycine ratio is kept at 1:2, as previously reported. A big crystallizing dish was used to combine the solutions of the metal nitrates and glycine. When it was time to evaporate and auto combust, the crystallizing dish was placed on top of a hot plate set at 200°C . An autocombustion reaction occurred within seconds of the complete evaporation of water, forming a sticky gel at the bottom of the dish (as-synthesized product). Thereafter, the powder was put to use in a variety of ways.

Citrate Precursor Method

Citrate precursor technique (CIT) synthesis was performed by dissolving cobalt nitrate and ferric nitrate in water. The citric acid water solution was added to the metal ion solution at a 1:2 ratio. A thick gel was created by evaporating the solution over a water bath. The cobalt ferrite powder was made by drying this precursor overnight in an oven at 100°C and then calcining it for four hours at 500°C .

Coprecipitation Method

Cobalt and iron nitrates were dissolved in distilled water and combined together in the coprecipitation method (CPP). Under steady magnetic stirring, a solution of 20% KOH solution was added drop-by-drop to this solution. Filtered and repeatedly rinsed with distilled water, a precipitate was produced and the pH was adjusted to 7. A 100°C oven was used to dry the precipitate overnight, and the result was a black powder.

2 Powder XRD Analysis

Figure 8 displays the Powder XRD patterns for the three distinct synthesized materials. For the sake of comparison, the XRD pattern for the sample generated using the traditional ceramic technique is also displayed. It is clear from the XRD patterns that all of the samples are made of cobalt ferrite, as there are no other reflections present. Materials generated by the coprecipitation and citrate synthesis procedures have a wide range of reflections, while samples prepared through the combustion approach have a narrower range, indicating that crystallite sizes in the low-temperature synthesized powders are smaller.

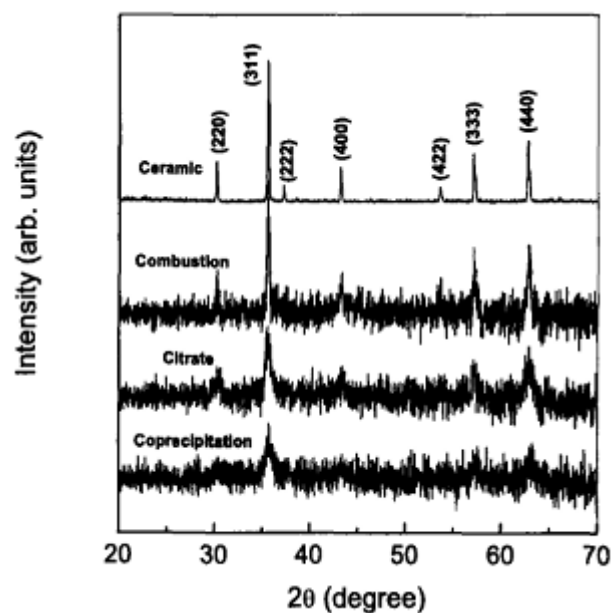


Figure 8: X-ray diffraction patterns of the samples synthesized by the low-temperature routes along with the one synthesized by the ceramic process

The Scherrer formula is used to estimate the average crystallite size. Coprecipitation, citrate, and combustion samples have crystallite diameters of 12, 15, and 45 nm, respectively, according to the calculations. Using a glycine:nitrate ratio closer to 0.5, Kikukawa et al. found comparable crystallite size in cobalt ferrite particles generated by the GNP technique. The higher flame temperature used in the combustion generated sample may have caused the particles to expand in size, as seen by the bigger crystallites found in this sample. The combustion of glycine as a fuel can produce temperatures as high as 1500°C .

3 TMA Analysis

Figure 9 shows the sintering curves of the samples made using various low-temperature procedures. Compacts made from Nanocrystalline powders should sinter differently than those made from smaller ceramic micro particles, because of the higher surface energy and bigger surface area of

nanoparticles. Chemical coprecipitation-created samples of NiCuZn ferrite can be sintered at a comparatively low temperature of 800°C. Sintering behavior of MgZnCu ferrite generated by the sol-gel combustion technique was investigated by Yue et al. and shown to be possible at a temperature of 950°C, which is considerably lower than previously thought. Using the procedures of coprecipitation (CPP) and citrate (CIT), the materials were synthesized in a way that differs from that of combustion and ceramic processes, as shown in figure 9. Sintering of CPP and CIT samples begins at 700°C and continues until 1300°C is reached. The sintering behavior of the combustion synthesized sample is quite similar to that of the bulk sample. There are nanometer-sized particles in this sample, as demonstrated by the presence of nanometer-sized crystallites in the XRD data. The synthesis circumstances can be used to explain this surprising behavior. In the midst of the combustion process, temperatures might rise to a dangerous level. As high as 1500 degrees Celsius have been reported by Chick et al during the combustion process, and this depends on the molar ratio of nitrates to glycine. A mole of metal ions is equivalent to two moles of glycine. The glycine/nitrate ratio is close to 0.5, which means that the flame temperature will be extremely high. The surface of the particles becomes non-active as a result of this high temperature created in a short period of time, even though the particle sizes are lower. As in the present case, urea and glycine have also been used to create oxide ceramics using the combustion method. While the particle size of the combustion synthesized sample is substantially smaller than that of the synthesized sample made using the ceramic approach, Shi et al. showed that the difference between the sintering temperature for combustion and ceramic samples was only 60°C.

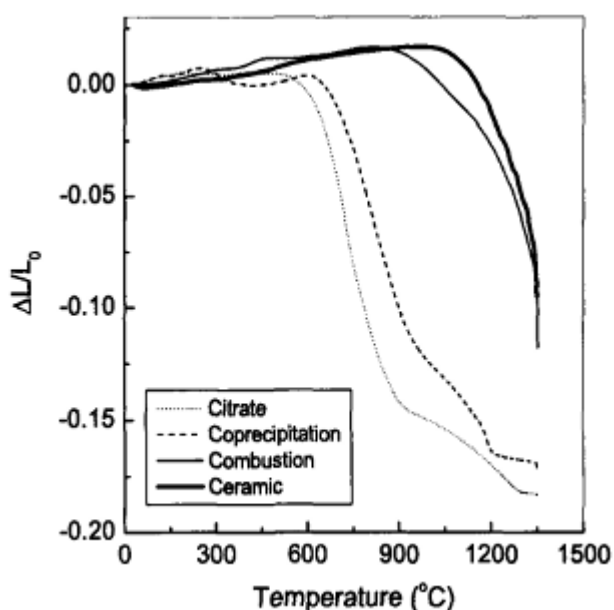


Figure- 9 Sintering behavior of cobalt ferrite prepared by different methods

When it was discovered through laboratory testing that the samples were only partially sintered at a temperature of 1350°C (see figure 9), the researchers decided to sinster all four samples at a higher temperature of 1450°C for 10 minutes to compare their results. The weight and volume of these disks are used to calculate the densities of the sintered pellets.

CONCLUSION

The magnetostrictive properties of sintered polycrystalline cobalt ferrite have been done in great detail. Magnetostrictive properties of the $\text{Co}_x\text{Fe}_{3-104}$ series were shown to be superior in compositions with $x = 1.0, 1.1,$ and 1.2 . Sintering temperatures must be raised in order to produce materials with increased density. A different production process and starting with Nanosized particles improved magnetostrictive characteristics in investigations on Nanosized cobalt ferrite. Cobalt ferrite Nano powders manufactured using three different low-temperature procedures exhibit improved magnetostrictive performance as compared to those synthesized using traditional high temperature methods. The magnetostriction and the microstructure of sintered materials have a strong link. As much as 197 parts per million (ppm) of magnetostrictive strain can be detected in combustion generated samples, which have been sintered to produce a microstructure with smaller-sized grains. Studies on ball milled cobalt ferrite confirm this. The microstructure and magnetostrictive properties of ball milled cobalt ferrite were studied in relation to sintering temperature, dwell duration, and sintering aids. Researchers found that sintering temperatures can be decreased to as low as 1100°C using the ball milling process, hence limiting grain formation and increasing the amplitude of the magnetostrictive strain. The results of the sintering aid tests further support the hypothesis that improving the magnetostrictive performance of cobalt ferrite necessitates the presence of small, uniform grains and higher sintered densities.

REFERENCES

- [1] D. Fiorani, Surface effects in magnetic nanoparticles (Springer Science + Business Media, Inc., New York 2005).
- [2] S. D. Tiwari and K. P. Rajeev, Thin Solid Films 505, 113 (2006).
- [3] R. W. Chantrell and K. O'Grady, in Applied Magnetism edited by R. Gerber, C. D. Wright, G. Asti (Kluwer Academic Publishers, The Netherlands, 1994).
- [4] M. Rasa, Eur. Phys. J. E 2, 265 (2000).

- [5] Q. A. Pankhurst, J. Connolly, S. K. Jones and J. Dobson, *J. Phys. D: Appl. Phys.* 36, R167 (2003).
- [6] C. Frandsen, C. W. Ostefeld, M. Xu, C. S. Jacobsen, L. Keller, K. Lefmann and S. Mørup, *Phys. Rev. B* 70, 134416 (2004).
- [7] F. Reif, *Fundamentals of Statistical and Thermal Physics* (McGraw Hill, Singapore, 1985).
- [8] I. S. Jacobs and C. P. Bean, in *Magnetism*, Vol.III edited by G. T. Rado and H. Suhl (Academic Press Inc., New York, 1963).
- [9] L. Néel, in *Low Temperature Physics*, edited by C. Dewitt, B. Dreyfus and P. D. de Gennes (Gordan and Beach, New York, 1962).
- [10] S. H. Kilcoyne and R. Cywinski, *J. Magn. Mater.* 140-144, 1466 (1995).
- [11] S. A. Makhlof, F. T. Parker and A. E. Berkowitz, *Phys. Rev. B* 55, R14717 (1997).
- [12] M. S. Seehra, V. S. Babu, A. Manivannan and J. W. Lynn, *Phys. Rev. B* 61, 3513 (2000).
- [13] M. S. Seehra and A. Punnoose, *Phys. Rev. B* 64, 132410 (2001).
- [14] N. J. O. Silva, V. S. Amaral and L. D. Carlos, *Phys. Rev. B* 71, 184408 (2005).
- [15] A. Punnoose, T. Phanthavady, M. S. Seehra, N. Shah and G. P. Huffman, *Phys. Rev. B* 69, 54425 (2004).

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