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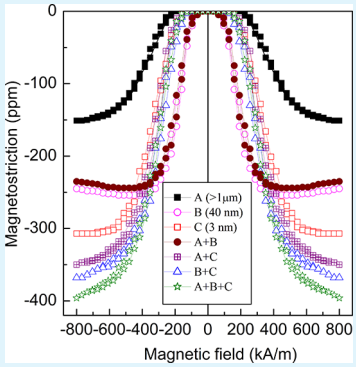
Enhancement in the Magnetostriction of Sintered Cobalt Ferrite by Making Self-Composites from Nanocrystalline and Bulk Powders

Kamal Khaja Mohaideen and Pattayil Alias Joy*

Physical and Materials Chemistry Division, National Chemical Laboratory, Pune 411008, India

Supporting Information

ABSTRACT: Sintered polycrystalline cobalt ferrite is a potential magnetostrictive smart material for applications as sensors and actuators. A novel concept of enhancing the magnetostrictive strain of sintered cobalt ferrite by making self-composites from nanosized and bulk powders with different particle sizes of the same material as components is reported. The self-composites give higher magnetostriction coefficient and strain derivative when compared to the sintered products obtained from the individual powders. The individual components give a maximum magnetostriction up to ~310 ppm, whereas up to ~370 ppm is obtained for a two-component system consisting of powders of two different sizes. On the other hand, a three-component self-composite made from starting powders of 3 nm, 40 nm and >1 μm give very high magnetostriction of ~400 ppm at 800 kA/m, suitable for making devices.



KEYWORDS: *magnetostriction, self-composite, cobalt ferrite, nanocrystalline, sintering*

INTRODUCTION

Magnetostriction is the change in the dimensions of a magnetic material in an external applied magnetic field.[1] Magnetostrictive smart materials can convert energy between the mechanical and the magnetic states and therefore, are used as sensors and actuators for various domestic and strategic applications.[2,3] Terfenol-D, an alloy of Tb, Dy, and Fe with the composition $Tb_{0.3}Dy_{1.7}Fe_2$ and magnetostriction up to 2000 ppm at room temperature in a magnetic field of 200 kA/m, developed by Naval Ordanance Laboratory, USA, in 1975,[4] is the most commonly used magnetostrictive material today for various applications. However, this material has limitations such as the high cost of Tb and Dy, requirement of single crystals for applications, high cost of production of single crystals, poor mechanical properties, etc. Oxide-based materials are suitable alternatives and among the various oxides, spinel type cobalt ferrite is the only oxide material exhibiting sufficiently large magnetostriction at room temperature.[5] Therefore, cobalt ferrite is proposed as an economical and viable alternative material to Terfenol-D.[6−10] Sintered polycrystalline cobalt ferrite is a feasible substitute for magnetostrictive applications over the currently used single crystals of Terfenol-D-based alloys, because of various advantages such as low cost, high mechanical stability, better coupling coefficient, low thermal conductivity, high electrical resistance, excellent corrosion resistance, and sufficiently large magnetostriction.

For sintered cobalt ferrite derived from bulk powders obtained by the ceramic method of synthesis and under simple processing conditions, so far at room temperature a maximum magnetostriction (λ) value of ~230 ppm is reported,[8] compared to the obtained magnetostriction constant (λ_{100}) of 500−600 ppm for single crystals.[11] A high maximum magnetostriction value of about ~400 ppm is reported recently for cobalt ferrite sintered after isostatically compacting the pellets at a very high pressure of ~150 MPa, sintering at 1350 °C for 24 h, and magnetic field annealing in a field of 8000 kA/m at 300 °C for 3 h.[12] Before magnetic field annealing, the maximum magnetostriction obtained was less than 200 ppm for the same pressure applied while making pellets. Apart from the magnitude of magnetostriction, the slope of the magnetostriction or strain derivative ($d\lambda/dH$) which is a measure of the magnetomechanical coupling factor is also an important factor for various applications as sensors and actuators.[9] Stress sensing applications require large magnetomechanical effect and high sensitivity to stress.[10] The use of cobalt ferrite as an alternate material for various applications is limited by the low value of magnetostriction and strain derivative obtained under simple processing conditions. Therefore, it is essential to increase the magnetostriction coefficient of sintered polycrystalline cobalt ferrite by suitable processing so that currently used expensive single crystals of Terfenol-D can be replaced by cheaper polycrystalline sintered cobalt ferrite having many other advantages. Enhancing the performance parameters of existing smart materials by following simple and novel processing techniques is always a matter of interest due to various advantages. Equally important factor is that the sintered material with high magnetostriction should be produced under simple processing conditions. There have been many

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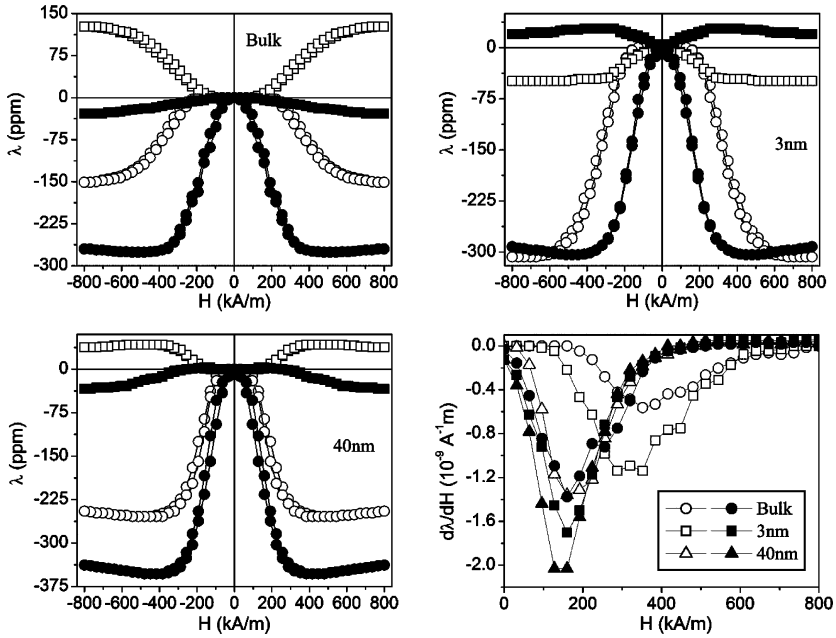

Figure 1. Magnetostriction of the individual components bulk, 3 nm, and 40 nm, as a function of magnetic field, measured parallel (circles) and perpendicular (squares) to the applied magnetic field before (open symbols) and after annealing in a field of 400 kA/m (closed symbols) and field derivative of magnetostriction along the parallel direction for the different samples.

studies in the recent past to enhance the magnetostriction coefficient and strain derivative of cobalt ferite by changing the processing conditions, magnetic field annealing, and by suitable substition at the Co and Fe sites.[6−10,12−24]

It has been reported that higher magnetostriction coefficient can be obtained if cobalt ferrite is sintered from nanocrystalline powders compared to the material derived from bulk powders.[23,24] In this communication, we show that much higher values of the magnetostriction coefficient can be obtained for sintered polycrystalline cobalt ferrite by a novel concept and simple process of making self-composites obtained by sintering a physical mixture of nanosized and micrometer sized particles of cobalt ferrite with different sizes. The self-composites made from nanosized particles and micrometer sized particles as starting materials show enhanced magnetostriction up to ∼400 ppm, without any magnetic field annealing and compacted under very low hydrostatic pressures. Also, there is a huge increment of the strain derivative for the self-composite. The self-composites are prepared with two components (mixture of powders with smaller and larger particles) as well as with three components (small, medium size and larger size particles). The highest magnetostriction of ∼400 ppm is obtained for a three component self-composite without any magnetic field annealing. Usually the maximum in the magnetostriction of sintered cobalt ferrite is reached at a magnetic field of 400 kA/m. However, in the case of the three-component self-composites, the maximum in the magnetostriction was not achieved even at the highest field of measurement (800 kA/m) indicating that there is further scope for improving the magnetostriction values at higher magnetic fields.

EXPERIMENTAL SECTION

Nanocrystalline cobalt ferrite was synthesized following the glycine-nitrate autocombustion process using the corresponding metal nitrates as the oxidizer and glycine as the fuel.[25] The particle size of cobalt ferrite powders synthesized by this method was varied by changing the fuel to oxidizer ratio in the combustion synthesis, as reported previously.[26] Lower particle size was obtained by using smaller glycine to nitrate (G/N) ratios. Stoichiometric amounts of AR grade cobalt nitrate, $Co(NO_3)_2{\cdot}6H_2O$, and ferric nitrate, $Fe(NO_3)_3{\cdot}9H_2O$, taken in the 1:2 molar ratio, were dissolved separately in minimum amounts of distilled water. Glycine, corresponding to the required G/N ratio was also dissolved separately in minimum amount of distilled water. All the three solutions were mixed thoroughly by ultrasonicating for 2 min. The mixed solution was then transferred to a crystallizing dish and the dish with its contents was subjected to heating on a hot plate at a temperature of about 200 °C. After complete evaporation of water, the resulting viscous liquid ignited automatically giving rise to a fluffy mass. This procedure was repeated for two different G/N ratios to get cobalt ferrite particles of different sizes. Bulk cobalt ferrite with particles of size >1 μm was obtained by the ceramic method of synthesis, as reported previously.[13] The cobalt ferrite self-composites were prepared by thoroughly mixing powders of cobalt ferrite with differently sized particles (very small, medium, and larger size particles). Individual components and the mixtures were compacted by cold uniaxial pressing the powders in cylindrical form at a pressure of 8 MPa. The resulting compacts were sintered at 1450 °C for 10 min, to obtain sintered cylindrical discs of size ∼7 mm dia × ∼10 mm length.

The as-synthesized powder samples were characterized for phase purity by powder X-ray diffraction (XRD) using Cu Kα radiation (Panalytical X'pert Pro). Magnetic measurements (DC magnetization measurements as a function of magnetic field in the range ±1200 kA/m at room temperature and as a function of temperature in a magnetic field of 8 kA/m in the temperature range 30−600 °C) were made on a vibrating sample magnetometer (model EG&G PAR 4500). Densities of the sintered discs were calculated from the volume and the weight of the discs as well as by the Archimedes method. Both methods gave comparable values of the densities. The relative density was calculated from the ratio of the measured density to the theoretical density calculated from the crystal structure parameters. Magnetostriction, $\lambda = \Delta L/L$, the relative change in the length of the sample in an applied magnetic field, was measured on the sintered pellets at room temperature using 350 Ω resistive strain gauges.[24] λ_{par} is the magnetostriction measured when the applied external magnetic field is parallel to the cylindrical axis of the sintered pellet and λ_{per} is for the magnetic field applied perpendicular to this direction. Magnetic field

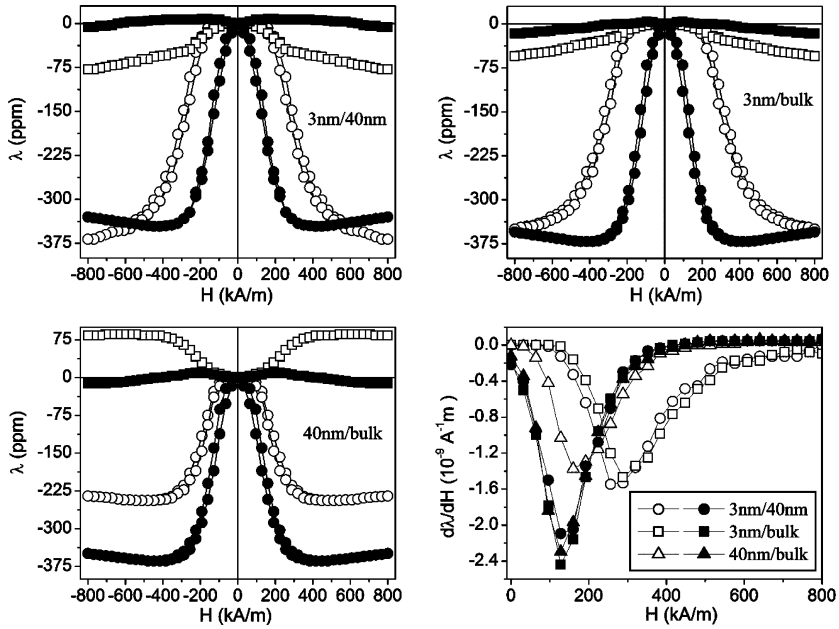

Figure 2. Magnetostriction of the two-component self-composites 3 nm/40 nm, 3 nm/bulk and 40 nm/bulk, as a function of magnetic field, measured parallel (circles) and perpendicular (squares) to the applied magnetic field before (open symbols) and after annealing in a field of 400 kA/m (closed symbols) and field derivative of magnetostriction along the parallel direction for the different composites.

annealing of the sintered pellets was carried out at 300 °C in a magnetic field of 400 kA/m for 30 min. The annealing field was applied perpendicular to the cylindrical axis of the sintered pellet which is perpendicular to the measurement direction as well as the direction of the measuring field in the case of λ_{par}.

RESULTS AND DISCUSSION

Nanoparticles of ∼3 nm size were obtained using G/N = 0.38 (sample code G1) and larger particles of ∼40 nm were obtained using G/N = 0.25 (sample code G2). Micron sized particles were obtained by the ceramic method of synthesis (sample code G0). Average crystallite size of G1 and G2 were calculated as 3 and 40 nm, respectively, from the widths of the peaks in the powder XRD patterns using the Scherrer formula $D = 0.9\,\lambda/\beta\cos\theta$, where D is the crystallite size in nm, λ is the wavelength of X-rays, β is the full width at half-maximum of the peaks corrected for instrumental contribution to line broadening, and θ is the Bragg angle.[24] The particle sizes were obtained from TEM images for G1 and G2 and from SEM image for G0 (see Figure S1 in the Supporting Information) and it was found that the calculated average crystallite sizes are comparable to the particle sizes obtained from TEM. Composites with two components were obtained by mixing the powders of G1 with G0 (sample code 3 nm/bulk), G2 with G0 (sample code 40 nm/bulk), and G1 with G2 (sample code 3 nm/40 nm) in the ratio of 80:20 by weight. Similarly, a three component composite was made by mixing G1, G2, and G0 in the ratio 80:10:10 by weight (sample code 3 nm/40 nm/bulk).

Sintered density is obtained as 89% for G0 (bulk), whereas for all other samples, the densities are around 80%. All the sintered samples were characterized by magnetic measurements (as a function of magnetic field at room temperature and as a function of temperature). The Curie temperature of the ceramic sample (bulk) is obtained as 520 °C. For all other samples, the Curie temperatures are obtained in the range 520 ± 5 °C, indicating almost comparable cation distribution in the tetrahedral and octahedral sites of the spinel lattice. Similarly, the saturation magnetizations of all sintered samples are almost comparable (80 ± 2 emu/g). The magnetic characteristics of different samples are compared in Table S1 (see the Supporting Information).

Figure 1 shows the room-temperature magnetostriction curves of the sintered samples 3 nm, 40 nm and bulk (made from the powder samples G1, G2, and G0, respectively), recorded up to a maximum magnetic field strength of 800 kA/m, in the parallel (λ_{par}) and perpendicular (λ_{per}) directions to the applied magnetic field, before and after annealing in a magnetic field. The magnetostrictive strain is negative along the parallel direction and the maximum strain value of ∼310 ppm is achieved for the sample 3 nm. The maximum value of magnetostriction is found to be strongly depends on the particle size of the starting powders. Sample 3 nm with the smallest particle size for the starting powder (3 nm) shows a maximum magnetostriction of 307 ppm, followed by sample 40 nm (254 ppm, starting particle size 40 nm) and then bulk (151 ppm, starting particle size >1 μm).

Magnetic field annealing has been shown to be very effective in enhancing the magnetostriction coefficient and strain derivative of cobalt ferrite due to the induced easy axis direction parallel to the annealing field, which affects magnetization processes and domain configuration.[10,12,16] Higher magnetostriction coefficient perpendicular to the direction of the annealing field can be achieved by magnetic field annealing because of the reorientation of the domains along the measurement direction. However, in the present case, there is no change in the maximum magnetostriction after field annealing of sample 3 nm, whereas 39 and 83% increases are observed for samples 40 nm and bulk, respectively. Similarly, about 50% increase in the strain derivative at low fields is observed after magnetic field annealing for samples 3 nm and 40 nm whereas 150% increase is observed for bulk, as shown in the Figure 1 and Table S1 (Supporting Information). These observations show that magnetic field annealing is effective in

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enhancing the magnetostriction and strain derivative for samples sintered from larger particles.

As shown in Figure 2, among the different combination of two-component self-composite samples (3 nm/40 nm, 3 nm/bulk and 40 nm/bulk), the 3 nm/40 nm and 3 nm/bulk self-composites show higher maximum magnetostriction values of 368 ppm and 350 ppm, respectively, without magnetic field annealing. On the other hand, the highest value of magnetostriction obtained for the individual components is 307 ppm for sample 3 nm (Figure 1 and Table S1 in the Supporting Information). For the self-composite 40 nm/bulk, the magnetostriction obtained is comparable to that for the sample 40 nm alone. Even though the sample 40 nm/bulk shows relatively lower maximum magnetostriction (245 ppm), higher magnetostriction value of 364 ppm is obtained after magnetic field annealing, comparable to the values obtained for the other two composites (~346 and 371 ppm, respectively, for 3 nm/40 nm and 3 nm/bulk). Also, unlike in the case of the individual components 40 nm and bulk, there is not much improvement in the magnetostriction of 3 nm/40 nm and 3 nm/bulk samples after magnetic field annealing, apart from the increase in the strain derivative. An important observation is that, whereever very small particles are used for the composites, higher magnetostriction is obtained with out magnetic field annealing. This shows that making the self-composites using smaller and larger particles of the same material is advantageous over magnetic field annealing.

When the self-composite is made from three starting powders of different particle sizes (3 nm/40 nm/bulk), a very high maximum magnetostrictive strain of ~400 ppm is obtained without any magnetic field annealing. Figure 3 shows the magnetostriction and strain derivative of the three-component system before and after field annealing. In fact, the maximum magnetostriction is reduced considerably (9%) for this composite after field annealing whereas the low-field magnetostriction is considerably increased without any major change in the strain derivative. The obtained highest value of magnetostrictive strain of ~400 ppm is almost closer to the values reported for single crystals of cobalt ferrite and double the value reported for sintered polycrystalline cobalt ferrite samples produced from larger particles.

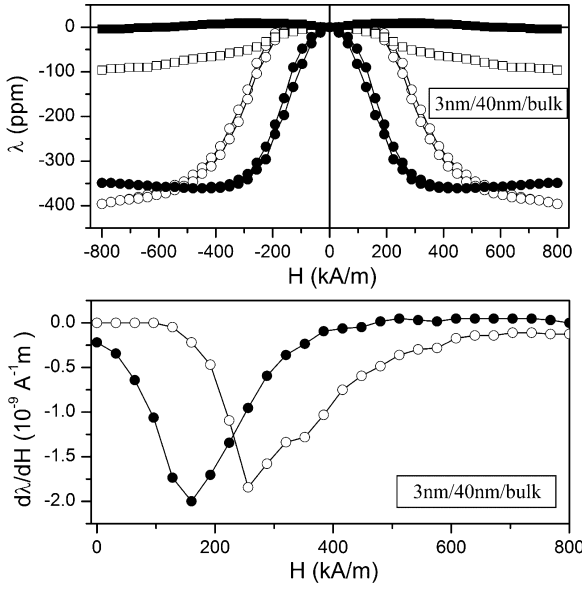

Figure 3. Magnetostriction of the three-component self-composite 3 nm/40 nm/bulk as a function of magnetic field, measured parallel (circles) and perpendicular (squares) to the applied magnetic field before (open symbols) and after annealing in a field of 400 kA/m (closed symbols) and field derivative of magnetostriction along the parallel direction.

The individual components G1 (3 nm), G2 (40 nm), and G0 (>1 μm) with different particle sizes in the increasing order after sintering give maximum values of magnetostriction of 307, 254, and 151 ppm, respectively indicating that the value of maximum magnetostriction decreases with increasing particle size of the starting powders (see Table S1 in the Supporting Information). On the other hand, the two-components systems give a maximum magnetostriction around 350−370 ppm when G1 with the smallest particle size of 3 nm is made in to a composite with larger particles and this value is enhanced to ~400 ppm for the sintered material derived from the three-component mixture (see Table S1 in the Supporting Information).

The effect of magnetic field annealing is to increase the magnetostriction at low fields for all samples. As mentioned, apart from the magnitude of magnetostriction, the slope of the magnetostriction ($d\lambda/dH$) or the magnetomechanical coupling factor is also an important factor for stress sensing applications. The strain derivative ($d\lambda/dH$) for different samples with applied magnetic field, before magnetic annealing shows that the highest value of strain derivative 2.0×10^{-9} A^{-1} m is obtained in the case of the three-component sample, which is higher than the previously reported values. After magnetic field annealing, all the self-composites show higher strain derivative of $2.0-2.4 \times 10^{-9}$ A^{-1}m.

From a comparison of the magnitude of maximum magnetostriction and strain derivative of the individual components and composites, it is found that when the 3 nm particles are used for compaction, the magnetostriction is not changed much whereas large changes are observed when larger particles are used (separately or in composites), after magnetic field annealing. Also, there is not much correlation between the changes in the magnitude of maximum magnetostriction and the strain derivative, except that magnetostriction at low fields is enhanced after annealing and maximum strain derivative is obtined at lower magnetic fields. This shows that the induced uniaxial anisotropy and the associated changes in the magnetization processes and domain configuration, as reported previously,[10,12,16] alone is not sufficient to explain the changes in the value of magnetostriction and strain derivative. A major observation is that the changes in the magnetostriction is very small after magnetic field annealing when the smallest particles (3 nm) are used while making the compacts. In fact, a decrease in the magnetostriction is observed for the three samples 3 nm (−1%), 3 nm/40 nm (−6%), 3 nm/40 nm/bulk (−9%). On the other hand, some increase in the strain derivative is observed for the first two samples. These unusual changes on magnetic annealing is likely to be coupled with the induced anisotropy as well as the microstructure, because the induced anisotropy can also be affected by the size, shape and orientation of the grains in the sintered samples. Eventhough there is not much difference in the microstructure of the different samples (see Figure S2 in the Supporting Information), there are some smaller grains present in the images of the composites prepared using the 3 nm particles, which could be the deciding factor for the changes in the magnetostriction and strain derivative of the composites. It is

possible that most of the domains in the smaller grains are aligned away from the direction of the measuring field so that there is not much effect of reorienting the domains after field annealing. Another possibility is that, if the direction of magnetization is already aligned in random directions in the smaller grains and is not influenced by magnetic field annealing, contribution from these smaller grains toward magnetostriction will not be influenced on field annealing. Similar effects may be the reasons for the unusual changes in the strain derivative also. However, these observations need to be verified by further detailed studies.

CONCLUSIONS

In conclusion, it has been shown that very high magnetostriction at room temperature can be achieved for polycrystalline sintered cobalt ferrite if compacts are made in to the form of a self-composite where the components in the composites are nano and micrometer sized powders of the same material. Larger maximum magnetostriction of ~400 ppm and maximum value of strain derivative of 2.0×10^{-9} A^{-1} m could be achieved for a self-composite made from powder particles of three different sizes in the nano and micrometer levels, whereas the individual components gave values less than 310 ppm. Unlike for the individual components, the magnetostriction is not saturated at the highest measuring field of 800 kA/m for the three-component composite, indicating that it is further possible to improve the magnetostriction of sintered cobalt ferrite at higher fields. Also, in the case of the composites, higher magnetostriction can be achieved with out any magnetic field annealing, thereby reducing the processing cost for various applications.

ASSOCIATED CONTENT

Supporting Information

Magnetic and magnetostrictive parameters of the sintered individual components and the self-composites of cobalt ferrite (Table S1), TEM and SEM images of the powder samples showing the particle size (Figure S1), SEM images of the different sintered samples (Figure S2), comparison of the magnetostriction (λ_{par}) of the individual components and self-composites before magnetic field annealing (Figure S3) and after magnetic field annealing (Figure S4). This material is available free of charge via the Internet at http://pubs.acs.org/.

AUTHOR INFORMATION

Corresponding Author

*E-mail: pa.joy@ncl.res.in.

Notes

The authors declare no competing financial interest.

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