Chapter 7

Conclusions and Future Perspectives

Magnetostrictive materials for sensors and actuators have been of great interest because of their variety of applications in the automobile, aerospace, domestic and medical industries such as position sensing, vibration control, stress sensing, magnetostrictive filters etc. Terfenol-D, which is an alloy containing the rare earth elements terbium and dysprosium along with iron, D is the currently available magnetostrictive material showing high magnetostrictive strain around 1500 ppm at a relatively low magnetic fields. However, this magnetostrictive material has several limitations and disadvantages including the high cost of the rare earth elements, high brittleness, requirement of single crystals for applications and therefore, the high production cost, etc. Furthermore, the material generates much greater response only when it is subjected to compressive loads, and the power requirement for this class of actuators is greater than those for piezoelectric materials. Therefore, the material is currently used only for strategic applications.

Ceramic oxide based magnetic materials are suitable cheaper alternatives over the currently used alloy-based materials for various applications. Among the different ceramic magnetic oxides, cobalt ferrite, CoFe$_2$O$_4$, is known for its high magnetostriction of 600 ppm for single crystals. In addition, this material is very cheap, has good mechanical hardness, chemical stability and can be processed into various shapes and sizes. There have been many attempts to make sintered polycrystalline cobalt ferrite with high magnetostriction at very low magnetic fields. So far only a magnetostriction value of 230 ppm and strain derivative of $1.3 \times 10^{-9}$ A$^{-1}$m is attained for sintered cobalt ferrite,
derived by simple processing conditions. It is necessary to achieve relatively large magnetostrictive strain as well as high strain derivative at room temperature for polycrystalline cobalt ferrite for use in various applications which can replace the costly Terfenol-D. The magnetostriction coefficient ($\lambda$) and strain derivative ($d\lambda/dH$) of sintered cobalt ferrite is known to depend on the processing parameters such as the method of synthesis, pressure applied while making the compacts for sintering, sintering atmosphere, temperature, and duration of sintering as well as on the microstructure. So far, there have been no attempts to study the effect of nanocrystalline cobalt ferrite powders as starting materials and the initial particle size on the magnetostriction coefficient. Similarly, there are no studies so far reported on the effect of method of synthesis and sintering conditions on the compacts derived from nanocrystalline materials. In the present work, we have studied the magnetostriction characterization of this material by changing the synthesis and processing conditions.

Nanocrystalline cobalt ferrite of varying particle size is synthesized by autocombustion method, using glycine as a fuel, to study the effect of initial particle size of the powders on the ultimate value of magnetostriction after sintering. The results showed that high values of the magnetostriction coefficient of 315 ppm and strain derivative of $1.97 \times 10^{-9}$ A$^{-1}$m are obtained for sintered compacts derived from particles of 4 nm obtained from the autocombustion method and sintered at 1450 °C for 10 minutes. The initial particle size is found to be one of the deciding factor the magnetostrictive behavior of cobalt ferrite. Nanocrystalline cobalt ferrite powders were also synthesized by co-precipitation and citrate methods in order to confirm the correlation between initial particle size and magnetostriction of sintered cobalt ferrite. However, comparison of the effect of the initial particle size derived from the three different methods of synthesis indicated that particle size alone is not the deciding factor for the high values of magnetostriction. Some correlation is observed when the microstructures and densities of the different samples are compared with the values of magnetostriction for the powders derived from the autocombustion method. The observed high magnetostriction value of 315 ppm is further improved to 345 ppm by using
magnetic field annealing at room temperature. Higher magnetostriction is achieved at lower magnetic field after field annealing. These are the highest values reported so far for sintered polycrystalline cobalt ferrite obtained under simple processing conditions.

To study the effect of sintering temperature on magnetostriction, single-stage as well as double-stage sintering studies have been performed. It was found that highest magnetostriction value of 315 ppm is obtained after sintering at 1450 °C under single-stage sintering conditions and the changes in the value of magnetostriction are somewhat correlated with the microstructure. In the case of double-stage sintering, grain size remains constant while density continuously increases, unlike in normal sintering in which final stage densification is always accompanied by rapid grain growth. Out of all the experiments, magnitude of magnetostriction value of 331 ppm is achieved for the sample sintered by the double-stage sintering method at 1450 °C (T₁) as the higher temperature and then at 1300 °C (T₂) as the lower temperature. It has been found that under suitable two stage sintering conditions, high value of magnetostriction of 331 ppm and strain derivative of $1.8 \times 10^{-9}$ A$^{-1}$m can be achieved. Magnetic field annealing has been shown to be very effective in enhancing the magnetostriction and strain derivative of single and two-stage sintered cobalt ferrite samples. Especially, the sample sintered at a low temperature of 1200 °C showed huge increment of magnetostriction as well as strain derivative compared to the two-stage sintered samples after magnetic field annealing. Thus, from the present study it is concluded that there is not much advantages on the two-stage sintering process over single stage sintering for getting higher magnetostriction and strain derivative for sintered cobalt ferrite.

For the first time, we have shown that much higher values of the magnetostriction coefficient can be obtained for sintered polycrystalline cobalt ferrite by making self-composites obtained by sintering a physical mixture of cobalt ferrite powders with different initial particle sizes. Larger maximum value of magnetostriction of $\sim$400 ppm and maximum value of strain derivative of $2.0 \times 10^{-9}$ A$^{-1}$m could be achieved for a self-composite made from powders of three different particle 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, it was found that annealing in a magnetic field reduces the magnetostriction coefficient. Thus, in the case of the self-composites, higher magnetostriction can be achieved without any magnetic field annealing, thereby reducing the processing cost for various applications.

Mn substitution is reported to be very effective in enhancing the strain derivative at the cost of the magnetostriction coefficient. Since higher magnetostriction coefficient and strain derivative could be attained for the sintered unsubstituted material derived from nanocrystalline powders, studies were made on Mn substituted cobalt ferrite powders of particle size 4 nm. The magnetic and magnetostrictive properties of Mn substituted cobalt ferrite, CoFe$_{2-x}$Mn$_x$O$_4$ and Co$_x$Mn$_{1-x}$Fe$_2$O$_4$, for $x$ varying from 0 to 0.3 in steps of 0.05, derived from nanocrystalline powders of size 4 nm, have been investigated. The magnetostriction coefficient as well as the strain derivative is found to be largely affected on substitution of Mn for Co. However, magnetostriction and strain derivative is not much affected when Fe is partially replaced by Mn. The field at which highest magnetostriction value is obtained is shifted to lower values for Mn substituted compositions. For CoFe$_{1.8}$Mn$_{0.2}$O$_4$, magnetostriction in the parallel direction is found to be comparable to that of unsubstituted cobalt ferrite with enhanced strain derivative when sintered at 1300 °C. This is the first such report of comparable magnetostriction values for unsubstituted and Mn substituted cobalt ferrite. Maximum value of magnetostriction and strain derivative is further increased after magnetic field annealing of CoFe$_{1.8}$Mn$_{0.2}$O$_4$. The present value of 262 ppm is the highest value of magnetostriction coefficient reported till date for Mn substituted cobalt ferrite, suitable for various applications.
Scope for future research

Based on the findings from the present studies on nanocrystalline powders, there is scope for further studies to improve the magnetostriction coefficient and strain derivative of sintered cobalt ferrite. Sintered samples derived from the auto-combustion method using glycine as the fuel is found to give very high magnetostriction coefficient and strain derivative compared to literature reports. Studies can be performed using other fuels which may control the surface characteristics of the nanoparticles because of the varying combustion characteristics of different fuels, and this may affect the properties of the sintered products. Similarly, a systematic study of the magnetostriction of sintered products derived from nanocrystalline powders of varying sizes synthesized by different wet chemical methods are required to optimize the best method of synthesis to attain the highest magnetostriction coefficient as well as strain derivative. Since the studies showed that the magnetostrictive properties are correlated with the microstructure of the sintered materials, a systematic study is required on low-temperature sintering and to achieve a suitable microstructure and for understanding the effect of grain size and morphology on magnetostrictive properties. Sintering at low temperatures is possible if the material is synthesized in nanocrystalline form and this can be effective for reducing the processing cost. The sintered materials are found to contain large number of intra-grain pores. These intra-grain and inter-grain pores might be detrimental to the desired properties, which needs to be investigated thoroughly. Similarly, it might be possible to achieve much higher magnetostrictive strains for the sintered products by controlling the grain size by optimizing the processing conditions such as sintering time and addition of sintering aids. Self-composites prepared by mixing nanocrystalline powders of different sizes obtained from different methods of synthesis may be efficient in improving the magnetostriction parameters. Finally, other important factors that need to be considered are the similar studies on substituted cobalt ferrite by replacing Fe by other elements. Enhancing the magnetostriction coefficient of sintered cobalt ferrite up to 500 ppm with high strain derivative may be an achievable target.