DESIGN, PROCESSING AND CHARACTERIZATION OF MECHANICALLY ALLOYED Galfenol & LIGHTLY RARE-EARTH DOPED FEGA ALLOYS AS SMART MATERIALS FOR ACTUATORS AND TRANSDUCERS

A Dissertation Presented

By

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ABSTRACT

Smart materials find a wide range of application areas due to their varied response to external stimuli [1–3]. The different areas of application can be in our day to day life, aerospace, civil engineering applications [4], and mechatronics [5] to name a few. Magnetostrictive materials are a class of smart materials that can convert energy between the magnetic and elastic states [2,6]. Galfenol is a magnetostrictive alloy comprised primarily of the elements iron (Fe) and gallium (Ga) [7]. Galfenol exhibits a unique combination of mechanical and magnetostrictive (magnetic) properties that legacy smart materials do not [8,9]. Galfenol’s ability to function while in tension, mechanical robustness and high Curie temperature (600 °C) is attracting interest for the alloy’s use in mechanically harsh and elevated temperature environments. Applications actively being investigated include transducers for down-hole use [10,11], next generation fuel injectors, sensing and energy harvesting devices [2].

Understanding correlations between microstructure, electronic structure and functional response is key to developing novel magnetostrictive materials for sensor and actuator technologies.

To this end, in the first part of this thesis we report successful fabrication and investigation on magnetic and magnetostrictive properties of mechanically alloyed Fe₈₁Ga₁₉ compounds. For the first time we could measure magnetostrictive properties of mechanically alloyed FeGa compounds. A maximum saturation magnetostriction of 41 ppm was achieved which is comparable to those measured from polycrystalline FeGa alloys prepared by other processing techniques, namely gas atomization and cold rolling. Overall, this study demonstrates the feasibility of large-scale production of FeGa
polycrystalline alloys powders by a simple and cost-effective mechanical alloying technique.

In the second part of this work, we report for the first time, experimental results pertaining to successful fabrication and advanced characterization of a series of Er/Gd-doped [110]-textured polycrystalline alloys of nominal composition, Fe$_{83}$Ga$_{17}$Er$_x$ (0$<x<$1.5) and Fe$_{83}$Ga$_{17}$Gd$_x$ (0$<x<$1). Experiments indicate an enhancement of more than $\sim$275 % from $\sim$45 ppm to 170 ppm for Er doped Galfenol and $\sim$160 % from $\sim$45 ppm to 120 ppm in the saturation magnetostriction ($\lambda_s$) of Fe$_{83}$Ga$_{17}$ alloys with the introduction of small amounts of Er and Gd. Moreover, it is noted that the low field derivative of magnetostriction with respect to applied magnetic field ($i.e.$ $d\lambda_s/dH_{app}$ for $H_{app}$ up to 1000 Oe) increases by $\sim$230 % with Er doping ($d\lambda_s/dH_{app,FeGa} = 0.045$ ppm/Oe ; $d\lambda_s/dH_{app,FeGaEr} = 0.15$ ppm/Oe). The origin of the enhanced magnetostrictive response in this materials system is discussed. Overall, this work provides guidelines to further improving FeGa alloys for potential sensor and actuators applications in multiferroic devices, particularly in harsh environments.

The goal of this project is 1) Developing new synthesis techniques including mechanical alloying for fabricating FeGa alloys and 2) To develop rare earth doped FeGa alloys with focus in Er and Gd as rare-earth which have a much lower price compared with the heavy rare earth magnetostrictive materials and are easier to use in harsh mechanical environments.
AUTHOR’S BIO

Parisa Taheri received her BSc and MSc degrees in Electrical Engineering from University of Guilan and Azad University of Tehran in 2003 and 2008 respectively. She joined Northeastern University in 2011 as a PhD student. Since then, she has been an applied researcher at the Center for Microwave Magnetic Materials & Integrated Circuits (CM3IC) on smart materials and permanent magnets of key social importance. She has been conducting research on Rare-Earth-free permanent magnetic materials for alternative energy technologies, as well as, magnetostrictive materials whose shapes depend on applied magnetic fields.

Coming from an interdisciplinary background, which includes past experience in radio frequency materials and electrical devices, she is able to examine complicated problems in Electrical Engineering and material science and find the most efficient and innovative solution. Her main research interests are magnetic materials, Nanotechnology and Semiconductor physics.

Parisa is also a GEL (Gordon Engineering Leader) Fellow, class of 2016 at Northeastern University. GEL fellowship’s mission is to train the emerging leaders of engineering breakthroughs of tomorrow.
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1 CHAPTER 1 INTRODUCTION

1.1. Overview

Smart materials are specialty-building materials whose properties tend to vary when subjected to external stimuli such as stress, temperature, moisture, pH, and magnetic field [1–3]. These materials are called smart materials because of the change inherent in them, and not due to an external force. Magnetostrictive materials are one of the most important part of smart materials which their shape is change during the process of magnetization [2,6]. Magnetostrictive materials have been on the market since World War II and serve a large number of applications mostly in actuators [12] (where a magnetic field is applied to cause a shape change) and sensors (which convert a movement into a magnetic field).

Functional materials systems that demonstrate large magnetostriction play an important role in a wide array of commercial applications ranging from acoustic sensors and linear actuators to electromechanical energy harvesters and sonar transducers. [13–16] One of the most successful magnetostrictive materials hitherto is the rare-earth compound, (Dy$_{0.7}$Tb$_{0.3}$)Fe$_2$ (also known as Terfenol D). [17] These alloys demonstrate a cubic C15 laves crystal structure and exhibit large room temperature magnetic-field-induced strains up to 2000 ppm (parts per million). [18] It is well known that Terfenol D has several major drawbacks that constrains its use in commercial devices to: (i) high cost and global shortage of the rare-earth elements, Tb and Dy; [19] (2) low mechanical integrity (high brittleness, low yield stress, low magneto-mechanical coupling) [20] and
To this end, a promising alternative to (Dy$_{0.7}$Tb$_{0.3}$)Fe$_2$ is the rare-earth-free, inexpensive, corrosion resistant Fe$_{1-x}$Ga$_x$ alloy (commercially known as Galfenol) that exhibits moderate magnetostriction (up to ~400 ppm) under very low magnetic field ~100 Oe [21,22] and high tensile strength ~500 MPa with limited variation in the temperature range of -20 to 80 $^\circ$C [21].

An intriguing characteristic of Fe$_{1-x}$Ga$_x$ is that its functional response is closely correlated with its microstructural and crystallographic properties [23]. The binary phase diagram of Fe$_{1-x}$Ga$_x$ indicates that the single phase terminal solid solution that possesses a chemically disordered body-centered cubic (bcc) crystal structure extends to Ga concentrations of 11 at.% at room temperature and as much as 35 at% of Ga at 1050 $^\circ$C. [24] In the composition range, ~27-28 at% Ga, the alloy exists as Fe$_3$Ga and exhibits a chemically tetragonal L1$_2$ crystal structure that undergoes polymorphic transformations to the ordered hexagonal D0$_{19}$ and cubic D0$_3$ phase upon heating. [25,26] Further, a B2 ordered cubic phase variant is also noted at high temperatures for compositions exceeding 32 at% Ga. [21] Depending upon the sample synthesis and processing technique employed, significant amounts of Ga (well in excess of the solubility limit) can be retained in metastable disordered bcc solid solution at room temperature. [21,26] High magnetostriction values ranging from 250 to 400 ppm have been reported in single crystals of bcc alloys of Fe$_{1-x}$Ga$_x$, where x ranges from 15 to 25. [27]

Over the last twenty years, attempts have been made to improve the magnetostrictive response of galfenol by addition of a wide variety of elements into its crystal lattice. [28–32] In almost all cases, ternary additions of 3d and 4d transition metals (V, Cr, Mn, Co, Ni, Rh, Mo) decreases the magnetostriction values, relative to that
of the parent binary FeGa alloy. [33,34] Conversely, trace amounts of small interstitial atoms (C, B or N) have a slight but favorable effect on the magnetostriction of FeGa, particularly at high atomic compositions of Ga. [29] To date, limited work has been performed on rare-earth doped FeGa systems. Recent studies indicate that the magnetostriction coefficient ($\lambda$) of FeGa alloys can be significantly increased (up to a 3 times enhancement), by adding small amounts (<0.5 at %) of the rare-earth elements, Tb, Dy, Ce or Y. [35–38] To add to the FeGa literature, here we present for the first time, an experimental study that aims at investigating the crystallographic, microstructural, magnetic and magnetostrictive properties of a series of Er-doped as well as Gd-doped polycrystalline alloys of composition, \((Fe_{83}Ga_{17})_{100-x}Er_x\) \((0<x<1.2)\) and \((Fe_{83}Ga_{17})_{100-x}Gd_x\) \((0<x<1)\). Results obtained in this research effort represents an exceptional ~275 % increase in the magnetostriction coefficient of [110]-textured \((Fe_{83}Ga_{17})_{100-x}Er_x\) alloys as well as ~160 % increase in the magnetostriction coefficient of [110]-textured \((Fe_{83}Ga_{17})_{100-x}Gd_x\) alloys. The origin of the enhanced magnetostrictive effect in this materials system is discussed in the context of the microstructure as well as the electronic structure of samples. Overall, this work provides pathways for tailoring the functional response of FeGa alloys.
1.2. Objectives of Research

The goal of this research work is to design, Processing and Characterization of FeGa alloys for actuators and transducers applications. We have had two different approaches regarding tuning the magnetostrictive behavior of FeGa alloys:

1.2.1 Approach 1: Investigating innovative sample fabrication methods (mechanical alloying)

As the first approach regarding making FeGa alloys using novel fabrication techniques we could make Galfenol alloys with the mechanical alloying technique using high energy ball mill. In that work, structure-magnetic property correlations and the magnetostrictive response of mechanically alloyed powders of composition $\text{Fe}_8\text{Ga}_{19}$ were investigated using a variety of structural and magnetic probes. Mechanical alloying, which is capable of producing micro- and Nano crystalline alloy powders, has the added advantage that it involves fewer processing steps and does not require the use of expensive instrumentation, unlike most other fabrication techniques. More details will be discussed in the next chapters.

1.2.2 Approach 2: Investigating the influence of rare earth doping on the magnetostrictive performance of Directionally FeGa Solidified Alloys

A lot of research has been done on transition and main group elements doped in FeGa compounds and most of them have led to either decreasing FeGa magnetostriction
properties or the magnetostriction properties remained unchanged. Very little studies have been done on rare-earth doped FeGa alloy. Our group with collaboration with Baotou Research Institute in China are working in rare-earth doped FeGa alloys. We have studied magnetostrictive properties of 3 different rare-earth (Tb [39], Er, Gd) which have been doped in FeGa and figured out an enhancement of 270% in the saturation magnetostriction of $Fe_{83}Ga_{17}Er_x$ alloys with the introduction of small amounts of Er.

My research objectives were mainly focused on fabricating, developing and studying the structure, magnetism and magnetostrictive properties of mechanically alloyed $Fe_{81}Ga_{19}$ and and studying the magnetostrictive properties of RE doped FeGa alloys. These studies are valuable in developing new magnetostrictive FeGa alloys as an alternative innovative magnetostrictive material for actuator and transducer applications.

1.3. Organization of Thesis

A brief review of the chapters in this thesis is given below. Chapter 1 includes a brief introduction about importance of smart materials and motivations for magnetostrictive material research. Chapter 2 covers technical terms and definition for studying magnetostrictive materials. Chapter 3 offers a comprehensive literature review on the previous works that have been done on tuning the magnetostrictive behavior of the FeGa alloys. Chapter 4 covers structure, magnetism, and magnetostrictive properties of mechanically alloyed $Fe_{81}Ga_{19}$. In chapter 5, investigating the influence of rare-earth doping on magnetostrictive performance of Directional Solidified FeGa alloys will be described. Chapter 6 explains market and impact assessment of the magnetostrictive and
smart materials. Chapter 7, represents the major conclusions of this study and states recommendations for future work.
2 CHAPTER2 TECHNICAL TERMS AND BASIC DEFINITIONS

2.1. Smart Material:

Smart materials are designed materials that have one or more properties that can be significantly changed in a controlled fashion by external stimuli, such as stress, temperature, moisture, electric or magnetic field [1–3]. Some examples of the most famous types of smart materials are as following:

- Piezoelectric
- Shape memory alloys
- Magnetostrictive materials
- Magnetic shape memory
- Magnetocaloric materials
- Thermoelectric materials
- Photomechanical materials
**Ferromagnetic material:** Ferromagnetism is the basic mechanism by which certain materials (such as iron) form permanent magnets, or are attracted to magnets. Ferromagnetic materials have a large, positive susceptibility to an external magnetic field. They exhibit a strong attraction to magnetic fields and are able to retain their magnetic properties after the external field has been removed. Ferromagnetic materials have some unpaired electrons so their atoms have a net magnetic moment [40,41].

They get their strong magnetic properties due to the presence of magnetic domains. In these domains, large numbers of atom's moments ($10^{12}$ to $10^{15}$) are aligned parallel so that the magnetic force within the domain is strong. When a ferromagnetic material is in the unmagnetized state, the domains are nearly randomly organized and the net magnetic field for the part as a whole is zero. When a magnetizing force is applied, the domains become aligned to produce a strong magnetic field within the part. Iron, nickel, and cobalt are examples of ferromagnetic materials. Components with these materials are commonly inspected using the magnetic particle method [40,41].

**Magnetostrictive material:** is a property of ferromagnetic materials that causes them to change their shape or dimensions during the process of magnetization.[42] This phenomenon for the first time has been discovered by James Joule. In 1842, James Joule found that Iron has magnetostrictive properties [43]. After this discovery, Various works have been done to study and develop the magnetostrictive material. As an example we can mention to ferromagnetic material as Fe, Ni, Co as an magnetostrictive material with low saturation magnetostriction properties. Besides that, there are rare earth-Fe2 alloys
such as Terfenol-D (Tb$_{0.3}$Dy$_{0.7}$Fe$_2$) that generates giant magnetostrictive strains on the order of 2000 x 10$^{-6}$ [17,44].

**Galfenol:** Galfenol is a technical term which is used for an alloy of Iron and Gallium. This name for the first time was given to the alloy of iron and gallium by the united states navy researchers in 1998. It was discovered by their scientist that adding gallium to iron can amplify magnetostrictive properties of the Galfenol to more than ten times [2,7–9].

**Mechanical Alloying:** Mechanical alloying is a powder processing technique that involves blending powders in a high energy ball mill in order to produce homogenous materials. Mechanical alloying is capable of synthesizing a variety of equilibrium and non-equilibrium alloy phases starting from raw powders. [45]

**Vacuum arc melting:** Is a fabrication technique that involves melting process for producing metal ingots. The basic design of the Vacuum arc melting furnace has been improved continuously over the years particularly in computer control and regulation with the objective of achieving a fully- automatic melting process. [46]

**Directional Solidification:** Is a fabrication process that involves removal of heat from the molten metal in one direction. Directional solidification can be used as a purification process [39,47].
Texture (crystalline): Texture is the distribution of crystallographic orientation of a polycrystalline samples. If these orientations for a specific sample is random is said that have no specific texture. And if the orientation for the sample have some preferred orientation either weak or strong then we can say that the sample have texture. There are two major type for texture materials: one perfect random crystallite oriented isotropic material and second single crystal anisotropic materials. [48]

Saturation magnetostriction: In magnetostrictive material, is the state that magnetostriction reached when external field increase.

SEM: Scanning Electron Microscope is kind of microscope that scan samples with the beam of electrons and produce an image of them [49]. The way that it works is that the electrons collide with atoms of the sample and originate signals. The produced signals carry some information about the surface topography and compositions of the sample surface.
**XRD:** X-ray Powder Diffraction is an analytical technique which is used to provide information on atomic and molecular structure of a crystal [50].

**PPMS:** Physical Property Measurement System which measures heat capacity and other physical properties of samples under magnetic field.

**EBSD:** Electron backscatter diffraction is a microstructural technique that study structure and crystal orientation of materials [36].
3 CHAPTER 3 LITERATURE REVIEW

3.1. Section 1: Different synthesis techniques have been used regarding tuning the magnetostrictive behavior of the FeGa alloys:

3.1.1 Suction Casting followed by low energy blade milling:

In a work that has been done by Walters et al. [51], the production process and the results of investigations into the microstructure and magnetic properties of epoxy-bonded iron–gallium (Galfenol) particulate composites is presented. The fabricated composites consist of powdered Fe$_{80}$Ga$_{20}$ alloy particles of three different size distributions (ranging from 20 to 200 µm), bonded in an epoxy matrix with a filling factor of 0.80. The filling factor is defined as the ratio of the volume of Fe–Ga powder to the total volume of the composite’s constituents. After the samples have been made, the magnetostrictive properties have been measured. What have been concluded in this paper is that the value of the magnetostriction of Fe can be greatly enhanced by the addition of Ga in the atomic volume of approximately 20 at.%. The investigations of the alloys and magnetostrictive measurements exhibited 70 ppm saturation magnetostriction for the bulk alloy and about 360 ppm for the composites. As they have reported in their paper, the composites exhibited strong magnetostriction hysteresis, probably due to: (a) samples being exposed to a pre-stress and (b) a complex mechanical interaction between the two composite phases. [51]
3.1.2 Zone Melting (FSZM):

Textured polycrystalline FeGa alloys can be produced by zone refining (FSZM) using growth rates (Etrema Products Incorporated) that are two orders of magnitude faster than single crystal growth rates (≈1 mm h\(^{-1}\)) and can be commercially viable, provided the actuation and sensing properties of polycrystals are not significantly inferior to that of single crystals. [52]

In a work that has been done by Atlsimha et al. not only the magnetostrictive behavior of FeGa alloys but also the actuation and sensing behavior of the typical polycrystalline Fe\(_{81.6}\)Ga\(_{18.4}\) alloys which have been manufactured by free stand zone melt (FSZM) was studied [52]. In this work, the actuation and sensing behavior of the polycrystalline magnetostrictive sample was modeled from its cross-section texture by treating the polycrystals as composed of multiple grains of single crystals, each with a different orientation to the loading axis.

The results for magnetostriction properties of the measured samples have shown that the maximum magnetostriction (\(\lambda_s\)) of the produced sample is about 200 ppm.

3.1.3 Modified Bridgman Technique (Directionally Solidified):

Although single crystalline materials inherently provide the maximum crystallographic texture and hence magnetostriction, the processing cost for high volume production would be very high and would stop broad commercialization due to low yield and non-uniform properties. [21,53] That is where the motivation from polycrystalline FeGa alloy specially in such a manner that the structure possesses a high degree of crystallographic
texture comes from. One of the techniques that seems to be promising include growth texturing in an as-cast structure and the preferential recrystallization of thin sheets. [21] Fe-Ga alloys can be directionally solidified at rates sufficiently fast to yield dendritic solidification along the length of the ingot. Dendritic solidification occurs along specific crystallographic directions, thereby aligning different crystals within the ingot with a common growth direction. In an attempt to make directional solidified FeGa alloys, a directionally solidified Fe$_{83}$Ga$_{17}$ specimen was grown in an alumina crucible by the modified Bridgman technique. The ingot was heated to the growth temperature and held for 1 hour to allow thorough mixing before withdrawing the sample from the heat zone at a rate of 100 mm/h. Following growth, the ingot was annealed at 1000°C for 168 hours then furnace cooled. A 50.8-mm long rod- shaped specimen having a 6.35-mm diameter was sectioned from the ingot using EDM. The rod’s longitudinal axis was approximately parallel with that of the ingot’s longitudinal axis. The directionally solidified specimen’s combination of modest magnetostrictive performance ($\lambda_s \sim 170$ ppm), and susceptibility to intergranular brittle failure indicates that this approach for producing a textured polycrystalline Fe-Ga alloy may not be ideal. Although adjustments might be made in the growth and annealing processes to improve results, other texturing methods were investigated for superior performance [21].

3.1.4 Melt Spinning:

Melt spinning is a fabrication technique that is used for rapid cooling of liquids. This method is one of the simplest method since it does not involve problems which is associated with using any solvent. In this method the polymer granules are melted and
then extruded through the spin head [54], the flow of molten liquid to the spin head can be controlled easily. From the very best benefits of the melt spinning technique we can mention to cost-effectiveness and high speed and solvent independent.

In a work that has been done by S. F. Cheng et al. the structure of melt spun FeGa alloys have been studied [55]. In this work, Fe Ga alloys were rapidly quenched by the melt-spinning technique to determine the maximum Ga concentration that retains the disordered bcc (α-Fe) phase at room temperature. The texture of the ribbons as a function of melt-spinning parameters and annealing was also extensively studied. All of the as-spun samples were found to be crystalline. It has been cleared that the Effect of Wheel Speed, Annealing and Sulfur have the most important effects on the texture in melt spun FeGa alloys.

This study showed that the phase is bcc at high wheel speed and DO3 at low speed. Besides the texture on the wheel side of the ribbon is close to random at high speed but increases with slower speed. For the different annealing temperatures, they concluded that 900 °C annealing reduces the tilt angle while 1100 °C annealing recrystallizes the grains and produces strong out of plane texture but randomizes the directionality in the plane. Moreover, annealing with sulfur addition was found to enhance the {100} texture but did not produce the desired along the longitudinal direction of the ribbon.

Finally, The saturation magnetostriction, $\lambda_s$, of as-spun Fe Ga and Fe Ga both having a disordered bcc structure and strong {100} texture was measured as 98 and 130 ppm, respectively, along the ribbon length [55].
3.1.5 Rolling Technique Followed by Annealing:

Till now, although significant research efforts have been done toward understanding and perfecting crystallographic texturing in Fe-based alloys very few works have been done on developing FeGa alloys with the crystallographic texture through the rolling process. Metals deformed by rolling primarily develop crystallographic texture through grain deformation, based on their active slip systems and work induced recrystallization events [21]. To facilitate the formation of a desired texture, a number processing parameters may be varied. Typical processing parameters include: material stoichiometry and impurities, rolling temperature, rolling speed, percent reduction, and intermediate and final heat treatments. Environmental conditions such as a reducing or oxidizing atmosphere are also regarded as having an important influence on impurity content [21].

3.1.5.1 Hot rolling:

In a work that has been done by R. Kellogg, FeGa alloys prepared with hot rolling techniques which have been followed by annealing. For making hot rolled FeGa alloys, the starting ingot was enclosed in a stainless steel can, backfilled with Argon gas, evacuated and sealed by welding to prevent oxidation of the specimen. To minimize diffusion bonding of the Fe-Ga specimen with the can during rolling, the can was pre-oxidized at 900°C in air for 1 hr. Following hot soaking at 1000°C for 30 min, the canned specimen was hot rolled to give a 55% reduction to a thickness of 4.2 mm over 72 passes. According to what they have reported, saturation magnetostriction in the rolling direction would be: \( \lambda_s = 95 \times 10^{-6} \) [21].
3.1.5.2 Warm rolling:

Warm rolling takes place in a lower temperature of about 300°C compared to the hot rolling. The magnetostriction properties for this technique would be lower and about: \( \lambda_s = 70 \times 10^{-6} \) [21]. The reason on the modest magnetostriction might be because texture development, while improving, is still inadequate [21].

3.1.5.3 Cold rolling:

Cold rolling technique which is mostly followed by annealing and heat treatment procedure were developed in a few studies for FeGa fabrications. It develops stronger <100> texture and the alloys will have better mechanical properties. The magnetostriction properties for this technique would be lower than warm rolling and about: \( \lambda_s = 30 \times 10^{-6} \) [21].

3.1.6 Gas atomization followed by annealing in the presence of a magnetic field:

In the work that has been done by Jiheng Li et al. [56], the microstructure of Fe–Ga powders and magnetostriction of bonded composites have been studied. In this work FeGa powders were prepared by gas atomization and the microstructure of as-atomized and annealed Fe–Ga powders and magnetostriction of composites were investigated. One of the most interesting parts of this research [56], besides the magnetostriction study is analyzing of particle morphology, and phase compositions of FeGa powders. They have noticed of the emerging of DO₃ phase. What have been concluded was that the quenching rate was not fast enough to maintain the A₂ structure. Still, a significant number of
particles remained polycrystalline in the structure. Moreover, they have seen the L\textsubscript{12} phase appeared in the annealed Fe\textsubscript{81}Ga\textsubscript{19} powders. This phase opposes any improvement in magnetostriction, but many single crystals were obtained due to grain growth during the thermal process, which resulted in an increase in the magnetostriction of composites containing annealed powders.

The maximum magnetostriction value of: \( \lambda_s = 64 \times 10^{-6} \) was obtained in the Fe\textsubscript{81}Ga\textsubscript{19} composite prepared by mixing the <25 \mu m annealed powders and epoxy. [56]

### 3.1.7 Sintering followed by annealing in the presence of a magnetic field:

Powder Metallurgy is a continually and rapidly evolving technology embracing most metallic and alloy materials, and a wide variety of shapes. The powder metallurgy process includes the consolidation of a particulate parent material followed by sintering to diffusion bond the particles [21].

In a study have been done by Kellogg [21], a high degree of <100> crystallographic texture has been developed in polycrystalline specimens utilizing powder metallurgy techniques. Analyzing the magnetic properties of all samples revealed that all size fractions of the powdered Fe-Ga alloy contained a significant number of particles having a dendritic and polycrystalline structure. the different powder fractions were annealed at 800\textdegree C for 4 hr in a furnace backfilled with ultra-high purity Argon gas because effective magnetic orientation of polycrystalline particles is not possible.

At the end, magnetostrictive properties have been measured by using strain gauge the maximum magnetostriction value of \( \lambda_s = 60 \times 10^{-6} \) was obtained [21].
3.1.8 Spark erosion:

One step production of optimized FeGa particles by spark erosion is another interesting research that has been done by J. I. Hong et al. [57]. In this research, Spherical Fe–Ga particles were prepared by spark erosion in liquid Ar, which directly incorporated the desirable rapid quench from high temperatures. In this work, Composites for magnetostriction measurements were made by mixing particles with epoxy and then they were cured in a mold to form a parallelepiped block. During process of curing at 100 °C, a magnetic field of 2 kOe was applied along the length of the block. The reason that magnetic field is applied is that, magnetic field promotes alignment of the particles in the epoxy in the field direction.

As a conclusion it was cleared that spark erosion of FeGa in liquid Ar produced spherical particles, mostly single crystals, with Ga concentrations reduced by around 2 at. % from that of starting alloy.

Different Ga concentration was used in this study and it was observed for bulk Fe–Ga alloys, magnetostriction depended on Ga concentration, with the largest values obtained for 19 at.% Ga which was: \( \lambda_s = 53 \times 10^{-6} \). With optimization of the particle concentration and spatial distribution in the polymer matrix, as well as better matching of the elastic properties of polymer and Fe–Ga particles, composites with even higher magnetostriction may be obtained [57].

3.1.9 Mechanical Alloying:

Mechanical alloying is a simple non-equilibrium sample processing method that involves cold welding, fracturing, and re-welding of powder particles in a high-energy ball mill
Powders prepared by mechanical alloying are promising as engineered materials as they provide a convenient form for the fabrication of magnetostrictive alloy-polymer matrix composites for magnetostrictive applications. Gaudet et al. [58] were the first to synthesize mechanically alloyed FeGa powders followed by Parisa T. et al. who measured and reported for the first time the magnetostrictive properties of mechanically alloyed FeGa alloys [23]. Next chapter will be completely devoted to the Structure, magnetism, and magnetostrictive properties of mechanically alloyed Fe$_{81}$Ga$_{19}$.

### 3.1.10 Hot Forging:

One of the deforming processing named extrusion is one of the production step used in forming wire out of many metals including Fe and Fe alloys. For developing crystallographic textured products with a high degree of mechanical anisotropy hot axial forging is using which causes a significant crystallographic reorientation and produces a dominant $<100>$ texture parallel to the direction of forging [21].

In another work by Kellogg [21], Forging of the Fe-Ga rod specimen was conducted. Considering the forged material’s complicated flow pattern, occurring over short distances relative to the diameter of the disk specimens, the saturation magnetostriction of each disk specimen was evaluated in multiple directions. The range of the magnetostriction value measured in the samples were between : $\lambda_s = 18 \times 10^{-6}$ to : $\lambda_s = 35 \times 10^{-6}$ [21]. In this study the low magnetostriction in the hot forged specimens is liked to a lack of favorable texture (or any texture) and possibly significant residual internal stress developed during quenching [21].
3.2. Section 2: Influence of ternary element addition on the magnetostrictive performance of FeGa compounds:

Clark and co-workers [22,59,60] have discovered that Fe–Ga (Galfenol) alloys possess the highest single crystalline magnetostrictive strain for a binary alloy (~13 times that of pure Fe) and unlike other magnetostrictive alloys retain significant ductility. After that, extensive works have been undertaken to improve magnetostrictive and magnetic properties of the FeGa alloys. In this sections, we are reviewing studies that have been done for the development of the Galfenol alloy system for magnetostriction applications including work on substitutional ternary alloying additions for magnetostrictive and magnetic property enhancement.

3.2.1 Effect of interstitial additions (C, B, N) on magnetostriction in FeGa alloys

In a study that has been done by Huang et al. [29], the additions of trace amounts of small interstitial atoms (carbon, boron, and nitrogen) to Fe–Ga Galfenol alloys, have been studied.

They found that the additions very small amounts of carbon, boron, and nitrogen atoms to Fe–Ga Galfenol alloys have a small but beneficial effect on the magnetostriction of Fe–Ga alloys especially at high Ga compositions. The revealed that for either slow cooled and quenched single crystal Fe–Ga–C alloys with Ga contents 18 at. %, saturated magnetostriction \((3/2)\lambda_{100}\) are about 10%–30% higher than those of the comparable binary Fe–Ga alloys. For boron and nitrogen additions, the magnetostriction of slow cooled alloys with Ga content 18 at. % were approximately 20% higher than those of the
binary Fe–Ga alloys.

What they have claim for this phenomena is that these small atoms enter interstitially into the octahedral site as in pure $\alpha$-Fe and inhibit chemical ordering, resulting in increased $\lambda_{100}$. Besides that, the thermal behavior of FeGa binary alloys and Fe-Ga-C ternary alloys have been analyzed. What they have found was that the addition of C into the Fe–Ga system decreases the formation kinetics of $D0_3$ and extends the disordered region beyond the maximum for slow cooled binary samples [61,62].

### 3.2.2 Magnetostriction of ternary Fe-Ga-X alloys (X=Ni, Mo, Sn, Al)

When it comes to large magnetostriction, the Fe–Ga and Fe–Al systems are supposedly unique among the Fe-based alloys despite the fact that Ga and Al are nonmagnetic. In the work that has been done by Restorf et al., [34], the effect of small additions of Ni, Mo, Sn, as well as larger additions of Al on the magnetostriction of single crystal $Fe_{100-x}Ga_x$ alloys ($x \approx 13$) have been investigated. Very small amount of Ni, Mo, Sn and Al has been substituted into the binary FeGa alloys for magnetostriction improvement. For each of the elements, there is a factual reason that why they have been chosen among all the elements in the periodic table.

Ni has been picked because in the Fe–Ga alloys $\lambda_{111}$ is negative and it makes it necessary to use either single crystal or highly textured polycrystals for reaching maximum performance. As Bozorth claimed [40], that the addition of Ni to Fe decreases the magnitude of the negative $\lambda_{111}$. As it was anticipated, Ni addition decreased the negative
value of $\lambda_{111}$ substantially but at the same time, it also lowered the value of $\lambda_{100}$.

Ga has a filled 3$d$ shell and the 3$d$ shell of Al is empty. Mo has been chosen to inspect the effect of a partially filled 3$d$ electron shell. Mo addition has made $\lambda_{111}$ more negative and reduced $\lambda_{100}$ for about 40% [34].

The atomic radius of Ga is 12% larger than Fe; Sn, whose atomic radius is about 30% larger than Fe, was selected as an addition to examine the effects of an even larger atom. It has been revealed that Sn addition neither decrease or increase $\lambda_{100}$ or $\lambda_{111}$ [34].

The reason that Al was chosen as a ternary addition was that Fe$_{100-x}$Al$_x$ ($x \sim 15$) alloys also have large magnetostrictions [60]. The amount of $\lambda_{100}$ has been increased at first that Al were added to FeGa. After specific amount of Al addition, $\lambda_{100}$ started to decrease.

Among all these four elements, Ni, Mo and Al show a drop in $\lambda_{100}$, while in case of Sn addition, $\lambda_{100}$ remained unchanged [34].

### 3.2.3 Magnetostriction of ternary Fe-Ga-X (X=C, V, Cr, Mn, Co, Rh)

In a study that has been done by E. Clark et al. [33] the effect of small additions of $x$=C, V, Cr, Mn, Co and Rh have been studied. It has been revealed that adding 2 at. % or greater of 3d and 4d transition elements which have either fewer valence electrons that Fe (V, Cr, Mo) or more valence electrons than Fe (Co, Ni, Rh) will reduce the saturation magnetostriction. What have been noticed in this study was that by adding V, Cr, Mn,
Co and Rh the tetragonal magnetostriction $\lambda_{100}$ will be decrease compared to the binary FeGa alloys [33]. Kawamiya and Adachi have been revealed that the D0$_3$ structure is stabilized by 3d transition elements with electron/atom ratios both less than iron and greater than iron [63] which is assumed to lessen the $\lambda_{100}$ magnetostriction [64].

What have been concluded at the end of this work was that addition of the V, Cr, Co, Mn and Rh does not increase magnetostriction. On the other hand, small Carbon addition to FeGa has an effect on the magnetostriction properties and processing steps. It means that by addition of Carbon has the same salutary effect on the magnetostriction as what quenching does. So by adding Carbon to FeGa alloys, the quenching step could be skipped. It can be conjectured that Carbon atoms enter interstitially and integrated into the FeGa alloys and can generate tetragonal distortions within the Fe lattice [65]. These tetragonal distortions are one of the most important reasons of magnetoelasticity and magnetostriction enhancement of FeGa alloys.

### 3.2.4 Influence of Be and Al on the behavior of FeGa alloys

FeAl and FeBe alloys have been widely recognized to have considerable magnetostrictive properties [66]. In this section we are going to cover the work has been done by Pinai Mungsantisuk et al. [30] and studies the influence of Be and Al on the magnetostrictive behavior of Fe Ga alloys. In this work, the effect of partially substituting Ga in FeGa alloys with Al and Be on the magnetostrictive behavior of FeGa alloys have been studied. Besides Al magnetic properties, one of the reasons that Al is of interest of researcher is that AL is less expensive than Ga and widely available. At this work we have seen that if
Ga in FeGa alloys is substituted with a small amount of Al and Be, magnetostriction properties won’t decrease significantly [30].

3.3. Section 3: Influence of rare-earth doping on magnetostrictive behavior of FeGa alloys

Since FeGa discovery, huge works have been done to improve magnetostrictive properties of Galfenol. Among these works we can mention to adding transition [33,34], main group [67], and interstitial elements to FeGa alloys [29], which none of them could increase magnetostriction property remarkably [68]. Recent works on adding rare earth to Galfenol may shed new light on improving magnetostrictive properties of Galfenol [68–70,70–74]. Below, a few works that has been done in rare earth addition to FeGa alloys have been reviewed before we explain our work on rare earth doped FeGa alloys in Chapter 5.

3.3.1 Influence of rare earth element Ce-doping on magnetostrictive behavior of FeGa alloys

In a recent work that has been done by Zhanquan Yao et al. [73], Ce as a rare earth is doped in FeGa alloys in order to improve magnetostrictive properties of Galfenol. Melt spinning technique was also applied on some of the samples later on for magnetostriction enhancement. The as-cast Fe$_{83}$Ga$_{17}$ and Ce-doped Fe$_{83}$Ga$_{17}$ alloys were prepared by arc melting. Then the as-cast Ce-doped Fe$_{83}$Ga$_{17}$ alloy was melt-spun by the melt-spinning
technique. Microstructure and magnetostriction of all samples have been studied to investigate the influences of rare earth element Ce-doping on Galfenol. For the as-cast Fe$_{83}$Ga$_{17}$ alloy, a single Fe(Ga) solid solution phase with bcc structure has been found. On the other hand, for the as-cast Fe$_{83}$Ga$_{17}$Ce$_{0.8}$ alloys the evolution of the CeGa$_2$ secondary phase was noticed during the microstructure analysis. For the melt spun Fe$_{83}$Ga$_{17}$Ce$_{0.8}$ alloys, Fe(Ga), CeGa$_2$ and asymmetrical DO$_3$ phase were found. In summary what have been concluded was that the CeGa$_2$ phase are formed as a result of Ce-doping while asymmetrical DO$_3$ phase are formed because of melt-spinning. Moreover, Ce doping into the Fe$_{83}$Ga$_{17}$ alloy caused stronger (100)-orientated texture of the alloy and lead to the magnetostrictive coefficient enhancement in the as-cast Fe$_{83}$Ga$_{17}$ alloy, which could be as a result of the formation of the CeGa$_2$ secondary phase and the preferred orientation along (100) direction. Whereas the improvement of magnetostriction for the Fe$_{83}$Ga$_{17}$Ce$_{0.8}$ alloy may mainly attribute to the formation of asymmetrical DO$_3$ phase caused by melt-spinning. All in all, FeGa alloys’ property heavily rely on the microstructure of alloy [73]. What it means is that as it is claimed in this work, the reason that saturation magnetostriction have been increased by Ce doping could be associated with microstructure variation that caused by Ce doping. Maximum magnetostriction of 382 ppm is achieved in the melt-spun Fe$_{83}$Ga$_{17}$Ce$_{0.8}$ alloy, which as it is claimed this value is 4.6 times larger than that of the as-cast Fe$_{83}$Ga$_{17}$ alloy.
3.3.2 Improved magnetostriction of Dy-doped Fe$_{83}$Ga$_{17}$ melt-spun ribbons

“Improved magnetostriction of Dy-doped Fe$_{83}$Ga$_{17}$ melt-spun ribbons” is the title of another work done by Tingyan Jin et al. [72]. In this work, (Fe$_{0.83}$Ga$_{0.17}$)$_{100-x}$Dy$_x$ ($0 \leq x \leq 0.42$) ribbons were prepared by the melt-spinning technique. The outcome of this rare earth addition has pointed out that the magnetostriction of Fe$_{83}$Ga$_{17}$ was notably enhanced by Dy addition. When a small amount of Dy added to FeGa alloys, an extraordinary enhancement in magnetostriction is acquired in the doped samples. A maximum saturation magnetostriction $\lambda$ of about 620 ppm is attained which is three times greater than that of the binary Fe$_{83}$Ga$_{17}$ ribbons. One of the most important theories about the origin of magnetostriction and magnetocrystalline anisotropy in ferromagnetic materials claims that it is from spin-orbit coupling [75]. Magnetic anisotropy plays a crucial role in magnetostrictive materials as the large magnetostriction material like T and Dy single crystals get their magnetostriction from [75]. It has been discovered previously that Tb additions to Fe$_{83}$Ga$_{17}$ ribbons could improve magnetostriction property significantly [70]. It is conjectured that the localized strong magnetocrystalline anisotropy of elements Tb and Dy [44,76] create the huge magnetostriction [72]. There are some similarities between element Tb and Dy in terms of electronic structure ($4f^8$ for Tb and $4f^9$ for Dy [77]), tremendously strong magnetocrystalline anisotropy and solid solubilities in Fe$_{83}$Ga$_{17}$ ribbons. Because of all these reasons that have been discussed, doping FeGa ribbons with Dy, causes enhancement in magnetostriction of Fe$_{83}$Ga$_{17}$ ribbons based on what it has been claimed in this work.
3.3.3 Tb doped FeGa

3.3.3.1 Microstructure and magnetostrictive properties of Tb doped Fe-Ga bulk alloys prepared by melt quenching

In a study that has been done by Shu-Xin Zhang et al. [69], the microstructure and magnetostrictive properties of Tb doped Fe$_{83}$Ga$_{17-x}$Tb$_x$ ($x = 0.05, 0.10, 0.20, 0.30, 0.40, 0.50$) bulk alloys which have been prepared by melt quenching have been studied. The magnetostrictive properties of all samples have been measured under different compressive pre stress from 0 to 30 MPa. What made this study interesting was that they found a correlation between saturation magnetostriction enlargement and the compressive pre stress. The maximum magnetostriction reaches to $\lambda_s = 106 \times 10^{-6}$ when the amount of the Tb doping is $x = 0.1$ under the 30 MPa compressive pre-stress. Magnetostriction measurements showed that with adding Tb, saturation magnetostriction first increased and then reached to maximum amount before it started to decrease. The reason, as they claim [69], should be related to the partial solution of Tb in the FeGa matrix. For the specific amount of Tb, the matrix could still retain it’s A$_2$ structure and after adding more Tb to FeGa bulk alloys, the second phase starts to grow which is undesirable and cause decrease in saturation magnetostriction.
3.3.3.2 Giant magnetostriction in Tb doped Fe$_{83}$Ga$_{17}$ melt spun ribbons.

FeGa ribbons are of interest of researchers around the world because of their high magnetostrictive properties compared to FeGa alloys. In a very recent work that has been done by Wei Wu et al. [70], large saturation magnetostriction property could be achieved in Fe$_{83}$Ga$_{17}$ ribbons made by melt spinning technique.

The spin-orbit coupling is the main reason of the magnetocrystalline anisotropy and the magnetostriction in ferromagnetic materials [75,78]. FeGa alloys by themselves do not have high magnetostriction and the reason is associated with relatively low spin-orbit coupling and quenched orbital moments [79], and the giant magnetostriction of rare-earth doped Fe alloys like TbFe$_2$ relates to the strong spin-orbit coupling of Tb, and an orbital moment [79]. That is part of the reason that Tb was chosen for doping into the Fe$_{83}$Ga$_{17}$ alloy. In this work, ribbons were prepared by melt spinning process and the magnetostriction property of all samples were measured along the direction of ribbons by standard resistance strain gauge technique. As the amount of Tb doping increased the saturation magnetostriction also elevated till it reached to saturation and that is where more Tb doping causes decrease in saturation magnetostriction. The maximum magnetostriction reaches to $\lambda_s = 886$ ppm when the amount of the Tb doping is $x = 0.23$. [70]
3.3.3.3 Magnetostriction of a Fe$_{83}$Ga$_{17}$ single crystal slightly doped with Tb.

As we have seen in the previous section, it is reported that the magnetostriction of Fe$_{83}$Ga$_{17}$ alloys could be incredibly increased by melt spinning with small amount of Tb [70]. Although the amount of the magnetostriction calculated is high, it is not easy to measure magnetostrictive property directly as a result of perpendicularly grown grains in the melt spun ribbons [71]. Besides that, a lot of work has been done on developing polycrystalline Fe$_{83}$Ga$_{17}$Tb alloys which have their own limitations in terms of magnetostriction properties, etc.

In a work that has been done by Chongzheng et al. [71], Fe$_{83}$Ga$_{17}$Tb single crystals in the [100] orientation have been prepared and it’s magnetostriction have been measured using standard strain gauge. A $\lambda_{100}$ of 195 ppm is measured for undoped Fe$_{83}$Ga$_{17}$ single crystal while the magnetostriction of the Fe$_{83}$Ga$_{17}$Tb0.5 single crystal is around 310 ppm which is 50% more than undoped one [71].

3.3.4 Giant heterogeneous magnetostriction in Fe-Ga alloys: Effect of trace element doping

In the previous sections we have studied the effect of a few rare earth including Ce, Tb and Dy doping on magnetostrictive behavior of FeGa alloys/ ribbons. In a very interesting study has been done by Yangkun He et al. [74] the effect of trace rare earth doping (Zr, La, Nd, Sm, Tb, Dy, Ti, Pb, Ce, Pr, Gd, Ho, Er, Tm, Yb) on magnetostriction behavior of FeGa alloys have been studied.
It has been proved that doping in FeGa with a third elements will change the magnetostriction [80] and recently has it been revealed that doping FeGa alloys with rare earth elements like Tb and Dy can elevate magnetostriction properties dramatically close to Terfenol-D [70,72]. Different reasons have been claimed for the saturation magnetostriction elevation including rare earth crystal field interaction and localized strong magnetostrictive anisotropy of rare earth [44] or the effect of Directional solidification [39,81]. So it requires to determine the structure of the FeGa alloys and to point out where the huge magnetostriction of rare earth doped FeGa alloys come from. That is where the motivation of this research by Yangkun He et al. comes from.

After some precise study on magnetostriction and microstructure of as mentioned rare earth doped FeGa alloys, has it been concluded that the magnetostriction in Fe\textsubscript{83}Ga\textsubscript{17} is controlled by fixed tetragonal nanoinclusions with Ga-Ga c-axis pairs [74].

So the remarkable enhancement in magnetostriction caused by rare earth doping are mostly associated with local stratin induced by these atoms. Among all rare earth elements that have been studied in this work, La has the largest size effect and the best dopants are the light rare earths Ce and Pr [74]. It is conjectured that we could extend this way of magnetostriction enrichment by adding selected trace dopants to other magnetostrictive alloys such as Fe-Co, Fe-Al, Fe-Ge and Fe-Si as well.
In this work, structure-magnetic property correlations and the magnetostrictive response of mechanically alloyed powders of composition Fe$_{81}$Ga$_{19}$ were investigated using a variety of structural and magnetic probes. X-ray diffraction analysis of the as-milled powders suggests the presence of a chemically-disordered body-centered cubic phase. Thermal annealing of powder compacts results in formation of a secondary phase that demonstrates the cubic ordered L1$_2$ crystal structure. Magnetostriction measurements indicate that the magnetoelastic properties of the polycrystalline Fe$_{81}$Ga$_{19}$ compacts can be tailored by increasing the milling time duration followed by an anneal of the as-milled powders at 900°C for 2 hours in an Ar gas environment (O$_2$<5 ppm). Under those conditions, the room temperature saturation magnetostriction was measured to be as high as 41 ppm at a low magnetic field of $H_{app}$ ~10 Oe. The magnetostrictive behavior of the mechanically alloyed Fe$_{81}$Ga$_{19}$ powders was found to be comparable with FeGa samples prepared by other non-equilibrium powder processing techniques. Based upon the results presented here, it is preferred that ball-milling offers a cost-effective pathway towards realizing large volumes of FeGa alloys having moderate values of magnetostriction.

4.1. Introduction:

Functional magnetic materials systems that demonstrate large magnetostriction play an important role in a wide range of applications, including sonar systems [13], force,
displacement and torque sensors [14,15], microelectromechanical actuators, and vibration energy harvesting and vibration control devices [16]. To this end, it is important to note that one of the most promising magnetostrictive materials hitherto is Galfenol, Fe$_{1-x}$Ga$_x$ (Galfenol) [22] – an inexpensive, corrosion resistant [82], machinable alloy that in single crystal form exhibits high tensile strength ($\sim$500 MPa) [21], and a moderate magnetostriction ($3/2 \lambda_{100} \sim 350$ ppm) under a low magnetic field of $\sim$100 Oe [21]. Studies conducted by Kellogg et al. indicate that the magnetomechanical properties of these intermetallic alloys show limited variation over a temperature range -20-80 °C and therefore it is understood that this materials system can withstand large shock loads in harsh operating environments [21]. It is well known that the excellent functional properties of this system are closely correlated with their microstructural and crystallographic properties [53]. In particular, the large magnetostriction in Fe$_{1-x}$Ga$_x$ near $x=19$ is ascribed to local short-range interactions between the Ga atoms along specific crystallographic directions in the disordered body-centered cubic (bcc) $\alpha$-Fe structure [24]. Further, it is commonly believed that the decrease in magnetostriction in FeGa compounds, as the alloy composition approaches $x=25$, may arise from the formation of the ordered D0$_3$ [25] and L1$_2$ [26] phases.

Over the past two decades, a variety of sample synthesis and processing techniques have been explored to provide a means for controlling the structural properties and hence the magnetostrictive behavior of this alloy system [53]. To this end, it is critical to realize that though single crystals are an ideal starting point for characterizing and modeling the functional response of the FeGa system, textured polycrystalline forms of this material are likely to be more commercially viable [21,53] [83]. While single
crystals of FeGa have been synthesized using either the Bridgman method or the optical zone melting method [8], textured polycrystalline samples (ingots, sheets, rods and ribbons) have been fabricated using a variety of methods including arc-melting followed by directional solidification, directional solidification using the modified Bridgman technique [21], cold rolling [84], melt-spinning [85], combinatorial sputtering [86], and powder processing involving agitation at elevated temperature in the presence of a magnetic field [56]. A consolidated table summarizing the experimental values of saturation magnetostriction of FeGa alloys synthesized using different processing techniques is provided as Table 4.1 with relevant references. It is intriguing to note that in spite of extensive investigations in this materials system, only one study in the literature has focused on the non-equilibrium sample synthesis technique, mechanical alloying [58].

Mechanical alloying is a simple non-equilibrium sample processing method that involves cold welding, fracturing, and re-welding of powder particles in a high-energy ball mill [45]. Powders prepared by mechanical alloying are promising as engineered materials as they provide a convenient form for the fabrication of magnetostrictive alloy-polymer matrix composites for magnetostrictive applications. Gaudet et al. were the first to synthesize mechanically alloyed FeGa powders and it was found that in the as-milled state the samples show the presence of a disordered body-centered cubic (bcc) A2 phase with no indication of any secondary phases [58]. Annealing studies conducted by this same research group showed that D03 and L12-like ordering of the Ga on the lattice occurs at elevated temperatures and thus it is construed that decrease in the short range Ga clustering of the lattice sites may lower the magnetostrictive performance of
mechanically alloyed powders, relative to that of corresponding bulk polycrystalline samples [58]. Since Gaudet et al.’s study does not characterize the magnetostrictive performance of their samples and to date, the relationship between the crystallographic, microstructural and magnetoelastic properties of mechanically alloyed FeGa powders remains unclear, the present study attempts to address this obvious need.

Here, we present a detailed report on the preparation and properties of mechanically alloyed Fe$_{81}$Ga$_{19}$. It is well known that ball milling process conditions (example: milling atmosphere, ratio of ball to powder mass, milling speed, milling ball size, and milling duration) are critical to achieving high quality mechanically alloyed powders [45]. Therefore, in this work, the structural, magnetic and magnetostrictive properties of mechanically alloyed as-milled powders and annealed compact samples, were examined as a function of milling time. Results obtained in this work provide pathways for tailoring the microstructure and magnetoelastic properties of FeGa compounds for potential magnetostrictive applications.
Table 4.1. Summary of FeGa alloy processing techniques with corresponding room temperature saturation magnetostriction values

<table>
<thead>
<tr>
<th>Synthesis Technique</th>
<th>Form of FeGa</th>
<th>Magnetostriction, $\lambda$ (ppm)</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>Bridgeman Technique</td>
<td>Single crystal ([100] oriented)</td>
<td>$\lambda_{100} \sim 400$</td>
<td>Clark et al. [9]</td>
</tr>
<tr>
<td>Suction casting followed by low energy blade milling</td>
<td>Epoxy-bonded composites containing polycrystalline powder</td>
<td>$\lambda_s \sim 360$ ppm</td>
<td>Walters et al. [51]</td>
</tr>
<tr>
<td>Zone melting (FSZM)</td>
<td>Polycrystalline rods (strong [100] and [310] texture)</td>
<td>$\lambda_s \sim 200$</td>
<td>Atulasimha et al. [52]</td>
</tr>
<tr>
<td>Modified Bridgeman Technique (directionally solidified)</td>
<td>Polycrystalline rods ((high degree of ⟨110⟩ texture))</td>
<td>$\lambda_s \sim 170$</td>
<td>Kellog, Ph.D. thesis[21]</td>
</tr>
<tr>
<td>Melt spinning</td>
<td>Polycrystalline ribbons (high degree of [100] texture)</td>
<td>$\lambda_s \sim 130$</td>
<td>Zhang et al. [85]</td>
</tr>
<tr>
<td>Hot rolling followed by annealing</td>
<td>Polycrystalline disks</td>
<td>$\lambda_{\parallel} \sim 95^\circ$</td>
<td>Kellog, Ph.D. thesis[21]</td>
</tr>
<tr>
<td>Warm rolling followed by annealing</td>
<td>Polycrystalline disks</td>
<td>$\lambda_{\parallel} \sim 70^\circ$</td>
<td>Kellog, Ph.D. thesis[21]</td>
</tr>
<tr>
<td>Suction casting followed by annealing</td>
<td>Polycrystalline sphere</td>
<td>$\lambda_s \sim 70$</td>
<td>Walters et al. [51]</td>
</tr>
<tr>
<td>Gas atomization followed by annealing in the presence of a magnetic field</td>
<td>Epoxy-bonded composites containing polycrystalline powder</td>
<td>$\lambda_s \sim 64$</td>
<td>Li et al. [56]</td>
</tr>
<tr>
<td>Sintering followed by annealing in the presence of a magnetic field</td>
<td>Polycrystalline powder</td>
<td>$\lambda_s \sim 60$</td>
<td>Kellog et al. [21]</td>
</tr>
<tr>
<td>Spark erosion</td>
<td>Epoxy-bonded composites containing polycrystalline powder</td>
<td>$\lambda_s \sim 53$</td>
<td>Hong et al. [57]</td>
</tr>
<tr>
<td>Mechanical alloying</td>
<td>PVA-bonded composites containing polycrystalline powder</td>
<td>$\lambda_s \sim 41$</td>
<td>Current work</td>
</tr>
<tr>
<td>Cold rolling followed annealing</td>
<td>Polycrystalline disks</td>
<td>$\lambda_{\perp} \sim 30-35^\circ$</td>
<td>Kellog et al. [21]</td>
</tr>
<tr>
<td>Hot Forging</td>
<td>Polycrystalline disks</td>
<td>$\lambda_{\parallel} \sim 18-35^\circ$</td>
<td>Kellog, Ph.D. thesis[21]</td>
</tr>
</tbody>
</table>
4.2. Experimental Methods:

Iron-gallium alloys of the nominal composition Fe$_{81}$Ga$_{19}$ were mechanically alloyed by a high-energy ball mill operating at room temperature. Starting materials employed in these experiments included: metal Fe powders of purity 99.9% with an average effective diameter of $\sim$10 $\mu$m and metal Ga of purity 99.99%. In the first step, Fe and Ga were mixed and mechanically alloyed by using a high-energy ball mill for durations from 1 to 15 hours. Stainless steel balls were used as the grinding medium. A combination of ten 10 mm diameter balls (36 grams each in mass) and ten 6 mm diameter balls (9 grams each in mass) were used in a ball-to-powder mass ratio of 10:1. Toluene was used as the process control agent. After milling, the powders were mixed with 5% poly-vinyl alcohol (PVA) and pressed in a 6mm die set under 1.5 metric tons of pressure. The compacted samples were annealed in an argon gas atmosphere at $T=900$ °C hours for 2 hours. The chemical composition and homogeneity of the powdered sample were confirmed by energy-dispersive X-ray spectroscopy in a scanning electron microscope (SEM-EDS, Hitachi S4800). X-ray diffraction patterns were obtained at room temperature for all samples using a standard Cu Kα radiation source ($\lambda=1.54$ Å). Bragg peaks obtained from the XRD pattern were fitted to a Pseudo-Voigt fitting function and a least-squares fit was applied to estimate lattice parameters [87]. Line broadening analysis using the Scherrer method was employed to estimate the crystallite size of the mechanically alloyed FeGa powders [87]. The magnetic behavior of the samples were investigated at room temperature in magnetic fields up to $H=1.2$ T using a vibrating sample magnetometer (Model: 7400 Series). Room temperature magnetostrictive properties of the annealed compacted samples were measured with the magnetic field ($H_{app}$ in the range, 0-1.2 T)
parallel to the sample plane using a traditional quarter-bridge technique with the strain gauge (Vishay micro-measurements P3 strain indicator) positioned atop the compact.

4.3. Results and discussions:

4.3.1 Structural & Morphological Properties

Figure 4.1 shows X-ray diffraction patterns of annealed iron gallium milled mixtures of nominal composition Fe$_{81}$Ga$_{19}$ together with the pattern collected from a high purity iron powder (as a crystallographic bcc reference standard) after milling times of 1 to 15 hours. The single phase FeGa bcc-like structure defined as an A2 structure from examination of the phase diagram [5], is identified by the three strongest peaks indexed to (110), (200), and (211) planes. As is seen, the polycrystalline Fe$_{81}$Ga$_{19}$ samples show a slight [110]-preferred crystallographic texture. Also, in Fig. 4.1, one observes a slight shift of the (110) reflection to larger d-spacing consistent with an increase in the lattice parameter to larger values with increased milling duration. After 6 hours, additional Bragg reflections corresponding to the cubic ordered L1$_2$ phase are observed and a decrease in the lattice parameter of the A2 phase is measured. Fig. 4.2 shows the evolution of the lattice parameters of the crystallographic phases found in the mechanically alloyed Fe$_{81}$Ga$_{19}$ samples. It is critical to note that the L1$_2$ phase was not detected in the Fe$_{81}$Ga$_{19}$ powders in the as-milled state, irrespective of milling time. Nonetheless, the A2 $\rightarrow$ A2 + L1$_2$ structural transition is consistent with the equilibrium FeGa phase diagram [53], and as such, it is construed that in the samples under consideration in this work, prolonged ball milling followed by thermal annealing
generates sufficient heat to drive the microstructure from the A2 phase field into the A2+L12 region of the phase diagram. It is worthwhile to mention that formation of the L12 phase has also been reported in annealed FeGa samples synthesized by other non-equilibrium methods, namely by rapid-solidification techniques such as melt-spinning [85], and gas [56] atomization.

Fig. 4.1. X-ray diffraction patterns of annealed Fe81Ga19 samples. The indexed Bragg reflections correspond to the disordered body-centered cubic (bcc) structure. Additional peaks corresponding to the cubic ordered L12 phase is observed in samples milled for time periods greater than 6 hours.
Fig. 4.2. Lattice parameter trends in the disordered body-centered cubic A2 phase found in the mechanically alloyed Fe$_{81}$Ga$_{19}$ samples. The * symbol represents samples where the A2 phase coexists with the ordered cubic L1$_2$ phase. The lattice parameter of the L1$_2$ phase found in the Fe$_{81}$Ga$_{19}$ powders milled for 15 hours is $a \approx 3.709 \pm 0.005$ Å.

Fig. 4.3 is a composite figure of several SEM micrographs of milled powder samples, before and after heat treatment. The annealed samples shown here were lightly etched using a dilute nitric acid solution to reveal the finer details of the microstructure. Images of the pure iron powder (ball-milled for a period of 1 hour under similar
conditions as the other sample mixtures) serve as a reference for the Fe$_{81}$Ga$_{19}$ samples. Iron, being considerably more malleable than the materials under study, behaves considerably differently than FeGa. Overall, the particle morphology of iron can be described as uniformly sized nodules with rounded and smooth surfaces. Upon heat treatment at 900 C for 2 hours, one observes considerable grain growth via Ostwald ripening with large grains retaining smooth surfaces. In sharp contrast to pure Fe, the particle morphology of ball milled iron gallium mixtures are more faceted – a signature of cold welding during the high-energy ball milling process. The sample milled for 15 hours has a larger average particle size (d>5 µm) than that milled for 6 hours (3-5 µm) - a feature that may be attributed to increased toughness due to dislocation pile-up caused by cold welding. Notwithstanding the large particle size, the crystallite size remains comparable for all milled samples at ~40-50 nm as determined by Scherrer analysis of the [110] diffraction peak.

Examination of the morphology of these samples following heat-treatment and etching shows a striking difference. In the annealed samples, one sees larger particles suggesting aggregation. Etching reveals, a fine structure on the particle surface suggesting an embedded nanostructure. The sample milled for 6 hours shows a honeycomb-like microstructure on the surface of the etched aggregates. The honeycomb character of the sample microstructure becomes more pronounced upon milling for longer time periods. This observation is tentatively ascribed to preferential etching of either the L1$_2$ or A2 phases relative to the other. Overall, the conclusions drawn from the SEM images shown in Fig. 4.3 are consistent with the XRD data that demonstrate an increase in the L1$_2$ phase concentration with increase in milling time.
Fig. 4.3. SEM micrograph of mechanically alloyed Fe and Fe₈₁Ga₁₉ powder samples, before and after heat treatment. Here, Fe serves as a reference standard.

4.3.2: Magnetic Properties

The field-dependent magnetic behavior of the mechanically alloyed powder samples in as-milled as well as annealed state were examined at room temperature. The parameters, coercivity ($H_c$), saturation magnetization ($M_s$), and saturation field were determined from the hysteresis loops and are summarized in Table 2. Fig. 4.4 (a,b) shows the evolution of $H_c$ and $M_s$ as a function of milling time. In considering the saturation magnetization values, one sees a clear trend of decreasing magnetization with increasing milling time, consistent with the appearance of the secondary L₁₂ FeGa phase. Though it remains to be confirmed, it is speculated in the FeGa literature that the intrinsic saturation magnetization value of the ferromagnetic L₁₂ FeGa phase is significantly lower than that of the A2 phase [88]. Heat treatment provides additional thermal energy for formation of the chemically disordered FeGa A2 phase and consequently an overall increase is observed.
in the $M_s$ of the annealed samples, relative to that of the corresponding as-milled powders (See Fig. 4.4 (a)).

Trends in the coercivity of the mechanically alloyed Fe$_{81}$Ga$_{19}$ powders, shown in Fig. 4.4 (b), are in agreement with the changing microstructure of the sample with increasing milling times and heat-treatments. As such, the overall $H_c$ of the as-milled samples are larger than that of their annealed counterparts. Upon post-annealing, all samples demonstrate coercive field values ranging from 20-30 Oe, with one exception in that at t=15h where co-existence of the A2 and the L1$_2$ FeGa phase is noted. These results suggest that the crystallite size of the A2 FeGa phase ($D\sim50$ nm as determined from the Scherrer equation) is above the single domain particle size where the coercivity depends upon both domain wall interactions within single crystallites and domain wall interactions that encompass clusters of crystallites [87].

Fig. 4.4. Evolution of the saturation magnetization (left) and coercity (right) of the as-milled and annealed Fe$_{81}$Ga$_{19}$ powders as a function of milling time duration
4.3.3 Magnetostrictive Properties

This study focuses on the magnetostrictive properties of annealed compacts of mechanically alloyed, Fe$_{81}$Ga$_{19}$ powders only. Fig. 4.5 shows the evolution of the magnetostrictive coefficient ($\lambda_s$) of the pure Fe powder and annealed FeGa powder compacts as a function of applied magnetic field and milling time. Here, Fe serves as a reference standard and its behavior is found to be in good agreement with that reported in literature (magnetostrictive coefficient, $\lambda_s = -8$ ppm [87]). The magnetostrictive coefficient increases as a function of ball milling time reaching a maximum value, ~41 ppm, for the 6 h milled sample. In agreement with previous reports in the literature that demonstrate a reduction in magnetostrictive performance in FeGa systems that exhibit coexistence of the A2 and L1$_2$ phases [56], Fig. 4.5 clearly indicates that the sample milled for 15 hours shows a dramatic reduction in $\lambda_s$ relative to that of other samples milled for shorter times. The experimental trends shown in Fig. 4.5 are in agreement with the X-ray diffraction data that indicate that the sample milled for 6 hours has the longest ball mill duration prior to the onset of the L1$_2$ phase (see Figures 1 and 2). The lattice parameter of this sample is closest to the A2 phase, which is known to have a high magnetostrictive value (a$_{\text{Fe}_{81}\text{Ga}_{19}}$ ~0.291 Å [25]). It is also critical to observe that the $t=6$ hours sample has the highest slope approaching saturation magnetostriction (0.0038 ppm/Oe) signaling its superior potential for application, as this would require a small bias field to reach maximum sensing performance.

Following the work of Cullity and Graham [87], who first reported the relationship between magnetostriction and magnetization for polycrystalline Fe samples could be
described by a power law relationship of the form \( \frac{\lambda}{\lambda_s} = \frac{3}{2} \left( \frac{M}{M_s} \right)^2 \), we plot the normalized magnetostriction as a function of the square of normalized magnetization in Fig. 6. In the high-field region, the plot of \( \lambda \) vs. \( M^2 \) may be reasonably approximated by a line. The reason for this behavior is that the magnetization of most specimens changes almost entirely by domain rotation in this high-field region, just as the magnetization of stressed specimens change by spin rotation over the range of \( M = 0 \) to \( M_s \) [87].

Fig. 4.5. Plot of magnetostriction as a function of applied magnetic field in annealed Fe\(_{81}\)Ga\(_{19}\) composites comprising of 5 wt\% PVA and mechanically alloyed powders.
The milling time duration was varied between 1 to 15 hours.

Fig. 4.6. Plot of normalized magnetostriction ($\lambda/\lambda_s$) as a function of the square of normalized magnetization ($M/M_s$)

4.4. Conclusion:

Mechanical alloying of Fe and Ga powders were investigated by high-energy ball milling under different milling durations. X-ray diffraction revealed that high energy milling for time periods up to 6 hours converts the elemental constituents to an alloy
dominated by the chemically disordered A2 phase. Prolonged milling and subsequent annealing beyond this point leads to the appearance of the cubic ordered L12 phase, which is consistent with the equilibrium phase diagram. A maximum magnetostriction of \(-41\) ppm was observed in Fe\(_{81}\)Ga\(_{19}\) composites containing annealed powders (see Fig. 4.5). This magnetostriction value is comparable to those measured from polycrystalline FeGa alloys prepared by other processing techniques, namely gas atomization and cold rolling (See Table 4.1). It has been proposed by many theoretical and experimental studies that the many-fold increase in FeGa magnetostriction, relative to that of pure Fe, may be due to emergence of short-range ordering of Ga atoms in the [100] crystallographic direction [59]. It is thus conjectured that the magnetostriction effect observed in mechanically alloyed FeGa powders may be enhanced by applying an external magnetic field during heat treatment. Future work to this end is planned. Overall, this study demonstrates the feasibility of large-scale production of FeGa polycrystalline alloys powders by a simple and cost-effective mechanical alloying technique.
5 CHAPTER 5 INVESTIGATING THE INFLUENCE OF RARE-EARTH DOPING ON THE MAGNETOSTRICTIVE PERFORMANCE OF DIRECTIONAL SOLIDIFIED FEGA ALLOYS

In this chapter, we will cover our work in collaboration with Baotou Research Institute of Rare Earth in China. This chapter will be divided into 3 sections. In all of the section, all of the samples were prepared with the same fabrication technique which is vacuum arc melting and directional solidification technique. In the first section, Tb doped Fe Ga alloys will be covered. This work has been done by Liping Jiang et al. [39] and studied the magnetostrictive properties of FeGa alloys which doped with a small amount of Terbium. In the second section, Er doped FeGa alloys will be explained in details. The last chapter will be devoted to the Gd doped FeGa alloys.

5.1. Terbium doped Galfenol:

Our group in CM3IC in collaboration with Baotou Research Institute in China has discovered that small amount of Tb addition to FeGa alloys can enhance magnetostrictive properties of the doped FeGa alloys to more than twice of the parent compound [39]. For consistency and also better understanding the material, in this section, first I am going to review their work [39,81] before I reveal new rare earth elements (Erbium and Gadolinium) that we have worked on that.
5.1.1 Introduction

Magnetostrictive materials are of interest for use in acoustic sensors and transducers, linear motors, actuators, damping devices, torque sensors, positioning devices, and magnetoelectric sensors and transducers [26,53]. Galfenol has particularly drawn wide attention in diverse fields due to unique combination of magnetostrictive and mechanical attributes. As we have seen in chapter 3, huge work have been done to improve the magnetostriction properties of FeGa alloys including different fabrication techniques, ternary element addition on FeGa alloys, etc. The magnetostriction could not be remarkably elevated either by addition of 3d and 4d transition elements such as Ni, V, Cr, Mn, Co, Mo, and Rh, [33,34] or the main group elements like Si and Ge, or the interstitial elements B, C and N [29]. On the other hand rare earth doping could make a huge difference in magnetostrictive properties of FeGa ribbons/alloys. In this work done by Liping Jiang et. al. [39] an experimentally verified improvement in magnetostriction of Tb doped FeGa alloys has been reported.

5.1.2 Experimental Methods

Polycrystalline samples of nominal composition $\text{Fe}_{83}\text{Ga}_{17}\text{Ta}_{x}$ $(0<x<0.8)$ were synthesized from constituent elements of 99.95% purity using vacuum arc melting and directional solidification techniques to grow polycrystalline alloys employing removal of heat from one direction. The casting process were done very quickly. The liquid metal was cooled primarily by rapid one dimensional heat extraction. Moderate growth of grains cause the formation of a columnar crystal having preferred crystalline orientation [39]. The alloys microstructural properties were analyzed by x-ray diffractometry (XRD),
energy dispersive x-ray spectroscopy (EDXS), scanning electronic microscopy (SEM), and magnetostriction measurements.

5.1.3 Experimental Results and Discussions

X-ray diffraction data of the Fe$_{83}$Ga$_{17}$Tb$_x$ alloys obtained from scanning the sample plane perpendicular to the growth direction, as shown in Fig. 5.1, indicates the presence of a single phase having the $bcc$ crystal structure for all samples of composition $x<0.2$. It is revealed that the primary peaks match with the A2 phase with $bcc$ structure, which is ferromagnetic phase. As the amount of Tb doping increases to more than 0.2, the evolution of secondary phase happens which can be observed in Fig. 5.1 Fig. 5.2 demonstrate the dependence of the x-ray intensity of different reflecting planes with Tb content. As can be seen in Fig. 5.2 polycrystalline alloys show a preferred orientation along the [110] growth direction that is formed by the Directional Solidification thermal gradient [39].
Fig. 5.1 Room temperature $\theta$-$2\theta$ X-ray diffraction (Cu ka-radiation) spectra of Fe$_{83}$Ga$_{17}$Tb$_x$ alloys with different Tb doping ($x$).

Fig. 5.2 Dependence of relative intensity of primary peaks on Tb content ($x$).
The scanning electron microscopy (SEM) were done on Fe$_{83}$Ga$_{17}$Tb$_x$ alloys ($0<x<0.8$) to visualize the distribution of the elements. Figures 5.3 (a1) and 5.3 (a2) show the determination of elements at the spot 1 (grain) and spot 2 (grain boundary). It is noticed that grains are mostly made up of Fe and Ga while the grain boundary is formed of Tb and Ga. What hav ebenn concluded by Liping Jiang’s group was that Tb atoms accumulated at the grain boundary and form (Fe)GaTb and intermetallic Ga-Tb alloys (possibly Ga$_6$Tb) that appear as the secondary phase in the XRD scans for $x>0.2$ [39].

![Fig. 5.3 SEM image depicting granular morphology for Fe$_{83}$Ga$_{17}$Tb$_x$ (x.0.2) alloy.](image)

In Fig. 5.4, the magnetostriction strain ($\lambda$) along the direction of growth of the Fe$_{83}$Ga$_{17}$Tb$_x$ alloys is plotted as a function of applied magnetic field. In all samples, $\lambda$ increases with applied field until a saturation magnetostriction value ($\lambda_s$) is obtained. Change in $\lambda_s$ with Tb content ($x$) for the Fe$_{83}$Ga$_{17}$Tb$_x$ alloys is shown in Fig. 5.5. Overall, $\lambda$ increases with Tb doping till the maximum of 160 ppm is achieved at $x=0.2$. Further
addition of Tb results in a decrease of \( \lambda_s \). These results represent an enhancement of more than \( \sim 200 \% \) in the saturation magnetostriction (\( \lambda_s \)) of Fe\textsubscript{83}Ga\textsubscript{17}Tb\textsubscript{x} alloys with the introduction of small amounts of Tb.

Fig. 5.4 Dependence of magnetostrictive coefficient on magnetic field.

Fig. 5.5 Change of magnetostriction constant with Tb content (x) for Fe\textsubscript{83}Ga\textsubscript{17}Tb\textsubscript{x} alloys.
5.1.4 Conclusions

In summary, Liping Jiang’s group in collaboration with our group in CM3IC reported for the first time a magnetostriction improvement of more than 128% in Tb doped FeGa alloys compared with the parent material. Besides magnetostriction enhancement, the slope of the magnetostriction versus applied magnetic field has increased notably which is very useful in practical applications [39].

5.2. Erbium doped Galfenol:

We report for the first time, correlations between the crystal structure, microstructure, magnetic properties and magnetostrictive response of lightly Er-doped FeGa alloys. In this study, a series of Er-doped [110]-textured polycrystalline alloys Fe$_{83}$Ga$_{17}$Er$_x$ (0$<x<$1.5) were fabricated by vacuum arc-melting and directional solidification techniques. Experiments indicate an enhancement of more than ~275% from ~45 ppm to 170 ppm in the saturation magnetostriction ($\lambda_s$) of Fe$_{83}$Ga$_{17}$Er$_x$ alloys with the introduction of small amounts of Er. Moreover, it is noted that the low field derivative of magnetostriction with respect to applied magnetic field (i.e. $d\lambda_s/dH_{app}$ for $H_{app}$ up to 1000 Oe) increases by ~230% with Er doping ($d\lambda_s/dH_{app,FeGa} = 0.045$ ppm/Oe; $d\lambda_s/dH_{app,FeGaEr} = 0.15$ ppm/Oe). The origin of the enhanced magnetostrictive effect in this materials system is discussed in the context of the microstructure as well as the electronic structure of the sample. Overall, this work provides guidelines to further improving FeGa alloys for potential magnetoelectric and multiferroic device applications.
5.2.1 Introduction

Magnetostrictive materials change its dimension when subjected to a change of the applied magnetic field, that whose properties change during the process of magnetization. They are widely used in actuators, sensors and transducers [26,53]. Galfenol has particularly drawn wide attention in diverse fields due to unique combination of magnetostrictive and mechanical attributes. As we have seen in chapter 3, huge work have been done to improve the magnetostriction properties of FeGa alloys including different fabrication techniques, ternary element addition on FeGa alloys, etc. The magnetostriction could not be remarkably elevated either by addition of 3d and 4d transition elements such as Ni, V, Cr, Mn, Co, Mo, and Rh, [33,34] or the main group elements like Si and Ge, or the interstitial elements B, C and N [29]. On the other hand rare earth doping could make a huge difference in magnetostrictive properties of FeGa ribbons/alloys. We have seen in the previous section that very small Tb doped in FeGa alloys could elevate magnetostriction properties of FeGa alloy dramatically. To date, very little attention has been given to Er-doped FeGa compounds.

To add to the FeGa literature, here we present for the first time, an experimental study that aims at investigating the crystallographic, microstructural, magnetic and magnetostrictive properties of a series of Er-doped polycrystalline alloys of composition, \((\text{Fe}_{83}\text{Ga}_{17})_{100-x}\text{Er}_x\) (0<x<1.2). Results obtained in this research effort represents an exceptional ~275 % increase in the magnetostriction coefficient of [110]-textured FeGa alloys. The optimal composition for the best magnetostrictive response was found to be \((\text{Fe}_{83}\text{Ga}_{17})_{100-x}\text{Er}_x\) (x=0.6).
5.2.2 Experimental Methods

Polycrystalline samples of nominal composition $\text{Fe}_{83}\text{Ga}_{17}\text{Er}_x$ ($0 < x < 2.5$) were synthesized from constituent elements of 99.9% purity using vacuum arc melting and directional solidification techniques. The bulk ingots were subsequently placed in an Ar atmosphere and annealed at 900°C for two hours to obtain the desired phase and microstructure. The arc-melted charges were then sliced into cuboid-shaped slabs $0.38" \times 0.38" \times 0.06"$ using a low-speed diamond saw for characterization of structural, magnetic and magnetostrictive attributes. Microstructural analysis was carried out on mechanically polished sample slices [27] using an Electron Backscatter Diffractometer consisting of a JEOL 700F SEM microscope equipped with a TSL OIM analysis unit and a laboratory CuK$_\alpha$ x-ray diffractometer (Rigaku Ultima III). Bragg peaks obtained from the x-ray diffraction pattern were least-squares fit to a Pseudo-Voigt function to estimate lattice parameters of the $\text{Fe}_{83}\text{Ga}_{17}\text{Er}_x$ alloys [28]. During electron back-scattering diffraction (EBSD) measurements, Kikuchi patterns were generated using an acceleration voltage of 20 kV, and recorded by means of a DigiView camera system at a recording speed of the order of 0.1 s/pattern. Slightly longer times were required for multi-phase analysis. The working distance was 20 mm, and the stepsize of the EBSD system was chosen to be 20 nm. More details regarding the measurement procedures may be found in references 23-25 [36–38]. The results of the EBSD measurements are presented in the form of maps, the most important are the so-called inverse pole figure (IPF) maps that indicate crystallographic orientation of individual foci.

Magnetic characterization was carried out using a Vibrating Sample Magnetometer (Lake Shore, Model 7400) in magnetic fields up to $H_{\text{app}} = +/-1.2$ T and in
the temperature range \(300 \, \text{K} \leq T \leq 1000 \, \text{K}\). The magnetic transition temperature \(T_t\) was determined as the inflection point in the derivative of magnetization \(M\) as a function of temperature \(T\) at an applied field of 1 Tesla and the magnetic anisotropy was determined using the law of approach to saturation method. During magnetostriction measurements, the strain gauge was bonded longitudinally to the Galfenol samples in a quarter-bridge configuration to measure the magnetostrictive coefficient along the direction of growth of the samples. A Vishay Micro-measurement P3 strain Indicator was employed to measure the magnetostrictive strain as the magnetic field was swept from 0 to 1 Tesla at room temperature (~300K).

5.2.3 Experimental Results and Discussion

5.2.3.1 Structural Attributes: Crystallographic & Microstructural Properties

X-ray diffraction data of the Fe\(_{83}\)Ga\(_{17}\)Er\(_x\) alloys obtained from scanning the sample plane perpendicular to the growth direction, as shown in Fig. 5.6 (a), indicates the presence of a single phase having the bcc crystal structure (lattice parameter, \(a=2.905 \pm 0.005 \, \text{Å}\)) for all samples of composition \(x<0.6\). An additional Bragg peak corresponding to a minor secondary phase is observed at \(2\theta\sim42^\circ\) as Er is increased to \(x>0.6\). As such, all the samples were found to be polycrystalline in character with a preferred orientation along the [110] growth direction – a feature attributed to the thermal gradient imposed by directional solidification.

Fig. 5.6 (b) illustrates the dependence of relative x-ray intensity of the Bragg planes, (110) and (200) with Er content. At all Er doping concentrations, the (110) plane
retains dominance. Nonetheless, it is interesting to note that the (200) plane increases in intensity and displays the largest value for the x=0.6 alloy. It is therefore concluded that Erbium favors occupation of the (200) planes at a critical concentration of x<0.6. These results are essential to further understanding the following measurements of magnetostriction as a function of Tb content, as will be discussed in the following paragraphs.

![XRD pattern and Bragg peak intensity graph](image)

**Fig. 5.6.** (a) XRD pattern of directional solidified bulk alloys of (Fe$_{0.83}$Ga$_{0.17}$)$_{100-x}$Er$_x$ (0<x<1). An additional Bragg peak corresponding to a minor secondary phase is observed as Er dopant concentration is increased to x>0.6; (b) Dependence of the relative intensity of the Bragg peaks corresponding to (110) and (200) planes on Er content (x).

The scanning electron microscopy (SEM) images of select Fe$_{83}$Ga$_{17}$Er$_x$ alloys (0<x<1) are shown in Fig. 5.7. The microstructure of the parent Fe$_{83}$Ga$_{17}$ alloy consists of a single solid solution with equiaxed grains of dimensions ~ 200 µm (Fig. 5.7 (a)).
Conversely, the morphology of the Er-doped FeGa alloys demonstrates columnar grains mainly composed of a matrix phase (i.e., gray area) and precipitates of a secondary phase (i.e., white area) deposited along the grain boundary. To determine the distribution of elements, the sample Fe$_{83}$Ga$_{17}$Er$_{0.6}$ was analyzed by EDXS. Fig. 5.8(a) and 5.8(b) show SEM morphology and the determination of the elements at spot 1 (grain boundary) and spot 2 (grain). It is noted that the grains are composed primarily of Fe and Ga, while the grain boundary consisting of Fe, Ga as well as a high relative percentage of Er. Stoichiometric determination using EDXS indicates that the Er atoms accumulate in the grain boundary region and form an intermetallic secondary phase, possibly Ga$_6$Er. Presence of the secondary phase in samples of relative high Er concentration is consistent with results obtained by x-ray diffraction analysis (see Fig. 5.6).

Fig. 5.7. Microstructure of Er-doped (Fe$_{0.83}$Ga$_{0.17}$)$_{100-x}$Er$_x$ (x=0, 0.2, 0.4, 0.6).
Fig. 5.8. (a) SEM morphology of Fe_{0.83}Ga_{0.17}. (b) SEM morphology of (Fe_{0.83}Ga_{0.17})_{100-0.6}Er_{0.6}. Grains are composed of Fe and Ga while Grain boundary primary consists of Ga and Er (Ga_6Er secondary phase).

Information regarding the texture of the Fe_{83}Ga_{17}Er_x alloys (0<x<1.5) were obtained using EBSD analysis. Kikuchi patterns obtained using this technique were indexed using material files pertaining to FeGa (based on bcc α-Fe structure; Pearson symbol: cI2) and Ga_6Er (based on tetragonal crystal structure; Pearson Symbol: tP14) structures. Here, it should be noted that we can observe the Ga_6Er phase already from the sample with x=0.2. This demonstrates the importance of a highly spatially resolved measurement. Fig. 5.9 shows the inverse pole figure maps along the [001] direction (i.e., perpendicular to the sample surface) and corresponding pole figures for the following compositions: Fe_{83}Ga_{17} (i.e., the parent compound), Fe_{83}Ga_{17}Er_{0.6} and Fe_{83}Ga_{17}Er_{1.2}. The inverse pole figures shown here provides the crystallographic orientation of the grains.
according to the stereographic triangles for each phase. In confirmation with results obtained by XRD and SEM-EDS, no Ga\textsubscript{6}Er phase is observed in the parent Fe\textsubscript{83}Ga\textsubscript{17} compound (Fig. 5.9 (a)). In Fe\textsubscript{83}Ga\textsubscript{17}Er\textsubscript{0.6}, the Ga\textsubscript{6}Er precipitates are present as indicated as small spots scattered over the scan area (Fig. 5.9 (b)). Conversely, significant aggregation of Ga\textsubscript{6}Er is also found in Fe\textsubscript{83}Ga\textsubscript{17}Er\textsubscript{1.2} (Fig. 5.9 (c)). The IPF maps and the pole figures indicate that while the Fe\textsubscript{83}Ga\textsubscript{17} parent compound demonstrates [001] texture, Fe\textsubscript{83}Ga\textsubscript{17}Er\textsubscript{0.6} and Fe\textsubscript{83}Ga\textsubscript{17}Er\textsubscript{1.2} samples do not exhibit preferred grain orientation. It is important to realize that grain size of both the FeGa and the Ga\textsubscript{6}Er phases in the Fe\textsubscript{83}Ga\textsubscript{17}Er\textsubscript{x} samples increase as a function of Er concentration. On increasing the dopant concentration x, Ga\textsubscript{6}Er forms a secondary phase in the grain boundary region (Fig. 5.9 (b) and (c)), and the orientation of the grains is found to be in (001) and (101) direction. In case, the Ga\textsubscript{6}Er is located within the matrix, the grains have the same orientation as the matrix - a feature attributed to the coherent relationship between the two phases. As the grain size of the FeGa and the Ga\textsubscript{6}Er phases increases, the crystallographic orientation between these phases becomes significantly different (see pole figures in Fig. 5.9 (c)) and thus it is inferred that the secondary phase precipitates are randomly oriented in the matrix phase in the large grained Fe\textsubscript{83}Ga\textsubscript{17}Er\textsubscript{x} alloys.
Fig. 5.9. Inverse pole figure maps and corresponding pole figures for FeGa and the Ga₆Er phases in samples of the following compositions: (a) Fe₈₃Ga₁₇ (parent compound); (b) Fe₈₃Ga₁₇Er₀.₆ and (c) Fe₈₃Ga₁₇Er₁.₂. The inverse pole figures shown here gives the crystallographic orientation of the grains according to the stereographic triangles for each phase.
5.2.3.2 Magnetic Attributes: Field and Temperature – dependent Magnetization

Experimental Results & Discussion

Addition of Er has noteworthy effects on the magnetic properties of [110] textured polycrystalline FeGa alloys. The magnetization behavior of Fe$_{83}$Ga$_{17}$Er$_x$ alloys (0<$x$<1.5) as a function of magnetic field at room temperature ($T$=300 K), shown in Fig. 5.10 (a), indicates that doping with Er increases the saturation magnetization ($M_s$) by approximately 10 % as compared to the Galfenol parent alloy. As shown as the inset to Fig. 5.10 (a), $M_s$ initially increases from 153.8 emu/g to 168.2 emu/g as the Er concentration increases from 0 to 0.6 atomic %. Further increase in Er doping decreases $M_s$ slightly – a feature attributed to the influence of the secondary Ga$_6$Er phase that appears in the boundaries of the Fe$_{83}$Ga$_{17}$ grains in samples of composition Fe$_{83}$Ga$_{17}$Er$_x$, where $x$>0.8. The temperature-dependent magnetization behavior of the Fe$_{83}$Ga$_{17}$Er$_x$ samples at an applied magnetic field of $H$=1000 Oe is shown in Fig. 5.10 (b). Consistent with previous reports, the Curie temperature of Fe$_{83}$Ga$_{17}$ was found to be ~990 K. [32] As such, the $T_c$ of the Fe$_{83}$Ga$_{17}$Er$_x$ alloys are independent of Er concentration.
Fig. 5.10. (a) Magnetization hysteresis loops of $(\text{Fe}_{0.83}\text{Ga}_{0.17})_{100-x}\text{Er}_x$ (x=0, 0.2, 0.6, 1). The inset shows the saturation moment as a function of Er doping amount. (b) Magnetization (emu/g) of $(\text{Fe}_{0.83}\text{Ga}_{0.17})_{100-x}\text{Er}_x$ at $H=10$ k Oe as a function of temperature for different amounts of Er doping.

5.2.3.3 Enhanced Functional Response: Magnetostriction Measurements at Room Temperature

In Fig. 5.11 (a), the magnetostriction strain ($\lambda$) along the direction of growth of the Fe$_{83}$Ga$_{17}$Er$_x$ alloys is plotted as a function of applied magnetic field. In all samples, $\lambda$ increases with applied field until a saturation magnetostriction value ($\lambda_s$) is obtained. In agreement with previous studies on directionally solidified [110] textured FeGa alloys [39], the $\lambda_s$ of Fe$_{83}$Ga$_{17}$ was found to be $\sim 45$ ppm. Change in $\lambda_s$ with Er content (x) for the Fe$_{83}$Ga$_{17}$Er$_x$ alloys is shown in Fig. 5.11 (b). Overall, $\lambda$ increases with Er doping till the maximum of 170 ppm is achieved at x=0.6. Further addition of Er results in a decrease of $\lambda_s$. These results represent a record enhancement of more than $\sim 275\%$ in the saturation magnetostriction ($\lambda_s$) of Fe$_{83}$Ga$_{17}$Er$_x$ alloys with the introduction of small
amounts of Er. For operation in actuators and sensors in low loss magnetoelectric and multiferroic devices such as those described in [31–37], magnetostrictive materials must be operated under mechanical and magnetic bias conditions to achieve maximum strain per unit magnetic field. Thus, permeability (μ) as realized from the derivative of magnetization/magnetostriction with respect to applied magnetic field (dM/dH_{app} or dλ/dH_{app}) is a desired figure of merit in magnetostrictive materials. To this end, it is critical to observe from Fig. 5.11 (a) that the low field derivative of magnetostriction with respect to applied magnetic field (dλ/dH_{app} for H_{app} upto 1000 Oe) increases by ~230% with Er doping (dλ/dH_{app,FeGa} = 0.045 ppm/Oe ; dλ/dH_{app,FeGaEr} =0.15 ppm/Oe).

Fig. 5.11. (a) Magnetostriction of the (Fe_{0.83}Ga_{0.17})_{100-x}Er_{x} (0<x<1) alloys as a function of the applied magnetic field. An enhanced λ_{s} of more than 250% is measured relative to the parent compound. (b) Change in saturation magnetostriction as a function of Er dopant concentration.
For FeGa single crystals, a maximum in magnetostriction is reported along the easy magnetic axis, \textit{i.e.}, along the \langle 1\,0\,0 \rangle crystallographic direction. Assuming the approximation of only dipole–dipole interactions within the material, the magnetostriction values for a \{1\,1\,0\}-textured polycrystalline materials may be calculated using the expression [38]:

\[
\lambda_{110} = \frac{1}{4} \lambda_{100} + \frac{3}{4} \lambda_{111} \tag{1}
\]

Where \(\lambda_{100}\) and \(\lambda_{111}\) are the saturation magnetostriction when the crystal is magnetized and the strain is measured along the \langle100\rangle and \langle111\rangle directions, respectively. In the absence of compressive pre-stress, the calculated values of \((3/2)\lambda_{100}\) and \((3/2)\lambda_{111}\) for Fe\(_{83}\)Ga\(_{17}\) are \(-311\text{ppm}\) and -20 ppm, respectively. [82] Note, that the factor \(3/2\) arises from the definition of magnetostriction as a deformation from a demagnetized state. [38]: It follows from equation (1) that the theoretical \(\lambda_{110}\) for polycrystalline sample of Fe\(_{83}\)Ga\(_{17}\) is \(-42\text{ ppm}\). These estimation are in full agreement with our presented magnetostriction value for the parent compound where \(\lambda_{110} \sim 45\text{ ppm}\) (see Fig. 5.11 (a)).

It is possible to estimate a maximal magnetostrictive coefficient, \((3/2)\lambda_{100}\), for the Er-doped Fe\(_{83}\)Ga\(_{17}\) samples using equation (1)]. Using the same \((3/2)\lambda_{111}\) value as the parent system [82], the \((3/2)\lambda_{100}\) magnetostrictive coefficient of Fe\(_{83}\)Ga\(_{17}\)Er\(_x\) (\(x = 0.6\)) is approximately predicted to be \(\approx 720\text{ ppm}\) – a value twice as high as the corresponding value for the \{100\} oriented \(\text{Fe}_{83}\text{Ga}_{17}\) single crystals (\(\lambda_{\text{single crystal}} \sim 311\text{ppm} [82]\)). It is critical to note that the use of Eq. (1) for the Fe\(_{83}\)Ga\(_{17}\)Er\(_x\) alloys is based on the broad postulation that the doped alloy has similar texturing degree as that of pure Fe\(_{83}\)Ga\(_{17}\) sample. A table summarizing the \((3/2)\lambda_{110}\) results of \{110\} textured rare-earth doped FeGa
alloys is provided in Table 5.1 with relevant references. It is important to note from Table 5.1 that with an exception of one report concerning Fe$_{83}$Ga$_{17}$Ce$_{0.8}$ [73], the magnetostriction response of the Fe$_{83}$Ga$_{17}$Er$_{0.6}$ is higher in magnitude than that reported by other bulk rare-earth-doped polycrystalline FeGa alloys of [110] texture synthesized to date.

Table 5.1. Experimentally determined magnetostriction coefficients of [110] textured rare-earth doped FeGa alloys

<table>
<thead>
<tr>
<th>Alloy</th>
<th>Fabrication technique</th>
<th>$\lambda_{110}$ (ppm)</th>
<th>Condition</th>
<th>References</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fe$<em>{83}$Ga$</em>{17}$</td>
<td>Directional solidification</td>
<td>45</td>
<td>Bulk; Pre-stressed</td>
<td>Current work</td>
</tr>
<tr>
<td>Fe$<em>{83}$Ga$</em>{19}$Tb$_{0.3}$</td>
<td>Directional solidification</td>
<td>85</td>
<td>Bulk; Pre-stressed</td>
<td>T. I. Fitchorov et al. [81]</td>
</tr>
<tr>
<td>Fe$<em>{83}$Ga$</em>{17}$Y$_{0.64}$</td>
<td>Directional solidification</td>
<td>133</td>
<td>Bulk; Compressed under 15 MPa</td>
<td>L. Jiheng et al. [92]</td>
</tr>
<tr>
<td>Fe$<em>{83}$Ga$</em>{17}$Tb$_{0.2}$</td>
<td>Directional solidification</td>
<td>160</td>
<td>Bulk; Pre-stressed</td>
<td>L. Jiang et al. [39]</td>
</tr>
<tr>
<td>Fe$<em>{83}$Ga$</em>{17}$Er$_{0.6}$</td>
<td>Directional solidification</td>
<td>170</td>
<td>Bulk; Pre-stressed</td>
<td>Current work</td>
</tr>
<tr>
<td>Fe$<em>{83}$Ga$</em>{17}$Ce$_{0.8}$</td>
<td>Directional solidification</td>
<td>200</td>
<td>Bulk; Pre-stressed; Sample not at saturation</td>
<td>Z. Yao et al. [73]</td>
</tr>
</tbody>
</table>

At the present time, the enhanced magnetostrictive response of the lightly doped Fe$_{83}$Ga$_{17}$Er$_x$ alloys is attributed to a combination of electronic and microstructural effects. Previous studies conducted by Clark et al. on binary FeGa alloys suggest that the large magnetostriction in this intermetallic alloy originates from local magnetocrystalline anisotropy induced by local short-range interactions between the Ga atoms along specific
crystallographic directions in the disordered body-centered cubic (bcc) α-Fe structure. Likewise, it is likely that the large number of 4f valence electrons and aspherical charge cloud distributions observed in Er atoms lead to enhanced magnetic anisotropy due to crystalline electric field effects. Considering that Er possesses larger atomic radii (178 pm [40]) relative to Fe (127 pm [40]) and Ga (140 pm [40]), it is possible that strain due to local lattice distortions influence the magnetic properties of the Fe$_{83}$Ga$_{17}$Er$_{x}$. In related compounds, namely Tb- and Ce-doped directionally solidified FeGa systems, increase in magnetostriction has been linked to improved grain orientation and morphology. [39,72] Optimal magnetostrictive performance in the Fe$_{83}$Ga$_{17}$Er$_{x}$ system merely requires a slight amount of Er. Excessive doping destroys magnetostriction in these alloys due to limited solid solubility of Er in the FeGa lattice (estimated as ~0.6 atomic % from XRD analysis, see Fig. 5.6) and subsequent formation of the intergranular Ga$_6$Er secondary phase. It is hypothesized that further enhancement of magnetostriction may be achieved either by the application of a compressive pre-stress or by increasing the solid solubility of Er in the bcc FeGa matrix through quenching during the cooling phase of the sample fabrication technique. Indeed, previous studies in the FeGa literature demonstrate that the saturation magnetostriction of Fe$_{83}$Ga$_{17}$ alloys can be remarkably increased by the melt spinning method [23, 26, 40] It is however critical to note that it is difficult to experimentally measure the magnetostriction of melt-spun ribbons as the grains in the sample usually grow perpendicular to the direction of sample growth. [71] Moreover, due to large demagnetizing effects, shape anisotropy in FeGa ribbon samples typically leads to high magnetic saturation fields. [71]
It is worthwhile to discuss the experimental results obtained in this study in the context of He et al.’s recently developed phenomenological model to predict magnetostrictive trends in FeGa alloys doped lightly with rare-earth elements. Accordingly to He et al., the enhanced magnetostrictive behavior of this family of FeGa ternary compounds is influenced by only two factors: microstructural strain induced due to the presence of large rare-earth atoms in the FeGa lattice and single-ion crystal field contribution due to the high magnetocrystalline anisotropy of these elements. If this were indeed true, then the magnetostrictive behavior of [110] textured directionally-solidified Fe$_{83}$Ga$_{17}$Tb$_x$ compounds investigated by Fitchorov et al. [41] or Jiang et al. [22] would be superior to that of the Fe$_{83}$Ga$_{17}$Er$_x$ samples examined in the current study. However, our experimental results suggest the opposite. Insight into a potential explanation for this contradiction may be obtained by examining the x-ray diffraction patterns of the Fe$_{83}$Ga$_{17}$Er$_x$ and Fe$_{83}$Ga$_{17}$Tb$_x$ systems that suggest that the limit of solid solubility of Er in the FeGa lattice (~0.6 atomic %, Fig. 5.6) is greater than that of Tb (~0.2 atomic %, reference [39]). Based on this observation, it is hypothesized that further enhancement of magnetostriction may be achieved by increasing the solid solubility of the rare earth atoms in the bcc FeGa matrix through faster quenching during the cooling phase of the sample fabrication technique. Indeed, previous studies in the FeGa literature demonstrate that the saturation magnetostriction of Fe$_{83}$Ga$_{17}$ alloys can be remarkably increased by synthesizing samples using the melt spinning technique. [23–26] Unfortunately, it is difficult to experimentally measure the magnetostriction of melt-spun ribbons as the grains in the sample usually grow perpendicular to the direction of sample growth. [41] Moreover, due to large demagnetizing effects, shape anisotropy in FeGa
ribbon samples typically leads to high magnetic saturation fields. [41] From the perspective of user inspired research, the directional solidification technique is more amenable for commercial production of rare-earth doped FeGa alloys.

5.2.4 Conclusions

In summary, here we present the effects of Erbium additives upon the microstructure, magnetic and microstructural properties of Fe$_{83}$Ga$_{17}$Er$_x$ alloys prepared by vacuum arc-melting and directional solidification methods. Data obtained in this experimental study indicate a room temperature magnetostriction value of 170 ppm in a [110]-textured polycrystalline sample of nominal composition Fe$_{83}$Ga$_{17}$Er$_{0.6}$ – a value that is ~275% higher than that of the corresponding parent Fe$_{83}$Ga$_{17}$ compound. Overall, addition of small amounts of Er into the FeGa lattice (less than 0.6 atomic %) results in an increase in saturation magnetization and magnetostriction and a reduction in the saturation field. These characteristics are beneficial for practical applications such as actuators in multiferroic magnetic field generators that use a converse magnetoelectric effect [90,91] or high-sensitivity magnetic field sensors that operate based on the direct magnetoelectric effect without the need for a bias dc field [89]. The enhanced magnetostrictive response of the lightly doped Fe$_{83}$Ga$_{17}$Er$_x$ alloys is ascribed to an amalgamation of electronic and microstructural factors, namely: (i) strong local magnetocrystalline anisotropy due to large spin-orbit coupling and the highly anisotropic localized nature of the 4f electronic charge distribution of the Er atom; (ii) improved grain orientation and morphology due to deposition of Er in the intergranular region and (iii) local strain effect that may arise due to incorporation of Er into the FeGa lattice.
Excessive Er doping (greater than 0.8 atomic %) destroys the improved magnetostriction in Fe$_{83}$Ga$_{17}$Er$_x$ alloys due to formation of an undesirable secondary phase that is identified as the intermetallic compound, Ga$_6$Er. Overall, these results highlight the potential for modifying the functional response of FeGa alloys by addition of tiny amounts of the rare-earth element, Erbium. To further understand the origin of the superior functional response of rare-earth doped FeGa systems, future work involving computational modeling of the magnetostrictive behavior of these compounds is desired.

5.3. Gadolinium doped Galfenol:

5.3.1 Introduction

Following our previous work that have been discussed in this chapter, we also introduced Gd as a third dopant in FeGa alloys and measured microstructural and magnetostriction properties of the doped FeGa alloys. In this study, a series of Gd-doped [110]-textured polycrystalline alloys Fe$_{83}$Ga$_{17}$Gd$_x$ (0<x<1) were fabricated by vacuum arc-melting and directional solidification techniques. Experiments indicate an enhancement of more than ~160 % from ~45 ppm to 120 ppm in the saturation magnetostriction ($\lambda_s$) of Fe$_{83}$Ga$_{17}$Gd$_x$ alloys with the introduction of small amounts of Gd. Moreover, it is noted that the low field derivative of magnetostriction with respect to applied magnetic field (i.e. $d\lambda_s/dH_{app}$ for $H_{app}$ up to 1000 Oe) increases notably.
5.3.2 Experimental Methods:

Polycrystalline samples of nominal composition Fe$_{83}$Ga$_{17}$Gd$_x$ (0<x<1) were synthesized from constituent elements of 99.9% purity using vacuum arc melting and directional solidification techniques. The bulk ingots were subsequently placed in an Ar atmosphere and annealed at 900°C for two hours to obtain the desired phase and microstructure. The arc-melted charges were then sliced into cuboid-shaped slabs 0.38" × 0.38" × 0.06" using a low-speed diamond saw for characterization of structural, magnetic and magnetostrictive attributes. A laboratory CuK$_\alpha$ x-ray diffractometer (Rigaku Ultima III) was used to analyze microstructure properties of doped alloys. A Vishay Micro-measurement P3 strain Indicator was employed to measure the magnetostrictive strain as the magnetic field was swept from 0 to 1 Tesla at room temperature (~300K). During magnetostriction measurements, the strain gauge was bonded longitudinally to the Galfenol samples in a quarter-bridge configuration to measure the magnetostrictive coefficient along the direction of growth of the samples.

5.3.3 Experimental Results and Discussion

5.3.3.1 Structural Attributes: Microstructural Properties

X-ray diffraction data of the Fe$_{83}$Ga$_{17}$Gd$_x$ alloys obtained from scanning the sample plane perpendicular to the growth direction, as shown in Fig. 5.12, indicates the presence of a single phase having the bcc crystal structure for all samples of composition x<0.4. An additional Bragg peak corresponding to a minor secondary phase is observed at 2θ~42° as Gd is increased to x>0.4. As such, all the samples were found to be
polycrystalline in character with a preferred orientation along the [110] growth direction – a feature attributed to the thermal gradient imposed by directional solidification.

Fig. 5.13 illustrates the dependence of relative x-ray intensity of the Bragg planes, (110) and (200) with Gd content. At all Gd doping concentrations, the (110) plane retains dominance. Nonetheless, it is interesting to note that unlike Tb and Er doped Fega alloys, in Fe$_{83}$Ga$_{17}$Gd$_x$ alloys, the (200) plane does not follow any pattern and therefore could be conjectured that Gd does not favor occupation of the (200) planes at a critical concentration of $x<0.4$.

![XRD pattern of directional solidified bulk alloys of (Fe$_{0.83}$Ga$_{0.17}$)$_{100-x}$Gd$_x$](image)

Fig. 5.12 XRD pattern of directional solidified bulk alloys of (Fe$_{0.83}$Ga$_{0.17}$)$_{100-x}$Gd$_x$ ($0<x<0.6$). An additional Bragg peak corresponding to a minor secondary phase is observed as Gd dopant concentration is increased to $x>0.4$;
5.3.3.2 Enhanced Functional Response: Megnetostriction Measurements at Room Temperature

In Fig. 5.14, the magnetostriction strain ($\lambda$) along the direction of growth of the Fe$_{83}$Ga$_{17}$Gd$_x$ alloys is plotted as a function of applied magnetic field. In all samples, $\lambda$ increases with applied field until a saturation magnetostriction value ($\lambda_s$) is obtained. In agreement with previous studies on directionally solidified [110] textured FeGa alloys [39], the $\lambda_s$ of Fe$_{83}$Ga$_{17}$ was found to be $\sim$ 45 ppm. Change in $\lambda_s$ with Gd content ($x$) for
the Fe$_{83}$Ga$_{17}$Gd$_x$ alloys is shown in Fig. 5.15 Overall, $\lambda$ increases with Gd doping till the maximum of 120 ppm is achieved at $x=0.4$. Further addition of Gd results in a decrease of $\lambda_s$. These results represent a record enhancement of more than ~160 % in the saturation magnetostriction ($\lambda_s$) of Fe$_{83}$Ga$_{17}$Gd$_x$ alloys with the introduction of small amounts of Gd.

As mentioned before, for operation in actuators and sensors in low loss magnetoelectric and multiferroic devices such as those described in [31–37], magnetostrictive materials must be operated under mechanical and magnetic bias conditions to achieve maximum strain per unit magnetic field. As observed in Fig. 5.14, in Fe$_{83}$Ga$_{17}$Gd$_x$ alloys like Fe$_{83}$Ga$_{17}$Er$_x$, the low field derivative of magnetostriction with respect to applied magnetic field ($d\lambda/dH_{app}$ for $H_{app}$ upto 1000 Oe) increases notably with Gd doping.
Fig. 5.14 Magnetostriction of the (Fe$_{0.83}$Ga$_{0.17}$)$_{100-x}$Gd$_x$ ($0<x<1$) alloys as a function of the applied magnetic field. An enhanced $\lambda_s$ of more than 160% is measured relative to the parent compound.

Fig. 5.15 Change in saturation magnetostriction as a function of Gd dopant concentration.
5.3.4 Conclusions

In summary, here we presented the effects of Gadolinium additives upon the microstructure and magnetostrictive properties of Fe$_{83}$Ga$_{17}$Gd$_x$ alloys prepared by vacuum arc-melting and directional solidification methods. Data obtained in this experimental study indicate a room temperature magnetostriction value of 120 ppm in a [110]-textured polycrystalline sample of nominal composition Fe$_{83}$Ga$_{17}$Gd$_{0.4}$ – a value that is ~160% higher than that of the corresponding parent Fe$_{83}$Ga$_{17}$ compound. Overall, addition of small amounts of Gd into the FeGa lattice (less than 0.6 atomic %) results in an increase in saturation magnetization and magnetostriction and a reduction in the saturation field. These characteristics are beneficial for practical applications such as actuators in multiferroic magnetic field generators that use a converse magnetoelectric effect [90,91] or high-sensitivity magnetic field sensors that operate based on the direct magnetoelectric effect without the need for a bias dc field [89]. Excessive Gd doping (greater than 0.8 atomic %) destroys the improved magnetostriction in Fe$_{83}$Ga$_{17}$Gd$_x$ alloys due to formation of an undesirable secondary phase. Overall, these results highlight the potential for modifying the functional response of FeGa alloys by addition of tiny amounts of the rare-earth element, Gadolinium.
6 MARKET AND IMPACT ASSESSMENT

Smart materials are specialty-building materials whose properties tend to vary when subjected to external stimuli such as stress, temperature, moisture, and magnetic field [1–3]. These materials are called smart materials because of the change inherent in them, and not due to an external force. Magnetostrictive materials is one of the most important part of smart materials which their shape is change during the process of magnetization [2,6]. Magnetostrictive materials have been on the market since World War II and serve a large number of applications mostly in actuators [10,11](where a magnetic field is applied to cause a shape change) and sensors (which convert a movement into a magnetic field) [12].

There are quite a few drivers contributing to the growth of the Global magnetostrictive material market including Galfenol. Rising demand from the sonar industry is driving the overall market. The applications of Galfenol magnetostrictive materials mostly fall in these main categories: Sensors [2,3,13,15,20,53,94], Energy harvesting [5,16] and transducers [7,10–12,53] and sonar systems [2,7,20,53].

This report on market and impact assessment of magnetostrictive material is based on in-depth qualitative and quantitative analysis of various market research. In this chapter market analysis has been done by using “Global Rare Earth Giant Magnetostrictive Global Rare Earth Giant Magnetostrictive Material” sample research done by QYR Research Center [95] and Global Smart Materials Market by Technavio Research [96]. The Qualitative analysis involves the application of various projection and sampling techniques, whereas quantitative analysis involves primary interviews, surveys, and vendor briefings. So the data analysis reported in this section is based on the author’s best
knowledge at this time and subject to change with different parameters in the market at any time.

6.1. Market Research Methodology:

For analyzing the data before preparing the report, primary as well as secondary research techniques was adopted to ascertain the size and vendor landscape of the Global and also US Magnetostrictive Materials Market. The information is obtained using a combination of the bottom-up and top-down approaches. The data is then corroborated with data obtained from various market participants and stakeholders across the value chain, including vendors, research facilities, related industries, and end-users.
6.2. Market Landscape:

The global market for smart materials totaled about $26 billion in 2014 and is expected to reach $42.2 billion in 2019, registering a compound annual growth rate (CAGR) of 10.2% for the period 2014-2019. Assuming that $1/10^{th}$ of the money goes to magnetostrictive materials, the Global magnetostrictive materials market is expected to grow at a CAGR of 2% percent during the forecast period. Since 40% of magnetostrictive market goes to Galfenol, there will be $1.688$ billion global market in it.
The US Magnetostrictive Materials market is expected to be vibrant during the forecast period. With the rising investment in R&D for product innovation and the rising demand from the air force and navy, the demand for magnetostrictive materials including Galfenol is expected to rise considerably during the forecast period. Additionally, high demand for the less rare-earth doped Galfenol as a potential substitute for heavy rare earth magnetostrictive materials is expected to drive market growth.

6.3. Market Growth Driver:

Some of the major growth drivers included in the US Magnetostrictive Materials market are discussed below:

- Increased demand from Navy and Military Sonar sector
- Increasing demand from energy sector
- Rising demand from Construction Industry

The demand for Galfenol consistently driven by the growing need for such materials from the Navy and Military and also department of energy sector. Galfenol is of interest to sonar researchers because magnetostrictive materials are used to detect sound, and amplifying the magnetostrictive effect could lead to better sensitivity of sonar detectors. That is why Galfenol with enhanced magnetostrictive properties are gaining demand in the sonar industries. Additionally, by solving the internal structure of Galfenol the use of
FeGa alloy technology for detecting sound will provide a huge boost to the magnetostrictive materials market globally.

| Market Size          | 2013: US$ 1.04 billion  
<table>
<thead>
<tr>
<th></th>
<th>2019: US$ 1.688 billion</th>
</tr>
</thead>
</table>
| Key Geographies      | APAC                   
|                      | EMEA                   
|                      | Americas               |
| Key Leading Countries | USA                    
|                      | China                  
|                      | Canada                 
|                      | UK                     
|                      | India                  |
| Key Customer Segments | Transportation         
|                      | Agriculture and Food   
|                      | Healthcare             
|                      | Construction and Infrastructure 
|                      | Leisure and Sports     |
| Key Applications     | Motors                 
|                      | Sensors                
|                      | Transducers            
|                      | Building Materials     |
| Key Market Drivers   | Military Aerospace Sector 
|                      | Navy                   
|                      | Energy Sector          |
| Key Market Challenges | Lack of Awareness of Magnetostrictive Materials |
| Key Buying Criteria  | Cost                   
|                      | Availability           
|                      | Efficiency             |
| Key Vendors          | Aerofit LLC            
|                      | Bayer Material Science 
|                      | Advanced Cerametrics   
|                      | Metglas                |
| Other prominent Vendors | Kyocera               
|                      | Fine tube              
|                      | Lord                   
|                      | M-Biotech              
|                      | Nikon Corp.            
|                      | Mitsubishi Industrial  |
Table 6.1: Smart materials market

6.4. Market Challenges: Lack of Awareness of Smart Material

Galfenol is a high performance magnetostrictive material that have numerous benefits in fields such as sonar system, energy harvesting, transduce, actuators, etc. However, their growth in the market is dependent on how well they are marketed. Many end-users are not aware of such high performance magnetostrictive material. Many other end-users who own magnetostrictive materials, but do not have well-planned strategies to sell their products and spread the awareness about the benefits of Galfenol over other magnetostrictive materials.

In the sound industry, builders are not reliably apprised of the benefits of Galfenol in their sound systems, especially in commercial applications. Additionally, in these industries Galfenol technologies are still at a nascent stage and innovation calls for proper planning, propaganda and appropriate skills. Similarly, in the Sports and Leisure industry, lack of awareness and understanding of the applications of smart materials prevails in many parts of the world and there is a dearth of published information on the use of smart materials in the market.
7  CHAPTER 7  CONCLUSION

7.1. Summary of work:

Magnetostrictive materials are one of the most important class of the smart materials. Magnetostrictive materials can convert magnetic energy to kinetic energy and that is why they play an important role in a wide range of commercial applications including acoustic sensors and transducers, linear motors, actuators torque sensors, energy harvesters, etc.

Cobalt shows the greatest room temperature magnetostriction among pure elements and (Dy$_{0.7}$Tb$_{0.3}$)Fe$_2$ (also known as Terfenol-D) which exhibits about 2000 microstrains is best known to have the highest magnetostriction among alloys. It is well known that Terfenol D has several major drawbacks that constrains its use in commercial devices to:

(i) high cost and global shortage of the rare-earth elements, Tb and Dy; [19] (2) low mechanical integrity (high brittleness, low yield stress, low magneto-mechanical coupling) [20] and (3) high fields required for magnetic saturation [21].

Galfenol which is an alloy of iron and gallium appears to be promising in filling the role as a mechanically robust material with favorable magnetostrictive capability [60]. Galfenol is rare earth free, inexpensive and corrosion resistant and that is why has particularly drawn wide attention in various applications as mentioned above [2,7–9]. After Galfenol was discovered In 1998, extensive work have been undertaken to improve it’s microstructure and magnetostrictive properties. Over the past two decades, a variety of sample synthesis and processing techniques have been explored [21,23,51,53,56–58,97] to provide a means for controlling the structural properties and hence the magnetostrictive behavior of this alloy system [53]. To this end, textured polycrystalline forms of this material are
likely to be more commercially viable [21] [83]. Textured polycrystalline samples (ingots, sheets, rods and ribbons) have been fabricated using a variety of methods that have been discussed in chapter 3, including arc-melting followed by directional solidification, directional solidification using the modified Bridgman technique [21], cold rolling [84], melt-spinning [85], combinatorial sputtering [86], and powder processing, etc.

Besides new fabrication technique’s investigation, the influence of ternary element addition on the magnetostrictive performance of FeGa compounds have also studied for magnetostriction improvement of FeGa alloys [29,30,33,34,60]. What have been found showed that, neither by addition of 3d and 4d transition elements such as Ni, V, Cr, Mn, Co, Mo and Rh nor the main group elements including Si, Ge and Sn or even the interstitial elements including B, C, and N, the saturation magnetostriction could not be enhanced notably. That is where the motivation for exploring new ways for magnetostriction improvement of FeGa alloys come from.

In the last few years, a few studies have been done on investigating the influence of rare earth doping on the magnetostrictive performance of FeGa compound [39,70,72–74]. Our collaborators Liping Jiang et. al. [39] in china in a work with our group could show that small amount of Tb doping could increase the magnetostrictive performance of FeGa alloys more than twice. Tb and Dy have the strong spin-orbital coupling of the 4f electrons and could cause strong local magnetocrystalline anisotropy which leads to magnetostriction enhancement. After some work that have been done on the effect of Tb and Dy doped FeGa, in this project we have worked and reported the influence of the Er and Gd doping on microstructure and magnetostrictive performance of FeGa alloys.


7.2. Conclusions:

In summary, in this project, we present the effects of Erbium and Gadolinium additives upon the microstructure, magnetic and microstructural properties of \( \text{Fe}_{83}\text{Ga}_{17}\text{Er}_x \) and \( \text{Fe}_{83}\text{Ga}_{17}\text{Gd}_x \) alloys prepared by vacuum arc-melting and directional solidification methods. Data obtained in this experimental study indicate a room temperature magnetostriction value of 170 ppm in a [110]-textured polycrystalline sample of nominal composition \( \text{Fe}_{83}\text{Ga}_{17}\text{Er}_{0.6} \) – a value that is ~275% higher than that of the corresponding parent \( \text{Fe}_{83}\text{Ga}_{17} \) compound and also a room temperature magnetostriction value of 120 ppm in a [110]-textured polycrystalline sample of nominal composition \( \text{Fe}_{83}\text{Ga}_{17}\text{Gd}_{0.4} \) – a value that is ~160% higher than that of the corresponding parent \( \text{Fe}_{83}\text{Ga}_{17} \) compound. Overall, addition of small amounts of Er into the FeGa lattice (less than 0.6 atomic %) results in an increase in saturation magnetization and magnetostriction and a reduction in the saturation field. The same phenomena happens for Gd doped FeGa alloys. These characteristics are beneficial for practical applications such as actuators in multiferroic magnetic field generators that use a converse magnetoelectric effect [90,91] or high-sensitivity magnetic field sensors that operate based on the direct magnetoelectric effect without the need for a bias dc field [89]. The enhanced magnetostrictive response of the lightly doped \( \text{Fe}_{83}\text{Ga}_{17}\text{Er}_x \) alloys is ascribed to an amalgamation of electronic and microstructural factors, namely: (i) strong local magnetocrystalline anisotropy due to large spin-orbit coupling and the highly anisotropic localized nature of the \( 4f \) electronic charge distribution of the Er atom; (ii) improved grain orientation and morphology due to deposition of Er in the intergranular region and (iii) local strain effect that may arise due to incorporation of Er into the FeGa lattice. Excessive Er doping (greater than 0.8 atomic
%) destroys the improved magnetostriction in $\text{Fe}_{83}\text{Ga}_{17}\text{Er}_x$ alloys due to formation of an undesirable secondary phase that is identified as the intermetallic compound, $\text{Ga}_6\text{Er}$. For $\text{Fe}_{83}\text{Ga}_{17}\text{Gd}_{0.4}$ alloys, same as $\text{Fe}_{83}\text{Ga}_{17}\text{Er}_x$, Gd doping more than 0.6 will lead to magnetostriction reduction as a result of the formation of a secondary phase.

Overall, these results highlight the potential for modifying the functional response of FeGa alloys by addition of tiny amounts of the rare-earth elements, Erbium and Gadolinium. To further understand the origin of the superior functional response of rare-earth doped FeGa systems, future work involving computational modeling of the magnetostrictive behavior of these compounds is desired.

### 7.3. Recommendations for future work:

FeGa (i.e., Galfenol) alloys, some of the most important functional magnetic materials, have only recently found their way into sonar systems; force, displacement, and torque sensors; and acoustic and tactile sensors [1–3,7,13,20,53,94]. In practical applications, sensors or transducers are required to work over a broad range of temperatures (-40 to 120 °C) [81]. This in turn requires magnetostrictive materials having high thermal stability. The temperature stability of $\text{Fe}_{81}\text{Ga}_{19}\text{Tb}_x$ (x = 0.3) and $\text{Fe}_{81}\text{Ga}_{19}$ (i.e. Galfenol) alloys is investigated over a temperature range from 10 to 1000 °C. It has been noticed that Tb doping stabilized magnetostriction properties of FeGa alloys [81]. It is predicted that we see the same trend with other rare earth elements including Er and Gd. More study needs to be done on the magnetostrictive behaviors of the FeGa alloys doped with Er and Gd.
Besides that, exploring other fabrication techniques for making rare earth doped FeGa other than Directional Solidification would be another approach for developing high magnetostrictive rare-earth doped FeGa alloys.
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