

# FERROIC MATERIALS- BASED TECHNOLOGIES

*Edited By*  
Inamuddin  
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# Ferroic Materials-Based Technologies

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# **Ferroic Materials-Based Technologies**

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**Inamuddin**  
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**WILEY**

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## Preface

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Ferroic materials have sparked widespread attention because they represent a broad spectrum of elementary physics and are employed in a plethora of fields, including flexible memory, enormous energy harvesting/storage potential, spintronic functionalities, spin caloritronics, and a large range of other multi-functional devices. Moreover, in multiferroic materials, two or more primary ferroic orderings—such as ferroelectrics; Dia-, Para-, Ferro-, Ferri-, and Antiferromagnetic materials; ferroelastic materials; and ferrotoroidicity as the fourth form of ferroic order—are all present simultaneously in the similar phase. Magnetic materials exhibit significant electro-mechanical coupling, pyro-electricity, and electro-optical characteristics, as well as spontaneous but switchable magnetic behavior, whereas ferroelectric materials exhibit spontaneous but switchable electric polarization.

With the application of new ferroic materials, a strong room-temperature ferroelectricity with high saturation polarization may be established in ferroelectric materials, and magnetism with significant magnetization can be accomplished in magnetic materials. Furthermore, magnetoelectric interaction between ferroelectric and magnetic orderings is high in multiferroic materials, which could enable a wide range of innovative devices. Magnetic, ferroelectric, and multiferroic 2D materials with ultrathin characteristics above ambient temperature are often expected to enable future miniaturization of electronics beyond Moore's law for energy-efficient nanodevices. This book addresses the prospective, relevant, and original research developments in the ferroelectric, magnetic, and multiferroic fields. Readers of this book will gain a better understanding of ferroic materials, their related technologies, and their various applications. In fields both specific and related to ferroic materials, this book serves as a great reference tool for students, physicists, academics, researchers, and professionals.

Chapter 1 gives a complete overview of ferroic materials, their history, and the latest progress. It discusses four main types, ferromagnetic, ferroelastic, ferroelectric, and multiferroic materials, while explaining their

properties and various applications like data storage, sensors, and more. The chapter also covers the current research pertaining to these materials.

Chapter 2 encapsulates the history and current presence of ferroic materials. This chapter gives details of ferroic materials, e.g., primary and secondary types of ferroic materials. Primary ferroic materials include ferromagnetic, ferroelectric, and ferroelastic, while secondary ferroic materials include multiferroics, ferromagnetoelectric, ferromagnetoelastic, and ferroelastoelectric materials, and all are addressed. The origin of ferroelectricity, ferroelasticity, ferromagnetism, scaling, and recent advances in ferroic materials is also outlined.

Chapter 3 covers an in-depth evaluation of the state of these materials currently and their promising future possibilities. This chapter offers a greater understanding of the possible improvements and applications of ferroic and multiferroic materials in a variety of industries, making it an invaluable resource for researchers and scientists.

Chapter 4 presents a brief history, working principle, theory, and various measurement techniques of electrocaloric effect (ECE) in ferroelectrics. Furthermore, it focuses on different strategies that are adopted to enhance ECE in various lead-based and lead-free ferroelectrics, relaxor ferroelectrics, and hafnia-zirconia-based ferroelectrics.

Chapter 5 discusses the preparation, improvement, and characterizations of ferroelectric and ferroelastoelectric materials. Several synthesis methods for ferroelectric and ferroelastoelectric materials are explained in detail. Improvements and applications of ferroelectric and ferroelastoelectric materials are also discussed.

Chapter 6 examines the elastocaloric impact (ECE) in the discipline of solid-state cooling. Ferroelectric materials are employed for solid-state cooling purposes due to their distinctive thermodynamic features and phase transition uses. Additionally, ECE is further divided into uniaxial and biaxial based on its behavior in the microstructure of materials.

Chapter 7 discusses the flexoeffect alterations in the ferroic nanosystem and their attributes that result from the inhomogeneity of order parameters. This effect exists spontaneously. The equation framework of FCT (flexoelectric coupling tensor) for various point groups using a direct matrix approach, including the quantity of non-zero independent components, is also covered.

Chapter 8 covers recent advancements in ferroic thin films, multi-layers, and hetero-structures, including their historical background, properties, and characterization methods. The significance of atomically controlled thin films and interfaces is emphasized, along with their applications in microelectronics, data storage, sensing, and energy conversion. The



chapter also reviews the ongoing research into the enhancement of their characteristics and the expansion of their usage in the future.

Chapter 9 deals with multiferroic materials, their origin, history, and present development, along with the origin of ferromagnetic, antiferromagnetic, and ferroelectric phases. Classification of multiferroics in single-phase and composite multiferroic materials based on their coupling is also addressed. Single-phase multiferroics classification in type I and type II multiferroics and their prominent examples are discussed, as are possible applications, such as magnetic field sensors, memory devices, and laser applications of multiferroics.

Chapter 10 delves into the basic concepts, formation mechanism, phase structure, feasibility, and classifications of ferroic materials. Furthermore, it elaborates on comparing primary and secondary ferroics along with multi-ferroics formation and their relation with both classes of ferroic materials. Applications of these ferroic materials in various fields, including nanotechnology, are also elaborated upon.

Chapter 11 discusses the importance of domain boundary engineering in multiferroic materials and how it affects the properties of these materials. Domain boundary engineering can be used to manipulate the domain structure and affect the interaction between various ferroic orders. The advantages and challenges of domain boundary engineering are also discussed.

In chapter 12, magneto-electric, dielectric, and optical features of ferro/antiferroelectric materials are explained in detail. Polarization curves for 0.96BaTi–0.04BaFO were studied after the samples had been treated at different temperatures. Additionally, dielectric characteristics of La-modified AFE PbZrO<sub>3</sub> thin films, BNTC22, PLZST-AFE material and BiMgFeCeO<sub>6</sub> are reviewed.

Chapter 13 details the rapid growth in smart electronic and optical devices based on metal-halide perovskites (MHPs), due to their auspicious and innovative semiconducting nature to show ferroelectric behavior. The theoretical and experimental evidence of the ferroic nature of MHPs, the dimension dimension-dependent ferroelectricity within MHPs, and their applications in devices are all covered thoroughly.

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# Ferroic Materials: From Past to Present

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## Abstract

The chapter provides an overview of the development and applications of ferroic materials. The chapter begins with a brief history of ferroic materials and their discovery and a detailed discussion of the four major types of ferroic materials: ferromagnetic, ferroelastic, ferroelectric, and multiferroic materials. The section on ferromagnetic materials covers their magnetic properties and applications in data storage, sensing, and medical imaging. The section on ferroelastic materials describes their mechanical properties and applications in actuators, sensors, and energy-harvesting devices. The section on ferroelectric materials explains their electrical properties and applications in capacitors, transducers, and memory devices. Finally, the section on multiferroic materials discusses their unique combination of multiple ferroic properties and their potential applications in next-generation devices such as spintronics, magneto-electric sensors, and nonvolatile memory. The chapter concludes by mentioning the present state of research and probable future directions for developing and applying ferroic materials. This chapter comprehensively introduces ferroic materials, their historical development, and their diverse applications across multiple fields. It will interest researchers, students, and materials science, physics, and engineering professionals.

**Keywords:** Ferromagnetic, ferroelectric, ferroelastic, multiferroic, piezoelectric sensors, magnetic sensors

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## 1.1 Introduction

Ferroic materials exhibit ferroic ordering, a long-range ordered state in which the material shows a spontaneous polarization, magnetization, strain, or other physical properties. Intense research has been done on these materials over the past few decades due to their potential for various technological applications.

One of the most critical applications of ferroic materials is in the field of data storage. Ferromagnetic materials, for example, are used extensively in hard disk drives, where they store digital information in magnetic domains. Ferroelectric materials, on the other hand, are used in nonvolatile memory devices. One example of a nonvolatile memory device is ferroelectric random access memory (FeRAM). It has faster access times and lower power consumption than conventional memory devices. In data storage, ferroelastic materials have some potential applications because they can undergo reversible strain, and this property can be utilized to develop data storage devices with high-density data [1, 2].

Besides data storage, ferroic materials have found applications in various other fields. For example, ferromagnetic materials are used in motors, transformers, and generators due to their ability to generate a magnetic field.

The study of ferroic materials has a long and rich history, dating back to the discovery of ferromagnetism in lodestones by the ancient Greeks. However, it was in the 1930s that the concept of ferroic materials as a class of materials with similar properties was established. Since then, the field has proliferated with the discovery of new materials and phenomena and the development of new characterization techniques [3].

Recently, ferroic materials came into the limelight due to their potential use in technologies such as nanoelectronics and spintronics. Developing new synthesis and fabrication techniques has caused the formation of new materials with novel properties and functionalities, such as multiferroics, which exhibit more than one type of ferroic ordering. The study of ferroic materials is a crucial research field with a wide range of practical applications across different industries and disciplines. The history of ferroic materials research dates back centuries, and recent developments in synthesis and characterization techniques have led to the discovery of new materials with novel properties and functionalities. The remaining sections of this chapter will provide a detailed overview of the different types of ferroic materials, their properties, and their applications.

## 1.2 Types of Ferroic Materials

Ferroic materials encompassed various types of ordered materials. Ferromagnetic materials, such as iron and nickel, possessed spontaneous magnetization even without an external magnetic field. Ferroelectric materials, like barium titanate and lead zirconate titanate, exhibited spontaneous electric polarization that could be reversed with an electric field. Ferroelastic materials, including shape memory alloys like Nitinol, showcased reversible deformation and strain. Moreover, multiferroic materials exhibited multiple ferroic properties simultaneously, allowing for coupling between different types of orderings. These materials offered promising potential for applications in diverse fields, including magnetoelectric sensors and memory devices [4]. Figure 1.1 shows the types of ferroic materials.

### 1.2.1 Ferromagnetic Materials

Ferromagnetic materials are a type of ferroic materials that exhibit spontaneous magnetization. This means that these materials have some magnetic behavior even when no external magnetic field exists. Ferromagnetic materials have been extensively studied over the past century due to their importance in technological applications.

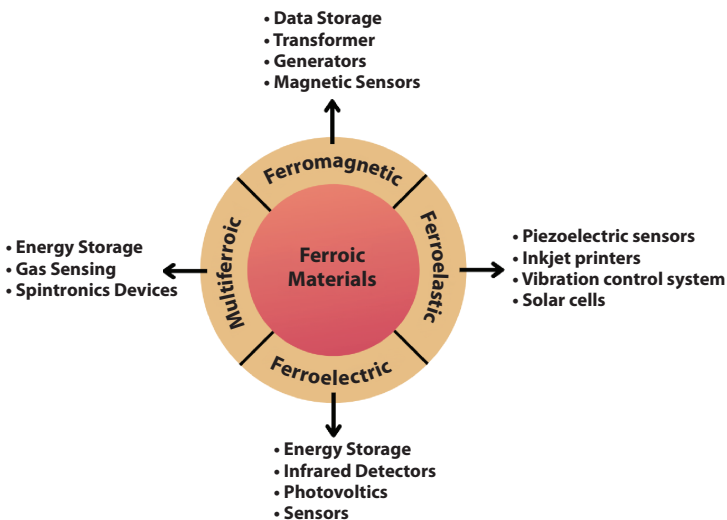


Figure 1.1 Types of ferroic materials.

### 1.2.1.1 *Past of Ferromagnetic Materials*

Ferromagnetism dates back to ancient times when the Greeks discovered that certain minerals could attract iron. However, it was not until the 19th century that the phenomenon was studied in detail. In 1820, Hans Christian Oersted saw a magnetic needle gets deflected when placed near a current-carrying wire, indicating a relationship between electricity and magnetism. This led to the development of electromagnetic theory and the discovery of the connection between electricity and magnetism.

In 1825, William Sturgeon developed the first practical electromagnet, which used a coil of wire to create a magnetic field. This was followed by the development of permanent magnets made of ferromagnetic materials such as iron, cobalt, and nickel. In 1915, the German physicist Wilhelm Lenz proposed the concept of ferromagnetism, which explained the phenomenon of spontaneous magnetization in certain materials [5].

Ferromagnetic materials have found numerous technological applications. One of the most important applications is in the field of data storage. Hard disk drives, for example, use ferromagnetic materials to store digital information in the form of magnetic domains. The development of high-density magnetic storage devices has been made possible by discovering new ferromagnetic materials and fabrication techniques.

Ferromagnetic materials are also used in various electrical and electronic devices, such as motors, transformers, and generators, due to their ability to generate a magnetic field. In addition, they are used in magnetic sensors and actuators, which are widely used in automotive, aerospace, and biomedical applications.

### 1.2.1.2 *Present of Ferromagnetic Materials*

Recent developments in ferromagnetic materials research have focused on discovering new materials with improved magnetic properties. The development of magnetic nanoparticles is one of the most promising research areas, with potential applications in magnetic resonance imaging (MRI), drug delivery, and magnetic hyperthermia. In addition, there has been significant progress in the development of spintronics. This field aims to utilize the electronic spin and its charge for information processing and storage. Ferromagnetic materials are crucial in spintronics, as they are used as magnetic electrodes and spin injectors [6].

Chiu and colleagues conducted research where they explored ferromagnetic shape memory alloys (FSMA) in actuating robots. Their findings indicated that Ni-Mn-Ga alloys were well-suited for this purpose, as they

exhibited a high work:volume ratio with rapid response rates. The alloys had a 5-modulated (5M) martensite phase, which could provoke martensite variant reorientation (MVR) when an external magnetic or stress field is applied. Additionally, the study revealed that 7–13 vol.% of the Ni-Mn-Ga alloy was necessary to initiate MVR [7].

Wang *et al.* found that the heterogeneous nanocrystalline Co/Ni sample exhibited a high permeability and good impedance similarity between permeability and permittivity, resulting in good absorption in the Ku-band (12–18 GHz). The CoNi microsphere sample displayed good absorption in the microwave region, also known as C-band (4–8 GHz) and X-band (8–11.5 GHz). On the other hand, CoNi microspheres with diameters greater than 2  $\mu\text{m}$  formed chain-like structures that demonstrated inadequate microwave absorption capability [8].

A  $\text{Fe}_3\text{O}_4$ -based aerogel was produced by Lo *et al.* via the sol-gel method and supercritical freezing. Loaded Ag enhanced its photocatalytic Fenton-oxidation and reduction activities, leading to the efficient removal of benzoic acid and the production of 4-aminophenol under visible light. The Ag-loaded porous structure of the aerogel provided a high surface area, many active sites, and many active radicals. The research provides valuable information on creating a highly effective aerogel catalyst that can be used for environmental clean-up purposes [9].

Choi *et al.* added carbon to FePt ferromagnetic grains to improve magnetic isolation and enable smaller grain sizes. This is important for developing high-density magnetic recording media, such as heat-assisted magnetic recording (HAMR) technology. This technology is used in hard disk drives and other data storage devices to increase capacity. By identifying the optimal carbon concentration for L10-ordered FePt films, the researchers have provided a valuable guide for designing media with high areal densities of 4 Tb/in<sup>2</sup> and beyond, which could lead to even higher capacity and more advanced data storage technologies in the future [10]. Fe/N codoping was used by Li *et al.* to alter the magnetic and electrical properties of graphdiyne (GDY) materials. The Fe-N-GDY achieved high conductivity as a ferromagnetic semiconductor with a Curie temperature of about  $-68^\circ\text{C}$ . Fe-N-GDY could be used as a conductive ink in printers and flexible field-effect transistors with a high mobility of  $215\text{ cm}^2\text{ V}^{-1}\text{ s}^{-1}$ . These results demonstrate an easy way of modulating the properties of GDY and promoting its potential in electronic devices [11]. A few more recent studies are mentioned in Table 1.1.

In conclusion, ferromagnetic materials are a class of ferroic materials that exhibit spontaneous magnetization. They have been extensively studied for their applications in modern-day technologies, such as



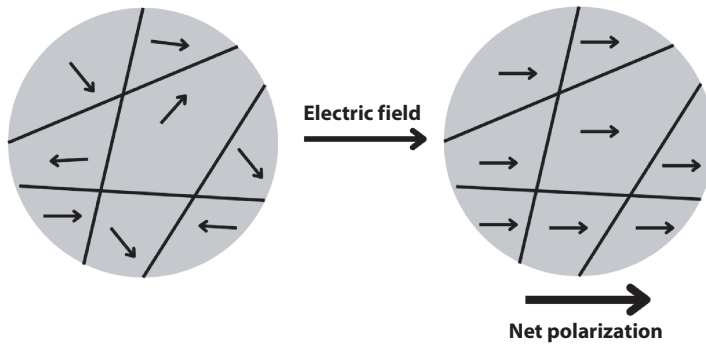
**Table 1.1** Some recent studies of various ferromagnetic materials.

S. no.	Application	Ferromagnetic material	Ref.
1	Soft robotics	Ni-Mn-Ga	[7]
2	Microwave absorption materials	Co/Ni nanocrystalline	[8]
3	Environmental remediation	Fe <sub>3</sub> O <sub>4</sub> aerogel	[9]
4	Magnetic data storage	FePt-C	[10]
5	Spin caloritronics	NiFe <sub>2</sub> O <sub>4</sub>	[12]
6	Flexible electronics	Fe-N-GDY	[11]
8	Energy storage	Fe <sub>3</sub> O <sub>4</sub> @C	[13]
9	Cancer therapy	FeNi-CNT	[14]
10	Magnetic sensors	VSe <sub>2</sub> -graphite/MoS <sub>2</sub>	[15]
11	Electromagnetic interference shielding	Co <sub>0.5</sub> Zn <sub>0.5</sub> Fe <sub>2</sub> O <sub>4</sub> / PANI-PTSA	[16]
14	Magnetic nano-devices	NiFe <sub>2</sub> O <sub>4</sub> nanocrystals	[17]

motors, sensors, and data storage. The history of ferromagnetic materials research dates back to the 19th century, and recent developments have focused on discovering new materials with improved magnetic properties and the development of spintronics. The remaining sections of this chapter will provide a detailed overview of the properties, applications, and recent developments in ferroelectric, ferroelastic, and multiferroic materials.

### 1.2.2 Ferroelectric Materials

Ferroelectric materials exhibit immediate electric polarization, which can be changed by applying an external electric field. This behavior arises due to the displacement of ions within the crystal lattice, leading to a net dipole moment. The ferroelectric behavior can occur at a specific temperature or below a critical size, known as the Curie temperature and Curie size. Figure 1.2 shows the working of ferroelectric materials



**Figure 1.2** Effect of electric field on ferroelectric materials.

#### 1.2.2.1 *Past of Ferroelectric Materials*

The study of ferroelectric materials began in the early 20th century with the discovery of piezoelectricity. The first ferroelectric material discovered was Rochelle salt, which exhibits ferroelectric and piezoelectric behavior. In 1920, the ferroelectric properties of Rochelle salt (potassium sodium tartrate) were successfully elucidated by the Curie brothers, marking a significant breakthrough. Subsequent investigations carried out during the 1940s by Valasek and Stevenson revealed the reversible polarization behavior that characterizes ferroelectric materials, with barium titanate being a prominent example. A momentous milestone arose in the 1950s with the discovery of lead zirconate titanate (PZT) by Jaffe, Cook, and Jaffe. PZT quickly garnered acclaim as a versatile ferroelectric material due to its exceptional attributes, including its piezoelectric, pyroelectric, and electrostrictive properties [18, 19].

Since then, extensive research has been carried out to explore the fundamental properties of ferroelectric materials and their potential applications.

Ferroelectric materials have numerous applications in various fields, including electronics, memory devices, energy harvesting, and sensors. For example, lead zirconate titanate (PZT) is a commonly used ferroelectric material for constructing electronic devices, including piezoelectric actuators and sensors. Another example is lithium niobate ( $\text{LiNbO}_3$ ), commonly used in optical modulators, switches, and sensors. Barium titanate ( $\text{BaTiO}_3$ ) is another crucial ferroelectric material used in capacitors, electromechanical transducers, and nonlinear optics.

### 1.2.2.2 Present of Ferroelectric Materials

Recent developments in ferroelectric materials research have focused on improving their properties and exploring new applications. One approach is to develop new ferroelectric materials with enhanced properties, such as high dielectric constant, high piezoelectric response, and high Curie temperature. For example, bismuth ferrite ( $\text{BiFeO}_3$ ) is a promising ferroelectric material with high spontaneous polarization, high Curie temperature, and magneto-electric solid coupling. Another approach is to engineer the interface between different ferroelectric materials to create novel properties and functionalities.

A metal/ferroelectric capacitor [(FE)- $\text{HfO}_2$ /IGZO/metal] was constructed by Mo *et al.* without atomic interdiffusion for three-dimensional high-density memory. The composite exhibited ferroelectricity with many endurance cycles and retention of up to 10 years. The lack of the wake-up effect improves the design and manufacturing process of the circuit. The asymmetric effect was caused by the varying band modulations in different states of IGZO [20].

In another example, researchers found a new method to develop a three-dimensional memory structure by self-rolling up single-crystalline ferroelectric oxides, which enhanced the information density more than 40 times. The " $\text{Pb}(\text{Zr,Ti})\text{O}_3$ /stressor" membranes also had a strong self-rolling up force, which increased the area ratio and allowed for high-density information storage of 102 Tbit. The study provided a new method for developing concise memory devices having high-density and three-dimensional memories from oxide materials [21].

In another study, the researchers achieved enormous pyroelectric performance in ceramics by changing the phase boundary made of ferroelectric-relaxor. They engineered the phase boundaries by introducing  $\text{BaTiO}_3$ , which broke the long-range antiferroelectric order. Due to the planned phase boundaries, ceramics exhibited a significant pyroelectric coefficient and figures of merit. The results promised potential applications for ultra-sensitive infrared detectors and some technological insights into pyroelectric ceramic design [22].

Huang *et al.* used a coaxial electrospinning technique to manage the distribution of polarization gradient in a  $\text{TiO}_2$  nanofiber and polymer hybrid nanocomposite system, significantly boosting the discharged energy storage density (Ue) from  $6.5 \text{ J cm}^{-3}$  to  $12.7 \text{ J cm}^{-3}$  [23].

Habib *et al.* achieved excellent room-temperature piezoelectric performance in  $0.67\text{Bi}_{1.03}\text{FeO}_3\text{-}0.33\text{Ba}_{1-x}\text{La}_x\text{TiO}_3$  ceramics with a very high temperature of  $482^\circ\text{C}$ . The researchers conducted a study where they slightly modified the piezoelectric strain within a temperature range of  $25^\circ\text{C}$  to

125°C, which resulted in hysteresis of low strain and a significant average electrostrictive coefficient. This development in non-lead ceramics provided an opportunity to advance temperature-insensitive piezoelectric properties, thus making it viable for high-temperature commercial applications [24]. Table 1.2 lists some ferroelectric materials with their applications.

Ferroelectric materials also have been explored for use in energy storage and conversion. For example, using ferroelectric materials in capacitors can lead to high energy-density storage devices with fast charging and discharging times. Ferroelectric materials have also been studied for photovoltaic devices, where their polarization can enhance the transformation efficiency of solar to electrical energy.

In summary, ferroelectric materials have significantly influenced various technological advancements and scientific discoveries. Studying these materials has led to a better understanding of their fundamental properties and potential for various applications. Ongoing research in this field continues to explore new materials, improve existing properties, and develop new applications for ferroelectric materials.

**Table 1.2** Some recent studies of various ferroelectric materials.

S. no.	Application	Ferroelectric material	Ref.
1	Nonvolatile memory	HfO <sub>2</sub> /IGZO	[20]
2	Ultrahigh-density data storage	PbZr <sub>0.3</sub> Ti <sub>0.7</sub> O <sub>3</sub>	[21]
3	Infrared detectors	Ferroelectric BaTiO <sub>3</sub>	[22]
4	Energy storage	Ferroelectric poly(vinylidene fluoride-trifluoroethylene)	[23]
5	Piezoelectric actuators	BiFeO <sub>3</sub> –BaTiO <sub>3</sub> ceramics	[24]
6	Ferroelectric memory	Ferroelectric thin films of BaTiO <sub>3</sub>	[25]
7	Sensor and actuator technology	Ferroelectric single crystals of LiNbO <sub>3</sub>	[26]
9	Ferroelectric tunnel junctions	Ferroelectric Hf <sub>0.5</sub> Zr <sub>0.5</sub> O <sub>2</sub>	[27]
10	Energy storage	Bi <sub>0.5</sub> Na <sub>0.5</sub> TiO <sub>3</sub> –Ba(Zr <sub>0.2</sub> Ti <sub>0.8</sub> )O <sub>3</sub> film	[28]
12	Photovoltaics	Pb <sub>0.93</sub> La <sub>0.07</sub> (Zr <sub>0.6</sub> Ti <sub>0.4</sub> ) <sub>0.9825</sub> O <sub>3</sub> (PLZT) thin films	[29]

### 1.2.3 Ferroelastic Materials

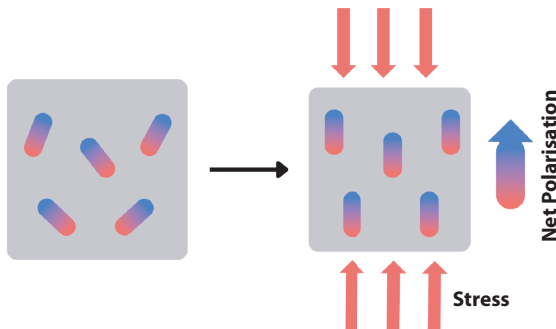
Ferroelastic materials are another class of ferroic materials that exhibit reversible deformation because of the electric or magnetic field. The term “ferroelastic” comes from the Greek word “elastos,” meaning capable of being stretched or compressed without breaking. In ferroelastic materials, the deformation is caused by the movement of domain walls, which can change the shape of the material.

The definition of ferroelastic materials has been refined over time, but it is generally accepted that these materials exhibit reversible deformation due to the applied electric or magnetic field. Ferroelastic materials are typically classified into soft and hard ferroelastic materials. Soft ferroelastic materials exhibit large deformations at low applied fields, while hard ferroelastic materials require higher areas to induce deformation. Figure 1.3 shows how ferroelastic materials function in stress.

#### 1.2.3.1 Past of Ferroelastic Materials

The history of ferroelastic materials research dates back to the early 20th century when researchers first discovered the phenomenon of reversible deformation in certain materials.

During the early 20th century, the term “ferroelasticity” was introduced by Auguste Brusconi to describe the reversible deformation observed in specific materials. Extensive research conducted in the 1950s and 1960s, led by James G. Simmons and colleagues, focused on investigating ferroelasticity in crystals and identifying materials that exhibited spontaneous strain and reversible phase transitions when subjected to external influences. Significant studies were carried out on potassium dihydrogen



**Figure 1.3** Effect of mechanical stress on ferroelastic materials.