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About the Author

Jing-Feng Li is Changjiang Scholar Distinguished Professor of the School of Materials Science and Engineering at Tsinghua University, Beijing, China, and also serves as deputy director of Tsinghua University-Toyota Research Center. Dr. Li has received master and doctor degrees in materials science and engineering both from Tohoku University (Japan) in 1988 and 1991 and a bachelor of engineering from Huazhong University of Science and Technology, China, in 1984. After temporarily working at Nihon Ceratec Co. Ltd., he was appointed to assistant professor in Tohoku University in 1992 and promoted to associate professor in 1997, then joined Tsinghua University as full professor in 2002. He also served as vice department chair (2005–2012) and vice school dean (2013–2016) of Materials Science and Engineering Department/School at Tsinghua University.

Dr. Li has conducted a wide range of research. His early work in Tohoku University focused on phase transition of zirconia ceramics, ceramic processing, and mechanical properties of silicon carbide and aluminum nitride ceramics, and ceramic microfabrication processing. From 2002 at Tsinghua, Li has been leading a research group with research interests on lead-free ferroelectric ceramics for piezoelectric and energy storage applications, piezoelectric films for micro-electromechanical system (MEMS) applications, thermoelectric materials, and microdevices for energy conversion, MEMS-based microfabrication processing. He has published >501 papers (H-index = 70) in prestigious journals and received several awards including distinguished young researcher award from the Japan Institute of Metals and the first-class science and technology award from the Chinese Ceramic Society, distinguished young scholars fund from National Natural Science Foundation of China, and Journal of the American Ceramic Society Loyalty Award.

He serves as Editor-in-Chief of Journal of Materiomics, associate Editor-in-Chief for Journal of the Chinese Ceramic Society, Reginal/Subject Editor for Journal of Materials Processing Technology (2005–2013), and editorial board member for NPG Asia Materials, Journal of Advanced Ceramics, Journal of Asian Ceramic Societies, Science China Technological Science, Energy Harvesting and Systems, Journal of Inorganic Materials, Electronic Components and Materials (Chinese), Powder Metallurgy Technology (Chinese). He has been elected to the President of Thermoelectric Materials and Applications Subsociety of Chinese Materials

Research Society and Vice President of Micro/Nano Technology Subsociety of Chinese Ceramic Society in 2018. He is a fellow of the American Ceramic Society, board member of International Thermoelectric Society, full member of International Institute for the Science of Sintering, and ferroelectric committee member of IEEE Ultrasonics, Ferroelectrics, and Frequency Control Society.

Foreword by Professor Longtu Li

Piezoelectric materials possess the functionality of interconversion between electrical energy and mechanical energy, which have been widely used in electronic information, communication, automobile, military defense, aeronautics and space technology, medical diagnostics, energy storage and harvesting, artificial intelligence, and advanced manufacturing, among other applications. The market-dominating piezoelectric ceramics are based on the $Pb(Zr,Ti)O_3$ (abbreviated as PZT) system, which is a big family with diverse chemical modifications designed for specific applications. PZT-based ceramics possess comprehensive excellent properties, but its environmental incompatibility has generated increasing concerns since the beginning of the twenty-first century. In addition, the European Union's legislation about Restriction of the use of certain Hazardous Substances (RoHS) in electrical and electronic equipment has accelerated the research and development of high-performance lead-free piezoelectric ceramics.

Piezoelectric ceramics and device applications have been one of the key research directions in the State-Key Laboratory of New Ceramics and Fine Processing, Tsinghua University. At Tsinghua University, our research groups mainly focused on lead-based piezoelectric ceramics and their applications before the twenty-first century. Since the new century I became deeply interested in lead-free piezoelectrics and have been heavily involved in the related research activities with several research groups within our state-key laboratory. Among them, Prof. Jing-Feng Li is the leader of the biggest research group working on lead-free piezoelectric ceramics since 2002 when he moved to Tsinghua University from Tohoku University. With the financial support from the National Natural Science Foundation and the Ministry of Science and Technology of China, Tsinghua University and Toyota Motor Corporation, Prof. Jing-Feng Li has been focusing on the $(K,Na)NbO_3$ lead-free piezoelectric system and made substantial progress in numerous research areas, including sintering process, characterization and manipulation of hierarchical structure, chemical modification, and piezoelectricity enhancement mechanism, etc. Because of these impressive achievements, he has received the first-class science and technology award from the Chinese Ceramic Society. Meanwhile, a start-up company was also founded by his former students quite recently to promote the mass production and industrial applications of the high-performance $(K,Na)NbO_3$-based piezoceramics.

Writing a book especially in foreign language is not easy, which requires not only extensive knowledge about the field but also hard work and perseverance. Prof. Jing-Feng Li has spent more than two years to complete this monograph about lead-free piezoelectric materials, which adds his contributions to the field of ferroelectrics and piezoelectrics. This book has systematically compiled the research progress of several promising lead-free piezoelectric systems, which could synchronize the perspectives of researchers from both academia and industry over the development of lead-free piezoelectric systems, and will undoubtedly inspire future research endeavors in both fundamental and application-oriented studies.

Owing to the increasing emphasis and requirement of green manufacturing and environmental friendly materials, study on the lead-free piezoelectric ceramics has become more popular around the world. Many significant results and findings of theoretical and experimental studies related to lead-free piezoelectric ceramics have been published. This book has captured some of the latest developments and most recent advancements in this exciting field. I hope and believe that readers will find interesting and useful information from this book.

Longtu Li
Professor, Tsinghua University
Member of Chinese Academy of Engineering

Foreword by Professor Jürgen Rödel

Piezoelectricity allows the generation of electrical charges on the surface of certain insulating materials in response to applied mechanical stress or, conversely, allows the generation of mechanical strain when subjected to an applied electric field. With such functionality, piezoelectric materials have been increasingly used nowadays in a wide range of technologies, as an intermediary between mechanical and electric energies. Typical examples include piezoelectric sensors and actuators in smartphones, piezoelectric probes in ultrasonic diagnostic machines, piezoelectric buzzers in industrial machines, and consumer electronics including toys, high-precision positioning units in scientific research equipment, ignitors for lighters, pressure sensors, and so on. $PbZrO_3$–$PbTiO_3$ solid solutions have formed a major commercial system, abbreviated as PZT. The PZT-based ceramics have dominated the market for about 70 years because of their excellent piezoelectric properties and a mature understanding of the processing technique. However, this "king" of piezoceramics has been challenged by the awareness of environmental protection, as European Union (EU) issued legislation on the restriction of hazardous substances (RoHS) in electrical and electronic equipment at the beginning of this century. RoHs and many other similar legislations throughout the world have stimulated the research searching for high-performance lead-free piezoceramics.

Significant progress has been witnessed in the past two decades. For select applications, replacements for PZT are being made available and some new materials even have advantages over PZT. For example, some of them feature higher fracture toughness, higher thermal conductivity, or simply lower density. However, transition into application demands from companies to run two production lines, one for PZT and one for the new material and customers need to be convinced. At present, there is no single system that can fully replace PZT. Nevertheless, there are competitive lead-free substitutions, such as $(K,Na)NbO_3$ (KNN), $(Bi_{0.5}Na_{0.5})TiO_3$ (BNT), and $BaTiO_3$-based (BT) systems. Prof. Jing-Feng Li has been working mainly on the KNN system, while my group is working on the BNT system. Interestingly, both systems have complementary piezoelectric properties: KNN-based ceramics possess high quasi-static or small-signal piezoelectric coefficients, whereas large piezoelectric strains can be achieved in BNT-based ceramics. For many years, we had intimate collaborations on research projects and academic exchange. I would like to mention how amazing our collaborations are, especially once we both worked as guest co-editors for a special issue about lead-free piezoelectrics in MRS Bulletin in August 2018.

I am very pleased to know that Prof. Jing-Feng Li has completed the writing of a specialized book on lead-free piezoelectric materials, which is truly a tough yet important task for our community. This comes at exactly the right time where first high-volume applications are expected in the next three years. I noticed that this book has two introductory chapters about the fundamentals of piezoelectricity and lead-free piezoelectrics. I particularly like the detailed descriptions on measurement technology, which is so important to newcomers into this field. The second chapter gives an overview of the lead-free piezoelectrics, including the background, the general classification, and the research progress of the lead-free piezoelectrics. These two chapters should be very helpful for young researchers who have just started working on research topics related to ferroelectrics and piezoelectrics. Four representative lead-free piezoelectric systems are introduced in the later chapters, which are then followed by a final chapter about lead-free piezoelectric applications. Such an arrangement is excellent. Explanations are clear, diagram and sketches are simple but insightful, and references are well-chosen and complete.

This book is not meant as a stand-alone. Scientists and engineers need to consider a basic book on ferroelectrics for all the fundamental physics and possibly a book on applications. However, this book by Jing-Feng Li is a definite must-read for graduate students and young researchers working on the research topics related to lead-free ferroelectric and piezoelectric materials. It suffices both as an introduction to the field as well as the first application-oriented book on piezoceramics. This work should also be a valuable reference for the industry who wishes to obtain a comprehensive picture of the development status of lead-free piezoceramics.

Jürgen Rödel
Professor, Department of Materials and Earth Sciences
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Guest Professor at Tsinghua University and Tokyo Institute of Technology
Member of German National Academy of Science and Engineering

Preface

Ferroelectric/piezoelectric materials have been a hot research topic for a diversity of fields not only due to their wide applications but also because of their fascinating physical and chemical nature. The market has been dominated by lead zirconate titanate (PZT) ceramics over decades, due to their excellent properties and flexibility in terms of compositional modifications. Since 2006, the European Union has already adopted some well-known directives, e.g. the Waste Electrical and Electronic Equipment (WEEE) directive and the Restriction of the use of certain Hazardous Substances (RoHS) in electrical and electronic equipment directive, to protect human health and the environment by prohibiting the uses of hazardous substances in electrical and electronic devices. Therefore, lead-free piezoelectrics have been attracting more and more interest since the beginning of the twenty-first century. Encouraging progress in the development of high-performance lead-free piezoelectrics has been witnessed over the last decade. Despite a very limited scale, lead-free piezoelectric ceramics have successfully entered the market, which is estimated to be US$ 172 million in 2019. Given the significant R&D progress of lead-free piezoelectrics, a renewal of the RoHS directive to terminate the exemption of lead-containing piezoelectric materials should be approaching soon, at least for some applications that do not require a comprehensively excellent performance of high piezoelectricity and good temperature stability, equivalent to those of the PZT-based materials.

I believe that now is the perfect time for reviewing the research of the lead-free piezoelectrics, which is not only important for the young generation of researchers who are looking for a good starting point but also valuable for those who are already in the fields to think and innovate new strategies for enhancing the piezoelectric performances. Certainly, there have been many excellent review articles but most of them rather focused on some specific topics in individual material systems. There are four promising lead-free piezoelectric systems, which are $BaTiO_3$, $(K,Na)NbO_3$, $(Bi_{0.5},Na_{0.5})TiO_3$, and $BiFeO_3$. These systems share similarities but they are not cut from the same cloth. To have a comprehensive picture of the world of the lead-free piezoelectrics, we need a book that covers the fundamental knowledge about piezoelectrics and also the cutting-edge research progress about lead-free piezoelectrics. With such motivation, I wrote this book.

This book consists of seven chapters, starting with two introductory ones about the fundamentals of piezoelectricity and lead-free piezoelectrics. These two chapters should be beneficial for the readers, especially for those who wish to reinforce their basic knowledge. The first chapter will provide the fundamental background for piezoelectricity, emphasizing on the piezoelectric effects, the relationship between ferroelectrics and piezoelectrics, the meanings of the piezoelectric parameters, and common characterization techniques. In the second chapter, an overview of the lead-free piezoelectrics will be given, including the background, the general classification, and the research progress of the lead-free piezoelectrics. Next, four representative lead-free piezoelectric systems will be introduced in the following chapters. Each chapter consists of a brief introduction of the history and crystal structure as well as the characteristics of the focused lead-free piezoelectric system. Finally, this book will overview some applications based on the lead-free piezoelectrics. By comprehensively covering the aforementioned contents, I expect this book to be informative to the readers. Other lead-free piezoelectric materials such as AlN and ZnO are not involved in this book, since they are non-perovskite-structured and largely differ from the focused material systems in properties and applications.

I would like to thank my group members for their contributions to this book. Special thanks go to Dr. Yichi Zhang (postdoc), Dr. Zhen Zhou (graduated Ph.D. student), Dr. Lei Zhao (postdoc), Dr. Lisha Liu (postdoc), and Dr. Ke Wang (associate professor) for their deep involvement in the writing of Chapters 3–7, respectively. Also, I deeply thank Mr. Hao-Cheng Thong (Ph.D. student), Dr. Qian Li (assistant professor), Mr. Yi-Xuan Liu (Ph.D. student), Dr. Qing Liu (graduated Ph.D. student), Dr. Fang-Zhou Yao (graduated Ph.D. student), Mr. Hua-Lu Zhuang (Ph.D. student) and Miss Jing Gao (Ph.D. student) for their great help in editing the manuscripts.

Finally, I also want to express my thanks to my family and colleagues for their continuous encouragement and extensive support. I sincerely wish my book will be helpful to the readers who are interested in ferroelectrics and piezoelectrics.

30 April 2020 *Jing-Feng Li*
Beijing, China

1

Fundamentals of Piezoelectricity

1.1 Introduction

In 1880, Pierre Curie and Jacques Curie discovered the (direct) piezoelectric effect in quartz (SiO_2) and other single crystals, which generates an electric charge proportional to a mechanical stress. The converse piezoelectric effect, a geometric strain proportional to an applied voltage, was also soon realized. Since then, quartz has been one of the most well-known and widely used piezoelectric materials. Many decades later, polycrystalline piezoelectric ceramics (oxides) have been discovered. The first one is $BaTiO_3$ that was discovered during the World War II, which was used as dielectric materials for solid condensers at first [1]. In 1947, Roberts found that $BaTiO_3$ ceramics (polycrystals) showed good piezoelectricity, about 100 times higher than that of quartz, after they were poled under a high voltage [2]. Since then, $BaTiO_3$ ceramics have been widely applied to transducers, sensors, and filters, particularly in Japan. In 1952, Shirane et al., reported that solid solutions can be formed between $PbTiO_3$ and $PbZrO_3$ [3, 4]. One year later, ferroelectricity and antiferroelectricity were found in the solid solutions [5]. In 1954, Jaffe et al. studied the piezoelectric properties of $PbTiO_3$–$PbZrO_3$ solid solution ceramics, and found that its piezoelectric constants were twice as high as that of $BaTiO_3$, and its Curie temperature (above which the piezoelectricity disappears) was over 300 °C [6]. Now, the $PbTiO_3$–$PbZrO_3$ solid solutions, abbreviated as PZT, are the most widely used piezoelectric ceramics [7–10]. The PZT ceramics show greatly enhanced piezoelectric and dielectric properties when the Zr/Ti ratio is close to 52/48, where exists a morphotropic phase boundary (MPB) separating the rhombohedral and tetragonal regions [7]. It is generally understood that the piezoelectricity enhancement stems from the effect of phase coexistence enabled by the existence of MPB.

Despite the facts that $BaTiO_3$ is lead-free and was also discovered before PZT, the markets of piezoceramic applications have been dominated by PZT-based ceramics mainly because of its following advantages compared with $BaTiO_3$: (i) excellent and adjustable piezoelectric properties, (ii) relatively high Curie temperature, and (iii) relatively low sintering temperature. Recently, environmental protection has become a major global concern, and environmental-friendly materials and technology are one of the main tasks to be resolved in this new century. The manufacturing,

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handling, and disposal of PZT ceramics, which contain >60 wt% of lead, pose harmful influences on the workers' safety and soil environment as well as water supply. That is why many countries have incentivized the development of lead-free piezoelectric materials [11–18].

For the R&D of lead-free piezoelectric materials, it is very important to get a full understanding of piezoelectric principles and the piezoelectric mechanisms of existing piezoelectric materials, especially PZT ceramics. However, because PZT ceramics have many important applications, and in some sense, its application research has moved faster compared with the fundamental research on its piezoelectric mechanism, there are still a lot of things remaining very unclear. For example, the phase diagram of PZT around the MPB has been renewed even after half a century passed since the discovery of PZT [19–21], and rigorous descriptions still lack for unambiguous understanding of the MPB's contribution to piezoelectricity. The fundamental structure–property mechanisms revealed in lead-containing piezoelectric materials can be also operational in lead-free systems and at a minimum, should be considered as starting guidelines for the development of lead-free piezoelectrics from the aspects of composition modification, microstructure tailoring, property characterizations, device applications, etc.

1.2 Piezoelectric Effects and Related Equations

The piezoelectric effect or piezoelectricity is the generation of electric charges on the surface of certain non-conducting materials in response to applied mechanical stress, or conversely, the generation of a mechanical strain in such materials when they are subjected to an electric field, as schematically shown in Figure 1.1 [17]. The piezoelectric effect is a reversible process, so the materials exhibiting the direct

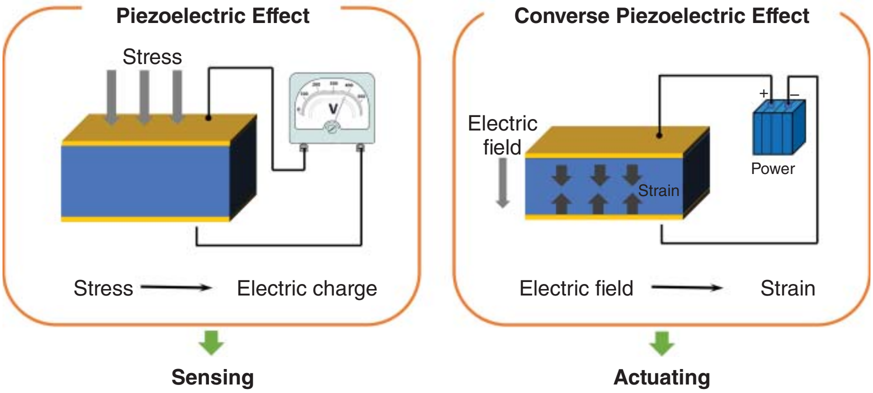


Figure 1.1 (a) The direct piezoelectric effect provides an electric charge upon application of a mechanical stress, whereas (b) the converse piezoelectric effect describes the situation where strain develops under an applied electric field. Source: Reproduced with permission from Roedel and Li [17]. Copyright 2018, Cambridge University Press.

piezoelectric effect also exhibit the converse piezoelectric effect. As such, piezoelectricity is referred to as both direct and converse effects, even though the word "piezoelectricity" often leads us to the meaning of the direct piezoelectric effect of the internal generation of electrical charges resulting from an applied mechanical force.

In a narrow sense, piezoelectricity can be understood as a linear electromechanical interaction between the mechanical and the electrical states. The constant for such a linearly proportional relation is defined as the piezoelectric coefficient d, which is a third-rank tensor coupling the first-rank tensor or vector (electric displacement or field) and the second-rank tensor (stress or strain). Hence, the piezoelectric equations may be written in the following form ($i, j, k = 1, 2, 3$) [22]

$$D_k = d_{kij} T_{ij} \tag{1.1}$$

$$S_{ij} = d_{kij}{}^{*} E_k \tag{1.2}$$

where D_i is electric displacement (C/m^2), E_i is electric field component (V/m), S_{ij} is strain component, T_{ij} is stress component (N/m^2), and d_{kij} or $d_{kij}{}^{*}$ is component of the piezoelectric charge or strain constant. It should be noted that the subscripts of piezoelectric constant are commonly expressed using the reduced Voigt matrix notation d_{km}, where k denotes the component of electric displacement D or field E in the Cartesian reference frame (x_1, x_2, x_3), and the index $m = 1, \ldots, 6$ is used to define the mechanical stress or strain. In this case, $m = 1$, 2, and 3 correspond to the normal stresses along the x_1, x_2, and x_3 axes, respectively, whereas $m = 4$, 5, and 6 stand for the shear stresses T_{23}, T_{13}, and T_{12}, respectively. Both d and d^* are called the piezoelectric constant or coefficient, but they have different units, which are pC/N and pm/V (here, p stands for 10^{-9}), respectively. It follows from thermodynamic considerations that $d_{km} = d_{km}{}^{*}$, namely, the coefficients that connect the field and strain are equal to those connecting the stress and the polarization.

In addition to the piezoelectric charge or strain constant, other forms of piezoelectric constants are also used in specialized design cases. Totally, there are four piezoelectric constants including the abovementioned piezoelectric charge or strain coefficient d, which are listed in Table 1.1 with their names and definitions [22]. These piezoelectric constants are defined as partial derivatives evaluated at constant stress (subscript T), constant electrical field (subscript E), constant electrical displacement (subscript D), or constant strain (subscript S). These conditions can be regarded as "mechanically free," "short circuit," "open circuit," and "mechanically clamped," respectively.

1.3 Ferroelectric Properties and Its Contribution to Piezoelectricity

Since most high-performance piezoelectric materials are also ferroelectric materials, it is necessary to review ferroelectric properties and their contribution to piezoelectricity [23–28]. Ferroelectricity is a character of certain materials that have a spontaneous electric polarization that can be reversed by the application of an external electric field. As illustrated in Figure 1.2, dielectrics are the big family

Table 1.1 Piezoelectric constants.

Symbol	Name	Definition
d	Piezoelectric charge coefficient or piezoelectric strain coefficient	$d_{ij} = \left(\frac{\partial D_i}{\partial T_j}\right)_E = \left(\frac{\partial S_j}{\partial E_i}\right)_T$
g	Piezoelectric voltage coefficient (voltage output constant)	$g_{ij} = -\left(\frac{\partial E_i}{\partial T_j}\right)_D = \left(\frac{\partial S_j}{\partial D_i}\right)_T$
e	Piezoelectric stress coefficient	$e_{ij} = -\left(\frac{\partial T_j}{\partial E_i}\right)_S = \left(\frac{\partial D_i}{\partial S_j}\right)_E$
h	Piezoelectric stiffness coefficient	$h_{ij} = -\left(\frac{\partial E_i}{\partial S_j}\right)_D - \left(\frac{\partial T_j}{\partial D_i}\right)_S$

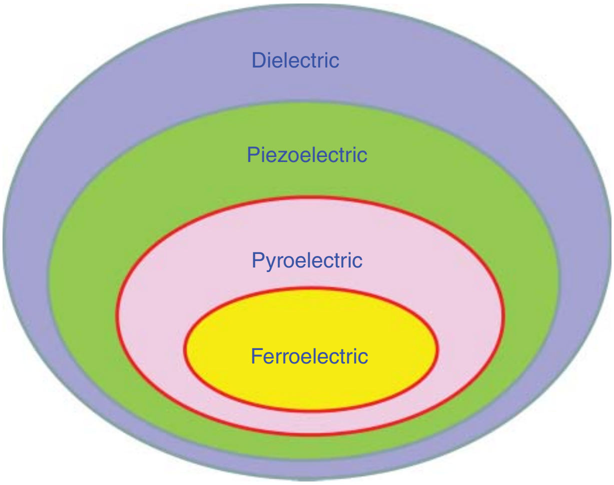


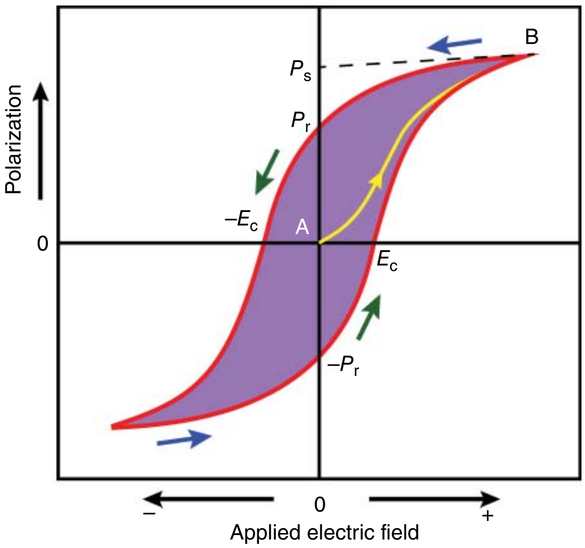
Figure 1.2 The relationship among dielectric, piezoelectric, pyroelectric, and ferroelectric materials.

with the core subset being ferroelectrics. Dielectric materials are basically electrical insulators, which become polarized by the peripheral application of electrical field when placed across the plates of a capacitor. Piezoelectric materials belong to the dielectric group, but a stress can create a net separation of positive and negative charges in a piezoelectric crystal that has a non-centrosymmetric crystal structure. Pyroelectrics are those materials with the ability to generate a temporary voltage when they are heated or cooled, since the polarization magnitude in a pyroelectric crystal can be thermally changed by the temperature change. By comparison, for a piezoelectric crystal, it is the mechanical stimuli resulting in the polarization change and as a consequence, charges build up at its surfaces. Ferroelectrics are an experimental subset of pyroelectric materials. All ferroelectric materials are pyroelectrics, and all pyroelectrics are piezoelectric; however, not all piezoelectric materials are pyroelectric and not all pyroelectrics are ferroelectric. It is known that crystal symmetry governs the aforementioned categorization. All crystalline substances belong to one of the 32 crystallographic point groups. There are 20 piezoelectric point groups and 10 ferroelectric point groups.

The direction of electric dipoles in both piezoelectric and pyroelectric (but not ferroelectric) materials cannot be changed, whereas it can be reversed by an electric field for ferroelectric materials. Therefore, the distinguishing feature of ferroelectrics is that the spontaneous polarization can be reversed by a sufficiently high applied electric field along the opposite direction. Furthermore, the polarization is dependent not only on the electric field but also on its history that the material has experienced, thereby yielding a hysteresis *P*–*E* (polarization–electric field) loop, as shown in Figure 1.3. Starting from point A, the polarization initially increases slowly with E-field, but turns to a sharp rise when the applied field is sufficiently high. Then, after a long and slow stage, the polarization reaches a saturation level (saturation polarization, P_s). The P_s is normally estimated by intersecting the polarization axis with the saturated linear part. The polarization does not go back to the starting point after the removal of E-field but instead results into non-zero values, which is defined as the remnant polarization, P_r. In order to reach a zero polarization state, an E-field applied along the opposite direction is required. This E-field is named as the coercive field, E_C, which stands for the magnitude of the applied electric field to reverse the direction of ferroelectric polarization.

The appearance of such a *P*–*E* loop is an important criterion to distinguish whether a material is ferroelectric or not. Ferroelectric materials display such a hysteretic behavior as a result of the response of electric domains to electric field, analogous to that of magnetic domains of a ferromagnetic material against a magnetic field. It should be emphasized that a polar material may be piezo-/pyro-electric but not ferroelectric if the direction of its dipoles is not switchable even under exceedingly high external electrical fields. For example, single crystalline quartz is a conventional piezoelectric material, but has no ferroelectric properties. Similarly, ZnO is a piezoelectric but non-ferroelectric material in general.

Figure 1.3 Polarization vs. electric field hysteresis loop in ferroelectric materials.



Once a ferroelectric crystal is cooled across the Curie temperature, a polarization develops. The ferroelectric phase transition is a structural phase transition, during which the displacements of ions produce lattice distortions and change the symmetry of the crystal. The magnitude of the ion displacements along certain crystallographic directions in the materials is specific to a given crystal structure and composition. If the polarization develops uniformly throughout the whole crystal, a depolarizing electric field will be produced. To minimize the electrostatic energy associated with this field, the crystal often splits into regions, called *domains*; a region in which the polarization is uniform is called a domain. The regions between two adjacent domains are called domain walls. Their thickness is typically of the order of 10–100 Å. Domain represents a region within a ferroelectric material in which the direction of polarization is uniform. The saturation polarization, P_s, corresponds to the total polarization at an extreme state where (almost) all domains are aligned along the direction of applied electric field. Some of these domains stay at the same direction even after the removal of electric field, resulting in the remnant polarization. It can be readily envisaged that a ferroelectric material at a state with remnant polarization can be used a piezoelectric material, since it can generate electric charges when subjected to mechanical stress. In other words, if a ferroelectric material, at least polycrystalline bulk materials should show no piezoelectric response if it has not been subjected to an electric field. This is because the charges will be canceled collectively if the domains are randomly distributed along different directions, resulting in zero change when the whole material receives mechanical deformation. As such, piezoelectricity can be regarded as one of the functionalities of ferroelectric materials, and in general, ferroelectric materials need to be poled before they can be used as piezoelectric materials. Therefore, electrical poling is an indispensable process for ferroelectric piezoelectric materials. During poling, a strong electric field is applied across ferroelectric materials and consequently, a majority of the domains switch their pristine polarization and become aligned along the electric field direction. Figure 1.4 schematically shows the poling process. The virgin materials are subjected to an electric field, which should be sufficiently higher

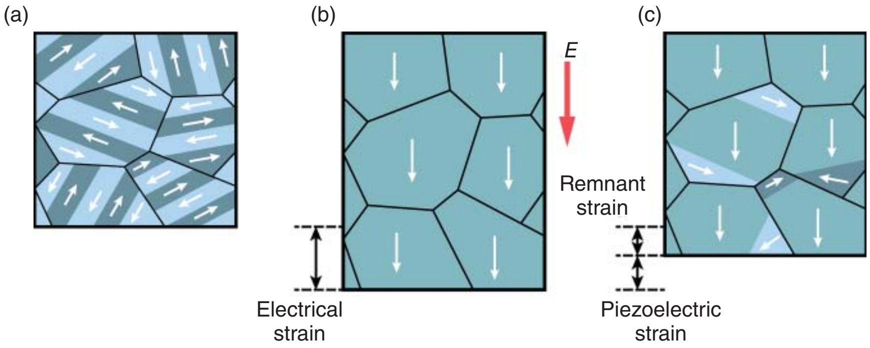


Figure 1.4 The schematic illustrations showing the alignment of ferroelectric domain and macroscopic strains when a ferroelectric material is subjected to a poling treatment under an electric field. (a) Virgin state. (b) Saturation state. (c) Remnant state.