

Domains in Ferroic Crystals and Thin Films

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Preface

With much excitement and great enthusiasm I introduce this thorough treatise on the major aspects of domain and domain wall phenomena in ferroics, mostly ferroelectrics, a major achievement for which there has been a long-standing need.

Ferroelectric materials possess spontaneous electrical polarization which is stable in more than one orientation and can be reoriented (switched) by an applied electric field. This property and its typical derivative characteristics, e.g., high piezoelectric response and large permittivity, make ferroelectrics exceedingly useful in diverse applications such as non-volatile memories, ultrasonic medical imaging, micro-electromechanical systems, and reconfigurable high-frequency electronics.

Typically, a ferroelectric material is divided into domains, which are regions in the material that are polarized in one of the symmetry-permitted polarization directions. The interfaces between adjacent domains, the domain walls, have a typical thickness of 1–2 unit cells. The behaviors of domains and domain walls are fundamental to ferroelectrics and dominate their properties: poling of ferroelectric ceramics, namely electrical aligning of the polar direction of ferroelectric domains, is essential for piezoelectric activity; periodically poled crystals are used as nonlinear optic materials for which the width of the inverted domains controls the desired wavelength of operation. The high permittivity of ferroelectrics widely used in capacitors is dominated by domain wall contributions, and domain wall dynamics is responsible for some 50% of the piezoelectric response in standard transducers and actuators.

Considering the vital role of domains and domain walls, the substantial body of data, and the resultant theoretical knowledge, it is surprising how limited is the space given to this subject in the classical books on ferroelectric materials. Even recent books rarely dedicate entire chapters to this topic. Meanwhile the importance of domains and domain walls is growing. Thus the study and manipulation of domain walls can be achieved with much enhanced detail using new techniques such as piezoelectric force microscopy; new thin-film growth techniques allow the control of their position, spacing, and response, and new computation methods aid in revealing their further potential.

It is therefore very timely for the ferroelectric community and for students and researchers interested in the field of ferroelectrics that the three most prominent authorities in the field have united to write this major book on ferroelectric domains in single crystals, ceramics, and thin films, covering all the important aspects of the field: basic theoretical descriptions of structural phase transitions that emphasize the symmetry and phenomenological aspects of their classifications, an overview of typical ferroic materials, a survey of experimental methods used to visualize domain patterns, aspects of domain formation and their typical shapes, and the static properties of domain walls are all addressed. A large section of the book covers theoretical and experimental aspects of switching and polarization response and overviews comprehensively domain-related properties of ferroelectric thin films.

This book will be of central importance to anyone interested in ferroelectrics and their applications: graduate students of materials science, physics, chemistry, mechanical and electrical engineering, as well as scientists and engineers, whether new to the field or simply in need of a systematic and thorough review of the vast, useful, and fascinating field of ferroic domains.

Nava Setter
7.2009, Lausanne

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Chapter 1

A Preview of Concepts and Phenomena

This book covers a large area of material properties and effects connected with static and dynamic properties of domains. These are relevant to materials referred to as ferroics. In textbooks on solid state physics, one large group of ferroics is customarily covered, namely those in which magnetic properties play a dominant role: magnetically ordered materials which include ferromagnetics and antiferromagnetics. Numerous books are specifically devoted to such materials and cover a wide spectrum of magnetic domain phenomena which also incorporate essential practical aspects such as magnetic memories. In contrast, in the present monograph attention will be concentrated on domain-related phenomena in nonmagnetic ferroics. These materials are still only inadequately represented in solid state physics textbooks—even those which offer the most interesting properties, namely ferroelectrics. Therefore before starting with a systematic description of domain phenomena, in the present chapter we wish to offer the reader an introduction into what this book is all about.

Domains are a special sort of crystal twins and a few general remarks on twinning seem appropriate.

The phenomenon of growth twinning in crystals has been a subject of interest for crystallographers since crystallography started to develop as a scientific branch. The obvious reasons are the beauty of external shapes of some of the twinned crystals as well as evident and challenging symmetry relations between their constituents. Essentially, we speak about a *twin* when two or more individual crystals of the same species intergrow in a crystalline aggregate. Such parts of the aggregate are referred to as *twin components* and it is obvious that the symmetry operation (referred to as *twinning operation*) which brings one crystal into coincidence with the other cannot be a symmetry operation of the crystal itself. Twins are often just the result of an accident during crystal growth: Ions newly arriving at the surface layer of the growing crystal may have a choice of sites in which to settle, and one or more of these choices may represent the nucleus of the same crystal species growing in a different orientation. We then speak about the *growth twins* and these were often classified according to the physical appearance of the twinned crystal. The concepts of *penetration twins* (in which components may be of irregular size and shape) and *lamellar twins*

(composed of uniform alternating layers and not infrequently named *polysynthetic twins*) are almost self-explanatory. The boundary separating two constituents of the twinned crystal is referred to as the *twin boundary* or *composition plane*. Figure 1.1 shows an example of a twinned as-grown crystal. Description and understanding of growth twins presented many challenges to mineralogy and crystallography but some of them were and still are also of practical concern. A good example is offered by crystals of quartz, SiO_2 : When twinned, its useful piezoelectric properties are deteriorated. This is because the piezoelectric responses in different twin components may partly compensate each other.

Twin components may differ in the orientation of crystallographic axes. Then, their unit cell dimensions would also differ with reference to the laboratory frame. Under applied mechanical force, therefore, the energies of two neighboring twin components may differ and if this is so one of the components may grow at the expense of the other. In fact, the applied force may lead even to nucleation of the more suitably oriented twin component, that is, to the formation of a twin starting from a single homogeneous crystal. This phenomenon is called *mechanical twinning*. It has been known for a long time, especially in some metals where twins can be relatively easily formed by gliding movement of a part of the crystal against the other, under a shear stress.

Whether we deal with growth twins or mechanical twins, their crystallographic description includes two essential issues: What are the symmetry relations between the twin components and what orientations the composition

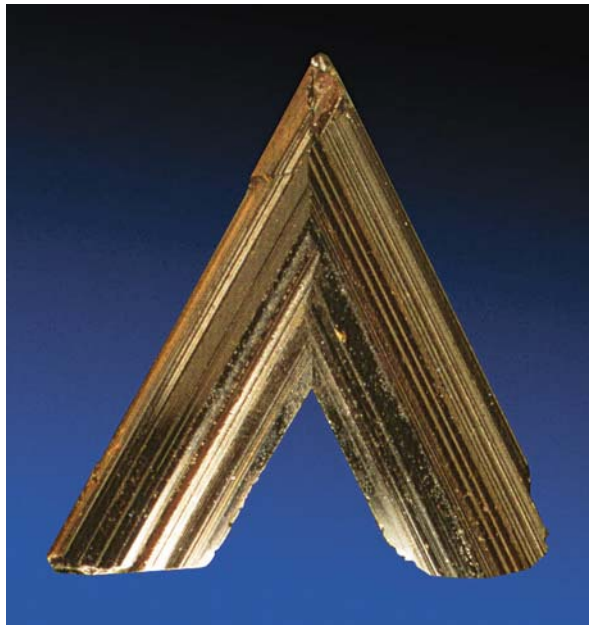


Fig. 1.1 Example of a twinned as-grown crystal (Rutil TiO_2)

plane may take. Detailed considerations lead to different classifications of twins and the topic has been treated in detail in a number of books on mineralogy and review articles (see, e.g., Cahn, 1954; Wadhawan, 1987; Shuvalov, 1988).

In this book we are concerned in the description of properties of a special kind of twins, traditionally referred to as transformation twins. Their essential feature is that the mentioned symmetry relations between their components are fully defined by specifying two crystal structures, say S_G and S_F , with two prominent properties: (i) the symmetry of S_F is *lower* than that of S_G and (ii) S_F arises from S_G by small distortions of the latter, for instance by small shifts of some of the ions. In a large number of crystalline compounds, the structure changes spontaneously from S_G to S_F at a certain *phase transition temperature* T_{TR} , simply to obey the rule that such structure is realized which, at a given temperature, corresponds to lower free energy of the material. Consider the simple example illustrated in Fig. 1.2. The structure S_G has a tetragonal unit cell. At the phase transition, this structure undergoes changes: The central ion shifts along the vertical c -axis. The actual displacements of particles may be very small (typically of the order of 10^{-2} – 10^{-3} nm, i.e., a very small fraction of the unit cell dimension), but even so they violate some of the symmetry operations of S_G and the resulting structure S_F has a *lower symmetry*. The shift of the central ion can have either sign so that two structures $S_F(A)$ and $S_F(B)$, denoted further on as S_A and S_B , can form. When no external forces are applied they have the same energy and therefore in an ideal sample it is unpredictable which of them will appear. These two structures, resulting from the *phase transformation* from a *phase* with the structure S_G to that with the structure S_F , represent *transformation twins*. Herein we will refer to these phases as G and F , respectively. The material undergoing a phase transition such as this one or similar to it is referred to as a *ferroic*. Twin components in a real sample which are formed due to a phase transformation in ferroics are called *domains*. To avoid misunderstandings, we stress already at this point that while in this hypothetic ferroic material only two *domain states* can exist, with structures S_A and S_B , in a sample of it we may have any number of twin components, i.e., any number of domains each of which represents either S_A or S_B .

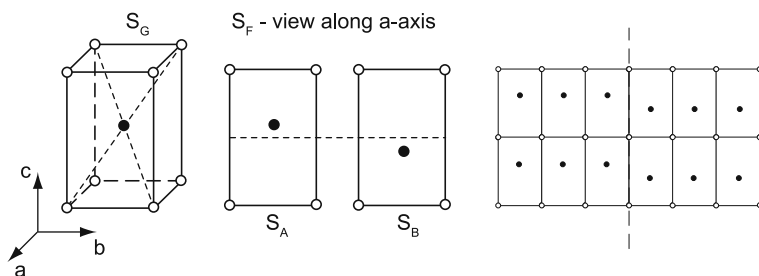


Fig. 1.2 Simple case of two ferroelectric domain states formed in a crystal lattice

Several thousands of crystalline materials are known to undergo phase transitions at which the symmetry is lowered, typically on cooling (Tomashewski, 1992a,b) or when the ambient hydrostatic pressure is changed (Tonkov, 1992). In all of them, domains may exist and there are manifold reasons for their occurrence. Static mechanical and electrical boundary conditions of a finite sample may lead to domain formation, in particular during the phase transformation process. Presence of defects incorporated into the crystal lattice during the crystal growth may prefer the coexistence of two domains next to each other. Metastable domain patterns may exist in a sample as remnants of dynamic processes which took place in it in the past. And, perhaps most important of all, domains can be formed intentionally by applying properly oriented mechanical and/or electrical forces.

Size of domains varies in wide limits, from tens of nanometers to millimeters; however, if a narrower region should be quoted as typical, linear dimension between 1 and 100 μm would seem a reasonable hint for the bulk materials, however, much smaller values are typical for thin films. While the number of domains is virtually unlimited, a very different rule applies to the count of “kinds of domains.” It is obvious from the Fig. 1.2 that, starting from a tetragonal cell, the shift of the central ion along the vertical axis can proceed in two ways only: upward or downward. This leads to just two possible structures, S_A and S_B ; these represent the only two possible *domain states*. Generally, the number of domain states may be larger than two. We shall show in the following chapter how it can be determined by simple symmetry considerations.

Compared to growth twins, domains excel in one aspect: The number of domain states and the symmetry relationship between them can be exactly formulated, knowing the symmetries of crystal structures S_G and S_F . We shall consider these symmetry aspects in some detail in the next chapter.

A phase transition between phases G and F can also be associated with a change of the form of the unit cell as illustrated in Fig. 1.3, where the unit cell in F phase becomes orthorhombic. Here the two possible structures of S_F phase,

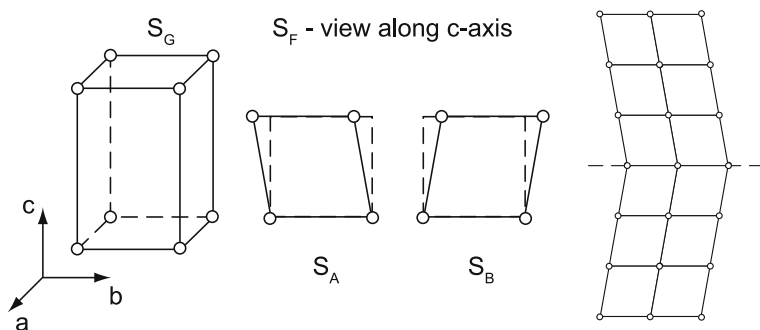


Fig. 1.3 Simple case of two ferroelastic domain states formed in a crystal lattice

S_A and S_B , differ from S_G by the sign of shear deformation in the plane normal to the fourfold axis of G phase.

What was a twin boundary or a composition plane in the general twinning narrative becomes a *domain wall* or *domain boundary* in the case of domains. But the concept of twin boundary is also frequently used, especially when speaking about two neighboring domains which differ in the shape of their unit cells, as illustrated in Fig. 1.3. Typically, having in mind nonmagnetic ferroics, the domain wall is an extremely thin region, its thickness ranging from one to several tens of lattice units. We wish to mention already at this point that, in a sample of a ferroic material, both phases (with the structures S_G and S_F) may coexist, usually within a restricted temperature interval around the phase transition temperature T_{TR} . In this book we shall reserve the term *phase boundary* for a narrow transition region separating these two structures.

Figure 1.4 shows an example of real domains. It is a microscopic image of domains in a plate of barium titanate; the sample surface was etched (Fousek and Safrankova, 1965). Here, dark and white stripes, which are several micrometers wide, correspond to domains representing two possible domain states. The photograph clearly demonstrates that domain walls are much thinner than the domain size.

It is obvious from what has been said that, under ideal conditions (perfect crystal lattice, no applied forces) the energy density of the crystal in the two domain states (or in any domain state allowed by symmetry), is the same. These are the *ground states* of the crystalline system in phase F , degenerate in energy. But within the domain wall—however thin it may be—the structure must be distorted, providing a passage between the two structures S_A and S_B . Therefore the wall is characterized by some extra energy; since the wall is very thin we consider it as a surface energy. It plays a significant role: What size and in particular what shape domains have largely depend on its magnitude and on the extent it varies with the wall orientation. If asked for a typical number, the wall energy density is usually estimated to be of the order between 1 and 10 erg/cm².

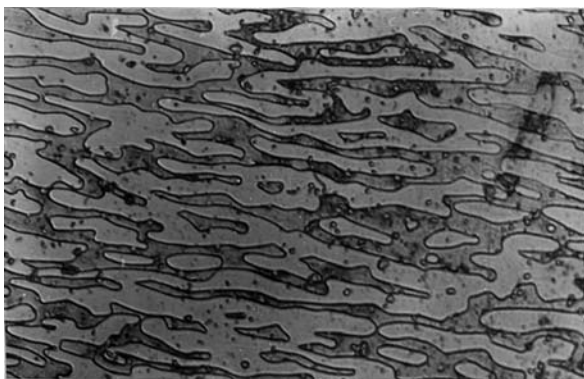


Fig. 1.4 Microscopic picture of domains in a c -plate of barium titanate; the sample surface was etched and observed in reflected light (Fousek and Safrankova, 1965)

Up to this point, domains and growth twins seem to have many similar properties. What makes domains unique are two features. First, the structural change from S_G to S_F is accompanied by fully predictable macroscopic tensor properties of the crystal. As a consequence, the difference in the tensor properties of different domain states (with structures S_A and S_B in our example) is well defined. Second, forces may be applied to the ferroic sample, which remove the energy degeneracy of domain states; again the nature and orientation of these forces are fully predictable. Often they can be easily realized and are capable of transforming the crystal from one domain state to another. This process is referred to as *domain state reorientation* but many alternative terms are employed such as *switching*.

Ferroic crystals, because of the existence of domains and possibility of reorientation, thus offer qualitatively new properties and effects which cannot be achieved with “normal” crystalline compounds that exist in one state only.

A simple and at the same time a very realistic illustration of what has been just said can be based again on the previous simple model. Assuming the central ion is positively charged, its shift is connected with formation of a dipole. Its dipole moment, when integrated over a unit volume, defines the polarization variation associated with the phase transformation. This polarization variation is customarily termed as *spontaneous polarization* \mathbf{P}_S , associated with the phase transition from S_G to S_F . Thus the structures S_A and S_B differ in the sign of \mathbf{P}_S . It is obvious that an applied electric field \mathbf{E} pointing downward prefers the structure S_A while the structure S_B is more favorable in the field of opposite sign. We expect that domains with structures preferred by the applied field, say S_A , will grow at the expense of domains with structures S_B . As a characteristic of this process, mapping average polarization vs. field results in the *hysteresis loop*. An example of such loop observed in a slowly varying field applied to a crystal of $\text{Gd}_2(\text{MoO}_4)_3$ (abbr. GMO) is shown in Fig. 1.5a (Kumada et al., 1970). It illustrates the process of *polarization reversal*. A ferroic with this property is said to be *ferroelectric*. Other ferroelectric crystals which serve as model materials for many aspects of domain properties are barium titanate, BaTiO_3 , and $(\text{CH}_2\text{NH}_2\text{COOH})_3\text{H}_2\text{SO}_4$ (triglycine sulfate — abbr. TGS).

Similarly, applying a properly oriented shear stress to the system illustrated in Fig. 1.3 we will make favorable one of the structures S_A and S_B , having different signs of the shear deformation of the unit cell. In practice, the shear stress is realized as a compressive stress along an axis making an angle of 45° with the crystal axes and its sign is reversed when compression is applied perpendicularly to the previous one. In this way we can achieve a hysteretic dependence of strain on stress, such as shown in Fig. 1.5b (Gridnev et al., 1990). A ferroic with this feature is called *ferroelastic*. Here we come very close back to the concept of mechanical twins but — since we now base our approach on the existence of the original unperturbed structure S_G — families of materials offering mechanical twins and ferroic materials are not identical. A model ferroelastic crystalline material is lead phosphate, $\text{Pb}_3(\text{PO}_4)_2$.

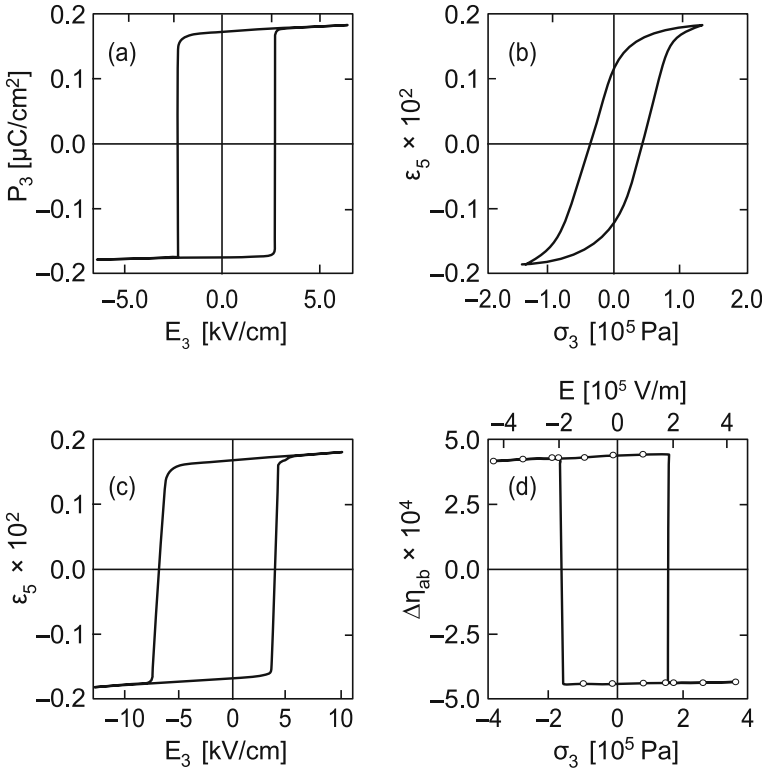


Fig. 1.5 (a) Ferroelectric hysteresis loop: hysteretic dependence of polarization on applied electric field (at a frequency of 1 mHz) in a crystal of gadolinium molybdate (GMO) (Kumada et al., 1970). (b) Ferroelastic hysteresis loop: hysteretic dependence of deformation on applied stress in a crystal of $\text{KH}_3(\text{SeO}_3)_2$ (Gridnev et al., 1990). (c) Hysteretic dependence of deformation on applied electric field in a crystal of GMO (Kumada et al., 1970). (d) Linear birefringence of a GMO crystal as a function of applied electric field or mechanical shear stress (Kumada et al., 1970)

Definitions given above are to a certain extent approximate. We shall pay more attention to this terminology in the following chapter where also other kinds of ferroics will be introduced.

The mentioned properties appear even more interesting when we look at some numerical values. In a normal dielectric like mica or rutile, with the relative permittivity value say 40, an electric field of 1 kV/cm induces polarization, equal to the surface charge density, in the amount of about $40 \mu\text{C}/\text{m}^2$. The same field can bring about polarization reversal in a ferroelectric sample with spontaneous polarization of $20 \mu\text{C}/\text{m}^2$ and this leads to the surface charge change of $40 \times 10^4 \mu\text{C}/\text{m}^2$, a value $10,000 \times$ higher. For a normal elastic material, whether sodium chloride or copper, the elastic compliance is of the order of $10^{-11} \text{m}^2/\text{N}$ so that an applied stress say $2 \times 10^4 \text{N}/\text{m}^2$ induces deformation

2×10^{-7} . The same strain can cause reversal of spontaneous strain of a ferroelastic crystal in the amount of 2×10^{-3} . For this impressive “amplification” of effects by a factor of 10^4 , however, we pay a price in terms of nonlinear and hysteretic behavior.

Appearance of the spontaneous polarization in F phase, depending on the symmetry of G phase, can lead to the deformation of the unit cell of the crystal. In the case of the structure shown in Fig. 1.2 this does not happen. However, adding more atoms to the unit cell of this structure thus lowering its symmetry, one can obtain a structure where the appearance of the spontaneous polarization along the c -axis will be entailed with a shear deformation in the perpendicular plane as shown in Fig. 1.3. It is obvious that in such structure, changing polarization by electric field may lead to reversing the shear strain at the same time. We thus observe a hysteretic dependence of strain on applied field. It is represented in Fig. 1.5c. This phenomenon can exist in ferroics which are simultaneously ferroelectric and ferroelastic. Barium titanate and GMO are well-studied representatives.

The two domain states in GMO differ also in birefringence and this fact manifests itself in yet another characteristic of domain reorientation, reproduced in Fig. 1.5d. Thus ferroics offer a large variety of characteristic macroscopic phenomena.

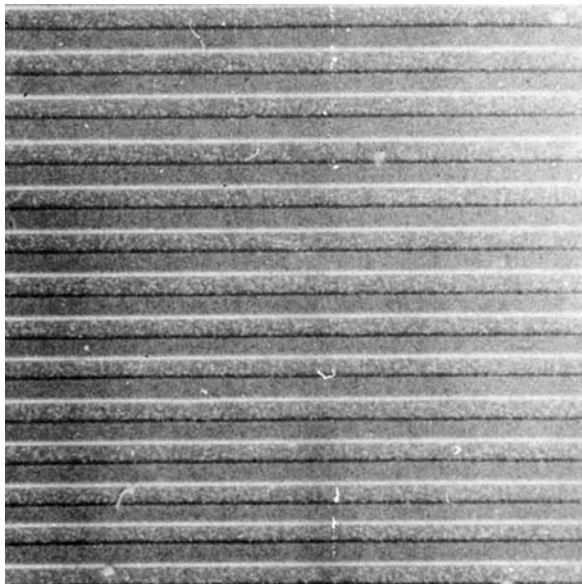
The hysteresis loop is often considered a defining feature of ferroics and of ferroelectrics in particular. The stability of either of two states when the applied force is zero is the basis of a memory device. Switching times of the order of tens or hundreds of nanoseconds are typically achieved in good single crystals at high fields. It has been established that domain walls can move faster than the velocity of sound. In thin films, switching times are not far from hitting the picosecond limit. A remarkable feature of a ferroelectric loop is that together with polarization a number of other “coupled” properties are switched, as we have just demonstrated. This opens a way to alternative methods of detecting in which state the memory device dwells at any given moment, as well as to many other application aspects. On the other hand, the polarization reversal is coupled with behavior of free charge carriers, making processes complicated; in ferromagnetics, this issue does not exist.

While the states on the hysteresis loop are transient, multidomain states can, of course, exist also in static conditions, often representing metastable states with a long lifetime. Multidomain structures which can live for very long time can also be created artificially. Figure 1.6 gives an example of an artificial regular domain pattern in a crystal of LiNbO_3 (Feisst and Koidl, 1985) “engineered” for nonlinear optical applications.

Because domain states differ in the orientation of crystallographic axes, there exist a large number of methods to observe domain structures, ranging from surface etching and decoration techniques, polarized light microscopy, and nonlinear optical scattering to high-resolution electron microscopic methods.

Domain reorientation phenomena as well as characteristics of samples in multidomain states offer manifold applications. Though, in this book, we are

Fig. 1.6 Artificially produced periodic domain pattern serves to enhance optical second harmonic generation. Etched surface of a LiNbO_3 crystal imaged by a scanning electron microscope. Reprinted with permission from Feisst and Koidl (1985). Copyright (1985), American Institute of Physics



not going to address practical applications of ferroic domain, let us shortly mention some of them. Domain reorientation is an absolutely essential process when preparing piezoelectric ceramics; note that a ceramic sample containing chaotically oriented grains of a typical piezoelectric material would reveal zero or negligible piezoelectric response. Only when grains are subject to ferroelectric poling which is just the process of domain reorientation pertinent to the $P(E)$ hysteresis loop, the sample becomes piezoelectric. Most of today's electroacoustic devices utilize such ceramics. Behavior of domain walls in low electric fields greatly enhances dielectric and piezoelectric response of multidomain systems, which allows reaching values of material coefficients like permittivity or piezoelectric constants, which cannot be realized within homogeneous samples. One of the most characteristic applications of ferroelectric hysteresis is non-volatile random access memory. Domain processes in ferroelectric ferroelastics make it possible to electrically control light propagation in the material, with a number of practical aspects. Engineered domain structures such as the one shown in Fig. 1.6 offer nonlinear optical elements with greatly enhanced efficiency of second harmonic generation. Many promising applications are in the research or development stages. For example, controlled polarization reversal makes it possible to fix holograms in photorefractive ferroelectrics. Fast switching processes are often accompanied by bursts of emitted electrons or light and these phenomena promise several practical aspects.

The goal of the preceding paragraphs was to give a qualitative and introductory overview of some of the topics to be discussed in detail in this book. In

what follows we start with introducing basic theoretical approaches to structural phase transitions, emphasizing the symmetry and phenomenological aspects of their classifications (Chapter 2) and give an overview of typical ferroic materials (Chapter 3). After a survey of experimental methods used to visualize domain patterns (Chapter 4) we shall review a number of aspects of domain formation and what their typical shapes are (Chapter 5). Chapter 6 will address the static properties of domain walls. The short Chapter 7 will be devoted to the experimental characterization of switching. The largest chapter of the book, Chapter 8, will cover the theoretical and experimental aspects of the polarization response of ferroelectrics. In Chapter 9, we have attempted to give a comprehensive overview of the domain-related properties of ferroelectric thin films. Originally, we planned to include the book chapters on domains in bulk ceramics, on domain issues in ferroics revealing an incommensurate phase and relaxors, and one which would cover practical applications of domain phenomena in ferroic; however, the time factor urged us to limit the scope of the book. These issues are only briefly mentioned in places.

This book is intended for students and researchers who are familiar with just a small part of the whole field or who are beginners. When writing it we have tried to follow a “bi-modal” approach. If something can be explained or derived in a relatively simple way, we present a detailed explanation or derivation. On the other hand, if the relevant story was, in our opinion, complicated, we present only the results referring the reader to the original papers for the explanations.

Perhaps we can end this chapter by referring to other literature, in the book form, on domain phenomena in nonmagnetic ferroics. The more recent books on ferroelectrics include works by Smolenskii et al. (1984), Xu (1991), Strukov and Levanyuk (1998), Wadhawan (2000), and by Rabe et al. (2007). In all of them the various domain issues are well treated, of course without going into details and using quite different approaches. Recently published books edited by Hong (2004), Alexe and Gruverman (2004), and Kalinin and Gruverman (2006) offer a wealth of information on domains on nanoscale and their characterization with Scanning Probe Techniques. The theoretical work of Toledano and Toledano (1988) provides the reader with the background required to analyze domain states on the basis of symmetry and thermodynamics. A small but very informative monograph on some aspects of ferroelectric domains has been published by Fesenko et al. (1990). Ferroelastic domain phenomena are treated extensively in Salje’s book (1990) on ferroelastics. A very informative book on the theory of domain-related phenomena was published by Sidorkin (2006). Close attention was paid to domain phenomena in several older monographs on ferroelectricity (Jona and Shirane, 1962; Fatuzzo and Merz, 1966; Lines and Glass, 1977; Burfoot and Taylor, 1979). There also exist a number of relevant review papers. They will be pointed out later in the corresponding chapters.

Chapter 2

Fundamentals of Ferroic Domain Structures

2.1 Structural Phase Transitions and Domain States: Basic Concepts and Classifications

2.1.1 Structural Changes at Phase Transitions: Ferroics

In this section we introduce the basic concepts required to discuss structural phase transitions in crystals on the basis of a symmetry approach. The latter is in fact closely connected with the Landau theory of phase transitions, to which we come later in this chapter. However, for the reader who is more oriented toward domain properties without studying the nature of phase transitions themselves, it may be practical to become acquainted with the symmetry approach in the first place. The analysis of domain states on the basis of symmetry gives essential information on the number of domain states and on how they can be distinguished. It is this information that forms the background of any considerations about domain reorientation processes, about domain walls, as well as about properties and applications of multidomain samples.

Speaking about a structural phase transition, we always compare two different crystal structures S_G and S_F between which the transition is realized. The difference between S_G and S_F is not trivial: We have in mind changes in the crystal structure, which cannot be described by a mere thermal expansion (due to change of temperature) or by a mere compression (due to change of hydrostatic pressure). Our structural changes are more dramatic, although they are also brought about by change of temperature or pressure. Such transitions are known to occur in several thousands of crystalline substances (Tomaszewski, 1992a,b; Tonkov, 1992). They can be classified according to a number of different criteria.

On the first level of categorization we have to distinguish between *distortive* and *reconstructive transitions* (Gränicher and Müller, 1971). In the latter case, the structures S_G and S_F have nothing in common except for chemical composition. A reconstructive transition requires indeed a complete reconstruction of the atomic structure so that chemical bonds are broken and because of that the process itself usually involves formation of dislocations and proceeds

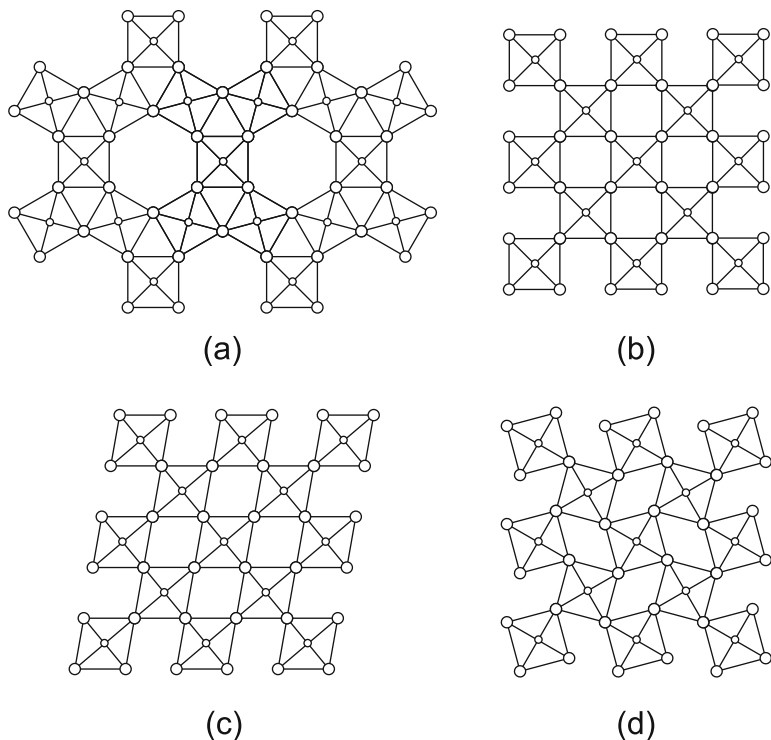


Fig. 2.1.1 Models of possible distortions of crystal structure

sluggishly. Figure 2.1.1 (in part reproduced from the book of Rao and Rao (1978)) shows schematically atomic arrangements in four different crystal structures. Transformation from the structure (a) to any of the other structures requires breaking of first coordination bonds and would represent a reconstructive transition. Well-known examples of such transitions include that between sphalerite- and wurtzite-type structures in ZnS , one between arsenolite and claudetite structures of As_2O_3 , or that between the β -phase (body-centered cubic) and hexagonal or rhombohedral modifications of titanium. Domain states as they are presented in this book do not concern reconstructive phase transitions.

In contrast, at a *distortive transition* the spatial system of crystal bonds forming the structure S_G becomes systematically distorted, without disrupting the linkage of the network. Thus, in Fig. 2.1.1, the structure (c) or (d) can be conceived as a slightly changed structure (b), due to coordinated shifts of atoms. By these distortions the crystal structure goes over into S_F and it is obvious that by doing so the crystal symmetry also changes, from symmetry group G to symmetry group F . Here G and F stand for the symbol of 32 point groups. As it is usual, we shall always use the symbol G or S_G when referring to the higher

symmetry phase and F or S_F when referring to the lower symmetry phase. Thus for distortive transition the group—subgroup relation holds, namely

$$F \subset G. \quad (2.1.1)$$

This is one of the essential features of distortive phase transitions and offers different ways for their further classifications. Logically now, the phase with the symmetry G (or shortly the phase G) is referred to as the *parent* or *prototypic* or *high-symmetry phase* while the phase with symmetry F (or shortly the phase F) is called *distorted* or *low-symmetry phase*.¹ Since the transition between the two phases is often monitored as a function of temperature (at some *transition temperature* T_{TR}) and, as a rule, the symmetry is lowered on cooling, phases G and F are often mentioned as *high-temperature* and *low-temperature phases*, respectively.

Before pursuing further the symmetry issues, however, we mention one further classification of distortive transitions. Depending on the basic type of thermal motion of the structural units related to the transition, one distinguishes *displacive* and *order–disorder transitions*. Speaking about the symmetry of a crystal, one considers the symmetry of the structure formed by the average positions of atoms involved in thermal motion. If the atoms controlling the symmetry change at the transition perform small harmonic oscillations² around their average positions, one classifies the transition as *displacive*. In this case, physically, the symmetry change at the transition is controlled by displacements of bottoms of the potential wells, where the atoms oscillate. If the atoms controlling the symmetry change at the transition perform thermally activated jumps between two or more equilibrium positions, one classifies the transition as *order–disorder*. In this case, the symmetry change is controlled by the distribution of the atoms between these positions: In the high-symmetry phase the atoms are equally distributed between them, whereas in the low-symmetry phase, this distribution becomes asymmetric resulting in a displacement of the average positions of atoms.

In real systems, both types of transitions are represented as well as more complicated cases with mixed behavior. To illustrate the modifications of a structure accompanying a real displacive phase transition, we will consider below the cubic–tetragonal transition in BaTiO_3 . Here we will follow the classical scenario of this transition; however, more complicated scenarios of it are also under discussion (Stern, 2004).

Figure 2.1.2a illustrates the perovskite-type structure of BaTiO_3 , in the cubic phase. On cooling, at $T_{\text{TR}} \cong 126^\circ\text{C}$ it transforms into the tetragonal phase. Choosing as a reference the positions of barium ions, what happens at T_{TR} (cf.

¹ Coupling a *parent* together with something *distorted* or *low symmetry* is somewhat ungraceful. Indeed Wadhawan's (1982) *daughter phase* would be more elegant.

² Since these oscillations occur around the equilibrium positions that are temperature dependent, it would be more rigorous to call such oscillation quasi-harmonic.

Fig. 2.1.2 Perovskite-type structure of BaTiO_3 : (a) unit cell in the cubic phase and (b) atomic displacements at cubic to tetragonal transition

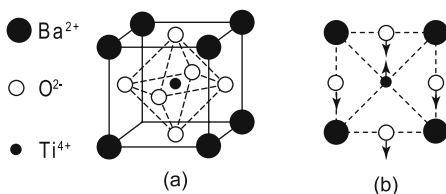
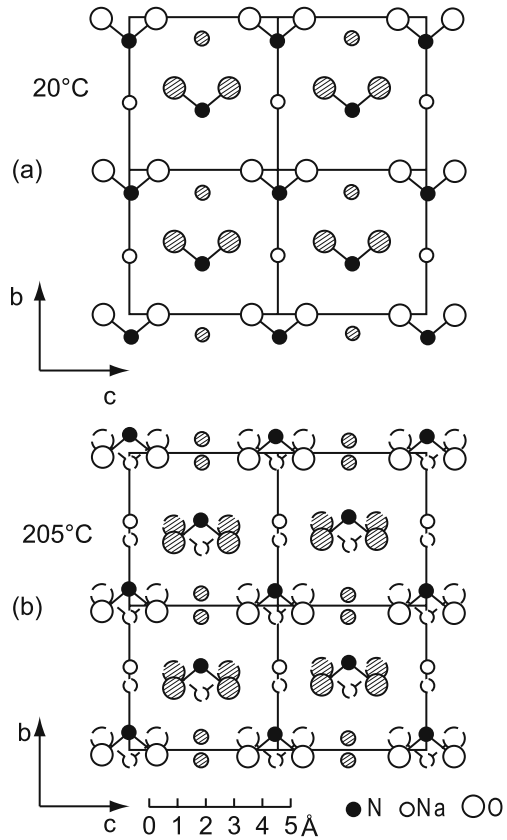


Fig. 2.1.2b) is that all titanium ions undergo a small shift along one of the cubic axes, say “upward.” There are two kinds of oxygen ions in nonequivalent positions, O_I and O_{II} ; both shift “downward,” though by different amounts. It is obvious that these shifts violate several symmetry operations of the original cell: center of symmetry, mirror plane (001), the twofold axis [010], to name a few which are obvious from this two-dimensional projection onto the (100) plane. Considering now the situation in three dimensions, as a result of these ionic displacements the point group symmetry $G = m\bar{3}m$ is lowered to $F = 4mm$ which of course is a subgroup of G .

A classical example of an order–disorder transition is provided by sodium nitrite, NaNO_2 . This crystal undergoes the order–disorder transition from $G = mmm$ to $F = mm2$ at about $T_{\text{TR}} = 163^\circ\text{C}$ (at this moment we disregard the intermediate phase which exists in a narrow temperature interval). In Fig. 2.1.3a, its unit cell is shown schematically in its ferroelectric phase. Here we assume that the NO_2 groups are fully ordered, their dipole moments all pointing along the direction of the b -axis. In fact there is partial disorder, since the probabilities of finding the NO_2 groups oriented against the b -axis is not zero so that the net dipole moment is less than maximum. Above T_{TR} the probabilities of finding the NO_2 groups in two symmetric positions become equal (Fig. 2.1.3b) so that the structure acquires an additional symmetry element — a mirror plane. Thus the net dipole moment disappears, and the average symmetry of the lattice becomes higher.

The difference between displacive and order–disorder transitions is vital when studying lattice dynamics and temperature dependences of some macroscopic properties. It does not seem to have a significant bearing on domain phenomena. On the other hand, properties of domains, their shapes, and dynamic behavior are closely related to the G – F relations. In this book, therefore, we shall base our classifications and many approaches on symmetry considerations. The symmetry approach is usually based on considering the point symmetries G , F but also on the possible change of the unit cell volume. Any phase transition fulfilling relation (2.1.1) is called a *ferroic transition* and F itself is the point group of the *ferroic* phase. Looking at the number of atoms in the unit cell, there are two possibilities. First, the number of molecular units in the primitive unit cell, or — less exactly — volume of the unit cell may not change. That is, the translational symmetry is preserved. Then we speak about a *ferrodistortive ferroic*. The phase transition from (b) to (c) in Fig. 2.1.1 obviously fulfills this requirement and the previously mentioned example of BaTiO_3 belongs to this category. Alternatively, even the translational symmetry

Fig. 2.1.3 Atomic structure of NaNO_2 . Projection along the a -axis: (a) ferroelectric phase. The NO_2 groups are planar and lying in the bc plane. The groups with the clear oxygen circles are in the plane of the figure; those with the shaded oxygen circles are displaced by a half of the lattice constant along the a -axis. The clear sodium circles are in the plane of the figure; those with the shaded sodium circles are displaced by a half of the lattice constant along the a -axis. (b) Paraelectric phase. NO_2 groups and Na ions are equally distributed between two positions shown with solid and dashed lines



may change at the phase transformation, as it is obvious in a hypothetical transition from (b) to (d) in Fig. 2.1.1. The crystal of lead zirconate PbZrO_3 provides a well-known example. In its parent phase, its cubic structure is identical with that of barium titanate shown in Fig. 2.1.2a and its unit cell contains just one formula unit. At temperature $T_{\text{TR}} \cong 230^\circ\text{C}$ the atomic structure undergoes changes primarily characterized by shifts of lead ions along one of the original $[110]$ directions which becomes the a -axis of the new orthorhombic phase of symmetry $mm2$. In neighboring cubic cells these shifts are antiparallel. This is an example of a phase transition which is referred to as *antiferrodistortive*. This type of distortion will be accompanied by an increase of the number of formula units in the primitive unit cell (from one to eight in the case of PbZrO_3). Naturally, this is the same as saying that the translational symmetry has changed. To describe the unit cell multiplication one introduces the factor

$$v = Z_G/Z_F \cong V_G/V_F, \tag{2.1.2}$$

where Z_A is the number of formula units and V_A is the volume of the primitive unit cell (neglecting the effect of thermal dilatation) in the phase of group

symmetry A . Materials are known in which the phase transition is accompanied only by a change of the translational symmetry while the point symmetry remains the same: $G = F$ but $v > 1$. These are referred to as *nonferroics* and in this book their properties will not be considered. As examples, we can mention potassium cyanide, KCN, ($v = 2$) or $\text{CH}_3\text{NH}_3\text{CdCl}_4$ ($v = 4$). In some cases, such a transition is characterized by a change of the space symmetry group but in others even that remains the same in both phases. Tolédano and Tolédano (1982) performed a symmetry analysis of all possible nonferroic phase transitions and gave a number of concrete examples.

In the following three sections we shall categorize ferroics according to macroscopic properties absent in the parent phase but newly revealed in the ferroic phase, which is the most significant aspect in understanding domain-related phenomena.

2.1.2 Ferroelectric Phase Transitions

In a way, ferroelectrics are the simplest ferroics since domain states in them differ in the orientation of a tensor of the lowest possible rank, a vector. Let us discuss the definition of a ferroelectric phase transition by which is usually meant a transition from a nonferroelectric phase G into a ferroelectric phase F . In an uncomplicated approach it is said that the *phase transition is ferroelectric* when, as a result of it, there exists *spontaneous polarization* \mathbf{P}_S in the phase F . In many cases this “ \mathbf{P}_S definition” is fully satisfactory from most points of view and we shall be using it—as almost everyone—as a shorthand. However, it does not respect the problem of determining the notion of polarization itself and fails to provide an appropriate basis for describing transitions from a phase which is already polar. We shall, therefore, discuss this point in more detail.

Polarization is customarily defined as the dipole moment per unit volume of the system of charges in the material. However, as it was recently realized (Tagantsev, 1987, 1991, 1993; Resta, 1994), for a medium with a periodic distribution of charge, the dipole moment density cannot be unambiguously introduced as a bulk property of the system. Clearly, for any finite and electro-neutral part of this structure, one can calculate, using the charge distribution, the average dipole moment density. However, the fact that the result of the calculation depends on the way in which the part was specified shows that this result does not represent a bulk property of the structure. On the other hand, a variation of the dipole moment density resulting from small changes of charge positions is defined unambiguously, not suffering from the aforementioned dependence. This enables an unambiguous definition of variation of polarization as that of the dipole moment density. Thus, any rigorous definition of the ferroelectric phase transition should deal with changes of polarization or its derivative with respect to other physical variables rather than with the polarization itself.

One possibility of such a definition is based on the *pyroelectric effect*. One considers the *pyroelectric coefficient* \mathbf{p} , a vector defined as the derivative of polarization with respect to temperature, at zero electric field in the material. Its components are

$$p_i = \left(\frac{\partial P_i}{\partial T} \right)_{E=0}. \quad (2.1.3)$$

Clearly, \mathbf{p} is a polar vector. The experimental manifestation of the pyroelectric effect is a change δQ of bound charge density on the surface of a plate-like sample cut obliquely to \mathbf{p} when its temperature is changed by δT . Since $\delta Q = \delta D_n = \varepsilon_0 \delta E_n + \delta P_n$, where δD_n , δE_n , and δP_n are changes of components (normal to the plane of plate) of the electric displacement, electric field, and polarization, respectively, the condition $E = 0$ implies $p = \delta Q / \delta T$.

The symmetry of a material puts serious restrictions on the existence and orientation of \mathbf{p} . It can only have nonzero components in samples of materials represented by one of the point symmetry groups 1, 2, m , $mm2$, 4, $4mm$, 3, $3m$, 6, $6mm$, or Curie groups ∞ and ∞m . These are referred to as *polar groups*. While point groups describe symmetries of crystalline media, the Curie groups ∞ and ∞m have been included since they play a role in nonuniform ferroelectric systems such as ceramics or polymers. If the group F is polar while G is not, we speak about a *ferroelectric phase transition*; F is then the symmetry of the *ferroelectric phase*. It may, however, happen that already G is a polar group and that on transforming from G to F the vector \mathbf{p} just acquires new components. We believe that it is reasonable to call the latter transition ferroelectric to have uniformity in the definition of all nonmagnetic phase transitions. Thus, we arrive at the following definition of a *ferroelectric transition*:

A phase transition is called ferroelectric if it results in a lower symmetry phase in which the vector of pyroelectric coefficients acquires new components which were zero, by symmetry, in the high-symmetry phase.

A convenient variable for a description of the properties of material in the ferroelectric phase is the vector of *spontaneous polarization* \mathbf{P}_S . At a given temperature T_f in the ferroelectric phase we define it as the change of polarization during cooling from a temperature in the paraelectric phase T_p down to T_f , i.e.,

$$\mathbf{P}_S(T_f) = \int_{T_p}^{T_f} \mathbf{p}(T) dT. \quad (2.1.4)$$

Concerning the accepted definition of spontaneous polarization the following remarks should be made.

First, as we will see in the section of this chapter devoted to the thermodynamic description of the phase transitions, this definition is in perfect correspondence with that accepted in phenomenological theories.³ Second, though

³ Spontaneous polarization at T_{TR} may appear discontinuously. This is so for transitions of the first order, as discussed in detail in Sect. 2.3. Then the corresponding component of \mathbf{p} at