Growth and Characterization of Lead Zirconate-Titanate (PbZr$_{1-x}$Ti$_x$O$_3$)-Based Novel Piezo-/Ferroelectric Single Crystals

by

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Abstract

Piezo-/ferroelectric materials form an important class of functional materials that can transduce mechanical energy to electrical energy and vice versa. PbZr$_{1-x}$Ti$_x$O$_3$ (PZT) ceramics are the most extensively used piezoelectric materials owing to their good piezoelectric and electromechanical properties near the morphotropic phase boundary (MPB). However, the microstructures of this class of materials and the atomistic phenomena that cause the outstanding performance have not been thoroughly understood yet. Therefore, it is of particular interest to grow single crystals of PZT, which are not only necessary for thorough characterization of the anisotropic properties of this system, but also are expected to exhibit superior piezo-/ferroelectric performance over their ceramic counterparts. In this work, PZT single crystals with compositions of $x = 0.54$ and $0.45$ were grown successfully by a top-seeded solution growth (TSSG) method, and characterized by X-ray diffraction, polarized light microscopy (PLM), piezoresponse force microscopy (PFM), and dielectric, ferroelectric, and piezoelectric measurements.

On the other hand, given that PZT ceramics used in industry are always chemically modified to obtain desired and enhanced properties for specific applications, we extended our work to grow donor ($\text{La}^{3+}$ and $\text{Bi}^{3+}$)- and acceptor ($\text{Mg}^{2+}$ and $\text{Mn}^{2+}$)-doped PZT single crystals and to investigate the effects of the doping on the structure and properties. The compositions and homogeneity of the as-grown doped PZT single crystals were investigated by laser ablation inductively coupled plasma mass spectrometry (LA-ICP-MS) and energy dispersive spectroscopy (EDS). The dielectric, ferroelectric and piezoelectric properties of these single crystals were investigated. These very first set of data on doped PZT single crystals not only provide a better understanding of structure-property relationship of PZT-based single crystals and their doping mechanisms, but also points to the possible applications of doped PZT single crystals as a new high-$T_C$, high-performance piezo-/ferroelectric material.

Moreover, there have been pressing demands for lead-free or lead-reduced replacement materials because of the environment concerns arising from the potential toxicity of the lead in high-performance piezo-/ferroelectric material such as PZT. In our search for high-temperature, lead-reduced piezoelectric materials, novel ferroelectric single crystals of complex perovskite ternary solid solution Bi($\text{Zn}_{0.5}\text{Ti}_{0.5}$)O$_3$-PbZrO$_3$-PbTiO$_3$ (BZT-PZ-PT) have been grown for the first time. The structure and properties of these crystals suggest that the BZT-PZ-PT ternary single crystals constitute a new family of high-$T_C$ ferroelectric materials, which are promising for various applications such as high-power electromechanical transducers that can operate in a wide temperature range.
**Keywords**: Perovskite; Ferroelectrics; Single Crystals; Donor/Acceptor Doping; Ternary; Solid Solution.
Dedication

To my dear parents,
Xingrong Wang and Nvdan Chen
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<tr>
<td>PZT</td>
<td>PbZr$_{1-x}$Ti$_x$O$_3$</td>
</tr>
<tr>
<td>BZT</td>
<td>Bi(Zn$<em>{0.5}$Ti$</em>{0.5}$)O$_3$</td>
</tr>
<tr>
<td>NBT</td>
<td>Na$<em>{0.5}$Bi$</em>{0.5}$TiO$_3$</td>
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<tr>
<td>PZ</td>
<td>PbZrO$_3$</td>
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<td>PT</td>
<td>PbTiO$_3$</td>
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<tr>
<td>KNN</td>
<td>K$<em>{0.5}$Na$</em>{0.5}$NbO$_3$</td>
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<tr>
<td>PMN</td>
<td>Pb(Mg$<em>{1/3}$Nb$</em>{2/3}$)O$_3$</td>
</tr>
<tr>
<td>PZN</td>
<td>Pb(Zn$<em>{1/3}$Nb$</em>{2/3}$)O$_3$</td>
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<tr>
<td>PIN</td>
<td>Pb(In$<em>{1/2}$Nb$</em>{1/2}$)O$_3$</td>
</tr>
<tr>
<td>PYN</td>
<td>Pb(Yb$<em>{1/2}$Nb$</em>{1/2}$)O$_3$</td>
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<tr>
<td>BS</td>
<td>BiScO$_3$</td>
</tr>
<tr>
<td>La-PZT</td>
<td>La$^{3+}$-doped PbZr$_{1-x}$Ti$_x$O$_3$</td>
</tr>
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<td>Bi-PZT</td>
<td>Bi$^{3+}$-doped PbZr$_{1-x}$Ti$_x$O$_3$</td>
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<td>Mg-PZT</td>
<td>Mg$^{2+}$-doped PbZr$_{1-x}$Ti$_x$O$_3$</td>
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<tr>
<td>Mn-PZT</td>
<td>Mn$^{2+}$-doped PbZr$_{1-x}$Ti$_x$O$_3$</td>
</tr>
<tr>
<td>BZT-PZ-PT</td>
<td>Bi(Zn$<em>{0.5}$Ti$</em>{0.5}$)O$_3$-PbZrO$_3$-PbTiO$_3$</td>
</tr>
<tr>
<td>PMN-PT</td>
<td>Pb(Mg$<em>{1/3}$Nb$</em>{2/3}$)O$_3$-PbTiO$_3$</td>
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<tr>
<td>PZN-PT</td>
<td>Pb(Zn$<em>{1/3}$Nb$</em>{2/3}$)O$_3$-PbTiO$_3$</td>
</tr>
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<td>PIN-PMN-PT</td>
<td>Pb(In$<em>{1/2}$Nb$</em>{1/2}$)O$<em>3$-Pb(Mg$</em>{1/3}$Nb$_{2/3}$)O$_3$-PbTiO$_3$</td>
</tr>
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<td>PMN-PZ-PT</td>
<td>Pb(Mg$<em>{1/3}$Nb$</em>{2/3}$)O$_3$-PbZrO$_3$-PbTiO$_3$</td>
</tr>
<tr>
<td>MPB</td>
<td>Morphotropic phase boundary</td>
</tr>
<tr>
<td>HTSG</td>
<td>High temperature solution growth</td>
</tr>
<tr>
<td>TSSG</td>
<td>Top-seeded solution growth</td>
</tr>
<tr>
<td>TCGS</td>
<td>Top-cooled solution growth</td>
</tr>
<tr>
<td>XRD</td>
<td>X-ray diffraction</td>
</tr>
<tr>
<td>HRXRD</td>
<td>High resolution X-ray diffraction</td>
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<tr>
<td>PLM</td>
<td>Polarized light microscopy</td>
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<tr>
<td>PFM</td>
<td>Piezoresponse force microscopy</td>
</tr>
<tr>
<td>EDS</td>
<td>Energy dispersive spectroscopy</td>
</tr>
<tr>
<td>LA-ICP-MS</td>
<td>Laser ablation inductively coupled plasma mass spectrometry</td>
</tr>
<tr>
<td>HRTEM</td>
<td>High resolution transmission electron microscopy</td>
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</tbody>
</table>
\( d_{33} \) Piezoelectric constant
\( k_{33} \) Electromechanical coupling factor
\( E_c \) Coercive field
\( P_r \) Remnant polarization
\( T_C \) Curie temperature
\( Q_m \) Mechanical quality factor
\( t \) Tolerance factor
\( G \) Free energy
\( \varepsilon' \) Dielectric permittivity
\( \tan\delta \) Dielectric loss
\( P_s \) Spontaneous polarization
\( f_r \) Resonance frequency
\( f_a \) Anti-resonance frequency
\( k_p \) Planar electromechanical coupling factor
\( P \) Polarizer
\( A \) Analyser
\( \Delta n \) Birefringence
\( R \) Retardation
\( \lambda \) Wavelength of light
\( FE \) Ferroelectric phase
\( PE \) Paraelectric phase
Chapter 1.

General Introduction

1.1. Piezoelectric Properties

The piezoelectric effect was first discovered by Jacques and Pierre Curie in the Rochelle salt (KNaC₄H₄O₆·4H₂O) single crystals in 1880.[1] The phenomenon whereby electric polarization is generated from an external stress is defined as the direct effect, whereas the fact that an internal strain induced by an electrical field is called the converse effect.[2], [3] Both direct and converse piezoelectric effects are linear effects, which can be expressed using the following equations:

\[
P_i = d_{ij} T_j \quad \text{(Direct Effect)} \quad (1.1)
\]

\[
S_i = d_{ij} E_j \quad \text{(Converse Effect)} \quad (1.2)
\]

where \( P_i \) is the electric polarization induced, \( T_j \) is the stress applied, \( S_i \) is the strain induced, \( E_j \) is the electric field applied, \( d_{ij} \) is the piezoelectric coefficient,[4], [5] \( i \) and \( j \) are the tensor notation of the physical properties of crystals. The piezoelectric coefficients measured in the direction of the applied field are called longitudinal coefficients \((ij = 11, 22, 33)\), and those measured in the direction perpendicular to the field are called transverse coefficient \((ij = 12, 23, 31)\). The remaining piezoelectric coefficients are shear coefficients \((ij = 14, 15, 16, \ldots 35, 36)\).[4]

Electromechanical coupling factor \( k \) specifies the conversion efficiency between electrical and mechanical energies. \( k \) is given by the expression:
\[ k^2 = \frac{\text{mechanical energy stored}}{\text{electrical energy applied}} \quad \text{or} \quad k^2 = \frac{\text{electrical energy stored}}{\text{mechanical energy applied}} \] 

The \( k \)-factors carry different subscripts depending on different measuring modes. For instance, \( k_{33} \) is the coupling factor for longitudinal vibrations of rod shaped piezoelectric materials, and \( k_p \) is the planar coupling factor for a thin disc in which the radial coupling is measured between electric field applied in the direction of ceramic internal polarization and the mechanical vibrations produced along the radial directions.

1.2. Ferroelectric Properties

1.2.1. Ferroelectric Curie temperature and phase transitions

Normally, ferroelectric single crystals only show ferroelectric properties below a certain temperature called the Curie temperature \((T_C)\), and above this temperature, the crystals are in a non-polar paraelectric phase. This high temperature non-polar phase is characterized by a single-well potential in the free energy \((G)\) versus polarization \((P)\) curve, with the minimum at \( P = 0 \) (Figure 1.1(c)). When the temperature decreases through the \( T_C \), a ferroelectric crystal undergoes a structural phase transition from a paraelectric phase to a ferroelectric phase. At this point, the potential curve becomes flattened (Figure 1.1(b)). It is generally believed that the ferroelectric structure of a crystal is created by a small distortion of the paraelectric structure such that the lattice symmetry in the ferroelectric phase is always lower than that in the paraelectric phase.[6] This low symmetry ferroelectric phase provides more than one possible polarization state with multiple equivalent local minima. The two-dimensional free energy diagram, in terms of \( G \) and \( P \), showing two minima, is illustrated in Figure 1.1(a) in the ferroelectric state.
Figure 1.1 Two dimensional free energy diagram, in free energy (G) and polarization (P) for a ferroelectric material (a) below $T_C$, (b) at around $T_C$ and (c) above $T_C$. The two minima in (a) correspond to the two possible polarization states $+P_s$ and $-P_s$.

When the temperature is in the vicinity of the $T_C$, the thermodynamic properties (such as dielectric, elastic, optical, and thermal properties) of a ferroelectric crystal show anomalies and the structure of the crystal changes. For example, the dielectric permittivity in most ferroelectric crystals has a very large (abnormal) value near their $T_C$. This phenomenon is usually called the "dielectric anomaly" (Figure 1.2).

Figure 1.2 An illustration of dielectric permittivity as a function of temperature for normal ferroelectrics. The sharp anomaly corresponds to the phase transition at $T_C$.

1.2.2. Ferroelectric domains and hysteresis loop

Ferroelectrics are a class of piezoelectric materials that exhibit a spontaneous polarization that is reorientable under an electric field. As shown in Figure 1.3(a), in
some regions of ferroelectric crystals, electric dipoles are aligned uniformly, while in other regions of the crystals spontaneous polarization may be in the reverse direction. Such regions with uniform polarization are called ferroelectric domains. The interface between two domains is called the domain wall (Figure 1.3(b)).[7]

Figure 1.3  (a) Schematic drawing of atomic displacements on either side of a boundary between domains polarized in opposite directions in a ferroelectric crystal; (b) view of a domain structure, showing boundaries/walls between 180° domains polarized in opposite directions (adapted from Ref. 7).

The orientation and type of domain walls depend on the polarization direction of the phases.[8], [9] For the tetragonal phase, the polarization is oriented along one of the six $<001>_{\text{cub}}$ directions, and the domain walls lie in the $(001)_{\text{cub}}$ and $(101)_{\text{cub}}$ planes.[5] The domain walls in the $(001)_{\text{cub}}$ planes are 180°-domain walls, because the polarizations of the domains separated by them are antiparallel. In the $(001)_{\text{cub}}$ planes, the domain wall are 90°-walls, separating domains of polarization oriented 90° to each other. The polarization in the rhombohedral phase is along the $<111>_{\text{cub}}$ direction, and the resulting domain walls are 180°- and 71°/109°- walls. Polarization in the orthorhombic phase lies in the $<001>_{\text{cub}}$ direction and consequently 180°-, 60°-, 90°-, and 120°-domain walls are permitted. Since the 180°-walls are parallel to the spontaneous polarization, the switching of them does not induce the ferroelastic deformation and the 180°-walls are called ferroelectric domain walls. The non-180°-domain walls are ferroelastic domain walls, and the switching of the polarizations of those domains may involve elastic deformation. Only the ferroelastic domain walls can be observed using polarized light microscopy (PLM).
As shown in Figure 1.4, one of the important characteristics of ferroelectrics is the ferroelectric hysteresis loop, i.e., the polarization (P) is a double-valued function of the applied electric field (E). If we first apply a small electric field, we will have only a linear relationship between P and E, because the field is not high enough to switch any domains and the crystal will behave as a normal dielectric material. This case corresponds to the segment OA of the curves in Figure 1.4. As the electric field increases, a number of the negative domains (which have a polarization opposite to the direction of the field) will be switched over in the positive direction (along the field direction) and the polarization will increase rapidly (AB) until all the domains are aligned in the positive direction (BC). This is a state of a saturation in which the crystal is composed of just a single domain.

As the field strength decreases, the polarization will generally decrease to the point D in the Figure 1.4, but does not return back to zero. When the field is reduced to zero, because some of the domains will remain aligned in the positive direction and the crystals will exhibit a remnant polarization $P_r$. This polarization in a crystal cannot be removed until the applied field in the opposite (negative) direction reaches a certain value (at the point E in the Figure 1.4). The strength of the field required to reduce the polarization to zero is called the “coercive field” $E_c$. Further increase of the field in the negative direction will cause a complete alignment of the dipoles in this direction and the cycle can be completed by reversing the field direction once again. Thus the relation between P and E is represented by a hysteresis loop (CDEFGC) as shown in Figure 1.4.[6], [10], [11]
1.3. Perovskite Structure

The most studied piezo-/ferroelectric materials are perovskite oxides. Perovskite is the name of the mineral calcium titanate (CaTiO₃). The oxide single crystals of this structure have a general chemical formula ABO₃, where O is oxygen, A represents a cation with a larger ionic radius, and B is a cation with a smaller ionic radius. As shown in Figure 1.5(a), in a cubic ABO₃ perovskite-type unit cell, large A cations usually sit at the corners of the cube (A site), small B cations occupy the center of the cube (B site), and the oxygens are located in the face centers of the cube. As mentioned before, the ferroelectric perovskites are in the cubic paraelectric phase above the Tc. As the temperature drops below Tc, there is a phase change from the high symmetry cubic phase to a lower symmetry phase, for example, the ferroelectric tetragonal structure (Figure 1.5(b)).
Figure 1.5  The perovskite $\text{ABO}_3$: (a) cubic paraelectric phase ($a = b = c$) and (b) tetragonal ferroelectric phase ($a = b \neq c$).

The tolerance factor ($t$) is used to determine the stability of perovskites as shown by the following equation:

$$t = \frac{r_A + r_O}{\sqrt{2}(r_B + r_O)}$$

[1.4]

where $r_A$, $r_B$, and $r_O$ are the respective ionic radii. It was concluded that the stability of the perovskite structure may be expected within the limits of $t = 0.88$ to 1.09.[12] General observations of a low symmetry distortion of the unit cell for ferroelectric perovskites indicate that for a rhombohedral or monoclinic structure, $t < 1$, while for a tetragonal structure, $t > 1$. In order to promote good piezo-/ferroelectricity and high permittivity, the A-site and B-site cations in a perovskite are usually the highly polarizable “active” ions, for example, $\text{Ti}^{4+}$, $\text{Zr}^{4+}$ and $\text{Nb}^{5+}$ ions with a $d^0$ electronic configuration and $\text{Pb}^{2+}$ and $\text{Bi}^{3+}$ ions possessing “lone-pair” electrons.[13]

1.4. $\text{PbZr}_{1-x}\text{Ti}_x\text{O}_3$ Solid Solution

A solid-solution is the continuous sequence of substances with compositions intermediate between two distinct solid phases, called end members. In a solid-solution series, the components may be thought to substitute for one another on a molecular level in the crystal structure; the intermediate members have properties that vary
continuously with composition from those of one end member to those of another.[14], [15]

An example is the reaction to produce a solid solution between the two end members PbZrO$_3$ and PbTiO$_3$:

$$(1 - x)PbZrO_3 + xPbTiO_3 → Pb(Zr_{1-x}Ti_x)O_3$$

The perovskite PbZrO$_3$ is antiferroelectric and exhibits an orthorhombic crystal structure while PbTiO$_3$ is ferroelectric with a tetragonal symmetry at room temperature. The substitution of the B-site cation Zr$^{4+}$ with Ti$^{4+}$ forms a binary solid solution of Pb(Zr$_{1-x}$Ti$_x$)O$_3$ (PZT) with $T_C$ varying from 220 °C to 490 °C, depending on the composition. And all the solid solutions containing more than 10 mole percent PbTiO$_3$ are ferroelectric at room temperature. PZT ceramics are the most widely used piezo-/ferroelectric materials in a wide range of industrial and technological applications. Figure 1.6 shows the phase diagram of PZT. One of the characteristics that make this system special is that the low temperature phase diagram is divided vertically into two regions of different symmetry, rhombohedral for the Zr-rich composition and tetragonal for the Ti-rich side.[15], [16] In the rhombohedral region, there is a transition from the high temperature $R3m$ phase to the low temperature $R3c$ phase, which is associated with the in-phase octahedral rotation around the $<111>$$_{cub}$ direction.

The term morphotropic phase boundary (MPB) was first proposed by Jaffe et al. to describe the boundary between the two phases in the PZT phase diagram.[17] MPB is particularly interesting for both applications and fundamental studies, because the useful properties such as piezoelectric coefficient ($d_{33}$), electromechanical coupling factor ($k_{33}$), dielectric permittivity ($\varepsilon'$) and remnant polarization ($P_r$) all reach a maximum value in the MPB. The highest piezoelectric response (~ 350 pC/N) in this system was found near the boundary between these two phases ($x = 0.47$).[18], [19]
Although PZT ceramics have been established in technical applications for decades, the microstructure of this class of materials is still under investigation and the atomistic phenomena that cause the strong extrinsic piezoelectric and ferroelectric effect are not yet understood, neither are the mechanisms of its degradation.[20] So far, there have been a number of theories proposed to explain the behaviour of ferroelectric PZT ceramics. Historically, Cao et al. believed that the increase of the dielectric permittivity near the MPB is because of the coexistence of the tetragonal and rhombohedral crystal structures with six and eight equivalent polarization directions, respectively.[21] It is argued that the coexistence of the two polymorphs leads to fourteen possible polarization directions and therefore fourteen directions into which the material can be polarized under the influence of an external electric field.

Noheda et al. suggested that the existence of a monoclinic phase in the region of the MPB is the origin of the outstanding ferroelectric properties.[22] It was found that by introducing this phase, the agreement between experimental and calculated data by Rietveld refinement method was significantly improved. Furthermore, the introduction of a new phase could provide more possible directions for the polarization. This explanation is consistent with the previously mentioned model proposed by Cao et al.
Later on, Jin et al. found that, in the case of ferroelectric micro-domains of tetragonal symmetry, a nano-scale coherent mixture of micro-domains can be interpreted as an adaptive ferroelectric phase, whose micro-domain-averaged crystal lattice is monoclinic.[23] And this model was further developed by the theoretical work of Wang concerning nano-twin super-lattices.[24] Many of the predictions of this theory has been confirmed by experimental investigations of (1-x)Pb(Mg$_{1/3}$Nb$_{2/3}$)O$_3$-xPbTiO$_3$ (PMN-PT) and (1-x)Pb(Zn$_{1/3}$Nb$_{2/3}$)O$_3$-xPbTiO$_3$ (PZN-PT) single crystals. Recently, Theissmann et al. combined ex situ and in situ transmission electron microscopy (TEM) and high resolution X-ray diffraction (HRXRD) to demonstrate that the extrinsic piezoelectric effect in MPB PZT ceramic is closely connected to the existence of nano-domains.[20] It is concluded, that the existence of nano-domains is a characteristic feature of the MPB region.

1.5. Modification on PbZr$_{1-x}$Ti$_x$O$_3$ Ceramics

The PZT ceramics are also used with a modified form to improve and optimize their basic properties for practical applications.[3] The possible modification includes making binary, ternary, and quaternary solid solutions as well as doping with different dopants.[25] The effect of doping depends markedly on the types of dopants (donor or acceptor) and defect structure because of their influence on domain wall motion.

Donor dopants are compensated by negatively charged defects, such as cation vacancies. As an example, when Nb$^{5+}$ is substituted for Zr$^{4+}$, vacancies on the Pb$^{2+}$ site result:

$$\text{Pb}_{1-0.5y} \Box_{0.5y} (\text{Zr}_{1-x-y} \text{Ti}_x \text{Nb}_y)\text{O}_3,$$  

where $\Box$ represents a lead vacancy.

The lead vacancies could minimize local stresses in the lattice, which in turn facilitates domain wall motion. In addition, defect dipoles could be formed between the negatively charged lead vacancies and dopant Nb$^{5+}$ ions. These defect dipoles should be immobile, since both species are immobile near room temperature.[26] Such immobile defect dipoles will produce random fields that locally destabilize the domain structure.[27] The lowered stability of the domain structure against external mechanical or electric fields then contribute to the increased mobility of domain walls. The dielectric and piezoelectric properties of PZT ceramics are closely related to the domain wall motion. In general,
donor doping leads to electrically “soft” PZT ceramics with large piezoelectric coefficients, large permittivity, high electrical losses, large electromechanical coupling factors, very high electrical resistance, low mechanical quality factors, and a low coercive field.[28]

On the other hand, acceptor dopants, such as Na\(^+\) replacing Pb\(^{2+}\), are compensated by positively charged defects, such as oxygen vacancies:

\[ Pb_{1-y}Na_{y}(Zr_{1-x}Ti_{x})O_{3-0.5y} \oplus_{0.5y}, \]  

\(\oplus\) represents an oxygen vacancy

Domain walls are pinned in acceptor-doped PZT ceramics because the defect dipoles are able to align in accordance with the domain structure. Dipoles consisting of oxygen vacancies and associated dopant ions are able to reorient more easily in acceptor-doped PZT ceramics. The explanation lies in the ease with which oxygen vacancies diffuse at temperatures below \(T_C\). This can be clearly seen from the perovskite crystal structure. Cations are completely surrounded by oxygens and are separated from the nearest cation site by an entire unit cell (~ 4 Å), making diffusion very difficult. Oxygen sites, on the contrary, are adjacent to one another, only 2.8 Å apart.[29] Hence, oxygen vacancies diffuse much faster than those cation vacancies thanks to the proximity of oxygen sites. Therefore, oxygen can easily move into nearby oxygen vacancies, realigning defect dipoles and pinning domain walls.[29], [30] Acceptor doping usually leads to an electrically “hard” PZT, which is characterized by low piezoelectric coefficients, low permittivity, low losses, low electrical resistivity and a high coercive field.[31]

1.6. Bi(Zn\(_{0.5}\)Ti\(_{0.5}\))O\(_3\)-Related Solid Solutions

PZT based piezoelectric materials are well known for their excellent piezoelectric properties. However, considering the toxicity of lead and its compounds, there is a general awareness for the development of environmental friendly lead-free and lead-reduced materials as evidenced from the legislation passed by the European Union on this effect.[32] The large piezoelectric response of PZT results from two factors. Primarily, the stereo-chemical activity of the 6s\(^2\) lone pair on the Pb\(^{2+}\) ion causes large structural distortions from the cubic perovskite phase that, in turn, results in strong coupling between the electronic and structural degrees of freedom.[33] Bi-based
compounds have similar or larger levels of ionic off-centering than Pb-based compounds, driven by the stereo-chemically active 6s\(^2\) lone pair on the Bi\(^{3+}\) ion. This leads to large ferroelectric polarization. In most common ferroelectrics, ionic off-centering and thereby the ferroelectricity is mainly contributed by the B-site cations so as to increase the chemical bonding between their valence d orbital and the surrounding oxygen 2p orbital.[34] Bismuth (Bi) is non-toxic in its oxide forms; indeed, the active ingredient of a popular antacid is bismuth salicylate.

Among the Bi-based perovskites, Bi(Zn\(_{0.5}\)Ti\(_{0.5}\))O\(_3\) (BZT) exceeds others for its high calculated spontaneous polarization \(P_s\) of 103 \(\mu\)C/cm and high tetragonality (c/a ratio) of 1.21. Its XRD refinement shows \(P4mm\) symmetry with a large Bi displacement of 0.88\(\AA\) and the Zn/Ti displacement of 0.6\(\AA\).[35], [36] However, BZT can only be synthesized at high pressure. Given that solid solution BZT cannot be made at ambient pressure by solid-state synthesis, many potential Bi-based perovskite compounds have been explored as end members in pseudo-binary or -ternary systems with other Pb-contained perovskite compounds.[37], [38]

1.7. Piezoelectric Single Crystals

1.7.1. Current status of piezoelectric single crystals

Figure 1.7 shows the history of the development of piezoelectric materials in terms of piezoelectric coefficient \(d_{33}\). The milestones are marked by the discoveries of BaTiO\(_3\) (BT) in the 1940s and Pb(Zr\(_{1-x}\)Ti\(_x\))O\(_3\) (PZT) ceramics in the 1950s. For almost 50 years, PZT-based systems have been the most widely used piezoelectric materials. However, their piezoelectric performance has only been improved slightly over this time.[39] A breakthrough occurred in the late 1990s when Park and Shrout reported, following an earlier work by Kuwata et al., that single crystals of relaxor ferroelectric (1-\(x\))Pb(Mg\(_{1/3}\)Nb\(_{2/3}\))O\(_3\)\(_x\)PbTiO\(_3\) (PMN-PT) and (1-\(x\)) Pb(Zn\(_{1/3}\)Nb\(_{2/3}\))O\(_3\)\(_x\)PbTiO\(_3\) (PZN-PT), with compositions near the MPB, could exhibit a very good performance, e.g. a high piezoelectric coefficient (\(d_{33} > 2500 \text{ pC/N}\)), extremely large strains (> 1.5%), and an exceptionally high electromechanical coupling factor (\(k_{33} > 94\%\)) compared to their ceramic counterparts.[40]–[44]
However, there are a number of technical hurdles to overcome before these single crystals can replace piezoelectric ceramics in some high-demanding commercial applications. One of the most important issues is that the low coercive field ($E_c$) along with the low Curie temperature ($T_C$) could limit the acoustic power of the device and the temperature range of operation and device fabrication processing.[45] In addition, the mechanical quality factor ($Q_m$) is low, which limits their application as high power transformers and transducers. There is an increased demand for new systems of single crystals with high $T_C$ and large $E_C$ for the replacement of the PMN-PT and PZN-PT single crystals in commercial applications.

![Figure 1.7](image)

**Figure 1.7** Historical development of perovskite-based piezoelectric materials in terms of piezoelectric constant $d_{33}$ [adapted from Ref.39].

For the PZT-based ceramics, the room temperature piezoelectric properties generally decrease with increasing $T_C$ (see Figure 1.8). Lead-free piezoelectric perovskites have a $d_{33}$ value around 200 pC/N or lower, except for textured $K_{0.5}Na_{0.5}NbO_3$ (KNN) ceramics, which has a $d_{33}$ reaching 400 pC/N.[46] Similar relationship between $d_{33}$ and $T_C/T_{MPB}$ ($T_{R-T}$) can be found for the relaxor-PT ferroelectric single crystals, as shown in the plot of piezoelectric coefficients as a function of $T_C$ in
Figure 1.9. The second generation of relaxor-based piezoelectric single crystals, e.g. the ternary Pb(In\(_{1/2}\)Nb\(_{1/2}\))O\(_3\)-Pb(Mg\(_{1/3}\)Nb\(_{2/3}\))O\(_3\)-PbTiO\(_3\) (PIN-PMN-PT) and Pb(Mg\(_{1/3}\)Nb\(_{2/3}\))O\(_3\)-PbZrO\(_3\)-PbTiO\(_3\) (PMN-PZ-PT) that are being developed show increased T\(_C\) and T\(_{MPB}(T_{R-T})\) compared to the binary crystals PMN-PT and PZT-PT.[47], [48] In addition, E\(_c\) is also increased. For example, PMN-PZT has an E\(_c\) of 5 kV/cm, which is more than twice of that of PMN-PT (2.3 kV/cm). Therefore, the second-generation ferroelectric crystals are thermally more stable for applications in a broader temperature range. Modification of PIN-PMN-PT crystals with Mn doping further increases the value of E\(_c\) to 6.4 kV/cm,[49] and the crystals are known as the third-generation piezoelectric single crystals. Mn-doping generates acceptor oxygen vacancies, which can pin the domain wall, prevent the polarization reorientation and thereby increase the E\(_c\).[50]

Figure 1.8 Piezoelectric coefficient as a function of Curie temperature (T\(_C\)) for various ferroelectric ceramics (BT = BaTiO\(_3\), NBT = Na\(_{0.5}\)Bi\(_{0.5}\)TiO\(_3\), and KNN = K\(_{0.5}\)Na\(_{0.5}\)NbO\(_3\)). (adapted from Ref.[51]).
Figure 1.9  Piezoelectric coefficient as a function of Curie temperature ($T_C$) for different classes ferroelectric ceramics (adapted from Ref.[51-53]).

1.7.2. Growth of piezoelectric single crystals

For commercial applications, it is desirable to grow crystals with good quality, large size and the correct compositions. Crystal growth techniques include (i) high temperature solution growth (HTSG) from flux, such as flux-Bridgman growth and top-seeded solution growth (TSSG), and (ii) growth directly from pure melts, such as Bridgman method and floating-zone melting method.[51]

The size of the crystal and the growth rate are the major concerns for the commercial production. It is possible to obtain large crystals with high quality by the Bridgman method.[52] Specifically, the charge of the desired crystal composition is sealed in a Pt crucible and heated to melt by a vertical tubular electric furnace. The crucible is then slowly lowered out of the heating region, so the molten metal oxides crystallizes from the bottom to the top.[53] So far, PMN-PT and PIN-PMN-PT single crystals have been commercially manufactured by the Bridgman method, the dimensions of which can reach 75-100 mm in diameter and 150-200 mm in length.[8] One of the problems for the Bridgman method is the compositional inhomogeneity in the
grown crystals due to the incongruent melting behavior of PMN-PT. As a result, only part of the crystal boule with the desired composition and good quality can be used, which has significantly increased the costs of the crystals.

For high temperature solution growth, the flux used is usually PbO or a mixture of PbO and B$_2$O$_3$.[54], [55] The crystallization occurs when the solution is supersaturated, which can be achieved by evaporation of PbO or by cooling. Compared with the growth from melts, the flux growth has the advantage of lowering the growth temperature, and it is suitable for growing crystals that melt incongruently at high temperatures, such as PZN-PT,[56], [57] PYN-PT (Pb(Yb$_{1/2}$Nb$_{1/2}$)O$_3$-PbTiO$_3$)[58] and BS-PT (BiScO$_3$-PbTiO$_3$)[59], [60] single crystals. Large size PZN-PT single crystals with 75 mm in diameter were synthesized by the flux-Bridgman method.[61] However, it is common to find PbO inclusions in some parts of the crystals, which diminishes the quality of the crystals. Another drawback of the flux-Bridgman method is that the orientation of the grown crystals varies with growth conditions due to the spontaneous nucleation during the growth.

The TSSG method developed in our lab to grow the PZN-PT single crystals with one growth direction by introducing a seed crystal to trigger nucleation.[62] Using this technique, it is also possible to lift the grown crystal from the solution, eliminating the process of separating the crystal from the flux and extending the life of Pt crucible.

1.8. Objectives and Organization of the Thesis

1.8.1. Objective of this work

Over the past two decades, ferroelectric single crystals such as PMN-PT and PZN-PT have drawn a lot of attention due to their ultra-high piezoelectric properties.[55], [63], [64] They outperform polycrystalline ceramics of PZT with a higher $d_{33}$ (1500 pC/N) and a larger $k_{33}$ (~ 0.90). However, their low $T_C/ T_{MPB}(T_{R-T})$ and low $E_c$ make them unsuitable for applications at high temperatures and under high electric field. Thus, ferroelectric crystals with high $T_C$, high $E_c$ and good piezoelectric properties need to be developed. It is well known that the PZT system has a higher $T_C$, but its single crystals are very difficult to grow. Previous attempts in growing single crystals of PZT were
mostly unsuccessful as the grown crystals had compositions far away from the MPB and their size was too small to perform meaningful characterization on them. Recently, the TSSG method has been developed in our lab, which can be applied to grow PZT single crystals. With the availability of PZT single crystals, measurements can be carried out to investigate the phases, domain structures and phase transitions in PZT single crystals. The objectives of part of my research are as follows: (1) grow PZT single crystals of various compositions by the TSSG method and optimize the properties of crystals by adjusting the growth conditions; (2) investigate the phase symmetry and domain structures of PZT single crystals with different compositions; (3) study the phase transition behavior in PZT single crystal.

In technological applications, PZT ceramics are always modified via doping with different (donor or acceptor) dopants to improve and optimize their electromechanical properties. “Hard” PZTs are formed when doped with acceptor ions such as K+ and Na+ ions replacing Pb2+, and Fe3+ replacing Zr4+ or Ti4+. “Soft” PZTs are produced by doping with donor dopants, for example, replacing Pb2+ with La3+, and Zr4+ or Ti4+ with Nb5+. However, many aspects of the origin of high piezo-response in doped-PZT ceramics still remain unclear. And in general, single crystals outperform their ceramic counterparts. Therefore, it is of particular interest to grow single crystals of doped-PZT, which are not only necessary for thorough characterization of the anisotropic properties of this system, but are also expected, to exhibit superior piezo-/ferroelectric performance. The second objective of this work is to synthesize the doped-PZT single crystals and to characterize their domain structures and phase transitions in order to understand the structure-property relations.

Furthermore, there have been pressing demands for lead-free or lead-reduced replacement materials because of the environment concerns arising from the potential toxicity of the lead oxides. Bismuth zinc-titanate, Bi(Zn0.5Ti0.5)O3 (BZT) has been reported to have a tetragonal symmetry with an extremely large c/a ratio (1.21) and a high calculated ionic polarization (103 μC/cm²). Unfortunately, this material is not stable in its pure form and cannot be prepared by ambient-pressure solid state synthesis. Our previous study shows that adding BZT into PZT forms the ternary solid solution Bi(Zn0.5Ti0.5)O3-PbZrO3-PbTiO3 (BZT-PZ-PT) of perovskite structure, and enhances its dielectric and ferroelectric properties in the ceramics of the MPB.
compositions.[66] My third project is the growth and characterization of the piezo-/ferroelectric single crystals of the new lead-reduced BZT-PZ-PT ternary system. We hope to find some improved properties in this lead-reduced system.

1.8.2. Organization of the Thesis

Following the general introduction of this chapter, we provide the principles of the main experimental techniques in Chapter 2, such as, laser ablation inductively coupled plasma mass spectroscopy, energy dispersive spectroscopy, X-ray powder diffraction, dielectric spectroscopy, ferroelectric hysteresis loop and piezoelectric properties measurements, and polarized light microscopy.

As above-mentioned, both high piezoelectric performance and a high $T_C$ are expected to be obtained in PZT single crystal with MPB compositions. However, the PZT single crystals are very difficult to grow due to its incongruently melting behaviour and high melting point. TSSG method has the advantage of lowering the growth temperature by using flux (PbO/B$_2$O$_3$), and controlling the growth direction by introducing a seed crystal. We have applied the TSSG method to the growth of PZT single crystals, and optimized the growth condition to obtain good quality crystals with desired compositions. Chapter 3 gives a detailed description of the growth of PZT single crystals with compositions of $x = 0.54$ and 0.45. Structural analysis of PZT crystals is performed by X-ray diffraction. The dielectric, ferroelectric and piezoelectric properties of the grown PZT crystals are also characterized in this chapter. The PZT ($x = 0.45$) crystal possesses overall better properties with a piezoelectric coefficient $d_{33} = 886$ pC/N, an electromechanical coupling factor $k_{33} = 0.80$, a large coercive field $E_c = 10$ kV/cm and a high $T_C = 381$ °C, making PZT single crystals a high-performance and high-$T_C$ piezoelectric material potentially useful for high-temperature and high-power electromechanical transducer applications.

Chapter 4 is focused on the domain structure study of the tetragonal PZT ($x = 0.54$) single crystal by the polarized light microscopy (PLM) and piezoelectric response force microscopy (PFM). Nanodominates are found to be present in this tetragonal PZT ($x = 0.54$) single crystal. They are arranged in such a way that they compensate each other almost completely along the $<001>_{\text{cub}}$ direction on the $(001)_{\text{cub}}$ platelet, but incompletely
on the (011)\textsubscript{cub} platelet. Upon application of an electric field in the <010>\textsubscript{cub} direction of the (001)\textsubscript{cub} platelet, square-shaped domains with edges oriented in <110>\textsubscript{cub} direction are observed by PLM. They are embedded in a tetragonal nanodomain matrix and are confirmed by PFM to be 180° ferroelectric domains with an average size of 12 μm. The formation of these domains is due to the nucleation and growth of 180° flux-closure state in the crystal. Three steps are involved in this process: (1) a circular 180° flux-closure domain is nucleated in the tetragonal nanodomain state; (2) the small circular flux-closure domain reaches its critical size and grows into a large one and (3) due to the anisotropic bonding in PZT crystal unit cell, the growth rate along the <001>\textsubscript{cub} direction is faster than along the <011>\textsubscript{cub}, leading to a square-shaped microdomain.

It is well known that the growth of PZT single crystals has been one of the biggest challenges in the ferroelectric field. Furthermore, doped PZT crystals are even more difficult to grow. We took on this challenge seriously and have systematically studied the chemical, thermodynamics and kinetic parameters for the growth of donor- and acceptor-doped PZT single crystals. We have successfully grown large-size La\textsuperscript{3+}- and Bi\textsuperscript{3+}-doped PZT single crystals for the first time and optimized their compositions and quality in Chapter 5. The compositions of the crystals are determined by means of laser ablation inductively coupled plasma mass spectrometry, and the dielectric and ferroelectric properties, and the domain structure of the grown crystals are characterized. The growth and characterization of acceptor-doped PZT single crystals by Mg\textsuperscript{2+} and Mn\textsuperscript{2+} are reported in Chapter 6. These very first set of data on doped PZT crystals not only provide a better understanding of structure-property relationship of PZT-based single crystals and possible doping, but also points to the possible applications of doped PZT single crystals as a new high-$T_C$, high-power piez-/ferroelectric material.

In order to develop new piezoelectric materials with a high-$T_C$ and reduced-lead content, chemical modification on the binary PZT system is a viable option. Bi(Zn\textsubscript{0.5}Ti\textsubscript{0.5})O\textsubscript{3} (BZT) is an unique lead-free compound with a high calculated $P_s = 103$ μC/cm², and its solid solution with PT exhibits a high $T_C$ (487 °C) and a large tetragonality ($c/a = 1.21$).[35], [67] The special features of BZT provide the basis of developing a new lead-reduced ternary system Bi(Zn\textsubscript{0.5}Ti\textsubscript{0.5})O\textsubscript{3}-PbZrO\textsubscript{3}-PbTiO\textsubscript{3} (BZT-PZ-PT). In Chapter 7, ferroelectric single crystals of BZT-PZ-PT system have been grown for the first time by three different methods. The chemical and thermodynamic
parameters, including the flux concentration, the soaking temperature and the cooling rate, have been optimized, leading to the growth of good quality BZT-PZ-PT crystals of pseudo-cubic morphology. A large size crystal of the dimensions of $2 \times 2 \times 0.5$ cm$^3$ has been obtained. The physical properties of the single crystals, such as $T_C$, and dielectric and ferroelectric properties are investigated. The high $T_C$ and large coercive field of the BZT-PZ-PT single crystals make this material a promising candidate for applications in high-power electromechanical transducers that can operate in a wider temperature range and at high fields.
Chapter 2.

Material Characterization: Principles and Techniques

2.1. Introduction

In this chapter, we will present the basic principles for the various experimental techniques used to investigate the structure and properties of the piezo-/ferroelectric single crystals prepared in this work. These techniques include chemical analysis by laser ablation inductively coupled plasma mass spectrometry (LA-ICP-MS) and energy dispersive spectroscopy (EDS), structural determination by X-ray diffraction (XRD), and characterization of physical properties and domain structures of the materials by dielectric spectroscopy, ferroelectric and piezoelectric measurements, polarized light microscopy (PLM) and piezoresponse force microscopy (PFM).

2.2. Laser Ablation Inductively Coupled Plasma Mass Spectrometry

Inductively coupled plasma mass spectrometry (ICP-MS) is an invaluable tool in a huge range of applications. ICP-MS exploits the fact that high-temperature argon plasmas ionize atoms in a sample very efficiently, so that different mass-to-charge ratios can be measured.[68] In general, the samples are introduced to the plasma as liquids. The solid sample can be digested by applying lasers and the coupling of laser ablation with ICP-MS (LA-ICP-MS) has shown great potential for the direct elemental analysis of solid samples.[69]

A typical LA-ICP-MS setup (Figure 2.1) has a 213 nm Nd-YAG laser either with argon or helium flowing through the sample chamber, coupled to a quadrupole ICP-
Usually, the samples are mounted on a slide together with reference standards, and the slide is then placed in the chamber. Software controls x-y-z movement of the ablation chamber and projects a video image of the inside of the chamber. Ablation patterns (lines, spots, or lines of spots) are drawn on the samples.

When the ablation starts, the material vaporized from the sample and ejected from the site of ablation is entrained in the helium stream flowing through the chamber. Outside of the sample chamber, the ablated aerosol joins the argon gas stream and eventually flows into the argon plasma of the ICP torch. Ions from the plasma then pass through the interface into the mass spectrometer.

![Diagram of a typical laser ablation-ICP-MS setup](image)

**Figure 2.1** Diagram of a typical laser ablation-ICP-MS setup (adapted from Ref. 68).

In this work, all the samples were sent to New Wave Research, Inc., Montana, USA, to carry out LA-ICP-MS characterization. The crystals were cut parallel to the (001)\textsubscript{cub} planes and polished using silicon carbide sand paper, followed by 3M lapping sheets. Bulk and spatial analysis was completed using NWR193 and NWR213 laser on the designated standard and samples.

### 2.3. Energy Dispersive Spectroscopy

Energy dispersive spectroscopy (EDS) is a technique used for quantitative elemental analysis. The principle of this technique is based on the fact that each element has its unique atomic structure and energy levels. For EDS experiment, as illustrated in
Figure 2.2, electron beam is focused onto the sample surface and the emission of characteristic X-rays from the sample is stimulated. Within the sample, electrons which exist in their ground state will be excited and ejected from the shell while creating an electron hole. An electron from outer higher energy shell will then fill the inner vacancy. Since the atomic energy levels are discrete, transfer of an electron from the higher energy level to the lower energy level can result in release of energy in the form of X-ray. The emitted X-rays from the sample can be detected by an energy-dispersive spectrometer. As different atom has its unique energy levels, the energy of the X-rays are also characteristic, which allows the elemental composition to be measured.

Figure 2.2  Schematic diagram demonstrating the principle of energy dispersive spectroscopy.

2.4. X-ray Diffraction

X-ray diffraction (XRD) is a powerful technique used widely for characterization of the structures of crystalline materials. This technique is based on the constructive interference of monochromatic X-rays from a crystalline sample. The conventional X-rays are generated by a X-ray tube.[72] In this tube, there is a heated filament (cathode), which can produce a source of free electrons. These electrons are accelerated by a high electric potential and then strike the target material (anode). When the electrons on the
K shell of the target atom are ejected by the electron beam, the electrons on the high energy level will drop to low energy level to occupy the vacancies. The decreased energy emits as X-ray radiation. In particular, electrons descending from L shell gives \( K_\alpha \) lines and the electrons from M shell gives \( K_\beta \) lines.[73] The wavelength of the X-ray radiation is determined by the target material. In our XRD instrument, a Bruker D8 Advanced Diffractometer, copper is used as target and the resulting \( K_\alpha \) radiation has a wavelength of 1.5418Å.

As illustrated by Figure 2.3, when a crystal is bombarded with X-ray at certain incident angles, the condition for producing intense peaks of diffracted radiation is that the scattered X-rays interfere constructively. This requires that the path difference is equal to an integer multiples of the wavelengths. In other words, if we consider a crystal with crystal lattice planar distance \( d \), the travel path length difference between the ray paths ABC and A'B'C' must be an integer number of wavelength. The general relationship between the wavelength \( \lambda \) of the incident X-rays, angle \( \theta \) of incidence and spacing \( d \) between the crystal lattice planes of atoms is known as Bragg’s Law:

\[
2d \sin \theta = n \lambda \tag{2.1}
\]

where \( n \) is an integer representing the order of diffraction. The diffraction pattern is usually plotted as the intensity of the diffracted X-ray vs. the angle 2\( \theta \). A diffraction pattern contains many distinct peaks, each corresponding to a set of planes with the same inter-planar spacing \( d \).[74]

![Diagram of diffraction of X-rays by a crystal (Bragg condition).](image)
2.5. Principles Used for Determining the Crystal Symmetry

The crystal structure of a material can be described in terms of its unit cell (Figure 2.4). The unit cell is represented in terms of its lattice parameters, which are the lengths of cell edges \((a, b, c)\) and the angles between them \((\alpha, \beta, \gamma)\). The restrictions of the lattice parameters of the seven crystal systems are listed in Table 2.1.[75]

![Figure 2.4 Space-lattice with lattice parameters labelled.](image)

Depending on the type of the structure adopted by the material, the relationship between \(d\)-spacing and lattice parameters varies. The \(d\)-spacing for a material with a crystal structure of orthogonal axes, i.e. cubic, tetragonal or orthorhombic, can be expressed as follows:

\[
\frac{1}{d_{hkl}^2} = \frac{h^2}{a^2} + \frac{k^2}{b^2} + \frac{l^2}{c^2}
\]  

(2.2)

where \(a, b\) and \(c\) are the lattice parameters of the unit cell, \(h, k, l\) are the Miller indices assigned to a set of planes with the inter-planar spacing \(d\). The refinement of the lattice parameters of the unit cell requires indexing the diffraction pattern, which is achieved by assigning Miller indices \((hkl)\) to each peak.[74] To achieve a good accuracy, it is better to index all the peaks and calculate the lattice parameters by regression analysis. We use
TOPAS Academic Software to determine the symmetry and refine the lattice parameters of the grown crystals.

Table 2.1 The seven crystal systems and their unit cell specification.

<table>
<thead>
<tr>
<th>Crystal System</th>
<th>Lattice Parameter Restrictions</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cubic</td>
<td>( a = b = c, \alpha = \beta = \gamma = 90^\circ )</td>
</tr>
<tr>
<td>Tetragonal</td>
<td>( a = b \neq c, \alpha = \beta = \gamma = 90^\circ )</td>
</tr>
<tr>
<td>Orthorhombic</td>
<td>( a \neq b \neq c, \alpha = \beta = \gamma = 90^\circ )</td>
</tr>
<tr>
<td>Monoclinic</td>
<td>( a \neq b \neq c, \alpha = \gamma = 90^\circ; \beta \neq 90^\circ )</td>
</tr>
<tr>
<td>Triclinic</td>
<td>( a \neq b \neq c, \alpha \neq \beta \neq \gamma \neq 90^\circ )</td>
</tr>
<tr>
<td>Hexagonal</td>
<td>( a = b \neq c, \alpha = \beta = 90^\circ; \gamma = 120^\circ )</td>
</tr>
<tr>
<td>Rhombohedral</td>
<td>( a = b = c, \alpha = \beta = \gamma \neq 90^\circ )</td>
</tr>
</tbody>
</table>

Most of the ferroelectric systems we have been studying in our group have the perovskite structure. X-ray diffraction patterns can be used to monitor chemical reactions and structural properties such as phase purity and change of symmetry. For example, in a cubic unit cell \((a = b = c)\), the calculated distance between \(\{100\}_{\text{cub}}\) planes is \(a\), between \(\{110\}_{\text{cub}}\) planes \(a/\sqrt{2}\), between \(\{111\}_{\text{cub}}\) planes \(a/\sqrt{3}\), etc. As a result, the \(\{100\}_{\text{cub}}\) reflection peak in the cubic phase is indistinguishable from the \(\{010\}_{\text{cub}}\) and \(\{001\}_{\text{cub}}\). In a similar way, it can be concluded that in the diffraction pattern of a cubic structure, all the three reflections, \(\{100\}_{\text{cub}}\), \(\{110\}_{\text{cub}}\), and \(\{111\}_{\text{cub}}\) show an overlapping single peak each.[72]

In a tetragonal crystal structure, the interaxial angles is still the same \((\alpha = \beta = \gamma = 90^\circ)\), but the length of the unit cell are no longer equal \((a = b \neq c)\). This will affect the \(d\)-spacing within the lattice, which in turn will result in the splitting or merging of peaks. As shown in Figure 2.5(a), the first one corresponds to the \(\{001\}_{\text{cub}}\) reflection and the second one, the \(\{100\}_{\text{cub}}\) and \(\{010\}_{\text{cub}}\) reflections. Figure 2.5 shows the splitting of the cubic \(\{100\}\), \(\{110\}\), and \(\{111\}\) reflection peaks when the crystal undergoes transition into a respective lower symmetry phase. Each vertical line represents the peak position with the relative intensity ratio. This characteristic XRD pattern can be used to identify the symmetry and phase components of the materials.
2.6. Dielectric Permittivity Measurements

Dielectric property measurements allow for the determination of phase transition temperatures, permittivity values, and dielectric loss. The dielectric properties are measured as a function of temperature and frequency using a Novocontrol Alpha high-resolution broad band dielectric spectrometer equipped with a high temperature system. The sample material is usually mounted in a sample cell between two electrodes forming a sample parallel-plate capacitor.

The schematic diagram of the circuit used in the dielectric permittivity measurements is shown in Figure 2.6. In this circuit, the voltage is applied by a signal generator across the pair of electrodes on the surfaces of a sample capacitor \( C_s \), with thickness \( d \) and a reference capacitor \( C_r \). The voltage across the reference capacitor \( V_r \) and the sample \( V_s \) is also measured by two separate voltmeters. Because the two capacitors are connected in series, the charge on the reference capacitor \( Q_r \) must be the same as the charge over the sample capacitor \( Q_s \). This means that the charge on the sample can be found by:
\[ Q = C_r \times V_r \]  

(2.3)

Once the charge on the sample \((Q)\) is obtained, the capacitance of this material can be calculated by using the following equation:

\[ C = \frac{Q}{V_s} \]  

(2.4)

The relative real permittivity, or dielectric permittivity \((\varepsilon_r)\), is determined based on the following equation:

\[ C = \varepsilon_r \varepsilon_0 \left( \frac{A}{d} \right) \]  

(2.5)

where \(C\) is the capacitance of the dielectric material between two parallel electrodes, \(\varepsilon_0\) is the permittivity of the free space, \(8.854 \times 10^{-12} \text{ F/m}\), \(A\) is the area of the plates of the parallel electrodes, and \(d\) is the distance between them.[74], [76]

![Typical frequency response analyzer circuit model.](image)

**Figure 2.6** Typical frequency response analyzer circuit model.

There is usually dielectric loss in the media due to the energy loss from the friction between the polarization and electric dipoles. Therefore, the leakage current also needs to be considered when writing the expression for permittivity.[6] In general, the
charge resulting from the leakage current is time dependent. Consequently, the dielectric permittivity must be expressed in complex form as a function of frequency ($f$):

$$
\varepsilon_r^*(f) = \varepsilon'(f) - i\varepsilon''(f) \quad (2.6)
$$

where $\varepsilon'$ is the real part of the dielectric permittivity, termed the dielectric constant, $i = \sqrt{-1}$, and $\varepsilon''$ is the imaginary part of the dielectric permittivity. The loss factor ($\tan \delta$) is defined as:

$$
\tan \delta = \frac{\varepsilon''}{\varepsilon'} \quad (2.7)
$$

where $\delta$ is the angle between the imaginary component and the real component of the permittivity, as illustrated in Figure 2.7. In this work the dielectric loss ($\tan \delta$) and permittivity ($\varepsilon'$) are measured as a function of temperature at various frequencies.

![Figure 2.7](image.png)

**Figure 2.7** The illustration of the loss angle $\delta$ with respect to the real part and imaginary part of the dielectric permittivity $\varepsilon_r^*$.

### 2.7. Ferroelectric Hysteresis Measurements

The ferroelectric properties of the single crystals prepared in this work are characterized using an RT66A Standard Ferroelectric testing system (Radiant Technologies Inc.), which performs measurements of polarization as a function of electric field. Figure 2.8 shows a schematic of a modified Sawyer-Tower circuit used to
display the hysteresis loops.[77] In this circuit, a step voltage ($V$) is applied by the signal generator across the pair of electrodes on the surfaces of a sample capacitor ($C_s$, with thickness $d$), and a RC circuit is connected in series with $C_s$, which compensates for any phase shift due to conductivity or dielectric loss in the sample.[78] An alternating voltage is applied across the two parallel electrodes of the sample.

![Modified Sawyer-Tower circuit](image)

Figure 2.8 A modified Sawyer-Tower circuit for the measurement of ferroelectric hysteresis loops, where $C_s$, $R_s$, $C_r$, $R$, $V$, and $V_r$ stand for the capacitance of the sample, the resistance of the sample, the capacitance of the reference, the resistor, the step voltage, and the voltage across the reference capacitor, respectively.

Spontaneous polarization could be defined by the value of charge per unit area on the surface perpendicular to the axis of spontaneous polarization. Since the testing sample and reference capacitor are connected in series, the charge on the sample capacitor must be the same as the charge on the reference capacitor. Once the charge on the sample is known, the polarization can be determined using following equation:

$$P = \frac{Q}{A}$$  \hspace{1cm} (2.8)

where $Q$ is the charge developed on the electrodes of the ferroelectric capacitor and $A$ is the area of the electrodes. In practical experiment, the collected digital data by computer give rise to a ferroelectric hysteresis loop shown in Figure 1.4 in Chapter 1.
2.8. Piezoelectric Measurement System

The piezoelectric coefficient \( d_{33} \) was measured by a quasi-static piezoelectric \( d_{33}/d_{31} \) meter (ZJ-6B, Institute of Acoustics Chinese Academy of Sciences). As described in Chapter 1.1, the piezoelectric coefficient can be expressed as:

\[
d_{33} = \frac{P_3}{T_3} \tag{2.9}
\]

where \( P_3 \) represents the charge density (C/m\(^2\)), and \( T_3 \) is the mechanical stress applied (N/m\(^2\)). The notation “33” means that the polarization was measured in the same direction as that of the applied stress.[79] Figure 2.9 illustrates a schematic diagram for the \( d_{33} \) measurement using the Piezo-Meter. The sample is usually poled at a high electric field for the sake of achieving the optimum alignment of the dipoles in the sample.

![Figure 2.9](image)

**Figure 2.9** A schematic diagram for the \( d_{33} \) measurement by a quasi-static method.

The electromechanical coupling factor \( k \) is determined by the resonance-antiresonance method using a Solarton 1260 impedance analyzer combined with a Solartron 1296 dielectric interface. The value of \( k \) indicates the efficiency of the conversion between electrical energy and mechanical energy. When an ac field is applied to a poled piezoelectric material, large amplitude oscillation happens near the resonance frequencies, where the efficiency of the energy conversion is the highest. Like the piezoelectric coefficient \( d \), the electromechanical coupling factor \( k \) carries a
subscript. $k_{33}$ is the longitudinal coupling factor, and the standard sample for the measurement is a long bar (or rod) with a height (h)/width (w) > 3 (see Figure 2.10). The mechanical vibration is measured along the longest dimension of the sample, which is the same direction of the applied ac field. The expression of $k_{33}$ is given by the following equation:

$$k_{33}^2 = \frac{\pi}{2} \cdot \frac{f_r}{f_a} \cdot \tan \left( \frac{\pi}{2} \cdot \frac{f_a - f_r}{f_a} \right)$$  \hspace{1cm} (2.10)$$

where the resonance frequency $f_r$ and anti-resonance frequency $f_a$ correspond to the maximum and minimum impedance, respectively. When a piezoelectric is working in the range of $f_r < f < f_a$, the energy-conversion between electrical and mechanical energy is the most efficient.

![Figure 2.10](image)

**Figure 2.10** Illustration of the (001)$_{\text{cub}}$-oriented bar (or rod) single crystal for $k_{33}$ measurement (with a typical aspect ratio $h/w > 3$).

### 2.9. Polarized Light Microscopy

Polarized light microscope (PLM) is a powerful instrument used to determine the symmetry and crystallographic group, observe the domain structure and measure the birefringence of the single crystals. The instrument used in this work is an Olympus BX60 PLM equipped with a Linkam HTMS600 heating/cooling stage. The PLM is equipped with both a polarizer (P), positioned in the light path somewhere before the
specimen, and an analyzer (A), which is placed in the optical pathway between the objective rear aperture and the observation tubes (Figure 2.11).[80]

![Diagram of polarized light microscope configuration](image)

**Figure 2.11  Polarized light microscope configuration (adapted from Ref.80).**

The interaction of plane-polarized light with a birefringent (or doubly-refracting) specimen can produce two individual wave components that are each polarized in mutually perpendicular planes. The orientations and velocities of the two decomposed rays depend on the crystalline optical axis. The ray with the polarization parallel to the optical axis is termed the extraordinary ray (e), and the other one with orientation perpendicular to the optical axis is the ordinary ray (o).[81] The two corresponding refractive indices $n_e$ and $n_o$ can be quantified by birefringence $\Delta n$, which is defined as:

$$\Delta n = |n_e - n_o|$$  \hspace{1cm} (2.11)

After exiting the specimen, the light components become out of phase, but are recombined with constructive and destructive interference when they pass through the analyzer. By measuring the retardation of the light by PLM, the birefringence value can be obtained through the following equation:
\[ R = t \times \Delta n \]  \hspace{1cm} (2.12)

where \( R \) is the retardation, and \( t \) is the thickness of the crystal.[82]

Different birefringent specimen or domains have different extinction direction. The extinction direction is such a direction, in which the polarization direction of optical indicatrix is align or perpendicular to the direction of P or A and the output imaging is in the dark field. Consider a beam of linearly polarized light incident normally on a thin plate of a birefringent sample cut parallel to the optic axis (along optic axis the velocity of the ordinary ray and the extraordinary ray are equal). The displacement vector \( D \) of the incident light (Figure 2.12) has an amplitude \( a \cos \omega t \) and makes an angle \( \theta \) with the optic axis \( x \).

Upon entering the crystal the displacement \( D \) breaks up into two components of amplitudes \( D_o = a \cos \theta \cos \omega t \) and \( D_e = a \sin \theta \cos \omega t \) in the directions of \( Ox \) and \( Oy \), respectively. After traversing in the crystal plate of thickness \( d \) the two orthogonal components will be out of phase by an amount \( \phi \). The two components will be then:

\[ D_o = a \cos \theta \cos \omega t \]  \hspace{1cm} (2.13)

and

\[ D_e = a \sin \theta \cos(\omega t - \phi) \]  \hspace{1cm} (2.14)

After traversing the analyzer, the light has the components \( A_o \) and \( A_e \) (Figure 2.12). The light intensity for a birefringent sample after the analyzer can be expressed as:

\[ I = I_0 \sin^2 2\theta \cdot \sin^2 \phi/2 \]  \hspace{1cm} (2.15)

\( \phi \) can be further be expressed as:
\[ \varphi = \left( \frac{2\pi}{\lambda} \right) \cdot d \cdot (n_e - n_o) = \left( \frac{2\pi}{\lambda} \right) \cdot d \cdot \Delta n \]  

(2.16)

where \( \lambda \) is the light wavelength; \( d \) is the sample thickness; \( n_e \) and \( n_o \) represent the refractive indices for the \( D_e \) and \( D_o \) components, respectively. The maximum contrast between opposite domains is reached at \( \varphi = \pi/2 \) for a fixed wavelength and extinction in one of the domains.[83]

![Diagram](image)

**Figure 2.12** The schematic illustration of decomposition and recombination of a polarized light.

For most of the samples considered in this thesis, the optical properties of the crystals are anisotropic and are related to the crystal symmetry. For example, in a complex perovskite sample with tetragonal \( 4mm \) phase, the intrinsic spontaneous polarization is along one of the six equivalent \( <001>_{cub} \) directions and the optical axes are also oriented parallel to \( <001>_{cub} \). When observed by PLM on a \((001)_{cub}\)-oriented crystal platelets, the cross section of the optical indicatrix, which is an sphere or ellipsoid surface defined by the indices of refraction, coupled to the crystallographic axes, will exhibit extinction directions parallel to \( <001>_{cub} \) (Figure 2.13(a)).[84] In the rhombohedral \( R3m/R3c \) phase, the intrinsic polarization is along one of the eight equivalent \( <111>_{cub} \) directions and the optical axes are also oriented parallel to the \( <111>_{cub} \) direction. The corresponding indicatrix in a \((001)_{cub}\)-oriented plate will exhibit extinction along the \( <110>_{cub} \) directions (Figure 2.13(b)).
2.10. Piezoresponse Force Microscopy

Piezoresponse force microscopy (PFM) is a powerful tool for high resolution characterization of topography and local behaviour of ferroelectric domains on a micrometer to nanometer scale. This technique utilizes the converse piezoelectric effect, where an electric field is applied to a piezoelectric material and strain is created. A Bruker Dimension Icon PFM and an Asylum Research Corp. Cypher PFM were used in this work. The PFM has a conductive cantilever probe that allows an AC field to be applied with or without a DC bias, which causes piezoelectric materials to deflect based on their piezoelectric effect.[85] If the polarization of the material is in the same direction as the electric field applied, the material will expand, and if the polarization is in the
opposite direction, the material will contract (Figure 2.14). For example, if the surface oscillations are in-phase with the tip voltage ($\varphi = 0^\circ$), the material will expand, and it will give a bright image. Conversely, when it is out-of-phase ($\varphi = 180^\circ$), the material will contract, and will give a dark image. Furthermore, a plot of amplitude versus voltage applied can provide information on the strain created as the voltage changes, which reveals a local piezoelectric response. A plot of phase angle versus voltage applied provides information on polarization switching in the material, which is indicative of ferroelectric behavior, at least on local scale.

Figure 2.14  Schematics of deformation in a piezoelectric material when the PFM tip bias is (a) zero, (b) positive and (c) negative (adapted from Ref.[86]).
Chapter 3.

Growth and Characterization of PbZr$_{1-x}$Ti$_x$O$_3$ (PZT) Single Crystals

3.1. Abstract

PbZr$_{1-x}$Ti$_x$O$_3$ (PZT) single crystals with compositions of $x = 0.54$ and 0.45 were grown by a top-seeded solution growth (TSSG) technique. The X-ray powder diffraction analysis shows that the PZT ($x = 0.54$) crystal has a tetragonal perovskite structure. The measurements of dielectric properties indicate that the crystal undergoes a single phase transition from the cubic to the tetragonal phase at Curie temperature, $T_C = 405$ °C upon cooling. A remnant polarization ($P_r$) of 58.0 μC/cm$^2$ is displayed with a high coercive field ($E_c$) of 43.3 kV/cm for the PZT ($x = 0.54$) crystal. On the other hand, the phase component and symmetry of the PZT ($x = 0.45$) crystal are much more complex, containing rhombohedral and monoclinic phases at room temperature, which is characteristic of the morphotropic phase boundary (MPB) behaviour. The paraelectric to ferroelectric phase transition of the PZT ($x = 0.45$) crystal occurs at $T_C = 381$ °C. It undergoes an additional ferroelectric-to-ferroelectric phase transition as revealed by the dielectric anomaly at 238 °C, which is due to a curved MPB. Furthermore, this crystal possesses better properties with a piezoelectric coefficient $d_{33} = 886$ pC/N, an electromechanical coupling factor $k_{33} = 0.80$, a coercive field $E_c = 10$ kV/cm and a high $T_C = 381$ °C. The high $T_C$ and high piezoelectric performance of the PZT single crystals qualify them as a promising material for high temperature and high power electro-mechanical transducer applications.
3.2. Introduction

PbZr\(_{1-x}\)Ti\(_x\)O\(_3\) (PZT) ferroelectric ceramics are the most extensively used piezoelectric materials owing to their good piezoelectric and electromechanical properties near the morphotropic phase boundary (MPB). Recently, relaxor ferroelectrics-based single crystals of the Pb(Mg\(_{1/3}\)Nb\(_{2/3}\))O\(_3\)-PbTiO\(_3\) (PMN-PT) and Pb(Zn\(_{1/3}\)Nb\(_{2/3}\))O\(_3\)-PbTiO\(_3\) (PZN-PT) solid solutions with compositions close to their respective MPBs have attracted a great deal of attention. Compared with PZT ceramics, these crystals have a higher piezoelectric coefficient (d\(_{33}\) > 1700 pC/N) and a larger electromechanical coupling factor (k\(_{33}\) > 0.90).[39] Even though their properties are superior to those of PZT ceramics, they exhibit some inherent drawbacks, such as a low MPB phase transition temperature (T\(_{MPB}/T_{RT}\) < 100 °C) and a low coercive field (E\(_c\) < 3 kV/cm), making them unsuitable for high temperature and high field (power) applications.

Since PZT (x = 0.46) system has a high T\(_C\) (≈ 380 °C), it is believed that its single crystals could achieve both excellent piezoelectric properties and high T\(_C\).

PZT solid solution is also important for fundamental research, and numerous studies have been carried out to unveil the mechanisms for its extraordinary piezoelectric properties in the MPB region. Investigations on crystal structure and its relationship with piezoelectric properties play an essential role for understanding this system, especially for the compositions around the MPB region. Several structural models have been proposed based on experimental approaches by means of transmission electron microscopy (TEM), and neutron and X-ray powder diffractions. It was discovered by Noheda et al. that a monoclinic phase with Cm symmetry exits in the MPB region, which bridges the high-Zr rhombohedral phase and high-Ti tetragonal phase. Later on, several structural models involving coexistence of monoclinic, rhombohedral and tetragonal phases were proposed.[87]–[89] However, all these studies were based on the ceramic samples, the structure of which is known to be dependent on the synthetic method, the texture of the grain and the microstructure of the grain boundary. For instance, it was found that the width of the MPB with coexisting phases is inversely proportional to the grain size of the ceramics.[21] According to this finding, one could expect the phase coexistence region in PZT single crystals should be very narrow and even non-existing. Therefore, structural studies on PZT single crystals
are much needed and it will provide us with more intrinsic experimental data about the MPB. Moreover, the availability of PZT single crystals with adequate size will allow us to characterize their various properties, and therefore to reveal the relationship between crystal structure and properties.

In this work, we have successfully grown perovskite PZT single crystals by a top-seeded solution growth (TSSG) technique. The thermodynamics and kinetics conditions have been optimized for the growth of PZT single crystals. It was found that by adjusting the growth temperature, the composition of PZT crystals can be controlled, leading to the growth of PZT crystals of tetragonal composition \((x = 0.54)\) and those of the morphotropic phase boundary (MPB) composition \((x = 0.45)\). The crystal structures and their electrical properties, e.g. dielectric, ferroelectric and piezoelectric properties have been studied.

### 3.3. Experimental

#### 3.3.1. Crystal growth

The TSSG method was applied for growing PZT single crystals. A PZT crystal with the \(<001>_{\text{cub}}\) orientation obtained from a previous growth was used as a seed crystal to trigger and control the nucleation. The seed crystal was tied to the end of an alumina rod by platinum wire. The flux used is a mixture of PbO and B\(_2\)O\(_3\) (with a molar ratio of 1:5). The starting chemicals weighed corresponding to the nominal composition PZT \((x = 0.6)\) were ground and calcined to form the perovskite structure. The mixture was loaded to a 100mL Pt crucible, which was then placed inside a growth furnace with the seed crystal hanging from the top, as shown in Figure 3.1.
As shown by the temperature profile in Figure 3.2, for growth Batch #1, the powder mixture was heated up to 1050 °C, dwelt for five days, and then cooled to 1030 °C at a cooling rate of 0.8 °C/h. The seed crystal was introduced into the solution at 1030 °C. During the subsequent growth process, the cooling rate was set as 4 °C/day. At the end of the growth (930 °C) after twenty five days, the grown crystal was pulled all the way out of the solution and then cooled down to room temperature at a rate of 20 °C/h. For growth Batch #2, the powder was first heated up to 1100 °C for two days and then cooled to 1080 °C, at which temperature the seed crystal was introduced into the solution. The growth was ended at 980°C and all the other thermodynamic parameters were kept the same as those for Batch #1.
Figure 3.2  Schematic thermal profile used for the PZT crystal growth by the TSSG method.

3.3.2. Measurements

For electrical characterization, the polished \((001)_{\text{cub}}\) crystal surfaces of the platelets were painted with a layer of silver paste and gold wires were then attached to both surfaces of the samples. The dielectric properties of the grown PZT crystals were measured as a function of temperature at various frequencies using a Novocontrol Alpha high-resolution broadband dielectric analyzer equipped with a Novotherm heating system. The ferroelectric hysteresis loops were displayed on the \((001)_{\text{cub}}\) platelets by means of a Radiant RT-66 standardized ferroelectric testing system. The sample was kept in a silicon oil bath to avoid electric arcing during the polarization switching. The sample was poled by a Stanton PS350 high voltage power source at room temperature in silicon oil. The piezoelectric coefficient \((d_{33})\) was measured by a quasistatic piezoelectric meter (ZJ-6B). The electromechanical coupling factor \((k_{33})\) was measured on a poled bar-shaped \((001)_{\text{cub}}\)-oriented Batch #2 crystal with dimensions of \(0.7 \times 0.7 \times 2.4 \text{ mm}^3\) by the resonance-antiresonance method using a Solartron 1260 impedance analyzer in conjunction with a Solartron 1296 dielectric interface.
3.4. Results and discussion

3.4.1. Crystal growth

Figure 3.3 shows the two batches of as-grown PZT single crystals obtained by the TSSG method. The Batch #1 crystals show a pseudo-cubic morphology with naturally grown (001)\textsubscript{cub} facets. The average size of a crystal is between 5.0 - 6.0 mm (the background scale is in 1 mm.). A bulk single crystal of large size of 1.5 x 1.5 x 0.5 cm\textsuperscript{3} is obtained from growth Batch #2, which appears to be of clear yellow colour. Our previous work has shown that as the compositions approaches the MPB region of PZT system, the colour of the crystals becomes lighter.[90] Therefore, the Batch #2 crystal is more likely to be in the MPB region.

![Figure 3.3](image)

Figure 3.3 As-grown PZT single crystals from growth Batches #1 and #2, respectively.

3.4.2. Structural analysis by XRD

The phase and structure of the grown Batch #1 PZT single crystals were analyzed by XRD on a fine powder obtained by grinding several small crystals. Figure 3.4 shows the XRD pattern and its Pawley fitting results, which indicate a pure perovskite-type phase for the as-grown crystals and the formation of the PZT solid solution. The small peaks at the 2-theta of about 28° arise from the solidified PbO flux on the surface of the crystal. The pattern shows splitting at the (100)\textsubscript{cub}, (110)\textsubscript{cub}, and (200)\textsubscript{cub} reflections while the (111)\textsubscript{cub} peak remains singlet. This kind of splitting is characteristic of a tetragonal symmetry. To confirm the symmetry of the crystal, the XRD pattern was further analyzed by the Pawley fitting method based on a model of tetragonal structure, and the refinement result is shown in Figure 3.4, where the
measured data are displayed in the black solid curve and the calculated result is represented by the red curve. The difference between the experimental and fitting data is indicated by the gray curve, which shows a good match between the experimental data and the calculated pattern. Accordingly, the structure of the Batch #1 PZT single crystal is determined to be of tetragonal symmetry with lattice parameters of \( a = 4.032 \pm 0.002 \) Å, and \( c = 4.141 \pm 0.002 \) Å. These values are very close to the data reported by Idemoto et al. for the unit cell of PZT ceramics with \( x = 0.55 \).[91] Therefore, the composition of the grown PZT (Batch #1) crystal is estimated to be \( x = 0.54 \sim 0.55 \).

**Figure 3.4** XRD pattern of ground Batch #1 PZT single crystals and the Pawley fitting results.

The XRD pattern of the Batch #2 single crystal (Figure 3.5) shows splitting at the \((100)_{\text{cub}}, (110)_{\text{cub}}, (111)_{\text{cub}},\) and \((200)_{\text{cub}}\) peaks, suggesting a mixture of phases, which is characteristic of the MPB composition. The small peaks at about 28° and 32.5° arise from the solidified PbO flux on the surface of the crystal. It is well known that for a rhombohedral phase, the \((110)_{\text{cub}}\) and \((111)_{\text{cub}}\) reflections are split into two peaks while the \((100)_{\text{cub}}\) reflection remains as a single peak, while a monoclinic phase is characterized by its triplet \((100)_{\text{cub}}\) and quadruplet \((110)_{\text{cub}}\) reflections as shown in Figure
2.5 of Chapter 2. In order to study the symmetry of the Batch #2 crystal at different temperatures, XRD was performed upon heating. As shown in Figure 3.5, there is no obvious change in the XRD patterns from 30 °C to 180 °C, indicating no structural phase transition. However, between 250 °C and 300 °C, additional reflection peaks are seen, suggesting that a new phase appears and that the composition of the Batch #2 crystal is indeed in the MPB region.

![XRD patterns of the Batch #2 single crystal measured at various temperature upon heating.](image)

**Figure 3.5** XRD patterns of the Batch #2 single crystal measured at various temperature upon heating.

The (100)\textsubscript{cub}, (110)\textsubscript{cub}, and (111)\textsubscript{cub} peaks of the Batch #2 crystal are enlarged and shown in Figure 3.6, for the sake of clearly viewing the phase change upon heating. It was found that for a MPB composition PZT, the structure at room temperature could either be a two-phase mixture of rhombohedral and monoclinic phases or a three-phase mixture of rhombohedral, tetragonal and monoclinic phases.[92] It can be seen that both
the (110)cub and (111)cub reflections split into two peaks and the (100)cub reflection remains as a single peak at 30 °C, which in general suggests a rhombohedral symmetry. However, more careful analysis found that the splitting peaks of the rhombohedral (110)cub and (111)cub reflections are broadened or further split, indicating the possible existence of a monoclinic phase. When the temperature reaches 180 °C, the splitting pattern of the (110)cub and (111)cub reflections remains the same, but the intensity ratios show explicit change. Moreover, the (100)cub reflection starts showing shoulders, which means that the amount of the monoclinic phase was gradually increasing at the expense of the rhombohedral phase and becoming the dominant phase upon heating. At 250 °C, the splitting peaks of the (110)cub and (111)cub reflections gradually merge to form a broaden single peak. Meanwhile, additional peaks appear at the (200)cub reflection, suggesting the formation of a new phase, which is most like a tetragonal phase. At this point, the crystal overall shows a mixture of a major monoclinic phase and a minor tetragonal phase. With further increase in temperature, the amount of the tetragonal phase increases gradually at the cost of the monoclinic phase. The crystal eventually changes to a cubic phase at higher temperatures (e.g. 400 °C and 450 °C). Therefore, the sequence of the phase transition in the Batch #2 PZT crystal in the measured temperatures range is concluded to be as follows: (Rhombohedral + Monoclinic) (30 °C - 180 °C) → (Monoclinic + Tetragonal) (250 °C - 300 °C) → Cubic (400 °C - 450 °C). In order to determine the proportion of each phase component, high resolution XRD data and more advanced analysis are needed. This phase transition sequence suggests that the ferroelectric to paraelectric phase transition temperature (T_C) of the Batch #2 PZT crystal should be between 300 °C and 400 °C. In addition, there is another phase transition from rhombohedral to tetragonal that occurs between 180 °C and 250 °C. These phase transition temperatures indicate an approximate MPB composition (x = 0.45 ~ 0.48) for the grown Batch #2 PZT crystal according to the well-established phase diagram.[22]
3.4.3. Electrical properties of PZT single crystals

Figure 3.7(a) and Figure 3.7(b) show the variation of dielectric permittivity as a function of temperature measured on a (001)$_{\text{cub}}$ platelet of Batch #1 crystal at various frequencies upon heating and cooling, respectively. The phase transition between the paraelectric cubic and ferroelectric tetragonal phases occurs at around 408 °C ($T_C$). The composition with this $T_C$ value is determined to be PbZr$_{0.46}$Ti$_{0.54}$O$_3$ (hereafter referred to as the PZT (x = 0.54)) according to the known PZT phase diagram.[22] The crystal structure of this composition below $T_C$ is supposed to be in the tetragonal region of PZT system.[22] These results are in a good agreement with the above mentioned XRD structural analysis. It is worth noting that there is a frequency dependent dielectric dispersion between 200 °C and 360 °C upon heating. And this dispersion is expanded to the temperature range of 175 °C and 360 °C when the measurement is performed on cooling. This kind of dispersion could arise from domain wall motion, mobile charge...
carriers, and/or possible crystal defects, which are known to contribute to dielectric permittivity of a non-relaxor ferroelectric material in general.[93]–[95]

Figure 3.7  Temperature dependence of the dielectric permittivity ($\varepsilon'$) upon (a) heating and (b) cooling of a (001)$_{\text{cub}}$ tetragonal PZT ($x = 0.54$) single crystal.

In order to further investigate the mechanisms of this phenomenon, dielectric measurements were carried out upon heating on the crystal after electric-field poling at room temperature. The frequency dependence of the sample at several characteristic temperatures is plotted in Figure 3.8. It can be seen that the dielectric permittivity is
nearly frequency-independent below 200 °C for both unpoled (Figure 3.8(a)) and poled (Figure 3.8(b)) samples. However, the frequency dependence in the temperature range of the dispersion, namely at 250 °C and 300 °C, is significantly attenuated by electric-field poling. This result indicates that the observed dispersion could more likely arise from domain wall motions as electric-field poling process could significantly reduce the density of the domain walls and thereby reduce their motions.[93] Meanwhile, it is worth mentioning that this kind of domain wall motion is an indirect sign of a minimized domain state, e.g. with a small domain size and high domain wall density, in the crystal. The domain state of this crystal will be studied in detail in Chapter 4.

To study the influence of possible crystal defects, the sample was annealed in the oxygen gas at 800 °C for four hours at a heating and cooling rate of 100 °C/h and 50 °C/h, respectively. It is found that oxygen annealing does not have observable effect on the dielectric dispersion, which also indicates that the grown single crystal is of good quality without a significant level of defects. However, the dielectric permittivity (at T > T_c) at low frequencies is reduced, suggesting that the conductivity contribution is diminished after annealing in O_2 (Figure 3.8(c)).
Figure 3.8  Frequency dependence of the dielectric permittivity ($\varepsilon'$) of the (001)$_{cub}$ PZT ($x = 0.54$) single crystal: (a) as-grown, (b) electric-field poled, and (c) annealed in oxygen atmosphere.

The dielectric properties of the Batch #2 crystal were also examined. Figure 3.9 displays the temperature dependence of the dielectric permittivity ($\varepsilon'$) and dielectric loss ($\tan \delta$) measured on heating for a (001)$_{cub}$-oriented single crystal platelet. The strongest peak at $T_C = 381 \, ^\circ C$ indicates the ferroelectric to paraelectric phase transition upon heating. The dielectric curve shows an additional anomaly at $T_{MPB}/T_{R-T} = 238 \, ^\circ C$, which corresponds to the MPB (from the (Rhombohedral + Monoclinic) to the (Monoclinic + Tetragonal)) phase transition. The composition with this $T_C$ and $T_{MPB}/T_{R-T}$ is determined to be PbZr$_{0.55}$Ti$_{0.45}$O$_3$ (hereafter referred to as the PZT ($x = 0.45$)) according to the known PZT phase diagram,[22] which is consistent with the composition deduced from the phase sequence by XRD (see Section 3.4.2). The dielectric response ($\varepsilon'$) at room temperature is found to be 1200 for this composition with a very low dielectric loss ($\tan \delta = 0.006$), attesting to the high quality of the grown crystals.
Figure 3.9 Temperature dependences of the dielectric permittivity ($\varepsilon'$) and dielectric loss (tan $\delta$) for a (001)$_{\text{cub}}$-oriented PZT ($x = 0.45$) single crystal, measured at various frequencies.

Ferroelectric properties were measured on the (001)$_{\text{cub}}$-oriented PZT single crystals. As shown in Figure 3.10, the ferroelectric properties of the PZT ($x = 0.54$) were displayed by the well-developed polarization-electric field hysteresis loops. Saturation of polarization is achieved at an electric field of $\pm85$ kV/cm at room temperature. The
remnant polarization reaches $P_r = 58 \ \mu\text{C/cm}^2$ with a coercive electric field $E_c = 43.8 \ \text{kV/cm}$. Both these values are much higher than those so far reported PZT single crystals by our group, which show a typical $P_r$ value of $57 \ \mu\text{C/cm}^2$ and an $E_c$ of $43 \ \text{kV/cm}$.\[90\] In particular, the higher $P_r$ value reflects the intrinsic ferroelectric properties of PZT, which can only be revealed in single crystals and will be useful as a reference for theoretical modeling. Besides, it also proves the high quality of the crystals. Note that the large coercive field is characteristic of the tetragonal phase of PZT. Because of the large coercive field, the sample is very hard to be poled completely. As a result, piezoelectric property measured on this crystal is rather mediocre ($< 400 \ \text{pC/N}$), which is expected for the tetragonal PZT.

![Ferroelectric hysteresis loop of the (001)$_\text{cub}$ PZT (x = 0.54) single crystal displayed at room temperature.](image)

**Figure 3.10** Ferroelectric hysteresis loop of the (001)$_\text{cub}$ PZT (x = 0.54) single crystal displayed at room temperature.

The polarization-electric field hysteresis loop of PZT (x = 0.45) shows typical MPB behaviour with a small coercive electric field $E_c = 10 \ \text{kV/cm}$ and a higher polarization $P_r = 33 \ \mu\text{C/cm}^2$ (Figure 3.11). It is known that in the tetragonal region of PZT, the space group is P4mm, with the polar axis along $<001>_{\text{cub}}$, while in the rhombohedral region, with space group R3m, the polar axis is along the pseudocubic
A continuous phase transition from the rhombohedral to the tetragonal is not allowed by symmetry (no group-subgroup relation). However, in the MPB PZT, there is a monoclinic phase with space group Cm, which is a subgroup of P4mm and R3m and allows the polar axis to lie anywhere between the \( <001>_{\text{cub}} \) and the \( <111>_{\text{cub}} \) directions.[22] Therefore, the monoclinic phase acts as a bridge between the rhombohedral and the tetragonal phases in the MPB region.[18] The free energy of these three phases is similar, in other words, the energy surface is flat. Hence, polarization rotation is allowed and a small field will cause a large change of polarization angle. Moreover, the PZT (\( x = 0.45 \)) crystal shows a better piezoelectric property with a piezoelectric coefficient \( d_{33} = 886 \) pC/N, which is much higher than any of the undoped PZT ceramics.[96]

![Polarization-electric field hysteresis loop](image)

**Figure 3.11** Polarization-electric field hysteresis loop of a \((001)_{\text{cub}}\) PZT \((x = 0.45)\) single crystal measured at room temperature, indicating ferroelectricity.

The resonance measurement was carried out on a \((001)_{\text{cub}}\)-oriented PZT \((x = 0.45)\) single crystal bar with the dimensions of \(0.7 \times 0.7 \times 2.4 \) mm\(^3\), by measuring the impedance and phase angle as a function of frequency. Prior to the measurement, the crystal was poled at an electric field of 30 kV/cm at room temperature. As shown in
Figure 3.12, the resonance and anti-resonance frequencies are found to be $f_r = 4.24 \times 10^5$ Hz and $f_a = 5.99 \times 10^5$ Hz, respectively. Accordingly, the longitudinal electromechanical coupling factor $k_{33}$ was calculated using Equation 2.10 in Chapter 2 and it reaches 80% for this sample. It is noticed that there are some fluctuations in the data points at high frequencies, which could be attributed to possible domain scattering, arising from an incomplete poling, could be taken into account as well.

![Figure 3.12 Variations of the impedance and phase angle as a function of frequency for a (001)$_{cub}$-oriented, poled PZT ($x = 0.45$) single crystal bar ($0.7 \times 0.7 \times 2.4$ mm$^3$).](image)

3.5. Conclusions

PbZr$_{1-x}$Ti$_x$O$_3$ (PZT) single crystals were grown by a top-seeded solution growth (TSSG) technique. The thermodynamics and kinetics conditions have been optimized for the growth of PZT crystals. It was found that by adjusting the growth temperature, the composition of PZT crystals can be controlled, leading to the growth of PZT crystals of morphotropic phase boundary (MPB) composition ($x = 0.45$) and those of tetragonal
composition \( (x = 0.54) \). The XRD analysis shows that the PZT \((x = 0.54)\) crystal has a tetragonal perovskite structure. The measurements of dielectric properties indicate that the crystal undergoes a single phase transition from the cubic to the tetragonal phase at \( T_C = 405 \) °C upon cooling. Meanwhile, this crystal exhibits significant dielectric dispersion at a temperature range between 200 °C and 400 °C, suggesting strong domain wall motions, which could have arisen from minimized domain states. A remnant polarization \((P_r)\) of 58.0 \( \mu \)C/cm\(^2\) is displayed with a high coercive field \((E_c)\) of 43.3 kV/cm for the PZT \((x = 0.54)\) crystal. The piezoelectric property measured on this crystal is rather mediocre (< 400 pC/N), which is expected for the tetragonal PZT.

On the other hand, the phase component and symmetry of the PZT \((x = 0.45)\) crystal are much more complex, containing rhombohedral and monoclinic phases at room temperature, which is characteristic of MPB behaviour. The paraelectric to ferroelectric phase transition of the PZT \((x = 0.45)\) crystal occurs at \( T_C = 381 \) °C upon cooling. It also undergoes an additional dielectric anomaly at 238 °C, which corresponds to the ferroelectric-to-ferroelectric MPB phase transition. The maximum dielectric response \((\varepsilon')\) at room temperature is found to be 1200 for this composition with a very low dielectric loss \((\tan \delta = 0.006)\). Moreover, this crystal possesses better properties with a piezoelectric coefficient \(d_{33} = 886\) pC/N, an electromechanical coupling factor \(k_{33} = 0.80\), a large coercive field \(E_c = 10 \) kV/cm and a high \( T_C = 381 \) °C.

The comparative results between the PZT \((x = 0.54)\) and PZT \((x = 0.45)\) crystals confirm that the MPB plays a favourable role in the enhancement of the piezoelectric performance in PZT solid solution. The high \( T_C \) and high piezoelectric performance of PZT single crystals qualify them as a promising material for high-temperature and high-power electro-mechanical transducer applications. Furthermore, even though PZT has been studied for several decades, the intrinsic properties of this solid solution system are still missing. The availability of PZT single crystals makes it possible to study the phase transitions by polarized light microscopy (PLM) and piezoresponse force microscopy (PFM), which will be described in the following chapters. The obtained results would be expected to be very useful for studying the fundamental physics of both the ferroelectricity and piezoelectricity.
Chapter 4.

Complex Meso-to-Nano Domain Structures and Related Phenomena in Tetragonal PbZr$_{1-x}$Ti$_x$O$_3$ ($x = 0.54$) Single Crystals

4.1. Abstract

Single crystals of PbZr$_{1-x}$Ti$_x$O$_3$ ($x = 0.54$) were grown by a top seeded solution growth (TSSG) method. The symmetry of the crystals was confirmed to be tetragonal by structural refinement based on X-ray diffraction data. However, the analysis of domain structure by polarized light microscopy (PLM) reveals that the (001)$_{\text{cub}}$ platelet of the crystal behaves isotropically, with extinction at any positions under the crossed polarizers, i.e. showing a seemingly cubic symmetry. On the other hand, the (011)$_{\text{cub}}$ platelet exhibits birefringence with extinctions at $0^\circ/90^\circ$ to the $<100>_{\text{cub}}$ direction, which is consistent with the optical feature of a tetragonal phase. These phenomena are attributed to the presence of differently oriented miniaturized domains or nanodomains of tetragonal symmetry. These nanodomains are arranged in such a way that they compensate each other almost completely along the $<001>_{\text{cub}}$ direction when observed on the (001)$_{\text{cub}}$ platelet, but incompletely along the $<011>_{\text{cub}}$ direction when observed on the (011)$_{\text{cub}}$ platelet. The induced birefringence on the (001)$_{\text{cub}}$ platelet is investigated by applying an electric field and an external stress in the $<010>_{\text{cub}}$ direction. Upon application of an electric field in the $<010>_{\text{cub}}$ direction, square-shaped domains with edges oriented in the $<110>_{\text{cub}}$ directions are observed by PLM. They are embedded in a tetragonal nanodomain matrix and are confirmed by piezoresponse force microscopy (PFM) to be $180^\circ$ ferroelectric domains with an average size of 12 μm. The formation of these domains is explained by the nucleation and growth of $180^\circ$ flux-closure state in the crystal. Three steps are involved in this process: (1) a circular $180^\circ$ flux-closure domain is nucleated in the tetragonal nanodomain state; (2) the small circular flux-closure
domain reaches its critical size and grows into a large one, and (3) due to the anisotropic bonding in PZT crystal unit cell, the growth rate along the \( \langle 001 \rangle_{\text{cub}} \) direction is faster than along the \( \langle 110 \rangle_{\text{cub}} \), leading to a square-shaped microdomain. In addition, a monoclinic (M\(_{\text{C}}\)) phase is induced in the tetragonal nanodomains by application of the electric field. Moreover, the variation of the induced birefringence versus the applied stress shows a linear and reversible relation.

4.2. Introduction

Lead zirconate titanate, PbZr\(_{1-x}\)Ti\(_x\)O\(_3\) (PZT), forms the basis of a family of the best known and most important piezoelectric materials. Its structure and properties have been studied extensively for several decades since its discovery.[97] In spite of all these efforts, the origin of high-performance piezoelectricity in this solid solution is still not well understood because of its structural complexity. The original phase diagram of PZT solid solution determined by Jaffe et al. shows a narrow phase boundary, called morphotropie phase boundary (MPB), between the Zr-rich rhombohedral (R) region and the Ti-rich tetragonal (T) region at \( x \approx 0.45 - 0.48 \).[28] In late 1990s, a major update was made to this diagram when an intermediate monoclinic (M) phase was discovered by Noheda et al. by means of synchrotron X-ray diffraction that exists in the MPB region of PZT.[22] This picture of MPB has since been considered as an accepted feature of the PZT phase diagram and the nature of the apparent M phase has undergone intense investigation. A great deal of experimental and theoretical studies on the MPB of PZT indicate that the high piezoelectric properties are closely related to the existence of the M phase.[18], [98]–[100] which is assumed to facilitate the polarization rotation in the vicinity of the MPB, rendering the PZT of MPB composition electrically active, and thereby highly piezoelectric.[101] Recently, Nan et al. found that the R and M phases coexist at all compositions across the Zr-rich area of PZT, and it is the monoclinic M\(_{\text{A}}\) phase that is more likely responsible for the high piezoelectricity.[92]

PZT has a cubic perovskite structure above its Curie temperature (\( T_C \)), which depends on the composition ratio of Zr/Ti. Upon cooling, it undergoes a phase transition from the high symmetry cubic paraelectric state to a low symmetry ferroelectric phase at \( T_C \). The symmetry losses with this phase transition are accommodated by the formation
of ferroelectric and ferroelastic domains. For the phase R (x < 0.45) of PZT, an electric dipole is generated in the \(<111>_{\text{cub}}\) directions, and the possible types of domains are 109°, 71°, and 180°. The orientation of the permissible uncharged walls, i.e., with a head-to-tail arrangement of the dipoles, is \({110}_{\text{cub}}\) planes for the 109° domains, \({001}_{\text{cub}}\) planes for the 71° domains and any plane parallel to the polarization vector (\(P_s\)) for the 180° domains. The electric dipole for a phase T (x > 0.48) is aligned in one of the \(<100>_{\text{cub}}\) directions, so the rotation of the \(P_s\) from one domain to the next can only be 90° or 180° in the T phase. Therefore, the permissible uncharged walls correspond to the \({110}_{\text{cub}}\) planes for the 90° domains and any plane parallel to the \(P_s\) for the 180° domain type. The domain and domain wall state in a M phase are much more complicated as it is a biaxial phase.

Recent studies have reported various domain configuration observed in PZT ferroelectrics, e.g., lamellar twins, bands of twins, needle-shaped and wedge-shaped. Various mechanisms have been proposed in order to explain the formation of these domains.[102]–[104] It was found that the domain width decreases as the composition approaches the MPB region.[89] Domains of a few nanometers size have been observed within microdomains in different MPB compositions of PZT.[20], [89], [105], [106] This type of “nanodomains” was also found in some other ferroelectrics, such as PMN-PT.[107] and doped PZT.[108]–[110] with compositions close to their respective MPBs. Recently, Jin et al. developed an adaptive ferroelectric phase theory to interpret these miniaturized domains with a mixed nanoscale structure.[23], [107] It was proposed that in an adaptive ferroelectric phase consisting of T and R domains, the microdomain-averaged symmetry is M. The crystal lattice parameters of this phase are dependent on those of the parent cubic phase and those forming microdomains.[23], [111] Since then, the mechanisms, which lead to the extraordinary piezoelectric properties of PZT have been commonly discussed in terms of the existence of nanodomains.[112]–[119]

On the other hand, flux-closure domain states (sometimes called ‘vortex domains’), which are commonly observed in ferromagnetics, were recently predicted to exist in ferroelectrics.[120]–[123] The driving force behind the formation of flux-closure domains in ferroelectrics is the minimization of depolarizing fields, achieved through the creation of head-to-tail dipole loops. If the local dipole orientation continuously rotates around a core, then a vortex state develops.[120]–[126] For pure ferroelectric materials,
obvious polarization rotation is perhaps most likely to occur in PZT system as its anisotropy near the MPB is expected to be lowered allowing for great polar malleability.[120]–[129] Indeed, Jia et al. have directly observed polarization rotation on PZT \((x = 0.80)\) thin film and McGilly et al. made similar observation in PZT \((x = 0.58)\) nanodots.[130], [131] However, such ‘flux-closure pattern’ has not been found in ferroelectric bulk PZT materials to date.

Most of the microstructural analyses of PZT were performed on ceramics due to the unavailability of single crystals. However, for a meaningful interpretation of the nanodomain structures and related properties, a thorough analysis of the macro- to meso-scopic structures, which determine the crystal physical properties, on good-quality single crystals is necessary. In the present work, the domain structure and properties of a PZT \((x = 0.54)\) single crystal are characterized by various methods. Most interestingly, square-shaped domain patterns are observed in this crystal, which could develop from the flux-closure moments in a \((001)_{\text{cub}}\) platelet with domains of nanoscale size. Careful analysis is carried out using polarized light microscopy (PLM) by applying an electric field along the \(<100>_{\text{cub}}\) direction through the two \([010]_{\text{cub}}\) edges of a \((001)_{\text{cub}}\)-cut single crystal platelet. Piezoresponse force microscopy (PFM) is also performed to confirm the polar nature of the observed domain patterns. In addition, stress induced birefringence is studied by applying a mechanical stress in the \(<100>\) direction of the PZT \((x = 0.54)\) \((001)_{\text{cub}}\)-cut single crystal platelet.

### 4.3. Experimental

Single crystals of PZT \((x = 0.54)\) were grown by a top-seeded solution growth (TSSG) method as described in Chapter 3. To study the optical properties, the crystals were cut parallel to the \((001)_{\text{cub}}\) and \((011)_{\text{cub}}\) platelets and polished to optical quality using silicon carbide sand papers and lapping sheets. PLM was performed with an Olympus BX 60 polarizing microscope equipped with Olympus UC 30 digital camera and compensators to image and analyze the domain structure, phase symmetry and phase transition of the \((001)_{\text{cub}}\) and \((011)_{\text{cub}}\) platelets. To differentiate small optical rotations visually by color, a sensitive tint plate \((1\lambda, \text{U-TP530, Olympus})\) was used.
To study the electric field effect, the two [010]$_{\text{cub}}$ edges (i.e. the (010)$_{\text{cub}}$ faces) of the (001)$_{\text{cub}}$ platelet are covered by silver paste (Figure 4.1). An external dc electric field was applied along the $<100>_{\text{cub}}$ direction through the two gold wires that are connected to the two edges as electrodes. The domain structure of the sample was studied by PLM under different electric fields.

![Figure 4.1 Schematic drawing of the (001)$_{\text{cub}}$ platelet for the electric field effects studies.](image)

Mechanical stress was also applied to the same (001)$_{\text{cub}}$ platelet of the PZT ($x = 0.54$) crystal by means of a Low Temperature Uniaxial Stress Application Device (courtesy of Prof. Hans Schmid, University of Geneva) on the two parallel [010]$_{\text{cub}}$ edges. The detailed technical description of this system can be found in a previous publication.[132] Figure 4.2 illustrates the direction of stress applied and that of the crystal between the sapphire jaws.
Figure 4.2  Sketch showing application of mechanical stress in the \(<100>_{\text{cub}}\) direction through a pair of sapphire jaws. The shaded area are \((010)_{\text{cub}}\) faces covered by silver paste as electrodes.

In order to probe the local domain configuration and demonstrate the switching of polarization, the same \((001)_{\text{cub}}\) platelet sample was analyzed by piezoresponse force microscopy (PFM) on a modified commercial atomic force microscopy system in piezoresponse mode (AFM, Dimension Icon, NanoScope V, Bruker, located at Xi’an Jiaotong University, China).

4.4. Results and discussion

4.4.1. Domain structure observation and analysis

The optically polished \((001)_{\text{cub}}\) and \((011)_{\text{cub}}\) PZT \((x = 0.54)\) single crystal platelets were examined by PLM to analyze their domain structure, phase symmetry and phase transitions. According to the XRD structural analysis, the crystal has a tetragonal symmetry, so birefringent domains with extinction angles at 0° and 90° to the \(<100>_{\text{cub}}\) direction are expected when observed on a \((001)_{\text{cub}}\) platelet. However, as shown in Figure 4.3(a) and Figure 4.3(b), the \((001)_{\text{cub}}\) crystal appears to be optically isotropic, showing extinction at any positions (angles) under crossed polarizers, which indicates an apparent cubic symmetry. The inserted photos in Figure 4.3(a) and Figure 4.3(b) were taken with a sensitive tint plate \((\lambda = 530 \text{ nm})\) placed between the sample and analyzer to
differentiate small optical rotations visually by color and to reveal the presence of the optically isotropic crystal under crossed polarizers. The birefringence observed in a small area on top-right part of the crystal seems to arise from an inclined (broken) edge, suggesting that platelets of other orientations might be birefringent.

The (011)\textsubscript{cub}-cut platelet was then examined by PLM. As shown in Figure 4.3(c) and Figure 4.3(d), the (011)\textsubscript{cub}-cut platelet appears to be birefringent and shows extinction only when the [010]\textsubscript{cub} edge is parallel to the polarizer or analyzer, suggesting that the axes of the optical indicatrix section are parallel to the [010]\textsubscript{cub} and [101]\textsubscript{cub} directions. This type of extinction is consistent with the tetragonal symmetry. The weak residual birefringence in Figure 4.3(c), where the sample is at extinction position, could be induced by the internal stress of the crystal. It vanishes at high temperature once the stress is released. Interestingly, no distinct domain boundaries are observed, and instead the crystal exhibits clean interference color fringes and appears to be homogenously “monodomain” [Figure 4.3(d)]. However, such a monodomain state is thermodynamically unstable and is normally unlikely to form. Instead, the homogeneous birefringent state may arise from the formation of very fine domains, as depicted from the fine lines observed at the extinction position in Figure 4.3(c) (see below for a more detailed explanation).
Figure 4.3  Room temperature PLM images of a (001)$_{\text{cub}}$ (a, b) and a (011)$_{\text{cub}}$ (c, d) the PZT (x = 0.54) platelets with different polarizer/analyzer configurations: (a) and (c): the polarizer/analyser are parallel to the $<010>_{\text{cub}}$ direction; (b) and (d): the polarizer/analyser are at 45° to the $<010>_{\text{cub}}$ direction. The inserted photos in (a) and (b) were taken with a sensitive tint plate ($\lambda = 530$ nm) placed between the sample and analyzer.

Upon heating, the birefringence gradually vanishes when the (011)$_{\text{cub}}$-cut platelet undergoes a phase transition from the anisotropic tetragonal phase to an isotropic cubic phase that shows extinction at any angles (Figure 4.4).
Figure 4.4  PLM images of a (011)\textsubscript{cub} platelet observed under the same positions (angles) of crossed polarizers upon heating at (a) 30 °C, (b) 100 °C, (c) 200 °C and (d) 400 °C.

The variation of the birefringence of the crystal as a function of temperature was measured simultaneously and the result is shown in Figure 4.5. The birefringence decreases continuously and drops to zero upon the phase transition from the ferroelectric tetragonal phase to the paraelectric cubic phase at $T_C = 406$ °C.
It is known that in a ferroelectric tetragonal phase of perovskite structure, there are six ferroelectric domain states corresponding to six spontaneous polarization directions ($P_S$). The $P_S$ vectors are oriented along the six equivalent $<001>_{\text{cub}}$ directions, which can be represented by the three pairs of points (1/2, 3/4, and 5/6) in Figure 4.6(a). The paired domain states that have antiparallel (180°) polarizations, like the states of pair 1/2, have the same lattice deformation or spontaneous strain, so they are ferroelastically identical. Therefore, in a ferroelectric tetragonal crystal, there are only three types of ferroelastic domain states, namely domain states a, b, and c, where “a” denotes the ferroelastic domain that involves the ferroelectric states 1/2, and “b” and “c” are the denotations for the other two ferroelastic domains with the ferroelectric domains 3/4, and 5/6, respectively. These ferroelastic domains can be distinguished by their optical indicatrices, which are represented by the revolutionary ellipsoids in Figure 4.6(a). The orientations of the indicatrices are coupled to the crystallographic axes according to the symmetry of the phase.

**Figure 4.5** Temperature dependence of the birefringence of a (011)$_{\text{cub}}$-oriented PZT ($x=0.54$) single crystal measured upon heating.
Intersection of the indicatrix with a major crystallographic plane [e.g. (001)\textsubscript{cub}, (011)\textsubscript{cub}, or (111)\textsubscript{cub}] of a sample is usually an ellipse with two perpendicular main axes representing the ordinary refractive index $n_o$ (perpendicular to the optical axis) and the extraordinary refractive index $n_e$ (along the optical axis). In a (001)\textsubscript{cub}-cut platelet of a tetragonal crystal, the configuration of the indicatrix sections of the three above-mentioned ferroelastic domain states is displayed in Figure 4.6(b). Specifically, $c$-domains on the (001)\textsubscript{cub} platelet would be optically isotropic under crossed polarizers as their crystallographic z-axis is aligned perpendicular to the plane of the platelet, i.e. their optical axis is parallel to the direction of observation. The indicatrix sections of a- and b-domains are practically perpendicular to each other and they appear to be birefringent ($\Delta n = n_e - n_o \neq 0$) with the extinction angle at $\theta = 0^\circ$ and/or $90^\circ$ to the $<001>$\textsubscript{cub} directions. In the case of a (011)\textsubscript{cub}-cut platelet, the three possible indicatrix sections of the three domain states are shown in Figure 4.6(c). They are oriented either parallel or perpendicular to each other with the extinction angles for all of them being at $\theta = 0^\circ$ and/or $90^\circ$ to the [101]\textsubscript{cub} directions.
Figure 4.6 (a) Ferroelectric domain states of a perovskite tetragonal P4mm phase represented by the spontaneous polarization (P_s) vectors (1-6). Three ellipsoids illustrate the optical indicatrices of the three ferroelastic domain states a, b and c, respectively. (b, c) The possible ferroelastic domains with the corresponding configurations of the indicatrix sections on a (001)_cub platelet and a (110)_cub platelet, respectively. Each of the ferroelastic domains may contain two ferroelectric domains.

To visualize the birefringence of a domain, there must be a difference between the values of n_e and n_o, in other words, Δn = n_e - n_o ≠ 0. When formed upon cooling through T_C, the three types of domains (a, b and c) have equal probabilities to develop. If the sizes of these domains are very small (close to nanometer scale), there will be a large number of domains stacking on top of each other even in a thin crystal platelet. The overall birefringence of the platelet is determined by Δn = Σ \{ (Δn_a + Δn_b + Δn_c) = Σ \{ [(n_e - n_o)a - (n_e - n_o)b] + (n_o - n_c)c \}, where “\iota” indicates an individual ferroelastic nanodomain a, b and c. For a (001)_cub-cut platelet, a stack of many a-, b- and c-domains may be realized as shown in Figure 4.7(a), which statistically leads to a zero net
birefringence ($\Delta n = 0$) on average, i.e., the crystal behaves like an optically isotropic medium.

In the case of a (011)$_{\text{cub}}$-cut platelet, the possible stacking of the a, b and c domains is schematically shown in Figure 4.7(b), giving rise to an overall birefringence of $\Delta n = \sum (\Delta n_{a_i} + \Delta n_{b_i} + \Delta n_{c_i}) = \sum [(n'_e - n_o)_{a_i} + (n'_e - n_o)_{b_i} - (n_e - n_o)_{c_i}]$. Even though the three different type domains are superimposed on each other, the compensation of the birefringence cannot be complete due to the different orientations and shapes of the indicatrix sections. As a result, a non-zero net birefringence appears when observed along the $<001>_{\text{cub}}$ direction, in other words, $\Delta n \neq 0$, leading to a relatively small net birefringence.

These two domain structure modes based on crystal optical principles and optical crystallographic analysis allow us to explain the unusual optical isotropic behaviour observed on the (001)$_{\text{cub}}$-cut PZT platelet of tetragonal symmetry and the optical anisotropy with a birefringence detected on the (011)$_{\text{cub}}$ platelet. It should be noted that the ferroelectric/ferroelastic domains are usually comparatively large (~μm size) and/or preferably oriented in normal ferroelectric crystals so that the polarized light ray passes through few domains having different directions of optical indicatrix.[134] As a result, the crystals are typically highly anisotropic even in a polydomain state. The effect of compensation of birefringence observed here suggests that the domains in this crystal must be miniaturized, and the size could be on nanometer scale. This provides the first evidence for the existence of nanodomains in a tetragonal PZT single crystal.
4.4.2. **Square-shaped polar microdomains**

In principle, application of an electric field to a ferroelectric crystal will result in domain rearrangements, and the changes in crystal lattice parameters and electron density, leading to changes in refractive indices and birefringence through the electro-optical effect. To study the effect of electric field on the domain structure of PZT (x = 0.54) crystals, a (001)\textsubscript{cub} platelet with two [010]\textsubscript{cub} edges covered by silver paste is used (see Figure 4.1). The thickness of the sample is 100 μm. As shown in Figure 4.8(a), at zero field, the (001)\textsubscript{cub} platelet of PZT (x = 0.54) crystal is optically isotropic due to the total compensation effect of the differently oriented tetragonal nanodomains, as explained above. When a dc field is applied along the <100>\textsubscript{cub} direction, the sample becomes brighter and brighter under crossed polarizers due to the domain reorientation, domain wall motion and possible electro-optical effect [Figure 4.8(b) and Figure 4.8(c)].
In addition, square-shaped “islands” become visible at different locations scattered across the entire sample surface [Figure 4.8(c) and Figure 4.8(d)]. It is clear that the edges of the islands are oriented in the $<110>$$_{cub}$ directions and the average size is measured to be about 12 μm. They appear to be isotropic or weakly birefringent in the electric field range of 1 to 15 kV/cm. After removal of the field, the induced square-shaped islands become invisible again and the crystal platelet returns to be homogeneously optically isotropic.
Figure 4.8  PLM micrographs of the (001)\textsubscript{cub} PZT (x = 0.54) single crystal platelet imaged with the crossed polarizers at 45 ° to the <100> cub direction under the application of electric field along the <100> cub direction (a) 0 kV/cm, (b) 5 kV/cm, (c) 10 kV/cm and (d) an enlarged view of the marked rectangle region in (c). (The spot marked by the red circle in (c) is where the experiment in Section 4.4.3 is performed.)

We suspect that these islands could arise from ferroelectric polar domains. In order to study the nature of these islands, the sample platelet is examined by PFM. Figure 4.9(a) and Figure 4.9(b) show the PFM out-of-plane phase images obtained on two different locations of the (001)\textsubscript{cub} platelet. We observe very similar square-shaped patterns with a sharp contrast to the surrounding area. Such a phase contrast indicates polar nature of the domains. The domains are slightly different in size and the smaller one shows a more rounded-corner square shape. The average size is about 12 μm and the edges are aligned in the <110>\textsubscript{cub} directions, which is consistent with the size and shape of the “islands” observed by PLM. In order to exclude the possible residual
influence of electric field, which was previously applied during the optical observation, PFM was performed on another (001)$_{\text{cub}}$ platelet cut from the same as-grown PZT (x = 0.54) single crystal. Again, similar domain patterns in terms of shape, size and orientation are observed. This confirms that these square-shaped domains are real and they exist in the sample prior to applying an electric field. For the both images in Figure 4.9(a) and Figure 4.9(b), the polarization of the dark square region is oriented downward, whereas, the surrounding (bright) region is polarized upward (out of paper).

**Figure 4.9** PFM out-of-plane phase images at two different locations across the sample surface. The directions of the polarizations inside and outside square domain are marked (lines are polishing scratches on the sample surface).

To study the reversible polarization switching phenomenon of the domains, a dc bias field of different magnitudes is applied on an area of $20 \times 20$ $\mu$m covering the square domain shown in Figure 4.9(a), through the conductive tip. As shown in Figure 4.10, the out-of-plane images were taken after poling with different bias voltages and polarities, $E = 10$ V, 20 V, 30 V, -10 V, -20 V, -30 V and -35 V. A positive voltage corresponds to a field pointing downward. With increasing positive voltage to 30 V, the bright region with an upward $P_s$ (pointing out the page) becomes dark, indicating that the polarization has been switched downward (into page) [Figure 4.10(c)]. A negative switching voltage is then applied to the same area to reverse the polarization. With increasing negative voltage, the dark monodomain gradually becomes brighter and brighter, and at -35 V, the area is completely switched to a homogeneously bright monodomain with polarization upward [Figure 4.10(f)]. The PFM results provide the evidence for the $180^\circ$ phase difference between the “islands” and the surrounding
regions, confirming the polar nature of the domains. Once the regions are polarized, the polarizations remain upward (bright area) or downward (dark area).

![Image](image1.png)

**Figure 4.10** Ferroelectric domain switching realized and imaged by PFM under an applied bias voltage of: (a) 10 V, (b) 20 V, (c) 30 V, (d) -10 V, (e) -30 V, and (f) -35 V.

One of the significant advantages of the PFM technique is that it can provide information for both a-domains (in-plane polarization) and c-domains (out-of-plane polarization) of a tetragonal phase. As shown in Figure 4.11, it seems that the square-shaped domain (marked by red square) is of c-type and it is embedded in a matrix consisting of a- and c-nanodomains. The optical indicatrix of this square-shaped domain is parallel to the $<001>_{\text{cub}}$ direction, therefore, it behaves optically isotropic and cannot be distinguished from the nanodomain matrix by PLM under crossed polarizers on the (001)$_{\text{cub}}$ platelet without electric field. However, the application of an electric field along the $<100>_{\text{cub}}$ direction could cause inclination of the indicatrix by a certain angle and consequently, the contrast between the “island” c-domains and the surrounding domains is enhanced, making the “islands” visible under PLM (see Figure 4.8).
The out-of-plane piezoresponse was measured as a function of applied voltage. The PFM hysteresis loops in terms of amplitude and phase vs. voltage are shown in Figure 4.12. Figure 4.12(a) and Figure 4.12(b) show the amplitude and phase variations with the field for the downward-polarized “island” domain (dark region), respectively. A symmetric butterfly shape is displayed for the amplitude response, revealing typical piezoelectric behaviour of a bipolar ferroelectric crystal, which is consistent with the observed single polar domain state. The phase response is also symmetrical with regard to the applied ± voltages, revealing a sharp switching of 180° polarization. Figure 4.12(c) and Figure 4.12(d) give the amplitude and phase response for the surrounding bright area (overall) upward-polarized, respectively. It can be seen that both curves are asymmetrical with regard to the applied ± voltages, and shifted toward the negative field, indicating a voltage offset which could arise from internal bias field due to the interaction of charged domain walls. Roelofs et al. has demonstrated that 90° domain walls represent an obstacle for the motion of 180° walls.[135] Since both a- and c-domains exist in the bright region, there must be both 90° and 180° domain walls. The electrostatic interaction between 180° and 90° domain walls can inhibit the motion and switching of the former by 180° domains, giving rise to an asymmetric butterfly and an off-set hysteresis loop. On the other hand, there might be charged “head-to-head” and “tail-to-tail” 90° domain walls, which could act as crystal defects in a multidomain sample.[7]
The existence of flux-closure domain states or vortex domains were theoretically predicted and experimentally observed in PZT within a wide range of composition.[131], [136]–[138] Recently, Jia et al. directly observed continuous rotation of the dipoles closing the flux of 180° domains in PZT thin films.[130] In our work, the domains are also on nanometer scale, so flux-closure domain state could possibly arise from finite size effects and boundary conditions.[138] On the other hand, under the influence of an external field, the domain can grow through the sidewise motion of the 180° domain wall.[139]–[141] The formation of square-shaped domains in this PZT (x = 0.54) single
crystal sample could have involved three steps (Figure 4.13): (1) a circular 180° flux-closure domain is nucleated in the tetragonal nanodomain state (Figure 4.13 (a)); (2) the small circular flux-closure domain reaches its critical size and grows into a large one (Figure 4.13(b)), and (3) due to the anisotropic bonding in the unit cell of the PZT crystal, the growth rate along the $<001>_{\text{cub}}$ direction is faster than along $<110>_{\text{cub}}$, leading to a square-shaped microdomains (Figure 4.13 (c)). The formed domain shape can be determined by the rate of wall motion steps, which is a function of the orientation of the boundary surface. From the view point of the oxide chemistry and local structure of PZT solid solution, there are strong bonding interactions between Zr/Ti atoms and O atoms along the $<001>_{\text{cub}}$ direction of the perovskite unit cell. However, along the $<110>_{\text{cub}}$ direction, the main force is the repulsive interactions between Zr/Ti atoms and Pb atom. Therefore, the domain growth velocities, which are governed by the interplay of bonding and repulsive interactions, are different. In the current case, the domain growth velocity in the $<100>_{\text{cub}}$ direction is faster than that in the $<110>_{\text{cub}}$ direction. As a result, the final domain is stabilized in a square shape with edges oriented in the $<110>_{\text{cub}}$ directions. This also explains the previous experimental observation that the smaller domains look more round-sided than the larger ones (see Figure 4.9). Although similar kind of square-shaped domains is observed in BaTiO$_3$ single crystals,[141], [142] it is the first time that this kind of domain patterns has been found in PZT ferroelectrics.

**Figure 4.13** Schematics showing the formation of square-shaped ferroelectric domains: (a) a circular flux-closure is nucleated; (2) the domain wall expands through side-wall motion; (c) a square-shaped domain formed due to the different growth velocities along the $<100>_{\text{cub}}$ and the $<110>_{\text{cub}}$ directions.
4.4.3. Electric field-induced monoclinic phase

The variations of birefringence and extinction angle were measured on the nanodomain region (marked by the red circle in Figure 4.8(c)) as a function of electric field applied in the \( <001>_{\text{cub}} \) direction. This induced birefringence is typically a linear function for most of ferroelectrics.[23] Here, as shown in Figure 4.14(a), it shows two different slopes, indicating two different phases. Specifically, when the applied field is less than 5 kV/cm, the birefringence increases linearly at a relatively smaller slope value \( (m_1 = 0.143) \) compared to that \( (m_2 = 0.203) \) at fields higher than 5 kV/cm. The extinction angle was measured with respect to the \( <100>_{\text{cub}} \) direction and plotted in Figure 4.14(b). When the electric field is less than 5 kV/cm, the platelet is in the extinction position with crossed polarizers at 90° to the \( <100>_{\text{cub}} \) direction, which is consistent with the optical behaviour of a tetragonal symmetry. It can be seen that the extinction angle undergoes an abrupt “jump” from 90° to 97° when the magnitude of the field reaches 5 kV/cm, and then continues to increase gradually with the further increase of the applied field. The “anomalies” in the birefringence and extinction angle suggest that a new phase has been induced in the tetragonal PZT \( (x = 0.54) \) platelet when the applied electric field reaches a critical value of \( E_c = 5 \text{kV/cm} \).
Figure 4.14 Variations of (a) the birefringence and (b) the extinction angle, measured on a (001)$_\text{cub}$ PZT (x = 0.54) platelet, as a function of electric field that is applied in the $<$100$>_{\text{cub}}$ direction.
The gradual increase of the extinction angle is a signature of a monoclinic (M) phase, whose polarization is allowed to rotate within one of the mirror plane, leading to the change in the extinction angle as a function of temperature. Among the three types of M phases, MA and MB belong to the Cm space group while MC belongs to the Pm space group. In addition, the polarizations (Ps) of both MA and MB lie in the (110)cub plane and the Ps of MC is in the (100)cub plane.[143] Therefore, it is reasonable to believe that the induced M phase in the PZT (x = 0.54) (001)cub platelet crystal is of MC type. Figure 4.15(a) and Figure 4.15(b) schematically illustrate the possible variants of the prototype cell deformation in the tetragonal P4mm (T) and monoclinic Pm (MC) phases, respectively. Each of the directions represents a ferroelastic orientation state and can be considered as parallel to the principle axis of the corresponding optical indicatrix. There are 3 ferroelastic domain states (denoted as a, b and c) and 6 ferroelectric domains in a T symmetry. In a MC symmetry, there are 12 ferroelastic domain states (denoted as 1, 2, …12), with each allowing two antiparallel polarization states, i.e. 24 ferroelectric domains in total.

Figure 4.15 Schematic drawing of the possible ferroelastic orientation states in the (a) tetragonal (T) P4mm phase (denoted as a, b and c), and (b) monoclinic (MC) Pm phase (denoted as 1, 2, …12). The arrows indicate one half of the possible ferroelectric domain state.

To distinguish the different phases we analyze the extinction positions and the directions of domain walls in the crystal plates. The possible extinction positions of the ferroelastic domains on a (001)cub platelet (as shaded in Figure 4.15(a) and Figure 4.15(b)), for the T and MC phases are shown in Figure 4.16(a) and Figure 4.16(b),
respectively. When an electric field is applied along the [100]\textsubscript{cub} direction, the $P_s$ opposite to the electric field will start to decrease in magnitude, but the involved ferroelastic domain states still stays as a tetragonal phase at low field. Thus, the sample shows extinctions at $\theta = 0^\circ$ and $90^\circ$ with respect to the $<100>_{\text{cub}}$ direction. Once the magnitude of the electric field reaches a threshold value (e.g. $E_c = 5$ kV/cm in this case), the $P_s$ in the perpendicular direction (state a) starts to rotate continuously, and consequently, a monoclinic $M_C$ phase with different extinction angles is induced. Upon further increase of electric field, the polarization of the $M_C$ phase continues to rotate within the mirror plane, causing the extinction angle to change accordingly. Note that, the maximum magnitude of the applied electric field (15 kV/cm) is much smaller than the coercive field (44 kV/cm), so the $P_s$ is not switched completely, and once the electric field is removed, the original domain state is restored. Therefore, the electric field induced T to $M_C$ phase transition is reversible under the field strength up to 15 kV/cm.

![Figure 4.16](image)

Figure 4.16 Possible extinction positions of domains on a (001)\textsubscript{cub} crystal platelet of (a) tetragonal and (b) monoclinic phases.

4.4.4. Birefringence induced by external stress

To investigate the effect of mechanical stress on the optical properties of the PZT ($x = 0.54$) single crystal, stress was also applied by means of a Low Temperature Uniaxial Stress Application Device. The detailed technical description of this system can be found in Ref.132.[132] The sample is nearly optically isotropic without stress due to the nanodomain compensation effect (Figure 4.17(a)), as explained in Section 4.4.1. With the increase of stress, birefringence appears in the middle region of the sample. Figure 4.17(b) and Figure 4.17(c) show the induced birefringence with an applied stress.
of $75 \times 10^7$ and $150 \times 10^7$ N/cm$^2$, respectively. The top and bottom parts of the crystal stay isotropic because the sapphire jaws were not completely in contact with the crystal edges, which is caused by a slight lack of parallelism of the larger (001)$_{\text{cub}}$ border facets. It is found that the birefringence disappears immediately after the removal of external stress. So this stress-induced birefringence is a reversible process.

![Figure 4.17](https://via.placeholder.com/150)

**Figure 4.17** (a) Photographs showing the direction of the applied stress with regard to the crystal orientation and induced birefringence by a stress of (b) $75 \times 10^7$ N/cm$^2$ and (c) $150 \times 10^7$ N/cm$^2$, with extinction at 45° to the $<100>_{\text{cub}}$ direction.

The variation of the induced birefringence versus the applied stress for the PZT $(x = 0.54)$ (001)$_{\text{cub}}$ platelet is presented in Figure 4.18, which shows a linear and reversible relation. This phenomenon is known as the piezo-optical effect of the materials.[144] The application of stress to crystals can in general give rise to a slight, thermodynamically reversible distortion of the crystal lattice, and thereby to an anisotropic deformation of the optical indicatrix, leading to a small induced birefringence. It is interesting to note that the square-shaped microdomains are not revealed by the applied stress.

The difference between employing a stress and applying electric field is that, the stress directly affects the unit cell while the electric field exerts an indirectly influence on the crystal lattice via rearrangements of the $P_S$ and the electron density. The results obtained here provide further evidence of the polarity of the square-shaped microdomains, which is not sensitive to stress and only give contrast or become visible under PLM by applying an electric field.
Figure 4.18 Linear and reversible variation of induced birefringence as a function of applied stress measured on a (001)$_{\text{cub}}$ platelet of the PZT (x = 0.54) crystal.

4.5. Conclusions

In conclusion, single crystals of PbZr$_{1-x}$Ti$_x$O$_3$ (x = 0.54) were grown by a top seeded solution growth (TSSG) method and the symmetry of the crystals was confirmed to be tetragonal by structural refinement based on X-ray diffraction data. However, the analysis of domain structure by polarized light microscopy (PLM) reveals that the (001)$_{\text{cub}}$ platelet of the crystal behaves isotropically, with extinction at any positions under the crossed polarizers, i.e. showing a seemingly cubic symmetry. On the other hand, the (011)$_{\text{cub}}$ platelet exhibits birefringence with extinctions at 0°/90° to the $<100>_{\text{cub}}$ direction, which is consistent with the optical feature of a tetragonal phase. These phenomena are attributed to the presence of differently oriented miniaturized domains or nanodomains of tetragonal symmetry. These nanodomains are statistically arranged in such a way that they compensate each other almost completely along the $<001>_{\text{cub}}$ direction on the (001)$_{\text{cub}}$ platelet, but incompletely along the $<001>_{\text{cub}}$ direction on the (011)$_{\text{cub}}$ platelet. The induced birefringence on the (001)$_{\text{cub}}$ platelet is investigated by applying an electric
field and an external stress in the $<100>_{\text{cub}}$ direction. Upon application of an electric field in the $<100>_{\text{cub}}$ direction, square-shaped domains with edges oriented in the $<110>_{\text{cub}}$ direction are observed by PLM. They are confirmed by piezoresponse force microscopy (PFM) to be 180° ferroelectric domains with an average size of 12 μm. The formation of these domains is due to the nucleation and growth of 180° flux-closure state in the crystal. Three steps are involved in this process: (1) a circular 180° flux-closure domain is nucleated in the tetragonal nanodomain state; (2) the small circular flux-closure domain reaches its critical size and grows into a large one, and (3) due to the anisotropic bonding in PZT crystal unit cell, the growth rate along the $<001>_{\text{cub}}$ direction is faster than along the $<110>_{\text{cub}}$, leading to a square-shaped microdomains. The different growth velocities along different direction are attributed to the corresponding interplay of bonding and repulsive interactions. Such a complex domain structure is observed for the first time in the tetragonal crystal and it reveals some fascinating insights into the microstructure of PZT single crystals. In addition, a monoclinic ($M_\text{C}$) phase is induced in the tetragonal nanodomains by application of the electric field. Moreover, the variation of the induced birefringence vs. the applied stress shows a linear and revisable relation for the $(001)_{\text{cub}}$ platelet of the single crystal. These results obtained on the PZT ($x = 0.54$) single crystal contribute to a better understanding the structure-property relationships of this technologically important system.
Chapter 5.

Growth and Characterization of Donor (La$^{3+}$ and Bi$^{3+}$)-Doped PbZr$_{1-x}$Ti$_x$O$_3$ (PZT) Single Crystals

5.1. Abstract

Donor (La$^{3+}$ and Bi$^{3+}$)-doped single crystals of PbZr$_{1-x}$Ti$_x$O$_3$ (PZT) have been successfully grown for the first time by a top-cooled solution growth method (TCSG) and a top-seeded solution growth method (TSSG). The compositions of the as-grown single crystals are analyzed, in terms of the ratio of Zr$^{4+}$ to Ti$^{4+}$, by laser-ablation inductively coupled plasma mass spectrometry (LA-ICP-MS) and energy dispersive spectroscopy (EDS). X-ray powder diffraction technique is used to analyze the structure of these crystals. The electrical properties of the crystals are studied by various methods. All three batches (#1, #2 and #3) of La$^{3+}$-doped PZT (La-PZT) single crystals are found to be Zr-rich and the symmetry is confirmed to be rhombohedral by X-ray powder diffraction. The highest paraelectric to ferroelectric phase transition temperature, the Curie temperature $T_C = 291 \, ^\circ C$, is obtained for La-PZT (#3) single crystals. The highest remnant polarization reaches $P_r = 24.5 \, \mu C/cm^2$ with a coercive electric field $E_c = 6.1 \, kV/cm$ for La-PZT (#2) crystals. The domain structure on a (001)$_{cub}$-cut platelet of the La-PZT (#1) single crystal is investigated by means of both polarized light microscopy (PLM) and piezoresponse force microscopy (PFM). On the other hand, the compositions of two batches (#1 and #2) of Bi$^{3+}$-doped PZT (Bi-PZT) single crystals are also found to be Zr-rich and their symmetry is confirmed to be rhombohedral by X-ray structural analysis. The $T_C$ values of Bi-PZT (#1) and Bi-PZT (#2) are 352 °C and 354 °C, respectively. The domain structure and phase transition behaviour of a (001)$_{cub}$-cut Bi-PZT (#1) crystals are investigated by PLM. The effects of Bi$^{3+}$ doping on the electrical properties of PZT single crystals are rather complex and different from the ceramics due to the multi-valence state of Bi ions.
5.2. Introduction

Lead zirconate-titanate solid solution, PbZr$_{1-x}$Ti$_x$O$_3$ (PZT), has been studied extensively over the past decades for fundamental research, but almost exclusively in the forms of ceramics because of the difficulties encountered in the growth of PZT single crystals.[97] On the other hand, in technological applications, PZT ceramics are always modified via doping with different (donor or acceptor) dopants to improve and optimize their electromechanical properties for specific application purposes.[3] In the case of donor doping, cation vacancies are created to achieve the electron neutrality condition of the perovskite structure. As an example, when Nb$^{5+}$ is substituting for Ti$^{4+}$, vacancies on the lead site will form. On the one hand, the lead vacancies could minimize local stresses in the lattice, which in turn facilitates domain wall motion. On the other hand, defect dipoles could be formed between the negatively charged lead vacancies and the dopant Nb$^{5+}$ ions. These defect dipoles should be immobile, since both species are immobile near room temperature.[26] Such immobile defect dipoles will produce random electric fields and strain that locally destabilize the domain structure.[27] As a result, the mobility of domain walls will increase thanks to the lowered stability of the domain structure against external mechanical or electric fields. It is well known that the domain wall motion plays an important role in the extrinsic contribution of the piezoelectric effect of PZT solid solution.

In general, donor doping leads to electrically “soft” PZT ceramics with large piezoelectric coefficients, large permittivity, high electrical losses, large electromechanical coupling factors, very high electrical resistance, low mechanical quality factors, and a low coercive field.[13], [28], [30] Among numerous attempts that have been made to improve the properties of PZT, lanthanum (La$^{3+}$) modification has proven itself to be one of the most successful techniques and is the most commonly used method for electro-optic applications due to its transparency.[26], [145] Meanwhile, it was found that La$^{3+}$ addition reduces the Curie temperature (T$_C$) in a linearly decreasing manner at a rate of approximately 37 °C per atom percent (at.% La$^{3+}$).[146], [147] Furthermore, for a PZT (x $\approx$ 0.35) ceramic, when the doping level of La$^{3+}$ is between 4-9 at.%, the ferroelectric to paraelecteric phase transition shows relaxor behaviour.[148] On the other hand, bismuth (Bi$^{3+}$) is of particular interest as a Pb$^{2+}$
alternative due to its stereochemically active 6s² “lone-pair” electrons.[149], [150] And Bi³⁺ (2 at.%)-doped PZT \((x \approx 0.35)\) ceramics possess excellent ferroelectric and piezoelectric properties.[151]

From the application point of view, single crystals are expected to exhibit superior piezo-/ferroelectric performance over their ceramic counterparts. Therefore, it is of particular interest to grow single crystals of donor-doped PZT. In this work, we have synthesized three batches of La³⁺-doped PZT (La-PZT) single crystals and two batches of Bi³⁺-doped PZT (Bi-PZT) single crystals. Their domain structures, phase transitions and electrical properties are characterized in order to understand the structure-property relations.

### 5.3. Experimental

The starting materials, PbO (99.9%), ZrO₂ (99.9%), TiO₂ (99.9%), Bi₂O₃ (99.9%), and La₂O₃ (99.9%), were mixed according to the stoichiometry of the nominal composition \(\text{Pb}_{0.97}X_{0.02}\left(\text{Zr}_{0.4}\text{Ti}_{0.6}\right)\text{O}_3\) \((X = \text{La}^{3+} \text{ or Bi}^{3+})\). These mixed oxides of calculated amounts were put in a 100 ml platinum crucible and calcined at 800 °C in a furnace for 4 hours. The mixture of PbO and B₂O₃ with a molar ratio of 4:1 was used as flux. The flux was added into the calcined mixture with a flux:charge molar ratio of 5:1 for the growth of La-PZT (#1). This ratio was changed to 4:1 in the growth of La-PZT (#2) and La-PZT (#3) single crystals. The flux to charge molar ratio for the growth of both Bi-PZT (#1) and Bi-PZT (#2) crystals was 5:1. The mixture of solute and solvent was loaded into a 100 ml platinum crucible. The top-cooled solution growth (TCSG) method (see Chapter 7 for details) was used for the growths of La-PZT (#1) and La-PZT (#2). The technique used for the growth of La-PZT (#3) was top-seeded solution growth (TSSG) method (as introduced in Chapter 3). The two batches of Bi-PZT (#1) and Bi-PZT (#2) crystals were grown by the TCSG method. The detailed thermodynamic parameters and growth condition are listed in Table 5.1.
<table>
<thead>
<tr>
<th>Growth Batch</th>
<th>Flux/Charge (mol %)</th>
<th>( T_1 (°C) )</th>
<th>( T_2 (°C) )</th>
<th>Cooling Rate ( R_1 (°C/day) )</th>
<th>Growth Method</th>
</tr>
</thead>
<tbody>
<tr>
<td>La-PZT (#1)</td>
<td>5:1</td>
<td>1150</td>
<td>1000</td>
<td>4</td>
<td>TCSG</td>
</tr>
<tr>
<td>La-PZT (#2)</td>
<td>4:1</td>
<td>1150</td>
<td>1000</td>
<td>4</td>
<td>TCSG</td>
</tr>
<tr>
<td>La-PZT (#3)</td>
<td>4:1</td>
<td>1150</td>
<td>1000</td>
<td>4</td>
<td>TSSG</td>
</tr>
<tr>
<td>Bi-PZT (#1)</td>
<td>5:1</td>
<td>1150</td>
<td>1090</td>
<td>4</td>
<td>TCSG</td>
</tr>
<tr>
<td>Bi-PZT (#2)</td>
<td>5:1</td>
<td>1130</td>
<td>1070</td>
<td>4</td>
<td>TCSG</td>
</tr>
</tbody>
</table>

The compositional homogeneity of the specimens was verified using laser ablation-inductively coupled plasma-mass spectrometry (LA-ICP-MS) and energy dispersive spectroscopy (EDS). The crystal structure of the as-grown crystals was analyzed by X-ray diffraction (XRD) on fine powder obtained by grinding a number of small crystals (Bruker D8 Advance Diffractometer). The resulting diffraction data was analyzed using TOPAS Academic Software to determine the symmetry and to refine the lattice parameters. Crystal platelets from each batch of La-PZT (#1), La-PZT (#2) and Bi-PZT (#1) were cut parallel to the \((001)_{\text{cub}}\) plane and polished to optical quality using silicon carbide sand paper and lapping sheets. The domain structure was examined by polarized light microscopy (PLM), using an Olympus BX60 microscope equipped with a Linkam THMS600 heating/cooling stage. Local piezo-/ferroelectric response was characterized on a \((001)_{\text{cub}}\) sample platelet of La-PZT (#1) by means of piezoresponse force microscopy (PFM) at room temperature, using a Bruker Dimension Icon microscope (located at Xi’an Jiaotong University, China). Moreover, the dielectric properties of the grown crystals were measured using a Novocontrol Alpha high-resolution broadband dielectric analyzer equipped with a Novotherm heating system. The ferroelectric properties of the donor-doped PZT single crystals were displayed on the \((001)_{\text{cub}}\) platelets by means of a Radiant RT-66 standardized ferroelectric testing system. The samples were kept in a silicon oil bath to avoid electric arcing during the polarization switching.
5.4. Results and discussion

5.4.1. Crystal growth and composition analysis

Figure 5.1 shows the as-grown La-PZT and Bi-PZT single crystals. For the La-PZT single crystals, all the thermodynamic parameters were the same for the growth of La-PZT (#1) and La-PZT (#2) except the flux/charge molar ratio. It can be seen that a relatively low flux to charge ratio has significantly improved the crystal size and quality. Therefore, a lower flux/charge ratio (4:1) was subsequently used in the growth of La-PZT (#3), for which a TSSG method was employed. In addition to the crystal size, the crystallinity of the as-grown single crystals is improved as well in the growth of La-PZT (#3). In the case of the Bi-PZT single crystals, the growth temperature ranges were adjusted so as to optimize the composition. It can be seen that Bi-PZT (#2), which was grown at a relatively low temperature, overall shows better morphology and crystallinity compared with the Bi-PZT (#1). According to our previous study,[90] the PZT crystals formed at a lower temperature tend to have a higher Ti$^{4+}$ concentration.

For compositional analysis by LA-ICP-MS, laser ablation was performed by several parallel line scans across the polished (001)$_{\text{cub}}$ platelets of the La-PZT (#1) and La-PZT (#3) crystal in Time Resolved Mode in order to detect the variation of composition from core to rim by looking at the time-resolved variation in signal response.
As shown in Figure 5.2(a), the signals of Ti$^{4+}$ and La$^{3+}$ show slight fluctuations while the other two elements (Pb$^{2+}$, Zr$^{4+}$) give a relatively smooth curve in the La-PZT (#1) crystal. The higher concentration of Ti$^{4+}$ (marked by gray circle) on the edges of the sample could arise from phase segregation. For the crystal of La-PZT (#2), laser ablation was carried out on ten different positions on the crystal surface. It was found that the concentrations of all ions exhibit fluctuations. In particular, the Ti$^{4+}$ ion varies up to ±20% across the sample surface. Figure 5.2(b) displays the ablation results of the La-PZT (#3) crystal, it is clearly seen that this crystal shows better homogeneity with stable signal response, which is not surprising as the TSSG method is known to be able to improve the crystal homogeneity.

An undoped PZT ($x = 0.54$) single crystal from previous growth (see Chapter 3) was used as reference to determine the concentrations of the Zr$^{4+}$ and Ti$^{4+}$ ions on the B-site in the La-PZT single crystals. The calculated percentages of Ti$^{4+}$ on the B-site of the perovskite structure are between 0.30 - 0.35 for all the sample of the three batches. Unfortunately, no single crystal containing La$^{3+}$ was available as reference and the doping level of La$^{3+}$ could not be determined quantitatively. However, the strong signal response of La$^{3+}$ detected by LA-ICP-MS confirmed the incorporation of La$^{3+}$ into the PZT single crystals.
Figure 5.2  LA-ICP-MS patterns of a (001)_{cub-cut} platelet of (a) La-PZT (#1) and (b) La-PZT (#3) single crystals, respectively.

The laser ablation signals of all the elements in the sample of Bi-PZT (#1) are very stable in general, showing good homogeneity (Figure 5.3). The small peaks (marked by asterisks) in the response curve of Bi^{3+} element, were believed to arise from an instrumental artifact. The calculated percentage of Ti^{4+} in the B-site of the perovskite
structure using PZT ($x = 0.54$) single crystal is around 0.31. Again, the doping level of Bi$^{3+}$ could not be determined due to the lack of proper reference.

![Graph](image)

**Figure 5.3** LA-ICP-MS patterns of a (001)$_{cub}$-cut platelet of Bi-PZT (#1) single crystals.

Energy dispersive spectroscopy (EDS) was performed on the surface of a Bi-PZT (#2) single crystal to analyze the elements present. As shown in Figure 5.4(a), elemental mapping of Pb$^{2+}$, Bi$^{3+}$, Zr$^{4+}$ and Ti$^{4+}$ indicates that these ions are distributed uniformly across the crystal. The corresponding EDS spectrum of these elements is shown in Figure 5.4(b). The composition analysis by this technique indicates that the Zr$^{4+}$/Ti$^{4+}$ ratio in this sample is around 62/38.
Figure 5.4  (a) Elemental mapping of Pb (green), Bi (brown), Zr (red), O (purple) and Ti (blue) using EDS on the surface of a Bi-PZT (#2) single crystal, and (b) EDS spectrum of Pb, Bi, Zr, and Ti.
5.4.2. Structure and property studies of La-PZT single crystals

5.4.2.1 Structural analysis

The structure of the as-grown La-PZT single crystals was analyzed by XRD. As shown in Figure 5.5, all three batches of La-PZT single crystals show a rhombohedral (pseudo-cubic) crystal structure with a broadened or asymmetric (111)$_{\text{cub}}$ peak. The small peaks indicated by the asterisks (*) are caused by flux oxides (PbO) attached onto the crystals, because XRD characterization was carried on the small-sized single crystals picked from the flux solids in order to preserve good-quality crystals. The resulting diffraction data was analyzed using TOPAS Academic Software to determine the symmetry and to refine the lattice parameters of the grown crystals.

![XRD patterns of the three batches La-PZT single crystals (on crushed powders).](image)

The refinement result for the (111)$_{\text{cub}}$ reflection is shown in Figure 5.6, where the measured data are displayed in the black solid curve, while the calculated result is
represented by the red dashed curve. The difference between the experimental and fitting data is indicated by the gray line. It is clear that La-PZT (#2) crystal shows a more obvious splitting compared with the other two crystals.

\[ \text{Figure 5.6} \quad \text{The enlarged XRD views of the } (111)_{\text{cub}} \text{ peaks of the three batches of La-PZT single crystals} \]

The calculated lattice parameters are listed in Table 5.2. It is noticed that the value of the rhombohedral distortion angle \( \alpha \) does not show any general trend while the lattice constant \( a \) decreases from 4.10797\( \text{Å} \) (La-PZT (#1)) to 4.10684\( \text{Å} \) (La-PZT (#3)). According to the information obtained from the Inorganic Crystal Structure Database,[152]–[154] both lattice constant \( a \) and distortion angle \( \alpha \) decrease with the concentration of Ti\(^{4+}\) in the rhombohedral region of undoped PZT solid solution. Therefore, it is concluded that La-PZT (#1) crystal possesses the highest Zr\(^{4+}\)/Ti\(^{4+}\) ratio among the three batches, while the La-PZT (#3) exhibits the lowest one. The abnormal behaviour of \( \alpha \) could be attributed to the incorporation level of La\(^{3+}\) ion into the A-site (Pb\(^{2+}\)) of the perovskite structure. Since the ionic radii of La\(^{3+}\) (1.03\( \text{Å} \)) and Pb\(^{2+}\) (1.19\( \text{Å} \)) ions are significantly different, the crystal unit cell must undergo distortion. And this distortion is reflected in the variation of angle \( \alpha \). The approximate compositions of the three batches crystals are also estimated based on their lattice parameters \( a \). As shown
in Table 5.2, all the three batches of crystals exhibit a very close $\text{Zr}^{4+}/\text{Ti}^{4+}$ ($\approx 67/33$) ratio, which is comparable with the previous LA-ICP-MS results. However, the slightly different $\text{Zr}^{4+}/\text{Ti}^{4+}$ ratios of these crystals could lead to difference in the temperature of the transition from ferroelectric to paraelectric phase as shown in the later experimental characterization of their dielectric properties.

Table 5.2 Calculated lattice parameters of the three batches of La-PZT single crystals.

<table>
<thead>
<tr>
<th>Batches</th>
<th>Zr/Ti</th>
<th>a (Å)</th>
<th>$\alpha$ (°)</th>
</tr>
</thead>
<tbody>
<tr>
<td>#1</td>
<td>66.72/33.28</td>
<td>4.10797 ± 0.00116</td>
<td>89.76258 ± 0.00395</td>
</tr>
<tr>
<td>#2</td>
<td>66.67/33.33</td>
<td>4.10785 ± 0.00283</td>
<td>89.72940 ± 0.00405</td>
</tr>
<tr>
<td>#3</td>
<td>66.23/33.77</td>
<td>4.10684 ± 0.00260</td>
<td>89.74219 ± 0.00566</td>
</tr>
</tbody>
</table>

5.4.2.2 Domain structures

The optical domain structure and phase transition of the La-PZT (#1) crystal were examined by means of polarized light microscopy (PLM) on a (001)$_\text{cub}$ platelet. The specimen is in extinction with crossed polarizers at 45˚ to the <100>$_\text{cub}$ direction, which confirms the rhombohedral symmetry of the single crystal [Figure 5.7(a)] (some inclusions could arise from undissolved oxide flux (PbO) attached to the sample platelet). Upon heating, the inner part of the sample (marked as A) changes to paraelectric isotropic phase at around 261 °C, while the outer region (marked as B) still remains anisotropic till 292 °C. Figure 5.7(b) displays the domain state at 280 °C, at which region A has turned to the cubic phase but region B is still in the rhombohedral state.
Figure 5.7 Domain structure of a (001)\textsubscript{cub} platelet of the La-PZT (#1) single crystal observed by PLM with crossed polarizers parallel to the <100>\textsubscript{cub} directions, (a) at room temperature, and (b) at 280 °C.

The variation of the birefringence of both regions as a function of temperature was measured upon cooling. As shown in Figure 5.8, both curves show discontinuous change at the paraelectric to ferroelectric phase transition, which indicates a first-order phase transition behaviour.[6] However, the drop in the birefringence is very small, suggesting the phase transition is a weakly first-order (or almost second-order).[155] This behaviour could be typically related to the disorder induced by the substitution of La\textsuperscript{3+} for Pb\textsuperscript{2+}. As introduced in the experimental part, the crystal was grown by slow cooling. Therefore, the rim of the bulk crystal must be formed at a relatively lower temperature compared with the core. The crystallization behaviour of the PZT binary system indicates that the Ti\textsuperscript{4+} content of the solid solution increases with decreasing growth temperature.[90] As a result, the outer region of a sample platelet presents a higher Ti\textsuperscript{4+} concentration compared to the inner part. This is also proved by the previous LA-ICP-MS analysis. It is not surprising to observe an almost 30 °C difference in phase transition temperature between regions A and B, which could be attributed to this phase composition segregation.
Figure 5.8  Birefringence of a (001)\textsubscript{cub}-cut La-PZT (#1) single crystal as a function of temperature measured upon cooling.

Piezoresponse force microscopy (PFM) was carried out on a (001)\textsubscript{cub} platelet of the La-PZT (#1) single crystal. Figure 5.9(a) shows the PFM topography obtained from the surface of the sample. Figure 5.9(b) and Figure 5.9(c) present the PFM phase and amplitude micrographs, respectively. In these micrographs, the dark region is polarized downward, whereas, the light region is polarized upward, indicating a 180° phase difference between two domain regions, resulting form the 180° ferroelectric domains. The average domain size of the sample is 4 - 5 \(\mu\)m.
Figure 5.9  Ferroelectric domain observation by PFM on a (001)\textsubscript{cub} platelet of the La-PZT (#1) single crystal: (a) Surface topography, (b) PFM amplitude, and (c) PFM out-of-plane phase images.

To explore the reversible polarization switching phenomenon, a square polarization pattern (10 × 10 μm\textsuperscript{2}) has been generated on an unpoled (001)\textsubscript{cub} platelet of the La-PZT (#1) single crystal of rhombohedral symmetry by poling with a dc bias of 30, 35 and -35 V, respectively, and then scanning the sample surface with a conductive tip. Figure 5.10(a\textsubscript{1}) shows the PFM out-of-plane phase image with a mixture of ferroelectric and ferroelastic domains before poling with an electric field. Figure 5.10(a\textsubscript{2}) represents its schematic drawing of permissible polarization vectors. In this unpoled state at room temperature, the polarization vectors randomly point along the eight body diagonals of the pseudocubic unit cell because of the rhombohedral symmetry, indicating two equivalent sets of eight out-of-plane directions (four upward and four downward). When a positive poling field of 30 V is applied to the crystal through the tip, both ferroelectric switching (180°) and ferroelastic switching (71° and 109°) take place and the polar vectors rotate upward on a large majority of the poled area (red box). Only a minority of the sample retains some of its original downward polarization, as shown and observed in Figure 5.10(b\textsubscript{1}) and Figure 5.10(b\textsubscript{2}). When a dc voltage of 35 V is applied, the polarization vectors completely change to upward [Figure 5.10(c\textsubscript{2})], as evidenced by the domain states image in Figure 5.10(c\textsubscript{1}) where a homogenously poled square domain is obtained. To demonstrate the effects of negative poling, a negative switching pulse is applied (-35 V) on a smaller inner 5 × 5 μm\textsuperscript{2} square inside the previously engineered upward-poled domain region. As shown in Figure 5.10(d\textsubscript{1}), the polarization is successfully switched to downward (yellow box) by the applied negative external electric field. Figure 5.10(d\textsubscript{1}) and Figure 5.10(d\textsubscript{2}) illustrate the orientations of the polarization vectors under this state and the observed PFM image.
Figure 5.10 Ferroelectric domain switching processes realized in a (001)$_{\text{cub}}$-oriented La-PZT (#1) single crystal, as revealed by PFM. Panels (a$_1$), (b$_1$), (c$_1$) and (d$_1$) are the in-plane phase images observed with the tip bias of 0, 30, 35, and -35V, respectively. Panels (a$_2$), (b$_2$), (c$_2$) and (d$_2$) are the corresponding schematics showing the poling direction of the cantilever and the polar vector states at different poling biases. The red arrows represent the spontaneous polarization vectors in the rhombohedral phase. The green arrows along the $<100>_{\text{cub}}$ represent the direction of scanning of the PFM phase images and the black arrows at the centre of the cubes stand for the direction of the electric field.

To verify the ferroelectric behaviour of the La-PZT (#1) single crystal, the out-of-plane and in-plane hysteresis loops were simultaneously recorded as a function of applied driving voltage. The obtained PFM amplitude and phase versus voltage loops of the La-PZT (#1) single crystals are presented in Figure 5.11. Both out-of-plane [Figure 5.11(a)] and in-plane [Figure 5.11(c)] PFM response amplitude loops possess a butterfly-like shape with saturated wings when the driving voltage reaches the value of the coercive voltage. The PFM response out-of-plane phase loop [Figure 5.11(b)] is of near rectangular shape with 180° change in the phase angle, which reflects the change of the sign of deformation coupled to the polarization reversal in the sample. As shown in Figure 5.11(d), the in-plane phase loop is also well-developed, showing an almost 180° domain switching. However, the coercive field of the in-plane phase loop is much smaller than that of out-of-plane phase loop, resulting in the narrowing of the in-plane PFM
response loop, which corresponds to the same tendency as in the behaviour of amplitude loops.

As mentioned above, when a (001)_{cub} cut single crystal with rhombohedral symmetry is poled along a nonpolar axis (e.g. <001>_{cub}), it adopts a multidomain structure, which is also called an “engineered domain structure”. It is well accepted that such domain configuration results in the large and enhanced piezoelectric response in PZT solid solution.[156] In the current case, an internal strain along the <001>_{cub} direction (out-of-plane) could be induced by the applied voltage because of the inverse piezoelectric effect. Consequently, an increased coercive field is obtained due to the induced internal strain.[157] In addition to strain effect, another important factor that affects the properties of phase loops is the distribution of the polarization under an applied electric field, which can lead to an inhomogeneous polarization switching, thereby a decrease in the coercive field.[158] Here, the switching process of the in-plane polarization is inhomogeneous, which makes the coercive field much smaller than the out-of-plane case. It is well known that the switching behaviour of the domains in PZT is strongly dependent on the additives and the Zr^{4+}/Ti^{4+} ratio.[159], [160] Our result shows that La^{3+} has enhanced the domain wall mobility in PZT single crystal, especially in the out-of-plane phase, making the polarization switching more energetically favourable.
Figure 5.11  Local hysteresis loops measured by PFM: (a) Amplitude- and (b) Phase (Polarization)- voltage hysteresis loops of out-of-plane signal. (c) Amplitude- and (d) Phase (Polarization)- voltage hysteresis loops of in-plane signal.

5.4.2.3  Dielectric and ferroelectric properties

Figure 5.12 illustrates the variations as a function of temperature of the dielectric permittivity of the three batches of La-PZT single crystals, measured at various frequencies. The dielectric permittivity ($\varepsilon'$) of the three batches of La-PZT crystals at room temperature are 383 (La-PZT (#1)), 436 (La-PZT (#2)), and 423 (La-PZT (#3)), respectively. As shown in Figure 5.12(a), the $T_C$ of the transition from the paraelectric to ferroelectric phase of the La-PZT (#1) crystal is at 261 °C. The $T_C$ of the La-PZT (#2) [Figure 5.12(b)] and La-PZT (#3) [Figure 5.12(c)] are 286 °C and 291 °C, respectively. According to the previous work[28], [90], the $T_C$ of the undoped PZT single crystal with a composition of $\text{Zr}^{4+}/\text{Ti}^{4+}$ ratio close to 67/33 is around 330 °C. Thus, the incorporation of
La$^{3+}$ into PZT has decreased the phase transition temperature of the system, which is expected from the known effects of donor-doping in PZT ceramics. The doping level of La$^{3+}$ in all three batches of crystals should be less than 2 at.% based on the results reported by Haertling for the ceramics.[145] However, there might be various factors responsible for the differences in $T_C$ of the three batches of crystals. On the one hand, a slight decrease in the Zr$^{4+}$/Ti$^{4+}$ ratio, in other words, an increase in the Ti$^{4+}$ content on the B-site, could increase the $T_C$ of the La-PZT (#2) and La-PZT (#3). On the other hand, the slight fluctuation in the doping levels of La$^{3+}$ could contribute to the obtained results as well.
Dielectric Permittivity ($\varepsilon'$) vs. Temperature (°C) for different frequencies:

- **(a)**: $T_c = 261$ °C
- **(b)**: $T_c = 266$ °C
- **(c)**: $T_c = 291$ °C
Figure 5.12 Temperature dependences of the dielectric permittivity ($\varepsilon'$) of (a) La-PZT (#1), (b) La-PZT (#2), and (c) La-PZT (#3) single crystals measured on a (001)$_{\text{cub}}$-cut platelet at various frequencies.

Figure 5.13 illustrates the variations as a function of temperature of the dielectric loss of the three batches of La-PZT single crystals, measured at various frequencies. The loss (tan$\delta$) of the three batches of La-PZT crystals at room temperature are 0.03 (La-PZT (#1)), 0.02 (La-PZT (#2)), and 0.03 (La-PZT (#3)), respectively. It is worth mentioning that La-PZT (#2) shows the highest dielectric permittivity among the three batches and its dielectric loss [Figure 5.13(b)] is comparable to that of La-PZT (#1) [Figure 5.13(a)] and La-PZT (#3) [Figure 5.13(c)]. This is mainly due to the relatively high concentration of La$^{3+}$ in the La-PZT (#2) as the donor dopant is meant to increase the concentration of lead vacancies, and thereby increase the dielectric permittivity at room temperature. The increase of lead vacancies can generate electrons and holes by ionization. Most of the holes from the lead vacancies are compensated by electrons from donor level to make the resistivity high and thereby the dielectric properties are known to be enhanced.[161] Although we are not able to determine the precise amount of La$^{3+}$ in all three batches crystals, the combined LA-ICP-MA analysis and lattice parameter values suggest that the La-PZT (#2) single crystal indeed has a higher La$^{3+}$ doping level than the other two. Furthermore, in the study of ceramics, it was found that the La$^{3+}$ concentrations between 4-9 at.% could make the dielectric peak frequency dependent, showing relaxor-like behaviour.[147] In the current data, the lack of relaxor behaviour confirms that the doping level of La$^{3+}$ should not be higher than 4 at.%.[110], [162] This agrees well with the previous conclusion made from the change of the $T_c$ values.
Figure 5.13  Temperature dependences of the dielectric loss (tanδ) of (a) La-PZT (#1), (b) La-PZT (#2), and (c) La-PZT (#3) single crystals measured on a (001)_{cub}-cut at various frequencies.
In terms of ferroelectric properties, it was found that the La-PZT (#1) crystal shows different shapes of polarization - electric (P-E) field hysteresis loops when displayed under different frequencies (Figure 5.14). In general, the sharpness of the loop tip (at the highest fields) indicates a high electric resistivity and in contrast, a blunt tip suggests that the conductivity of the sample is relatively high. In addition, it is noticed that the (ac) conductivity is lower when the hysteresis measurement period is 10 ms (high frequency) and greater when it is 50 ms (low frequency). This phenomenon indicates that there are defect dipoles and vacancies existing in the crystal that contribute to the ac conductivity which in turn depends on the frequency of the applied voltage. Thus differently-shaped hysteresis loops are realized under different frequencies. This result is acceptable as there must be cation vacancies originated from the incorporation of La$^{3+}$.[163] The loop is saturated under an electric field of ±25 kV/cm with a remnant polarization of $P_r = 30.3 \, \mu\text{C/cm}^2$ and a coercive field of $E_c = 7.2 \, \text{kV/cm}$ when the field hysteresis period is 10 ms. However, based on the above discussion, part of the measured "remnant" polarization could be attributed to the conductivity in the sample.

![Figure 5.14](image)

**Figure 5.14** Polarization vs. electric field (P-E) hysteresis loops displayed on a (001)$_{\text{cub}}$-oriented La-PZT (#1) single crystal at different periods.
Contrary to the La-PZT (#1) crystal, the La-PZT (#2) and La-PZT (#3) crystals possess well developed polarization-electric field hysteresis loops. As shown in Figure 5.15(a), the La-PZT (#2) sample shows better hysteresis behaviour both in terms of polarization and coercive field at different frequencies. And the sharp tip of the loops suggests the high electrical resistivity of the crystals. Saturation of polarization is achieved at an electric field of ± 40 kV/cm at room temperature. The remnant polarization reaches $P_r = 24.5 \mu$C/cm$^2$ with a coercive electric field $E_c = 6.1$ kV/cm for the La-PZT (#2) crystal. Both $P_r$ and $E_c$ of La-PZT (#3) (Figure 5.15(b)) single crystal fluctuate slightly under different frequencies. The highest value of $P_r = 11.3 \mu$C/cm$^2$ is obtained at an electric field of ± 25 kV/cm at room temperature with $E_c = 6.8$ kV/cm for the La-PZT (#3) crystal.
Figure 5.15  Polarization vs. electric field (P-E) hysteresis loops displayed on the (001)$_{\text{cub}}$-oriented (a) La-PZT (#2) and (b) La-PZT (#3) single crystals.

Considering the ferroelectric behaviour of all three batches of single crystals, it can be seen that the dopant La$^{3+}$ has changed the switching characteristics of hysteresis loop by forming different defect structures. Hardtl et al. found that A-site vacancies predominate in La$^{3+}$ substituted-PZT ceramic solid solutions and the formation of B-site vacancies is favoured under increased PbO vapor pressure[164], [165] In this work, the
flux to charge ratio for the growth of La-PZT (#1) is 5:1, which is higher than that of La-PZT (#2) and La-PZT (#3). A higher flux to charge ratio could decrease the melting point of the system, which in turn increases the vapour pressure of the system. Meanwhile, the molar fraction of PbO component is increased with the increasing concentration. Overall, the partial pressure of PbO is greater in La-PZT (#1) than that of La-PZT (#2) and La-PZT (#3). Consequently, more B-site vacancies are expected in the La-PZT (#1) single crystal. This could explain why the La-PZT (#1) crystal shows a very different behaviour compared with the La-PZT (#2) and La-PZT (#3) crystals.

In our previous work, single crystals of undoped PZT with Zr$^{4+}$/Ti$^{4+}$ ratios of 68/32 and 65/35 have been grown.[90] The La-PZT (#2) (Zr$^{4+}$/Ti$^{4+}$ $\approx$ 67/33) single crystal is used to compare the dielectric and ferroelectric properties with that of undoped PZT single crystals. Table 5.3 lists the obtained $P_r$, $E_c$, and $T_C$ values for these crystals. It can be seen that both $E_c$ and $T_C$ are lowered by the presence of La$^{3+}$ while the value of $P_r$ is increased slightly. Therefore, softening is successfully achieved in this work by La$^{3+}$ doping. Unfortunately, the piezoelectric properties of the three batches of La-PZT single crystals are rather mediocre ($d_{33} \leq 300$ pC/N), which is mainly because the composition of the crystals are away from the MPB region. We believe that it is still possible to improve the piezoelectric property by adjusting the Zr$^{4+}$/Ti$^{4+}$ ratio in the future growths.

<table>
<thead>
<tr>
<th>Growth Batches</th>
<th>Dielectric permittivity ($\varepsilon''$)</th>
<th>Loss (tan$\delta$)</th>
<th>$E_c$ (kV/cm)</th>
<th>$P_r$ ($\mu$C/cm$^2$)</th>
<th>$T_C$ ($^\circ$C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>PZT (x = 0.32)</td>
<td>244</td>
<td>0.135</td>
<td>7.0</td>
<td>19.2</td>
<td>337</td>
</tr>
<tr>
<td>PZT (x = 0.35)</td>
<td>339</td>
<td>0.034</td>
<td>11.4</td>
<td>23.5</td>
<td>352</td>
</tr>
<tr>
<td>La-PZT (x = 0.33)</td>
<td>436</td>
<td>0.024</td>
<td>6.1</td>
<td>24.5</td>
<td>285</td>
</tr>
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</table>

### 5.4.3. Structure and properties of Bi-PZT single crystals

#### 5.4.3.1 Structural analysis

The symmetry of the as-grown Bi-PZT single crystals was analyzed by XRD. As shown in Figure 5.16, both batches of Bi-PZT single crystals show a rhombohedral
(pseudo-cubic) crystal structure with a broadened or asymmetric \((111)_{\text{cub}}\) peak. The resulting diffraction data was analyzed using TOPAS Academic Software to determine the symmetry and to refine the lattice parameters of the grown crystals.

Figure 5.16  XRD patterns of the two batches of Bi-PZT single crystals.

The refinement results for the \((110)_{\text{cub}}\) and \((111)_{\text{cub}}\) reflections of Bi-PZT (#1) and Bi-PZT (#2) are shown in Figure 5.17(a) and Figure 5.17(b), respectively. The measured data are displayed in the black solid curves, while the calculated results are represented by the red curves. The difference between the experimental and fitting data is indicated by the gray curves. It is clear that the splitting of the \((110)_{\text{cub}}\) peak of Bi-PZT (#1) is less significant than that of Bi-PZT (#2). This different splitting behaviour also indicates the possible difference in composition between the two batches of crystals. The calculated lattice parameters are shown in Table 5.4.
Figure 5.17  Enlarged views of the splitting \((110)_{\text{cub}}\) and \((111)_{\text{cub}}\) peaks for the (a) Bi-PZT (#1) and (b) Bi-PZT(#2) single crystals.
Table 5.4  Calculated lattice parameters of the two batches of Bi-PZT single crystals.

<table>
<thead>
<tr>
<th>Batches</th>
<th>Zr/Ti</th>
<th>a (Å)</th>
<th>α (°)</th>
</tr>
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<tbody>
<tr>
<td>#1</td>
<td>69/31</td>
<td>4.11411 ± 0.00079</td>
<td>89.69546 ± 0.00257</td>
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<tr>
<td>#2</td>
<td>62/38</td>
<td>4.10074 ± 0.00115</td>
<td>89.66415 ± 0.00184</td>
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</table>

5.4.3.2  Domain structures

The optical domain structure and phase transition of the Bi-PZT (#1) crystals are examined by means of PLM on a (001)\textsubscript{cub} platelet. As shown in Figure 5.18, the specimen is in extinction with crossed polarizers at 45° to the <100>\textsubscript{cub} direction, which confirms the rhombohedral symmetry of the single crystal.

![Image of domain structure](image)

Figure 5.18  Domain structure of a (001)\textsubscript{cub} platelet of Bi-PZT (#1) observed by PLM with crossed polarizers: (a) parallel, and (b) at 45°, to the <100>\textsubscript{cub} direction.

In order to clearly show the domain patterns and domain walls, a region (marked by red rectangle in Figure 5.18) is enlarged. As shown in Figure 5.19(a), the lamellar domains are parallel to the <100>\textsubscript{cub} and <010>\textsubscript{cub} directions, corresponding to two sets of differently oriented domain states (labeled as “a” and “b”). Figure 5.19(b) shows a sketch of the domain patterns with the representative optical indicatrix section (birefringence) marked on. The optical indicatrix sections of the two domain states are aligned perpendicular to each other. The domain walls separating these two domain
states are inclined and look thicker than normal ones. Upon heating, the domain walls start to move slowly and at higher temperatures, relatively large scale domains are developed at the expense of smaller domains (Figure 5.19(c)). The domain walls are found to remain clearly stable even near the phase transition from ferroelectric to paraelectric phase at $T_C = 350 \, ^\circ\text{C}$, which could be attributed to the suppression of domain wall motions by the $\text{Bi}^{3+}$-doping.

Figure 5.19  (a) The domain patterns observed by PLM for a (001)$_{\text{cub}}$ platelet of Bi-PZT (#1) at room temperature, (b) A sketch of the domain structure and the orientation of optical indicatrix, and (c) The domain pattern near phase transition temperature 350 $^\circ\text{C}$. 
It is noticed that when the temperature decreases from 370 °C, the birefringence value increases very slowly till 352 °C, and then it continuously increases to about 0.032 at room temperature upon further cooling (Figure 5.20). The tail between 370 °C and 352 °C could be attributed to residual stresses in the crystal arising from the growth process. Moreover, in a compound with perovskite structures (ABO$_3$), the relatively small Bi$^{3+}$ ions not only create B-site vacancies, but also lead to distortions of the unit cell structure.[166] As a result, a slight stress could exist and cause the residual birefringence even in a cubic phase (above T$_C$).

![Figure 5.20](image)

**Figure 5.20** Variations of the birefringence as a function of temperature measured on a (001)$_{\text{cub}}$-cut Bi-PZT (#1) single crystal platelet upon cooling.

### 5.4.3.3 Dielectric and ferroelectric properties

Figure 5.21 illustrates the variations as a function of temperature of the dielectric permittivity and loss of the two batches of Bi-PZT single crystals, measured at various frequencies. It can be seen that the T$_C$ of the transition from the paraelectric to ferroelectric phase of Bi-PZT (#1) and Bi-PZT (#2) are 352 °C and 354 °C, respectively. Overall, the Bi-PZT (#2) shows a relatively better dielectric property with a higher dielectric permittivity ($\varepsilon' = 340$, at room temperature) and a higher T$_C = 354$ °C. On the other hand, it is evident from Figure 5.21(a) and Figure 5.21(b) that the dielectric permittivity peak of the Bi-PZT (#1) is much wider than that of the Bi-PZT (#2) single
crystal. Meanwhile, the magnitude of the dielectric permittivity decreases with increasing frequency in the Bi-PZT (#1) single crystal. It is known that Bi$^{3+}$ doping could introduce dielectric relaxation behaviour in some other perovskite systems.[166]–[169] The diffuse phase transition of the Bi-PZT (#1) could be a consequence of a relatively higher concentration of Bi$^{3+}$.

![Dielectric and loss temperature dependence](image)

**Figure 5.21** Temperature dependences of the dielectric permittivity ($\varepsilon'$) and loss (tanδ) of (a) Bi-PZT (#1), and (b) Bi-PZT (#2) single crystals.
Figure 5.22  (a) Polarization vs. electric field (P-E) hysteresis loop displayed on a (001)_{cub}-oriented Bi-PZT (#1) single crystal, and (b) Plot of the $P_r$ and $E_c$ values vs. different hysteresis periods.

Figure 5.22(a) displays the polarization vs. electric field (P-E) hysteresis loops of the Bi-PZT(#1) crystal under an electric field of 65 kV/cm at various hysteresis periods.
The dependence of $P_r$ and $E_c$ on hysteresis periods is plotted in Figure 5.22(b). It is found that as the hysteresis period increases (the frequency decreases), the value of $P_r$ increases while $E_c$ decreases. The loop is saturated under an electric field of $\pm 80$ kV/cm with $P_r$ and $E_c$ of $37.9 \mu$C/cm$^2$ and $31.3$ kV/cm, respectively. In the case of Bi-PZT (#2) single crystals, there is no obvious dependence of $P_r$ and $E_c$ on the measuring frequency (Figure 5.23). The obtained $P_r$ and $E_c$ values are $13.4 \mu$C/cm$^2$ and $9.0$ kV/cm, respectively. The large coercive field and high remnant polarization of the Bi-PZT (#1) single crystal suggest that “hardening” is more likely achieved by the Bi$^{3+}$ doping. It is known that the valence electron configuration of Bi$^{3+}$ is $6s^26p$. Therefore, Bi-based compounds contain two $6s^2$ lone-pair electrons outside a closed shell in an asymmetric hybrid orbital. In other words, Bi$^{3+}$ is in pyramidal coordination with oxygens in the doped PZT compounds and this special crystal chemistry bonding environment enhances the spontaneous polarization, making PZT solid solution “soft”. Somehow, these effects seem to have been “smeared out”, or “suppressed” by the defect dipoles in single crystals in which “hardening” become the dominant effect.

![Figure 5.23](image-url)  

Figure 5.23  Polarization vs. electric field (P-E) hysteresis loop displayed on the (001)$_{\text{cub}}$-oriented Bi-PZT (#2) single crystal.
Table 5.5 summarizes the obtained $P_r$, $E_c$, and $T_C$ values for the Bi-PZT single crystals. They are also compared with those of undoped PZT single crystals with similar compositions. The single crystal of Bi-PZT (#1) with $x = 0.31$ overall shows better ferroelectric property, but its dielectric permittivity is lower compared with undoped ones. On the other hand, it seems that the Bi-PZT (#2) with $x = 0.38$ has maintained its dielectric property, but the ferroelectric property has been significantly decreased. Therefore, no obvious trend has been found for Bi$^{3+}$ doping effects in this system.

Table 5.5  Dielectric and ferroelectric properties of the (001)$_{cu}$-oriented undoped PZT and Bi-PZT single crystals.

<table>
<thead>
<tr>
<th>Growth Batches</th>
<th>Dielectric permittivity ($\varepsilon'$)</th>
<th>Loss (tan$\delta$)</th>
<th>$E_c$ (kV/cm)</th>
<th>$P_r$ ($\mu$C/cm$^2$)</th>
<th>$T_C$ (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>PZT ($x = 0.32$)</td>
<td>244</td>
<td>0.135</td>
<td>7.0</td>
<td>19.2</td>
<td>337</td>
</tr>
<tr>
<td>PZT ($x = 0.35$)</td>
<td>339</td>
<td>0.034</td>
<td>11.4</td>
<td>23.5</td>
<td>352</td>
</tr>
<tr>
<td>PZT ($x = 0.42$)</td>
<td>232</td>
<td>0.056</td>
<td>5.0</td>
<td>32.0</td>
<td>372</td>
</tr>
<tr>
<td>Bi-PZT (#1) ($x = 0.31$)</td>
<td>125</td>
<td>0.039</td>
<td>31.3</td>
<td>37.9</td>
<td>352</td>
</tr>
<tr>
<td>Bi-PZT (#2) ($x = 0.38$)</td>
<td>336</td>
<td>0.010</td>
<td>9.0</td>
<td>13.4</td>
<td>354</td>
</tr>
</tbody>
</table>

It must be emphasized here that the perovskite structure with a general formula of $\text{ABO}_3$ correlates to large-sized A cation (1.10-1.80 Å) and a small-sized B cation (0.62-1.00 Å).[12] Bismuth ions can occur as Bi$^{3+}$ or Bi$^{5+}$. Their ionic radius varies between 1.11 Å and 0.74 Å depending on their valence and coordination number. Due to this variation, it is possible to incorporate Bi on either A-site or B-site of the perovskite lattices. In addition, the 6s$^2$ lone pair can produce a local distortion or even hybridization between Bi-6s-orbitals and O-2p-orbitals, leading to the block of the movement of electrons.[33] Therefore, bismuth doping in PZT single crystals may not follow the same “softening” mechanisms as expected from the ceramics and from the other donors.

5.5. Conclusions

Donor (La$^{3+}$ and Bi$^{3+}$)-doped single crystals of PbZr$_{1-x}$Ti$_x$O$_3$ (PZT) have been successfully grown by two different techniques: the top-cooled solution growth (TCSG) and the top-seeded solution growth (TSSG) for the first time. The compositions of the
as-grown single crystals have been determined by the laser ablation inductively coupled plasma mass spectrometry (LA-ICP-MS) and energy dispersive spectroscopy (EDS). All the three batches of La$^{3+}$-doped PZT (La-PZT) single crystals exhibit a very close Zr$^{4+}$/Ti$^{4+}$ ($\approx 67/33$) ratio, but the doping level of La$^{3+}$ in the La-PZT (#2) single crystals is slightly higher. The Zr$^{4+}$/Ti$^{4+}$ ratios of the two batches of Bi$^{3+}$-doped PZT (Bi-PZT) single crystals are found to be 69/31 (Bi-PZT (#1)) and 62/38 (Bi-PZT (#2)), respectively.

The structure of the donor-doped PZT single crystals are characterized by means of X-ray powder diffraction and the resulting data is analyzed using the TOPAS Academic Software to refine the lattice parameters. All the structures of the as-grown doped PZT single crystals are found to be rhombohedral. The optical domain structure and phase transition of the La-PZT (#1) are examined by means of polarized light microscopy (PLM) on a (001)$_\text{cub}$ platelet. An almost 30 °C difference in phase transition temperature are observed between the inner and outer part of the platelet, which could be attributed to the composition segregation of the Ti$^{4+}$ content. Piezoresponse force microscopy (PFM) is also performed on the (001)$_\text{cub}$ platelet of the La-PZT (#1) single crystal. It seems that La$^{3+}$ has enhanced the domain wall mobility in PZT single crystal, especially in the out-of-plane phase, making the polarization switching more energetically favourable. The incorporation of the La$^{3+}$ dopant into PZT could decrease the paraelectric to ferroelectric phase transition temperature (Curie temperature, T$_C$). In addition, the dielectric and ferroelectric properties of the PZT single crystals have been significantly impacted by the La$^{3+}$ doping. The highest paraelectric to ferroelectric phase transition temperature (T$_C$ = 291 °C) is obtained for the La-PZT (#3) single crystal. The highest remnant polarization reaches $P_r = 24.5 \mu$C/cm$^2$ with a coercive electric field $E_c = 6.1$ kV/cm for the La-PZT (#2) crystal.

Lamellar domains corresponding to two differently oriented sets of domain states are observed in a (001)$_\text{cub}$-cut platelet of the Bi-PZT (#1) single crystal by PLM. They are aligned parallel to the $<100>_{\text{cub}}$ and $<010>_{\text{cub}}$ directions. The T$_C$ values of Bi-PZT (#1) and Bi-PZT (#2) are 352 °C and 354 °C, respectively. However, it looks like that the Bi$^{3+}$ doping to PZT leads to rather complex behaviour and different effects from the ceramics and from other donor dopants. These different results of the two dopants could arise from the different electronic structure of La$^{3+}$ ([Xe]6s$^0$6p$^0$) and Bi$^{3+}$ ([Xe]6s$^2$6p$^0$) and the resulted different defect formations and distributions in the crystal lattice. The 6s$^2$ lone pair of Bi$^{3+}$ can produce a local distortion or even hybridization between Bi-6s-orbitals and O-2p-orbitals, leading to the block of the movement of charges and thereby the
domain walls. Another possible reason for the complex behaviour of Bi$^{3+}$ doping is its multiple valence states as Bi ions can occur as Bi$^{3+}$ or Bi$^{5+}$. Their ionic radius varies between 1.11 Å and 0.74 Å depending on their valence and coordination number. Due to this variation, it is that Bi occupies either A-site or B-site of the perovskite lattices.

In summary, our work has shown that the doping effects in PZT single crystals are not necessarily the same as in ceramics. In order to further understand the mechanisms of donor doping in PZT single crystals, more detailed characterizations on crystal local structure, e.g. by high resolution transmission electron microscopy (HRTEM) and high resolution x-ray diffraction (HRXRD), are needed.
Chapter 6.

Growth and Characterization of Acceptor (Mg$^{2+}$ and Mn$^{2+}$)-Doped PbZr$_{1-x}$Ti$_x$O$_3$ (PZT) Single Crystals

6.1. Abstract

Acceptor (Mg$^{2+}$ and Mn$^{2+}$)-doped PbZr$_{1-x}$Ti$_x$O$_3$ (PZT) single crystals have been successfully grown for the first time by a top-seeded solution growth (TSSG) method. The compositions of the as-grown single crystals are analyzed in terms of the ratios of Zr$^{4+}$ to Ti$^{4+}$ by energy dispersive spectroscopy (EDS). X-ray powder diffraction technique is used to determine the structure of these crystals. The electrical properties of the crystals are studied by various methods, including dielectric, ferroelectric and piezoelectric measurements. The paraelectric to ferroelectric phase transition temperature, i.e. the Curie temperature ($T_C$) of the two batches of Mg$^{2+}$-doped PZT (Mg-PZT) single crystals is found to be 338 °C (Mg-PZT (#1)) and 324 °C (Mg-PZT (#2)), respectively. The Mg-PZT single crystals show “peanut-shaped” polarization - electric field hysteresis loops, which are reminiscent of the “double” hysteresis loops of antiferroelectric-like behaviour. The loops open up with the increase of temperature and applied electric field and eventually become regular ferroelectric hysteresis loops. This phenomenon is attributed mainly to the “pinning” effect of oxygen vacancies that are introduced by the Mg$^{2+}$ (donor) doping. A remnant polarization ($P_r$) of 20 μC/cm$^2$ with a coercive field ($E_c$) of 7.0 kV/cm is obtained at 210 °C with an electric field of ±20 kV/cm for the Mg-PZT (#1) single crystal. At room temperature, when a ±50 kV/cm field is applied on a (001)$_{\text{cub}}$-cut Mg-PZT (#1) single crystal platelet, the achieved $P_r$ and $E_c$ values are 12 μC/cm$^2$ and 20 kV/cm, respectively. On the other hand, the two batches of Mn$^{2+}$-doped PZT (Mn-PZT) single crystals show a transition from the paraelectric to ferroelectric phase upon cooling at 326 °C (Mn-PZT (#1)) and 330 °C (Mn-PZT (#2)), respectively.
respectively. The dielectric permittivity and loss tangent of Mn-PZT (#1) at room temperature are 200 and 0.004, while those values for Mn-PZT (#2) at room temperature are 250 and 0.01, respectively. Furthermore, the Mn-PZT single crystals show a much higher conductivity compared with that of Mg$^{2+}$-doped ones, which could be due to the existence of multi-valence states of Mn$^{2+}$, Mn$^{3+}$ and Mn$^{4+}$, which favours electron hopping among the B-sites, leading to a high conductivity. Overall, the remnant polarization of the PZT single crystals is dramatically diminished by Mn$^{2+}$ doping.

6.2. Introduction

Since the discovery of the phenomenon of ferroelectricity in the Rochelle salt single crystal in 1921, there have been continuous efforts to investigate both the fundamental and application aspects of ferroelectric behaviour, resulting in the development of a large variety of ferroelectric materials. Nowadays, ferroelectric materials have found a wide range of applications, from microwave devices, to piezoelectric transducers, sensors and actuators. Lead zirconate titanate solid solution, PbZr$_{1-x}$Ti$_x$O$_3$ (PZT), is considered as an important material because of its high spontaneous polarization and high Curie temperature ($T_C$), well above room temperature, providing it with good thermal stability during operation, high electromechanical coupling coefficient, etc. Modification of the various properties of PZT ceramics by addition of dopants has been researched extensively for further improvement of dielectric and piezoelectric properties, so as to make them suitable for various specific applications such as actuators, transducers and ceramic capacitors.

The dopants are classified as isovalent, acceptor or donor. For isovalent doping, the substituting ion has the same valence and the same or similar ionic size as the replaced ion, for example, Sn$^{4+}$ substituting for (Zr$^{4+}$, Ti$^{4+}$) and Ca$^{2+}$ substituting for Pb$^{2+}$, which have been shown to enhance the dielectric properties of PZT ceramics. According to the defect dipole model, the introduction of an acceptor or donor dopant disturbs the electroneutrality condition. Therefore, donors (higher valence cations), such as La$^{3+}$ for A (Pb$^{2+}$) site modification or Nb$^{5+}$ for B (Zr$^{4+}$, Ti$^{4+}$) site modification, are compensated by negatively charged defects, such as lead vacancies.
(see details in Chapter 5). Acceptors (lower valence cations), such as the Fe$^{3+}$ or Mg$^{2+}$ substituting for Zr$^{4+}$/Ti$^{4+}$ or Na$^+$ substituting for Pb$^{2+}$, are compensated by positively charged defects, such as oxygen vacancies, to maintain the overall electroneutrality.

In a perovskite structure, cations are completely surrounded by oxygens and are separated from the nearest cation site of the same kind by an entire unit cell (~ 4Å), making ionic diffusion very difficult. The oxygen sites, on the other hand, are adjacent to one another only at 2.8 Å apart.[30] Hence, the oxygen ions can easily move into nearby oxygen vacancies. As a result, dipoles consisting of oxygen vacancies and associated dopant ions are able to move and reorient more easily in acceptor-doped PZT solid solution. An enhancement of the internal bias under an applied electric field can be expected due to the increase in the concentration of alignable defect dipoles. Domain walls in the acceptor-doped PZT are then pinned by the internal bias, leading to an electrically “hard” PZT.[179] A hard PZT is characterized by low piezoelectric coefficients, low permittivity, low losses, low electrical resistivity, and a high coercive field and a large polarization.[13]

The improved ferroelectric and pyroelectric properties in Mn-doped PZT thin films were reported by Zhang et al.[180] It was concluded that Mn doping has significant effects on the ferroelectric and pyroelectric properties of PZT (x = 0.7) and Mn-doped thin films can be considered as an excellent candidate for both memory devices and pyroelectric detectors. On the other hand, it was found that the addition of a low concentration of MgO into PZT solid solution could improve the dielectric property.[181] However, many aspects of the effects of Mn$^{2+}$-doping and Mg$^{2+}$-doping on the structure and properties of PZT single crystals remain unknown, and the mechanisms of the acceptor-doping in general are poorly understood. Therefore, it is of particular interest to grow single crystals of acceptor-doped PZT, which are not only necessary for thorough characterization of the anisotropic properties of this system, but are also expected to exhibit superior piezo-/ferroelectric performance over their ceramic counterparts. In the present study, we have synthesized two batches of Mg$^{2+}$-doped PZT (Mg-PZT) single crystals and two batches of Mn$^{2+}$-doped PZT (Mn-PZT) single crystals and characterized their domain structures, phase transitions and electrical properties.
6.3. Experimental

The starting materials, PbO (99.9%), ZrO\textsubscript{2} (99.9%), TiO\textsubscript{2} (99.9%), MgO (99.9%), and MnO (99.9%), were mixed according to the stoichiometry of the nominal composition Pb((Zr\textsubscript{0.4}T\textsubscript{0.6})\textsubscript{1-0.05}M\textsubscript{0.05})O\textsubscript{3} (M = Mg\textsuperscript{2+} or Mn\textsuperscript{2+}). These mixed oxides of calculated amounts were put in a 100 ml platinum crucible and calcined at 800 °C in a furnace for 4 hours. The mixture of PbO and B\textsubscript{2}O\textsubscript{3} with a molar ratio of 4:1 was used as flux. The flux was added into the calcined mixture with a flux:charge molar ratio of 4:1 for all the growths. The mixture of solute and solvent was loaded into a 100 ml platinum crucible. The top-seeded solution growth (TSSG) method (see Chapter 3 for more details) was used. The detailed thermodynamic parameters and growth condition are listed in Table 6.1.

<table>
<thead>
<tr>
<th>Growth Batch</th>
<th>Flux/Charge (mol %)</th>
<th>T\textsubscript{1} (°C)</th>
<th>T\textsubscript{2} (°C)</th>
<th>Cooling Rate R\textsubscript{1} (°C/day)</th>
<th>Growth Method</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mg-PZT (#1)</td>
<td>4:1</td>
<td>1130</td>
<td>1000</td>
<td>4</td>
<td>TSSG</td>
</tr>
<tr>
<td>Mg-PZT (#2)</td>
<td>4:1</td>
<td>1140</td>
<td>1000</td>
<td>4</td>
<td>TSSG</td>
</tr>
<tr>
<td>Mn-PZT (#1)</td>
<td>4:1</td>
<td>1070</td>
<td>970</td>
<td>4</td>
<td>TSSG</td>
</tr>
<tr>
<td>Mn-PZT (#2)</td>
<td>4:1</td>
<td>1060</td>
<td>1020</td>
<td>4</td>
<td>TSSG</td>
</tr>
</tbody>
</table>

The homogeneity of the specimens was verified using energy dispersive spectroscopy (EDS). The crystal structure of the as-grown crystals was analyzed by X-ray diffraction (XRD) on fine powder obtained by grinding a number of small crystals (Bruker D8 Advance Diffractometer). The resulting diffraction data was analyzed using the TOPAS Academic Software to determine the symmetry and to refine the lattice parameters. In addition, the dielectric properties of the grown crystals were measured using a Novocontrol Alpha high-resolution broadband dielectric analyzer equipped with a Novotherm heating system. The ferroelectric properties of the acceptor-doped PZT single crystals were displayed on the (001)\textsubscript{cub} platelets by means of a Radiant RT-66 standardized ferroelectric testing system. The samples were kept in a silicon oil bath to avoid electric arcing during the polarization switching.
6.4. Results and discussion

6.4.1. Crystal growth and compositional analysis

Figure 6.1 shows the photographs of the as-grown Mg-PZT and Mn-PZT single crystals. The chemical and thermodynamic parameters used for the four growth experiments are listed in Table 6.1. A large bulk single crystal of dimensions of approximately $2 \times 3 \times 0.8 \text{ cm}^3$ is obtained for the Mg-PZT (#1). Unfortunately, the Pt wire that hung the seed broke and the crystal fell into the flux solution right before the completion of the growth. Therefore, there is some solidified flux attached on the surface of the crystal. The bulk crystal size of Mg-PZT (#2) is approximately $2 \times 2.5 \times 0.8 \text{ cm}^3$. It can be seen that the bottom part of the crystal shows more a regular cubic morphology than that of the top part. It is believed that the growth started on the faces of the seed crystal when the super-saturation was reached during slow cooling. This single-nucleated growth continued as the dominant process at the bottom part of the crystal during the growth, leading to the formation of a pseudo-cubic shape. However, spontaneous nucleation occurred around the top part of the growing crystal, which led to a few not-fully-developed cubic-shaped crystals with a degenerated morphology. The bulk Mn-PZT (#1) single crystal also shows multiple nucleation and orientations with an average size of $2 \times 2\times 0.8 \text{ cm}^3$. However, the naturally grown facets of the single crystals are the $\{001\}_\text{cub}$ faces, which are identifiable. The size of Mn-PZT (#2) single crystals is relatively small ($3 - 5 \text{ mm}$), which was due to an interruption of growth as a result of a power outage during the growth process.
Energy dispersive spectroscopy (EDS) was performed on the surface of the grown single crystals to analyze the elements and their relative amounts. Figure 6.2(a) illustrates the elemental mapping of Pb, Zr, Ti, and Mg in Mg-PZT (#1) and it can be seen that these elements are distributed uniformly across the crystal. The corresponding EDS spectrum of these elements is shown in Figure 6.2(b). The compositional analysis by this technique indicates that the Zr/Ti ratio in Mg-PZT (#1) is around 66/34. It is noticed that the peak of Mg (1.253 keV) is not obvious in the EDS spectrum, which could be due to a low concentration. This result also suggests that the doping level of Mg\(^{2+}\) is not very high. Similar analysis was carried out on a Mg-PZT (#2) single crystal and the Zr/Ti ratio was found to be 72/28. In the case of Mn-PZT single crystals, all the elements are distributed homogeneously in the sample. The Zr/Ti ratios were found to be 68/32 for Mn-PZT (#1) and 69/31 for Mn-PZT (#2).
Figure 6.2 (a) Elemental mapping of Pb (red), Zr (blue), Ti (purple) and Mg(brown) using EDS on the surface of a Mg-PZT (#1) single crystal, and (b) the EDS spectrum of Pb, Zr, Ti and Mg.
6.4.2.  **Structure and properties of Mg-PZT single crystals.**

The phase and structure of the Mg-PZT single crystals were determined by powder XRD on ground crystals. Figure 6.3(a) illustrates the XRD pattern of Mg-PZT (#1) and its Pawley Fit results using the TOPAS Academic software. The XRD pattern of the Mg-PZT (#1) single crystal shows a singlet \((100)_{\text{cub}}\) peak, and a broadened \((111)_{\text{cub}}\) reflection, which is characteristic of a rhombohedral symmetry. Therefore, the fitting was carried out based on a model of rhombohedral phase. The measured data are displayed in the black solid curve, while the calculated result is represented by the red dashed curve. The difference between the experimental and fitting data is indicated by the gray curve. The XRD pattern of Mg-PZT (#2) shows some noisy background (between \(22.5^\circ\) and \(30^\circ\)), which could be attributed to the solidified flux (PbO) on the crystal surface and the oxides inclusions in the crystal. The fitting for Mg-PZT (#2) single crystal was also carried out based on a model of rhombohedral structure. The small noisy peaks were excluded from fitting (Figure 6.3(b)). The calculated lattice parameters of the two batches of Mg-PZT single crystals are listed in Table 6.2.
Figure 6.3  XRD patterns and Pawley Fitting results of (a) Mg-PZT (#1) and (b) Mg-PZT (#2) single crystals.
Table 6.2  Calculated lattice parameters of the Mg-PZT single crystals.

<table>
<thead>
<tr>
<th>Batches</th>
<th>Zr/Ti</th>
<th>a (Å)</th>
<th>α (°)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mg-PZT (#1)</td>
<td>66/34</td>
<td>4.1144 ± 0.0006</td>
<td>89.8954 ± 0.0007</td>
</tr>
<tr>
<td>Mg-PZT (#2)</td>
<td>72/28</td>
<td>4.1174 ± 0.0005</td>
<td>89.9377 ± 0.0007</td>
</tr>
</tbody>
</table>

Figure 6.4(a) and Figure 6.4(b) show the variations as a function of temperature of the dielectric permittivity and loss tangent of Mg-PZT (#1), respectively, measured at various frequencies. As shown in Figure 6.4(a), the Mg-PZT (#1) crystal exhibits a sharp peak in the temperature dependence of dielectric permittivity, corresponding to $T_C$ (338 °C) of the phase transition from the paraelectric to ferroelectric phase upon cooling. The dielectric permittivity and loss tangent at room temperature are 350 and 0.004, respectively. The dielectric permittivity and loss tangent of Mg-PZT (#2) as a function of temperature are shown in Figure 6.4(c) and Figure 6.4(d). It can be seen that the phase transition from paraelectric to ferroelectric phase of Mg-PZT (#2) occurs at a relatively lower temperature (324 °C) compared with that of Mg-PZT (#1), which is mainly due to the lower Ti concentration. The dielectric permittivity and loss tangent at room temperature of the Mg-PZT (#2) single crystal are 323 and 0.006, respectively. Overall, the Mg-PZT (#1) shows better dielectric property with a higher $T_C$ and a larger dielectric permittivity, and a lower loss.
Figure 6.4  Temperature dependences of the dielectric permittivity ($\varepsilon'$) of (a) Mg-PZT (#1) and (c) Mg-PZT (#2), and of the loss tangent (tan $\delta$) of (b) Mg-PZT (#1) and (d) Mg-PZT (#2) single crystals.

The polarization versus electrical field hysteresis loops (P-E loops) of the Mg-PZT (#1) crystals were measured at various temperatures under a field of ±20 kV/cm. As shown in Figure 6.5, a very narrow loop is obtained at 30 °C. With increasing temperature, the loop starts to open up and shows double hysteresis-like behaviour (e.g. at 90 °C and 150 °C), which is known to be characteristic of antiferroelectric behaviour. However, when the sample was further heated up to 210 °C, a regular ferroelectric hysteresis loop is displayed.
Figure 6.5  P-E loops of Mg-PZT (#1) at different temperatures under a field of ±20 kV/cm with a period of 100ms.

In order to further explore the origin of the double hysteresis behavior, the sample was cooled down to room temperature and its P-E loop was measured again. As shown in Figure 6.6, the loop broadens slightly, but still maintains an irregular “peanut” shape at ±20 kV/cm. With increasing electric field, the loop gradually opens up and eventually becomes a regular ferroelectric hysteresis loop at ±50 kV/cm.
The basic idea of the defect chemistry model is that the electroneutrality condition is disturbed by introducing foreign ions with a different valence from the ions they replace. Here, it is expected that the acceptor ions (Mg$^{2+}$) are compensated with positively charged oxygen vacancies.[182] According to the defect chemistry model, oxygen vacancies are the only mobile ionic species in the lattice. Therefore, defect dipoles associated with oxygen-vacancy-acceptor-ions can be aligned since oxygen vacancies can easily change their position. These defect dipoles will then contribute to the gradual development of the internal bias.
Without an external electric field, these defect dipoles act like individual dipoles in antiferroelectric materials, which are oriented antiparallel to their adjacent dipoles. Hence, a nearly zero net polarization is obtained. When an external field is applied, the antiparallel defect dipoles can be reoriented when the magnitude of the field reaches a critical value. However, the defect dipoles in the crystal restore their antiparallel configuration once the field decreases to the critical value. As a result, a field-induced ferroelectric hysteresis loop appears at high positive or negative fields, giving rise to the double hysteresis loop at 90 °C and 150 °C, as shown in Figure 6.5. With the increase of temperature, the alignment of the defect dipoles becomes random instead of antiparallel. Therefore, a regular ferroelectric hysteresis loop is displayed at 210 °C in Figure 6.5.

On the other hand, it is obvious that the orientations of defect dipole have been affected by the thermal treatment as an asymmetric loop is obtained when the crystal is cooled down to 30 °C (Figure 6.6). Meanwhile, it seems that a relatively high electric field (40 kV/cm and 50 kV/cm in Figure 6.6) could also disturb the antiparallel alignment of the defect dipoles, leading to normal ferroelectric hysteresis loops. Overall, a $P_r$ of 20 $\mu$C/cm$^2$ with an $E_c$ of 7.0 kV/cm is obtained at 210 °C under an electric field of ±20 kV/cm. At room temperature, when a 50 kV/cm field is applied, the achieved $P_r$ and $E_c$ values are 12 $\mu$C/cm$^2$ and 20 kV/cm, respectively.
Figure 6.7  P-E loops of the Mg-PZT (#2) single crystal measured under different fields at room temperature with a period of 100ms.

The P-E loops of Mg-PZT (#2) were first measured at various fields at room temperature. As shown in Figure 6.7, the crystal also displays double hysteresis loop due to the “pinning” effect of internal bias. With the increase of the applied electric field, the loop gradually widens out. The applied electric field was kept up to 40 kV/cm in order to protect sample from breaking down. The obtained $P_r$ is 13 μC/cm² with an $E_c$ of 10 kV/cm.
Figure 6.8  P-E loops of the Mg-PZT (#2) single crystal measured at different temperatures under a field of 20 kV/cm with a period of 100 ms.

Internal bias “pinning” effect was also observed in the Mg-PZT (#2) single crystal at different temperatures under an electric field of ±40 kV/cm. As shown in Figure 6.8, the crystal displays a “peanut”-shaped loop at 30 °C and 80 °C. With further increase of temperature, the loop gradually becomes a normal ferroelectric hysteresis loop at 140 °C. The \( P_r \) and \( E_c \) values under this condition are 29 \( \mu \text{C/cm}^2 \) and 7 kV/cm, respectively.

6.4.3.  Structure and properties of Mn-PZT single crystals.

The phase and structure of the Mn-PZT crystals were determined by powder XRD on ground crystals. Figure 6.9(a) and Figure 6.9(b) illustrate the XRD patterns of Mn-PZT (#1) and Mn-PZT (#2), respectively. Both experimental patterns show a broadened \((111)_{\text{cub}}\) peak and the data are analyzed based on a rhombohedral structure.
using the Pawley Fitting method. Again, the data show some noisy background between 22.5° and 30° of Mn-PZT (#1), which could arise from solidified flux (PbO) and inclusions and were excluded from fitting. The excluded data region of Mn-PZT (#2) is between 27.5° and 30°. The measured data are displayed in the black solid curve, while the calculated result is represented by the red dashed curve. The difference between the experimental and fitting data is indicated by the gray curve.

Figure 6.9  XRD patterns and Pawley Fitting results of (a) Mn-PZT (#1) and (b) Mn-PZT (#2) single crystals.
The calculated lattice parameters of the two batches of Mn-PZT single crystals are listed in Table 6.3. It is worth noting that Mn-PZT (#1) is very similar to Mn-PZT (#2) in terms of lattice parameters, which in general means that the compositions of the two batches of crystals are very close. Additionally, the analysis by EDS has shown almost similar composition for the two batches of Mn-PZT single crystals.

### Table 6.3 Calculated lattice parameters of the Mn-PZT single crystals.

<table>
<thead>
<tr>
<th>Batches</th>
<th>Zr/Ti</th>
<th>(a) (Å)</th>
<th>(\alpha) (°)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mn-PZT (#1)</td>
<td>68/32</td>
<td>4.1024 ± 0.0003</td>
<td>89.7276 ± 0.0004</td>
</tr>
<tr>
<td>Mn-PZT (#2)</td>
<td>69/31</td>
<td>4.1050 ± 0.0009</td>
<td>89.7640 ± 0.0005</td>
</tr>
</tbody>
</table>

The variations of the dielectric permittivity and loss tangent as a function of temperature of Mn-PZT (#1) are shown in Figure 6.10(a) and Figure 6.10(b), respectively. The data are measured at frequencies of 1 kHz, 10 kHz and 100 kHz. As shown in Figure 6.10(a), the Mn-PZT (#1) crystal exhibits a sharp peak in the temperature dependence of dielectric permittivity, corresponding to \(T_C\) (326 °C) of the phase transition from the paraelectric to ferroelectric phase upon cooling. The dielectric permittivity and loss tangent of Mn-PZT (#1) at room temperature are 200 and 0.004, respectively. The dielectric permittivity and loss tangent of Mn-PZT (#2) as a function of temperature are shown in Figure 6.10(c) and Figure 6.10(d), respectively. It can be seen that the phase transition from the paraelectric to ferroelectric phase of Mn-PZT (#2) occurs at a higher temperature (330 °C) compared with that of Mn-PZT (#1), which could be due to a higher Ti concentration. The dielectric permittivity and loss tangent at room temperature of Mn-PZT (#2) are 250 and 0.01, respectively.
Figure 6.10  Temperature dependences of the dielectric permittivity ($\varepsilon'$) of (a) Mn-PZT (#1) and (c) Mn-PZT (#2), and the loss tangent (tan $\delta$) of (b) Mn-PZT (#1) and (d) Mn-PZT (#2) single crystals.

The polarization versus electrical field hysteresis loops (P-E loops) of Mn-PZT (#1) were measured under different fields at room temperature. As shown in Figure 6.11, the hysteresis loop shows blunt tips at high fields, which suggests that the conductivity of the Mn-PZT (#1) crystal is high. Mn has been investigated extensively as an effective dopant for the PZT-based ceramics because Mn ions can have different valence states from Mn$^{4+}$ to Mn$^{2+}$.\[183]\] In this work, the starting valence state of the dopant is Mn$^{2+}$, which could be oxidized to Mn$^{3+}$ or Mn$^{4+}$. The high conductivity is expected to be due to the existence of Mn$^{2+}$, Mn$^{3+}$ and Mn$^{4+}$ on the B-sites, which favours electron hopping. The electron transfer between the multivalent states of the Mn ions in the lattice can contribute to the conductivity of the Mn-PZT (#1) single crystal. The obtained $P_r$ and $E_c$ values for the Mn-PZT (#1) are 3.5 $\mu$C/cm$^2$ and 10.8 kV/cm, respectively.
Figure 6.11  P-E loops of the Mn-PZT (#1) single crystal measured under different fields at room temperature with a period of 100ms.

The polarization versus electrical field hysteresis loops (P-E loops) of the Mn-PZT (#2) crystal were measured under a field of ±40 kV/cm at different frequencies. The frequency does not seem to affect significantly the shape of the loop. A $P_c$ value of 8.4 $\mu$C/cm$^2$ is obtained with an $E_c$ of 10.8 kV/cm for the Mn-PZT (#2) single crystal. Overall, it is clear that the ferroelectric properties of the Mn-PZT single crystals are inferior to those of the Mg-PZT single crystals. There could be several factors that are responsible for the outcome of the Mn$^{2+}$ doping. First, as previously mentioned, a certain percentage of Mn$^{2+}$ could be oxidized to Mn$^{3+}$ or Mn$^{4+}$, providing potential charge carriers for electrical conductivity. In addition, the different ionic radii of Mn$^{2+}$, Mn$^{3+}$ and Mn$^{4+}$ could lead to lattice distortions, which then limits the space for the cation displacement. Therefore, the polarization properties are diminished. Furthermore, the structural distortion arising from the Jahn-Teller effect should be taken into consideration as well due to the possible existence of Mn$^{3+}$, a Jahn-Teller ion.
Figure 6.12  P-E loops of the Mn-PZT (#2) single crystal measured under different fields at room temperature with a period of 100ms.

6.5. Conclusions

Acceptor (Mg$^{2+}$ and Mn$^{2+}$)-doped PbZr$_{1-x}$Ti$_x$O$_3$ (PZT) single crystals have been successfully grown for the first time by a top-seeded solution growth (TSSG) method. Large bulk size single crystals with dimensions of approximately $2 \times 3 \times 0.8$ cm$^3$ and $2 \times 2.5 \times 0.8$ cm$^3$ are obtained for the Mg-PZT (#1) and Mg-PZT (#2), respectively. The bulk Mn-PZT (#1) single crystal shows multiple nucleation and orientations with an average size of $2 \times 2 \times 0.8$ mm$^3$. The size of the Mn-PZT (#2) single crystals is relatively smaller (3 - 5 mm), which was due to an interruption of growth as a result of a power outage during the growth process. The compositional analysis by energy dispersive spectroscopy (EDS) indicates that the Zr/Ti ratios in Mg-PZT (#1) and Mg-PZT (#2) are 66/34 and 72/28, respectively. Similar analysis was carried out on the Mn$^{2+}$-doped PZT single crystals and the Zr/Ti ratio was found to be 68/32 for Mn-PZT (#1) and 69/31 for Mn-PZT (#2). The phase and structure of the acceptor-doped PZT single crystals were investigated by powder XRD on ground crystals. The resulting data are analyzed using
the TOPAS Academic software to determine the symmetry and to refine the lattice parameter. All the as-grown acceptor-doped PZT single crystals show a rhombohedral phase with slightly different lattice parameters. The Curie temperature (T_C) of the two batches of Mg^{2+}-doped PZT (Mg-PZT) single crystals are 338 °C (Mg-PZT (#1)) and 324 °C (Mg-PZT (#2)), respectively. The ferroelectric hysteresis loops of the Mg-PZT single crystals show “peanut-shaped” hysteresis loops, which are similar to the “double” hysteresis loops of antiferroelectric-like behaviour. The loops open up with the increases of temperature and applied electric field and eventually become regular ferroelectric hysteresis loops. A remnant polarization (P_r) of 20 μC/cm^2 with an coercive field (E_c) of 7.0 kV/cm is obtained at 210 °C with an electric field of ±20 kV/cm for the Mg-PZT (#1) single crystal. At room temperature, when a ±50 kV/cm field is applied on a (001)_{cub}-cut Mg-PZT (#1) single crystal platelet, the achieved P_r and E_c values are 12 μC/cm^2 and 20 kV/cm, respectively. The enhancement of the E_c is mainly due to the “pinning” effect of oxygen vacancies that are introduced by the Mg^{2+} (acceptor) doping. In other words, “hardening” is achieved by Mg^{2+} doping in the PZT single crystals. On the other hand, the two batches of Mn^{2+}-doped PZT (Mn-PZT) single crystals show phase transitions from the paraelectric to ferroelectric phase upon cooling at 326 °C (Mn-PZT (#1)) and 330 °C (Mn-PZT (#2)), respectively. The dielectric permittivity and loss tangent of the Mn-PZT (#1) at room temperature are 200 and 0.004, respectively, while those values for the Mn-PZT (#2) crystal at room temperature are 250 and 0.01. Overall, the P-E hysteresis loops of the Mn-PZT single crystals show leakage behaviour due to high conductivity and the ferroelectric properties are inferior to that of Mg-PZT single crystals. The possible reason is that a certain percentage of Mn^{3+} could be oxidized to Mn^{5+} or Mn^{4+}, providing potential charge carriers for electrical conductivity and thereby diminishing the polarization properties. Furthermore, the structural distortion arising from the Jahn-Teller effect should be taken into consideration as well due to the possible existence of Mn^{3+}, a Jahn-Teller ion.
Chapter 7.

Growth and Characterization of Bi(Zn_{0.5}Ti_{0.5})O_3-PbZrO_3-PbTiO_3 Ternary Ferroelectric Single Crystals

The following chapter is a revised version of the paper published by Bixia Wang, Yujuan Xie, Jian Zhuang, Xiaoqing Wu, Wei Ren and Zuo-Guang Ye, Journal of Applied Physics, 115, 084104 (2014) and the paper published by Bixia Wang, Xiaoqing Wu, Wei Ren and Zuo-Guang Ye, IEEE Transactions on Ultrasonics, Ferroelectrics, and Frequency Control, 62, 1016-1021, (2015). The use of these papers is permitted by the publisher of American Institute of Physics and IEEE.

7.1. Abstract

Four batches ferroelectric single crystals of a new lead-reduced Bi(Zn_{0.5}Ti_{0.5})O_3-PbZrO_3-PbTiO_3 (BZT-PZ-PT) ternary solid solution system have been grown for the first time by three different methods, namely high temperature solution growth (HTSG, or flux method), top-cooled solution growth (TCSG) and top-seeded solution growth (TSSG). The chemical and thermodynamic parameters, including the flux concentration, the soaking temperature and the cooling rate, have been optimized, leading to the growth of good quality BZT-PZ-PT crystals of pseudo-cubic morphology. A large size crystal of the dimensions of 2 × 2 × 0.5 cm³ has been obtained by the TSSG technique for the Batch #1. The compositions and homogeneity of the as-grown BZT-PZ-PT single crystals are studied by laser ablation inductively coupled plasma mass spectrometry (LA-ICP-MS). All the four batches of BZT-PZ-PT single crystals are found to be in the PbZrO_3 (PZ)-rich region of this ternary system. The structure of the as-grown crystals is determined to be rhombohedral by means of X-ray diffraction (XRD). The domain structure and phase transitions of the crystals are studied by the optical examination of a (001)ₖₙₜ platelet by
polarized light microscopy (PLM). Large size and very uniform strain-induced domains are observed in the Batch #3 and Batch #4 of BZT-PZ-PT single crystal. These domains are not stable with respect to the heat treatment. Contrary to the increase of the transition temperature with BZT substitution in PbTiO₃ (PT), the Curie temperature (Tᵥ) of the PZT single crystal is decreased by the substitution of BZT. The highest ferroelectric Tᵥ of the grown crystals is found to be 320 °C by means of dielectric measurements for the Batch #3. A remnant polarization of 32 μC/cm² is displayed with a coercive field of 15.4 kV/cm for the Batch #1 crystal. The high Tᵥ and large coercive field of the BZT-PZ-PT single crystal make this material a promising candidate for applications in high power electromechanical transducers that can operate in a wider temperature range and at high fields.

7.2. Introduction

Perovskite ABO₃-type materials have been extensively studied because of their technical importance and the fundamental interest in the physics of their phase transitions.[184] The Pb-based perovskite ceramics Pb(ZrₓTi₁₋ₓ)O₃ (PZT) with compositions near its morphotropic phase boundary (MPB) have dominated the market of ferroelectrics and piezoelectrics for decades, being used in a wide range of applications including actuators, sensors, and memory devices, thanks to their high Curie temperature (Tᵥ ≈ 350 °C), larger remnant polarization, good piezoelectric and electromechanical properties.[185] So far, several PZT-based ternary and quaternary systems have been prepared and studied to meet various requirements for practical applications, such as Pb(Mn₁/₃Sb₂/₃)O₃-PZT[186], Pb(Mg₁/₃Nb₂/₃)O₃-Pb(Zn₁/₃Nb₂/₃)O₃-PZT[187] and Pb(Zn₁/₃Nb₂/₃)O₃-PZT.[188] However, there have been pressing demands for Pb-free or Pb-reduced replacement materials because of the environment concerns arising from the potential toxicity of the lead oxides.[46], [189] Due to the similar “inert-pair” 6s² electronic configuration of Bi³⁺ to that of the Pb²⁺ cation, Bi-based perovskites are considered to be promising alternatives to Pb-based ferroelectrics.[149], [150] Among these materials, Bismuth zinc-titanate, Bi(Zn₁/3Ti₂/3)O₃ (BZT) has been reported to have a tetragonal symmetry with an extremely large c/a ratio (1.21) and a high calculated ionic polarization (103 μC/cm²).[35], [36], [65] Unfortunately, this material is not stable in its pure form and cannot be prepared by ambient-pressure solid state
Therefore, formation of a solid solution between a Pb-based perovskite and BZT may help stabilize BZT while presenting or enhancing the ferroelectric properties of the former.

Recently, PZT ceramics and films substituted with Bi-based perovskites have received intensive attention. For instance, in the $x$Bi(Zn$_{0.5}$Ti$_{0.5}$)O$_3$-(1-$x$)PbTiO$_3$ (BZT-PT) system, both the phase transition temperature ($T_C$) and the tetragonality significantly increase with increasing BZT content, with the highest values of $T_C$ ($\approx 700 \, ^\circ$C) and tetragonality ($c/a = 1.11$) being obtained at the solubility limit ($x = 0.4$). On the other hand, it was found that the substitution of BZT for the antiferroelectric PbZrO$_3$ (PZ) perovskite lowers the $T_C$ and stabilizes the ferroelectric phase without changing the orthorhombic structure. Our previous study shows that adding BZT into PZT forms the ternary solid solution Bi(Zn$_{0.5}$Ti$_{0.5}$)O$_3$-PbZrO$_3$-PbTiO$_3$ (BZT-PZ-PT) of perovskite structure, in which two MPB connecting the orthorhombic and tetragonal (MPB$_{O-T}$) phases and tetragonal and rhombohedral (MPB$_{T-R}$) phases, respectively, were observed and enhanced dielectric and ferroelectric properties were found in the ceramics of the MPB compositions. In present work, four batches of BZT-PZ-PT ternary single crystals have been grown by different methods. Both the crystal quality and properties has been optimized by adjusting the compositions.

### 7.3. Experimental

The Batch #1 single crystal of BZT-PZ-PT was grown using high temperature solution growth (HTSG, or flux method). The starting materials, PbO (99.9%), Bi$_2$O$_3$ (99.9%), ZrO$_2$ (99.9%), TiO$_2$ (99.9%), and ZnO (99.9%), were mixed according to the stoichiometry of the nominal composition 13BZT-50PZ-37PT. The mixture of PbO and H$_3$BO$_3$ was used as flux with a flux:charge molar ratio of 2:1. The mixture of solute and solvent was loaded into a 50 ml platinum crucible. The loaded platinum crucible was then put into a large alumina crucible, which was sealed using alumina cement to prevent evaporation of the flux due to the high volatility of PbO at high temperatures. The growth experiments were carried out in a cylindrical crystal growth furnace equipped with an automatic temperature controller. Figure 7.1 gives a typical thermal profile used, which consists of: (a) heating from room temperature to $T_1 = 1150 \, ^\circ$C at a rate $R_1 = 250$
\( ^\circ \text{C}/\text{h} \), (b) dwelling time \( t_d = 24\text{hrs} \), (c) cooling at \( R_2 = 10 \ ^\circ\text{C}/\text{day} \) to \( T_2 = 1000 \ ^\circ\text{C} \), and (d) cooling to room temperature at \( R_3 = 300 \ ^\circ\text{C}/\text{h} \). The grown crystals were separated from the flux by leaching in dilute hot \( \text{HNO}_3 \) solution.

![Temperature profile](image)

**Figure 7.1** Typical temperature profile used for the growth of BZT-PZ-PT crystals.

The Batch #2 was grown by top-cooled solution growth (TCSG) method. The starting oxides of stoichiometric 13BZT-50PZ-37PT were mixed with the flux (\( \text{PbO} \) and \( \text{H}_2\text{BO}_3 \)) with an optimum ratio of flux:charge = 4:1 (which was obtained after a number of trials). The mixture was ground homogeneously with a mortar and pestle and loaded into a platinum crucible of 100 ml, which was then put into a large alumina crucible. The alumina crucible was placed inside a single crystal grow furnace with a platinum wire hanged on the top, as shown in Figure 7.2. The top-cooling was achieved by the excellent thermal conduction of the platinum wire, which triggered nucleation around it. The thermal profile given in Figure 7.1 was used with two modified thermal parameters: \( T_2 = 1090 \ ^\circ\text{C} \) and \( R_2 = 5 \ ^\circ\text{C}/\text{day} \). At the end of the growth process, the grown crystals attached on the wire were pulled out of the melt surface and then annealed to the room temperature at a fast cooling rate of 500 \( ^\circ\text{C}/\text{h} \).
The top-seeded solution growth (TSSG) technique was employed to grow crystals with nominal compositions of 15BZT-49PZ-36PT (Batch #3) and 10BZT-52PZ-38PT (Batch #4). The experimental procedure and the furnace set-up were similar to those used in the TCSG method. A small single crystal obtained from a TCSG batch was used as seed, which was tied to the end of an alumina rod by platinum wire. Several experiments were usually necessary to find out the exact saturation growth temperature at which the seed crystal was introduced into the solution (1 cm below the surface of the melt) to trigger nucleation. The saturation growth temperature was determined as the highest temperature at which the seed crystal remains undissolved, and the lowest temperature at which no spontaneous nucleation occurs. During the growth process, the cooling rate was set between 0.2 and 0.5 °C/h. The growing crystal was rotated at a speed of 0 - 30 rpm. At the end of the growth ($T_2 = 1090 °C/h$), the grown crystal was pulled all the way out of the solution and cooled down to room temperature at the rate of $R_3$ (Figure 7.1).

The composition and homogeneity of the crystals were examined by laser ablation inductively coupled plasma mass spectrometry (LA-ICP-MS). The crystal structure of the as-grown crystals was analyzed by X-ray diffraction (XRD) on fine powder obtained by grinding a number of small crystals (Bruker D8 Advance)
Diffractometer, 40mA, 40kV, step size = 0.01°/step, 2θ = 10° - 80°). The resulting diffraction data were analyzed using TOPAS Academic Software to determine the symmetry and refine the lattice parameters of the grown crystals. In order to confirm the orientation of the as-grown crystals, X-ray diffraction analysis was carried out on the naturally grown facet of the Batch #1 and Batch #3 crystals.

The optical domain structure and phase transitions of the BZT-PZ-PT crystals were examined by means of polarized light microscopy (PLM). A crystal from each growth was cut parallel to the (001)cub plane and polished to optical quality using silicon carbide sand paper (220, 400 and 600 grit), followed by 3M lapping sheets (3 - 9 μm). PLM was performed with an Olympus BX 60 polarizing microscope equipped with Olympus UC 30 digital camera and a Linkham (THMS600) heating stage to study the domain structure, phase symmetry and phase transition of the grown crystals.

To perform electrical characterization, the polished (001)cub crystal surfaces of the platelets were painted by a layer of silver paste and gold wires were then attached to both surfaces of the samples. The dielectric properties of the grown crystals were measured using a Novocontrol Alpha high-resolution broadband dielectric analyzer equipped with a Novotherm heating system. The ferroelectric hysteresis loops were displayed on the (001)cub platelets by means of a Radiant RT-66 standardized ferroelectric testing system. The sample was kept in a silicon oil bath to avoid electric arcing during the polarization switching.

7.4. Results and discussion

7.4.1. Crystal growth

Figure 7.3 shows the four batches as-grown BZT-PZ-PT single crystals obtained by the three different methods. The chemical and thermodynamic parameters used for the four growth experiments are listed in Table 7.1.
Table 7.1 Chemical and thermodynamic parameters used for the growth of BZT-PZ-PT single crystals by three different techniques (Referring to Figure 7.1 for characteristic temperature and cooling rate).

<table>
<thead>
<tr>
<th>Growth Batch</th>
<th>Nominal BZT/PZ/PT (mol %)</th>
<th>Flux/Charge (mol %)</th>
<th>T₁ (°C)</th>
<th>T₂ (°C)</th>
<th>Cooling Rate R₁ (°C/day)</th>
<th>Growth Method</th>
</tr>
</thead>
<tbody>
<tr>
<td>#1</td>
<td>13/50/37</td>
<td>2:1</td>
<td>1150</td>
<td>1000</td>
<td>10</td>
<td>HTSG</td>
</tr>
<tr>
<td>#2</td>
<td>13/50/37</td>
<td>4:1</td>
<td>1150</td>
<td>1090</td>
<td>5</td>
<td>TCSG</td>
</tr>
<tr>
<td>#3</td>
<td>15/49/36</td>
<td>4:1</td>
<td>1150</td>
<td>1090</td>
<td>5</td>
<td>TSSG</td>
</tr>
<tr>
<td>#4</td>
<td>10/52/38</td>
<td>4:1</td>
<td>1150</td>
<td>1100</td>
<td>5</td>
<td>TSSG</td>
</tr>
</tbody>
</table>

Only small crystals (of about 1.0 - 1.5 mm size) were obtained from the flux growth (Figure 7.3 (a)). They were formed around the crucible walls on the surface of molten flux. This indicates that the super-saturation, and hence the spontaneous nucleation, started at this place as a result of flux volatilization at high temperature.[39], [195] No crystal was found inside the solidified solution, suggesting that the solute might not have melted completely. However, due to the temperature limitation of our growth furnace, a higher dwelling temperature could not be reached. In previous single crystal growth work, it was found that decreasing the charge to flux ratio cause the perovskite crystallization temperature range to decrease.[196] Thus, the flux to charge ratio was increased to 4:1 in the following three growth batches, in order to bring down the melting point of the system.
Figure 7.3  BZT-PZ-PT crystals grown from the four batches: (a) Batch #1, (b) Batch #2, (c) Batch #3 and (d) Batch #4, respectively.

One of the difficult issues encountered in the growth from high temperature solution (HTSG or flux growth) is the formation of a large number of nuclei resulting from spontaneous nucleation, leading to crystal of small size. It is therefore necessary to control and restrain nucleation in order to grow larger crystals. Therefore, an alternative growth process, namely the top-cooled solution growth (TCSG), was used for the growth of BZT-PZ-PT single crystals. The crystals grown from the TCSG method (Batch #2, Figure 7.3(b)) exhibit a larger size (3.0 - 5.0 mm) and better quality compared with Batch #1. This confirms that the platinum wire in TCSG provided a nucleation spot in the solution, which initiated the growth around it, inhibiting the formation of spontaneous nuclei upon cooling. In addition, the grown crystals were pulled out from the solution before cooling down to the solidification temperature of the solution, eliminating the need for leaching the crystals in dilute HNO₃, and averting the damage to the crystals, which could be caused, by the acidic solution.[197]

The TSSG method offers some advantages in growing single crystals of good quality, high compositional homogeneity and controlled morphology thanks to its unique
convection process of the solute under a specially designed temperature field and its slow growth. The size and quality of the crystal were further improved when grown by the TSSG method. As shown in Figure 7.3 (c), a single crystal of large size of $2 \times 2 \times 0.5 \text{ cm}^3$ was obtained in Batch #3. This result indicates that the nucleation process was significantly modified and effectively controlled by the use of the seed crystal in the TSSG technique. It is believed that when the super-saturation was first reached during slow cooling, the growth started on the faces of the seed crystal by liquid-phase epitaxy, which developed into a more stable crystal. This single-nucleated growth continued as the dominant process during the growth process, leading to the formation of a large crystal of BZT-PZ-PT.

The growth layers in the crystal were curved in a direction concave from the point of the origin seed as can be seen in Figure 7.3(c). This curvature arises because of the higher super-saturation at corners and edges which can lead to an increase of growth rate with distance from the centre of the plane. This growth steps leads to a rough surface of the as-grown Batch #3 crystal. At the late stage of the growth, spontaneous nucleation occurred around the growing crystal, which led to a few crystals of not-fully-developed cubic shape attached to the central crystal. A few crystals were found on the bottom of the crucible, which was triggered at a second step by super-saturation resulting from a slight temperature gradient. Unfortunately, the Batch #4 was interrupted during growth process due to seed rod broken, so the size is relatively smaller compared with the Batch #3 one.

In general, growth morphology of a crystal is determined by the relative growth rates of all possible crystal faces, fast-growing faces disappear and slowing growing faces remaining.[198] For perovskite crystals, slowing-growing $\{100\}_{\text{cub}}$ faces form cubes, the fast growing $\{111\}_{\text{cub}}$ and $\{110\}_{\text{cub}}$ face grow out and disappear. As a result, perovskite crystals grown under stable growth condition should have a cubic morphology.[196] In order to confirm the orientation of the as-grown crystals, X-ray diffraction analysis was carried out on the naturally grown facet of the Batch #2 and Batch #3. As shown in Figure 7.4, only three clear $\{00\}_{\text{cub}}$ peaks appear in the pattern, confirming the $\{001\}_{\text{cub}}$ orientation for the as-grown facets.
Figure 7.4  X-ray diffraction patterns indicating the \{001\}_{\text{cub}} naturally grown facets of the BZT-PZ-PT crystals of Batches #2 and Batch #3.

### 7.4.2. Composition determination

The LA-ICP-MS analysis results are shown in Figure 7.5. In general, all four batches of crystals show very strong signal response indicating the presence of Bi, Pb, Zn, Zr and Ti elements in the sample. In particular, Batch #1 crystal has good homogeneity with smooth and stable signal response in the inner part of the sample. However, as indicated by the ellipse in Figure 7.5, there are fluctuations at the beginning and end of the ablation, which correspond to the edge area of the crystal. This might be due to composition segregation during the later stage of growth. A relatively high concentration of Bi, Zn and Ti could lead to a different crystal structure, which can be confirmed by carrying out XRD structure characterization and optical domain observation. The small fluctuation (marked by *) in Batch #2 and #3 could result from the metal oxides inclusion (PbO, Bi$_2$O$_3$) in the crystals.
A dense and high-purity 13BZT-50PZ-37PT ceramic was used as reference. The ICP-MS response of Bi, Pb, Ti, Zn, and Zr (CPS) in the reference ceramic was recorded and compared to the response of those elements in the sample. The concentration of each element in the reference sample is known and the relation between the concentration and the ICP-MS response is linear. Once the ICP-MS response of the sample is measured, the concentration of each element can be calculated according to the concentration/response ratio obtained for the reference sample. The composition ratio between each element within sample is then calculated based on a perovskite structure $\text{ABO}_3$. The calculated actual compositions of the four batches crystals are listed in Table 7.2. The nominal compositions of Batch #1 and Batch #2 are same, but there is a huge difference between the actual compositions of these crystals, which most possibly is due to the effect of the flux concentration. The $\text{B}_2\text{O}_3$ additive formed by
decomposition of $\text{H}_3\text{B}_2\text{O}_3$ in the flux could prevent the evaporation of PbO by increasing the viscosity of the solution.[196] The higher flux-to-charge-ratio growths seem to form single crystals with a higher PZ-PT concentration, but a lower BZT concentration single crystals.

**Table 7.2 Calculated compositions of the four growths batches of BZT-PZ-PT single crystals**

<table>
<thead>
<tr>
<th>Growth Batches</th>
<th>BZT (mol %)</th>
<th>PZ (mol %)</th>
<th>PT (mol %)</th>
</tr>
</thead>
<tbody>
<tr>
<td>#1</td>
<td>0.974 ± 0.008</td>
<td>70.976 ± 0.197</td>
<td>28.079 ± 0.194</td>
</tr>
<tr>
<td>#2</td>
<td>0.530 ± 0.007</td>
<td>65.267 ± 0.245</td>
<td>34.203 ± 0.238</td>
</tr>
<tr>
<td>#3</td>
<td>0.578 ± 0.003</td>
<td>66.232 ± 0.179</td>
<td>33.189 ± 0.176</td>
</tr>
<tr>
<td>#4</td>
<td>0.433 ± 0.005</td>
<td>61.898 ± 0.332</td>
<td>37.668 ± 0.326</td>
</tr>
</tbody>
</table>

Both the nominal and actual compositions of the four batches of BZT-PZ-PT crystals are plotted in the phase diagram of the ternary system. According to the studies on the ceramics, with the addition of a certain amount BZT (about 1 mol %), the MPB region of this ternary system exists over a wide compositions region from 45 to 60 mol % PZ content.[66], [199] This suggests that the as-grown BZT-PZ-PT single crystals of all the four batches are in the rhombohedral instead of MPB region, thus, the properties of the crystals might not be the best of this ternary system.
Figure 7.6  Phase diagram of BZT-PZ-PT ternary system with the nominal and actual compositions of the four batches crystals indicated by black and red spots, respectively.

As can be seen from Figure 7.6, that all four batches of crystals seem to have a relatively higher PZ, but lower BZT and PT content compared with those starting nominal compositions. The studies on the PZ-PT binary system indicated that, with temperature cooling down below the liquidus line, the compositions of crystals change from Zr-rich side to Ti-rich side, because of phase segregation.[200] The crystal growth studies on the PZ-PT also confirmed that the Ti content of the solid solution increases with decreasing crystallization temperature.[90] As a result, the growth temperature range (1100–1090 °C) is favourable for forming PZ-rich crystals. BZT-PZ-PT single crystals of a MPB composition could be obtained by lowering the growth temperature.

7.4.3.  Structural studies

The phase and structure of the BZT-PZ-PT crystals were determined by powder XRD on ground crystals. The XRD pattern of the crystals from Batch #1 shows split at the (100)\text{cub}, (110)\text{cub} and (111)\text{cub} peaks. It is known that for a rhombohedral phase the (110)\text{cub} and (111)\text{cub} reflections are split, whereas the (100)\text{cub} reflection remains a single peak. In contrast, for a tetragonal phase the (100)\text{cub} and (110)\text{cub} reflections split into two
peaks, while the $(111)_{\text{cub}}$ reflection remains as a single peak. Therefore, the observed doublet peaks at all the $(100)_{\text{cub}}$, $(110)_{\text{cub}}$ and $(111)_{\text{cub}}$ reflections indicate a mixture of rhombohedral and tetragonal phases.

![Figure 7.7] Pawley Fitting of the X-ray powder diffraction pattern of one of the Batch#1 crystals. The black solid curve represents the experimental data. The red dashed curve is the calculated result. The difference between the experimental and fitting data is indicated by the gray curve. Inset is an enlarged view to clearly show the $(110)_{\text{cub}}$ peak splitting of Batch #1 crystal.

To confirm this, the XRD pattern was further analyzed by a Pawley Fit method using software TOPAS Academic. The fitting was carried out based on a model of coexisting rhombohedral and tetragonal phases. The refinement result is shown in Figure 7.7, where the measured data are displayed in the black solid curve, while the calculated result is represented by the red dashed curve. The difference between the experimental and fitting data is indicated by the gray curve (the small peak at 28° (marked by *) most possibly resulted from the solidified lead oxide on the surface of the crystal). Inset in Figure 7.7 is an enlarged view to clearly show the $(110)_{\text{cub}}$ peak splitting of Batch #1 crystal. The first asymmetric peak at about 30.8° belongs to the rhombohedral phase of the crystal. The presence of the second (31.5°) and third (32.3°) peaks is most likely caused by the $(110)_{\text{cub}}$ reflections of the tetragonal phase. It can be seen that the rhombohedral structure possesses a higher intensity than that of the
tetragonal phase. This result suggests the presence of coexisting rhombohedral phase in majority and tetragonal phase in minority in the crystals of Batch #1.

By narrowing down the growth temperature range to 1150 - 1090 °C, pure rhombohedral crystals were obtained for the other three growths. The XRD patterns of the crystals of Batches #2, #3 and #4 show an asymmetric (111) peak (Figure 7.8), confirming the rhombohedral structure. The calculated lattice parameters of the rhombohedral phase for all the four batches are listed in Table 7.3.

**Figure 7.8** X-ray diffraction patterns the BZT-PZ-PT single crystals from Batch #2, Batch #3 and Batch #4, respectively.

<table>
<thead>
<tr>
<th>Batch</th>
<th>BZT/PZ/PT</th>
<th>a (Å)</th>
<th>α (°)</th>
</tr>
</thead>
<tbody>
<tr>
<td>#1</td>
<td>0.974/70.976/28.079</td>
<td>4.1046 ± 0.0003</td>
<td>89.77 ± 0.03</td>
</tr>
<tr>
<td>#2</td>
<td>0.530/65.267/34.203</td>
<td>4.1157 ± 0.0009</td>
<td>89.700 ± 0.03</td>
</tr>
<tr>
<td>#3</td>
<td>0.578/66.232/33.189</td>
<td>4.1083 ± 0.0009</td>
<td>89.701 ± 0.006</td>
</tr>
<tr>
<td>#4</td>
<td>0.433/61.898/37.668</td>
<td>4.1138 ± 0.0009</td>
<td>89.697 ± 0.003</td>
</tr>
</tbody>
</table>
7.4.4. Domain structure and phase transitions behaviour

The domain structure and phase transition of the crystals of Batch #1 were studied by the optical examination of the crystal platelets by PLM. Figure 7.9(a) and Figure 7.9(b) show the image of a (001)$_\text{cub}$ platelet with crossed polarizers parallel and at 45˚ to the $<100>_{\text{cub}}$ direction, respectively. The platelet is in extinction with crossed polarizers at 45˚ to the $<100>_{\text{cub}}$ direction, which is consistent with the optical behaviour of a rhombohedral symmetry. However, there is a small region on the right edge of the sample (as marked by a dashed red ellipse in Figure 7.9(b)) that exhibits tetragonal symmetry with extinction being at 90˚.[133] This is in good agreement with the above-mentioned results from XRD refinement.

![Figure 7.9 Domain structure of a (001)$_\text{cub}$ platelet from Batch #1 observed by polarized light microscopy with crossed polarizers: (a) parallel, and (b) at 45˚, to the $<100>_{\text{cub}}$ direction, respectively.](image)

Upon heating to about $T_C = 300$ °C, the birefringence of the (001)$_\text{cub}$ platelet changes abruptly to zero, which indicates a first order phase transition from the (rhombohedral) ferroelectric to the paraelectric phase.[201] In contrast, the tetragonal part of the crystal does not transform into the cubic phase until above 520 °C. Therefore, the coexistence of the rhombohedral and tetragonal phases is not related to the morphotropic phase boundary (MPB) behaviour. The tetragonal crystal could be formed at a later stage of growth due to composition segregation that led to a higher
concentration of PT, and BZT content as revealed by the LA-ICP-MS results. On the other hand, the studies on the ceramics of the BZT-PZ-PT system confirmed that a relatively higher amount PT or BZT could lead to a higher phase transition temperature.[66]

![Figure 7.10](image)

**Figure 7.10** Domain structure of a (001)$_{\text{cub}}$ platelet from Batch #2 observed by PLM (a) with crossed polarizers parallel to the <100>$_{\text{cub}}$ direction, (b) an enlarged view of region A in Figure 7.10(a), and (c) an enlarged view of region B in (a).

Figure 7.10(a) illustrates the domain structures observed on a (001)$_{\text{cub}}$ platelet in the <001>$_{\text{cub}}$ direction. The domain structure in the top part of the sample (Figure 7.10(b)) cannot be clearly described, since the domains are too small and random. However, in the bottom part of the sample, as illustrated in Figure 7.10(c), clear domain patterns are revealed. At the position where the arrow is pointing to, layered twin interweaving domain configuration is observed. The domain wall orientation is in the <100>$_{\text{cub}}$ direction and the stacking of two 90° rotated twins produces a cross-hatching pattern under PLM. These are the typical 109° domain walls in the rhombohedral structure.[202] Birefringence of Batch #2 crystal as a function of temperature was measured upon cooling. As shown in Figure 7.11, at around $T_C$, the birefringence of the
(001)$_{\text{cub}}$ platelet changes abruptly to zero. However, this drop in birefringence is very small, suggesting a weak first order phase transition.[90]

![Figure 7.11](chart.png)

**Figure 7.11** Temperature dependence of the birefringence of (a) (001)$_{\text{cub}}$-oriented Batch #2 single crystal.

The Figure 7.12 displays the domain structure of Batch #3 single crystals at different temperatures. At the room temperature (Figure 7.12(a)), there are two types of domain configurations with different orientations. As illustrated by the white arrow in Figure 7.12(b), the domains look like tweed structures at an angle about 45° with respect to the (100)$_{\text{cub}}$ edge. Since orientation of these domain walls is in the $<110>$$_{\text{cub}}$ direction, they are most likely 71° domain. On the other hand, wedge shaped domains (marked by the red arrow) are displayed parallel to the (100)$_{\text{cub}}$ edge, which is aligned in the $<100>$$_{\text{cub}}$ direction. These are the 109° domains of the sample.[203] As the temperature increases, the 71° domain walls start to diminish and the 109° domain walls become clearer. Figure 7.12(c) is the domain structure at 310 °C, it can be seen that the 71° domains, which are aligned at 45° to the (100)$_{\text{cub}}$ edge, completely disappear and leave only 109° domain patterns (marked by white arrows in Figure 7.12(d)) behind. The 109° domain walls vanish above the phase transition temperature when the sample is in isotropic paraelectric phase.
Figure 7.12  Domain structure of a (001)\textsubscript{cub} platelet from Batch #3 observed by PLM with crossed polarizers parallel to the $<100>$\textsubscript{cub} direction (a) at room temperature, (b) an enlarged view of rectangle marked region A in Figure 7.12(a), (c) at 310 °C, (d) an enlarged view of rectangle marked region B in Figure 7.12(c) and (e) after cooling back to room temperature.

However, when the sample was cooled back to the room temperature, all the previous domain structures are completely gone. New formed domains are very different and fine (Figure 7.12(e)) and it is hard to describe their shape. This phenomenon suggests that the domain structure observed in the sample before might be caused by the internal stress, which can be introduced either in growth cooling or polishing. And these stress induced domains are not stable with respect to temperature once the stress is released.
In the case of Batch #4 single crystal, the (001)\textsubscript{cub}-oriented platelet is in extinction with crossed polarizers at 45° to the \textless 100\textgreater\textsubscript{cub} direction, which is consistent with the optical behavior of a rhombohedral symmetry. As shown in Figure 7.13(a), very clear and uniform wedge-shaped domains are revealed under PLM observation. The red and black arrows are used to indicate the two types of twin domains with different orientations in the platelet. The domain walls are oriented parallel to the [100]\textsubscript{cub}/[010]\textsubscript{cub} edges. The domain structure varies with temperature, becoming thinner and shorter with increasing temperature as indicated in Figure 7.13(b). As marked by white arrow in Figure 7.13(c), on the evidence of appearance of fine domains inside the large domains, the stress is released around 300 °C due to precursor effect of phase transition. After the sample was kept at 400 °C for 30 mins, and then cooled down to room temperature, a very different domain structure developed consisting of very fine domains, as shown in Figure 5.13(d). This phenomenon suggests that the original domain structure with large domain size observed in the sample could be again caused by internal mechanical
stress introduced during the polishing process. These stress-induced domains are not stable with respect to temperature. Upon heating up to 400 °C, the internal stress is released and the crystal exhibits fine and dense domain structure when cooled down to room temperature. The birefringence of the crystal as a function of temperature was measured upon heating and cooling, respectively, and the result is shown in Figure 7.14. The value of birefringence changes continuously at the phase transition between the ferroelectric and paraelectric phases, indicating a second order phase transition.[93] It is also noticed that the birefringence value at room temperature before heating up is slightly larger than that of after cooling back, which could also be attributed to the effect of the internal stress which induces additional structural anisotropy.

![Figure 7.14](image.png)

**Figure 7.14** Temperature dependence of the birefringence of a \((001)_{\text{cub}}\)-oriented platelet of Batch #4 BZT-PZ-PT single crystal.

### 7.4.5. Dielectric and ferroelectric properties

Figure 7.15 shows the variations as a function of temperature of the dielectric permittivity and loss, of the Batch #1 and #2 of BZT-PZ-PT single crystals, measured at various frequencies. The tetragonal part of the crystal from Batch #1 was removed by polishing all facets prior to carrying out the dielectric measurement. As shown in Figure
both crystals exhibit a sharp peak in the temperature dependence of dielectric permittivity, corresponding to the T_c of the phase transition from the paraelectric to ferroelectric phase upon cooling. It can be seen that the T_c values of the Batch #1 and Batch #2 crystals are very close: T_c = 292 °C and T_c = 298 °C, respectively. Generally, the close T_c indicates a similar composition of the two samples, but the LA-ICP-MS characterization result reveals that the Batch #1 and Batch #2 crystals have different compositions: Batch #1 is rich in BZT while Batch #2 has a relatively higher PT content. Therefore, the actual composition of the first two growth single crystals is different, and as a result the dielectric and ferroelectric properties are different.

It is noticed that the temperature dependence of the dielectric loss of Batch #1 crystals (Figure 7.15) shows a frequency-dependent shoulder at around 200 °C, which might suggest some kind of relaxor behavior. However, the temperature dependences of the real part and imaginary part of the dielectric permittivity measured at different frequencies (not shown here) show that no frequency-dependent anomaly can be observed either on the real part or on the imaginary part of the dielectric permittivity in the temperature range from 150 to 250°C. This result confirms that the observed dispersion in the dielectric loss is not due to a relaxor crossover, and accordingly the material is not a relaxor ferroelectric. Therefore, the “bumps” in the dielectric loss curves must be caused by the different increase rates of the real and imaginary parts of the dielectric permittivity as the temperature increases. Nevertheless, we do see a slight dispersion in the real part of dielectric permittivity occurring before the phase transition (220 - 280°C), especially when plotted in a log_{10}-scale. It could result from the domain wall motion, mobile charge carriers, and/or crystal defects, which are known to contribute to dielectric permittivity. This kind of dispersion is also observed in our studies of other systems, for example the PbZr_{0.46}Ti_{0.54}O_3 single crystals (see Chapter 3 for more details).
Figure 7.15  Temperature dependences of the dielectric permittivity ($\varepsilon'$) and loss (tan$\delta$) of the Batch #1 and Batch #2 of BZT-PZ-PT single crystals.

Figure 7.16 show the variations as a function of temperature of the dielectric permittivity and loss tangent of Batch #3 and Batch #4 of BZT-PZ-PT crystals, measured at various frequencies. The $T_c$ of the Batch #3 crystal is slightly higher: $T_c = 320$ °C. According to our studies on the ceramics of the ternary system around the MPB region,[66] the higher $T_c$ might be associated with a higher concentration of PT arising from severer composition segregation. The Batch #4 single crystal sample exhibits a
sharp and frequency-independent peak in the temperature dependence of dielectric permittivity, corresponding to the $T_C = 313 \, ^\circ C$ of the phase transition from the paraelectric to ferroelectric phase upon cooling. According to the well-established PZT phase diagrams,[16], [21], [22] the $T_C$ of the PZT with original composition ($x = 0.42$) is around $370 \, ^\circ C$. An expected decrease of PT content could be attributed to this result. Meanwhile, it seems that the addition of BZT into PZT decreases the $T_C$. This result is opposite to the effect of BZT substitution in PT where $T_C$ was found to increase by about 90 $^\circ C$ with 20 mol% substitution.[204] However, in both BZT-modified PZ and PZT ceramics within the MPB compositions,[194], [205] the $T_C$ was reported to be lowered by the substitution. Therefore, the result of this work confirms that BZT substitution does not always increase the $T_C$ of the solid solutions despite its large tetragonality. Its overall effect on the $T_C$ of a complex system depends also on the nature of the other end member.
Figure 7.16  Temperature dependences of the dielectric permittivity ($\varepsilon'$) and loss (tan$\delta$) of the Batch #3 and Batch #4 of BZT-PZ-PT single crystals.
Figure 7.17 Ferroelectric hysteresis loops of the four batches (#1, #2, #3, and #4) of BZT-PZ-PT single crystals.

The ferroelectric properties of the BZT-PZ-PT crystals were demonstrated by the well-developed polarization-electric field hysteresis loops, as shown in Figure 7.17. Saturation of polarization for Batch #1 and Batch #2 is achieved at an electric field of ±55 kV/cm at room temperature. The remnant polarization reaches $P_r = 32 \mu$C/cm$^2$ with a coercive electric field $E_C = 15.4$ kV/cm for Batch #1 crystal. The corresponding values for the Batch #2 crystal are $P_r = 36 \mu$C/cm$^2$ and $E_C = 11.1$ kV/cm, respectively. The Batch #1 and #2 crystals have a higher degree of loop squareness compared with the crystal of Batch #3 ($P_r = 23 \mu$C/cm$^2$ and $E_C = 7.3$ kV/cm), indicating a better composition homogeneity of the crystals. Overall, as shown in Figure 7.17(d), the Batch #4 has both higher remnant polarization $P_r = 28 \mu$C/cm$^2$ and larger coercive electric field $E_C = 23.1$ kV/cm. It has been reported that the MPB region of PZT is not changed by BZT.
substitution,[205] which means that the obtained BZT-PZ-PT crystals are not located in the MPB of the complex system. However, it is noticed that the coercive field of these BZT modified-PZT single crystal has been significantly enhanced compared with PZT crystals in the vicinity of this composition ($x = 0.35$ and $0.42$).[90]

From the viewpoint of crystal chemistry, several factors may be responsible for the enhancement of the Curie temperature, remnant polarization and coercive field found in this ternary system. First, the Zn$^{2+}$ ion on the B-site of complex perovskite Bi(Zn$_{1/2}$Ti$_{1/2}$)O$_3$ is known to be ferroelectrically active due to its $d^{10}$ electronic configuration, which favours covalent bonding between zinc and oxygen. Thus, the presence of Zn$^{2+}$ in the BZT-PZ-PT ternary solid solution could enhance the degree of ferroelectric order of the material, as recently shown in the Zn-doped PMN-PT ceramics.[206] The partial substitution of Zn$^{2+}$ and Ti$^{4+}$ for Zr$^{4+}$ increases the concentration of ferroelectrically active cations on the B-site, leading to a strong coupling between the A-site and B-site off-center distortion, which in turn could also contribute to a high $T_C$ value. Second, in the ternary system, both A-site cations (Bi$^{3+}$ and Pb$^{2+}$) possess the stereochemically active 6s$^2$ “lone-pair” electrons, which inherently enhance its spontaneous polarization and stabilize the ferroelectric order, leading to a higher $T_C$. It is also found that the replacement of the larger ionic radius Pb$^{2+}$ ion (1.49 Å) by the smaller Bi$^{3+}$ ion (1.35 Å) could increase the A-site cation displacement, increasing the spontaneous polarization. On the other hand, the spontaneous off-center displacement of B-sites cation Zn$^{2+}$ (0.5 Å) is considerably larger than that of Ti$^{4+}$ (0.34 Å), due to the strong hybridization of the 4s and 4p orbitals of Zn with the 2p orbitals of O atom.[192], [207]

The piezoelectric coefficient $d_{33}$ measured at room temperature for these crystals are lower than 300 pC/N. One possible reason for such a relatively low $d_{33}$ value for a single-crystal sample is that its composition is away from the MPB region of the ternary system. In addition, the sample might not be fully poled because of conduction, which could also lead to a low apparent piezoelectric coefficient. On the other hand, the absence of the rhombohedral-tetragonal (R-T) phase transition also diminishes the piezoresponse at room temperature, while extending the temperature of potential applications up to $T_C$, taking the full advantage of the high-$T_C$ feature of the crystals. More work could be done to improve the piezoelectric properties of the BZT-PZ-PT
single crystals by adjusting the composition of the grown crystals and by optimizing the electric-field poling process.

7.5. Conclusions

Novel ferroelectric single crystals of complex perovskite ternary solid solution BZT-PZ-PT were grown by three different techniques: the high-temperature solution growth (HTSG, or flux method), the top-cooled solution growth (TCSG) and the top-seeded solution growth (TSSG), respectively. The crystal purity and quality is significantly improved by narrowing down the growth temperature range. The largest crystal was grown from the TSSG with the dimensions of $2 \times 2 \times 0.5$ cm$^3$, and (001)$_{\text{cub}}$ faces. The crystal structure is found to be rhombohedral by means of X-ray powder diffraction. The examination of (001)$_{\text{cub}}$ platelets of Batch #3 and Batch #4 BZT-PZ-PT single crystals by polarized light microscopy has revealed the domain structure of rhombohedral symmetry with large and regular domains, which turn into finer lamellar domains upon heating above $T_C$ and cooling back to room temperature. The dielectric properties of the crystals measured as a function of temperature at various frequencies revealed the paraelectric to ferroelectric phase transition (upon cooling) at the Curie temperature $T_C = 292 ^\circ C$, $298 ^\circ C$, $320 ^\circ C$ and $313 ^\circ C$ for the Batch #1, #2, #3 and #4 crystals, respectively. The paraelectric to ferroelectric phase transition temperature $T_C$ is found to decrease with the substitution of BZT from the $T_C$ of the PZT ceramics of similar compositions. Although the value of the piezoelectric coefficient $d_{33}$ appears to be low compared with the relaxor-based piezocrystals, the ferroelectric properties are enhanced by the BZT substitution with the largest remnant polarization $P_r$ of 36 $\mu$C/cm$^2$ found in the Batch #2 crystal (with a coercive field $E_C = 11.1$ kV/cm). The results suggest that the BZT-PZ-PT ternary single crystals satisfy the widely held requirements of large remnant polarization and high operation voltage, while maintaining a relatively high Curie temperature with the absence of the rhombohedral-tetragonal phase transition. These features make them a promising candidate for a wide range of applications in high-power electromechanical transducers that can operate in a wider temperature range and at high fields.
Chapter 8.

General Conclusions and Future Directions

8.1. General Conclusions

The research on piezoelectric materials involves the design and synthesis of new or modified materials with high performance and the study of the relationship between structure and physical properties. Piezoelectric single crystals generally outperform their ceramic counterparts with excellent piezoelectric properties, making them the most promising materials for applications in piezo-devices that require high sensitivity, efficiency and power. In this thesis, PbZr$_{1-x}$Ti$_x$O$_3$ (PZT) single crystals with compositions of $x = 0.54$ and $0.45$ were grown successfully by a top-seeded solution growth (TSSG) method, and characterized by X-ray diffraction, polarized light microscopy (PLM), piezoresponse force microscopy (PFM), and dielectric, ferroelectric, and piezoelectric measurements. Moreover, donor- and acceptor-doped PZT single crystals were also grown for the first time by the TSSG technique and a top-cooled solution growth (TSSG) method. The compositions and homogeneity of the as-grown doped PZT single crystals are investigated by laser ablation inductively coupled plasma mass spectrometry (LA-ICP-MS) and energy dispersive spectroscopy (EDS). The dielectric, ferroelectric and piezoelectric properties of these single crystals are characterized. Finally, ferroelectric single crystals of a new lead-reduced Bi(Zn$_{0.5}$Ti$_{0.5}$)O$_3$-PbZrO$_3$-PbTiO$_3$ (BZT-PZ-PT) ternary solid solution system have been grown for the first time by three different methods, namely TSSG and TCSG, and high temperature solution growth (HTSG, or flux method). The domain structure, phase transition behaviour and the dielectric, ferroelectric and piezoelectric properties are investigated by various methods. The main results and contributions of this thesis work can be highlighted as follows:
1. Perovskite PZT single crystals were grown by the TSSG technique. The thermodynamics and kinetics conditions have been optimized for the growth of PZT single crystals. It was found that by adjusting the growth temperature, the composition of PZT crystals can be controlled, leading to the growth of PZT crystals of tetragonal composition \((x = 0.54)\) and those of the morphotropic phase boundary (MPB) composition \((x = 0.45)\). The XRD analysis confirms that the PZT \((x = 0.54)\) crystal has a tetragonal perovskite structure. The measurements of dielectric properties indicate that the PZT \((x = 0.54)\) crystal undergoes a single phase transition from the cubic to the tetragonal phase at \(T_C = 405 \degree C\) upon cooling. The PZT \((x = 0.54)\) crystal exhibits significant dielectric dispersion at a temperature range between 200 \degree C and 400 \degree C, suggesting strong domain wall motions, which could arise from minimized or nano-scale domain states. In contrast, the phase component and symmetry of the PZT \((x = 0.45)\) crystal are much more complex, containing rhombohedral and monoclinic phases at room temperature, which is characteristic of the MPB behaviour. The paraelectric to ferroelectric phase transition of the PZT \((x = 0.45)\) crystal occurs at \(T_C = 381 \degree C\). It undergoes an additional phase transition as revealed by the dielectric anomaly at 238 \degree C, which corresponds to the MPB phase transition. Furthermore, the PZT \((x = 0.45)\) crystal exhibits a much higher dielectric and piezoelectric properties with a \(d_{33}\) value reaching 886 pC/N. The high \(T_C\) and high piezoelectric performance of PZT single crystals qualify them as a promising material for high temperature and high power electro-mechanical transducer applications. On the other hand, availability of PZT single crystals makes it possible to study the complex domain structures and phase transitions by polarized light microscopy (PLM) and piezoresponse force microscopy (PFM).

2. The symmetry of the \(\text{PbZr}_{1-x}\text{Ti}_x\text{O}_3\) \((x = 0.54)\) single crystals was confirmed to be tetragonal by structural refinement based on X-ray diffraction data. However, the analysis of domain structure by PLM reveals that the \((001)_{\text{cub}}\) platelet of the crystal behaves isotropically, with extinction at any positions under the crossed polarizers, i.e. showing a seemingly cubic symmetry. On the other hand, the \((011)_{\text{cub}}\) platelet exhibits birefringence with
extinctions at 0°/90° to the <100>\text{cub} direction, which is consistent with the optical feature of a tetragonal phase. These phenomena are attributed to the presence of differently oriented miniaturized domains or nanodomains. These nanodomains are arranged in such a way that their birefringences compensate each other almost completely along the <001>\text{cub} direction on the (001)\text{cub} platelet, but incompletely on the (011)\text{cub} platelet. Birefringence on the (001)\text{cub} platelet can be induced by applying an electric field and an external stress applied in the <010>\text{cub} direction. Upon application of an electric field in the <010>\text{cub} direction, square-shaped domains with edges oriented in the <110>\text{cub} direction are observed by PLM. They are embedded in a tetragonal nanodomain matrix and are confirmed by PFM to be 180° ferroelectric domains with an average size of 12 μm. The formation of these domains is explained by the nucleation and growth of 180° flux-closure states in the crystal. Three steps are involved in this process: (1) a circular 180° flux-closure domain is nucleated in the tetragonal nanodomain state; (2) the small circular flux-closure domain reaches its critical size and grows into a large one, and (3) due to the anisotropic bonding in the PZT unit cell, the growth rate along the <001>\text{cub} direction is faster than along the <011>\text{cub}, leading to a square-shaped microdomain. The different growth velocities along different directions are attributed to the corresponding interplay of bonding and repulsive interactions. Such a complex domain structure is observed for the first time in a tetragonal ferroelectric crystal and it reveals some fascinating insights into the microstructure of PZT single crystals. In addition, a monoclinic (M\text{C}) phase is induced in the tetragonal nanodomains by application of the electric field. These results contribute to a better understanding of the structure-property relationships of this technologically important material system.

3. Given that PZT ceramics used in industry are always chemically modified to obtain enhanced properties for specific applications, it was a natural extension of our work to grow donor- and acceptor-doped PZT single crystals and to investigate the effects of the doping on the structure and properties. Donor (La$^{3+}$ and Bi$^{3+}$)-doped single crystals of PbZr$_{1-x}$Ti$_x$O$_3$
were grown by the TCSG and TSSG methods for the first time. The compositions of the as-grown single crystals were determined by LA-ICP-MS and EDS. The domain structure of the crystals was investigated by PLM and PFM. It was found that the incorporation of La\(^{3+}\) dopant into PZT could decrease the paraelectric to ferroelectric phase transition temperature (Curie temperature, \(T_C\)), as expected from the "softening" effects of donor-doping. In addition, the dielectric and ferroelectric properties of the PZT single crystals are significantly affected by La\(^{3+}\) doping. The highest Curie temperature, \(T_C = 291\) °C is obtained for the La-PZT (#3) single crystals. The highest remnant polarization (\(P_r\)) of 24.5 \(\mu\)C/cm\(^2\) with a coercive field (\(E_c\)) of 6.1 kV/cm is obtained for the La-PZT (#2) single crystals. The \(T_C\) values of the Bi-PZT (#1) and Bi-PZT (#2) crystals are 352 °C and 354 °C, respectively. It is found that the Bi\(^{3+}\) doping to PZT leads to rather complex behaviour and different effects from the La\(^{3+}\)-doping. These different results of the two donor dopants could arise from the different electronic structures of La\(^{3+}\) ([Xe]6s\(^0\)6p\(^0\)) and Bi\(^{3+}\) ([Xe]6s\(^2\)6p\(^0\)) and the resulted different defect distributions in the crystal lattice. The 6s\(^2\) lone pair can produce the local distortion or even hybridization between Bi-6s-orbitals and O-2p-orbitals, blocking the movement of electrons. Another reason for the complex behaviour of Bi\(^{3+}\) doping is the possible multiple valence states of bismuth ions as they can occur as Bi\(^{3+}\) or Bi\(^{5+}\). Their ionic radius varies between 1.11 Å and 0.74 Å depending on their valence and coordination number. Due to this variation, it is possible to incorporate bismuth ions on either A-site or B-site of the perovskite lattices. Our work has shown that the donor-doping effects in PZT single crystals are not always the same as in ceramics. In order to further understand the doping mechanisms in PZT single crystals, more detailed characterizations on crystal local structure by means of such techniques as high-resolution transmission electron microscopy (HRTEM) and high resolution x-ray diffraction (HRXRD), are needed.

4. Acceptor (Mg\(^{2+}\) and Mn\(^{2+}\))-doped single crystals of PZT have been successfully grown for the first time by the TSSG method. Large bulk size single crystals with dimensions of approximately 2 × 3 × 0.8 cm\(^3\) and 2 ×
2.5 × 0.8 cm³ are obtained for Mg-PZT (#1) and Mg-PZT (#2), respectively. The bulk Mn-PZT (#1) single crystal shows multiple nucleation and orientations with an average size of 2 × 2× 0.8 mm³. The size of Mn-PZT (#2) single crystals is relatively small (3 - 5 mm), which was due to an interruption of growth as a result of a power outage during the growth process. The Curie temperature, $T_c$, of the two batches of Mg$^{2+}$-doped PZT (Mg-PZT) single crystals is found to be 338 °C (Mg-PZT (#1)) and 324 °C (Mg-PZT (#2)), respectively. The polarization versus electric field hysteresis loops of the Mg-PZT single crystals show “peanut-shaped” hysteresis loops, which are reminiscent of the “double” hysteresis loops of antiferroelectric-like behaviour. The loops open up with the increases of temperature and applied electric field and eventually become regular ferroelectric hysteresis loops. A $P_r$ value of 20 μC/cm² with an $E_c$ of 7.0 kV/cm is obtained at 210 °C under an applied electric field of ±20 kV/cm for the Mg-PZT (#1) single crystal. At room temperature, when a ±50 kV/cm field is applied on a (001)$_{cub}$-cut Mg-PZT (#1) single crystal platelet, the achieved $P_r$ and $E_c$ values are 12 μC/cm² and 20 kV/cm, respectively. The enhancement of the $E_c$ is mainly due to the “pinning” effect of oxygen vacancies that are introduced by the Mg$^{2+}$ (donor) doping. In other words, “hardening” is achieved by Mg$^{2+}$ doping in PZT single crystals. On the other hand, the two batches of Mn$^{2+}$-doped PZT (Mn-PZT) single crystals exhibit phase transitions from the paraelectric to ferroelectric phases upon cooling at 326 °C (Mn-PZT (#1)) and 330 °C (Mn-PZT (#2)), respectively. The dielectric permittivity and loss tangent of Mn-PZT (#1) at room temperature are 200 and 0.004, respectively, while those values for Mn-PZT (#2) are 250 and 0.01. Overall, the P-E hysteresis loops of the Mn-PZT single crystals show high conductivity and the ferroelectric properties are inferior to that of Mg-PZT single crystals. A possible reason is that a certain percentage of Mn$^{2+}$ could be oxidized to Mn$^{3+}$ or Mn$^{4+}$, providing potential charge carriers for electrical conductivity and diminishing the polarization properties. Furthermore, the structural distortion arising from the Jahn-Teller effect should be taken into consideration as well due to the possible existence of Mn$^{3+}$, a Jahn-Teller ion.
5. In search for high-temperature, lead-reduced piezoelectric materials, novel ferroelectric single crystals of complex perovskite ternary solid solution Bi(Zn$_{0.5}$Ti$_{0.5}$)O$_3$-PbZrO$_3$-PbTiO$_3$ (BZT-PZ-PT) were grown by three different techniques: HTSG or flux method, TCSG and TSSG, respectively. The largest crystal was grown from the TSSG technique with the dimensions of 2×2×0.5 cm$^3$ that exhibited naturally grown {001}$_{cub}$ faces. The crystal purity and quality is significantly improved by narrowing down the growth temperature range. The dielectric properties of the crystals measured as a function of temperature at various frequencies revealed the paraelectric to ferroelectric phase transition (upon cooling) at the Curie temperature $T_C$ = 292, 298, 320 and 313 °C for the Batch #1, #2, #3 and #4 crystals, respectively. The ferroelectric properties of the grown crystals were displayed by well-developed (square) polarization - electric field hysteresis loops, with the largest remnant polarization $P_r$ of 36 µC/cm$^2$ found in the Batch #2 crystal (with a coercive field $E_C$ = 11.1 kV/cm). The results suggest that the BZT-PZ-PT ternary single crystals constitute a new family of high-$T_C$, lead-reduced ferroelectric materials, which are promising for various applications such as high-power electromechanical transducers that can operate in a wide temperature range.

8.2. Future directions

Piezoelectric single crystals with extraordinarily high piezoelectric performance will continue to be the focus of the developments of novel and improved materials for electromechanical transduction applications in the future. In particular, for high-efficiency and high-power applications, piezoelectric crystals with a high $T_C$ and a large $E_c$ are desired. In our work, PZT single crystals have been successfully grown using the TSSG method. The MPB crystals with composition $x = 0.45$ exhibits a high $T_C$ (381 °C) and a high $E_c$ (10 kV/cm). However, the piezoelectric properties of PZT crystals, with $d_{33} = 886$ pC/N and $k_{33} = 0.80$, are not high compared with the relaxor-based Pb(Mg$_{1/3}$Nb$_{2/3}$)O$_3$-PbTiO$_3$ (PMN-PT) and Pb(Zn$_{1/3}$Nb$_{2/3}$)O$_3$-PbTiO$_3$ (PZN-PT) single crystals. This is reasonable given that the piezoelectric properties of pure PZT ceramics are rather mediocre and in practical PZT ceramics need to be chemically modified to obtain
enhanced properties for specific applications. By doping PZT with higher valence cations (donors), such as replacing Pb$^{2+}$ with La$^{3+}$, and Zr$^{4+}$/Ti$^{4+}$ with Nb$^{5+}$, the properties can be “softened” with high piezoelectric coefficients (e.g. $d_{33}$), low coercive field and low conductivity. On the other hand, lower valence cations (acceptor), such as Na$^+$ replacing Pb$^{2+}$, and Mg$^{2+}$ substituting for Zr$^{4+}$/Ti$^{4+}$, can “harden” the properties with a large coercive field. In our work, we have successfully grown donor (La$^{3+}$ and Bi$^{3+}$)- and acceptor (Mg$^{2+}$ and Mn$^{2+}$)-doped PZT single crystals. Unfortunately, the actual compositions of the grown crystals are away from the MPB region due to constitutional segregation which is more severe in the presence of dopants. This has prevented us from realizing the best properties of PZT crystals. Therefore, one of the most important tasks in the near future is to grow doped PZT single crystals with compositions within the MPB region. To achieve this objective, it is necessary to study the thermodynamic behaviour of the PZT systems in the presence of various dopants by differential thermal analysis (DTA) and/or differential scanning calorimetry (DSC) in order to establish the relevant high-temperature phase diagrams. These phase diagrams will provide invaluable information on the phase segregation rate and the appropriate chemical, thermodynamic and kinetic parameters to compensate it. Moreover, for the fabrication of the electromechanical transducers in commercial and industrial applications, it will be necessary to increase the size and to improve the quality of the PZT and doped PZT single crystals. Studies also need to be performed to facilitate the transition from laboratory growth to a scale-up operation.

In this work the phase transitions in the donor-doped PZT single crystals have been investigated by PLM, and dielectric, ferroelectric and piezoelectric measurements. Some important experimental data and results have been obtained. However, many questions about the donor-doped PZT systems still remain open, which need to be further studied and clarified. In particular, the defect structure and the doping level of the dopants play an important role in determining the electrical properties of the doped PZT single crystals. It is necessary to investigate the doping levels of donors, such as La$^{3+}$ and Bi$^{3+}$ by using proper references before moving on to more advanced analysis. Laser ablation inductively coupled plasma mass spectrometry (LA-ICP-MS) can be employed to determine the composition and doping level of these crystals. In addition, the basic properties, such as the dielectric, ferroelectric properties have been investigated for acceptor (Mg$^{2+}$ and Mn$^{2+}$)-doped PZT single crystals. The polarization versus electric
field hysteresis loops of the Mg$^{2+}$-doped PZT single crystals show “peanut-shaped” hysteresis loops, which is arisen from the defect dipoles formed between oxygen vacancies and acceptor ions. Besides, the P-E hysteresis loops of the Mn$^{2+}$-doped PZT single crystals show high conductivity as a certain percentage of Mn$^{2+}$ could have been oxidized to Mn$^{3+}$ or Mn$^{4+}$. Electron paramagnetic resonance spectroscopy (EPR) is a powerful technique to investigate the local coordination environment and valence states of the dopants, in particular of the mixed valence states of the Mn ions. This study will help shed light on the complex doping effects.

The availability of the doped PZT single crystals makes it possible to study the structure-property relationship by carrying out a series of characterizations. It will be of particular interest to study the local structures of both undoped and doped PZT crystals by means of high-resolution transmission electron microscopy (HRTEM), which can obtain diffraction patterns and images of domains on nanoscale. The results will be of particular importance for developing the mechanisms of doping in single crystals. PFM is also a useful tool for imaging and examining ferroelectric domains microscopically, and it is a particularly effective way for studying how the local domains with different orientations respond to an external field drive. The electrical properties can be further studied by more advanced characterization methods, such as Rayleigh method to separate intrinsic and extrinsic contributions. Furthermore, it seems that donors and acceptors have different impacts on the phase transition behavior of the PZT single crystals. More theoretical analysis could be done to further explore the mechanism.We believe that a combination of these characterizations, together with our results obtained in this work on the macro- and meso-sopic properties, will lead to a better understanding of the doping mechanisms in the PZT single crystals, and thereby provide meaningful guidance for designing high performance piezoelectric materials in the future.

Because of environmental concerns about the presence of lead in PZT-based electronic materials, intensive research has been conducted on lead-free or lead-reduced piezoelectric systems in the last decade, with a view to replacing the Pb-based materials. In this work, novel ferroelectric single crystals of a lead-reduced ternary solid solution of BZT-PZ-PT have been successfully grown by three different methods. The BZT-PZ-PT system is confirmed to be a promising candidate for high-$T_c$ and high-power applications. It is believed that its electrical properties can be optimized by adjusting the
compositions, so as to grow single crystals within the ternary MPB region (with increased BZT content). Moreover, it is worth investigating the domain structure and phase transitions by PLM and PFM, which will provide a better understanding of the structure and property relation of this ternary system. Finally, keeping with the spirit of developing lead-free piezoelectrics, we believe that bismuth-based systems, represented by BZT, need to be investigated in more detail. With its $6s^2$ lone electron pair which is expected to enhance the polarization and piezoelectricity, $\text{Bi}^{3+}$ ion seems to be the most promising candidate for replacing $\text{Pb}^{2+}$ in piezo-ferroelectric materials. However, the solid state synthesis and crystal chemistry of bismuth compounds are far from being understood. Therefore, more studies should be performed on BZT-based solid solution systems in order to explore lead-free high-performance piezo-/ferroelectrics and to unveil the complex crystal chemistry (bonding nature, local structure, reaction mechanisms, etc.) and structure-property relations of bismuth-containing complex oxides.
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