Synthesis and Characterization of Piezo-/ferroelectric Lead Zirconate-Titanate (PZT) Single Crystals and Related Ternary Ceramics

by

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Abstract

PbZr$_{1-x}$Ti$_x$O$_3$ (PZT) single crystals with compositions across the morphotropic phase boundary (MPB) have been successfully grown by a top-seeded solution growth (TSSG) technique. The growth conditions are optimized in terms of chemical, thermodynamic and kinetic parameters. The growth temperature is found to be the key factor for controlling the composition of the crystals. The PbZr$_{0.54}$Ti$_{0.46}$O$_3$ crystals exhibit the best properties, with a piezoelectric coefficient $d_{33} = 1223$ pC/N, an electromechanical coupling factor $k_{33} = 0.8$, a high coercive field $E_c = 7$ kV/cm and a high Curie temperature $T_C = 395$ °C, making them a potentially material for high temperature and high power electromechanical transducer applications.

The availability of the PZT single crystals has allowed us to perform a series of characterization of their physical properties. Dielectric measurements of the PbZr$_{0.80}$Ti$_{0.20}$O$_3$ crystal show that the phase transition between rhombohedral octahedron-tilted ($R3c$) and untilted ($R3m$) phases is of the first order, which is evidenced by a thermal hysteresis upon heating and cooling. The tricritical behaviour of this composition is revealed by the birefringence measurements, showing a slightly discontinuous phase transition in (001)$_{cub}$ platelet and a continuous phase transition in the (110)$_{cub}$ platelet.

The domain structures and phase transitions of the PZT single crystals with compositions near the MPB are investigated by polarized microscopy (PLM). Continuous polarization rotation within the (110)$_{cub}$ plane was observed in both PbZr$_{0.58}$Ti$_{0.42}$O$_3$ and PbZr$_{0.54}$Ti$_{0.46}$O$_3$ crystals. Tetragonal nanodomains observed in the PbZr$_{0.54}$Ti$_{0.46}$O$_3$ crystal can be explained by Imry and Ma’s random field theory, which suggests that quenched random field related to structural disorder can break the system into nanodomains that are more energetically favored.

In our search for new lead-reduced piezoelectric materials, the ternary ceramics of Bi($Zn_{1/2}Ti_{1/2}$)O$_3$-PbZrO$_3$-PbTiO$_3$ [BZT-PZ-PT] were synthesized and investigated.
The introduction of BZT into the PZT binary system brings the MPB to a lower PT content and enlarges the composition range of the MPB region. Enhanced piezoelectric and ferroelectric properties are obtained in the MPB region with the highest BZT content (= 15 mole%), with $d_{33} = 275$ pC/N, $P_r = 33 \mu$C/cm$^2$ and $E_c = 26$ kV/cm.
To my dear parents, Zequan Xie and Ming Tian
and my beloved husband, Weilong Yang.
“Now bring me that horizon.”
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<tr>
<th>Abbreviation</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>PZT</td>
<td>PbZr(_{1-x})Ti(_x)O(_3)</td>
</tr>
<tr>
<td>MPB</td>
<td>morphotropic phase boundary</td>
</tr>
<tr>
<td>TSSG</td>
<td>top-seeded solution growth</td>
</tr>
<tr>
<td>XRD</td>
<td>X-ray diffraction</td>
</tr>
<tr>
<td>PLM</td>
<td>polarized light microscopy</td>
</tr>
<tr>
<td>(d_{33})</td>
<td>piezoelectric coefficient</td>
</tr>
<tr>
<td>(k_{33})</td>
<td>electromechanical coupling factor</td>
</tr>
<tr>
<td>(E_c)</td>
<td>coercive field</td>
</tr>
<tr>
<td>(P_r)</td>
<td>remnant polarization</td>
</tr>
<tr>
<td>(T_C)</td>
<td>Curie temperature</td>
</tr>
<tr>
<td>BZT</td>
<td>Bi(Zn(<em>{1/2})Ti(</em>{1/2}))O(_3)</td>
</tr>
<tr>
<td>PZ</td>
<td>PbZrO(_3)</td>
</tr>
<tr>
<td>PT</td>
<td>PbTiO(_3)</td>
</tr>
<tr>
<td>(\epsilon')</td>
<td>dielectric constant</td>
</tr>
<tr>
<td>(\chi)</td>
<td>dielectric susceptibility</td>
</tr>
<tr>
<td>(G)</td>
<td>free energy</td>
</tr>
<tr>
<td>(P_s)</td>
<td>spontaneous polarization</td>
</tr>
<tr>
<td>(E)</td>
<td>electric field</td>
</tr>
<tr>
<td>(t)</td>
<td>tolerance factor</td>
</tr>
<tr>
<td>(\tan \delta)</td>
<td>dielectric loss</td>
</tr>
<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>
</tr>
<tr>
<td>(Q_m)</td>
<td>mechanical quality factor</td>
</tr>
<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>
</tr>
</tbody>
</table>
BS  BiScO₃
fr  resonance frequency
fa  anti-resonance frequency
kp  planar coupling factor
P   polarizer
A   analyzer
Δn  birefringence
R   retardation
λ   wavelength of light
FE  ferroelectric phase
PE  paraelectric phase
C   Curie constant
β   critical exponent
Chapter 1

General Introduction

This thesis presents the growth and characterization of PbZr$_{1-x}$Ti$_x$O$_3$ (PZT) single crystals. With excellent properties and high Curie temperature, PZT single crystals with composition near morphotropic phase boundary (MPB) can be potentially used as electromechanical sensors, high-performance transducers and actuators. Other than industrial applications, studies of PZT single crystals also provide important experimental data for understanding the relationship between structure and properties. New PZT-based perovskite ceramics are also developed with improved properties near the expanded MPB region.

This chapter will introduce the background and some important concepts, including the piezoelectricity, ferroelectricity, order of phase transition, perovskite structure, PZT solid solution and its modification, and the current status of research and development of piezoelectric single crystals.

1.1 Piezoelectric Properties

Piezoelectric effect was discovered by Pierre and Jacques Curie in 1880s when studying natural crystals, such as tourmaline, quartz, topaz and Rhochelle salt [1]. The prefix “piezo” comes from the Greek word “pressure”. By applying pressure to a piezoelectric crystal, a charge flow can be induced in the measuring circuit. On the other hand, if an electric field is applied to the crystal, a strain will be induced, which is the converse piezoelectric effect [2]. Piezoelectric is a linear effect, and it can be expressed using the
following equations [3]

\[ D_i = d_{im}X_m \]  \quad (Direct effect) , and

\[ x_m = d_{mi}E_i \]  \quad (Converse effect) ,

where \( X_m \) is the applied stress, \( D_i \) is the resulting charge density along the \( i \) direction, \( E_i \) is the applied electric field along the \( i \) direction, \( x_m \) is the developed strain, and \( d_{mi} \) is the piezoelectric coefficient. \( m \) is the reduced notation form for the stress or strain, which follows the Voigt conversion [4]. Usually the piezoelectric coefficient measured in the direction of the applied field is called longitudinal coefficient (im=11, 22, 33), and that measured in the direction perpendicular to the field is called transverse coefficient (im=12, 23, 31). The remaining piezoelectric coefficients are shear coefficients (im=14, 15, 16,...35, 36).

Electromechanical coupling factor \( k \) specifies the conversion efficiency between electrical and mechanical energies. \( k \) is given by the expression:

\[ k^2 = \frac{\text{mechanical energy stored}}{\text{electrical energy applied}} \quad \text{or} \quad k^2 = \frac{\text{electrical energy stored}}{\text{mechanical energy applied}} . \]  \quad (1.3)

Electromechanical coupling factors carry different subscripts depending on different measuring modes. For instance, \( k_{33} \) is the coupling factor for longitudinal vibrations of a rod, and \( k_p \) is the planar coupling factor for a thin disc.

## 1.2 Ferroelectric Properties

### 1.2.1 General Properties of Ferroelectrics

Of the twenty piezoelectric crystal classes (point groups), ten have a unique polar axis, i.e., they possess a spontaneous polarization \( (P_s) \). Spontaneous polarization is temperature dependent, thus, charges will be generated on the surfaces of a polar crystal with changing temperature, which is called the pyroelectric effect. Ferroelectrics belong to the pyroelectric family, the polarization direction of which can be reversed by an electric field [5]. A ferroelectric will lose its ferroelectricity and become paraelectric if heated to above its Curie temperature \( (T_C) \). The direction of polarization is usually not the same throughout the whole crystal without poling. The regions with the polarization aligned along the same direction are called ferroelectric domains, which are formed during paraelectric-ferroelectric phase transition upon cooling below \( T_C \). The formation
of domains with opposite or different orientations is to minimize the electrostatic and elastic energy.

One of the most important characteristics of ferroelectrics is the ferroelectric hysteresis loop which displays the variation of polarization \( (P) \) with electric field \( (E) \). As shown in Figure 1.1, the initial polarization is zero when no \( E \)-field is applied (point A). With increasing \( E \)-field, the domains with the orientation that opposes to the \( E \)-field start to reorient in the direction of the field (BC). The saturated polarization \( (P_s) \) is reached when all the domains are aligned and the crystal becomes single domain (CD). When the \( E \)-field is reduced, the total polarization decreases (DE). However, even at zero field, there is still some remaining polarization \( P_r \) (point E). The opposite \( E \)-field required to cancel this polarization is called coercive field \( E_c \) (point F).

![Figure 1.1: Ferroelectric hysteresis loop: variation of polarization as a function of an applied alternative electric field (Adapted from [3]).](image)

The relationship between dielectric displacement \( D \), electric field \( E \), and polarization \( P \) is given by

\[
D = E + P .
\]  
(1.4)

The static dielectric constant \( \epsilon' \) is the derivative of dielectric displacement \( D \) with respect to the field \( E \). The dielectric susceptibility \( \chi \) is defined as the derivative of polarization \( P \) with respect to field \( E \). Therefore, \( \epsilon' \) and \( \chi \) have the following relationship [5]

\[
\epsilon' = 1 + \chi .
\]  
(1.5)
The value of dielectric constant $\epsilon'$ of ferroelectrics depends on the $E$-filed strength. However, at a small field, $\epsilon'$ is constant since there is no polarization reversal, the value of which can be calculated from the slope of the AB curve in Figure 1.1. Above $T_C$, $\epsilon'$ follows the Curie-Weiss law [3],

$$\epsilon' = \frac{C'}{(T - T_0)} \quad ,$$

(1.6)

where $C'$ is a constant and $T_0$ is the Curie-Weiss temperature. $T_0$ is not exactly coincident with the Curie temperature, but depends on the equilibrium behaviour of the paraelectric-ferroelectric transition. Since $\epsilon \gg 1$, the susceptibility $\chi = \epsilon' - 1 \simeq \epsilon'$ can be given by

$$\chi = \frac{C}{(T - T_0)} \quad ,$$

(1.7)

where $C$ is the Curie constant [6].

In Landau theory, the free energy ($G$) around the phase transition can be expanded in terms of the polarization with a series of coefficients [7],

$$G = \frac{1}{2} a P^2 + \frac{1}{4} b P^4 + \frac{1}{6} c P^6 - EP \quad .$$

(1.8)

The minimum of $G$ is obtained by differentiating the above equation with respect to $P$:

$$\frac{\partial G_P}{\partial P} = 0 \quad ,$$

(1.9)

which gives

$$E = aP + bP^3 + cP^5 \quad .$$

(1.10)

Since $\chi$, $P$ and $E$ are related by

$$\chi = \frac{\partial P}{\partial E} \quad ,$$

(1.11)

we obtain

$$\frac{1}{\chi} = \frac{\partial E}{\partial P} = a + 3bP^2 + 5cP^4 \quad .$$

(1.12)

For $T > T_0$ and $P = 0$, if combined with Curie-Weiss law (in Equation 1.7), Equation 1.12 results in

$$\frac{1}{\chi} = a = \frac{(T - T_0)}{C} \quad .$$

(1.13)

Therefore, Equation 1.8 can be rewritten as

$$G = \frac{(T - T_0)}{2C} P^2 + \frac{1}{4} b P^4 + \frac{1}{6} c P^6 - EP \quad .$$

(1.14)

Since $C$ and $c$ in Equation 1.14 are both positive in all ferroelectrics [8,9], the sign of $b$ determines whether the paraelectric-ferroelectric transition is continuous or discontinuous.
1.2.2 Second-order Transition

For the case \( b > 0 \), the paraelectric-ferroelectric phase transition is of second order, i.e., \( P \) is a continuous function of temperature (see Figure 1.2(b)). The corresponding free energy curve is illustrated in Figure 1.2(a). The spontaneous polarization can be calculated by setting \( E = 0 \) in Equation 1.14, in which the high power term \( cP^5 \) can be neglected since all the parameters are positive. Thus, from Equation 1.14, the spontaneous polarization \( (P_s) \) is obtained [10]

\[
P_s = \pm \left[ \frac{1}{C \cdot b} (T - T_0) \right]^{\frac{1}{2}}.
\]

(1.15)

As temperature decreases from \( T = T_0 \) to \( T < T_0 \), \( P_s \) will increase gradually from zero to \( P_0 \). Combining Equations 1.15 and 1.12, we have

\[
\frac{1}{\chi} = 2 \frac{(T_0 - T)}{C}.
\]

(1.16)

![Figure 1.2: Second-order phase transition. (a) The free energy as a function of polarization; (b) \( P_s \) as a function of temperature; and (c) The susceptibility \( \chi \) and its inverse as a function of temperature.](image)

Reciprocal susceptibility on both sides of the transition temperature are given in Equation 1.13 and 1.16 (see Figure 1.2(c)). The slope in the ferroelectric region \( (\frac{1}{2C}) \) is twice that in the paraelectric region \( (\frac{1}{C}) \). There is no latent heat, thus the phase transition temperatures on heating and cooling are both at \( T_0 = T_C \).
1.2.3 First-order Transition

If $b < 0$, for $T > T_0$ it is possible for the free energy curve to have a minimum with nonzero $P_s$ that coexists with a minimum with $P = 0$. As $T$ decreases from $T > T_0$ to $T < T_0$, the coefficient $\frac{(T-T_0)}{2c}$ in Equation 1.14 changes from positive to negative, and the corresponding free energy curves are illustrated in Figure 1.3(a). The phase transition from the non-polar state to the polar state does not happen at $T_0$, where the minimums of free energy corresponding to $P_s = 0$ and nonzero $P_s$ become equal, but at $T = T_C > T_0$ instead. In this case, the polarization jumps from zero to some nonzero value at $T_C$, which means the polarization changes discontinuously, as shown in Figure 1.3(b). There is a latent heat at the phase transition, i.e., the phase transition is of the first order [7].

Figure 1.3: First-order phase transition. (a) The free energy as a function of polarization; (b) $P_s$ as a function of temperature; (c) The susceptibility $\chi$ and its inverse as a function of temperature.

1.3 Ferroelectric Perovskites

Perovskite oxides are the most studied group of ferroelectrics. The perovskite compounds have the general chemical formula ABO$_3$, where A cations have the valance from +1 to +3 (e.g., $K^+$, Ba$^{2+}$, Pb$^{2+}$, Bi$^{3+}$, La$^{3+}$, etc.) and B cations have the valance from +3 to +6 (e.g., Ti$^{4+}$, Zr$^{4+}$, Sn$^{4+}$, Ta$^{5+}$, Nb$^{5+}$, etc). The perovskite structure is shown in Figure 1.4(a), where A cations occupy the corners of the cube, B cations are at
the centers and oxygen anions are at the centers of each face. The structure can also be described by a linked BO$_6$ octahedral network with A cations occupying the large cavities. As temperature drops below $T_C$, there is a phase change from high symmetry cubic phase to a lower symmetry phase. Taking PbTiO$_3$ for example, above $T_C$, it has a paraelectric cubic structure, with space group $Pm\bar{3}m$. Upon cooling, it transforms from a cubic phase to a ferroelectric tetragonal phase (with space group $P4mm$) at 487 °C, with small ionic displacements of Ti ions with respect to the oxygen octahedral network (see Figure 1.4(b)).

![Figure 1.4: The perovskite structure ABO$_3$ (for example PbTiO$_3$): (a) Cubic paraelectric phase ($a = b = c$); (b) Tetragonal ferroelectric phase ($a = b \neq c$).](image)

The stability of the perovskite structure is determined by the relative sizes of both the cations A and B and anion O$^{2-}$, with the B cation fitting into the oxygen octahedra, while A cation filling the space between the octahedra. The indicator for the stability of perovskite structure is called the tolerance factor $t$, given by [11]

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

where $r_A$, $r_B$ and $r_O$ are the ionic radii of the A, B and oxygen ions, respectively. The perovskite phase will be stable if the value of $t$ is between 0.88 and 1.09. If $t > 1$, the structure determined by A-O distance and the B cation is too small for the oxygen octahedron, which will lead to a small polar distortion. If $t < 1$, A cation will be too
small for the hole between oxygen octahedra, therefore rotations and tilting of the oxygen octahedra will be favoured [12].

1.4 PbZr$_{1-x}$Ti$_x$O$_3$ (PZT) Solid Solution

1.4.1 PZT Phase Diagram and Morphotropic Phase Boundary

PbZr$_{1-x}$Ti$_x$O$_3$ (PZT) ceramics are the most widely used piezoelectric and ferroelectric materials in a wide range of industrial and technological applications. As shown in Figure 1.5 of PZT phase diagram [13], PbTiO$_3$ (PT) and PbZrO$_3$ (PZ) can form continuous solid solutions over the whole composition range, $0 \leq x \leq 1$ [13]. PZ is antiferroelectric with an orthorhombic non-polar structure, which changes to rhombohedral ferroelectric with a small addition of PT ($x < 0.1$). 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 $\langle 111 \rangle_{cub}$ direction. The rhombohedral and the tetragonal phases are separated by a nearly vertical morphotropic phase boundary (MPB) at about $x = 0.47$. MPB is particularly interesting for both applications and fundamental studies, because the useful properties such as piezoelectric coefficients ($d_{33}$), electromechanical coupling factor ($k_{33}$), dielectric constant ($\epsilon'$) and remnant polarization ($P_r$) all reach a maximum value in the region of MPB.

A monoclinic phase was discovered by Noheda et al. [14] in the narrow range of composition in the MPB region using high-resolution synchrotron X-ray diffraction. The updated phase diagram around MPB is shown in Figure 1.6 [15]. The intermediate monoclinic phase allows the symmetry to change from rhombohedral $R3m$ to tetragonal $P4mm$ via their common subgroup, $Cm$. In the monoclinic $Cm$ phase, the Pb atom is free to move in the symmetry plane, therefore, polarization rotation can be induced if an electric field is applied. Theoretical calculation revealed that the high strain induced by the polarization rotation is the origin of large piezoelectric response at the MPB [16]. Recently, Glazer et al. suggested that local monoclinic symmetry exists in the compositions away from MPB, which cannot be easily detected by X-ray or neutron diffraction [17]. The monoclinic phase was found to increase in ratio with composition moving toward MPB [18]. However, by far no boundary and phase transition between the rhombohedral and monoclinic phases were reported. Also, the experimental results of structural analysis can be affected by the synthetic procedures of PZT ceramics. It
is reported by Kakegawa et al. [19] that phase coexistence is present in the ceramics synthesized by the conventional method, but absent in the ceramics prepared from a precipitation process. Based on the experimental data, Cao and Cross [20] proposed a model which predicted that the width of the MPB with coexistence of phases is inversely proportional to the grain size of the PZT ceramics. If PZT single crystals were available, it would have a very narrow MPB.

As mentioned previously, ferroelectric materials have spontaneous polarization and induced strain below $T_C$. In anisotropic crystals, domain structures will form to reduce the internal energy of the system. It is found that the rotational polarization instabilities in the monoclinic phase can lead to vanishing, or reduction, of the crystallographic anisotropy around the MPB [21,22]. The energy of domain walls is therefore decreased, and the system becomes an adaptive state, which is microscopically inhomogeneous, but macroscopically homogeneous [23, 24]. Transmission electron microscopy (TEM) investigations found that minimized domain structure, rather than normal micron-sized domains, exists in the MPB region of PZT [25]. The presence of miniaturization of the domain structure can facilitate the reorientation of the domains and result in the enhanced piezoelectric properties.
The phase transition behaviour of PZT as a function of composition and/or temperature is also interesting to investigate. Recently, the availability of PZT single crystals synthesized in our laboratory has made it possible to obtain the elastic data of PZT crystals. Kim et al. performed Brillouin light scattering on two PZT single crystals with composition near MPB: $x = 0.42$ and $x = 0.45$ [26]. They found that the ferroelectric to paraelectric phase transition at $x = 0.45$ is of second order, while it is of first order at $x = 0.42$, which means there is a tricritical point between these two compositions. An updated phase diagram around the MPB was also proposed with the new data points added. To reveal the nature of phase transition for the overall composition, further investigations need to be carried out.

1.4.2 Modifications on PZT Ceramics

To meet the specific requirements for different applications, PZT ceramics are usually modified by doping with various ions, such as Nb$^{5+}$, La$^{3+}$, Li$^+$, Fe$^{3+}$, etc., resulting in “hard” or “soft” PZTs. “Hard” PZT is formed when doped with acceptor ions such as K$^+$ and Na$^+$ for the replacement of Pb$^{2+}$, and Fe$^{3+}$ for the replacement of Zr$^{4+}$ or Ti$^{4+}$ (Table 1.1). In this case, oxygen vacancies are created, which form defect
dipoles. These defect dipoles can be aligned during the poling process, which stabilizes the domain structure and thereby leads to a high coercive field $E_c$. Hard doping also increases the mechanical quality factor ($Q_m$) and decreases dielectric constant ($\epsilon'$) and loss ($\tan \delta$). On the other hand, donor dopants create cation vacancies by replacing Pb$^{2+}$ with La$^{3+}$, and Zr$^{4+}$ or Ti$^{4+}$ with Nb$^{5+}$, which enhances the domain wall motion under an electric field. Therefore, donor doping “softens” the properties with high piezoelectric coefficients ($d_{33}$), high electromechanical coupling factor ($k_p$), low coercive field ($E_c$) and high dielectric loss ($\tan \delta$).

Table 1.1: Modifications of PZT with ‘soft’ and ‘hard’ doping adopted from [27].

<table>
<thead>
<tr>
<th>Dopant</th>
<th>$T_C$ (°C)</th>
<th>$\epsilon_{33}'/\epsilon_0$</th>
<th>$\tan \delta$, $10^{-3}$</th>
<th>$k_p$</th>
<th>$d_{33}$ (pC/m)</th>
<th>$Q_m$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Soft</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Nb$^{5+}$</td>
<td>365</td>
<td>1700</td>
<td>15</td>
<td>0.60</td>
<td>374</td>
<td>85</td>
</tr>
<tr>
<td>Sb$^{5+}$</td>
<td>&gt; 350</td>
<td>1510</td>
<td>15</td>
<td>0.46</td>
<td>410</td>
<td>95</td>
</tr>
<tr>
<td>Nd$^{3+}$</td>
<td>330</td>
<td>1600</td>
<td>20</td>
<td>0.60</td>
<td>355</td>
<td>100</td>
</tr>
<tr>
<td>Hard</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Fe$^{4+}$</td>
<td>300</td>
<td>820</td>
<td>4</td>
<td>0.59</td>
<td>240</td>
<td>500</td>
</tr>
<tr>
<td>Ni$^{3+}$</td>
<td>330</td>
<td>1000</td>
<td>8</td>
<td>0.50</td>
<td>200</td>
<td>350</td>
</tr>
</tbody>
</table>

By adding a complex perovskite, such as Pb(Mg$_{1/3}$Nb$_{2/3}$)O$_3$, Pb(Zn$_{1/3}$Nb$_{2/3}$)O$_3$ or Pb(Fe$_{1/2}$Ta$_{1/2}$)O$_3$, to PZT, a ternary piezoelectric ceramic system can be formed with modified properties. The B-sites of the complex perovskite compounds are generally occupied by two cations that have valences other than 4+. Due to the charge fluctuation of different cations, those complex systems can show relaxor behaviour and/or diffused ferroelectric-paraelectric phase transition. The addition of these complex compounds to PZT brings desired features of the ceramics, such as low sintering temperature, small grain size and high density. Furthermore, improved properties can be found in an enlarged MPB by adjusting the composition in a wide range. Some lead-free perovskite, such as BiFeO$_3$, LaAlO$_3$, KNbO$_3$ and AgSbO$_3$ can also form solid solutions with PZT with improved properties. For example, a high dielectric constant ($\epsilon' > 2000$) and a large mechanical coupling factor ($k_p > 75\%$) are obtained in the AgSbO$_3$-PZT ternary ceramics [6].
1.5 Bi(Zn$_{1/2}$Ti$_{1/2}$)O$_3$ Related Solid Solutions

Bi-based perovskite solid solutions are regarded as a promising substitution for Pb equivalent since Bi$^{3+}$ possesses the similar 6$s^2$ electron configuration, which can result in the electron lone pair that facilitates the local distortion and favours a polar structure. Therefore, Bi$^{3+}$ is a viable substitution for Pb$^{2+}$ on the A-site of the perovskite lattice to reduce the Pb-content. Among the Bi-based perovskites, Bi(Zn$_{1/2}$Ti$_{1/2}$)O$_3$ outstands 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 Å and the Zn/Ti displacement of 0.6 Å. However, BZT can only be synthesized at high pressure [28]. By forming solid solution with PbTiO$_3$, BZT can be stabilized in the perovskite structure. Different from the solid solution with other Bi-based perovskites, BZT-PT shows an increased $T_C$ of 487 °C with 40% BZT addition [29]. It was proposed by Suchomel et al. [29] that the high $T_C$ is resulted from the strong displacement coupling between the A- and B-site ions when the B-sites are completely occupied by ferroelectrically active ions (Zn$^{2+}$, Ti$^{4+}$, and Fe$^{3+}$).

1.6 Piezoelectric Single Crystals

1.6.1 Current Status of Piezoelectric Single Crystals

Figure 1.7 illustrates the historical development of piezoelectric materials in terms of piezoelectric coefficient $d_{33}$. For a long time, PZT ceramics had been the dominant material, and the piezoelectric property was only slightly increased by doping and modification. The breakthrough of piezoelectric performance occurred in 1997 with the discovery of relaxor-PT single crystals of 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) [30–33]. Compared with their ceramics, the single crystals show enhanced properties, such as high piezoelectric coefficient (> 1500 pC/N), and large electromechanical coupling factors $k_{33}$ (≈ 0.90) [16, 30, 34, 35]. However, the PMN-PT and PZN-PT single crystals have some drawbacks that limit their applications in the devices. Firstly, their Curie temperature $T_C$ and morphotrophic phase transition temperature (between rhombohedral and tetragonal phases) $T_{R-T}$ are low, which restricts the temperature range of operation for transducer devices. Secondly, their low coercive field $E_c$ increases the chance of depoling when an external electric
field is applied. As a result, to increase the polarization stability, a dc bias field is usually required. However, this would introduce complexity in designing the device and increase the manufacturing costs [36]. Another issue related to the performance of device is that their mechanical quality factor $Q_m$ is low, which limits their application as high power transformers and transducers. New systems of single crystals with high $T_C$ and large $E_c$ are desired for the replacement of the PMN-PT and PZN-PT single crystals in commercial applications.

![Figure 1.7: Development of piezoelectric materials in terms of piezoelectric coefficient $d_{33}$ (from [36]).](image)

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 [37]. Similar relationship between $d_{33}$ and $T_C/T_{R-T}$ 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, i.e. 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-PZT) that are being developed show increased $T_C$ and $T_{R-T}$ compared to the binary crystals PMN-PT and PZN-PT [38, 39]. 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 more thermally 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 [40], 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 [41] and thereby increase the $E_c$.

![Figure 1.8: Piezoelectric coefficient as a function of Curie temperature $T_C$ for ferroelectric ceramics [37,39,42–60].](image)

### 1.6.2 Growth of Piezoelectric Single Crystals

For commercial applications, it is desirable to grow crystals with good quality, large size and right compositions. Crystal growth techniques include (i) high temperature solution growth from flux, such as flux-Bridgman growth and top-seeded solution growth (TSSG), and (ii) growth directly from pure melts, such as Bridgman method, Czochralski growth and floating-zone melting method [61].

For commercial production, the size of crystal and growth rate are the major concerns. The Bridgman method that grows crystal directly from melt is a viable way to obtain large crystals with high quality [62]. Typically, the charge with the same
Figure 1.9: Piezoelectric coefficient as a function of Curie temperature $T_C$ for ferroelectric single crystals and ceramics. [40–43,61].
composition as the desired crystal 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 ingot crystallizes from the bottom to the top [63]. So far, PMN-PT and PIN-PMN-PT single crystals can be commercially manufactured by the Bridgman method, the dimensions of which can reach 75-100 mm in diameter and 150-200 mm in length [64]. One of the problems for the Bridgman method is the compositional inhomogeneity in the grown crystals due to the incongruent melting behaviour 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$_3$ [32,65]. 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 [66,67], PYN-PT (Pb(Yb$_{1/2}$Nb$_{1/2}$)O$_3$-PbTiO$_3$) [68] and BS-PT (BiScO$_3$-PbTiO$_3$) [69,70] single crystals. Large size PZN-PT single crystals with 75 mm in diameter were synthesized by the flux Bridgman method [71]. However, it is common to find PbO inclusions in some parts of the crystals, which degenerates the quality of the crystals. Another drawback is that the orientation of the grown crystals varies with growth conditions due to the spontaneous nucleation during the growth. The TSSG method was developed in our lab to grow PZN-PT single crystals with one growth direction by introducing a seed crystal to trigger nucleation [72]. 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 crucibles.

1.6.3 Domains in Ferroelectric Crystals

Domain pattern in a ferroelectric crystal is formed during the phase transition from paraelectric phase with a high symmetry to the ferroelectric phase with a lower symmetry. The orientation and type of domain walls depend on the polarization direction of the phases [64,73]. For the tetragonal phase, the polarizations are oriented along one of the six [001]$_{cub}$ directions, and the domain walls lie in the (001)$_{cub}$ and (101)$_{cub}$ planes [3]. The domain walls in the (001)$_{cub}$ planes are 180°-domain walls, because the polarizations of the domains separated by them are antiparallel. In the (101)$_{cub}$ planes, the domain
walls are 90°-walls, separating domains of polarizations oriented 90° to each other. The polarization in the rhombohedral phase is along the [111]_cub direction, and the resulting domain walls are 180°- and 71°/109°-walls. Polarization in the orthorhombic phase lies in the [011]_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 involves elastic deformation. Only the ferroelastic domain walls can be observed under the polarized light microscope (PLM). The availability of crystals makes it possible to observe and investigate the domain patterns and structures and to analyze the crystal symmetry of the phases by PLM.

1.6.4 Polarization Rotation

To explain the high piezoelectric response in relaxor-PT single crystals, Fu and Cohen [16] proposed the polarization rotation mechanism. They studied the PZN single crystals and did calculations using the first-principles linearized augmented plane wave (LAPW). Figure 1.10(b) shows the calculated free energy \(U\) under zero electric field as a function of the polarization path. If an electric field is applied, the total free energy \(G = U - PE\) can be decreased with the polarization rotating to the direction of the electric field. For a rhombohedral PZN crystal with an electric field applied along the [001]_cub-direction, the polarization can rotate via two paths, i.e., \(a \rightarrow f \rightarrow g \rightarrow e\) and \(a \rightarrow b \rightarrow c \rightarrow d \rightarrow e\) (see Figure 1.10(a)). It can be seen that the polarization is more easily to rotate along directions \(a \rightarrow f \rightarrow g \rightarrow e\) since its energy profile is flatter. The structural instability due to this flatter energy profile can lead to a large strain by a small electric field. As such, the piezoelectric coefficient calculated from polarization rotation along the path \(a \rightarrow f \rightarrow g \rightarrow e\) is five times higher than that of the path \(a \rightarrow b \rightarrow c \rightarrow d \rightarrow e\). This polarization rotation can be driven by composition, stress, electric field and temperature. The MPB phases (rhombohedral, monoclinic and tetragonal phases) of PZT have very close energy, thus the polarization can rotate in the anisotropically flattened free energy profile [74].
Figure 1.10: (a) Schematic illustration of polarization rotation path; (b) Free energy as a function of polarization direction (from [16]).

1.7 Objectives and Organization of the Thesis

1.7.1 Objectives of This Work

Over the past decade, ferroelectric single crystals such as PMN-PT and PZN-PT have drawn a lot of attention due to their ultra-high piezoelectric properties [30,31,33]. They outperform polycrystalline ceramics of PZT with a higher $d_{33}$ (1500 pC/N) and a larger $k_{33}$ ($\approx 0.9$). However, their low $T_C/T_{R-T}$ 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 PZT system has a high $T_C$, but its single crystals are very difficult to grow [75]. 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 characterizations on them. Recently, the top-seeded solution growth (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 this 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 behaviour in PZT; (4) update the PZT phase diagram based on the single crystal data.

The second part of this thesis work is to develop a new ternary solid solution system, namely Bi(Zn$\frac{1}{2}$Ti$\frac{1}{2}$)O$_3$-PbZrO$_3$-PbTiO$_3$ (BZT-PZ-PT). By modifying PZT with BZT, we hope to find some improved properties in this Pb-reduced system. Since BZT cannot form solid solution with PZT at any ratio, we will firstly find out the solubility limit of BZT in this ternary system. We will then focus on the compositions near the ternary MPB region, and systematically study the addition of BZT affects the dielectric, ferroelectric and piezoelectric properties of the PZT system.

1.7.2 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 X-ray powder diffraction, dielectric spectroscopy, ferroelectric hysteresis loop and piezoelectric properties measurements and polarized light microscopy.

As mentioned previously, both high piezoelectric performance and a high $T_C$ are expected to be obtained in PZT single crystals with MPB compositions. However, the PZT single crystals are very difficult to grow by Bridgman and related techniques due to its incongruently melting behaviour and high melting point. TSSG method has the advantage of lowering the growth temperature by using flux (PbO or PbO/B$_2$O$_3$), and controlling the growth direction by introducing a seed crystal. We applied the TSSG method to the growth of PZT single crystals, and optimized the growth condition to obtain crystals with desired compositions and good quality. Chapter 3 gives a detailed description of the growth of PZT single crystals under different conditions. The effects of growth parameters on the composition and morphology of the grown crystals are investigated and discussed. Structural analysis of PZT crystals with different compositions is performed by X-ray diffraction. The dielectric, ferroelectric and piezoelectric properties of the grown PZT crystals are also characterized in this chapter.

Chapter 4 is focused on the study of rhombohedral PZT crystals with composition around $x = 0.20$. On the PZT phase diagram, the rhombohedral region is separated to low temperature $R3c$ phase and a high-temperature $R3m$ phase. The difference between these two phases is that the oxygen octahedrons in $R3c$ show a successive rotation along
the \((111)_{\text{cub}}\) axis, which results in a subtle change in symmetry. It is interesting to study this phase transition in the PZT single crystal with \(x = 0.20\). Combining the results of polarized light microscopy (PLM) and dielectric measurements, we investigate the phase transition behaviour of the \(R3c-R3m\) and FE-PE phase transitions. The change of domain structures and variation of birefringence with temperature are also studied by PLM on two crystals with different orientations: \((001)_{\text{cub}}\) and \((110)_{\text{cub}}\).

Polarization rotation mechanism has been proposed to explain the high piezoelectric response in ferroelectric single crystals [16]. The monoclinic \(M_A\) phase with \(Cm\) symmetry in the MPB of PZT is a subgroup of both rhombohedral \((R3m)\) and tetragonal \((P4mm)\) phases. Theoretically, symmetry change from \(R3m\) to \(Cm\), and \(Cm\) to \(P4mm\) can be realized by polarization rotations from \(\langle 111 \rangle_{\text{cub}}\) to \(\langle 001 \rangle_{\text{cub}}\) direction in the \((110)_{\text{cub}}\) plane, since the three MPB phases have very close energy [74]. So far, no experimental data regarding the observation of the polarization rotation in PZT have been reported. This is because the polarization rotation is largely canceled out in PZT ceramics with randomly oriented domains. In a single crystal with all the unit cell perfectly arranged along one direction, it is possible to study the MPB phase transitions in crystals with different orientations by PLM. As such, Chapter 5 is focused on the study of the rhombohedral to monoclinic and monoclinic to tetragonal phase transitions in the two crystals with compositions \(x = 0.42\) and \(x = 0.46\), respectively. The path and mechanism of thermally induced polarization rotation for these two compositions are discussed by combining the results of dielectric measurements and optical observation. It is found that the domain structure becomes more complex as the composition approaching MPB, and nanodomains were observed in the tetragonal phase of the MPB region. The evolution of domain structure with the MPB phase transitions is also investigated on the crystals with these two compositions.

In order to develop new piezoelectric materials with a high \(T_C\) and a reduced lead content, chemical modification on the binary PZT system is a viable option. BZT is an unique lead-free compound with a high calculated \(P_s = 103 \ \mu \text{C/cm}^2\), and its solid solution with PT exhibits a high \(T_C\) (487 °C) and a large tetragonality \((c/a = 1.21)\) [28, 76]. The special features of BZT provide the basis of developing a new lead-reduced ternary system BZT-PZ-PT. In Chapter 6, the ceramics of this ternary system are synthesized by solid-state reaction. The solubility limit of BZT in the binary system is determined, and the ceramics with composition along the solubility limit curve are studied by means
of XRD, and dielectric, piezoelectric and ferroelectric measurements. Further systematic
ical studies of this system are focused on three series of compositions in the expanded
ternary MPB region, which is reported in Chapter 7. The physical properties of the
ceramics, such as $T_C$, and dielectric, ferroelectric and piezoelectric properties are inves-
tigated. By comparing the properties among the three series, ceramics with the best
properties can be selected to meet the requirements of different potential applications.
Chapter 2

Materials Characterization: Principles and Techniques

2.1 Introduction

This chapter will introduce the techniques and principles used for characterizing the structure and physical properties of the piezo-/ferroelectric materials prepared in this work, including X-ray diffraction, dielectric spectroscopy, ferroelectric and piezoelectric measurement and polarized light microscopy.

2.2 X-ray Diffraction (XRD)

X-ray powder diffraction is a nondestructive structural characterization technique of crystalline materials, which can be used to determine the crystal structures, symmetry, and lattice parameters. Two XRD instruments are used for characterizing our samples: Rigaku MSC Diffractometer and Bruker D8 Advanced Diffractometer. The X-ray radiation is produced by the bombardment of the target (anode) with a beam of accelerated electrons generated from the filament (cathode). The target material determines the wavelength of the X-ray. Both of the two XRD instruments use copper as target, and the resulting Cu-K$_\alpha$ radiation has a wavelength of 1.5418Å. The incident X-ray is emitted on the sample and a movable detector (Bruker) or photographic film (Rigaku) collects the intensities of the diffracted X-rays at different directions.
High intensity is obtained when incident X-rays and the diffracted X-rays are completely in phase and reinforced by each other, i.e., the path difference between the scattered X-rays and the incident X-rays is an integer multiple of wavelength $\lambda$. As shown in Figure 2.1, the constructive interference is at a maximum when Bragg’s Law is satisfied

$$2d_{hkl} \sin \theta = n\lambda, \quad (2.1)$$

where $d_{hkl}$ is the distance between the $(hkl)$ planes, $\theta$ is the angle between the incident beam and the crystal plane, $n$ is the order of reflection. The diffraction pattern is usually plotted as the intensity of the diffracted X-rays vs. the angle $2\theta$. A diffraction pattern contains many distinct peaks, each corresponding to a set of planes $(hkl)$ with the same interplanar spacing, $d$.

![Figure 2.1: Illustration of diffraction of X-rays by a crystal (Bragg condition).](image)

The seven crystal systems can be distinguished by their specific combination of the lengths of axes $(a, b, c)$ and the angles $(\alpha, \beta, \gamma)$ between them (Figure 2.2). Table 2.1 lists the seven crystal systems with their restrictions of lattice parameters. The refinement of the lattice parameters of the unit cell requires indexing the diffraction pattern, which is realized by assigning Miller indices $(hkl)$ to each peak. The lattice parameters are related to the Miller indices and d-spacings by an equation depending on the crystal system. For example, the expression for an orthorhombic unit cell is

$$\frac{1}{d_{hkl}^2} = \frac{h^2}{a^2} + \frac{k^2}{b^2} + \frac{l^2}{c^2}, \quad (2.2)$$

where $a$, $b$ and $c$ are the lattice parameters of the unit cell, $hkl$ are the Miller indices assigned to a set of planes with the interplanar spacing $d$. To achieve a good accuracy,
it is better to index all the peaks and calculate the lattice parameters by regression analysis. We use a program MDI Jade to refine our XRD data.

The ferroelectric systems we study have the perovskite structure. Since the formation of perovskite phase is determined by the tolerance factor $t$ calculated from the radii of the cations and anion (see Equation 1.16). To form a stable perovskite structure, $t$ should fall in the range of $0.88 < t < 1.09$, and lattice parameters $(a, b, c)$ corresponding to the dimensions of the unit cell should have very close values. However, the symmetry of the unit cell may vary with temperature or composition. For a cubic unit cell $(a = b = c)$, as calculated using Equation 2.2, the 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. So on the diffraction pattern, all the three reflections show a single peak each. When the structure changes to a lower symmetry, for example tetragonal, the lattice parameters along three axis are no longer identical, $a = b \neq c$. Therefore, at $\{100\}_{\text{cub}}$ position there are two distinguishable peaks. Figure 2.3 shows the splittings of the $\{100\}_{\text{cub}}$, $\{110\}_{\text{cub}}$ and $\{111\}_{\text{cub}}$ peaks for different symmetries. Therefore, based on the peak splitting and profile of the key reflections, it is possible to deduce the symmetry of the phase.
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>$a = b = c$</td>
</tr>
<tr>
<td></td>
<td>$\alpha = \beta = \gamma = 90^\circ$</td>
</tr>
<tr>
<td>Tetragonal</td>
<td>$a = b \neq c$</td>
</tr>
<tr>
<td></td>
<td>$\alpha = \beta = \gamma = 90^\circ$</td>
</tr>
<tr>
<td>Orthorhombic</td>
<td>$a \neq b \neq c$</td>
</tr>
<tr>
<td></td>
<td>$\alpha = \beta = \gamma = 90^\circ$</td>
</tr>
<tr>
<td>Monoclinic</td>
<td>$a \neq b \neq c$</td>
</tr>
<tr>
<td></td>
<td>$\alpha = \gamma = 90^\circ; \beta \neq 90^\circ$</td>
</tr>
<tr>
<td>Triclinic</td>
<td>$a \neq b \neq c$</td>
</tr>
<tr>
<td></td>
<td>$\alpha \neq \beta \neq \gamma \neq 90^\circ$</td>
</tr>
<tr>
<td>Hexagonal</td>
<td>$a = b \neq c$</td>
</tr>
<tr>
<td></td>
<td>$\alpha = \beta = 90^\circ; \gamma = 120^\circ$</td>
</tr>
<tr>
<td>Trigonal</td>
<td>$a = b = c$</td>
</tr>
<tr>
<td></td>
<td>$\alpha = \beta = \gamma = 90^\circ$</td>
</tr>
</tbody>
</table>

Figure 2.3: XRD peak splittings for the \{100\}_cub, \{110\}_cub and \{111\}_cub reflections for different symmetries.
2.3 Dielectric Spectroscopy

The measurement of dielectric properties (permittivity and loss factor) at various frequencies and temperatures provides us with information about polarization behaviour and phase transitions in a ferroelectric material. The dielectric spectrum is measured using a Novocontrol high-resolution broad band dielectric spectrometer equipped with a high temperature system. The schematic of the circuit of a typical frequency response analyzer is shown in Figure 2.4. The sample is connected to the two electrodes, and a voltage \( U \) with angular frequency \( \omega \) is applied to the measured sample. The voltage is in the range of \( 1 \, V \sim 3 \, V \) with frequency varying between \( 3 \, \mu Hz \) and \( 20 \, MHz \). The amplitude and phase of the voltage and the current flowing in the sample are measured by phase sensitive voltmeters. The second voltmeter measures the voltage signal across the resistance \( R \). The signals are output to the computer and the complex impedance \( Z \) is calculated by

\[
Z = \frac{U}{I}. \tag{2.3}
\]

Since \( Z \) and \( C \) have this relationship:

\[
Z = \frac{1}{j\omega C}, \tag{2.4}
\]

the complex dielectric constant can then be given by

\[
\epsilon = \epsilon' - j\epsilon'' = C \frac{d}{\epsilon_0 A}, \tag{2.5}
\]

where \( d \) is the thickness, and \( A \) is the area, of the sample.

When a time-varying electric field is applied to a dielectric capacitor, the current \( i \) flows through the capacitor is given by

\[
i = j\omega \epsilon_C E \quad (j = \sqrt{-1}), \tag{2.6}
\]
where $C_0$ is the capacitance of the capacitor without dielectric material filled in (i.e. in vacuum), and $\epsilon_r$ is the relative dielectric constant. There is usually dielectric loss in the media due to the energy loss from the friction between the polarization and electric dipoles. Thus, $\epsilon_r^*$ is a complex number depending on $\omega$:

$$\epsilon_r^*(\omega) = \epsilon'(\omega) - j\epsilon''(\omega),$$

(2.7)

where $\epsilon'(\omega)$ and $\epsilon''(\omega)$ are the real part and imaginary part of the dielectric constant, respectively. The loss factor (tan $\delta$) (Figure 2.5) is defined as

$$\tan \delta = \frac{\epsilon''}{\epsilon'},$$

(2.8)

which is general expression for the loss in practical use. The total current density $J$ is

$$J = \sigma E + j\omega\epsilon_0\epsilon'E = \omega\epsilon_0\epsilon''E + j\omega\epsilon_0\epsilon'E,$$

(2.9)

where $E$ is the dc electric field, and $\sigma$ is the electric conductivity of the material.

2.4 Ferroelectric Measurements

The primary characterization of polarization ($P$) reversal in ferroelectrics is the ferroelectric hysteresis loop, i.e. $P$-$E$ loops. In this work, $P$-$E$ loops are measured using
an RT66A Standard Ferroelectric Testing System (Radiant Technologies Inc.). Figure 2.6 shows a modified Sawyer-Tower circuit which is used to observe the $P$-$E$ hysteresis loops. In the circuit, $C_x$ is the capacitance of the sample to be measured, and an RC circuit is connected in the series with $C_x$, which can compensate phase shift due to conductivity or dielectric loss in the sample. An alternating voltage is applied across the two parallel electrodes of the sample. The voltage takes the form of a single triangle wave. As shown in Figure 2.7, one preset cycle is applied to the sample to ensure a known initial location for the loop. After one second delay for settling to the quiescent states, the measurement loop is executed. The electric field across the sample is outputted to the horizontal plates ($X$ axis) of the oscilloscope. The voltage $V_r$ across the reference capacitor $C_r$ is proportional to the polarization $P$ of the sample:

$$V_r = \frac{Q}{C_r} = \frac{AP}{C_r},$$

(2.10)

where $A$ is the area of the electrode. This voltage is displayed by the vertical plates ($Y$ axis) of the oscilloscope. In our experiments, digital data are collected. A typical $P$-$E$ loop is displayed in Figure 1.1.

Figure 2.6: Schematic circuit of modified Sawyer-Tower circuit for the measurement of $P$-$E$ hysteresis loop.
2.5 Piezoelectric Measurements

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 defined in Section 1.1, the piezoelectric coefficient can be expressed as:

\[
d_{33} = \frac{D_3}{X_3},
\]

(2.11)

where \(D_3\) is the charge density (C/m\(^2\)), and \(X_3\) is the mechanical stress applied (N/m\(^2\)). The notation “33” means that the direction of the applied stress is the same as the direction of the polarization measured.

The electromechanical coupling factor \(k\) is determined using a Solartron 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 a.c. 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 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 \((w)\) > 4 (see Figure 2.8). The mechanical vibration is measured along the longest dimension of the sample, which is the same direction of the a.c. field applied. The expression of \(k_{33}\) is given by the following equation [77]

\[
k_{33}^2 = \frac{\pi}{2} \cdot \frac{f_r}{f_a} \cdot \tan \left( \frac{\pi}{2} \cdot \frac{f_a - f_r}{f_a} \right),
\]

(2.12)
where the resonance frequency \( f_r \) and anti-resonance frequency \( f_a \) correspond to the maximum and minimum impedance, respectively. For ceramic samples, the electromechanical coupling factor is expressed by \( k_p \), which is the planar coupling factor, given by [77]

\[
k^2_p = 2.5 \cdot \frac{f_a - f_r}{f_r}.
\]

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 2.8: Illustration of the (001)cube-oriented bar (or rod) single crystal for \( k_{33} \) measurement (with a typical aspect ratio \( h/w > 4 \)).](image)

2.6 Polarized Light Microscopy (PLM)

We use polarized light microscopy to determine the symmetry and crystallographic group, observe the domain structure and measure the birefringence of the single crystals. The instrument used is an Olympus BX60 polarized light microscope (see Figure 2.9) equipped with a Linkam HTMS600 heating/cooling stage (temperature range \(-170^\circ C\) to \(600^\circ C\)) to control the temperature variations. There are two polarizing filters in the microscope: the polarizer \( P \) and analyzer \( A \), which are situated below the specimen stage and above the objective lens, respectively. The polarizer and analyzer are perpendicular to each other (crossed). Therefore, no light can go through the analyzer without
an anisotropic crystal (birefringent substance) inserted in between. For isotropic crys-

tals, the index of refraction is the same in all directions. For anisotropic crystals, light
entering the crystals is double refracted and decomposed into two polarized rays, the
orientations and velocities of which depend on the crystalline optical axis. The ray with
the polarization parallel to the optical axis is called the extraordinary (e) ray, and the
other ray with orientation perpendicular to the optical axis is the ordinary (o) ray [79].
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} (2.14)

The birefringence can be obtained by measuring the retardation of the light, which is
calculated using the following equation:

$$R = t \times \Delta n,$$  \hspace{1cm} (2.15)

where $R$ is the retardation, and $t$ is the thickness of the crystal.

If a crystal is placed between $P$ and $A$ at the position that its optical axis is parallel
to one of the polarizers, no light can go through since the polarized light is blocked by
either analyzer or the birefringent crystal that is perpendicular to it. In this situation,
the crystal is dark or extinct under the microscope. If the crystal is inserted between the crossed $P$ and $A$ with its optical axis at an angle ($\theta$) to the polarizer, some light can pass through the analyzer. Figure 2.10 shows the schematic of the decomposition and recombination of light during propagation. Suppose that the polarized light from polarizer has the vector $D = a \cos \omega t$, and its vibration direction has a $\theta$ angle to the optical axis of the crystal. The light goes through the crystal and splits into two rays with the amplitude $D_o = a \cos \theta \cos \omega t$ and $D_e = a \sin \theta \cos \omega t$ in their propagating plane. Due to the refraction, in the crystal one ray travels faster than the other, thus the two rays are out of phase by an angle $\phi$. These two rays are recombined by the analyzer, and the light intensity ($I$) of the sample can be expressed by [80]

$$I = I_0 \sin^2 2\theta \sin^2 \phi/2, \quad (2.16)$$

where $I_0$ is the intensity of the light from the polarizer, and the phase difference $\phi$ of the two rays is given by

$$\phi = (2\pi/\lambda) \cdot t \cdot \Delta n, \quad (2.17)$$

where $\lambda$ is the wavelength of light, $t$ is the thickness of the crystal and $\Delta n$ is the birefringence of the crystal. The maximum brightness can be reached when the crystal is oriented at 45° angle with respective to both analyzer and polarizer. Therefore, by checking the extinction position of a crystal, we can determine the orientation of its optical axis and therefore determine its crystallographic symmetry. The orientation of the crystal axis is related to the symmetry of the anisotropic crystal. For example, the rhombohedral crystal with symmetry $R3m/R3c$ has the spontaneous polarization along one of the $\langle 111 \rangle_{cub}$ directions. Its optical axis is also parallel to the $\langle 111 \rangle_{cub}$ direction. For a (001)$_{cub}$-oriented crystal platelet, the extinction occurs when the $[100]_{cub}/[010]_{cub}$ edges is at 45° angle to the polarizer or analyzer. For a (011)$_{cub}$-oriented crystal platelet, the extinction happens when the $[\overline{1}10]_{cub}$ edge is at 35.3° or 0° to the polarizer or analyzer. Table 2.2 summarized the extinction position and symmetry of the possible phases in PbZr$_{1-x}$Ti$_x$O$_3$ [81]. The retardation is measured when the crystal is at its brightest positions using a compensator. The compensator is an anisotropic crystal with known birefringence, and it is inserted at a right angle with the optical axis of the crystal. The birefringence of the compensator can be changed by adjusting its tilting angle, and total compensation is achieved when the birefringence of compensator equals the birefringence of the crystal. For many ferroelectric crystlas, birefringence decreases with increasing
temperature. When the temperature is increased to above the Curie temperature $T_C$, the structure changes to cubic and the crystal becomes isotropic, giving rise to an extinction at any position under crossed polarizers. By measuring the birefringence with changing temperature, we can study the symmetry change and the phase transition behaviour.
Table 2.2: Extinction angles ($\theta_e$) of different phases in the (001)$_{\text{cub}}$- and (110)$_{\text{cub}}$-oriented single crystals of different symmetry. (In (001)$_{\text{cub}}$ platelet $\theta_e$ is defined as the angle between [010]$_{\text{cub}}$ and analyzer when a crystal is at its extinct position; In (110)$_{\text{cub}}$ platelet $\theta_e$ is defined as the angle between [110]$_{\text{cub}}$ and analyzer when a crystal is at its extinct position.)

<table>
<thead>
<tr>
<th>Polarization direction</th>
<th>Rhombohedral</th>
<th>Tetragonal</th>
<th>Monoclinic ($M_A$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\theta_e$ in a (001)$_{\text{cub}}$ platelet</td>
<td>45°</td>
<td>0°/90°</td>
<td>45°</td>
</tr>
<tr>
<td>$\theta_e$ in a (110)$_{\text{cub}}$ platelet</td>
<td>0°/35.3°</td>
<td>0°/90°</td>
<td>Not specific</td>
</tr>
</tbody>
</table>
Chapter 3

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

3.1 Abstract

PbZr$_{1-x}$Ti$_x$O$_3$ (PZT) single crystals with a wide range of compositions ($0.2 \leq x \leq 1.00$) across the morphotropic phase boundary (MPB) region were grown by a top-seeded solution growth (TSSG) technique. To minimize the composition segregation, each growth was programmed to take place upon cooling within a certain temperature range, and it was found that the composition of grown crystals is mainly determined by the growth temperature. X-ray diffraction (XRD) analysis of the crystal powders shows that the structure changes from a rhombohedral to tetragonal symmetry with increasing Ti content. The dielectric, ferroelectric and piezoelectric properties of the (001)$_{\text{cub}}$-oriented PZT crystals were measured. The best properties were found in the MPB composition $x = 0.46$, with a Curie temperature $T_C = 395 \, ^\circ\text{C}$, an electromechanical coupling factor $k_{33} = 0.80$ and piezoelectric coefficient $d_{33} = 1223 \, \text{pC/N}$. This overall performance makes the PZT single crystals the best high-$T_C$, high piezoelectric material useful for high power electromechanical transducer applications.
3.2 Introduction

PbZr$_{1-x}$Ti$_x$O$_3$ (PZT) ferroelectric ceramics have been widely used in actuators, and sensors because of their high piezoelectric properties in the compositions close to the morphotropic phase boundary (MPB). Recently, relaxor ferroelectrics-based single crystals of the Pb(Mg$_{1/3}$Nb$_{2/3}$)$_3$O$_3$-PbTiO$_3$ (PMN-PT) and Pb(Zn$_{1/3}$Nb$_{2/3}$)$_3$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 ($k_{33} > 0.90$) [36]. Even though their properties are superior than those of PZT ceramics, they exhibit some inherent drawbacks, such as a low MPB phase transition temperature ($T_{MPB} < 100$ °C) and a low coercive field ($E_c < 3$ kV/cm), making them unsuitable for high temperature and high field (power) applications. Since PZT system has a high $T_C$ ($\sim 380$ °C at $x = 0.46$), 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 plays an essential role for understanding this system, especially for the compositions around MPB region. Many structural models have been proposed based on experimental approach: transmission electron microscopy (TEM), neutron diffraction and X-ray powder diffraction. 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 have been proposed [25, 82, 83]. However, all these studies were based on the ceramic samples, the structure of which is known to be dependent on the synthetic method. For instance, it was found that the width of the MPB with coexisted phases shows inversely proportional to the grain size of the ceramics [20]. According to this finding one could expect the phase coexistence region in PZT single crystals should be very narrow and even missing. Therefore, structural study on PZT single crystal is needed and it will provide us with more convincing 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 terms of crystal growth, various methods have been developed for synthesizing ferroelectric crystals of different systems, such as the Bridgman method and the flux growth. Initially, PMN-PT and PZN-PT crystals were mainly grown by the flux method [39,40]. Yamashita et al. used a modified the Bridgman technique and obtained crystals large enough for medical transducer applications [84,85]. However, the Bridgman and related techniques still have some disadvantages, such as the high cost associated with the Pt crucibles which are not reusable and the long growth period. Compared with other ferroelectric systems, PZT crystals are even more difficult to synthesize due to its high melting point and incongruent melting behaviour. As shown in the high temperature phase diagram of PZT (Figure 3.1) [86], with temperature cooling down below the liquidus, the composition of crystals change from Zr-rich side to Ti-rich side because of phase segregation. Other than the compositional segregation, multinucleation is also a problem to overcome. ZrO has a very high melting point (2715 °C), and cannot easily dissolve thoroughly even above the liquidus curve. During the growth, the ZrO powders serve as seeds for nucleation leading to very small crystals from multinucleation. So far, the PZT single crystals of desired composition have not been available because the control of composition and the multinucleation have been the major obstacles to overcome.

To solve the above problems, we took on the challenge in this work to grow PZT crystals with good quality, by means of the top-seeded solution growth (TSSG) method that was developed in our lab. The mixture of PbO and B$_2$O$_3$ is used as flux to lower the melting point of the system, and a bar of PZT crystal with (001)$_{cub}$ orientation, obtained from preliminary flux growth, was used as seed for the nucleation. We undertook a series of growth at different conditions and systematically investigated the growth mechanism and the effects of the chemical, thermodynamic and kinetic parameters on the growth results. The structure and electrical properties of the grown crystals were characterized by XRD and dielectric, ferroelectric and piezoelectric measurements. More detailed studies of phase transition behaviour in PZT on specific compositions will be reported in the following two chapters.
3.3 Experimental

The top-seeded solution growth method was used for the growth of PZT single crystals. The flux employed was a mixture of PbO and B$_2$O$_3$ with a molar ratio of 1:4. PbO has a low melting point (888 °C), and it is an effective solvent for growing Pb-based ferroelectric crystals because the melting point of the system can be lowered without introducing other element to the PZT crystals. The addition of B$_2$O$_3$ can decrease the melting point even lower and prevent the high evaporation of PbO at high temperature by increasing the viscosity of the solution [72, 87]. Since the radius of B$^{3+}$ ion is too small to enter the unit cell lattice of PZT, it will not affect the perovskite structure and properties of PZT. PbZr$_{1-x}$Ti$_x$O$_3$ ceramics with composition $x = 0.60$ were pre-synthesized by solid state reaction. The starting reagents used were high-purity (99.99%) powders of PbO, ZrO$_2$, and TiO$_2$. These oxides of stoichiometric amount were well mixed and pressed into pellets. After calcination at 800 °C for 4 h to form the perovskite phase, the pellets were put into a 100 ml platinum crucible together with the flux (PbO+B$_2$O$_3$) powders (see Table 3.1 for details). Figure 3.2 shows the schematic side-section view of the tube furnace and the set-up used for the top-seeded solution growth. Figure
3.3 gives the vertical temperature gradient inside the furnace measured with a thermal
couple attached to the seeding rod at a set temperature of 1100 °C. The temperature in
the furnace is stabilized at 1050 °C for the middle part of the furnace (≈ 15-5 cm from
the bottom). As the position lowers to the bottom, the temperature shows an slight
increase to 1075 °C. The platinum crucible (height ≈ 5 cm) is placed at the bottom
of the furnace, therefore, a vertical temperature gradient was created in molten oxides.
The crystal growth process was controlled by a cooling program as shown in Figure 3.4.
The soaking temperature is set at 5 °C higher than the seeding temperature. After
soaking for 5 days the PZT solute at bottom was found to gradually dissolve in the
flux and the saturation was reached at that temperature. The temperature was then
lowered 5 °C to reach the super-saturation state. The seed used for the growth was
a (001),cub-oriented PZT crystal from the previous growth (see Figure 3.7 (a)). It was
attached to the end of a straight alumina rod using platinum wires, and dipped into the
melt to trigger nucleation. As temperature was lowered at a very slow rate (4 °C/day),
the crystal gradually grew from the seed. After 25 days of slow cooling process, the
crystal was pulled out from the melt, and the temperature was decreased down to room
temperature at a slow rate of 20 °C/day to avoid the formation of cracks during faster
cooling.

X-ray powder diffraction was performed on the crushed crystals using a Rigaku MSC
diffractometer. The temperature dependences of the dielectric permittivity $\epsilon'$ and loss
factor (tan $\delta$) were measured at several frequencies (1 kHz-100 kHz) by a Novocontrol
Alpha high resolution broadband dielectric analyzer equipped with a high temperature
system. The ferroelectric hysteresis loops were measured using a Radiant Technologies
RT66A standardized ferroelectric testing system. The samples were poled by a Stant-
ton PS350 high voltage power source at room temperature in silicone oil. Piezoelectric
efficiency was measured by a quasistatic piezoelectric meter (Model ZJ-6B). The elect-
tromechanical coupling factor ($k_{33}$) as measured on a poled bar-shaped (001),cub-oriented
crystal with a dimensions of 0.4 × 0.4 × 1.7 mm$^3$ by the resonance-antiresonance method
using a Solartron 1260 impedance analyzer in conjunction with a Solartron 1296 dielectric
interface.
Figure 3.2: Schematic side-section view of the tube furnace and the set-up used for the top-seeded solution growth (TSSG).

3.4 Effects of Thermodynamic Parameters on the Growth of PZT Crystals

The overall phase diagram of the whole multi-component system is very complicated, which involves three pseudo-binary systems, namely PbO-PbZrO$_3$, PbO-PbTiO$_3$ and PbZrO$_3$-PbTiO$_3$. As mentioned previously, PbZrO$_3$ (PZ) and PbTiO$_3$ (PT) can form solid solution over the entire range of composition. In the high temperature phase diagram (Figure 3.1), PbZrO$_3$ melts incongruently at 1570 °C, above which it decomposes to ZrO$_2$ and a liquid phase. Therefore, above the crystallization temperature of PZT with composition $x > 0.1$, there exists a two phase region, liquid+ZrO$_2$. The situation is similar for the PbO-PZ system. As shown in Figure 3.5 (a), for high temperature liquid phase with a composition of PZ > 10%, with decreasing temperature, ZrO$_2$ crystallizes until the temperature drops below 1570 °C, at which PZ begins to crystallize. For the system PbO-PT, the equilibrium of P+PT+L occurs at a eutectic point 838 °C (see Figure 3.5 (b)).

To better understand the possible mechanism for the growth of PZT crystals from
Figure 3.3: Vertical temperature gradient of the furnace measured for a controller-displayed temperature of 1100 °C.

Figure 3.4: Schematic thermal profile used for the PZT crystal growth by top-seeded solution growth.
the melts, we reconstructed the pseudo binary phase diagram of PZT-(PbO+B_2O_3) (see Figure 3.6), based upon the ternary phase diagram of PZ-PT-PbO [86]. The solubility of PZT in the solvent follows the path of the liquidus curve with changing temperature, as shown in Figure 3.6. Thus, the concentration of PZT in the melt is only determined by temperature, but not by the ratio of PZT:flux in the starting reagents. When the seed was introduced and the cooling program was initiated, the PZT crystal grew from the seed since the saturation solubility of PZT in flux decreases with decreasing temperature.

The exact crystallization pathways leading to PZT crystals of specific compositions were very difficult to determine due to the complex phase diagram of the whole system. Nevertheless, we were able to establish some empiric relationships between the composition of the grown crystals and the growth parameters.

Table 3.1 summarizes the growth conditions and growth results. The compositions of the grown crystals are in the range of 0.2 ≤ x ≤ 1.00, which were determined from the T_C values of the crystals obtained by dielectric measurements according to the well-established phase diagram of the PZ-PT solid solution [13, 15]. It can be seen that the crystals grown at high temperatures tend to have a higher Zr content, while those grown at low temperatures tend to have a higher Ti content. The relationship between the growth temperature and the composition reflects the crystallization behaviour of the PZT binary system, since its phase diagram (Figure 3.1) shows that the Ti content of
the solid solution increases with decreasing crystallization temperature. Figure 3.7 (b)-(f) displays some pictures of the grown PZT crystals. They all have pseudo-cubic shape with (001)_{cub} facets. The crystals with compositions close to the MPB are yellow in colour, while those with composition away from the MPB appear to be of darker colour. This variation in colour is associated with the wavelength of the light transmitted by the crystals. It was found that the band gap decreases with increasing crystallographic symmetry [88], and the narrower the band gap is the higher its ability to absorb visible light [89]. Since the low-symmetry monoclinic phase exists in the MPB region, it has a wider band gap than high-symmetry rhombohedral and tetragonal phases. Therefore absorbance of light is lower in monoclinic crystals than in rhombohedral and tetragonal crystals. Also, it was observed that cracks are more easy to form in the crystals of the MPB compositions due to the high internal stresses produced by the slight compositional variation.

Figure 3.6: Pseudo-binary phase diagram of PbO(B_{2}O_{3})-PZT reconstructed based on the PbO-PT-PZ ternary phase diagram [86].
Table 3.1: Summary of growth parameters and growth results of the PbZr$_{1-x}$Ti$_x$O$_3$ single crystals.

<table>
<thead>
<tr>
<th>Growth batch</th>
<th>Initial PZ/PT (mol%)</th>
<th>Flux (B$_2$O$_3$/PbO) (mol%)</th>
<th>PZT/Flux (mol%)</th>
<th>Growth temperature (°C)</th>
<th>Cooling rate</th>
<th>PT content (x)</th>
</tr>
</thead>
<tbody>
<tr>
<td>21</td>
<td>40 /60</td>
<td>1/ 4</td>
<td>1/5</td>
<td>1220-1120</td>
<td>4°C/day</td>
<td>0.20</td>
</tr>
<tr>
<td>31</td>
<td>40 /60</td>
<td>1/4</td>
<td>1/5,2</td>
<td>1200-1100</td>
<td>4°C/day</td>
<td>0.32</td>
</tr>
<tr>
<td>23</td>
<td>40 /60</td>
<td>1/4</td>
<td>1/5</td>
<td>1180-1080</td>
<td>4°C/day</td>
<td>0.35</td>
</tr>
<tr>
<td>19</td>
<td>40 /60</td>
<td>1/4</td>
<td>1/5</td>
<td>1000-900</td>
<td>4°C/day</td>
<td>0.42</td>
</tr>
<tr>
<td>8 (by X. Long et al.)</td>
<td>40 /60</td>
<td>1/ 4</td>
<td>1/6</td>
<td>1070-1000</td>
<td>5°C/day</td>
<td>0.46</td>
</tr>
<tr>
<td>24</td>
<td>40 /60</td>
<td>1/4</td>
<td>1/5.7</td>
<td>1050-950</td>
<td>4°C/day</td>
<td>0.47</td>
</tr>
<tr>
<td>4 (by X. Long et al.)</td>
<td>35 /65</td>
<td>1/4</td>
<td>1/6</td>
<td>1060-980</td>
<td>5°C/day</td>
<td>0.62</td>
</tr>
<tr>
<td>28</td>
<td>0/100</td>
<td>1/4</td>
<td>1/5.7</td>
<td>1060-1000</td>
<td>4°C/day</td>
<td>1</td>
</tr>
</tbody>
</table>

Figure 3.7: Pictures of selected PbZr$_{1-x}$Ti$_x$O$_3$ crystals with different compositions (b-f), as well as a seed crystal attached to the Pt rod (a) on millimeter grid paper.
3.5 XRD Patterns of PZT Single Crystals

The powder XRD patterns of the crashed PZT crystals measured at room temperature are shown in Figure 3.8. The indices corresponding to the diffraction peaks are marked on the pattern, indicating that the grown PZT single crystals are of pure perovskite-type structure. The rhombohedral structure of the crystals with composition \( x = 0.20 - 0.42 \) is characterized by the non-symmetric \((111)_{\text{cub}}\) peaks/splitting at around \( 2\theta = 38^\circ \) and a single \((200)_{\text{cub}}\) peak at \( 2\theta = 44^\circ \). Crystals with composition from \( x = 0.47 \) to \( x = 1.0 \) show doublet peaks at the \((200)_{\text{cub}}\) reflection and a single peak at the \((111)_{\text{cub}}\) reflection, consistent with a tetragonal symmetry (space group \( P4mm \)). At room temperature the MPB exists in the narrow composition range from \( x = 0.45 \) to \( x = 0.48 \), where the intermediate monoclinic (\( Cm \)) phase was found to exist by high-resolution synchrotron X-ray diffraction [15]. Confined by the low resolution of the XRD available, the monoclinic structure cannot be resolved here. However, polarized light microscopic examinations have confirmed the monoclinic phase in the MPB composition with \( x = 0.46 \). More details on the observation of the monoclinic phase and related phase transitions will be discussed in Chapter 5.

3.6 Electrical Properties of PZT Single Crystals

For the measurements of electrical properties, platelets of PZT crystals were cut parallel to the crystallographic \((001)_{\text{cub}}\) facets, polished and then sputtered with gold electrodes. Figure 3.9 displays the temperature dependence of the dielectric constant \( \epsilon' \) and loss factor (\( \tan\delta \)) measured on cooling for crystals with compositions \( 0.2 \leq x \leq 0.60 \). The conductivity of the pure \( \text{PbTiO}_3 \) crystal was too high, so impedance on heating could not be successfully measured. The maximum dielectric constant on the curves indicates the paraelectric to ferroelectric phase transition at \( T_C \). For the MPB crystals with compositions \( x = 0.42, x = 0.46 \) and \( x = 0.47 \), the dielectric curves shows an additional anomaly below \( T_C \), which corresponds to the phase transitions from rhombohedral to monoclinic phase for \( x = 0.42 \) and from monoclinic to tetragonal phase for \( x = 0.46 \) and \( x = 0.47 \), respectively. The room temperature dielectric constant at 1 kHz was also plotted as a function of PT content \( x \), as shown in Figure 3.11. According to the PZT phase diagrams, the rhombohedral region with a high Zr content is separated into two rhombohedral phases with different space groups, \( R3c \) and \( R3m \), respectively. The
Figure 3.8: XRD patterns of PbZr$_{1-x}$Ti$_x$O$_3$ crystals with compositions $0.2 \leq x \leq 1.00$. 
phase boundary between the two phases is around the composition \( x = 0.35 \), where a slight increase of dielectric constant is observed. As expected, the maximum dielectric response \( \epsilon' = 971 \) is found at the MPB composition \( x = 0.46 \) with a very low dielectric loss \( \tan \delta = 0.0095 \), attesting to the high quality of the grown crystals.

Ferroelectric properties are measured on (001)_{cub}-oriented PZT crystals of various compositions. As shown in Figure 3.10, all the compositions studied (0.2 \( \leq x \leq 0.60 \)) display well-saturated ferroelectric hysteresis loops at room temperature. The near rectangle shape of the loops indicates the sharp switching of domains in the single crystals. Table 3.2 summarizes the dielectric, ferroelectric and piezoelectric properties of PZT crystals with different compositions. The coercive field \( E_c \) in the tetragonal crystals is much higher than that in the rhombohedral crystals, which is due to the high domain wall energy in the tetragonal phase [90]. The highest piezoelectric constant \( d_{33} = 1223 \) pC/N is found in the MPB composition \( x = 0.46 \), which confirms the well-known trend of \( d_{33} \) as a function of composition established in the PZT ceramics [91]. More discussions about the relationship between the domain structure and the electrical properties in the PZT crystals will be presented in Chapter 4 and Chapter 5.

On the phase diagram of PZT, \( T_C \) shows an increase with increasing PT content (see Figure 1.5). The compositions of PZT single crystals are determined by the value of their \( T_C \) using the phase diagram. The crystal (Batch \#24) with \( T_C = 378 \) °C should have a lower PT content than crystal with composition \( x = 0.46 \) (Batch \#8), which has a \( T_C = 395 \) °C. However, the XRD patterns show very clear splitting peak at the (002)_{cub} reflection for \#24PZT, while a broad single peak for \( x = 0.46 \), which indicates that the \#24PZT is on the tetragonal side and should have a PT content higher than 46%. The composition of \#24PZT is then determined to be \( x = 0.47 \) by its \( T_{MPB} = 150 \) °C on the PZT phase diagram [14]. The change of \( T_C \) of these two compositions (\( x = 0.46, 0.47 \)) does not follow the trend that crystal with a higher PT content should have a higher \( T_C \). Similar observation of unusual change of \( T_C \) was found in the PZT crystals with composition near the tricritical point on the high PZ side [92]. Since the PZT crystal with composition \( x = 0.46 \) is also close to the tricritical point at MPB [26], this anormal increase of \( T_C \) could be a common phenomena for phase transitions near a tricritical point.

The resonance measurement was carried out on a (001)_{cub}-oriented PbZr_{0.54}Ti_{0.46}O_{3} single crystal bar with the dimensions of \( 0.4 \times 0.4 \times 1.7 \) mm\(^3\), by measuring the impedance
Figure 3.9: Temperature dependences of the dielectric constant $\varepsilon'$ and dielectric loss $(\tan \delta)$ for (001)$_{\text{cub}}$-oriented PbZr$_{1-x}$Ti$_x$O$_3$ (PZT) single crystals with different compositions.
Figure 3.10: Ferroelectric hysteresis loops of PbZr$_{1-x}$Ti$_x$O$_3$ (PZT) single crystals with different compositions.
Table 3.2: Dielectric, piezoelectric and ferroelectric properties of the (001)\textsubscript{cub}-oriented PbZr\textsubscript{1−x}Ti\textsubscript{x}O\textsubscript{3} (PZT) single crystals of various compositions.

<table>
<thead>
<tr>
<th>Growth Batch #</th>
<th>PT(x)</th>
<th>Dielectric constant</th>
<th>Loss tangent</th>
<th>$E_c$ (kV/cm)</th>
<th>$P_r$ (µC/cm\textsuperscript{2})</th>
<th>$d_{33}$ (pC/N)</th>
<th>$T_{MPB}$ (°C)</th>
<th>$T_c$ (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>21</td>
<td>0.20</td>
<td>293</td>
<td>0.0380</td>
<td>5.7</td>
<td>17.0</td>
<td>223</td>
<td>300</td>
<td></td>
</tr>
<tr>
<td>31</td>
<td>0.32</td>
<td>244</td>
<td>0.0135</td>
<td>7.0</td>
<td>19.2</td>
<td>230</td>
<td>337</td>
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</tr>
<tr>
<td>23</td>
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<td>339</td>
<td>0.0336</td>
<td>11.4</td>
<td>23.5</td>
<td>190</td>
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</tr>
<tr>
<td>19</td>
<td>0.42</td>
<td>232</td>
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<td>335</td>
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</tr>
<tr>
<td>8</td>
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<td>971</td>
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<td>7.0</td>
<td>23.0</td>
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<td>180</td>
<td>394</td>
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<tr>
<td>24</td>
<td>0.47</td>
<td>606</td>
<td>0.0107</td>
<td>28.0</td>
<td>48.8</td>
<td>350</td>
<td>150</td>
<td>378</td>
</tr>
<tr>
<td>4</td>
<td>0.60</td>
<td>116</td>
<td>0.0113</td>
<td>43.0</td>
<td>57.0</td>
<td>216</td>
<td>426</td>
<td></td>
</tr>
</tbody>
</table>

Figure 3.11: Variations of the dielectric constant and loss factor (tan $\delta$) as a function of composition for PbZr\textsubscript{1−x}Ti\textsubscript{x}O\textsubscript{3} (PZT) single crystals.
and phase angle as a function of frequency. As shown in Figure 3.12, the resonance and antiresonance frequencies are found to be $f_r = 6.12 \times 10^5$ Hz and $f_a = 9.71 \times 10^5$ Hz, respectively. Accordingly, the longitudinal electromechanical coupling factor $k_{33}$ was calculated using Equation 2.21 in **Chapter 2**, and it reaches 80% for this composition. Compared with PMN-PT and PZN-PT single crystals which show $k_{33}$ values of $\approx 0.9$, PbZr$_{0.54}$Ti$_{0.46}$O$_3$ single crystal has a lower $k_{33}$, but much higher $T_C = 395$ °C and $E_c = 7$ kV/cm.

![Figure 3.12: Impedance and phase angle as a function of frequency for a (001)$_{cub}$-oriented, poled PbZr$_{0.53}$Ti$_{0.46}$O$_3$ single crystal bar with dimensions of 0.4 × 0.4 × 1.7 mm$^3$.](image)

**3.7 Conclusions**

PbZr$_{1-x}$Ti$_x$O$_3$ (PZT) single crystals with various compositions were grown by the top-seeded solution growth (TSSG) method. The improved TSSG method has shown to be successful in growing PZT crystals with good quality and homogeneous composition. The chemical, thermodynamics and kinetics conditions have been optimized for the growth of
PZT crystals. In particular, it is found that the crystals grown at a higher temperature tend to have a higher PZ content. Therefore, by adjusting the growth temperature, the composition of PZT crystals can be controlled, leading to PZT crystals of a wide range of compositions \((0.2 \leq x \leq 1.0)\), i.e. from rhombohedral to MPB and to tetragonal phase. The XRD analysis shows that all the grown crystals have the perovskite structure, and the symmetry of crystals changes from rhombohedral to tetragonal with the MPB region in between. The measurements of dielectric properties indicate that the crystals with composition around the MPB undergo an additional phase transition below \(T_C\), which corresponds to the rhombohedral to monoclinic phase transition for \(x = 0.42\) and the monoclinic to tetragonal phase transition for \(x = 0.46\). The MPB crystals with composition \(x = 0.46\) exhibit the best dielectric, ferroelectric and piezoelectric properties. Compared with PMN-PT and PZN-PT single crystals, \(\text{PbZr}_{0.54}\text{Ti}_{0.46}\text{O}_3\) has a higher \(T_C = 395^\circ\text{C}\) and a larger \(E_c = 7\ \text{kV/cm}\), as well as good piezoelectric properties \(d_{33} = 1223\ \text{pC/N}\) and \(k_{33} = 0.8\), which qualify the PZT single crystals as a promising material for high temperature and high power electro-mechanical transducer application.

The availability of PZT single crystals makes it possible to study the phase transitions by polarized light microscopy (PLM). The domain structure and phase transitions of the rhombohedral crystals \((x = 0.20)\) and MPB crystals \((x = 0.42, x = 0.46)\) will be discussed in Chapter 4 and Chapter 5, respectively. Based on our experimental data, an updated phase diagram around MPB will be proposed in Chapter 8.
Chapter 4

Domain Structure and Phase Transition Behaviour in PZT Single Crystals with Rhombohedral Symmetry

4.1 Abstract

$\text{PbZr}_{0.8}\text{Ti}_{0.2}\text{O}_3$ single crystals of rhombohedral symmetry were investigated by X-ray diffraction, dielectric measurements, polarized light microscopy (PLM) and ferroelectric measurements. The results of dielectric measurements reveal a first order phase transition between the low-temperature tilted rhombohedral phase ($R\bar{3}c$) and the high-temperature untilted rhombohedral phase ($R3m$), evidenced by a significant thermal hysteresis upon heating and cooling. Ferroelectric hysteresis loops were measured on heating, and the saturation polarization ($P_s$) is found to be lower in the $R\bar{3}c$ phase than in the $R3m$ phase, due to the pinning of domain mobility and switching in the $R3m$ phase. The domain structures are different in crystals with different orientations: the $(110)_{\text{cub}}$ platelet has wedge-domain structure with straight domain walls, while in the $(001)_{\text{cub}}$ platelet, domains with different orientations overlap, leading to a decrease in the measured birefringence. The ferroelectric (FE) to paraelectric (PE) phase transition behaviour in the $(001)_{\text{cub}}$ and $(110)_{\text{cub}}$ platelets is also different, showing a weak first order and second order behaviour around $T_C$, respectively. The ratio of Curie constants
(C+/C−) from the dielectric fitting is 3.4, which is close to the value 4 predicted for the FE-PE transition at a tricritical point.

4.2 Introduction

Pb(Zr,Ti)O₃ (PZT) ceramics are the most widely used ferroelectric materials in industrial applications. Extensive experimental and theoretical studies have been performed to understand the relationship between the structure and properties. In the rhombohedral region of the PZT phase diagram (see Figure 4.1), two ferroelectric phases are known to exist: the low temperature phase with tilted octahedrons FR(LT), and the high temperature phase with untilted octahedrons FR(HT). The oxygen octahedron-tilted rhombohedral phase, with space group R3c, is characterized by an opposite rotation of the successive oxygen layers along the ⟨111⟩cub direction, denoted as a−a−a− [93]. The octahedral rotation results in a doubling of the perovskite unit cell which has been observed by neutron and TEM diffraction on both PZT ceramics [94,95] and single crystals [96], as evidenced by superlattice peaks at (211/212)cub. On heating, the tilted rhombohedral phase (R3c) transforms into the untilted rhombohedral phase (R3m), and it was found that the R3c-R3m transition changes from first order to second order with composition approaching the MPB, during which the cation shifts, and the octahedral distortion and tilting vary gradually [97]. Also the order of rhombohedral ferroelectric to cubic paraelectric phase transition varies with the composition moving from the PZ-rich side to the MPB, from 1st order in x = 0.10 [12] to 2nd order in x = 0.25 [98], meaning that in the rhombohedral region 0.10 < x < 0.25, there is a tricritical point at which the order of phase transition changes from the first order to the second order.

Although the structure of the rhombohedral phase has been well studied, the property change related to the octahedral tilting is still poorly understood. Antiferroelectric behaviour characterized by the double hysteresis loops was found in the rhombohedral region, which was explained by the random octahedral rotations that disrupt the long-range polar order, resulting in the instability to sustain a net remnant polarization [99]. However, a recent study found that the pinched hysteresis loop is due to the oxygen vacancies, and after oxygen compensation by annealing, the electrical properties can be improved [100]. The defects and oxygen vacancies in ceramics impede the study of the intrinsic property change associated with to the octahedron-untitled to octahedron-tilted phase transition. To resolve this problem, it is highly desirable to perform the relevant
measurements on single crystals, in which defects and oxygen vacancies can be avoided. Other than the symmetry change, the domain structure also plays an important role in the macroscopic properties of ferroelectrics, but its investigation has not been realized because of the lack of PZT single crystals. Recently, PbZr$_{0.80}$Ti$_{0.20}$O$_3$ single crystals with good quality were synthesized in our lab by the top-seeded solution growth (TSSG) method (see Chapter 3). The availability of PZT single crystals allows us, in this work, to characterize systematically the FR(LT)-FR(HT) and FE-PE phase transitions and the domain structure of the PbZr$_{0.80}$Ti$_{0.20}$O$_3$ single crystals by dielectric measurements and polarized light microscopy. Ferroelectric hysteresis loop measurement has also been performed with variation of temperature, and the effects of oxygen octahedral rotations on the polarization of the solid solution system have been discussed.

4.3 Experimental

The TSSG technique is suitable for the PZT crystal growth due to its incongruent melting behaviour. PZT seed crystal oriented in the (001)$_{cub}$ direction was obtained from conventional flux growth by spontaneous nucleation. The flux used for the crystal growth
was a mixture of PbO and B$_2$O$_3$ (1 : 5 molar ratio). The PZT ceramics with a composition of $x = 0.60$ were calcined to form the perovskite phase. The ceramics together with the powders of PbO and B$_2$O$_3$ (purity of 99.99%) were put to a 100 ml Pt crucible and heated in a tube furnace to obtain a homogeneous melt. Then the seed was introduced into the melt at a temperature just above the saturation temperature of 1220 °C. The crystal growth took place upon cooling from 1220 °C to 1120 °C at a rate of 4 °C/day. The grown crystals were pulled out of the melt and cooled slowly to room temperature. The grown bulk consisted of several crystals with the largest dimensions of 8 × 3 × 4 mm$^3$. More details on the growth of PZT single crystals are provided in Chapter 3.

X-ray powder diffraction was performed on crushed crystals using a Bruker D8 Advance diffractometer with a wavelength of $\lambda = 1.5418$ Å. The crystals were cut and polished for properties measurements. For dielectric permittivity characterization, gold layers were sputtered on the major crystallographic facet as electrodes. The permittivity as a function of temperature was measured with a Novocontrol broadband dielectric spectrometer upon heating or cooling between 25 °C and 550 °C. Optical domain investigations were carried out on platelets with (001)$_{\text{cub}}$ and (110)$_{\text{cub}}$ orientations, using an Olympus BX60 polarized light microscope (PLM) equipped with Berek and Senarmont compensators. A Linkam THMS600 optical heating stage was used for temperature variable observations and measurements. The ferroelectric hysteresis loops were displayed using a Radiant RT66A standardized ferroelectric testing system (Radiant Technologies Inc.).

### 4.4 Structural Analysis

The XRD pattern for the powders of Pb(Zr$_{0.80}$Ti$_{0.20}$)O$_3$ single crystal is shown in Figure 4.2. The peak positions indicate a single-phase perovskite structure. The ratio of the relative intensities of the (100)$_{\text{cub}}$ and the (110)$_{\text{cub}}$ reflections are higher compared with the ceramic samples, which is due to the preferred (100)$_{\text{cub}}$ cleavage during grinding. The enlarged selected regions of the XRD pattern are shown in Figure 4.3. The single peak at the (100)$_{\text{cub}}$ reflection and the split peaks at the (110)$_{\text{cub}}$ and (111)$_{\text{cub}}$ reflections imply a rhombohedral symmetry (see Chapter 2 Figure 2.3). The lattice parameters are refined to be $a = 4.12$ Å and $\alpha = 89.72^\circ$. On the PZT phase diagram (see Figure 1.5), the ferroelectric phase of the composition $x = 0.20$ has a tilted rhombohedral phase ($R3c$) at room temperature, and the transition from the $R3c$ phase to the high
temperature $R3m$ phase is confirmed by our dielectric measurements (see below). Due to the small ionic displacements associated with the oxygen octahedral rotation in the $R3c$ phase, there should be a $(\frac{311}{222})_{cub}$ superlattice reflection at around $2\theta = 37^\circ$ (marked with an arrow in Figure 4.2). However, we did not observe this superlattice peak in our XRD pattern, which is due to the low scattering factor of oxygen by X-rays that makes the reflection discernible. Neutron diffraction needs to be carried out and to reveal the superlattice peak in the $R3c$ phase in the future.

![Figure 4.2: XRD pattern of the powder made of Pb(Zr$_{0.80}$Ti$_{0.20}$)O$_3$ single crystals.](image)

### 4.5 Dielectric Properties of Pb(Zr$_{0.80}$Ti$_{0.20}$)O$_3$ Single Crystals

#### 4.5.1 $R3c$-$R3m$ Phase Transition

Figure 4.4 shows the temperature dependences of the dielectric constant and dielectric loss ($\tan \delta$) of the (001)$_{cub}$-oriented Pb(Zr$_{0.80}$Ti$_{0.20}$)O$_3$ single crystal measured at 1 kHz. In order to achieve a good accuracy, the measurements were performed with a very slow...
heating and cooling rate (0.2 °C/min). A dielectric permittivity peak can be clearly seen at $T_C = 300$ °C associated with a loss anomaly, indicating the phase transition from the ferroelectric to paraelectric phase.

Figure 4.5 (a) shows the details of the variation of dielectric constant at low temperatures ($190$ °C < $T_C < 230$ °C). An anomaly can be observed at 201 °C on cooling and at 217 °C on heating. According to the PZT phase diagram (Figure 1.5), this anomaly is related to the phase transition between the two rhombohedral phases with different space groups: $R_3c$ and $R_3m$. It is important to note here that in our subsequent PLM studies, the rhombohedral domain structure is observed for the entire temperature range below $T_C$, which confirms that the phase transition at $T_{R-R}$ indeed involves only two phases of the same rhombohedral system. On heating, the dielectric constant $\varepsilon'$ increases by a small amount as the symmetry changes from $R3c$ to $R3m$, indicating a small increase of mobility or amplitude of charges in the untilted phase. In PZT, the ionic substitution of Ti$^{4+}$ for Zr$^{4+}$ on the B-site can lead to a symmetry change in the sequence of $R3c$, $R3m$, $Cm$ and $P4mm$ [14, 101]. Thomas et al. [102] studied the stability of the crystal structure with respect to the volume change of the octahedra ($V_B$) and the cuboctahedra ($V_A$), and found that for a space group with no tilting, such as $P4mm$, $R3m$, $Cm$ and
Figure 4.4: Variations of dielectric constant and loss factor as a function of temperature at 1 kHz for the (001)\textsubscript{cub}-oriented Pb(Zr\textsubscript{0.80}Ti\textsubscript{0.20})O\textsubscript{3}\textsubscript{3} single crystal.

\(Pm3m\), the ratio of \(V_A\) over \(V_B\) is 5. For the tilted phase \(R3c\) \((a^-a^-a^-)\), this ratio is lower than 5, which is due to the systematic tilting of octahedrons along the [111]\textsubscript{cub} direction. The relationship between \(V_A/V_B\) and the tilting angle \(\omega\) is given by [102]

\[
\frac{V_A}{V_B} = 6K^2 \cos^2 \omega - 1 ,
\]

where \(K\) is the constant factor with a value close to 1. Therefore, at the \(R3c-R3m\) phase transition temperature, there must be a change in the volume due to the rearrangement between the octahedron and cuboctahedron, which causes the change in the dielectric response of the single crystal. Other than the intrinsic contribution from the shift of the ions at the unit cell level, the dielectric response also depends on the extrinsic contribution from the motion of domain walls. Eitel et al. applied the Rayleigh law analysis to quantify the ferroelectric domain contribution to the dielectric permittivity in the tilted and untilted rhombohedral phases [103]. They found that in the tilted rhombohedral phase, the mobility of the reversible domains is reduced and the activation energy is increased. Therefore, the overall extrinsic dielectric response of the whole crystal is suppressed in the \(R3c\) phase.
Figure 4.5: Temperature dependence of the dielectric constant at 1 kHz for the (001)_cub-oriented Pb(Zr$_{0.80}$Ti$_{0.20}$)O$_3$ single crystal measured at different heating/cooling rates: (a) 0.2 °C/min, (b) 0.4 °C/min and (c) 0.8 °C/min.
It is also found in this work that the $R3c-R3m$ phase transition temperature and the extent of thermal hysteresis vary significantly with different heating/cooling rates: 0.2 °C/min, 0.4 °C/min and 0.8 °C/min (see Figure 4.5). For each run, after the temperature was stabilized at 550 °C the measurement on cooling at a given rate was firstly taken, which is then followed by the measurement on heating at the same rate. Since the measurements started at a temperature far above $T_C$, the thermal history from the previous run could be erased. It is found that the slower is the rate of temperature variation, the higher is the $R3c-R3m$ transition temperature, and more significant is the thermal hysteresis, namely $\Delta T = 11$ °C at 0.8 °C, $\Delta T = 13$ °C at 0.4 °C and $\Delta T = 16$ °C at 0.2 °C.

4.5.2 Tricritical Behaviour

In Chapter 1, we have introduced the dielectric behaviour of the first order and the second order phase transitions based on the Landau-Devonshire approach. For the case $b < 0$ in Equation 1.12, the polarization changes discontinuously during the phase transition. If $b > 0$, the phase transition is continuous and the dielectric susceptibility ($\chi$) and temperature ($T$) has the following relationship:

\[ \chi^{-1} = \frac{2(T_C - T)}{C} \quad \text{for } T < T_C , \quad (4.2) \]

and

\[ \chi^{-1} = \frac{(T - T_C)}{C} \quad \text{for } T > T_C , \quad (4.3) \]

where $C$ is a constant. If we plot the $\chi^{-1}$ versus $T$, the slope for $T < T_C$ should be twice of that for $T > T_C$, which provides a way for determining the second order phase transition.

There is still one more possibility with $b = 0$, which corresponds to the tricritical point between a continuous and a discontinuous phase transition [92]. In this case, the polarization below $T_C$ is given by

\[ P_0 = \left(1/c \cdot C\right)^{1/4}(T_C - T)^{1/4} . \quad (4.4) \]

Combining it with Equation 1.12 and the Curie-Weiss Law, we have

\[ \chi^{-1} = \frac{(T - T_C)}{C} \quad \text{for } T > T_C , \quad (4.5) \]
and
\[ \chi^{-1} = \frac{4(T_C - T)}{C} \quad \text{for } T < T_C. \] (4.6)

For a tricritical phase transition, if we plot \( \chi^{-1} \) versus \( T \), the slope for \( T < T_C \) should be four times of that for \( T > T_C \).

The plot of the measured inverse dielectric permittivity, \( \epsilon'^{-1} \), versus temperature is shown in Figure 4.6 for the composition \( x = 0.20 \). The value of the susceptibility \( \chi \) (\( \approx \epsilon' \)) should be zero at \( T_C \), which in real situation cannot be reached due to the defects and imperfection in the crystal. According to the Curie-Weiss law, the susceptibility can be expressed by
\[ \chi(\approx \epsilon') = C^+(T - T_C)^{-1} \quad T > T_C, \] (4.7)
\[ \chi(\approx \epsilon') = C^-(T_C - T)^{-1} \quad T < T_C, \] (4.8)
where \( C^+ \) and \( C^- \) are Curie constants above and below \( T_C \), respectively. The Curie constants were obtained from the temperature region away from \( T_C \) since the plot is not linear near \( T_C \) due to the non-mean-field critical behaviour and possible defect contributions [104]. The ratio of \( C^+/C^- \) from linear fitting is found to be 3.4 (see Figure 4.6). Compared with \( C^+/C^- = 2 \) for the second order phase transition, this ratio is closer to the ratio of 4 for the tricritical point, suggesting that the ferroelectric-paraelectric phase transition at \( T_C \) in Pb(Zr_{0.80}Ti_{0.20})O_3 is closer to a tricritical behaviour.

### 4.6 Domain Structure and Phase Transition in Pb(Zr_{0.80}Ti_{0.20})O_3 Crystals

#### 4.6.1 Phase Transition in a (001)\textsubscript{cub} Crystal

The symmetry of a crystal can be determined by examining its domain structure and domain wall orientations under polarized light microscope (PLM). For a rhombohedral crystal, the direction of the optical axis in one domain is the same as the polarization direction, which is along the \( \langle 111 \rangle \text{cub} \) crystallographic direction. The crystal shows extinction when the axes of the corresponding cross-section of its indicatrix are parallel to either the polarizer or the analyzer. The extinction angle in a (001)\textsubscript{cub} platelet is defined as the angle between the \( [010] \text{cub} \) and the optical axis. Therefore, for a rhombohedral crystal observed along the [001]\textsubscript{cub} directions, the extinction angle should be 45°. Figure 4.7 displays the PLM images of a (001)\textsubscript{cub} platelet (53 \( \mu \)m thick) of Pb(Zr_{0.80}Ti_{0.20})O_3.
Figure 4.6: Temperature dependence of inverse dielectric constant \((1/\epsilon')\) for the \(\text{Pb}(\text{Zr}_{0.80}\text{Ti}_{0.20})\text{O}_3\) single crystal.

The crystal shows extinction at \(45^\circ\) to the \([001]_{\text{cub}}\) direction, indicating a rhombohedral symmetry. The interference colour of the crystal is related to the magnitude of the optical retardation. The inhomogeneous colour is due to the cancellation of the overlapping domains along the thickness of the crystal. Figure 4.8 illustrates schematically the two situations of the overlapping domains. In the case where the polarizations (and thereby the optical indicatrix directions) in the two superimposing domains lie in the same \((110)_{\text{cub}}\) plane (see Figure 4.8(b)), the birefringence measured on the \((001)_{\text{cub}}\) crystal is enhanced. If the polarizations in the two overlapping domains are in the different \((110)_{\text{cub}}\) and \((\bar{1}10)_{\text{cub}}\) planes as shown in Figure 4.8(a), the birefringence is reduced, and a total cancellation can be reached if the two kinds of domains have the same thickness.

Figure 4.9 shows the PLM images of the domain structure of the \((001)_{\text{cub}}\) platelet observed at different temperatures. With increasing temperature, neither the extinction direction nor the structure of the domains change, indicating that the crystal symmetry remains rhombohedral through the \(R3c-R3m\) phase transition. This result confirms that the phase transition at \(T_{R-R}\) occurs between two phases of the same rhombohedral
Figure 4.7: PLM images of a (001)\textsubscript{cub}-oriented Pb(Zr_{0.80}Ti_{0.20})O\textsubscript{3} crystal observed under different positions of crossed polarizers at room temperature.

Figure 4.8: Schematic illustration of overlapping domains giving rise to the (a) reduction and (b) enhancement of birefringence on a (100)\textsubscript{cub}-oriented rhombohedral single crystal.
crystal system so that the directions of their optical axis are the same. The polarization
colour of the crystal seen in the microscope changes with the diminishing birefringence
on heating. At 309 °C the FE to PE phase transition takes place with some part of the
crystal transforming into the isotropic cubic phase; while the other part of the crystal
still remains bright, giving rise to a clear boundary between the PE and FE phases. The
Curie temperature of the left edge is higher than the major part of the crystal, which is
probably due to some the compositional inhomogeneity in the crystal.

![Image of crystal under different temperatures](image)

Figure 4.9: PLM images of the (001)$_{cub}$-oriented Pb(Zr$_{0.80}$Ti$_{0.20}$)O$_3$ crystal observed
under different positions of crossed polarizers at different temperatures.

4.6.2 Phase Transition in a (110)$_{cub}$ Crystal

The extinction angle on a (110)$_{cub}$ platelet is determined as the smaller angle between
the direction of the axes of the corresponding cross-section of optical indicatrix and the
[\bar{1}10]_{cub} crystallographic axis, as shown in Figure 4.10. In optically uniaxial R phase, the symmetry axis of optical indicatrix collinear to the spontaneous polarization is aligned along one of the (111)_{cub} crystallographic directions, the extinction angle of which is 35.3°/−35.3°. Figure 4.10 shows the PLM images of a (110)_{cub} platelet (30 µm thick) of Pb(Zr_{0.80}Ti_{0.20})O_3 single crystal at room temperature. The domains are wedge-shaped and oriented along the [001]_{cub} directions, which is the typical domain configuration for a rhombohedral phase. The neighbouring domains extinct at 35.3° and −35.3° alternatively, and the two domain walls forming one wedge domain start at the top edge of the crystal and intersect at some point in the crystal. In the right lower part of the crystal, there are some domain walls oriented along the [111]_{cub} direction, which are bright at any positions under crossed polarizers. These [111]_{cub}-oriented domain walls contain domains in a different (110)_{cub} plane intersecting the polished (110)_{cub} surface of the crystal. Figure 4.11 shows the PLM images of domains at different temperatures during the first heating run. With increasing temperature, these [111]_{cub}-oriented domain walls disappear at 285 °C, and were replaced by the [001]_{cub}-oriented domain walls. The [111]_{cub}-oriented domain walls did not reappear when the crystal was cooled back down to room temperature, implying that the [001]_{cub}-oriented domain walls are more favoured in the thin (110)_{cub} platelet. It should be noted here that, the same as in the (001)_{cub} platelet, no evidence of the R3m-R3c phase transition can be observed in the (110)_{cub} platelet upon heating and cooling. This confirms that R3c and R3m phases cannot be distinguished optically as they belong to the same crystal system.

![PLM images](image_url)

Figure 4.10: PLM images of (110)_{cub}-oriented Pb(Zr_{0.80}Ti_{0.20})O_3 crystal under different positions of crossed polars at room temperature.
With the temperature increased to around 310 °C, the whole crystal gradually become isotropic with extinction at any position, indicating a second order phase transition into the cubic paraelectric phase. The FE-PE phase transition in the (110)$_{\text{cub}}$ crystal is continuous, which is very different from that in the (001)$_{\text{cub}}$ platelet showing a discontinuous change of birefringence at $T_C$ (see below). Thus, in these two Pb(Zr$_{0.80}$Ti$_{0.20}$)O$_3$ crystals, we have observed both the first order and the second order phase transitions. This observation supports our previous conclusion on the Curie-Weiss behaviour by dielectric studies: the FE-PE phase transition in Pb(Zr$_{0.80}$Ti$_{0.20}$)O$_3$ is close to the tricritical point.
4.6.3 Birefringence Measurements on \((001)_{\text{cub}}\) and \((110)_{\text{cub}}\) Single Crystals

In a stress free crystal, the birefringence and polarization have this relationship [105]

\[ \Delta n = \text{constant} \times P_s^2. \] (4.9)

The phase transition behaviour near the critical point can be described by [106]

\[ \Delta n = B(T_C - T)^{2\beta} \quad (T < T_C), \] (4.10)

where \(\beta\) is the critical exponent for the temperature dependence of the order parameter. By measuring the variation of the birefringence with temperature, we can find out the exponent of order parameter \(P_s\). The value of the critical exponent can help us predict the closeness of the phase transition to the tricritical points. The value of \(\beta\) is expected to be 0.5 in a second order phase transition, while \(\beta = 0.25\) for the tricritical point. Figure 4.12 presents the temperature dependence of the birefringence measured on the \((001)_{\text{cub}}\)- and \((110)_{\text{cub}}\)-oriented single crystals. At the same temperature, the birefringence of the \((110)_{\text{cub}}\) crystal is higher than that of the \((001)_{\text{cub}}\) crystal, which can be explained by the fact that the polarization of the rhombohedral phase lies in the \((110)_{\text{cub}}\) plane. The best fit curve (solid curve) is determined by the least-squares fits using the power law (Equation 4.10). The values of \(\beta\) and \(T_C\) obtained from the birefringence fitting are \(\beta = 0.275\), \(T_C = 309^\circ\text{C}\) for the \((001)_{\text{cub}}\) platelet, and \(\beta = 0.29\), \(T_C = 310^\circ\text{C}\) for the \((110)_{\text{cub}}\) platelet, respectively. The dielectric measurements have been done on these two crystals and it is found that they have the same \(T_C\) value. The small difference in the \(T_C\) values from the birefringence measurements might be due to the instrumental error from the temperature controller. According to our studies of many crystals, \(T_C\) values obtained from birefringence measurement are usually higher than from dielectric measurements. For the dielectric measurement, the sample is placed in a heating chamber together with the thermal couple, and the temperature in the heating chamber is uniform. For the birefringence measurement, the sample is heated from the bottom, and the thermal couple is placed below the sample and close to the heating stage. Therefore, for the optical measurements the displayed temperature is usually lower than the actual temperature of the sample. The difference would be larger when the crystal is thicker. Around \(T_C\), the birefringence of the \((001)_{\text{cub}}\) platelet changes abruptly to zero (see Figure 4.9(d)). However, this drop in birefringence is very small suggesting
a weak first order phase transition, which is close to the tricritical point. The (110)\textsubscript{cub} platelet shows a birefringence tail above $T_C$. The residual small birefringence might be due to the anisotropic fluctuations, which is usually associated with a second order phase transition [107]. The observation of the first and second order phase transitions in the two crystals confirms that the composition $x = 0.20$ is close to the tricritical point.

4.7 Ferroelectric Properties

Antiferroelectric-like behaviour, characterized by the double hysteresis loops, was found in the PZT ceramics with compositions in the range of $0.20 < x < 0.40$ [99], which arises from the AFE nature of PZ. The pinched hysteresis loop is caused by the randomly distributed oxygen vacancies in the ceramics, which prevent the switching of the polarization by an electric field [100]. In a single crystal, the oxygen deficiency can be avoided or minimized, and regular ferroelectric hysteresis loops can be displayed. Therefore we can measure the hysteresis loops on heating to investigate the ferroelectric properties associated with the $R3c$ and $R3m$ phases. Figure 4.13 shows ferroelectric hysteresis ($P-E$) loops displayed on the (001)\textsubscript{cub}-oriented Pb(Zr\(_{0.80}\)Ti\(_{0.20}\))O\(_3\) single crystal at several temperatures. Well-saturated $P-E$ loops were obtained under the field $E = 40$ kV/cm in the temperature range of 50-210 °C. The hysteresis loop above 230 °C shows a rounded shape, indicating some charge contribution arising from the conductivity of the crystal. The variations of $P_r$ and $E_c$ as a function of temperature are shown in Figure 4.14. $E_c$ shows a gradual decrease with increasing temperature, which can be explained by the fact that as the energy barrier separating the bipolar states decreases, upon heating, the domain wall motion and polarization reversal become more energetically favourable with increasing temperature, as they are thermally activated processes. $P_r$ decreases with increasing temperature up to 125 °C, which follows the normal trend towards a paraelectric phase. However, above $T_{R-R} = 125$ °C, $P_r$ starts to increase on further heating. Rayleigh analysis found that the antiphase domain boundaries in $R3c$ is pinned at the ferroelectric domain boundaries, therefore the domain mobility and switching are restricted [103]. With the symmetry changing from $R3c$ to $R3m$ at $T_{R-R}$, this suppression effect becomes smaller, leading to the increase of remnant polarization above 125 °C, as shown in Figure 4.14.
Figure 4.12: Temperature dependence of the birefringence of (a) (001)_{cub}-oriented and (b) (110)_{cub}-oriented Pb(Zr_{0.80}Ti_{0.20})O_3 crystals. Solid line: the fitting result to Equation 4.10; Open circle: the measured birefringence.
Figure 4.13: Ferroelectric hysteresis loops of (001)\textsubscript{cub}-oriented Pb(Zr\textsubscript{0.8}Ti\textsubscript{0.2})O\textsubscript{3} crystals measured at different temperatures.
Figure 4.14: Temperature dependences of the remanent polarization \( P_r \) and coercive field \( E_c \) of \((001)_{\text{cub}}\)-oriented \( \text{Pb(Zr}_{0.8}\text{Ti}_{0.2})\text{O}_3 \) crystals.
4.8 Conclusions

PbZr$_{0.8}$Ti$_{0.2}$O$_3$ single crystals were grown by the TSSG method. The rhombohedral symmetry of the crystal was determined by both XRD and the polarized light microscopy. The temperature dependence of the dielectric properties shows an anomaly at $T_{R-R} \approx 200 \, ^\circ\text{C}$ (heating/cooling rate = 0.2 °C) below $T_C$, which corresponds to the first order phase transition from the oxygen octahedron-tilted $R3c$ phase to untitled $R3m$ phase. It was also found that with a smaller heating/cooling rate, the $R3c$-$R3m$ phase transition takes place at a higher temperature while the thermal hysteresis becomes more significant. The ratio of Curie constants ($C^+/C^-$) obtained from the fitting of the dielectric data is 3.4, which is close to the ratio of 4 predicted by Landau theory for a tricritical point. The PLM studies of two crystals with different orientations reveal that the phase transition behaviour from ferroelectric to paraelectric phase in these crystals is close to the critical behaviour: in the (001)$_{cub}$ platelet the birefringence changes slightly discontinuously, indicating an almost first order phase transition, while in the (110)$_{cub}$ platelet the birefringence changes more continuously, suggesting the onset of a second order phase transition. From the fitting of the temperature dependence of birefringence, the critical exponent $\beta$ was found to be 0.275 for the (001)$_{cub}$ platelet and 0.29 for the (110)$_{cub}$ platelet, consistent with the tricritical behaviour predicted by the Landau-Devonshire theory. Well-saturated $P$-$E$ hysteresis loops were displayed at temperature below 230 °C, confirming the ferroelectric behaviour. The remnant polarization $P_r$ value in the low temperature $R3c$ phase is smaller than that in the high temperature $R3m$ phase, which is due to the suppression of domain mobility in the octahedron-tilted phase.
Chapter 5

Phase Transitions Behaviour in PZT Single Crystals with Compositions near the MPB

5.1 Abstract

PbZr$_{1-x}$Ti$_x$O$_3$ (PZT) single crystals with compositions around morphotropic phase boundary (MPB), namely $x = 0.42$ and $x = 0.46$, were grown using top-seeded solution growth method, and their phase transitions were studied by polarized light microscopy and dielectric measurements. At room temperature, the macroscopic symmetry of the PbZr$_{0.58}$Ti$_{0.42}$O$_3$ crystal is rhombohedral with the revolutionary axis of the optical indicatrix oriented along the pseudocubic $\langle 111 \rangle_{\text{cub}}$ direction; at and above $T_{R-M} = 200$ °C, the optical indicatrix axis rotates gradually from the $\langle 111 \rangle_{\text{cub}}$ towards $\langle 001 \rangle_{\text{cub}}$ direction as the structure undergoes the following sequence: from rhombohedral (R), to monoclinic (M$_A$), to tetragonal (T) and finally to cubic (C). These observations point to a temperature-driven polarization rotation within the monoclinic unique mirror plane, which is an analogy to the recently reported electric-field-driven polarization rotation theory [16]. The monoclinic phase is confirmed by the domain walls forming an angle of 30° with the $\langle 001 \rangle_{\text{cub}}$ direction. The highest piezoelectric properties are found in PbZr$_{0.54}$Ti$_{0.46}$O$_3$ crystal, which has a monoclinic symmetry at room temperature. The monoclinic to tetragonal phase transition happens at around 150 °C, which is accompanied by a significant decrease of birefringence and a continuous change of the polarization.
direction. The domain size in the tetragonal phase is found to be anomalously small and the domains are randomly oriented, leading to an unusual optical isotropic state in the \((001)_{\text{cub}}\) crystal. The formation of miniaturized domains can be explained by Imry and Ma’s theory, which suggests that quenched random field related to structural disorder can break the system into nanodomains that are more energetically favored.

5.2 Introduction

The \(\text{PbZr}_{1-x}\text{Ti}_x\text{O}_3\) (PZT) perovskite solid solution system has been studied extensively over the past decades for both industrial applications and fundamental research. Investigations on the structural evolution with composition \((x)\), temperature \((T)\) and electric field \((E)\) have been carried out to explain the high piezoelectric response in the PZT ceramics of compositions close to the morphotropic phase boundary (MPB), separating the non-group-subgroup related Zr-rich rhombohedral \((R)\) \(R3m\) and Ti-rich tetragonal \((T)\) \(P4mm\) phases in the phase diagram of the solid solution system [108–110]. One possible mechanism for the large piezoelectricity in PZT and other high-performance piezoelectric materials with an MPB is the polarization rotation mechanism [34] proposed based on the first-principles calculations for \(\text{BaTiO}_3\) single crystal, in which large polarization rotation was shown to be induced by an external electric field, giving rise to a large intrinsic electromechanical response [16]. Using high-resolution synchrotron X-ray diffraction, Noheda et al. found a monoclinic \(M_A\) phase (with \(Cm\) symmetry) in the MPB composition range of PZT between the \(R\) and \(T\) phases [14]. This discovery is in good agreement with the polarization rotation theory since the polarization vector of the \(M_A\) phase lies within \((110)_{\text{cub}}\) pseudocubic plane, bridging the \((111)_{\text{cub}}\)-directed polarization of \(R\) phase and the \((001)_{\text{cub}}\)-directed polarization of \(T\) phase, and thereby facilitating polarization rotation from the \((111)_{\text{cub}}\)-towards \((001)_{\text{cub}}\)-direction. Similar intermediate monoclinic phases were also discovered at the MPB of other high-performance piezoelectric materials, e.g. in relaxor-based solid solutions of \(\text{Pb(Mg}_{1/3}\text{Nb}_{2/3})\text{O}_3\)-\(\text{PbTiO}_3\) and \(\text{Pb(Zn}_{1/3}\text{Nb}_{2/3})\text{O}_3\)-\(\text{PbTiO}_3\) [111].

Based on the detailed electron diffraction measurements on PZT ceramics, Glazer \textit{et al.} suggested that as the MPB is approached, short-range order monoclinic unit cells begin to cluster, which can only be detected when the clusters exceed a certain size [17]. The subsequent Rietveld refinements of the neutron powder diffraction data were carried out on PZT ceramics and the \(R\) region was found to be composed of a mixture of the
$R3m$ and $Cm$ phases [18,112]. These results could account for the missing R-M$_A$ phase boundary on the PZT phase diagram [14]. However, it is reasonable to believe that there is an R-M$_A$ phase transition as the composition and temperature vary, since the fraction of the monoclinic phase increases as the composition approaches the MPB. One possible reason for the missed observation of the R-M$_A$ phase transition is that the effects arising from the R-M$_A$ transition, such as the polarization rotation, could be largely attenuated in randomly oriented ceramics [16]. Moreover, the short range order of the M$_A$ domains [113] or nano-domains [25] of MPB can cause anomalous peak broadening and splitting, making it difficult to refine the structural diffraction data reliably.

On the other hand, it is especially important to know the macroscopic symmetry of materials because it determines the piezoelectric, dielectric and other crystal physical properties. In materials with complex domain structure of submicrometer and/or nanometer scale (like in PZT), macroscopic symmetry may be different from the symmetry determined by conventional methods, e.g. X-ray, neutron or electron diffractions. In contrast, polarized light microscopy (PLM) is an effective nondestructive way to examine macroscopic symmetry. However, comparatively large and good quality single crystals are required for PLM investigations, which had not been available until recently. In this chapter, we study the PZT single crystals with composition close to the MPB, namely, $x = 0.42$ and $x = 0.46$, which were grown using top-seeded solution growth (TSSG) technique [72]. PLM and dielectric measurements are carried out in order to gain some insights into the nature of the R-T and M$_A$-T phase transitions around the MPB. It is found that continuous polarization rotation takes place between the rhombohedral ($R3m$) and tetragonal ($P4mm$) phases via the intermediate monoclinic (M$_A$) symmetry.

5.3 Experimental

The TSSG technique was used for the growth of PZT crystals. A PZT seed crystal oriented in the $\langle 001 \rangle_{cub}$ direction obtained from conventional flux growth by spontaneous nucleation was used for the crystal growth with a mixture of PbO and $B_2O_3$ (1:5 molar ratio) as flux. The PZT ceramics with composition $x = 0.60$ were calcined to form a perovskite phase and then loaded in a 100 ml platinum crucible with powders of PbO and $B_2O_3$ (purity of 99.99%). The crucible was then heated in a tube furnace to above the seeding temperature to get a homogeneous melt, and then the seed was introduced into the melt. The crystal growth took place upon cooling from at a rate of 4 °C/day.
The grown crystals were pulled out of the melt and cooled slowly to room temperature. More details on the growth of PZT single crystals are provided in Chapter 3.

The (001)$_{\text{cub}}$ and (110)$_{\text{cub}}$ oriented crystal platelets were cut and polished. For permittivity characterization, gold layers were sputtered as electrodes. The permittivity as a function of temperature was measured with a Novocontrol broadband dielectric spectrometer upon heating and cooling from 25 to 550 °C. Optical investigations were made using Olympus BX60 polarizing microscope equipped with Berek and Senarmont compensators. A Linkam THMS600 optical heating stage was used for high-temperature optical observations and measurements.

5.4 Dielectric Properties

Figure 5.1 shows the temperature dependences of the dielectric permittivity ($\varepsilon'$) and the loss factor (tan $\delta$) at 1 kHz for a (110)$_{\text{cub}}$ Pb(Zr$_{0.58}$Ti$_{0.42}$)O$_3$ single crystal. The permittivity shows a maximum at $T_C = 372$ °C, which indicates the Curie point ($T_C$). Apart from the paraelectric-to-ferroelectric transition at $T_C$, we also found a shoulder near $T_{R-M} = 335$ °C both in the permittivity and loss, which suggests another phase transition between the MPB phases, confirming that the composition of the crystal is indeed in the MPB range. Our PLM study of the same crystal (see Section 5.5 for more details), reveals that the symmetry of the phase above $T_{MPB}$ is of monoclinic $M_A$ symmetry. Therefore, the dielectric anomaly at $T_{MPB} = 335$ °C arises from the MPB transition between the R and $M_A$ phases.

Figure 5.2 gives the variations of the dielectric constant ($\varepsilon'$) and loss (tan $\delta$) as a function of temperature of a (100)$_{\text{cub}}$-oriented Pb(Zr$_{0.54}$Ti$_{0.46}$)O$_3$ single crystal. It can be seen that, there is an anomaly at around 180 °C, which is related to the phase transition from the $M_A$ to T phase, within the MPB range. The $M_A$-T phase transition shows an obvious thermal hysteresis between heating and cooling, indicating a first order nature for the phase transition. The maximum dielectric peak at $T_C = 395$ °C is attributed to the ferroelectric tetragonal to paraelectric cubic phase transition.
Figure 5.1: Variations of the dielectric permittivity ($\epsilon'$) and the loss factor ($\tan \delta$) as a function of temperature at 1 kHz for a Pb(Zr$_{0.58}$Ti$_{0.42}$)O$_3$ single crystal of (110)$_{cub}$ orientation.
Figure 5.2: Variations of the dielectric permittivity ($\varepsilon'$) and the loss factor ($\tan \delta$) as a function of temperature measured at 1 kHz for a Pb(Zr$_{0.54}$Ti$_{0.46}$)O$_3$ single crystal of (001)$_{cub}$ orientation.
5.5 Rhombohedral to Monoclinic Phase Transition in Pb(Zr$_{0.58}$Ti$_{0.42}$)O$_3$ Single Crystals

5.5.1 Identification of Different MPB Phases by PLM

The orientation of the optical indicatrix depends on the macroscopic symmetry. By determining the optical indicatrix direction of the crystals using polarized light microscopy, we can identify the phases of different symmetry [81]. We study the (110)$_{cub}$ platelets based on the following considerations. In PZT single crystal with an MPB composition $x = 0.42$, it is possible to observe thermally induced phase transition from R to M$_A$ phase. The optical indicatrix axes of the M$_A$ phase can lie anywhere between the \( \langle 111 \rangle_{cub} \) - and \( \langle 001 \rangle_{cub} \)-directions in the (110)$_{cub}$ plane. On a (001)$_{cub}$ platelet, a crystal with M$_A$ symmetry can show extinction at many possible positions, including the position with its \( \langle 001 \rangle_{cub} \)-edge forming an angle of 45° to either of the crossed polarizers, which is also the extinction position for an R crystal [81]. So it is difficult to distinguish M$_A$ from R phase on a (001)$_{cub}$ crystal, especially when a phase transition takes place between these two phases. In addition, in both the R and M$_A$ phases, the birefringence of a (001)$_{cub}$ platelet corresponds to a projection of the indicatrix, while in a (110)$_{cub}$ platelet, the birefringence arises from a cross section of the indicatrix itself, giving the maximum value. So any phase transition between the room-temperature R phase and the high-temperature M$_A$ phase can be more accurately studied by monitoring the change of both the birefringence and extinction angle on a (110)$_{cub}$ platelet.

In the optically uniaxial R and T phases, the revolutionary symmetry axis of optical indicatrix collinear to the spontaneous polarization ($P_s$) is aligned along one of the \( \langle 111 \rangle_{cub} \) (in the R phase) or \( \langle 001 \rangle_{cub} \) (in the T phase) crystallographic directions. The extinction angle is determined as the smaller angle between the axes of the cross section of optical indicatrix (vibration directions) of the domain and the [110]$_{cub}$ crystallographic axis. Figure 5.3 shows that for the R symmetry the extinction angle is at 35.3°/−35.3° and for the T phase the extinction angle is at 90°/0°. For the biaxial M$_A$ phase, the single two-fold rotation axis is perpendicular to the (110)$_{cub}$ mirror plane. The other two axes are perpendicular to the 2-fold axis and can lie anywhere within the (110)$_{cub}$ mirror plane. So if a region of crystal shows extinction at neither 35.3°/−35.3° nor 90°/0°, one can conclude that it corresponds to a monoclinic phase. If the platelet contains several non-180° domains with differently oriented indicatrixes along the way of propagating
light, one will observes no extinction at all [96]. This may happen in the MPB crystals containing overlapping domains of different symmetry (e.g., overlapping domains of T and R phases or R and MA phases).

Figure 5.3: Crystal optical characterization of the low-temperature rhombohedral (R), tetragonal (T) or monoclinic Cm (MA) phase formed from paraelectric cubic phase. Crystallographic directions and cubic unit cell of the paraelectric phase are shown. (a) Possible directions of the particular axis (bold lines) of optical indicatrix. (b) Possible extinction positions of the domains on a (110)cub crystal platelet.

5.5.2 PLM Observation on (110)cub Crystal

Figure 5.4 shows the PLM images of a (110)cub platelet of Pb(Zr0.58Ti0.42)O3 crystal at the brightest (diagonal) and extinction positions observed at several temperatures. Before the optical measurement, the crystal was annealed at 600 °C for 30 min to eliminate the internal stress. At room temperature the majority of the crystal shows a clear extinction at 35°, indicating a macroscopic R phase with optical indicatrix oriented along the ⟨111⟩cub direction. With increasing temperature the interference colour changes in a certain order, arising from a decrease of birefringence. As the temperature increases to above 300 °C, the extinction angle starts to increase, as a result of the rotation of optical indicatrix. As shown in Figure 5.4 (c) and (d), the extinction angles at 325 °C and 365 °C are 45° and 59°, respectively. This means that the direction of optical indicatrix rotates off the ⟨111⟩cub-direction, indicating that the R symmetry has transformed into
a lower symmetry (M_A). This gradual increase in extinction angle is a signature for the occurrence of a monoclinic phase. Note that, besides M_A (Cm), two other types of monoclinic phase have been observed in perovskite ferroelectrics, namely M_B (with space group Cm, with polarization P_s in (110)_cub plane) and M_C (with space group Pm, and polarization P_s in (100)_cub plane) [114–116]. However, the transition between R (R3m) and T (P4mm) phases can only take place via an M_A (Cm) phase since it is a subgroup of both R3m and P4mm, and the direction of its polarization can rotate continuously between the T⟨001⟩ and R⟨111⟩ directions (see Figure 5.5). Therefore, the monoclinic phase observed in the PZT crystal is confirmed to be of M_A type.

To measure the temperature dependence of birefringence, a region of the crystal with complete extinction at room temperature was selected. Figure 5.6 shows that the birefringence decreases continuously with increasing temperature in the R phase up to \( T = 300 \, ^\circ\text{C} \), while the extinction angle varies only slightly. The variation of the extinction angle becomes more pronounced at and above 300 \( ^\circ\text{C} \), which indicates the onset of the monoclinic phase and associated polarization rotation within it. This R-M_A phase transition is also revealed in the variation of permittivity (Figure 5.1), as the broad peak in \( \epsilon' \) and a bump in loss factor (\( \tan \delta \)) at around 335 \( ^\circ\text{C} \). As the temperature increases to above 372 \( ^\circ\text{C} \) (\( T_C \)), the birefringence decreases to almost zero. However, careful measurements show that the extinction angle continues to increase towards 90°, which implies the occurrence of the tetragonal phase before the crystal reaches the cubic phase. A tail of birefringence is observed above \( T_C \), indicating that the transition from the ferroelectric (T) to the paraelectric (C) phase in the Pb(Zr_{0.58}Ti_{0.42})O_3 crystal is diffuse.

### 5.5.3 Monoclinic Domains in Pb(Zr_{0.58}Ti_{0.42})O_3 Single Crystal

Studying the domain wall orientations can provide another solid confirmation on the symmetry of the monoclinic phase and thereby the nature of the R-M_A phase transition. The rhombohedral domain walls are usually energetically favourable parallel to the \( \langle 001 \rangle_{\text{cub}}, \langle 011 \rangle_{\text{cub}} \text{ and } \langle 111 \rangle_{\text{cub}} \) directions due to the corresponding elastic and electric compatibility requirements, while in the lower symmetry monoclinic phase, domain walls of other directions are permitted [117]. The enlarged domain structures of the \( \langle 001 \rangle_{\text{cub}} \)-oriented \( \text{Pb(Zr}_{0.58}\text{Ti}_{0.42})\text{O}_3 \) crystal (Figure 5.4) at 21 \( ^\circ\text{C} \) and 325 \( ^\circ\text{C} \) are shown in Figure 5.7 (a) and (b). At room temperature, most of the domain walls align along
Figure 5.4: PLM images of a (110)cub platelet (0.047 mm thick) of Pb(Zr_{0.58}Ti_{0.42})O_3 crystal observed at different positions under crossed polarizers and various temperatures.
Figure 5.5: Scheme showing the magnitude and rotation of the spontaneous polarization vector as a function of temperature in PZT with \( x = 0.42 \). The polarization is shown at \( T_1 < T_2 < \ldots < T_7 \) by thick arrows of different colours (green, blue and red for the R, \( M_A \) and T phases, respectively) and \( \vec{P}_s \equiv \vec{0} \) in the cubic phase.

Figure 5.6: Variations of birefringence and extinction angle as a function of temperature for a \((110)_{\text{cub}}\) platelet of \( \text{Pb(Zr}_{0.58}\text{Ti}_{0.42})\text{O}_3 \) single crystal.
the [001]\textit{cub} crystallographic direction, indicating a typical rhombohedral domain configuration, which is consistent with our previous result based on the extinction angle. However, in the rhombohedral domain structure, some short lines exist forming an angle of 30° with the [001]\textit{cub} direction, which is only allowed for the low symmetry M\textit{A} phase. As the temperature increases up to around 200 °C, no noticeable change of the R domain structure occurs even though the extinction angle starts to increase slightly. When the temperature increases to above 300 °C, the R domain walls become shorter and then disappear, while the domain walls of the M\textit{A} phase appear. Other than the domain wall change no sharp change in the domain contrast was observed at the transition between the R and M\textit{A} phases, which is related to the birefringence difference between the two phases. This suggests that the magnitude of the macroscopic polarization changes continuously between the two phases. On the other hand, the extinction angle clearly undergoes a pronounced increase as the temperature exceeds 300 °C, as shown in Figure 5.6, which indicates that the polarization vector rotates significantly away from the [111]\textit{cub} direction when the crystal enters the monoclinic phase. As the temperature increases above \(T_{R-M}\), the M\textit{A} domain pattern becomes clearer (see Figure 5.7(b)), with the 30° domain walls that are favoured in the M\textit{A} phase. Upon further heating, no obvious domain wall motion or domain pattern changes were observed while the rotation of optical indicatrix, i.e. the polarization, continues, which means that the thermally driven polarization rotation arises from the evolution of the crystal structure of the M\textit{A} phase as a function of temperature within the monoclinic domains. It is worth noting that our observation of the formation of 30° M\textit{A} domain walls and the disappearance of R domains in the Pb(Zr\textsubscript{0.58}Ti\textsubscript{0.42})O\textsubscript{3} crystal provide evidence that M\textit{A} phase is a distinctive phase that exists independently from the R phase. This result contradicts the adaptive phase theory by Wang \textit{et al.} [118], which suggests that the M\textit{A} phase observed from diffraction methods were actually generated from the R or T nanotwin domains with very low domain wall energy. Moreover, if there were R or T nanotwin domains, the overall birefringence of the crystal would be very low due to the cancellation effect, which was indeed the case for the T phase of the Pb(Zr\textsubscript{0.54}Ti\textsubscript{0.46})O\textsubscript{3} crystal, as discussed in the following part of this Chapter.

Kisi \textit{et al.} [119] predicted theoretically that the phase transition from R to M\textit{A} phase should be discontinuous, however, our experimental evidences suggest that there is no clear boundary between the R and M\textit{A} phases, and birefringence changes continuously
in the whole temperature range below $T_C$. Based on the experimental results, Ragini et al. questioned the existence of a distinct rhombohedral phase because of the missing evidence of monoclinic-rhombohedral boundary [120]. According to our observation, the rhombohedral and monoclinic phases in PZT are two distinct phases with characteristic domain configurations. The question how the microscopic structure changes during the R to $M_A$ transition remains open. Most recently, Glazer et al. proposed that the monoclinic $M_A$ phase is originally at the local unit cell level in the R and T phases, which grow in to a size sufficiently large so that diffraction techniques can distinguish it [17]. This proposal supports our observation that the monoclinic domain walls can exist in a rhombohedral phase due to the aggregates of some local monoclinic unit cells. The reason we have only observed macroscopic R phase at low temperature may be that the local monoclinic distortion is not strong enough to form a monoclinic domain and to affect the macroscopic crystal optical property. As the temperature increases, the monolinic unit cells aggregate to form mesoscopic domains that are large enough to be observed by PLM.
5.6 Monoclinic to Tetragonal Phase Transition in Pb(Zr$_{0.54}$Ti$_{0.46}$)O$_3$ Single Crystals

5.6.1 PLM Observation on (001)$_{cub}$ Crystal

As presented in Chapter 3, the PZT single crystals with MPB composition $x = 0.46$ exhibit the best piezoelectric properties with $d_{33} = 1230$ pC/N and $k_{33} = 0.80$. This high piezoelectric response is explained by the rotation of polarization direction from the ⟨111⟩$_{cub}$ toward the ⟨001⟩$_{cub}$ direction via an intermediate monoclinic phase. This rotation is believed to be realized by the easy reorientation of small microdomains because of their high domain-wall mobility [121]. However, the correlation between the macroscopic structure in the MPB region and the observed high piezoelectric properties is still unclear. The availability of the PZT single crystals of the MPB composition allows us to gain some new insights into this issue. Figure 5.8 displays the PLM images of a (001)$_{cub}$ platelet of Pb(Zr$_{0.54}$Ti$_{0.46}$)O$_3$ at room temperature. The extinction happens when the [010]$_{cub}$ edge is at 45° to the polarizer. As mentioned previously, the R and M$_A$ phases cannot be distinguished on a (001)$_{cub}$ platelet, as both show an extinction at 45°.

By studying the (110)$_{cub}$ platelet of the same composition, we have confirmed that this phase is of M$_A$ symmetry since the extinction occurs at 57° (see Figure 5.11), i.e., neither at 35° for the R phase nor at 0°/90° for the T phase. On heating, the (001)$_{cub}$ crystal undergoes a phase transition at about 150 °C (see Figure 5.9), from the M$_A$ phase to the T phase. The phase transition first starts at the upper-left corner of the crystal. On heating, the boundary between these two phases moves to the lower-right corner. The phase transition from the M$_A$ phase to the T phase implies that the polarization rotates from the ⟨111⟩$_{cub}$ to the ⟨001⟩$_{cub}$ direction in the (110)$_{cub}$ plane. Since the polarization rotates in the (110)$_{cub}$ plane which is perpendicular to the (001)$_{cub}$ surface of the crystal, the extinction angle remains unchanged when observed along the [001]$_{cub}$ direction.

It is of interest to note that the high-temperature tetragonal phase behaves like optically isotropic, showing extinction at any position under the crossed polarizers. The crystal remains optically isotropic in whole temperature range above $T_{M-T}$, so that no change can be observed when it undergoes the tetragonal to cubic phase transition at $T_C$. The apparent “isotropic phase” of tetragonal symmetry can be related to the formation of very small domains in the T phase. The orientations of tetragonal domains have the equal possibilities along the [001]$_{cub}$, [010]$_{cub}$, [001]$_{cub}$, T$_X$ (domain X), [010]$_{cub}$, T$_Y$ (domain Y) and
[100]_{cub}T_{z} (domain Z) directions (see Figure 5.10). Since the orientation of domain Z ($T_{z}$) is perpendicular to the (001)_{cub} plane, it is optically isotropic when observed along the [001]_{cub} direction, and has no contribution to the optical retardation. Domain X and domain Y are oriented perpendicular to each other, therefore, the net optical retardation ($R$) of a (001)_{cub} tetragonal crystal can be calculated by

$$R = \Delta n(\sum d_{X} - \sum d_{Y}),$$

(5.1)

where $\Delta n$ is the “intrinsic” birefringence of a single domain, and $\sum d_{X}$ and $\sum d_{Y}$ are the thickness of the X and Y domain, respectively. In a defect-free tetragonal single crystal, the spontaneous polarization has the equal possibilities to be oriented along the $T_{x}$ and $T_{y}$ directions. If the domain size is much smaller than the thickness of the crystal, $\sum d_{X} = \sum d_{Y}$ can be satisfied statistically, which leads to a zero net retardation $R$. The crystal thereby looks like optically isotropic due to the domain compensation effect, even though its crystallographic symmetry is tetragonal.

Figure 5.8: PLM images of the (001)_{cub} platelet (60 μm thick) of Pb(Zr\textsubscript{0.54}Ti\textsubscript{0.46})O\textsubscript{3} crystal at room temperature.

5.6.2 PLM Observation on (110)_{cub} Crystal

In order to study the change of polarization direction in the (110)_{cub} plane during the monoclinic to tetragonal phase transition, we prepared a (110)_{cub} crystal of composition PbZr\textsubscript{0.54}Ti\textsubscript{0.46}O\textsubscript{3}. As shown in Figure 5.11, at room temperature the crystal shows an extinction at 57°, indicating a monoclinic phase since the extinction angle is neither 35° for a rhombohedral phase nor at 90°/0° for a tetragonal phase. The size of monoclinic
domains is small compared with the rhombohedral domains with a high Zr content (see Chapter 4). The same trend was also found by TEM studies [25, 122] which showed that domain size becomes smaller as the composition approaches MPB of PZT. The miniaturized domains can facilitate the polarization switching due to the low domain wall energy. On heating, the extinction angle starts to increase as the temperature increases to above 100 °C, indicating that the polarization starts to rotate towards [001]cub in the (110)cub plane. The extinction angle continues to increase with increasing temperature and reaches a constant value at 180 °C. The related phase transition at this composition is confirmed to be from monoclinic phase to tetragonal phase, consistent with the PZT phase diagram [101]. The high-temperature phase shows extinction at an angle of 80.6°, which is different from 90°/0° as expected for the tetragonal structure. One possible reason is that the energy profile flattens as the MPB is approached [74], thus defects and local electric field in the crystal can change the minimum position of the energy profile and drive the polarization away from its theoretically calculated direction. The change of the extinction angle is accompanied with the dramatic decrease of birefringence, which is due to the formation of micro-size domain in the tetragonal phase. If the same amount of domains with mutually perpendicular orientations overlap, the birefringence would be zero, which is the case for the (001)cub crystal, as described in
Figure 5.10: Schematics of the possible orientation states in the tetragonal phase of PbZr$_{0.54}$Ti$_{0.46}$O$_3$ crystal (a), and the cancellation of retardation in the (001)$_{\text{cub}}$ (b) and (110)$_{\text{cub}}$ platelets (c).
Section 5.6.1. However, unlike the (001)$_{\text{cub}}$ crystal, the tetragonal phase in the (110)$_{\text{cub}}$ crystal is not completely isotropic. As shown in Figure 5.10, the net optical retardation in the (110)$_{\text{cub}}$ crystal can be calculated by

\[ R = \Delta n \sqrt{\frac{\sqrt{2}}{2}} (\sum d_X + \sum d_Y) - \Delta n \sum d_Z, \quad (5.2) \]

where $\sum d_X$, $\sum d_Y$ and $\sum d_Z$ are the thicknesses of the X, Y and Z domains, respectively. Since the polarizations of domains X and Y are not on the (110)$_{\text{cub}}$ plane (see Figure 5.10), their birefringences in (110)$_{\text{cub}}$ plane need to be multiplied by $\frac{\sqrt{2}}{2}$. Given that the polarizations have the equal possibilities to be oriented along the three directions and the domains are very small, the thickness of the three kinds of domains can be statistically considered to be equal. Therefore, $\frac{\sqrt{2}}{2} (\sum d_X + \sum d_Y) - \sum d_Z > 0$, leading to a decreased but non-zero net retardation.

![Figure 5.11: PLM images of the (110)$_{\text{cub}}$ platelet (50 $\mu$m thick) of Pb(Zr$_{0.54}$Ti$_{0.46}$)O$_3$ crystal at room temperature.](image)

The phase sequence of PZT was studied by Glazer et al. [17] with respect to the short- and long-range orders of Pb displacements across the MPB region. They found that the rhombohedral and tetragonal phases in MPB region are of monoclinic ($Cm$) symmetry at the local level. On the Zr-side of the MPB region, with increasing Ti/Zr ratio, the small monoclinic regions increase in size and become long-range ordered, resulting in a macroscopic monoclinic symmetry that can be detected by scattering experiments, such as X-ray or neutron diffraction. With the increase of the Ti/Zr ratio the range of monoclinic order decreases, and once the average size of the ordered regions drops below the
Figure 5.12: PLM images of the (110)$_{cub}$ platelet (50 µm thick) of Pb(Zr$_{0.54}$Ti$_{0.46}$)O$_3$ crystal at various temperatures.
Figure 5.13: Variations of the birefringence and extinction angle as a function of temperature for a Pb(Zr\textsubscript{0.54}Ti\textsubscript{0.46})O\textsubscript{3} single crystal of (110)\textsubscript{cub} orientation.
coherence length of the diffraction, the macroscopic structure will be refined as tetragonal. It should be noted here that in the unit cell level the symmetry is still monoclinic, but with Pb atoms are displaced toward the near-[001]_{cub} direction, the crystal macroscopically is tetragonal. As observed on the (110)_{cub}-oriented Pb(Zr_{0.54}Ti_{0.46})O_{3} crystal in this work, the thermally-driven polarization rotation is characterized by the continuous change of the extinction angle. As the polarization rotates towards the [001]_{cub} direction, the average size of the ordered monoclinic regions decreases. Once the size of monoclinic region is smaller than the critical value, and all the Pb atoms displaced towards the near-[001]_{cub} direction, the structure will average out to be tetragonal on the macroscopic scale. A new domain structure will be energetically favoured as a consequence of the symmetry change.

The effects of random fields in ferromagnets has been studied by Imry and Ma using a theoretical approach [123]. They showed that for a system with a second order phase transition and a continuous symmetry of the order parameter, the ordered state is unstable against an arbitrary weak random fields conjugate to the order parameter. Therefore, the system tends to break down into small domains and the crystal remains disordered on the macroscopic scale. This theory can be applied to ferroelectrics since electric dipoles behave, in many respects, in an analogous manner to the magnetic dipoles. In PZT with compositions close to the MPB, the symmetry of ferroelectric order parameter is expected to be continuous due to the closeness of energies of three different phases (rhombohedral, tetragonal and monoclinic). The polarization rotation we observed experimentally in crystals with composition \( x = 0.46 \) proved the flattening of energy profile between the R and M_{A} phases on the Zr-rich side, and the M_{A} and T phases on the Ti-rich side. For the Pb(Zr_{0.54}Ti_{0.46})O_{3} crystal, the room-temperature monoclinic phase becomes unstable with increasing temperature and the long-range order of monoclinic phase gradually disappears. This structural disorder may lead to the formation of local random fields. As a result, the system is energetically favoured to break down into domains of small size. The new tetragonal phase develops as the formation of the miniaturized domains, the orientation of which will be randomly along the three possible directions [001]_{cub}, [010]_{cub} and [001]_{cub}. As discussed previously the domain size is anomalously small compared to the thickness of the crystal, and when observed under polarized light microscope, the crystals will display some cancellation effects due to overlapping domains with different orientations, leading to the isotropic state and the reduced retardation observed in the
(001)\textsubscript{cub}-oriented and (110)\textsubscript{cub}-oriented crystals, respectively.

5.7 Conclusions

We have studied the two MPB crystals of Pb(Zr\textsubscript{0.58}Ti\textsubscript{0.42})O\textsubscript{3} and Pb(Zr\textsubscript{0.54}Ti\textsubscript{0.46})O\textsubscript{3} by polarized light microscopy and dielectric measurements. In the (110)\textsubscript{cub} Pb(Zr\textsubscript{0.58}Ti\textsubscript{0.42})O\textsubscript{3} crystal, we observed the rotation of the optical indicatrix from [111]\textsubscript{cub} to [001]\textsubscript{cub}, which indicates a thermally activated polarization rotation during the phase sequence of R$\rightarrow$M$\rightarrow$T$\rightarrow$C upon heating. The formation of the monoclinic phase in the crystal of composition $x = 0.42$ was confirmed by the observation of the 30°-domain walls which appear around 300 °C with the disappearance of rhombohedral domain walls. Even though the birefringence and extinction angle show no abrupt change when going through the R-M\textsubscript{A} transition on heating, the R and M\textsubscript{A} phases are found to be two distinctive phases with very different domain configurations. The local aggregates of monoclinic unit cells nucleate within the rhombohedral phase and can only be optically detected when they have grown large enough to form a macroscopic domain. In the Pb(Zr\textsubscript{0.54}Ti\textsubscript{0.46})O\textsubscript{3} crystal, the M\textsubscript{A} to T phase transition is accompanied by a significant change in both the extinction angle and birefringence with increasing temperature. Anomalously small domains with random orientations form in the high-temperature T phase, resulting in total cancellation of birefringence on the (001)\textsubscript{cub} platelet, and partial cancellation on the (110)\textsubscript{cub} platelet. As explained by Imry and Ma’s theory [123], random field related to the structural disorder developed as the long-range order monoclinic phase becomes unstable, leading to miniaturized domains which is more energetically favoured for the system. The ferroelectric phase transitions from R to M\textsubscript{A} in Pb(Zr\textsubscript{0.58}Ti\textsubscript{0.42})O\textsubscript{3} and from M\textsubscript{A} to T in Pb(Zr\textsubscript{0.54}Ti\textsubscript{0.46})O\textsubscript{3} were also characterized by dielectric permittivity measurements, which show a broad peak for both $\epsilon'$ and loss ($\tan \delta$). Our studies have revealed some peculiar features of the R-M\textsubscript{A} and M\textsubscript{A}-T phase transitions between the morphotropic phases, which will lead to a better understandings of the origin of the high piezoelectric properties of PZT through polarization rotation.
Chapter 6

Synthesis and Properties of New Bi(Zn$_{1/2}$Ti$_{1/2}$)O$_3$-PbTiO$_3$-PbZrO$_3$ Ternary Ceramics

The following chapter is a revised version of the paper published in Transactions on Ultrasonics, Ferroelectrics, and Frequency Control, IEEE Transactions on (TUFFC) by Yujuan Xie, Ling Chen, Wei Ren, and Zuo-Guang Ye, (Ultrasonics, Ferroelectrics and Frequency Control, IEEE Transactions on, vol. 58, no. 9, pp. 1882-1887, 2011) [124]. The use of this article is by permission of the publisher of IEEE (Home website: www.ieee.org).

6.1 Abstract

Ceramics of a new ternary solid solution system $x$Bi(Zn$_{1/2}$Ti$_{1/2}$)O$_3$$-y$PbTiO$_3$$-z$PbZrO$_3$ ($xBZT$$-y$PT$$-z$PZ) with compositions within the solubility limit were prepared by solid-state reaction and sintering method. Morphotropic phase boundary (MPB) separating a rhombohedral and a tetragonal phase exists over a wide compositions region ($0.45 \leq z \leq 0.6$), as revealed by X-ray diffraction (XRD) and dielectric measurements. Enhanced dielectric and ferroelectric properties are found at different compositions around MPB with Curie temperature, $T_C$ ranging from 260°C to 290°C. The dielectric constant reaches a maximum value ($\epsilon' = 1250$) on the tetragonal majority side of the MPB. The highest remnant polarization ($P_r = 34.2 \mu$C/cm$^2$) is shown in the composition at the
center of the MPB where the rhombohedral and tetragonal phases coexist in almost equal quantity.

6.2 Introduction

Pb(Zr,Ti)O$_3$ (PZT) ceramics are the most extensively used piezoelectric material owing to their high Curie temperature ($T_C \approx 350 \, ^\circ$C), good piezoelectric and electromechanical properties with compositions near its morphotropic phase boundary (MPB) [125]. So far, several PZT-based ternary and quaternary system have been prepared and studied to meet the various requirements for practical applications, such as Pb(Mn$_{1/3}$Sb$_{2/3}$)O$_3$-PZT, Pb(Mg$_{1/3}$Nb$_{2/3}$)O$_3$-Pb(Zn$_{1/3}$Nb$_{2/3}$)O$_3$-PZT and Pb(Zn$_{1/3}$Nb$_{2/3}$)O$_3$-PZT [126–128].

On the other hand, there have been pressing demands for lead-free piezoelectric materials because of environmental concerns.

Bismuth zinc-titanate, Bi(Zn$_{1/2}$Ti$_{1/2}$)O$_3$ (BZT), a lead free ferroelectric material crystallizes in the complex perovskite structure with tetragonal symmetry. It exhibits a extremely large c/a ratio of 1.21 and a high calculated ionic polarization of 150 $\mu$C/cm$^2$ [28]. However, BZT cannot be obtained by ambient pressure solid-state synthesis. Recently, it was shown that BZT can be stabilized in solid solution with other perovskite end members [29,129,130]. In the $(1-x)$PbTiO$_3$-$xBi$(Zn$_{1/2}$Ti$_{1/2}$)O$_3$ system, both the phase transition temperature ($T_C$) and the tetragonality significantly increase with increasing BZT content, the highest value of $T_C$ ($\approx 700 \, ^\circ$C) and tetragonality ($c/a = 1.11$) being obtained at the solubility limit ($x = 0.4$) [29]. On the other hand, it was found that the substitution of BZT for antiferroelectric PbZrO$_3$ perovskite lowers the $T_C$ and stabilizes the ferroelectric phase without changing the orthorhombic structure [129]. Since the structures of both BZT-PT and BZT-PZ solid solution are different at solubility limit, it is reasonable to believe that interesting structures can be found in the MPB of a new ternary solid solution system of BZT-PT-PZ. In particular, a ternary MPB is expected to form in this lead-reduced system.

In the present work, two series of the $x$BZT-$y$PT-$z$PZ ($x + y + z = 1$) ceramics have been synthesized by solid-state reaction and sintering method, and their structural phase transition, dielectric and ferroelectric properties have been studied. As shown in the ternary phase diagram (Figure 6.1), the line with fixed PT/PZ ratio ($y/z = 47/53$) was chosen to find out the solubility limit of BZT in the PZT binary system around the MPB region. The other series with compositions along the solubility curve experiences
the phase transition from orthorhombic to tetragonal phase.

Figure 6.1: The ternary phase diagram of BZT-PZ-PT and the compositions studied.

6.3 Experimental

Two series of $x$BZT-$y$PT-$z$PZ ceramics with compositions shown in Fig.1 were prepared from analytical grade oxide powders of PbO, Bi$_2$O$_3$, ZrO$_2$, TiO$_2$ and ZnO. The oxide powders were weighed in stoichiometric proportion and then ground and homogenized in ethanol. The resulting mixtures were dried and calcined between 700 °C and 800 °C for 4 h. The products were reground to fine powder with 5 wt% PVA binder added, pressed into small pellets and then sintered between 1080 °C and 1150 °C for 4 h. After sintering, the circular surfaces of the ceramics were polished and sputtered with gold layers as electrodes for electric characterization. The phases of the sintered ceramics were analyzed using a Rigaku MSC diffractometer with Cu $K_{\alpha}$ radiation. The dielectric
properties were measured by means of Solartron 1260 impedance analyzer combined with a Solartron 1296 dielectric interface. The ferroelectric hysteresis loops were measured with a RT66 ferroelectric test system (Radiant Technologies Inc.) under the virtual ground mode with a high voltage interface.

6.4 Results and Discussion

6.4.1 Phase Analysis

Figure 6.2 shows the XRD patterns of the \( x \)BZT-(1 - \( x \))(PbZr\(_{0.53}\)Ti\(_{0.47}\)O\(_3\)) with \( x = 0 - 0.2 \). It was found that the introduction of BZT into PbZr\(_{0.47}\)Ti\(_{0.53}\)O\(_3\) does not affect the crystal structure of the system. However, a small amount of secondary nonperovskite phase is observed for \( x > 0.15 \), indicating that the solubility limit of this pseudobinary system is about \( x = 0.15 \). Since this composition does not fall on the straight line connecting the solubility points of BZT-PZ and BZT-PT binary systems, it can be concluded that the solubility limit in the ternary diagram is not a linear line.

Figure 6.3 shows XRD patterns for the second series of \( x \)BZT-yPT-zPZ (\( x/y/z \)) ceramics with the compositions along the solubility limit curve connecting the solubility limit points of the two binary systems BZT-PT and BZT-PZ. As shown in Figure 6.3, all the ceramic samples exhibited a single perovskite phase, indicating that BZT is stabilized in these compositions. Composition BZT-PT-PZ (10/0/90) crystallizes in an orthorhombic (\( Pbam \)) phase, whereas BZT-PT-PZ (10/10/80) has a rhombohedral (\( R3m \)) phase. Therefore, a morphotropic phase boundary MPB\(_{O-R} \), must exist between these two compositions. With increasing \( x \) and \( y \) (and decreasing \( z \)), the rhombohedral phase gradually transforms into tetragonal phase (\( P4mm \)), which can be seen by the peak splitting of such reflections (100)\(_{cub} \), (110)\(_{cub} \), (200)\(_{cub} \), etc. Figure 6.4 depicts the detailed diffraction profiles of the three representative pseudo-cubic reflections (111)\(_{cub} \), (200)\(_{cub} \) and (220)\(_{cub} \) in the composition range 0.4 \( \leq z \leq 0.7 \) showing the evolution from rhombohedral phase to tetragonal phase. It is known that the XRD pattern of rhombohedral phase shows splitting peaks at (111)\(_{cub} \) reflection and only a single peak at (200)\(_{cub} \) reflection, while in the contrast the tetragonal phase shows two peaks at (200)\(_{cub} \) reflection and one peak at (111)\(_{cub} \) reflection. The asymmetric peaks at both (111)\(_{cub} \) and (200)\(_{cub} \) reflections for BZT-PT-PZ (11/29/60) and BZT-PT-PZ (13/37/50) indicate a mixture of phases, that is, a second MPB that separates R and T phases,
Figure 6.2: XRD patterns of $(1-x)$PbZr$_{0.53}$Ti$_{0.47}$O$_3$-xBZT ceramics with $0 \leq x \leq 0.20$. 
Figure 6.3: XRD patterns of $x$BZT-$y$PT-$z$PZ ($x/y/z$) ceramics along the solubility limit curve, indicating two morphotropic phase boundaries MPB$_{O-R}$ and MPB$_{R-T}$.

MPB$_{R-T}$. For composition (15/40/45), the $(111)_{cub}$ peak is a singlet, while $(200)_{cub}$ is a doublet, suggesting a tetragonal structure. However, the $(111)_{cub}$ peak is broader than that for composition (17/43/40), indicating that the $(111)_{cub}$ peak for (15/40/45) may not be singlet. It is worth mentioning here that in PZT [131] and PMN-PT [132] ceramics, a monoclinic phase ($Pm$) was found to coexists with the tetragonal phase in the MPB region. The possibility of coexistence of tetragonal phase with the monoclinic phase in the MPB composition (15/40/45) also cannot be ruled out here. However, this can only be resolved using high-resolution synchrotron XRD data. Compared with pure PZT (MPB$_{R-T}$ at PT/PZ = 47/53), the MPB$_{R-T}$ of the BZT-PZ-PT ternary system at room temperature happens at a lower PT/PZ (≈ 40/60) ratio, and is enlarged to a wide range of compositions (PZ = 0.45–0.6) instead of a narrow region. The change in lattice parameters and unit cell volume is shown in Figure 6.5. It is seen that the unit cell volume increases with the composition approaching the PZ-rich side with a lower BZT content in the BZT-PZ-PT system. This can be explained by the fact that Pb$^{2+}$ (1.49 Å) has a larger ionic radius than Bi$^{3+}$ (1.35 Å), whereas Zr$^{4+}$ (0.72 Å) is bigger than the average radius of Zn$^{2+}$ (0.74 Å) and Ti$^{4+}$ (0.605 Å) [133]. On the tetragonal side
Figure 6.4: Evolution of the profiles of the (111)$_{cub}$, (200)$_{cub}$ and (220)$_{cub}$ reflections for the $xBZT$-$yPT$-$zPZ$ ($x/y/z$) ($0.4 \leq z \leq 0.7$) ceramics. The characteristic tetragonal and rhombohedral peaks are marked with arrows and asterisks, respectively.
(\(z \leq 0.45\)), the samples show a decrease in parameter \(c\) and increase in parameters \(a\) and \(b\) when approaching MPB_{R,T}, except the composition \(z = 0.45\), in which a relatively large increase was found in the parameters \(a\) and \(b\) and the unit cell volume.

Figure 6.5: Variations of lattice parameters and unit cell volume of the \(x\)BZT-\(y\)PT-\(z\)PZ (\(x/y/z\)) ceramics along the solubility limit curve as a function of PZ content (\(z\)).

6.4.2 Dielectric Properties

Figure 6.6 illustrates the variation of the dielectric constant and loss tangent of \(x\)BZT-(1-\(x\))(PbZr_{0.53}Ti_{0.47}O_{3}) (\(x = 0 - 2.0\)) versus temperature as a function of temperature, measured at 1 kHz upon cooling. In all cases, \(T_C\) shows a decrease from 390 °C to 300 °C with increasing BZT content from \(x = 0\) to \(x = 0.15\). As the amount of BZT in the solid solution increases, the dielectric peak becomes broader, indicating a diffuse phase transition from paraelectric (PE) to ferroelectric (FE) phase. This can be attributed to the disorder in the arrangements of cations on the A-site which is occupied by Pb\(^{2+}\) with Bi\(^{3+}\), and B-site occupied by Zr\(^{4+}\), Ti\(^{4+}\) and Zn\(^{2+}\), leading to a microscopic heterogeneity in the composition, which, in turn, results in a broad distribution of different local Curie point and thereby a diffuse phase transition [134]. For the samples with a high
BZT content, no frequency dispersion of dielectric constant or variation of $T_C$ with frequency (100 Hz - 10 MHz) near the dielectric maximum was observed, indicating a normal ferroelectric phase transition at $T_C$. The value of loss tangent ($\tan \delta$) at room temperature shows an increase with increasing BZT content. It should be noted that the loss value of composition $x = 0.15$ is nearly independent of the temperature below $T_C$. Figure 6.7 shows the temperature dependence of dielectric constant and loss tangent of the $x$BZT-$y$PT-$z$PZ ceramics. With decreasing PZ content, the peak temperature ($T_C$) shifts towards higher temperature, and the maximum dielectric constant at $T_C$ increases with $z$ increasing to $z = 0.6$, and then drops. The shape of $\tan \delta$ is a pointed

![Figure 6.6: Dielectric constant ($\epsilon'$) and loss ($\tan \delta$) as a function of temperature for $x$BZT-$y$PT-$z$PZ ceramics with $0 \leq x \leq 0.15$.](image)

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single peak in both rhombohedral and tetragonal single-phase regions while it is broad or double peaks in the two-phase MPB region. Combined with XRD analysis, the dielectric results confirm that the MPB region exists in the BZT-PT-PZ ceramics at $z = 0.45 - 0.6$. Figure 6.8 shows the variations of room temperature dielectric constant

![Figure 6.7: Variation of dielectric constant ($\epsilon'$) and loss tangent (tan $\delta$) as a function of temperature for the $xBZT$-$yPT$-$zPZ$ ceramics along the solubility limit curve. The insect shows the composition (PZ content) dependence of $T_C$ for the ceramics.](image)

and loss as a function of PZ content ($z$) measured at 1 kHz. The maximum dielectric constant was found at the tetragonal composition (15/40/45) rather than at the center of the MPB region. From the XRD analysis it is known that the unit cell volume increases as the composition approaches MPB from the tetragonal side. However, this increase is abnormally significant at composition $z = 0.45$ due to the increase of the lattice parameters $a$ and $b$. This increase leads to a large volume of the B-O$_6$ cage that leaves relatively large room for B-site cations to rattle around in response to an applied...
electric field leading to a large dielectric constant.

Figure 6.8: Dielectric constant and loss tangent (\(\tan \delta\)) as a function of PZ content (\(z\)) for the \(x\)BZT-\(y\)PT-zPZ ceramics along the solubility limit curve.

6.4.3 Ferroelectric Properties

The room temperature polarized-electric field (\(P - E\)) loops of the BZT-PT-PZ ceramics of the compositions along the solubility limit curve are shown in Figure 6.9 For composition (10/0/90) with an orthorhombic phase, the \(P - E\) loop displays a weak ferroelectric behaviour with a small remnant polarization (\(P_r = 0.5 \, \mu\text{C/cm}^2\)), which is reminiscent of the antiferroelectric character of PZ. The hysteresis loop opens up as the structure becomes rhombohedral at composition (10/10/80). Well-saturated \(P - E\) loops are obtained for the compositions \(z \leq 0.90\), indicating good ferroelectric properties. Since the intervals between composition points are large, saturations for different compositions are achieved at different electric field.

Figure 6.10 presents the values of remnant polarization (\(P_r\)) and coercive field (\(E_c\)) as a function of PZ content (\(z\)). The \(P_r\) value increases with the composition approaching the MPB\(_{R-T}\) from both rhombohedral and tetragonal sides and reaches the maximum
Figure 6.9: $P-E$ hysteresis loops displayed at room temperature for the $xBZT-yPT-zPZ$ ($x/y/z$) ceramics along the solubility limit curve.

value of $34.2 \mu C/cm^2$ at the MPB$_{R-T}$ composition (13/37/50). From the XRD analysis, ceramics with composition (13/37/50) contains almost same amount of rhombohedral and tetragonal phases according to the intensity of the peaks for each phase. The appearance of the largest polarization is believed to be associated with the coexistence of rhombohedral and tetragonal phases, where 14 possible spontaneous polarization directions exist and the energy states of both phases are close to each other. Another possible explanation for this maximum in $P_r$ is the presence of the local monoclinic (M) symmetry, which allows continuous polarization rotation between the [001]$_{cub}$ and [111]$_{cub}$ limiting directions within the same phase [101]. The value of $E_c$ shows a significant increase when the structure becomes predominantly tetragonal on the Ti-rich side. This is due to the increased domain size of the tetragonal structure as a result of higher domain wall energy making it difficult to reverse the polarization at a low electric field [135].
Figure 6.10: Remnant polarization ($P_r$) and coercive field ($E_c$) as a function of PZ content ($z$) for the $x$BZT-$y$PT-$z$PZ ($x/y/z$) ceramics along the solubility limit curve.

6.5 Conclusions

The $x$BZT-$y$PT-$z$PZ ternary ceramics with compositions across the MPB$_{O-R}$ and MPB$_{R-T}$ were obtained with pure perovskite phase. The XRD data reveal that MPB$_{R-T}$ exists in a wide range of compositions ($z = 0.45 - 0.6$) along the solubility limit curve. Substitutions of Bi$^{3+}$ for Pb$^{2+}$ and ($Zn_{1/2}Ti_{1/2}$)$^{3+}$ for Zr$^{4+}$ leads to a decrease in lattice parameters a and b and unit cell volume. With the addition of BZT into PZT system, the phase transition from FE to PE phase becomes more diffuse due to the microscopic heterogeneity in the composition caused by the disorder in the arrangement of different cations. The maximum value of dielectric constant $\epsilon'$, was found at the MPB$_{R-T}$ composition (13/37/50) on the tetragonal side. Maximum value of remnant polarization $P_r = 34.2 \mu C/cm^2$ was found at the center of the MPB$_{R-T}$ where equal amounts of rhombohedral and tetragonal phases exist. In the future study of this ternary system, it is an interest to investigate the compositions in the expanded MPB$_{R-T}$ area below the solubility curve, where high piezoelectric properties are expected to be found.
Chapter 7

Characterization of the Bi(Zn$_{1/2}$Ti$_{1/2}$)O$_3$-PbZrO$_3$-PbTiO$_3$ Ternary Ceramics around the MPB

7.1 Abstract

Bi(Zn$_{1/2}$Ti$_{1/2}$)O$_3$-PbZrO$_3$ -PbTiO$_3$ (BZT-PZ-PT) ternary solid solution was synthesized in the form of ceramics by solid state reaction and investigated by X-ray diffraction (XRD), dielectric spectroscopy, and ferroelectric and piezoelectric measurements. Studies were focused on three series of compounds, 0.05BZT-0.095PZT, 0.1BZT-0.9PZT and 0.15BZT-0.85PZT, which have their compositions around the morphotropic phase boundary (MPB), with varying Zr/Ti ratio. It is found that the introduction of BZT into the PZT system makes the paraelectric to ferroelectric phase transition more diffuse, brings the MPB to a lower PT content and enlarges the MPB region. The maximum room temperature dielectric constant of $\epsilon' = 1490$ is found in the 0.1BZT-0.9PZT series. Enhanced ferroelectric and piezoelectric properties are found in the MPB region of 0.15BZT-0.85PZT series, with $P_r = 35 \mu$C/cm$^2$ and $d_{33} = 275$ pC/N.
7.2 Introduction

Pb(Zr\(_{1-x}\)Ti\(_x\))O\(_3\) (PZT) ceramics are the most extensively used piezo-/ferroelectric material owing to its high Curie temperature (\(T_C \approx 350^\circ C\)), good piezoelectric and electromechanical properties near its morphotropic phase boundary (MPB) [13]. PZT-based ternary solid solutions, such as Pb(Mn\(_{1/3}\)Nb\(_{2/3}\))O\(_3\)-PZT, Pb(Mn\(_{1/3}\)Sb\(_{2/3}\))O\(_3\)-PZT and Pb(Cd\(_{1/3}\)Nb\(_{2/3}\))O\(_3\)-PZT [136, 137], were investigated to meet the requirements of practical applications in piezoelectric actuators, ultrasonic motors and piezoelectric transducers. These ternary ceramics exhibit a higher mechanical quality factor (\(Q_m\)) with an enhanced piezoelectric coefficient (\(d_{33}\)) and electromechanical coupling factor (\(k_p\)).

Recently, Bi-based perovskite systems, such as PbTiO\(_3\)-BiFeO\(_3\), PbTiO\(_3\)-BiScO\(_3\) and PbTiO\(_3\)-Bi(Mg,Ti)O\(_3\), were studied intensively because of their large polarization and multiferroic properties [29, 76, 138]. Bi\(^{3+}\) ion possesses a similar electron configuration ([Xe] 6\(s^26p^0\)) to that of Pb\(^{2+}\), which, due to the stereochemical activities of the 6\(s^2\) lone electron pair, can induce a large polarization in the perovskite materials. The smaller size of Bi\(^{3+}\) cation (1.35 Å) compared with that of Pb\(^{2+}\) cation (1.49 Å) limits the stability of the perovskite structure. Therefore, it is necessary to use an end member that has a stable perovskite structure, in order to stabilize Bi-based compounds. Among the Bi-based systems, \(x\)Bi(Zn\(_{1/2}\)Ti\(_{1/2}\))O\(_3\)-(1 - \(x\))PbTiO\(_3\) (BZT-PT) (with \(x \leq 0.4\)) presents a significant increase in \(T_C\) (700 \(^\circ\)C) compared with 490 \(^\circ\)C of PT and in the tetragonality (\(c/a = 1.11\)) [139]. Density functional theory (DFT) calculations showed that the theoretical spontaneous polarization can reach 127 \(\mu\)C/cm\(^2\), which is much higher than that of PT (52 \(\mu\)C/cm\(^2\)). Our previous study has revealed that adding BZT into PZT host can form a ternary solid solution system, in which the MPB compositions exhibit enhanced ferroelectric and dielectric properties (see Chapter 6). In this chapter, we have continued our investigation of this ternary system with focus on the extended ternary MPB region within the solubility limit (\(y = 0.15\)). As shown in Figure 7.1, three series of ternary compounds \((1 - y)(1 - x)\)PbZrO\(_3\) - \(x\)PbTiO\(_3\)-yBi(Zn\(_{1/2}\)Ti\(_{1/2}\))O\(_3\) with \(y_1 = 0.05\), \(y_2 = 0.1\) and \(y_3=0.15\) and varying \(x\), have been synthesized by solid state reaction method. Dielectric, ferroelectric and piezoelectric properties of the materials have been characterized and correlated with the structural change across the MPB.
Figure 7.1: Ternary phase diagram of \((1 - y)(1 - x)\text{PbZrO}_3 - x\text{PbTiO}_3\)-\(y\text{Bi}(\text{Zn}_{1/2}\text{Ti}_{1/2})\text{O}_3\), showing the compositions studied in this work: diamonds represent \(y = 0.05, 0.425 \leq x \leq 0.475\); circles represent \(y = 0.10, 0.40 \leq x \leq 0.47\); and triangles represent \(y = 0.15, 0.375 \leq x \leq 0.45\).
7.3 Experimental

Ceramic samples of the \((1-y)[(1-x)\text{PbZrO}_3-x\text{PbTiO}_3] - y\text{Bi(Zn}_{1/2}\text{Ti}_{1/2})\text{O}_3\) ternary system with compositions around the MPB of PZT binary system were synthesized by the solid state reaction, as shown in Figure 7.1. In each of the three pseudo-binary series with constant BZT content, \(y_1 = 0.05\), \(y_2 = 0.1\) and \(y_3 = 0.15\), the PT/PZ ratio (x) was adjusted in the range from 37.5/62.5 to 50/50 so that the specimens experienced a transition from the rhombohedral to the tetragonal phase across the MPB. Analytical grade PbO, Bi\(_2\)O\(_3\), ZrO\(_2\), TiO\(_2\) and ZnO were used as starting materials. The oxide powders were weighed in stoichiometric proportions and homogenized in ethanol. The resulting mixtures were dried and calcined between 700 °C and 800 °C for 4 hours. The products were reground to fine powder with 5 wt% PVA binder, pressed into small pellets and then sintered between 1080 °C and 1150 °C for 4 hours. After sintering, the circular surfaces of the ceramics were polished and sputtered with gold layers as electrodes for electric characterization. The phases of the sintered ceramics were identified and analyzed using a Rigaku MSC diffractometer with Cu K\(_\alpha\) radiation (\(\lambda = 1.5418\) Å). The dielectric properties were measured by a Solartron 1260 impedance analyzer combined with a Solartron 1296 dielectric interface. The ferroelectric hysteresis loops were displayed using an RT66 ferroelectric test system (Radiant Technologies Inc.) under the virtual ground mode with a high voltage interface. Piezoelectric coefficient \(d_{33}\) was measured by a quasistatic piezoelectric meter (Model ZJ-6B, Institute of Acoustics, Chinese Academy of Sciences).

7.4 Results and Discussion

7.4.1 Phase Analysis

As shown in Chapter 6, pure perovskite structure can be obtained for compositions with BZT ≤ 15 mole% around the MPB of BZT-PZ-PT [124]. The \((111)_{\text{cub}}\) and \((200)_{\text{cub}}\) reflections for different compositions of the three series \(y = 0.05\), \(y = 0.1\) and \(y = 0.15\) are plotted in Figure 7.2, which shows the evolution of phases from the rhombohedral (space group \(R3m\)) phase to the tetragonal (space group \(P4mm\)) phase with increasing PT content. According to the unit cell symmetry, a rhombohedral structure shows split peaks for the \((111)_{\text{cub}}\) reflection and only a single peak for the \((200)_{\text{cub}}\) reflection.
In contrast with the rhombohedral phase, the tetragonal phase shows two peaks for the \((200)_{\text{cub}}\) reflection and one peak for the \((111)_{\text{cub}}\) reflection (see Figure 2.3). The presence of the split or asymmetric peaks for both \((111)_{\text{cub}}\) and \((200)_{\text{cub}}\) reflections in Figure 7.2 suggests that the structure consists of a mixture of rhombohedral and tetragonal phases, which is the characteristic of a morphotropic phase boundary behaviour. Therefore, the composition of these three series fall into the ternary MPB region. It is important to note that intermediate monoclinic \(M_A\) phase with space group \(Cm\) is found to coexist with rhombohedral \((R3m)\) and tetragonal \((P4mm)\) phases in the MPB of PZT, which play a crucial role in explaining the extraordinary piezoelectric properties [18,140]. Therefore, it is reasonable to expect that in the MPB of similar ternary system BZT-PZ-PT, the monoclinic \((M_A)\) phase could exist as well. However, its clear identification would require unconventional diffraction techniques like synchrotron and/or neutron diffraction.

For the compositions with the same Zr/Ti ratio \(x = 0.44\) of the three series, the splitting of the \((200)_{\text{cub}}\) reflection becomes more significant with the addition of BZT, indicating an increase in the tetragonality \((c/a\) ratio\) with the increasing BZT content, which confirms our initial concept that BZT could enhance the tetragonal distortion of the PZT. This enhanced tetragonality with BZT addition could be due to a stronger coupling between A site cations (\(\text{Pb}^{2+}\) and \(\text{Bi}^{3+}\)) and B-site cations (\(\text{Zn}^{2+}\) and \(\text{Ti}^{4+}\)), which favours the cation displacement and strengthens the tetragonal phase [141]. The phase evolution from the rhombohedral structure into the MPB region (with a mixture of rhombohedral and tetragonal phases) might occur in the vicinity of \(x = 0.44\) for the \(y = 0.05\) series, and \(x = 0.425\) for the \(y = 0.10\) series. For the compositions \(x = 0.375\) and \(x = 0.4\) in the series \(y = 0.15\), both \((111)_{\text{cub}}\) and \((200)_{\text{cub}}\) reflections are broad, making it difficult to determine the exact phase boundary between the rhombohedral and tetragonal phases. This broadening could be due to the increase of local internal strain from the lattice mismatching between the local tetragonal and rhombohedral phases. The local tetragonal distortion is caused by the hybridization of the \(\text{Zn}\ 4s\) and \(4p\) orbitals and the \(\text{O}\ 2p\) orbitals forming the short covalent \(\text{Zn-O}\) bonds [139], which increases the off-center \((100)_{\text{cub}}\) displacement of A-site and B-site ions in the perovskite structure.
Figure 7.2: The (111)\textsubscript{cub} and (200)\textsubscript{cub} reflections of the \((1−y)((1−x)\text{PbZrO}_3−x\text{PbTiO}_3)−y\text{Bi(Zn}_{1/2}\text{Ti}_{1/2})\text{O}_3\) ceramics for three constant-BZT content series: (a) \(y = 0.05\), (b) \(y = 0.10\) and (c) \(y = 0.15\).

### 7.4.2 Dielectric Properties

Figure 7.3 shows the dependence of the relative dielectric constant on temperature measured at 1 kHz on cooling for the ceramic samples of \((1−y)(\text{PZ-PT})−y\text{BZT}\) system \((y = 0.05, 0.10\) and \(0.15\)) with the compositions across the MPB. The dielectric constant exhibits a maximum value at Curie temperature \(T_C\) corresponding to the transition from the paraelectric (PE) to ferroelectric (FE) phase. In addition to these major peaks, broad dielectric peaks also occur at temperatures between 175 °C and 250 °C in the \(y = 0.05\) and \(y = 0.10\) series (shown by the arrows in Figure 7.3), respectively, which can be related with the rhombohedral-to-tetragonal transition temperature \((T_{R-T})\) \([15]\). This confirms that these compositions fall into the MPB range. Upon increasing the PT content, \(T_{R-T}\) decreases while \(T_C\) becomes higher. The decrease of \(T_{R-T}\) with the increasing PT concentration indicates that the upper limit of the MPB region of the BZT-PZT pseudo-binary system is curved, which is similar to the cases of other PbTiO\(_3\)-based solid solution systems, like \(\text{Pb(Mg}_{1/3}\text{Nb}_{2/3})\text{O}_3\)-PbTiO\(_3\), \(\text{Pb(Zn}_{1/3}\text{Nb}_{2/3})\text{O}_3\)-PbTiO\(_3\), etc. By comparing the dielectric response of these three series, we can see that the dielectric peaks become more broadened with the addition of BZT, which is more obvious in the series of
0.15BZT-0.95PZT. The broadening of the peaks indicates that the ferroelectric to paraelectric phase transition becomes more diffuse, which is indicative of a more disordered perovskite structure for the ternary solid solution. The increased disorder in the arrangements of cations on both the A-site occupied by Pb$^{2+}$ and Bi$^{3+}$, and the B-site occupied by Zr$^{4+}$, Ti$^{4+}$ and Zn$^{2+}$ is expected to lead microscopic heterogeneities in the local composition, which, in turn, results in a distribution of different local Curie points [139,142]. It is also worth noting that, with increasing BZT concentration ($y = 0.5, 0.10$ and $0.15$), the dielectric loss at high temperature is significantly reduced and its temperature dependence becomes more stable below $T_C$. This result indicates that the addition of BZT into PZT helps improve the dielectric properties, probably by reducing the formation of lattice defects under the thermal activation [143], which would contribute to dielectric loss. This improved dielectric property provides advantages to the ternary materials for high temperature piezoelectric applications. The variation of dielectric constant ($\epsilon'$) and loss ($\tan \delta$) as a function of PT content are shown in Figure 7.4. For all the three series, $\epsilon'$ first increases and then decreases with the increasing PT content in the MPB region. For the series $y = 0.05$ and $y = 0.10$, the dielectric constant shows a sharp increase in the MPB, with the maximum values $\epsilon' = 1460$ found at $x = 0.46$ in the series $y = 0.10$, and $\epsilon' = 1300$ at $x = 0.46$ in the series $y = 0.05$, respectively. While in the $y = 0.15$ series, the change of dielectric constant across the MPB is more gradual and the maximum value of dielectric constant is slightly smaller than that of the $y = 0.10$ series. Referring to the XRD analysis, the highest dielectric constant is obtained in the samples with a composition closer to the tetragonal side of the MPB region.

7.4.3 Ferroelectric Properties

Figure 7.5 presents the room temperature $P$-$E$ (polarization-electric field) loops of the (1-$y$)PZT-$y$BZT ceramics for the three constant-BZT series: (a) $y = 0.05$, (b) $y = 0.10$ and (c) $y = 0.15$. All the compositions exhibit well-saturated $P$-$E$ loops at an alternating electric field of ±55 kV/cm, indicating the ferroelectricity at room temperature. The values of remnant polarization $P_r$ and coercive field $E_c$ are obtained from the $P$-$E$ loops and their variations as a function of PT content are shown in Figure 7.6. The maximum $P_r$ values in the respective series are 20 $\mu$C/cm$^2$ at $x = 0.46$ and $y = 0.05$, 28 $\mu$C/cm$^2$ at $x = 0.44$ and $y = 0.10$ and 33 $\mu$C/cm$^2$ at $x = 0.375$ and $y = 0.15$, and their corresponding $E_c$ values are 12 kV/cm, 17 kV/cm and 23 kV/cm, respectively. The
Figure 7.3: Temperature dependences of dielectric constant ($\epsilon'$) and loss factor (tan $\delta$) for three different constant-BZT series: (a) $y = 0.05$, (b) $y = 0.10$ and (c) $y = 0.15$, with various PT content ($x$).
Figure 7.4: Room-temperature dielectric constant $\epsilon'$ (filled symbols) and dielectric loss ($\tan \delta$) (open symbols) of the $(1-y)[(1-x)\text{PbZrO}_3 - x\text{PbTiO}_3] - y\text{Bi(Zn}_{1/2}\text{Ti}_{1/2})\text{O}_3$ ternary ceramics.
variation of \( P_r \) with PT content shows a maximum in each of the series, which is similar to the variation of dielectric constant \( (\epsilon') \) with PT (Figure 7.4). The only difference is that in the series with higher BZT content \( (y = 0.10 \text{ and } y = 0.15) \) the \( P_r \) values attain maxima at the compositions in which the rhombohedral phase predominate in the MPB regions. The highest \( P_r \) value found in the series with \( y = 0.15 \) confirms that the addition of BZT into PZT enhanced the spontaneous polarization. The variation of the coercive field \( E_c \) values with the PT and BZT concentrations indicates that large \( E_c \) values (up to 23 kV/cm) were obtained for the tetragonal compositions with a high BZT content. This could be attributed to the enhanced tetragonality, which leads to a larger strain associated with the switching the 90° domains, and thereby, a higher coercive field.

### 7.4.4 Piezoelectric Properties

Figure 7.7 shows the variation of the piezoelectric coefficient \( d_{33} \) as a function of PT concentration for the \((1 - y)[(1 - x)\text{PbZrO}_3 - x\text{PbTiO}_3]-y\text{Bi(Zn}_{1/2}\text{Ti}_{1/2})\text{O}_3\) ceramics. The maximum piezoelectric coefficient \( d_{33} = 275 \) pC/N is found in the composition with \( x = 0.425 \) and \( y = 0.15 \), which is in the MPB region of the series with the highest BZT content. The values of electromechanical coupling factor \( k_p \) of several MPB compositions obtained from the resonance measurements are listed in Table 7.1. The highest \( k_p \) value of 45.6% is also found in the composition of \( x = 0.425 \) and \( y = 0.15 \), indicating a high efficiency of the material in converting electrical energy to mechanical energy, and vice versa. The large piezoelectric response in the MPB compositions can be explained by the free energy model [74]. In the MPB compositions with mixed phases, the free energy profile flattens, and the small energy barriers facilitate polarization rotation from \( \langle 111 \rangle_R \) to \( \langle 100 \rangle_T \) via a \( (110)_{cub} \) plane, giving rise to high piezoelectricity. In addition to the intrinsic contributions, the domain structure in the MPB region plays an important role in the enhanced piezoelectric properties as well. Transmission electron microscopy studies showed that domain size decreases as the composition approaches the MPB of the PZT [25]. The same situation is expected to occur in the MPB of the current ternary system, in which the domain wall energy is reduced and the domain wall motion and domain switching are facilitated, giving rise to high piezoelectric performance.
Figure 7.5: Polarization-electric field (P-E) hysteresis loops for the \((1-y)(1-x)\)PbZrO\(_3\) - \(x\)PbTiO\(_3\) - \(y\)Bi\((Zn_{1/2}Ti_{1/2})O_3\) ceramics of three constant-BZT series \((y = 0.05, 0.10 \text{ and } 0.15)\) with various PT content \((x)\).
Figure 7.6: Variation of the remnant polarization $P_r$ and coercive field $E_c$ as a function of PT concentration for the $(1-y)[(1-x)\text{PbZrO}_3 - x\text{PbTiO}_3]-y\text{Bi(Zn}_{1/2}\text{Ti}_{1/2})\text{O}_3$ ceramics.
7.5 Pseudo-binary Phase Diagram of BZT-PZ-PT system

Combining the X-ray diffraction, dielectric, ferroelectric and piezoelectric data, we can conclude that the MPB with mixed rhombohedral, tetragonal and possibly monoclinic phases, exists in the BZT-PZ-PT ternary solid solution system between $x = 0.44$ and $x = 0.46$ for $y = 0.05$, $x = 0.425$ and $x = 0.46$ for $y = 0.10$, and $x = 0.40$ and $x = 0.44$ for $y = 0.15$. Figure 7.8 shows the variation of the Curie temperature $T_C$ as a function of PT concentration ($x$) for the three series, with their corresponding MPB regions shaded. It represents the pseudo-binary phase diagram for each of the series with $y = 0.05, 0.10$ and 0.15, which delimits the R, T and C phases, as well as the MPB region with curved R-T phase boundary for $x = 0.05$ and $x = 0.10$. As expected, in each series the $T_C$ increases with increasing PT content. It is also found that the addition of BZT content enlarges the MPB region and moves the MPB to the lower PT content, as shown by the shaded areas in the phase diagram.

Table 7.1 lists the dielectric, ferroelectric and piezoelectric properties of several
Figure 7.8: Compositional dependences of $T_C$ for $(1 - y)[(1 - x)\text{PbZrO}_3 - x\text{PbTiO}_3] - y\text{Bi(Zn}_{1/2}\text{Ti}_{1/2})\text{O}_3$ ceramics.
ternary compositions in the MPB region, in which the properties of pure PZT ceramics [6, 144] were added for comparison. It can be seen that the ferroelectric and piezoelectric properties are enhanced in the compositions with higher BZT content, although the value of \( T_C \) is decreased. It should be noted here that \( E_c \) is dramatically increased with the addition of BZT, which is due to the increased tetragonality in the MPB region as shown in the XRD analysis. Pure PZT ceramics have a relatively low \( E_c \) of 9 kV/cm, and the increase of its \( E_c \) is usually realized by chemical modifications using hard doping: by introducing the acceptor ions such as K\(^+\), Na\(^+\) and Fe\(^{3+}\), oxygen vacancies can be created, which act as defect dipoles and stabilize the domain structure during poling. The modification of PZT by the addition of BZT has the same effect as hard doping, but at the same time, other properties such as \( \epsilon' \), \( d_{33} \) and \( P_r \) are improved as well. It is found that the MPB composition \((x = 0.425)\) in the \( y = 0.15 \) series exhibits the best properties with improved \( \epsilon' = 1248 \) and \( d_{33} = 275 \) pC/N, and a large \( P_r = 33 \) \( \mu \)C/cm\(^2\), as well as a relatively high \( T_C \) (286 °C) and high \( E_c \) (23 kV/cm), making it a promising material for high-power piezoelectric applications.

Table 7.1: Dielectric \( \epsilon' \) and \( \tan \delta \), ferroelectric \((P_r \text{ and } E_c)\) and piezoelectric \((d_{33} \text{ and } k_p)\) properties of selected MPB compositions of the \((1 - y)\)\((1 - x)\)PbZrO\(_3\) - \( x \)PbTiO\(_3\) - \( y \)Bi(Zn\(_{1/2}\)Ti\(_{1/2}\))O\(_3\) ceramics.

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<th>Composition</th>
<th>( x ) (Ti/Zr)</th>
<th>( y ) (BZT)</th>
<th>( \epsilon' )</th>
<th>Loss (( \tan \delta ))</th>
<th>( d_{33} ) (pC/N)</th>
<th>( P_r ) (( \mu )C/cm(^2))</th>
<th>( E_c ) (kV/cm)</th>
<th>( k_p )</th>
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<td>26</td>
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7.6 Conclusions

The BZT-PZ-PT ternary ceramics with compositions within an extended MPB region were synthesized by solid state method and the structural change across the MPB is
determined by XRD analysis. The coexistence of the rhombohedral and tetragonal phases in the MPB region is evidenced by the non-symmetric peaks at both $(111)_{\text{cub}}$ and $(200)_{\text{cub}}$ reflections. The compositions with a higher BZT content show a diffuse-type FE to PE phase transition. The dielectric constant reaches the maximum value in the compositions on the tetragonal phase-side of the MPB. The remnant $P_r$ with the maximum value is found to be close to the rhombohedral phase-side of the MPB. Based on the XRD, dielectric and ferroelectric results, the pseudo-binary phase diagram for the three series has been constructed. The addition of BZT is found to shift the binary MPB of the PZT system to the lower PT content, and to enlarge the MPB region. The dielectric constant ($\epsilon'$) reaches maximum values in the composition on the tetragonal phase-side of the MPB. The remnant polarization ($P_r$) also shows an increase as composition approaches the MPB region, but the maximum value is found to be close to the rhombohedral phase-side. The value of $T_C$ is not increased by the addition of BZT as we expected initially, however, the ferroelectric and piezoelectric properties are enhanced in the series with the highest BZT content ($y = 0.15$). In terms of material properties, the ceramics of the MPB composition $x = 0.425$ and $y = 0.15$, exhibit a high dielectric constant ($\epsilon' = 1248$), a reasonably high piezoelectric coefficient ($d_{33} = 275 \text{ pC/N}$), and a large remnant polarization ($P_r = 33 \text{ µC/cm}^2$) with a relatively high Curie temperature ($T_C = 286 ^\circ\text{C}$) and a high coercive field ($E_c = 23 \text{ kV/cm}$). The enhanced properties show that the BZT-PZ-PT ceramics are potential for applications as electromechanical transducers working under high power and at high temperatures.
Chapter 8

General Conclusions and Future Directions

8.1 General Conclusions

The research on piezoelectric materials involves the design and synthesis of new materials with high properties and studying 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 requires high sensitivity, efficiency and power. In this thesis, PbZr$_{1-x}$Ti$_x$O$_3$ (PZT) single crystals with various compositions were grown successfully by top-seeded solution growth (TSSG) method, and characterized by polarized light microscopy (PLM) and dielectric, ferroelectric and piezoelectric measurements. New Bi(Zn$_{1/2}$Ti$_{1/2}$)O$_3$-PbZrO$_3$-PbTiO$_3$ ternary ceramics were also synthesized by solid-state reaction, and the dielectric, ferroelectric and piezoelectric properties in the extended MPB region were characterized. The main results of the thesis can be summarized as follows:

1. Perovskite PZT single crystals with compositions across MPB have been grown by the TSSG method. The growth conditions in terms of the chemical, thermodynamic and kinetic parameters were systematically studied and optimized. It was found that the growth temperature is the most important parameter for controlling the composition of the PZT crystal. Crystals with a high Ti-content tend to grow at lower temperatures, while crystals with a high Zr-content tend
to grow at high temperature. X-ray diffraction patterns of PZT crystals indicate a structural change from the rhombohedral to tetragonal phase with increasing PT content. The Curie temperature $T_C$, corresponding to the dielectric constant peak, of the PZT single crystals shows the same variation as PZT ceramics. For the compositions in the MPB region, additional dielectric anomalies can be observed below $T_C$. The PLM analysis reveals that the low-temperature FE-FE phase transitions are between rhombohedral to monoclinic for $x = 0.42$ and monoclinic to tetragonal for $x = 0.46$. The MPB composition $x = 0.46$ exhibits the best piezoelectric properties, with piezoelectric constant $d_{33} = 1223 \text{ pC/N}$ and an electromechanical factor $k_{33} = 0.8$. Compared with relaxor-based single crystals, such as 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, PZT single crystals exhibit a higher $T_C = 395 \degree\text{C}$ and a larger $E_c = 7 \text{ kV/cm}$ (see Figure 8.1), making the PZT single crystals a promising material for high temperature and high power electromechanical transducer applications.

2. Phase transitions in the rhombohedral PZT crystals with composition $x = 0.2$ were studied by dielectric, ferroelectric measurements and PLM analysis. The dielectric results reveal that the phase transition between the octahedron tilted rhombohedral $R3c$ phase and the untilted rhombohedral $R3m$ phase is of first order. The small dielectric jump at $T_{R-R}$ is due to the rearrangement of the volume between octahedra and cuboctahedra in the crystal lattice, which causes the change of dielectric response. It was also observed that the remnant polarization $P_r$ in low-temperature $R3c$ is lower than that in the $R3m$ phase. This was explained by the pinning effect of the antiphase domain boundaries in the tilted $R3c$ phase, which restricts the domain mobility and switching. The ratio of $C^+/C^- = 3.4$ was found from the fitting of the inverse of dielectric constant, indicating that this composition is close to the tricritical point. The phase transitions and domain structures in two crystals with $(001)_{cub}$ and $(110)_{cub}$ orientations, respectively, were studied by PLM. At room temperature, the $(110)_{cub}$ platelet displays typical wedge domain structure with clear domain boundaries. The domain boundaries in $(001)_{cub}$ platelet is not clear due to the overlapping effects of domains with different orientations. The temperature dependences of the birefringence show that the two crystals have very close $T_C$, but the PE-FE phase transition is slightly
Figure 8.1: Piezoelectric coefficient as a function of Curie temperature $T_C$ for ferroelectric single crystals (the data point of PZT is indicated by a star on the figure) [40–43, 61].
discontinuous (weak first order) in the \((001)_{cub}\) platelet and continuous (second order) in the \((110)_{cub}\) platelet, indicating the composition \(x = 0.20\) is close to a tricritical point.

3. \(\text{PbZr}_{1-x}\text{Ti}_x\text{O}_3\) crystals with compositions around MPB region \((x = 0.42\) and \(x = 0.46\)) were investigated by dielectric measurements and PLM analysis. It was found that the \((110)_{cub}\) platelet of \(\text{PbZr}_{0.58}\text{Ti}_{0.42}\text{O}_3\) single crystal is of rhombohedral symmetry at room temperature, which is evidenced by the extinction position at 35º under polarized light microscope. As temperature increases to around 200 ºC, the extinction angle starts to increase, indicating a symmetry change from rhombohedral \((R3m)\) to monoclinic \((Cm)\) phase. The monoclinic phase was also confirmed by the 30º domain walls, which appeared above 300 ºC. The rhombohedral to monoclinic phase transition is also evidenced by an dielectric anomaly around 335 ºC below \(T_C\). Although \(R3m\) and \(Cm\) are two distinct phases with different symmetries, the temperature dependence of both birefringence and extinction angle show gradual change during the phase transition, since the monoclinic phase can only be optically detected when its unit cells aggregate and grow large enough at high temperature. The PZT single crystals with composition \(x = 0.46\) is of monoclinic symmetry at room temperature. At around 180 ºC, the structure changes to tetragonal, which is accompanied by a significant change of birefringence. The monoclinic to tetragonal phase transition is confirmed to be of first order by the dielectric results displaying a thermal hysteresis of \(T_{M-T}\) upon heating and cooling. The tetragonal phase in the \((001)_{cub}\) platelet behaves like isotropic, which is due to the cancellation effect of overlapped tetragonal domains with random orientations. In \((110)_{cub}\) platelet, the birefringence is none-zero since the cancellation effect is partial. The formation of miniaturized domains can be explained by Imry and Ma’s random field theory [123], which suggests that quenched random field related to structural disorder can break the system into nanodomains that are more energetically favored.

Combining the dielectric results and PLM observation, an updated phase diagram of \(\text{PbZr}_{1-x}\text{Ti}_x\text{O}_3\) around MPB has been constructed (see Figure 8.2). In the phase diagram proposed by Noheda et al. [15], there was no phase boundary between the rhombohedral and monoclinic phases. The rhombohedral to monoclinic phase transition is not as significant as the monoclinic to tetragonal phase transition,
which makes it hard to be observed in PZT ceramics by structural analysis. In our work, the phase transition between rhombohedral and monoclinic phases was clearly observed by PLM and dielectric measurements. On the new phase diagram, the MPB region is a narrow region with monoclinic symmetry ($M_A$) which is separated by two phase boundaries with the rhombohedral and the tetragonal regions, respectively.

Figure 8.2: Updated phase diagram of PbZr$_{1-x}$Ti$_x$O$_3$ showing an extended MPB region, based on the studies of PZT single crystals by PLM and dielectric measurements.

4. In search for high-temperature, lead reduced piezoelectric materials, the new $x$Bi($Zn_{1/2}Ti_{1/2}$)O$_3$-$y$PbTiO$_3$-$z$PbZrO$_3$ ($x/y/z$) ternary perovskite ceramics have been synthesized by the solid-state reaction method. The solubility limit was determined to be a curve in the phase diagram. X-ray diffraction results reveal that with decreasing PZ content, the structure along the solubility curve changes from orthorhombic to rhombohedral at $z = 0.85$ and then to tetragonal at $z = 0.50$. The substitution of Bi$^{3+}$ for Pb$^{2+}$ and ($Zn_{1/2}Ti_{1/2}$)$^{3+}$ for Zr$^{4+}$ results in a decrease in the lattice
parameters $a$ and $b$ and unit cell volume. For the MPB$_{R-T}$ compositions, a low-temperature phase transition between rhombohedral and tetragonal phases was observed by dielectric measurements, which occurs at lower temperature with increasing PT content. Compared with the binary system PZT, the MPB region of BZT-PZ-PT exists over a wide composition range between $z = 0.45$ and $z = 0.60$. The maximum remnant polarization $P_r = 34.2 \, \mu\text{C/cm}^2$ is found in the MPB composition (15/40/45), while the maximum dielectric constant is obtained at the composition (13/37/50) which is close to the tetragonal side.

Further investigation of the $(1 - y)\{(1 - x)\text{PbZrO}_3 - x\text{PbTiO}_3\} - y\text{Bi(Zn}_{1/2}\text{Ti}_{1/2})\text{O}_3$ ternary ceramics is focused on the MPB regions of three series with variable BZT content ($y = 0.05$, $y = 0.10$ and $y = 0.15$). It was found that the addition of BZT shifts the MPB to the lower PT content and enlarges the MPB region. X-ray diffraction shows an increase of tetragonality with the addition of BZT, while $T_C$ decreases, as opposed to our preassumption. The dielectric loss (tan $\delta$) in the series with higher BZT content shows little variation with temperature, which means that these ceramics have better electrical stabilization at high temperature. The phase transition from ferroelectric to paraelectric phases becomes diffuse in the higher BZT series, which is due to the microscopic heterogeneity in the composition caused by the disorder in the arrangement of different cations. The highest dielectric constant at room temperature is obtained at $x = 0.46$ in series $y = 0.10$ with the value $\epsilon' = 1460$. The MPB composition, $x = 0.42$, $y = 0.15$ exhibits the best piezoelectric property with $d_{33} = 275 \, \text{pC/N}$, with a high $E_c = 25 \, \text{kV/cm}$ and a high $T_C = 286 \, ^\circ\text{C}$, which makes it a promising material for high-temperature applications as electromechanical transducers.

### 8.2 Future Directions

Piezoelectric single crystals with extraordinarily high piezoelectric performance will continue to be the focus of the development of novel piezoelectric materials in the near 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 crystals have been successfully grown using the TSSG method. The MPB crystal with composition $x = 0.46$ exhibits high $T_C$ ($395 \, ^\circ\text{C}$) and high $E_c$ ($7 \, \text{kV/cm}$). However, the piezoelectric properties
of PZT crystals, with $d_{33} = 1223$ pC/N and $k_{33} = 0.8$, are not high compared with the PMN-PT and PZN-PT single crystals. This is reasonable given that the piezoelectric properties of pure PZT ceramics are also low, and PZT ceramics used in industry are usually chemically modified to obtain enhanced properties. By doping PZT with higher valence cations, such as replacing Pb$^{2+}$ with La$^{3+}$, and Zr$^{4+}$ or Ti$^{4+}$ with Nb$^{5+}$, the properties can be “soften” with high piezoelectric coefficient ($d_{33}$), low conductivity and low coercive field ($E_c$). Therefore, future growth can be designed to grow doped PZT single crystals. Moreover, for commercial applications in the compact ultrasonic devices, the size and quality of the PZT single crystals still needs to be improved.

The availability of the PZT single crystals makes it possible to study the structure-property relationship by carrying out a series of characterizations. In this work the phase transitions in PZT single crystals with compositions in rhombohedral and MPB regions have been investigated by polarized light microscopy, and dielectric, ferroelectric and piezoelectric measurements. Some important experimental data and results have been obtained. However, there are still many questions about the PZT system which need to be further studied and clarified. Our experiments are mainly focused on the macroscopic structure and properties of the crystals. It will be of particular interest to study the local structures of PZT crystals by means of high-resolution transmission electron microscopy (HRTEM), which can obtain diffraction patterns and images of domains on nanoscale. Piezoresponse force microscopy (PFM) is also a useful tool for detecting ferroelectric domains microscopically, and it is an alternative way to observe how the local domains with different orientations respond to an external field drive. It is believed that our macroscopic study combined with the future microscopic characterizations will lead to a clearer understanding of the mechanism of high piezoelectric property in the MPB of PZT, and therefore provide guidance for designing high performance piezoelectric materials in the future.

Because of environmental concerns, more research has been concentrated on lead-free or lead-reduced piezoelectric systems. In this work, a lead-reduced ternary system, BZT-PZ-PT, has been developed with desired properties that can be optimized and tuned within the expanded MPB region. The BZT-PZ-PT system is a promising candidate for single crystal growth. The mixture of PbO and Bi$_2$O$_3$ has a lower melting point, which can be used as flux for the growth. Since Bi$^{3+}$ and Pb$^{2+}$ are both the A-site ions in the perovskite structure, the complex flux would not bring contamination. Both the
piezoelectric coefficient $d_{33}$ and coercive field $E_c$ were found to increase with the addition of BZT content, therefore, the MPB composition in the series with the highest BZT content can be selected to grow single crystals. Moreover, the availability of BZT-PZ-PT single crystals will make it possible to investigate the domain structure and phase transitions by PLM and PFM, which will provide a better understanding of the MPB of this ternary system.
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