Journal of Alloys and Compounds 509 (2011) 3398–3402

Contents lists available at ScienceDirect

Journal of Alloys and Compounds

journal homepage: www.elsevier.com/locate/jallcom

Rhombohedral–monoclinic phase transition related to grain orientation in Zr-rich $Pb(Zr_xTi_{1-x})O_3$ thin films

J.N. Wang, W.L. Li, X.L. Li, W.D. Fei*

State Key Laboratory of Welding Production Technology, School of Materials Science and Engineering, Harbin Institute of Technology, No. 92, West Da-Zhi Street, Harbin 150001, PR China

ARTICLE INFO

Article history:
Received 9 July 2010
Received in revised form
12 December 2010
Accepted 15 December 2010
Available online 22 December 2010

Keywords:
Phase transitions
Thin films
Sol–gel processes
Ferroelectrics

ABSTRACT

$Pb(Zr_xTi_{1-x})O_3$ thin films with mixed orientations of (1 1 1) and (1 0 0) were prepared on Pt/Ti/SiO_2/Si substrate by sol–gel technique. The compositions of PZT thin films are chosen as $x = 0.55$ and $x = 0.58$. Both of the compositions are in the rhombohedral phase region of the $Pb(Zr_xTi_{1-x})O_3$ phase diagram, but the former is near the monoclinic phase existence region, and the latter is far from the monoclinic phase existence region. Rhombohedral–monoclinic phase transitions are reported in both of the thin films. The results show that the phase transition is related to the grain orientation. Phase transitions in the films are clearly identified: rhombohedral phase transforms to M_B phase in (1 1 1)-oriented grains, and rhombohedral phase transforms to M_A phase in (1 0 0)-oriented grains. The remnant polarization is determined by the content of (1 1 1)-oriented grains. It is shown that the remnant polarization is greater in the film with higher content of (1 1 1)-oriented grains.

1. Introduction

$Pb(Zr_xTi_{1-x})O_3$ (PZT) system which can be considered as the solution of $PbZrO_3$ and $PbTiO_3$ has been intensively studied because of their high piezoelectric and ferroelectric properties [1,2]. In the temperature–composition phase diagram proposed by Jaffe et al. [3], rhombohedral (R) phase and tetragonal (T) phase are separated by morphotropic phase boundary (MPB). After the discovery of low symmetrical monoclinic phase (M phase) with the space group of C_m near MPB [4], Noheda et al. [5] systematically studied the phase compositions of $Pb(Zr_xTi_{1-x})O_3$ with different x values, and built a new phase diagram of PZT system, where M phase exists in the range $0.52 \leq x \leq 0.54$ near the MPB at room temperature. The phase diagram (above 200 K) with the similar structure given by Noheda et al. [5] was confirmed by first principle simulation [2]. The M phase has been considered to be the origin of the giant piezoelectric properties of PZT ceramics and some other ferroelectrics owing to the symmetry-allowed rotation of the polarization direction of M phase [6–8]. In this case, the study of M phase has attracted much attention.

Two approaches introducing M phase in perovskite ferroelectrics have been proved. One is to apply pressure on ferroelectric ceramics, e.g. the T–M phase transition can be found in $PbTiO_3$ (PT) ceramic under the condition of hydrostatic press [9]. The other is to substitute the cation with different ionic radii one, e.g. the M phase can be obtained in PZT with $x \sim 0.50$, in which the Ti cations with smaller radii are partially substituted by the Zr cations with larger radii. The substitution is called the effect of chemical pressure [9].

The residual stress is an intrinsic feature of thin films deposited on substrates, because of both the lattice mismatch and the discrepancy in thermal expansion coefficient between film and substrate. Therefore, the phase composition of perovskite films may be affected by the residual stress. Unfortunately, M phase in PZT film materials has not been studied extensively, although ferroelectric thin films have very important applications. Up to 2006, the M phase was just experimentally confirmed in some epitaxy PZT films [10].

It is important to study the phase transition of PZT thin films with the compositions falling in R phase region. Firstly, the previous studies about PZT phase transition behavior mainly focus on the PZT with the composition near the MPB [6,10], however, few studies about PZT in R phase region have been reported. Secondly, the thin films provide a condition of quasi two-dimensional stress state, therefore, we can study the effect of plane stress on the phase transition. Thirdly, the study on the relationship between phase transition and preferred orientation of thin films is limited. At last, the most important reason is that it is very difficult to directly use Rietveld refinement to study the phase composition of films in a θ–2θ scan XRD curve, because the diffraction peaks of thin films may belong to different-orientation grains, and the residual stress of different-orientation

---

* Corresponding author. Tel.: +86 451 86418647; fax: +86 451 86418647.
E-mail address: wdfei@hit.edu.cn (W.D. Fei).

0925-8388/$ – see front matter © 2010 Elsevier B.V. All rights reserved.
doi:10.1016/j.jallcom.2010.12.084

grains may differ. Based on the last reason, the study of phase composition about PZT has mainly focused on bulk and powder materials so far [4], however, the study about PZT films is much less.

The present study aims to investigate the phase transition in PZT films with the composition in R phase region of the phase diagrams [2,5]. The compositions of PZT thin films studied in the present paper are chosen as $x = 0.55$ (denoted as PZT55/45) and $x = 0.58$ (denoted as PZT58/42). The former composition is near by the M-included region, and the later is far from the M-included region in the phase diagram [5].

2. Experimental

PZT films used in this study were prepared on the highly (1 1 1)-oriented Pt/Ti/SiO_2/Si substrate using sol–gel method. Lead acetate trihydrate, zirconium *n* propoxide and titanium isopropoxide were used as the raw materials and 2-methoxyethanol [2-$CH_3OCH_2CH_2OH$] as the solvent. The 10 mol% excess Pb solution was used to overcompensate for any Pb volatility during high temperature annealing. The PZT precursor solution was firstly spin-coated on the substrate with the spin rate of 4000 rpm for 9 s, and then the wet film was pyrolyzed at 500 °C on a hot plate for 2 min. The above two processes were repeated for three times to attain the desired film thickness. Finally, PZT films were crystallized at 650 °C for 3 min through rapid thermal annealing technique in O_2 ambient. The thicknesses of PZT films were about 150 nm, which were measured by X-ray reflectivity curve and scanning electric microscope.

The XRD analysis of the films was carried out on a Philips X'Pert diffractometer with the Cu K_α radiation operated at 40 kV and 40 mA, and θ–2θ scan XRD curves were measured at different tilt angles, ψ, where ψ is the tilt angle of the scattering vector of XRD to the normal direction of the film. Obviously, the conventional θ–2θ scan XRD curve is corresponding to $\psi = 0°$. The Raman spectral excitation was provided by an Ar-ion laser with the wave length of 458 nm. The scattered light was analyzed with a Jobin Yvon HR800 spectrometer. Ferroelectric properties of the films were characterized using a Radiant (trade mark) LC ferroelectric analysis system.

3. Results and discussion

Fig. 1(a) shows XRD curves of PZT55/45 and PZT58/42 films at $\psi = 0°$, where only Pt and perovskite PZT phase diffraction peaks can be found. To simplify, the PZT film diffraction peaks are indexed using pseudo cubic coordinate system which is denoted by subscript 'C'. In Fig. 1(a), only $1\,0\,0_C$, $2\,0\,0_C$ and $1\,1\,1_C$ diffraction peaks of PZT films can be seen, indicative of possibly mixed textures of (1 0 0) and (1 1 1). To confirm the mixed orientations, $1\,1\,0_C$ diffraction peaks at different ψ angles were measured, and the curves of integral intensity (I_ψ) of $1\,1\,0_C$ diffraction versus ψ angle are given in Fig. 1(b). $I_\psi \sim \psi$ curves can be clearly separated into two peaks with the positions at about 35° and 45°. The interplanar angle between $\{1\,1\,0\}_C$ and $\{1\,1\,1\}_C$ planes is about 35°, and about 45° between $\{1\,1\,0\}_C$ and $\{1\,0\,0\}_C$ planes. Moreover, the preferential orientation is axisymmetric about the film normal direction. In this case, the result shown in Fig. 1(b) confirms the mixed orientations of (1 1 1) and (1 0 0) [11]. From the Gaussian fitting of $I_\psi \sim \psi$ curve, it can be found that the two peaks are narrow, suggesting highly preferential orientations of (1 1 1) and (1 0 0). In addition, the content of (1 0 0)-oriented grains in PZT55/45 film is higher than that in PZT58/42 film.

Up to now, only R, M and T phases have been confirmed for PZT system at room temperature, so the phase transition may be R → T or R → M. $2\,0\,0_C$ diffraction peak of R phase is single, but $2\,0\,0_C$ diffraction peaks of both M phase and T phase are not single, therefore, the phase transition can be easily judged by the $2\,0\,0_C$ diffraction peak splitting. In addition, $1\,1\,1_C$ diffraction peak of T phase is single among the three phases, so $1\,1\,1_C$ diffraction is helpful to estimate the transition product.

To analyze the phase transition in PZT films, the fine scan XRD curves of $2\,0\,0_C$ and $1\,1\,1_C$ diffraction peaks at different ψ angles were measured with the scan rate of 0.002 °/s. Fig. 2(a) and (b) shows $\{1\,1\,1\}_C$ and $\{2\,0\,0\}_C$ normal direction distributions for (1 1 1)- and (1 0 0)-oriented grains. The phase transition in (1 1 1)-oriented grains can be characterized by the $1\,1\,1_C$ diffraction at $\psi = 0°$ and $2\,0\,0_C$ diffraction at $\psi = 55°$, and the phase transition in (1 0 0)-orientated grains can be characterized by the $2\,0\,0_C$ diffraction at $\psi = 0°$ and $1\,1\,1_C$ diffraction at $\psi = 55°$. It can be clearly found that the $2\,0\,0_C$ diffraction peaks of both (1 1 1)- and (1 0 0)-oriented grains split into two peaks on the both sides of corresponding R phase diffraction peaks [5], which suggests that the phase transition takes place in both PZT55/45 and PZT58/42 films [see Fig. 2(c) and (d)]. Furthermore, $1\,1\,1_C$ diffraction peaks are not single for both the (1 1 1)- and (1 0 0)-oriented grains, so the transition may be not R → T transition [see Fig. 2(e) and (f)].

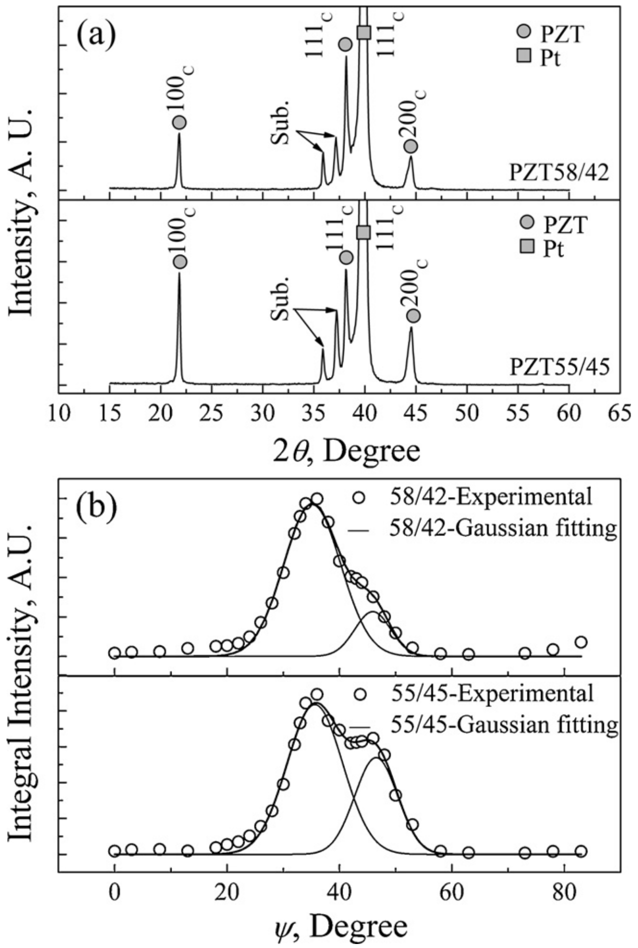


Fig. 1. θ–2θ scan XRD curves for PZT55/45 and PZT 58/42 films at $\psi = 0°$ (a), and relationship between $\{1\,1\,0\}_C$ diffraction integral intensity (I_ψ) and tilt angle (ψ) (b), in which the Gaussian fittings are also presented.

In Fig. 2(c) and (d), the peak symmetry of $2\,0\,0_C$ diffraction ($\psi = 55°$) of (1 1 1)-oriented grains is opposite to that of $2\,0\,0_C$ diffraction ($\psi = 0°$) of (1 0 0)-oriented grains, indicating the difference of phase transition between (1 1 1)- and (1 0 0)-oriented grains. According to previous studies [12,13], we analyze the peak shapes of $2\,0\,0_C$ and $1\,1\,1_C$ diffractions of R, M_A and M_B phases for different preferential orientations, as shown in Table 1. Comparing the experimental results in Fig. 2 with the peak shapes in Table 1, we think that the phase transitions in PZT55/45 and PZT58/42 thin films are as follows: R → M_B phase transition in (1 1 1)-oriented grains, and R → M_A transition in (1 0 0)-oriented grains.

In order to further confirm the phase transitions discussed above, Raman spectrum tests were conducted. According to the Raman spectra in Fig. 3, it can be concluded that the two films

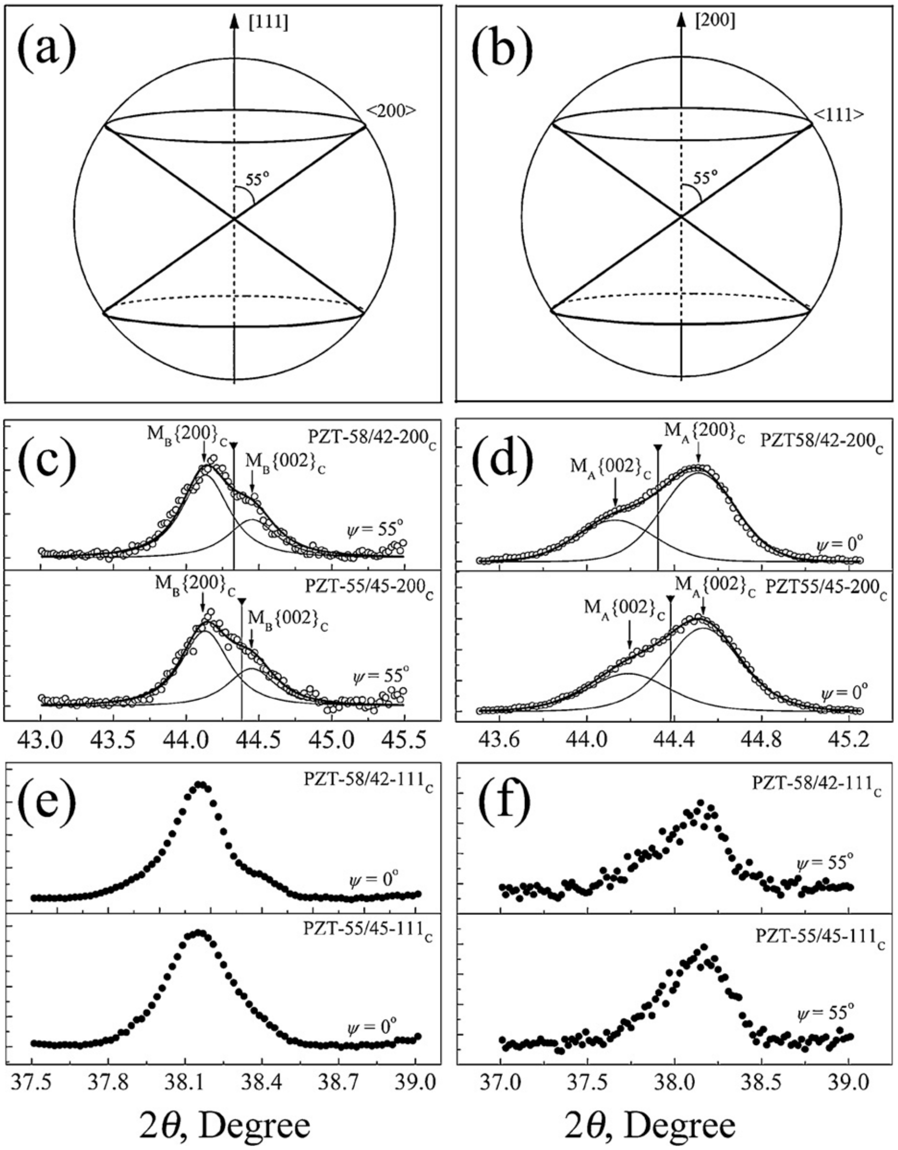


Fig. 2. Comparison of PZT thin film 2 0 0$_C$ and 1 1 1$_C$ XRD-diffraction patterns at different tilt angles (ψ), (a) shows the {1 1 1}$_C$ and {2 0 0}$_C$ normal direction distributions in (1 1 1)-oriented grains, and (b) the distributions in (1 0 0)-oriented grains. ▼ represents the 2 0 0$_C$ peak positions of R phase given by Noheda et al. [5].

exhibit the similar profiles, which means that the two films have the similar phase composition. The relative intensity of the bands A_1(1LO) and E(2TO) of PZT55/45 and PZT58/42 films exhibits the similar characteristics to that of PZT53/47 with M phase at 300 K [14]. It implies that monoclinic phase exists in PZT55/45 and PZT58/42 films. In addition, the profiles of Raman spectra of the two films are also similar to that of PZT53/47 at 50 K and 80 K [14], which shows another evidence of existence of monoclinic phase. As a result, the Raman spectra indicate that R → M phase transitions take place in both PZT55/45 and PZT58/42 films.

Fig. 4 shows ferroelectric properties of PZT55/45 and PZT58/42 thin films. As shown in Fig. 4(a), the ferroelectric hysteresis loops have excellent shape even at the driving electric field of 2000 kV/cm, indicating the good quality of the films. The remnant polarization ($2P_r$) values at different external electric fields are given in Fig. 4(b). As the driving electric field increases, the $2P_r$ values for both PZT55/45 and PZT58/42 films increase quickly at relatively low electric field region and slowly at relatively high electric field region. Some literatures claim that $2P_r$ decreases with the Zr

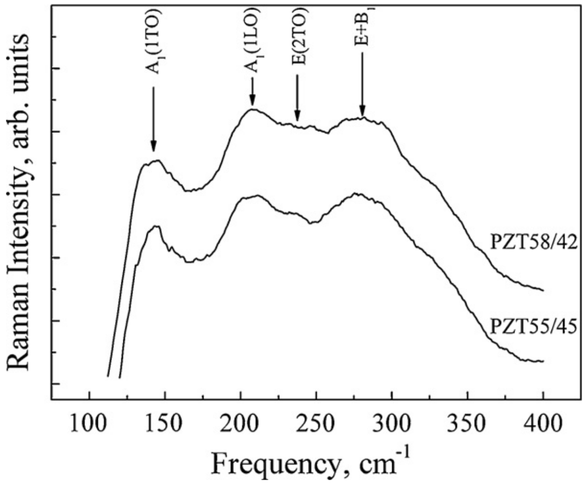
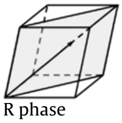
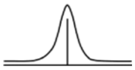
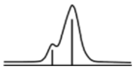
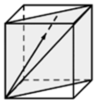
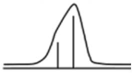
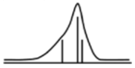
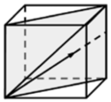
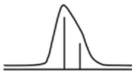
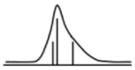


Fig. 3. Raman spectra of PZT55/45 and PZT58/42.

Table 1
Peak shapes of 2 0 0_C and 1 1 1_C diffractions in R, M_A and M_B phases for different orientations.

Crystal structure[a]	2 0 0_C peaks	1 1 1_C peaks
 R phase	Any preferential textures 	No preferential textures 
 M_A phase	(1 0 0) and (1 1 1) textures 	(1 0 0) texture 
 M_B phase	(1 0 0) and (1 1 1) textures 	(1 1 1) texture 

[a] The arrows represent spontaneous polarization.

content increasing for PZT with $0.55 \leq x \leq 0.60$ [15,16], but the $2P_r$ of PZT58/42 thin film is higher than that of PZT55/45 thin film in the presented study. For oriented films studied in this paper, the measured $2P_r$ values can be approximately considered as the average of spontaneous polarization (P_s) projections in $[1\,1\,1]_C$ direction of (1 1 1)-oriented grains and those in $[1\,0\,0]_C$ direction of (1 0 0)-oriented grains, because the films exhibit (1 1 1) and (1 0 0) mixed orientations. For M_A and M_B phases, the P_s projections in $[1\,1\,1]_C$ direction of (1 1 1)-oriented grains are similar, and larger than those in $[1\,0\,0]_C$ direction of (1 0 0)-oriented grains. In PZT58/42 thin film, the content of (1 1 1)-oriented grains is much larger than that in PZT55/45 film. Therefore, it is easy to understand that the $2P_r$ value of PZT58/42 thin film is higher than that of PZT55/45 thin film.

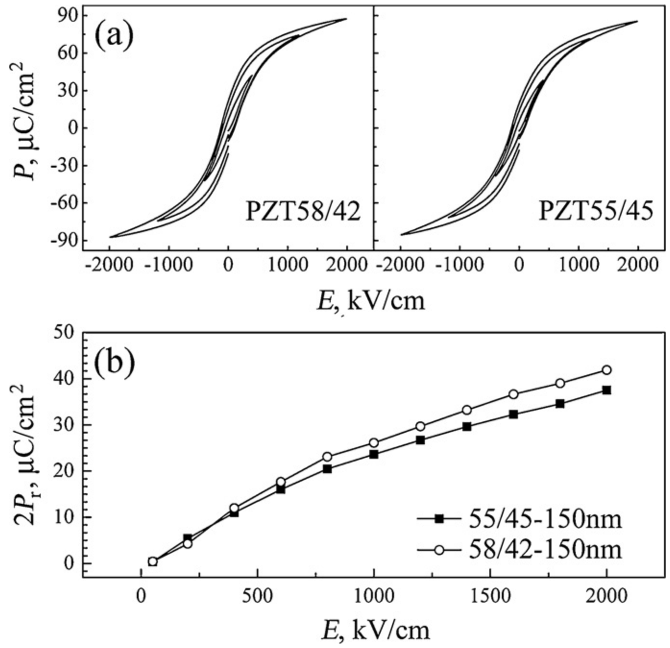


Fig. 4. Typical ferroelectric hysteresis loops of the PZT films (a), and $2P_r$ as functions of external electric field for the films with different x values (b).

4. Conclusions

PZT55/45 and PZT58/42 thin films prepared by sol–gel technology contain mixed orientations of (1 1 1) and (1 0 0). Although the compositions of thin films fall in R phase region of the phase diagram [2,5], the phase compositions of the PZT films are confirmed as M phase. Furthermore, phase transitions in the films are clearly identified: R → M_B phase transition in (1 1 1)-oriented grains and R → M_A transition in (1 0 0)-oriented grains. Finally, it is shown that the $2P_r$ value is greater in the film with higher content of (1 1 1)-oriented grains.

Acknowledgements

The work was supported by Excellent Youth Foundation of Heilongjiang Scientific Committee of China. Thanks are given for Dr. Q. Sun for his help on the preparation of PZT sols.

References

[1] K. Uchino, Piezoelectric Actuators and Ultrasonic Motors, Kluwar Academic Press, Boston, 1996.
[2] I.A. Kornev, L. Bellaiche, P.-E. Janolin, B. Dkhil, E. Suard, Phase diagram of Pb(Zr,Ti)O_3 solid solutions from first principles, Phys. Rev. Lett. 97 (2006) 157601.
[3] B. Jaffe, W.R. Cook, H. Jaffe, Piezoelectric Ceramics, Academic, London, 1971, p. 136.
[4] B. Noheda, D.E. Cox, G. Shirane, J.A. Gonzalo, L.E. Cross, S.-E. Park, A monoclinic ferroelectric phase in the $Pb(Zr_{1-x}Ti_x)O_3$ solid solution, Appl. Phys. Lett. 74 (1999) 2059.
[5] B. Noheda, D.E. Cox, G. Shirane, R. Guo, B. Jones, L.E. Cross, Stability of the monoclinic phase in the ferroelectric perovskite $PbZr_{1-x}Ti_xO_3$, Phys. Rev. B 63 (2000) 014103.
[6] B. Noheda, J.A. Gonzalo, L.E. Cross, R. Guo, S.-E. Park, D.E. Cox, G. Shirane, Tetragonal-to-monoclinic phase transition in a ferroelectric perovskite: the structure of $PbZr_{0.52}Ti_{0.48}O_3$, Phys. Rev. B 61 (2000) 8687.
[7] R. Guo, L.E. Cross, S.-E. Park, B. Noheda, D.E. Cox, G. Shirane, Origin of the high piezoelectric response in $PbZr_{1-x}Ti_xO_3$, Phys. Rev. Lett. 84 (2000) 5423.
[8] H.X. Fu, R.E. Cohen, Polarization rotation mechanism for ultrahigh electromechanical response in single-crystal piezoelectrics, Nature 403 (2000) 281–283.
[9] M. Ahart, M. Somayazulu, R.E. Cohen, P. Ganesh, P. Dera, H.-K. Mao, R.J. Hemley, Y. Ren, P. Liermann, Z. Wu, Origin of morphotropic phase boundaries in ferroelectrics, Nature 451 (2008) 545–552.
[10] L. Yan, J. Li, H. Can, D. Viehland, Low symmetry phase in $Pb(Zr_{0.52}Ti_{0.48})O_3$ epitaxial thin films with enhanced ferroelectric properties, Appl. Phys. Lett. 89 (2006) 262905.
[11] W.D. Fei, C.Q. Liu, M.H. Ding, W.L. Li, L.D. Wang, Characterization of fiber texture by omega-scan X-ray diffraction, Rev. Sci. Instrum. 80 (2009) 093903.
[12] Y.U. Wang, Diffraction theory of nanotwin superlattices with low symmetry phase: application to rhombohedral nanotwins and monoclinic M_A and M_B phases, Phys. Rev. B 76 (2007) 024108.

[13] H.W. Jang, S.H. Baek, D. Ortiz, C.M. Folkman, R.R. Das, Y.H. Chu, P. Shafer, J.X. Zhang, S. Choudhury, V. Vaithyanathan, Y.B. Chen, D.A. Felker, M.D. Biegalski, M.S. Rzchowski, X.Q. Pan, D.G. Schlom, L.Q. Chen, R. Ramesh, C.B. Eom, Strain-induced polarization rotation in epitaxial (0 0 1) $BiFeO_3$ thin films, Phys. Rev. Lett. 101 (2008) 107602.

[14] A.G. Souza Filho, K.C.V. Lima, A.P. Ayala, I. Guedes, P.T.C. Freire, F.F.A. Melo, J. Mendes Filho, E.B. Araújo, J.A. Eiras, Raman scattering study of the $PbZr_{1-x}Ti_xO_3$ system: rhombohedral–monoclinic–tetragonal phase transitions, Phys. Rev. B 66 (2002) 132107.

[15] S. Yokoyama, Y. Honda, H. Morioka, S. Okamoto, H. Funakubo, T. Lijina, H. Matsuda, K. Saito, T. Yamamoto, H. Okino, O. Sakata, S. Kimura, Dependence of electrical properties of epitaxial $Pb(Zr,Ti)O_3$ thick films on crystal orientation and Zr/(Zr + Ti) ratio, J. Appl. Phys. 98 (2005) 094106.

[16] M.J. Haun, Z.Q. Zhuang, E. Furman, S.J. Jang, L.E. Cross, Electrostrictive properties of the lead zirconate titanate solid–solution system, J. Am. Ceram. Soc. 72 (1989) 1140.