

Chapter 4

Mechanical characterization of single crystal BaTiO₃ film and in-situ XRD observation of microstructure change due to mechanical loading

4.1 Introduction

Ferroelectric materials have many technological applications, which utilize their switchable spontaneous polarization and their very high dielectric constants. In recent years ferroelectric thin films have inspired great interest due to their potential applications in microelectronics and microelectromechanical (MEMS) technology. These practical applications of ferroelectric materials in thin film form to piezoelectric actuators, electro-optic devices, and nonvolatile memories are basically related with the switching behavior of spontaneous polarization which usually consists of contributions from both 180° and 90° domains.

It is well known that many properties of ferroelectric materials such as dielectric constant, dielectric loss, coercive field, piezoelectric constant, switching time, etc., are related to the domain structure and the motion of domain walls. The spatial distribution, relative volume fraction, and dynamic motion of these domains often control physical properties of ferroelectric thin films. In particular, 90°-domain switching gives rise to

field-induced change in birefringence and strain required for electro-optic and piezoelectric devices, respectively. Nevertheless, it also contributes to degradation of polarization such as fatigue in ferroelectric random access memory (FRAM) application. Therefore, understanding of 90°-domain motion under applied electric field and/or mechanical loading is of great significance to design functional ferroelectric devices suitable for specific use. It is therefore of great importance that ferroelectric domain structures should be examined.

Much effort has been devoted to investigate the domain structures and dynamic motion of 90° and 180° domains in ferroelectric ceramics using various techniques such as polarization optical microscopy, transmission electron microscopy, atomic force microscopy, and x-ray diffraction (XRD). Among them, XRD is advantageous for in situ observation of 90°-domain switching dynamically and quantitatively under applied mechanical (stress/strain) field.

Several recent experiments have demonstrated that the response of ferroelastic domain walls to a dynamically applied load can be resolved successfully using x-ray diffraction techniques. Yet, the link between the macroscopic deformation and the microstructure as well as quantified relations between the mechanical loading and 90° domain wall motion need further study. The nature of the interaction between ferroelastic domain walls and surfaces is an area of active research.

In this work, the pressure bulge setup is used to apply the mechanical loading and the *in situ* X-ray diffraction is used to monitor the process of 90° domain switching. The results of single crystal barium titanate free standing thick film with 100 microns in

thickness are presented. In particular the following issues are discussed: the mechanical characterization process to determine the elastic modulus, and the use of this technique to quantify the relation between mechanical loading and 90° domain switching.

4.2 Materials

4.2.1 Single crystal BT thick film by ion implantation-induced layer transfer method

Two single crystal barium titanate (BaTiO₃) films were used in the experiments. These ferroelectric films were provided by Y.B. Park and H. Atwater. They were made by ion implantation-induced layer transfer method, separating a layer from a bulk crystal. The nominal thickness of each of these films was around 100 μm.

For each sample, the surface which is separated from the bulk crystal is relatively rough, with 50 nm fluctuation in surface profile, while the other surface is well-polished, since the bulk crystal surfaces were polished. Micro polishing was done on the rough surfaces on both samples. After X-ray diffraction experiments, the samples are mostly *a*-oriented, i.e., the domains are oriented along [100] or in-plane directions. The polishing stress made in-plane orientation favorable such that the *c*-domains were changed into *a*-domains by 90°-domain switching. However, the switch cannot be recovered without external electric field or mechanical load in the perpendicular direction. As a result, heat treatment was done on both samples, by heating them above 120°C, keep the temperature overnight, then cool down, in order to have multiple domains, including *c*-domains.

The samples were manually fixed on silicon wafers with pre-etched square windows using silver paste. Due to the different geometry of each sample, windows of different sizes were chosen. For sample 2, the tested and observed area was 2 x 2 mm. The mounting for sample 1 was more complicated. The thick film was 1 x 3 mm in rectangular shape. Two 1 x 1 mm pre-etched silicon square windows with 1 mm space in between were chosen to mount it. All sides of sample 1 were fixed to the silicon wafer while the whole 1 x 3 mm area can be pressurized.

Different experiments were carried out on these 2 samples with specific purposes respectively. For sample 1, pressurized bulge test was carried out under a Michelson interferometer to characterize the elastic modulus. For sample 2, in situ X-ray diffraction experiment was carried out with pressurized loading to capture the quantified relation between the driving force (pressure) and the 90° domain switching.

4.2.2 Sample holder

The small pressure chamber consists of a cylindrical chamber made of aluminum whose dimensions (diameter 5.1 cm, thickness 7.4 mm) are designed to fit inside the X-ray setup. A small flexible tube compatible with the X-ray machine shield holes is used to connect this chamber to the pressure-handling module (figure 4.1). The main drawback of this chamber is the absence of a sample-fixing system: double-sided tape had to be used, which can lead to leak, if high pressure loading were desired.

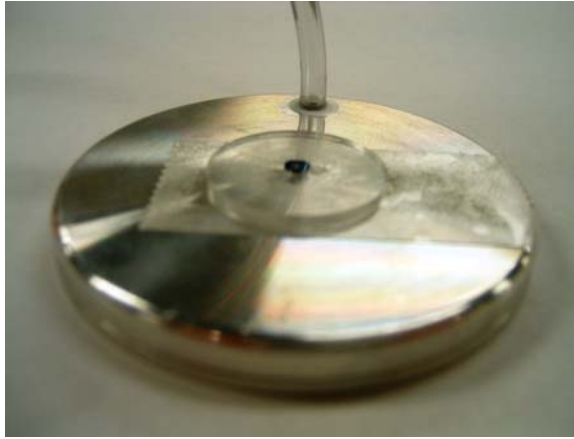


Figure 4.1. Pressure chamber with thick film barium titanate sample.

4.3 Experimental

Three tests were carried out to quantify the relation between the driving force (stress) and the volume fraction of the induced 90° -domain switching. All these three tests were performed under the pressure loading. The following measurement techniques were used to characterize the thick film: the micro-interferometry measurement to determine the real time displacement profile, the X-ray diffraction (XRD) to examine 90° domain switching, and polarized light microscopy (PLM) to observe the domain pattern evolution caused by the mechanical loading.

4.3.1 Pressure bulge setup

This setup is designed in order to be able to apply a differential pressure to a variety of thin films (figure 4.2). The basic functions of this setup are, delivering the pressure, measuring the pressure, and maintaining the thin film or thick film samples in multiple setups such as XRD and PLM equipments.

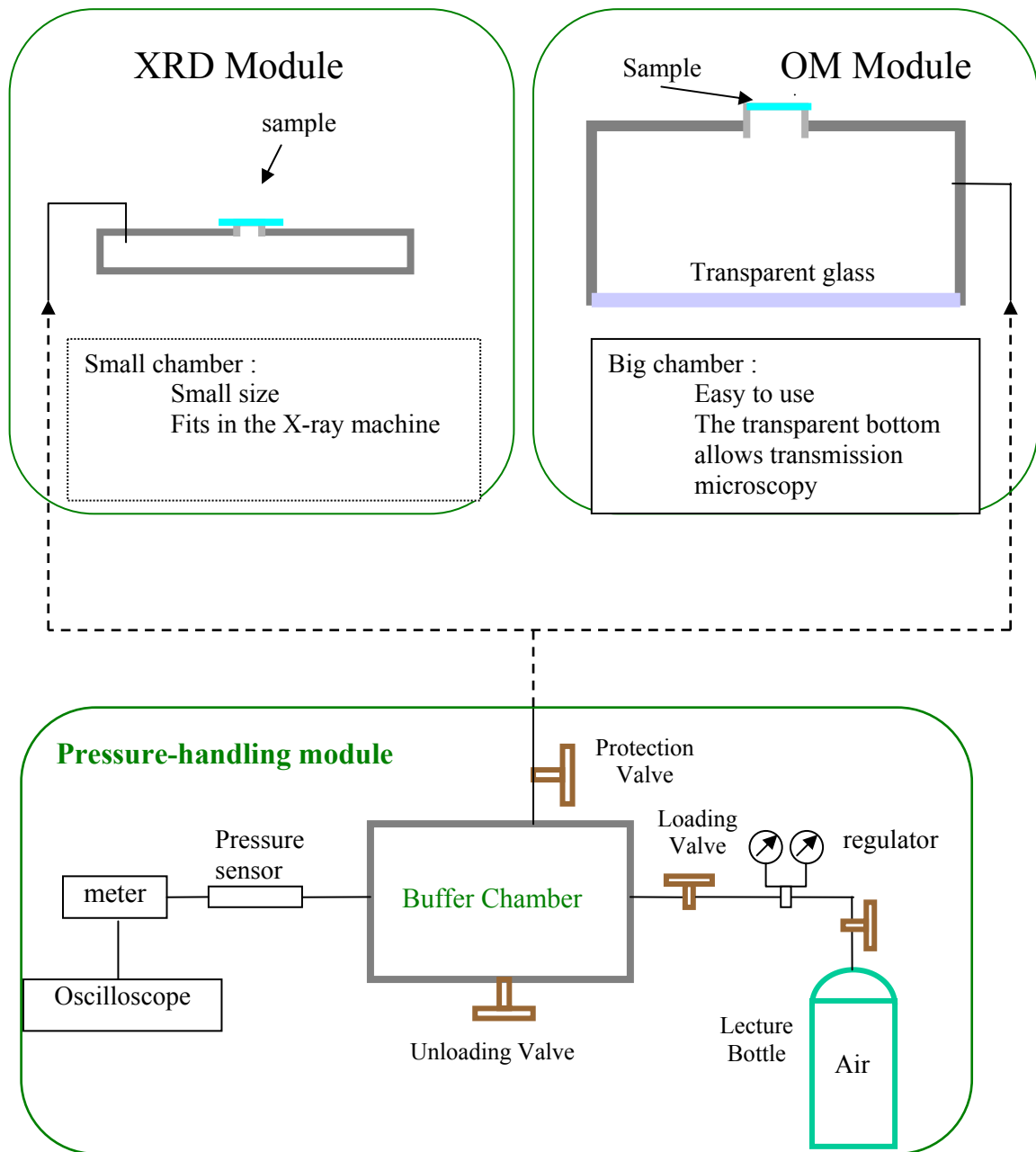


Figure 4.2. Schematic of the pressure bulge setup.

In order to meet the different requirements imposed by the different setups in which the film may be examined, a modular design was adopted. The pressure-handling module

delivers pressure and measures it, and the film-handling module holds the thin film and transmits the pressure to it. The two parts are connected with a flexible pipe.

4.3.2 The interferometry setup

A Michelson interferometer is used to measure the deflection of the thin films (figure 4.3). The main elements are a source of visible light at a fixed wavelength $\lambda=546$ nm (Nikon, Plan 5x), a beam splitter, a reference mirror, a long working distance microscope, and a CCD camera. This setup is similar to the one used by Mitchell [1]. The whole setup is mounted on a pressurized air table to avoid vibrations. The images from the CCD camera (Sony XC750) are recorded on a computer. The computer is also used to send a trigger signal to the oscilloscope which records the pressure.

The incident light beam is split into two components. One of these components reflects off the surface of the thin film and reenters the interferometer, where it combines again with the other component which has reflected off a reference mirror. Depending on the path length difference between the two beams, they will interfere either constructively or destructively with each other. As a result of the interference, a series of dark and bright fringes are observed, as shown in figure 4.4. Each white (or black) fringe corresponds to a displacement of $\lambda/2$.

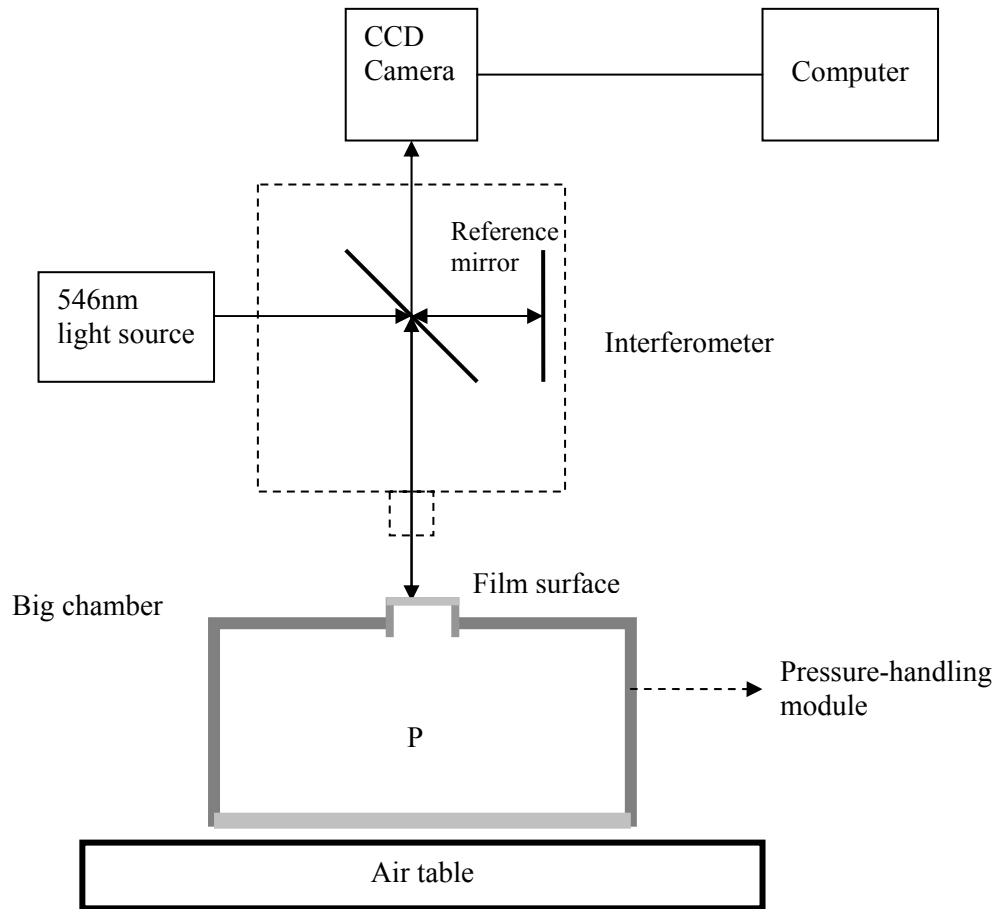


Figure 4.3: Schematic of the interferometry setup

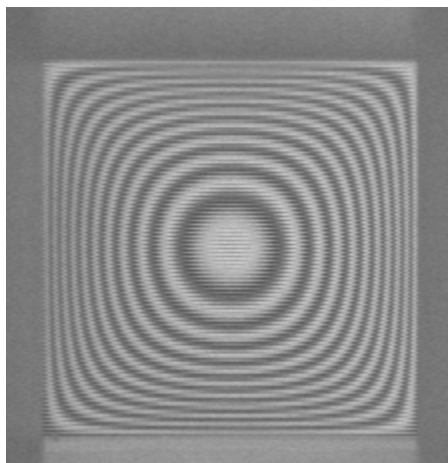


Figure 4.4. Typical interference patterns during the bulging of a thin film.

4.3.3 Principle of XRD

X-ray diffractometry is a common method to characterize the microstructure of crystalline materials. An incident x-ray beam is sent to the surface of a crystal. Since the beam can penetrate only first few micrometers of a crystal, part of the beam will reflect on each one of the crystal lattice plane (figure 4.5).

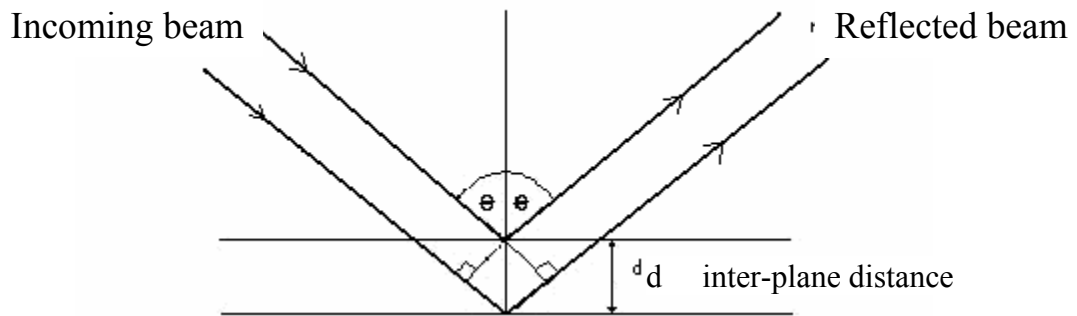


Figure 4.5. Principle of x-ray diffractometry.

As a result, a large number of reflected beams will interfere. Because of this large number of coherent interfering beams, the interference will be destructive in all the cases, except when all the reflecting beams are in phase. This condition provides the Bragg condition for a constructive interference between the reflected beams:

$$n\lambda = 2d \sin(\theta) \quad (4.1)$$

During an experiment, the intensity of the reflected beam is measured for a continuous range of angles. Different peaks of intensity are observed, corresponding to the different inter-planar distances present in the crystalline sample.

The XRD apparatus used to perform the experiments is a Phillips, PW3040-PRO. This is a closed system, which means that the x-ray specimen chamber is separated from the outside by a shield. The experiments are completely remote-controlled via a computer. The XRD instrument automatically scans a given range of angles between the x-ray source, the sample and the detector. A typical scan from 5° to 80° takes approximately 4 minutes. The resulting data is analyzed using the software provided by Phillips Corporation.

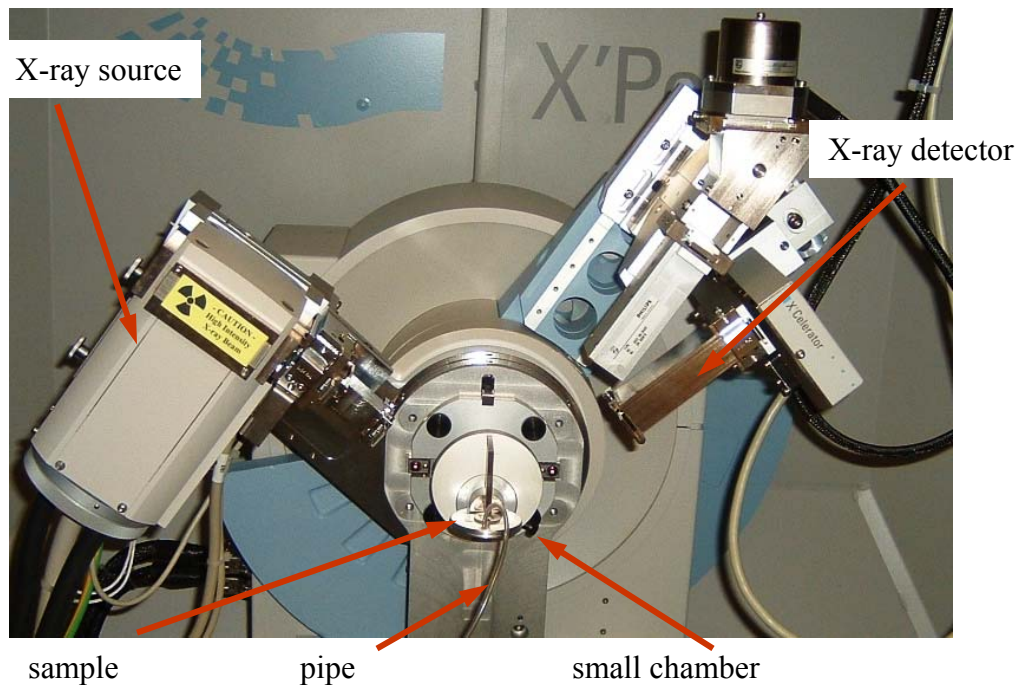


Figure 4.6. Photo of the x-ray diffractometry setup combined with the bulging setup.

The small pressure chamber is designed to have the same shape as the standard sample holders used with this machine, in order to fit inside the XRD equipment (see figure 4.6). This allows for applying real time pressure loading on the film during in situ XRD.

4.3.4 Polarized light microscopy

A long working distance microscope and two crossed polarizers are used to observe the orientation of domains in ferroelectric films. The two polarizers are oriented at 90° from each other, the light transmitted through the first polarizer is blocked by the second one. During the experiment, the light goes through the first polarizer, then through the thin film, and finally through the second polarizer (also called analyzer). The emerging beam is observed with a microscope.

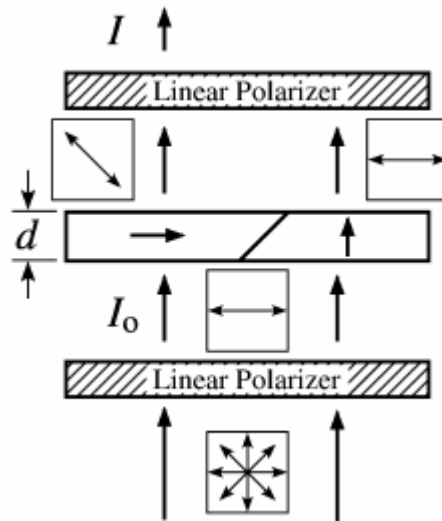


Figure 4.7. Polarized light microscopy setup (adopted from reference [2]).

If the polarization of the film is out-of-plane, then the film is optically isotropic in that direction and the corresponding image remains dark (figure 4.7). On the contrary, if the film polarization is in-plane oriented, the film is optically anisotropic in transmission. Therefore it will cause a rotation of the optical polarization direction, allowing the light to go through the second polarizer (figure 4.7). The details of the technique have been described by Burcsu [3].

The polarization microscopy experiment requires the thickness of the film to be large enough to make the orientation of the light rotate. For barium titanate, this occurs at a few μm . For illustrative purpose, an image acquired on a bulk barium titanate crystal is shown in figure 4.8. In this image, the out of plane (c) orientation domains appear dark while the in-plane oriented domains appear bright.

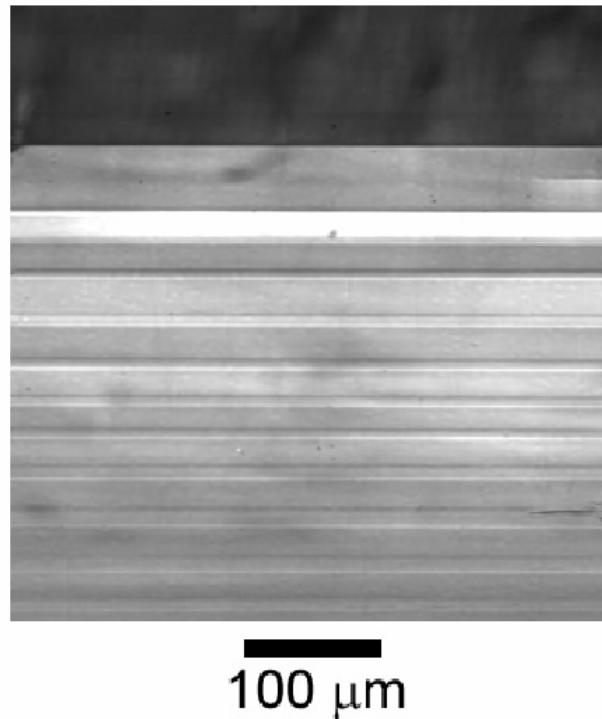


Figure 4.8: Domain pattern in single crystal barium titanate photographed using a polarizing microscope [2, 3].

4.4 Results

4.4.1 Mechanical characterization of single crystal thick film

A pressure bulge experiment (see Chapter 3) was carried out on a sample of barium titanate (BaTiO_3 , BT) single crystal film to determine the mechanical properties of barium titanate. The thick film sample of BT (thickness~100 μm) was prepared by wafer bonding method which involves hydrogen ion-beam-implantation and wafer transfer method [4]. Based on the ratio of the film thickness and the lateral dimension of the film, the corresponding mechanical problem of this experiment is the thin plate bending problem under uniformly distributed transverse load. Furthermore, from the interferometry measurement results shown later in this chapter, the maximum center displacement is about 0.5 μm , which is much less than the sample thickness, therefore, the problem satisfies the small deformation assumption for mechanical analysis. Thus, the elastic modulus of the film can be extracted from the relation between the load and maximum deformation [5].

The process of performing the mechanical characterization using pressure bulge loading assumes that the BT sample behaves linear elastically under loading. However, for this active material, high stress in the film due to pressure loading can induce 90°-domain switching resulting in inelastic behavior and the linear elastic deformation assumption will no longer be satisfied. The characterization method needs to examine the loading process to avoid the non-linearity during loading if one plans to use linear analysis to interpret the behavior of thin films of BT. Thus, for this sample two methods

are used to monitor the evolution of domain structure during pressure loading, (a) in-situ X-ray diffraction (XRD) and (b) polarized light microscopy (PLM).

The thick film was first visualized using polarized light microscopy. The applied pressure was increased from 0 kPa to 123 kPa. During this loading, no noticeable change was observed in domain structure, as shown in figures 4.9 and 4.10. The parallel and perpendicular black lines that can be seen on the pictures are thought to be either 180° domain walls going through the thickness of the film or out-of-plane domains between two parallel 90° domain walls close to each other. X-ray diffractometry was therefore used to measure the repartition of domains and thus quantify domain switching, if any. As in the case of the PLM, no change was observed during the same loading process. The intensity of the diffraction peaks remained constant indicating no change in microstructure during the entire loading process (figure 4.11).

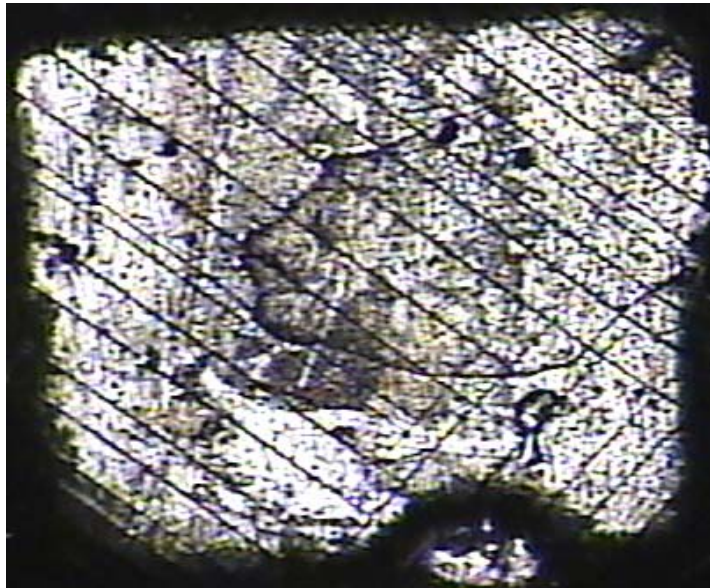


Figure 4.9. BT film under polarized light microscopy before loading (5X).

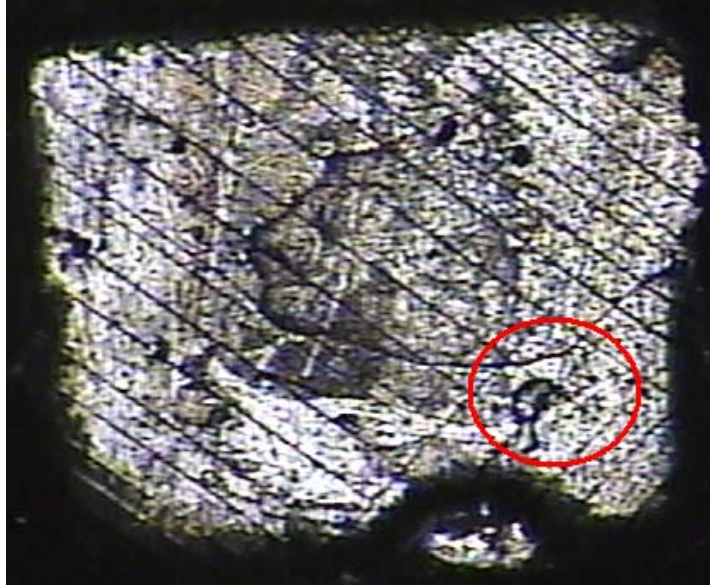


Figure 4.10. BT film (same as the one in figure 4.9) under pressure (123 kPa) loading (5X).

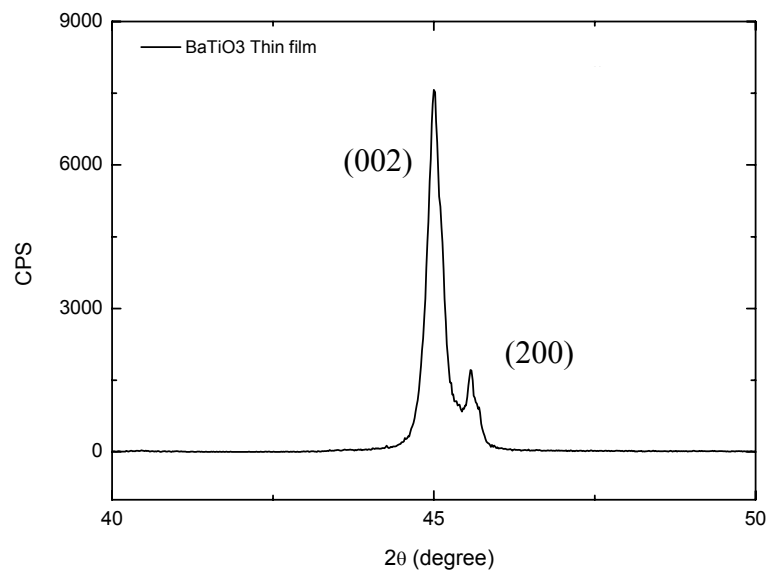


Figure 4.11. Second order diffraction peaks following unloading after pressurizing the film to 123 kPa.

From the above two experiments, one can conclude that for this thick sample of BT, pressure smaller than 123 kPa can not induce any noticeable change of the domain

structure. That is, the material remains in the linear elastic range with no change in microstructure. As a consequence, the pressure bulge experiment on this thick film can be used to determine the material properties accurately.

During the pressure bulge experiment, the film was loaded up to 117 kPa. Careful analysis indicates that the maximum fringe difference from the boundary is between 1.6 and 2 fringes. This uncertainty is caused by the complicated profile of the sample surface. Thus, the maximum deflection of the 1mm by 3mm thin plate at 117 kPa is 0.49 micron, since the fringe constant is 273 nm corresponding to half the wavelength of the light source ($\lambda=546$ nm).

For a rectangular plate, the maximum deflection (w_{\max}) can be determined from the following equation (4.2),

$$w_{\max} = \frac{\alpha p b^4}{E t^3} \quad (4.2)$$

where α is the function of the ratio between long and short side of the thin plate, p is the applied pressure, b is the length of the short side, E is the Young's modulus, and t is the plate thickness, i.e., 100 μm for both sample 1 and sample 2.

For the sample used in the present experiment, $a=3$ mm, $b= 1$ mm, p is 117 kPa, w_{\max} is 0.49 microns, and α is 0.248. Thus, the Young's modulus E can be computed using equation (4.2) which results in a value of 59.2 MPa. This value agrees reasonably well with the elastic modulus of single crystal barium titanate bulk material, which is 67 GPa [6]. The disagreement in value of the modulus may be due to the uncertainty in the

thickness of the sample and as well the number of fringes, which is used for computing the maximum deflection. For other samples of BT used in further investigation, the above value of the Young's modulus will be utilized when needed.

The maximum stress (at the center of the long edge) (σ_{\max}) and the stress in the center (σ_c), are

$$\text{Max } \sigma = -\frac{\beta_1 p b^2}{t^2} = 5.85 \text{ MPa} \quad (4.3)$$

$$\sigma_c = \frac{\beta_2 p b^2}{t^2} = 2.90 \text{ MPa} \quad (4.4)$$

where β_1 and β_2 are parameters depend on the ratio of length and width of the plate. For a 3 mm by 1 mm thin plate, β_1 and β_2 are 0.4980, 0.2480, respectively. For 2 mm by 2mm square plate, β_1 and β_2 are 0.3078, 0.1386, respectively. For the thick film BT used in this investigation, the values computed for σ_{\max} and σ_c are 5.85 and 2.90 MPa, respectively.

4.4.2 Direct observation of stress induced 90°-domain switching under XRD

The pressurized bulge experiment was performed on another thick film BT sample under *in-situ* XRD exam and PLM examination was carried out on this sample prior and following the pressure loading.

The thick BT film with dimension 2 mm x 2 mm x 100 μm is fixed on the sample holder as shown in figure 4.1, and mounted inside the X-ray diffractometer as shown in figure 4.6. The loading is between 0 and 27.2 kPa. The pressure loading history is shown

as a function of time in figure 4.12. The *in-situ* X-ray diffractometry (XRD) data (figure 4.13) was used to compute the evolution of domains.

In the XRD result, the intensity peaks of *a*-domain (200) or *c*-domain (002) indicate the relative population of these microstructures respectively, among the scanned beam spot area. The 90° domain switch can be caused by tensile or compressive stress in the film. However, due to the in-plane stress status, this 90° domain switching will only happen from *c*-domain switch to *a*-domain and is irreversible without external electric field. As a result, the volume fraction of *a*-domain will increase and therefore the intensity of *a*-peak (200) will also increase.

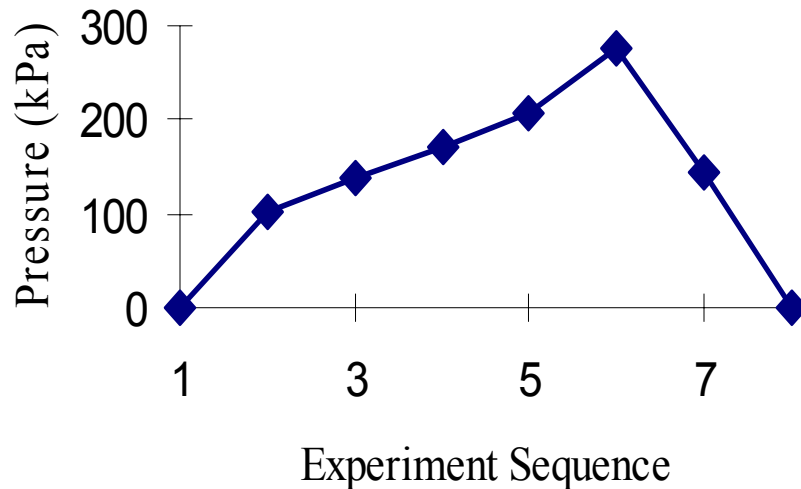


Figure 4.12. Pressure loading history.

Another important issue about explaining the XRD results of single crystal with multiple domains is that the relative intensity may change dramatically even by slightly changing in translation or rotation of samples. To avoid false information of domain

switching due to this artifact, in situ XRD scans are made under different pressure loadings while the sample is kept at the exactly same place. In the XRD result shown in figure 4.13, the intensity of a -domain increases significantly. This clearly shows the volume fraction increase in a -orientation (200) which is caused by 90° domain switching.

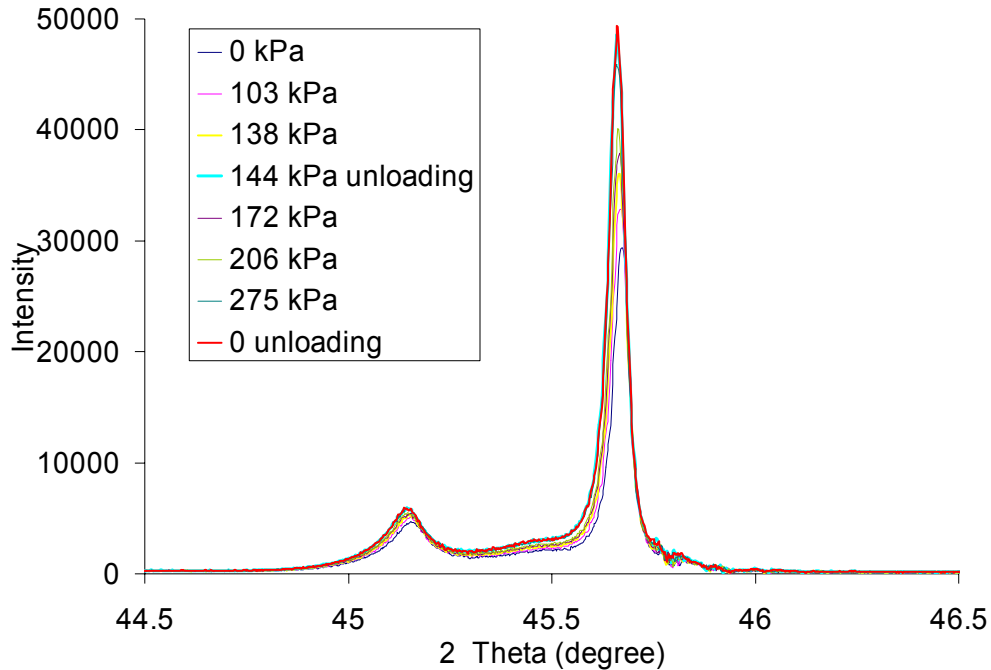


Figure 4.13. *In-situ* XRD results: the evolution of 2nd order diffraction peaks of c - (002) and a - (200) orientations during the sequence of loading shown in figure 4.12.

Assume the intensities of (002) and (200) orientations to be proportional to the population of the corresponding domains, namely c - and a -domains respectively [7]. I_c and I_a are the intensities of the diffraction peaks corresponding to c - (002) and a - (200) domains, respectively. Let $R=I_c/I_a$ before loading, then the percentage N of c -domain which is switched by the applied stress satisfies,

$$N = \frac{95(R' - R)}{1 + R'} \times 100 \quad (4.5)$$

where R' is the ratio of intensities of the (002) and (200) orientations after loading. The percentage change caused by pressure loading is shown in figure 4.14.

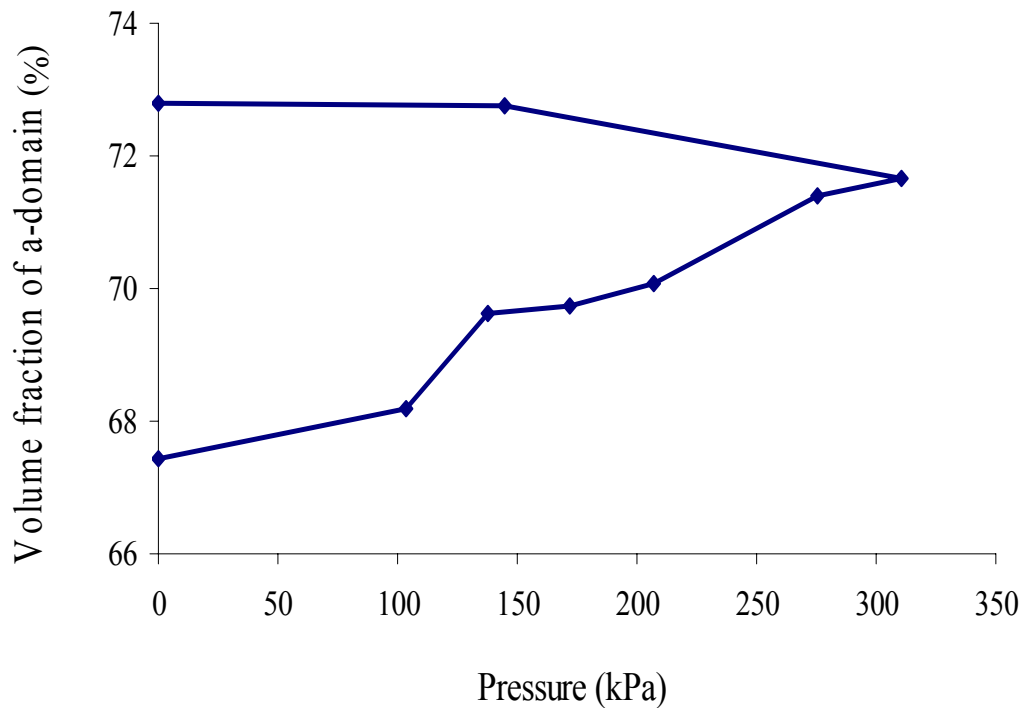


Figure 4.14. Pressure induced domain switching: Percentage change in a -domain due to applied stress.

Using the value of the Young's modulus (E) computed earlier, 59.2 GPa, the maximum stress and the stress in the center can be calculated by equations (4.3) and (4.4). Due to the differences in the geometry, the same pressure will generate much larger stress in this sample in comparison to the sample used for mechanical characterization (Section 4.4.1). As a consequence, the change in the XRD peaks and domain patterns are anticipated and observed.

At 0.22 MPa compressive stress, the 90° domain switching is initiated and fully developed at 1.1 MPa [8]. However, in results of this study, for sample 1 which has 2.9 MPa tensile stress in center, no domain re-participation was observed. For sample 2, in which 5.6 MPa tensile stress is applied at center at 101 kPa, significant change in domain re-distributions are observed. One can conclude that the stress to initiate 90° domain switching under tensile stress is between 2.9 MPa and 5.6 MPa. This discrepancy of the critical stress observed in other research group may be due to different loading mechanism. In current work, instead of compressive stress, most area of the sample is subject to tensile stress due to bending, especially near the center region, where the x-ray beam incidents. And the in-plane stress caused by bending moments is not uniform through out the thickness. The studied region, which is at the top surface near center of the sample, is subjected to non-uniform tensile stress.

Before and after each *in-situ* XRD experiment, the sample was mounted on the pressure chamber for the microscope, and polarized light microscopy (PLM) observation was carried out to observe the domain structure change, if any. The domain evolution patterns are shown in figures. 4.15 (a) (b) (c) for various levels of pressure loading.

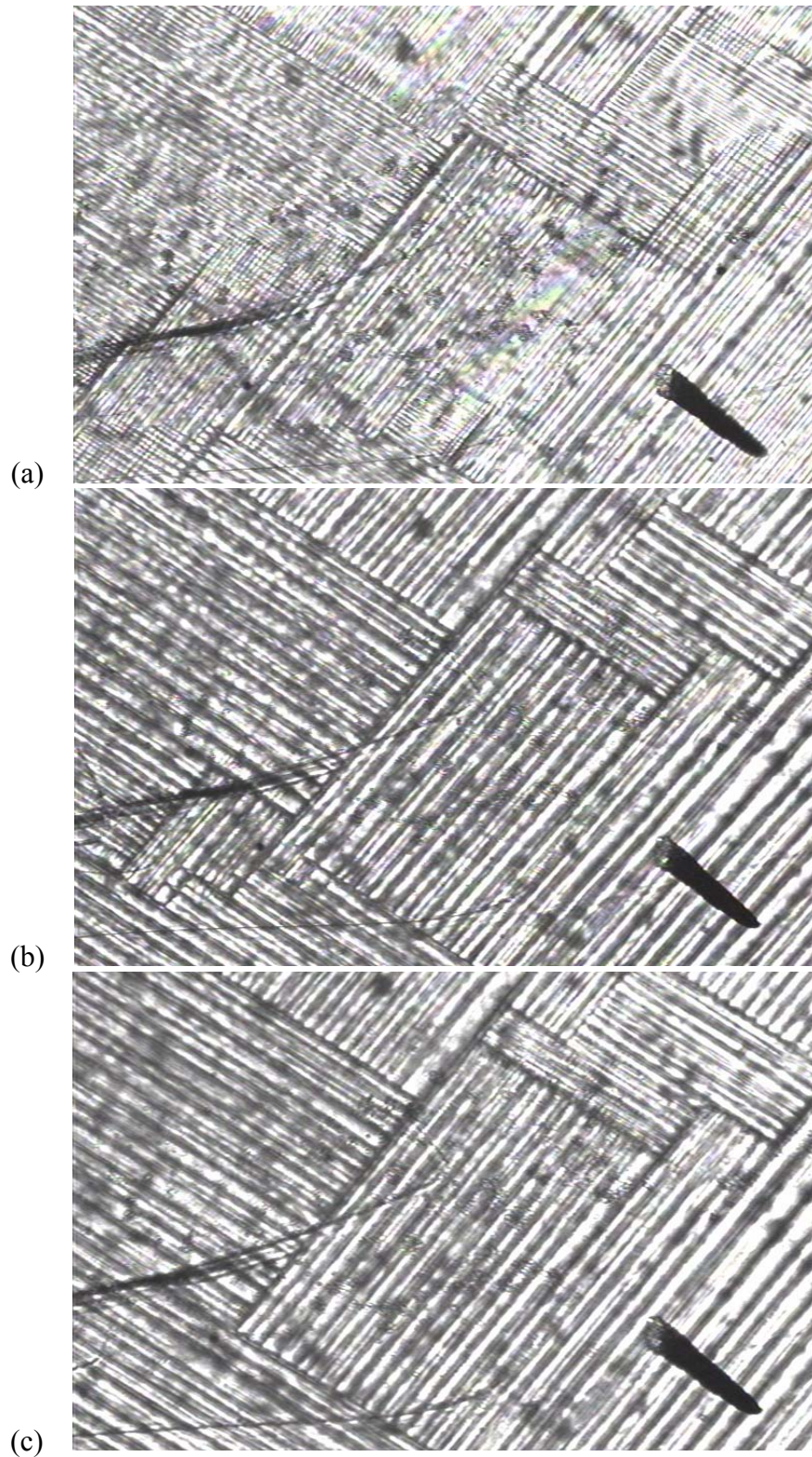


Figure 4.15. Domain patterns observed using polarized light microscopy (PLM), (a) 0 kPa (b) after 123 kPa (c) after 272 kPa

4.5 Discussion and conclusion

By utilizing the pressure bulge method, the Young's modulus of a barium titanate single crystal thick film ($\sim 100 \mu\text{m}$) fabricated by the wafer bonding method was characterized. The value of this modulus, 59.2 GPa, is smaller than the bulk crystal of the same material. Direct evidence of 90° domain switching were obtained from the *in-situ* XRD results of the intensity change in both (002) and (200) orientations. Obvious changes in domain patterns were observed by using the polarized light microscopy. At 272 kPa pressure, the stress in the center of the film is 15.3 MPa and more than 18% of the *c*-domains switched into *a*-domains. Quantified relations between the stress in the thick film and the microstructure change are also reported.

4.6 References

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