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Ceramics International 38 (2012) 4579–4585

CERAMICS INTERNATIONAL

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# Mechanically controlled domain structure in PZT piezoelectric ceramics

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Received 9 December 2011; received in revised form 8 February 2012; accepted 14 February 2012
Available online 21 February 2012

## Abstract

The influence of the mechanically applied load on the piezoelectric properties and domain switching characteristics has been investigated experimentally using a soft lead zirconate titanate (PZT) piezoceramic, which de-poled to make randomly orientated domain structures. Mechanical loads were applied to rectangular PZT ceramics under compressive and tensile stresses. With the applied stress, 90° domain switching occurred in many locations in the PZT ceramics, where the higher stress caused more severe domain switching. The domain switching occurred with different directions, depending on the stress direction. For instance, the (2 0 0) peak increased and the (0 0 2) peak decreased when more severe compressive stress was applied. The opposite trend was detected as more severe tensile stress was applied; the (2 0 0) peak decreased and the (0 0 2) peak increased. With the applied loading process, the domains (long tetragonal *c*-axis) were orientated regularly in the PZT ceramics. Furthermore, like the electrically poled PZT ceramics, the domain orientations were more aligned when the sample surfaces were constrained during the loading process.



*Keywords:* C. Piezoelectric properties; D. PZT ceramic; Domain orientation; Domain switching; XRD analysis

## 1. Introduction

In recent years, piezoelectric ceramics have been widely used as actuators, buzzers and sensors [1]. In particular, lead zirconate titanate piezoelectric (PZT) ceramics have been used more and more because of their high Curie temperature, high material strength and low sintering temperature. Since both sensor and actuator need to be reliable and durable, high quality piezoelectric properties are required. The material properties of PZT ceramics as used in the above devices are often subjected to self-induced or external stress [2]. Higher piezoelectric coefficients are especially appropriate for positioning actuator and ultrasonic motor applications [3]. The material properties of piezoelectric ceramics under combined electro-mechanical loading have been discussed to model the constitutive response and optimize the actuator performance [4]. Piezoelectric ceramics consist basically of crystals subdivided into domains separated by domain walls. A domain is formed by a group of unit cells with the same crystal structure and the domain direction is controlled by the polarization process. The domain orientation and domain wall motion are also believed to significantly affect the piezoelectric properties. It is reported that nonlinear electromechanical behavior occurs due to polarization switching and/or domain wall motion [5], and there is a relationship between the severity of the poling process and the stiffness of PZT ceramics [6]. The domain walls are found to be aligned in the PZT ceramic perpendicular to the poling direction. Such domain wall characteristic affects the change of crack growth behavior. Crack growth occurs mainly along the domain walls {1 1 0} because of the high stress concentration between the domain walls.

The application of the electric field or mechanical loading in excess of a critical magnitude can induce a dipole rotation inside a domain, leading to domain switching. The effect of the domain configuration on the material properties defines the electromechanical properties by manipulating the stress. This is crucial for the design of the related ceramic for specific engineering applications [7]. To date, several investigators have studied the dielectric and piezoelectric response of ferroelectric materials under combined mechanical loading. It is important to enhance the dielectric and piezoelectric performance for low values of pre-stress. For PZT thin films on a thick substrate, the

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0272-8842/$36.00 
doi:10.1016/j.ceramint.2012.02.036

piezoelectric coefficients of interest ($d_{33eff}$ and $d_{31eff}$) are dependent on the material's mechanical properties due the plane stress state [8]. To investigate the mechanical properties of PZT thin films, e.g., Young modulus, nanoindentation tests have been carried out [9]. The multilayer ceramic actuators using PMN-PZT ceramics present the non-linear ferroelectric behaviors when electric field and compressive stress are simultaneously applied to the ceramics [10]. Another approach was executed by Zhou and Kamlah, where high electric field induced polarization and strain responses were experimentally evaluated for a soft PZT material subjected to cyclic loading. One of their results is that the polarization and strain outputs are found to monotonically decrease with an increase in stress amplitude until mechanical loading completely impedes the piezoelectric response [11].

Several experimental approaches have been carried out to investigate the 90° domain switching contribution to the dynamic polarization and piezoelectric behavior in ferroelectric materials. Significantly, the 90° domain switching can occur anywhere in the PZT ceramics, and this process contributes to the accumulation of strain and consequent change of the material properties. The domain switching characteristics are clearly revealed by X-ray and electron back scattered diffraction analysis. The piezoelectric properties (electromechanical coupling coefficient, piezoelectric constant and permittivity) are apparently changed by the domain structure [12].

To obtain good piezoelectric properties for ferroelectric ceramics, the electrical poling processes are carried out with a high electric field, typically DC 5 kV/mm for 10 min in silicon oil. Furthermore, relaxor based ferroelectric single crystal piezoelectrics have been synthesised to create good piezoelectric properties [13]. Piezoelectric $Pb((Zn_{1/3}Nb_{2/3})_{0.91}Ti_{0.09})O_3$ single crystals 40 mm in diameter were successfully made by the Bridgman method. The electromechanical coupling coefficients for single crystal ceramics are 79–88%, which are larger than for conventional PZT ceramics, <70% [14]. Domain switching in ferroelectric single crystal ceramics under electromechanical loading has been investigated, and 90° domain switching zones were obtained near the crack tip, arising from the concentration of the electromechanical field [15]. The tensile stress due to polarization reorientation could cause crack growth under pure electrical loading [16], resulting in the change of piezoelectric properties. The strain characteristics caused by domain switching and reverse domain switching were experimentally investigated under mechanical loading [17]. Li and Rajapakse have successfully incorporated a switching assumption into the constrained domain switching model to account for the non-symmetry of their stress–strain curves [18].

From previous work, it appears that the domain orientation (or direction of the long tetragonal *c*-axis) can be changed by domain switching [19]. If there is reversible effect of domain switching, the domain orientation can be controlled by the mechanical applied load, and this could improve the piezoelectric properties. Hence, in the present work, an attempt has been made to control the domain orientation in PZT ceramics by the mechanical applied load. The piezoelectric properties of the PZT ceramics with domain structures orientated by electrically and mechanically applied load were further discussed.

## 2. Experimental

### 2.1. Material and experimental procedures

The material selected for the present study was a commercial soft tetragonal PZT ceramic of nominal composition $PbZrTiO_3$ made by Fuji Ceramics Corporation. The PZT ceramics were sintered at 1200 °C to give an average grain size of 5 μm, a density of 7.65 g/cm$^3$ and Curie point of 295 °C. Silver-based electroplated layers were attached to two sides of the specimens by a firing process in ambient atmosphere. In the present work, de-poled PZT ceramics were employed to make randomly orientated domain structures. The PZT ceramics adopt a perovskite tetragonal structure with aspect ratio $c/a = 1.014$ ($a = b = 0.4046$ nm and $c = 0.4103$ nm). The material properties of the PZT ceramics after polarization were measured by an impedance analyzer (Agilent Technologies, 4294A) giving: (i) effective elastic constant ($c_{33}^E$) 5.14 GPa, (ii) electromechanical coupling coefficient ($k_{33}$) 0.29, (iii) piezoelectric constant ($d_{33}$) 272 pm/v and (iv) dielectric constant ($\varepsilon_{33}/\varepsilon_0$) 5271). The piezoelectric properties, resonance frequency $f_r$, anti-resonance frequency $f_a$ and electrostatic capacity $C^T$ were measured by an impedance analyzer. In this case, $f_r$, $f_a$ and $k_{33}$ are expressed by

$$k_{33} = \sqrt{\frac{1}{a(f_r/(f_a - f_r)) + b}} \tag{1}$$

where $a$ and $b$ are coefficients depending on the vibration mode. On the other hand, the piezoelectric constant, $d_{33}$, can be described as:

$$d_{33} = k_{33}\sqrt{\frac{\varepsilon_{33}}{c_{33}^E}} \tag{2}$$

where $\varepsilon_{33}$ is the dielectric constant and $c_{33}^E$ is the elastic coefficient. These quantities are evaluated by the following formulas:

$$\varepsilon_{33} = \frac{C^T t}{A} \tag{2a}$$

$$c_{33}^E = (2lf_r)^2\rho \quad \text{for a rectangular shaped sample} \tag{2b}$$

where $t$ is the distance between the two electrodes, $A$ is the area of the electrode, $l$ is the length of the rectangular rod, and $\rho$ is the density of the PZT ceramic.

Fig. 1 shows a schematic illustration of the specimens. Two different rectangular shape specimens were employed for (a) the bending test and (b) the compressive test. The domain orientation for both specimens was examined in different regions, as indicated by the hatching in Fig. 1a and b. In this case, the domain orientations were investigated before and after the stress was applied. The X-ray diffraction system was employed to measure the domain orientation. In the XRD

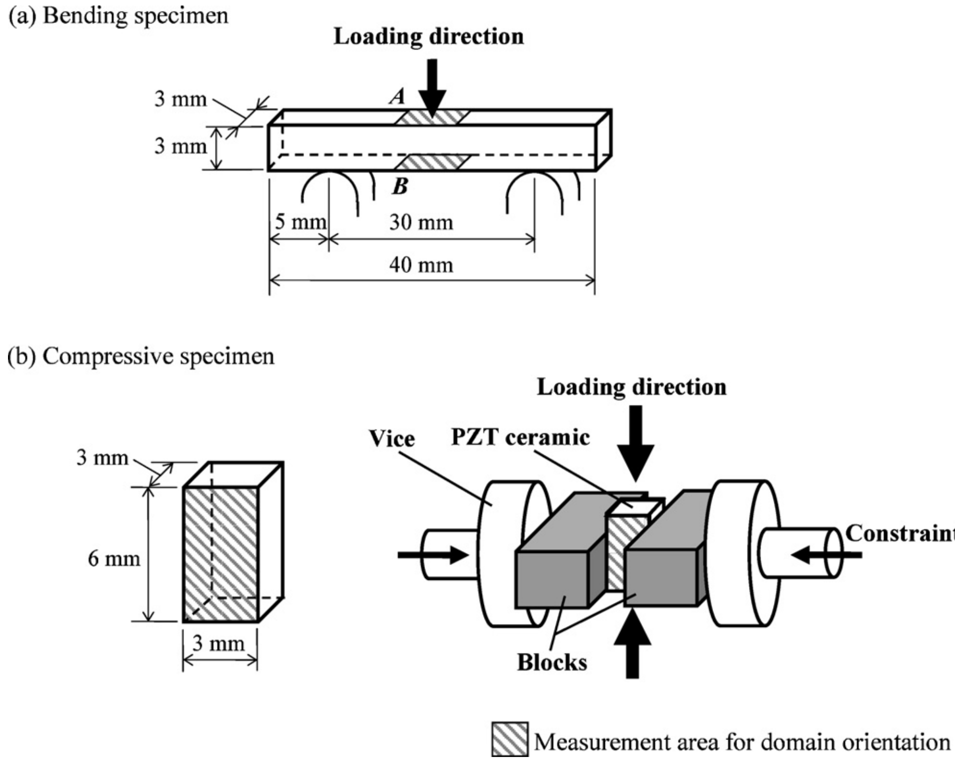


Fig. 1. Schematic diagrams of the specimen dimensions and experimental setup for (a) bending specimen and (b) compressive specimen.

analysis, an X'Pert Pro system (Panalytical Inc.) with a Cu tube source was utilized at 8 keV and $\lambda \sim 1.54$ Å.

The static bending and compressive loadings were performed in air with stroke control at 1 mm/min for the examination of the domain switching characteristics. The applied loading was conducted using a screw driven type EZ-Graph universal testing machine with 10 kN capacity (Shimazu Co.). The resolutions of the load and displacement in this testing machine are 0.01 N and 1 μm, respectively. The stress values were measured using a commercial load cell. The specimen surfaces were held using a special fixture to control the switching direction, as shown in Fig. 1b.

### 2.2. Finite element analysis (FEA)

Finite element analysis was conducted to examine the effect applied stress on the domain switching. In this analysis, stress–strain distribution was analyzed under plain strain criterion. The FE model was designed based on the bending specimen geometry shown in Fig. 1a. Two-dimensional finite element simulation with 4-noded elements was employed. The mesh size of the specimen, especially in the high stress region, was determined as small as 40 μm$^2$. The material properties of Young's modulus and Poison's ratio of the PZT ceramic were $Y_{33}$ = 49 GPa and $\nu$ = 0.32, respectively [20]. It should be noted first that the Young's modulus of $Y_{33}$ was selected in this analysis. The $Y_{33}$ is the modulus under the following criterion: the loading direction is parallel to the poling direction. The $Y_{33}$ value is about 20% smaller than the $Y_{11}$ value of this PZT ceramic ($Y_{11}$: the loading direction is perpendicular to the poling direction). In the previous works, the Young's modulus of the related PZT films has been examined by nanoindentation, where Young's modulus is apparently altered depending on the orientation direction [21,22].

## 3. Experimental results

### 3.1. Domain switching characteristics

Fig. 2 gives the X-ray diffraction analyses, showing the (2 0 0) and (0 0 2) peaks for the de-poled PZT ceramics (bending specimen) obtained in the tensile and compressive loading regions (Region *A* and *B*). In this case, the reorientation of the domains by 90° domain switching from the *c*- and *a*-direction can be identified and is given by the diffraction intensity ratio at the 2$\theta$ positions 43.63° and 44.88°. From Fig. 2, it is clear that different domain formation can be observed by the 90° domain switching. As the compressive stress is applied in Region *A*, the (2 0 0) peak decreases and the (0 0 2) peak increases. In contrast, the (2 0 0) peak increases and the (0 0 2) peak decreases in Region *B*. Such a change of domain switching pattern is affected by the different applied stress, i.e., compressive stress vs. tensile stress, as shown in Fig. 3.

Fig. 4 presents the X-ray diffraction analyses, showing the (2 0 0) and (0 0 2) peaks for the de-poled PZT ceramics (bending specimen) obtained at different positions. It is clear that the severity of domain switching is different. As seen, the 90° domain switching occurs most obviously near the loading position although the extent of domain switching is weakened in the measurement area far away from the loading position.

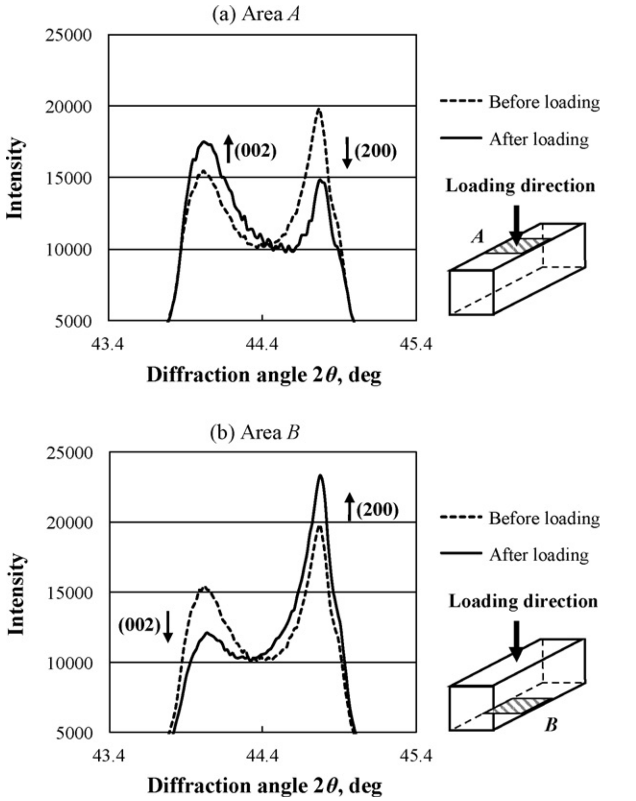


Fig. 2. X-ray diffraction profiles of de-poled bending specimens before and after applied loading in (a) Area $A$ and (b) Area $B$.

There is no clear domain switching in the both measurement areas (Area $A$ and $B$) more than 10 mm far away from the loading point. The reason for this is believed to be the reduction in the stress level. In a similar way to the results of Fig. 2, the domain switching direction is altered, depending on the stress direction.

To understand clearly the stress effect on the domain switching characteristic, a FE analysis was carried out. Fig. 5 displays the stress distribution ($\sigma_x$) of the bending specimen. As seen, the high stress level is distributed around the centers in Area $A$ and $B$, and the stress level decreases in the area far away from the loading position. The actual stress values obtained at 0 mm, 5 mm, 10 mm and 15 mm are computed by the following equations: $3Pl/bh^2$, where $P$ is applied load level; $l$ is beam span; $b$ is width of the specimen and $h$ is height of the specimen. The obtained values are summarized in Table 1. Because the domain switching occurs strongly near the loading position, i.e., less than 5 mm from the loading point, the stress value to make the domain switching could be estimated as more than 78 MPa. The stress value may be reasonable for the domain switching in PZT ceramics, as it is reported that domain switching is detected in the PZT ceramics under an applied load of 50 MPa [23].

Fig. 6a displays the variation of the intensity of the (2 0 0) and (0 0 2) peaks as a function of the compressive stress. Note the dashed lines in Fig. 6a are X-ray profiles for the electrically poled PZT ceramic. In this approach, the specimens in the unconstrained and constrained condition were employed, as shown in Fig. 1b. It should be pointed out that the sample cannot

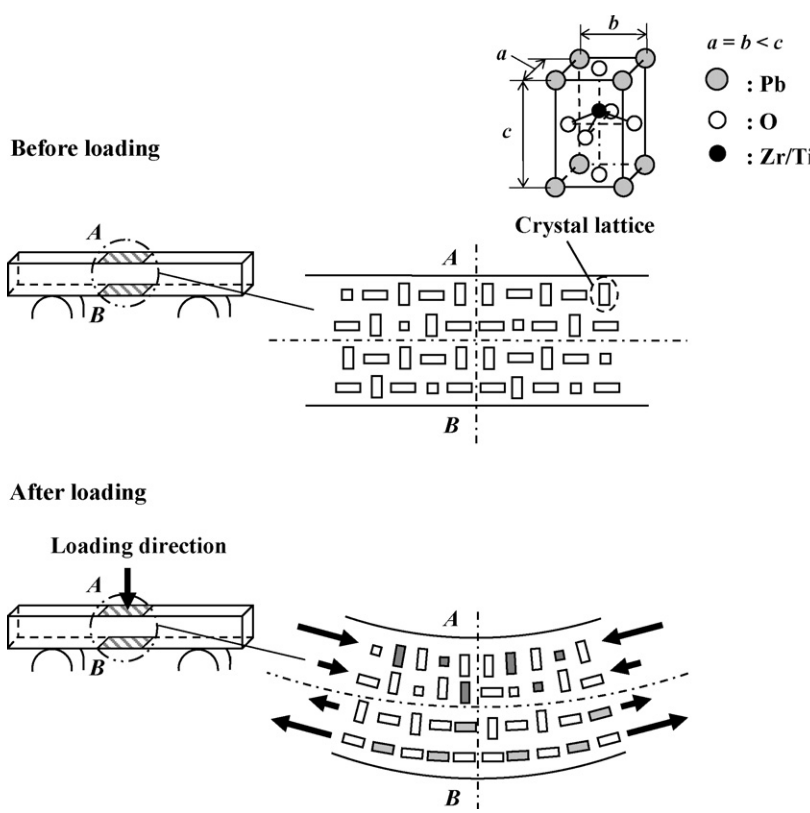


Fig. 3. Schematic illustration of the domain switching characteristics in the bending specimen before and after applied load.

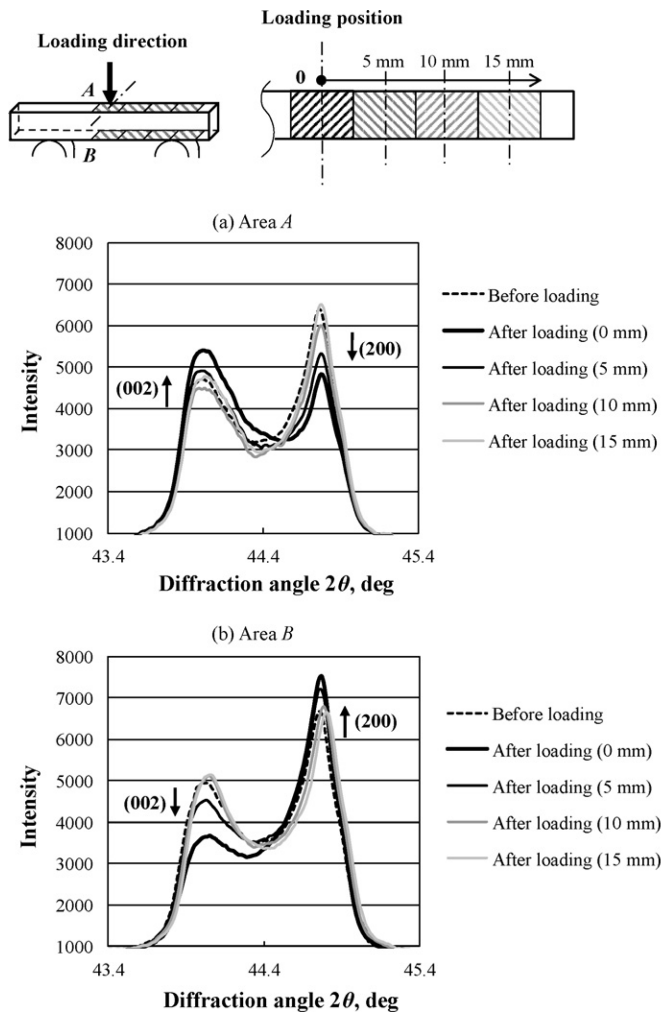


Fig. 4. X-ray diffraction profiles of de-poled bending specimens at different measurement positions on (a) Area *A* and (b) Area *B*.

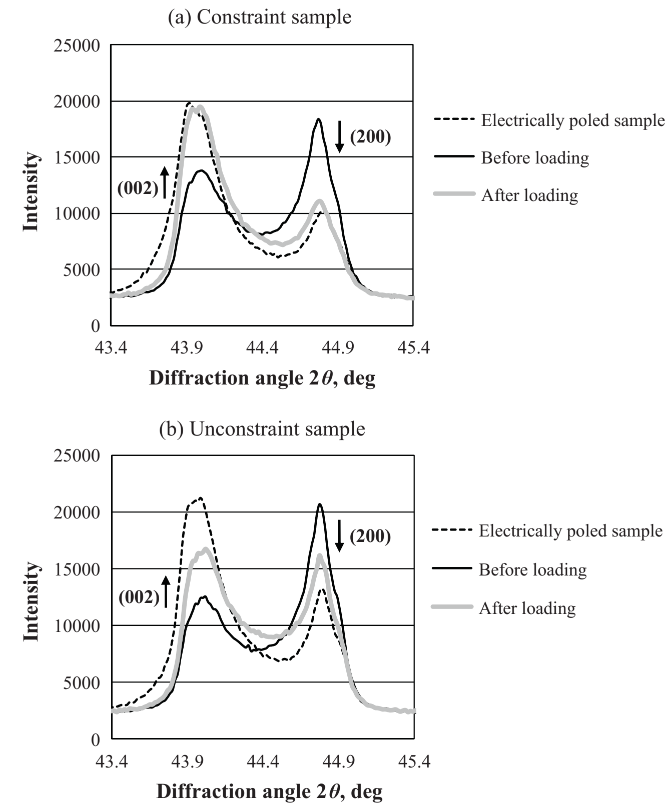


Fig. 6. X-ray diffraction profiles of de-poled compressive specimens before and after the loading process for (a) constrained and (b) unconstrained conditions.

be strained to the constraint surface directions, since the sample surfaces were firmly held by the high strength ceramics. As in Fig. 6a, a change of X-ray profiles is detected as a function of stress level. Significant 90° domain occurs with increasing applied stress, especially for the constrained sample, and the intensity of the (0 0 2) peak at maximum stress is almost equal to that for the electrically poled PZT ceramic. On the other hand, although improved domain orientation is detected for the unconstrained sample (Fig. 6b), the strongest peaks (2 0 0) and (0 0 2) are almost half the intensity of those for the electrically poled PZT ceramics. On the basis of this experimental approach, it is believed that the domain direction (*c*-axis) in the PZT ceramics can be readily orientated perpendicular to the loading direction, whereas the domain direction cannot be aligned to the constrained surface directions, as seen in Fig. 7. This result implies that the domain orientation can be controlled by the mechanical loading process.

With the domain orientation produced after the mechanical loading, the PZT ceramic may have excellent piezoelectric properties. To verify this, the piezoelectric properties of the PZT ceramics were investigated for the unconstrained and constrained samples used in Fig. 6. Fig. 8 represents the piezoelectric properties ($f_a$ and $f_r$). Even though distinct peaks at (2 0 0) and (0 0 2) are obtained, just like the electrically poled PZT ceramics, the piezoelectric properties cannot be seen

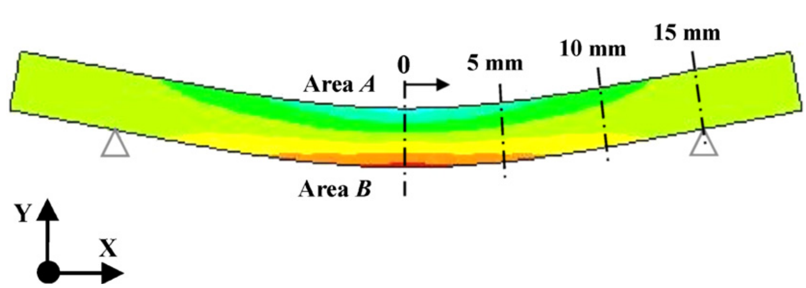


Fig. 5. Finite element stress distribution ($\sigma_x$) for PZT ceramics after bending loading.

Table 1
Finite element stress value ($\sigma_x$) at different positions in Fig. 5.

| Position, mm | Stress ($x$ axis), MPa | |
|---|---|---|
| | Area $A$ | Area $B$ |
| 0 | −117 | 117 |
| 5 | −78 | 78 |
| 10 | −39 | 39 |
| 15 | 0 | 0 |

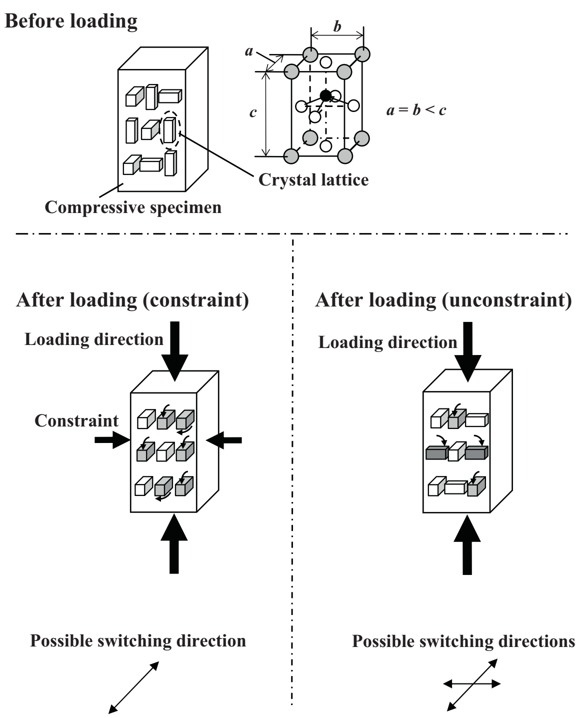


Fig. 7. Schematic illustration showing domain switching characteristics after compressive loading for unconstrained and constrained conditions.

clearly in both PZT ceramics. The reasons behind this are not clear at the moment, but it may be attributed to the constitution of the perovskite structure, possibly the position of the center ion in the perovskite structure. In this case, the long tetragonal $c$-axis direction would be confined to the same direction, but the

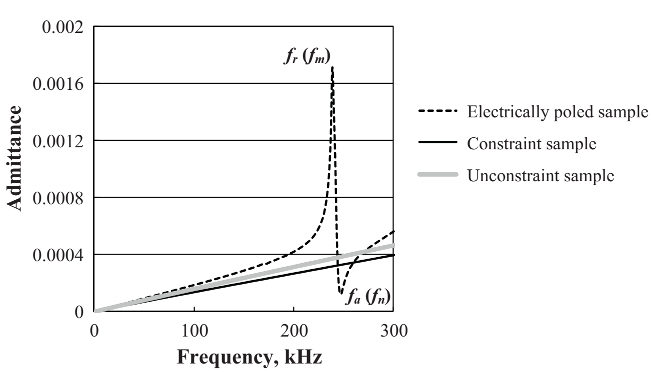


Fig. 8. Waveforms of admittance for the unconstrained and constrained samples after compressive loading.

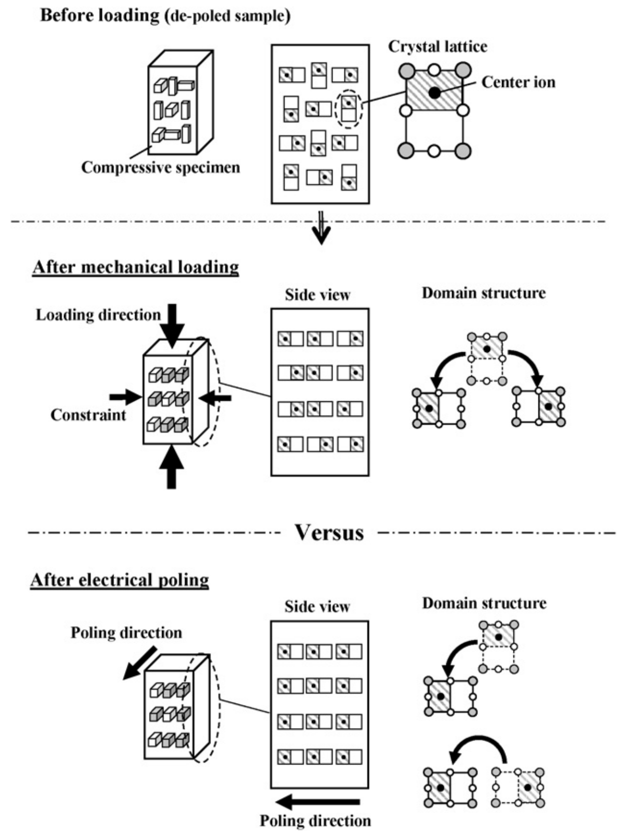


Fig. 9. Schematic illustrations showing the domain orientations after mechanical loading and the electrical poling processes. After both poling processes, the domain structures are aligned, but the position of the center ion is altered for the mechanical loading process.

position of the center ion in the perovskite structure could be altered in two possible ways (to the right-hand side or left-hand side). This is different compared to the PZT ceramic electrically poled one, as shown in Fig. 9. Further study will be required to understand clearly this in the future.

## 4. Conclusions

The domain switching characteristics of lead zirconate titanate (PZT) ceramics have been examined. Based upon the experimental results and discussion, the following conclusions can be drawn:

1) Different trends of domain switching pattern are obtained, depending on the stress direction. As the compressive stress is increased, the (2 0 0) peak decreases and the (0 0 2) peak increases. An opposite trend of domain switching pattern is detected in the tensile stress area, in which the (2 0 0) peak increases and the (0 0 2) peak decreases.
2) The domain switching occurs most significantly near the loading point, but the severity of the domain switching decreases in the measurement area far away from the loading position because of the reduction in the stress level.
3) The domain orientation (long tetragonal $c$-axis) can be aligned by the mechanical applied load. Although a clear peak at (2 0 0) and (0 0 2) appears, as with the electrically

poled PZT ceramic, the piezoelectric properties cannot be determined. The reason for this may be attributed to a randomized position of the central ion in the tetragonal perovskite structure.

## Acknowledgements

The authors would like to express the appreciation to Prof. F. Narita at Tohoku University for his helpful comments and suggestions on this work.

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