Piezoelectric properties of lead zirconate titanate ceramics at low and high temperatures

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ABSTRACT
The material properties and damage characteristics of lead zirconate titanate (PZT) ceramics were investigated at various temperatures. A positive voltage was obtained when the sample was cooled from 20°C to −190°C, while a negative voltage was obtained when the sample was heated from −190°C to 180°C. The difference between the positive and negative values depended on the thermal stress. Compressive stress generated a more positive voltage in the cooling process, while tensile stress led to a more negative voltage in the heating process. The voltage values also depended on the cooling (or heating) rate of the sample, e.g. the greater the cooling (or heating) rate, the greater the voltage. When cyclic loading was conducted mechanically at −190°C, the voltage reduced, but it was recovered after heating to 20°C. Damage of the PZT ceramic (90° domain switching) was detected when the sample was cooled to −190°C due to the high thermal stress.

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Introduction
Lead zirconate titanate (PZT: Pb(Zr,Ti)O₃) ceramics have seen widespread use in a large number of engineering applications, such as in various actuators for precision positioning, vibration suppression equipment, power transducers and vibration sensors. In these applications, PZT ceramics are sometimes used under severe conditions, e.g. at high (or low) temperatures and high humidity. Because the perovskite structure is highly crystalline, ferroelectric lead titanate films have recently been used at high temperatures [1]. Using X-ray diffraction analysis, the crystallization temperatures of piezoelectric ceramics of different chemical compositions, lead titanate (PT), lead zirconate (PZ) and PZT, have been shown to increase in the sequence PT < PZ < PZT at temperatures in the range of 380–500°C [2]. The piezoelectric properties of PZT worsen, resulting in a low value of $k_{33}$, as heating to the Curie temperature (300°C) occurs, due to a change of the lattice system from tetragonal to cubic [3]. The fabrication of capacitive ultrasonic transducers using surface micromachining techniques and a low-temperature process has been investigated [4]. The piezoelectric properties of PZT ceramics decrease when the sample is cooled. Zhang et al. [5] examined the dielectric and piezoelectric properties of PZT ceramics at temperatures from −268.8°C to 27°C. They found that the material properties converge as the temperature is decreased down to the temperature of liquid helium. Yakushev and Shalimov [6] reported that an improvement of the piezoelectric properties of PZT ceramics occurs with low temperature cyclic treatment. Various sensors made by PZT ceramics have been considered to employ for the performance and intrinsic characteristics of engineering devices. Wei et al. have examined the AE characteristics in liquid nitrogen, as the AE nondestructive testing method could be used to monitor the health of special vessels in the future, such as rocket tanks with liquid oxygen or hydrogen in space exploration [7]. Some researchers have examined the temperature-dependent behaviour of the piezoelectric properties in constitutive relations using a thermodynamic approach [8]. They found that the electrostriction coefficient is affected by the chemical composition. From our literature survey, the material properties of PZT ceramics under different conditions are significantly important to make design of PZT ceramics for various engineering devices. In particular, the temperature dependence of the piezoelectric properties of PZT ceramics under different conditions are significantly important to make design of PZT ceramics for various engineering devices. In particular, the temperature dependence of the piezoelectric properties of PZT ceramics plays a significant role in their design for engineering applications, although there is little information on this available. In particular, information about the change of the piezoelectric properties of PZT ceramics at low and high temperatures could be significant for the design process. Therefore, the material properties of PZT ceramics were investigated over
a wide temperature range under the static and cyclic loading.

Materials and experimental procedures

Piezoelectric ceramic

Figure 1 shows a schematic illustration of the piezoelectric ceramic and the experimental setup used in this work. The piezoelectric ceramics used were a commercial circular membrane PbZrTiO₃ base ceramic (φ25.0 mm × 0.23 mm) and a bulk PZT ceramic (5 mm × 3 mm × 3 mm), produced by Murata Manufacturing Co., Ltd and Fuji Ceramics Co., respectively. The circular membrane ceramic was attached to a thin brass plate (φ35.0 mm × 0.3 mm), and silver-based electrode plating was coated on its surface. The ceramic had a convex shape with a deflection value of 0.2 mm, see Figure 1(a). The material properties of the ceramic, brass and silver are as follows: (i) elastic constant (E): 82 [9], 103 and 82.7 GPa; (ii) thermal expansion coefficient (α): 17.5 × 10⁻⁶ K⁻¹, 7.5 × 10⁻⁶ K⁻¹, and 19.7 × 10⁻⁶ K⁻¹. The ceramic consisted of a tetragonal structure with aspect ratio c/a = 1.014. The nominal grain size of the ceramic was about 5 μm in diameter.

Experimental conditions

To examine the electric charge generation characteristics of the PZT ceramics, static and cyclic mechanical loading were applied using a screw-driven universal testing machine with 50 kN capacity (Shimadzu, AG-Xplus). Mechanical loading was applied at the centre of the sample, see Figure 1(b). Static loading was applied to the sample at 1 mm min⁻¹, and cyclic loading was applied with an R ratio of 0.05 with a frequency of 0.25 Hz. The maximum cyclic loading (Pₘₐₓ), was determined by the bending yield strength (Pᵧ) of the ceramic, so that Pₘₐₓ < 0.8 Pᵧ. The voltage generated from the ceramics was measured using a digital multimeter (8846A, Fluke). In this work, the mean maximum voltage was used as a parameter to evaluate electrical power generation. Details of this approach can be found elsewhere [10].

Figure 1. Schematic diagrams of (a) the PZT ceramic plate, (b) the mechanical loading process, and (c) the cooling and heating processes for investigating the voltage.
The piezoelectric properties were further investigated at various temperatures (−190°C to 180°C). The ceramic was cooled to the low temperatures using liquid nitrogen (20°C to −190°C), and heated to the high temperatures using a heater (20–180°C), as shown in Figure 1(c). A ceramic heater heated to about 800°C was used. To re-heat the sample from −190°C to 20°C, the sample was put into cold water. The different heating methods were used in order to change the heating rate.

**Failure analysis**

The microstructural and damage characteristics of the PZT ceramics were examined using electron backscatter diffraction (EBSD). The sample surfaces were polished to a mirror finish using colloidal silica. The EBSD analysis was executed using a JEOL-JSM-7001F SEM with an acceleration voltage of 15 kV, a beam current of 10 nA and a step size of 0.1 μm. The profiles of PZT plates at room temperature were measured using a stylus profilometer at 0.6 mm s⁻¹ (SURFCOM 1500DX2, Tokyo Seimitsu Co., Ltd); and those profiles at the low temperatures were measured using the screw-driven universal testing machine.

To understand the stress–strain characteristics at low temperature, finite element (FE) analysis was conducted using a software of Autodesk Inventor Professional 2020. In this analysis, three-dimensional FE simulation of the specimen geometry was executed using tetrahedral elements with mesh sizes 1.5 mm. The FE model was designed on the basis of the circular membrane PbZrTiO₃ base ceramic.

Poisson’s ratio for the PZT ceramic and brass plate were determined as ν = 0.32 and 0.35, respectively. Other material properties used in this analysis was shown in Section 2.1. Because of the different thermal expansion coefficient between PZT and brass, thermal stress generates with cooling process.

**Results and discussion**

**Static loading**

Figure 2 shows how the voltage (V) varied during static bending loading at −190°C and 20°C. The ceramics were loaded until a sample deflection of about 1.8 mm was achieved. As seen in the early loading stage at 20°C, the electric voltage increased to about 3.5 V, at which time the ceramic was deflected by 0.2 mm. With further loading, the voltage decreased to 0 and then with further loading still, generated a negative voltage. Similar variation of the voltage was seen at −190°C; however, the maximum voltage (about 2.7 V) was lower than that at room temperature, and a negative voltage was not obtained. The different positive and negative voltages were generated due to different amounts of stress. Differences in the voltages at −190°C and 20°C were related to the material properties, which will be discussed in a later section of this paper. It is interest to mention that the reduction of the voltage value occurs as the shape of the PZT plate is altered from convex to concave shape as illustrated schematically in Figure 2. The reason behind this is affected by the change of the stress direction in the PZT ceramic (from compressive to tensile stress).

Figure 3(a) shows the profile of the ceramic before and after bending loading. Note that profile is symmetrically indicated from the edge of ceramic to the centre one, indicated in Figure 3(a). The convex shape of the ceramic is formed at 20°C before the loading. The deflection of the convex shape is about 0.2 mm, as shown in Figure 1, but the profile is altered after the loading, which causes the ceramic to be deformed permanently to a concave shape, shown by the yellow lines. Compressive stress occurs early in the loading process due to the convex shape of the ceramic, while tensile stress is generated later in the process, because of the permanent deformation. This causes the voltage to change from positive to negative (Figure 2).

Figure 3(a) also shows the profile of the ceramic plate at −190°C before mechanical loading (see the blue dotted line). It can be seen that the ceramic is significantly bent with a convex shape, due to the high stress caused by the different thermal expansion coefficients of the brass plate and PZT ceramic. As severely bent PZT ceramic results in high compressive stress during the loading process, negative voltages were not obtained for the ceramic at −190°C, as shown in Figure 2. To verify the shape of the PZT ceramic at the low temperature, FE analysis was conducted. Figure 3(b) shows the deformation shape of the PZT ceramic at −190°C. As seen, the high strain is obtained...
on top of the PZT ceramic, resulting in the convex shape of the PZT ceramic.

Figure 4 shows how the maximum voltage varies as a function of the sample temperature. Figure 4(a) shows that the voltage increases to about 40 V immediately after the sample is put in liquid nitrogen and is cooled from 20°C to 0°C. Upon further cooling to about −100°C, the voltage is relatively stable. This may be an effect of heat insulation, due to the air gap created around the sample surface. The voltage increases to 100 V when the sample temperature is decreased from −120°C to −190°C, and the cooling rate increases to about −70°C s⁻¹. However, the voltage decreases to 0 when the sample temperature becomes stable at −190°C for a certain period of time, i.e. a spontaneous electric polarisation cannot be reversed in the presence of an electric field.

Figure 4. Variation of voltage with sample temperature: (a) cooling from 20°C to −190°C; (b) heating from −190°C to −20°C; and (c,d) heating from 20°C to 180°C.
When the ceramic, cooled to $-190^\circ C$, is put into water Figure 4(b), a negative voltage ($-80$ V) is generated rapidly in the temperature range of $-190^\circ C$ to $-150^\circ C$. This is followed by a decrease of the voltage during heating to $-20^\circ C$, while the rate of increase of the sample temperature decreases. In this case, the sample heating was stopped at $-20^\circ C$, as the electric voltage did not increase as heated more than $-20^\circ C$.

This could be due to the weak electric field of the PZT ceramic, i.e. the lower the heating rate, the lower the electric generation. Note that the reason for the negative electric voltage is considered to be the thermal tensile stress applied to the PZT ceramic.

The ceramic was further heated from $20^\circ C$ to $180^\circ C$ using the heater, and the voltage increased slowly without saturation, Figure 4(c). This is unlike the result of the heating process in water ($-190^\circ C$ to $-20^\circ C$). This reason is the low heating rate of about $10^\circ C$ s$^{-1}$ when using the heater ($20^\circ C$–$180^\circ C$). To verify this, the PZT sample was heated at $30^\circ C$ s$^{-1}$, and the obtained result is shown in Figure 4(d). From this, high electric voltage of about $-105$ V was detected, which is more than twice higher than that with the heating at $10^\circ C$ s$^{-1}$ (Figure 4(c)). Moreover, the high heating rate of $20^\circ C$ s$^{-1}$ ($-190^\circ C$ to $-20^\circ C$) made the high electric voltage (Figure 4(b)).

It is of interest to note that the rate of increase of the voltage changes at around $70^\circ C$, as indicated by the dashed circle. This may be due to a change in the lattice or material characteristics [11]. It is reported in our previous study [12] that the domain switching occurs during heating around $83^\circ C$, which is slightly

![Figure 5. Variation of the electric voltage generated by the PZT ceramic under cyclic loading at $-190^\circ C$ and $20^\circ C$.](image)

![Figure 6. EBSD analysis of the PZT ceramic before and after static loading, showing the 90° domain switching.](image)
higher than that for the present work. This may be caused by the different stress distribution arising from the different sample shape and different heating condition. However, there is no clear evidence of this, so further discussion will be required in the future.

**Cyclic loading**

The voltage was further investigated under cyclic loading at low temperatures (−190°C) and room temperature (before and after cooling to −190°C). Figure 5 shows the voltage obtained during the cyclic loading. Note first that the cyclic loading at −190°C was performed in liquid nitrogen. Figure 5 shows that a lower voltage was detected at the lower temperature ($V_{max} = 15$ V). This is about 70% lower than the voltage obtained at 20°C ($V_{max} = 45$ V). The low voltage at −190°C is due to the thermal stress at low temperatures, as shown in Figure 3. In previous work, piezoelectric properties were measured in a temperature range between −288.8°C and the Curie point on undoped and Fe-doped PZT samples, and a pronounced relaxation below 127°C occurred due to domain wall vibrations [13]. Zhang et al. have also examined dielectric and piezoelectric properties of modified lead titanate zirconate ceramics at temperatures between −288.8°C and 27°C, and piezoelectric properties, including the piezoelectric constant, worsened with decreasing sample temperature [5,14].

The voltage of the ceramic increases at 20°C after heating from −190°C (Figure 5(b)); however, the maximum voltage is slightly lower than that obtained before cooling to −190°C (see the red line vs. the blue dashed line). This may be attributed to damage of the ceramic (90° domain switching), arising from the high thermal stress. To verify this, the thermal stress of the ceramic was calculated. The different strain values ($\varepsilon$) caused by the different thermal shrinkages of the brass and the PZT ceramic result in high stress on the PZT ceramic. The thermal stress can be estimated using the formula $\varepsilon = \alpha \times \Delta T$. It is clarified using this formula that $\varepsilon_{PZT} = 0.0016$ and $\varepsilon_{brass} = 0.0037$. Knowing the different strain values, the thermal stress of the PZT ceramic can be calculated using the formula $\sigma = \varepsilon_{PZT} \times (E_{PZT} - \varepsilon_{brass})/2 = 82 \text{ GPa} \times 10^3 \times (-0.00105) = -86.1 \text{ MPa}$ (in compressive stress). In addition, the stress value was numerically analysed by FEA. The obtained mean normal stress in the PZT ceramic is found to be about −101.9 MPa, which is relatively in good agreement with the above calculation.

To examine whether or not 90° domain switching occurs in the PZT ceramic, an attempt was made to analyse the crystal orientation characteristics using the bulk PZT ceramic after compressive stress (86.1 MPa) was mechanically applied. The crystal orientations obtained before and after application of compressive stress are shown in Figure 6. The observations were made in the same area of the sample before and after loading. Figure 6 shows that the crystal orientations were changed after the application of compressive stress, and 90° domain switching occurred (see the pole figures with the lattice formations). From this result it can be inferred that the decrease of the electric voltage after the cooling process is influenced by material failure, i.e. domain switching. One of the authors has examined the domain switching characteristics using a similar PZT ceramic [15]. In that study, domain switching was detected when the bending loading was more than 0.8 $P_y$ (bending yield strength).

**Conclusions**

In this work, the material properties and damage characteristics of PZT ceramics were investigated under static and cyclic loading at low and high temperatures (−190°C to 180°C). The results can be summarised as follows:

1. A positive voltage was generated when the sample was cooled from 20°C to −190°C, whereas a negative voltage was generated when the sample was heated from −190°C to 180°C. The change in the voltage was attributed to different thermal stress, i.e. compressive stress of the ceramic generated the positive voltage, whereas tensile stress led to the negative voltage. The voltage was also affected by the cooling (or heating) rate of the sample, i.e. the greater the cooling (or heating) rate, the greater the voltage.

2. Upon cyclic loading, the voltage of the ceramic decreased when the sample was cooled to −190°C, although the voltage was recovered after heating the sample to room temperature (20°C). However, damage of the ceramic occurred when the sample was cooled to −190°C, due to high thermal stress (90° domain switching), which resulted in a reduction of the voltage.

**Disclosure statement**

No potential conflict of interest was reported by the author(s).

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