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Phase Transformation of PZST-86/14-5-2Nb Ceramic Under Quasi-Static Loading Conditions

Scott T. Broome, Stephen J. Bauer, Stephen T. Montgomery, Timothy W. Scofield, John H. Hofer

Prepared by
Sandia National Laboratories
Albuquerque, New Mexico 87185

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Scott T. Broome, Stephen J. Bauer, and John H. Hofer
Geomechanics Department

Stephen T. Montgomery
Solid Mechanics

Timothy W. Scofield
High Integrity SW Systems

Sandia National Laboratories
P.O. Box 5800
Albuquerque, NM 87185

Abstract

Specimens of poled and unpoled PZST ceramic were tested under hydrostatic loading conditions at temperatures of -55 , 25 , and 75°C . The objective of this experimental study was to obtain the electro-mechanical properties of the ceramic and the criteria of FE (Ferroelectric) to AFE (Antiferroelectric) phase transformations of the PZST ceramic to aid grain-scale modeling efforts in developing and testing realistic response models for use in simulation codes. As seen in previous studies, the poled ceramic from PZST undergoes anisotropic deformation during the transition from a FE to an AFE phase at -55°C . Warmer temperature tests exhibit anisotropic deformation in both the FE and AFE phase. The phase transformation is permanent at -55°C for all ceramics tests, whereas the transformation can be completely reversed at 25 and 75°C . The change in the phase transformation pressures at different temperatures were practically identical for both unpoled and poled PZST specimens. Bulk modulus for both poled and unpoled material was lowest in the FE phase, intermediate in the transition phase, and highest in the AFE phase. Additionally, bulk modulus varies with temperature in that PZST is stiffer as temperature decreases. Results from one poled-biased test for PZST and four poled-biased tests from PNZT 95/5-2Nb are presented. A bias of 1kV did not show noticeable differences in phase transformation pressure for the PZST material. However, with PNZT 95/5-2Nb phase transformation pressure increased with increasing voltage bias up to 4.5kV .

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1. Introduction

Mixed oxide ceramics based on compositional modifications of lead zirconate (PbZrO_3) are known to undergo ferroelectric (FE) to antiferroelectric (AFE) phase transitions on hydrostatic compression (Fritz and Keck, 1978). Extensive studies have been conducted to characterize the effects of temperature, stress, electric field, and fabrication method on a composition called PZT 95/5-2Nb, having the chemical formula $\text{Pb}_{0.99}\text{Nb}_{0.02}(\text{Zr}_{0.95}\text{Ti}_{0.05})_{0.98}\text{O}_3$, formed from PbZrO_3 and lead titanate (PbTiO_3) with ~2 mole% added niobium in order to provide a thorough understanding of phase transformations exhibited by this material needed to construct useful response models for analyzing ceramic responses seen in applications (Fritz and Keck, 1978; Zeuch *et al.* 1992, 1994, 1995, 1999a, b & c; Lee *et al.* 2003, 2004, 2006).

A rich structure of phases exists for PZT 95/5-2Nb ceramic (Avdeev *et al.* 2006). These phases are described relative to the high temperature cubic perovskite reference structure exhibited by pure PbTiO_3 and PbZrO_3 . Both crystals are paraelectric (PE) at high temperature. As PbTiO_3 is cooled below a certain temperature spontaneous displacements of Pb and Ti ions occur that distort the original unit cell and result in the formation of a permanent electric dipole within the crystal. One possible direction that can be taken by this dipole is along a body diagonal of the cubic unit cell and the FE is called the high temperature rhombohedral ferroelectric phase (F_{RHT}) due to the distortion of the unit cell produced. A similar circumstance occurs when PbZrO_3 is cooled below ~230 °C. Spontaneous displacements of the Pb and Zr ion occur and a complex pattern is formed for which spontaneous orthorhombic distortion and alternating charge displacements are produced on unit cell face diagonals. The number of PbZrO_3 formula units needed to describe the unit cell increases but no net electric polarization is produced in this case which is called the orthorhombic antiferroelectric phase (A_0). There is a modification of the F_{RHT} that occurs as the crystal is cooled below ~60 °C where positions of the oxygen ions surrounding the central Zr or Ti ion at the center of the unit cell are displaced. This displacement is most simply visualized as a ‘rigid’ rotation around the body diagonal of the unit cell and results in an increase in a doubling of the formula units needed to specify any distortions that slightly modify the magnitude of the spontaneous polarization resulting in a new phase called the low temperature rhombohedral ferroelectric phase (F_{RLT}). This description of phases in terms of distortions observed for pure crystal remains valid for PZT 95/5-2Nb which has compositional disorder produced by substituting roughly 5 mole% of the Zr ions with Ti ions.

Anomalous dielectric constant and loss measurements observed at transformations between the various phases described above were used to establish the first extensive pressure-temperature phase diagram for a single PZT 95/5-2Nb composition at pressures between 0 and 1,000 MPa and temperatures between -50 °C and 230 °C (Fritz and Keck, 1978). A transformation from the F_{RLT} to the A_0 was observed at ~300 MPa when the applied pressure was increased while holding the ceramic at room temperature. When the pressure was released, the reverse transformation, from the A_0 to the F_{RLT} , was seen to occur at a lower pressure of ~100 MPa on unloading. Cooling the ceramic from room temperature at ambient pressure produced a transformation from the F_{RLT} to the A_0 phase at about -20 °C, and then increasing the temperature recovered the F_{RLT} at a slightly higher temperature than produced the original transformation to the A_0 phase. Heating the ceramic from room temperature at ambient pressure

produced a transformation from the F_{RLT} to the F_{RHT} phase at about 60 °C. Continuing to heat the ceramic at ambient pressure eventually produced a transformation for the F_{RHT} phase to the PE phase at about 230 °C. Testing various pressure and temperature paths allowed mapping of the boundaries between the various phases for the ceramic. Significant hysteresis was observed in the location of the phase boundaries as pressure-temperature conditions traversed the phases. The least amount of hysteresis was seen in the PE- F_{RHT} and the PE- A_O phase boundaries. The F_{RLT} , F_{RHT} , and A_O phase boundary combinations appear to merge for pressures between 300 and 400 MPa and temperatures between 50 °C and 100 °C.

The transformation between the FE phases and the A_O phase is marked by a dielectric anomaly as well as a decrease in the volume and change in shape of the unit cell. Consequently, the phase transformation should be indicated by a decrease in the volume strain, occurring at the same time as a dielectric anomaly, and a possible dependence on shear stress. The next extensive series of tests on PZT 95/5-2Nb ceramic were conducted to examine these observations for various stress loading paths at room temperature (Zeuch *et al.* 1992, 1994, 1995, 1999a, b & c). Several different PZT 95/5-2Nb compositions formed by controlling material porosity through the additions of pore forming materials removed during ceramic firing were examined to understand the effect of porosity on the phase boundary measurements. It was established that the onset of the volume strain anomaly coincided with the anomaly in the dielectric constant for the onset of the F_{RLT} to A_O phase transformation. Also, it was determined that the onset of this transformation was modified by the shear stress present on the material and it was suggested that a maximum compressive stress dependent on crystal orientation could explain the results observed when components of shear stress were present. Consequently the mean stress at onset of the transformation was not generally equal to the corresponding pressure for the onset of the transformation under hydrostatic conditions. It was shown that increasing the porosity apparently lowered the pressure needed for the transformation under hydrostatic conditions as might be expected since the stresses in the solid matrix of the ceramic are magnified when the same pressure is applied to jacketed samples of ceramic with increasing porosity.

The role of shear stress, temperature, and electric field bias on the locations of the phase boundaries for various stress, temperature, and electric field conditions were examined in another series of studies (Lee *et al.*, 2003, 2004, 2006). These studies used various PZT 95/5-2Nb ceramics fabricated using newly developed methods for preparation of the ceramic powers (Voigt *et al.*, 1999). The tests characterized the effect of hydrostatic pressure, shear stress, and electric field on the phase transformation boundaries across a range of temperatures between -60 °C and 75 °C. The measurements of the phase boundaries obtained in these tests confirmed previous findings on the effect of temperature and shear stress. The effect of temperature, pressure, and shear stress were consistent with previous measurements but the specific values measured for different materials showed significant variation, perhaps due to a strong influence on spontaneous polarization due to subtle variations in stoichiometric composition. A new observation from these studies was that the apparent hydrostatic pressure required for the F_{RLT} to A_O transformation was increased by approximately 0.0168 MPa/V when the electric field was aligned with the initial direction of remnant polarization for two PZT 95/5-2Nb compositions with markedly different transformation pressure in the absence of an electric field bias (Lee and Montgomery, 2006).

In this study the effect of pressure, shear stress, temperature, and electric field on the phase boundaries for the mixed oxide compositions called PZST 86/14-5-2Nb, having the chemical formula $\text{Pb}_{0.99}\text{Nb}_{0.02}[(\text{Zr}_{0.86}\text{Sn}_{0.14})_{0.95}\text{Ti}_{0.05}]_{0.98}\text{O}_3$, formed from PbZrO_3 and lead titanate (PbTiO_3) with 14% of the Zr replaced by Sn and ~2 mole% added niobium. The pressure-temperature phase diagram for one ceramic fabricated with this composition has been established (Fritz and Keck, 1978). The primary objective of this work is to establish the stress-temperature phase boundary for a specific batch of PZST 86/14-5-2Nb ceramic and compare the results with the previous study. A new feature of study was a modification to the experimental loading used to include unload-reload paths in order to further illuminate the extent of the phase transformation under different conditions. Finally, the results of a small number of tests to examine the effect of an electric field bias at elevated temperature on the hydrostatic pressure on the transformation pressure for the F_{RLT} to A_{O} transformation is examined for this ceramic.

2. Sample Preparation and Characterization

2.1 Sample materials and preparations

The PZST ceramic specimens were manufactured by Honeywell. The average tested density of PZST material was 7.70 g/cm^3 . Two types of specimens were tested from PZST material. The first type was rectangular parallelepiped specimens fabricated from poled and unpoled slugs of PZST. The specimens have nominal dimensions of $10.8 \times 10.8 \times 25.4 \text{ mm}$. The dimensions fall within the range of nominal length-to-width ratio (2 to 2.5), which assures uniform stress and strain measured in the middle of the sample. The second type of specimen was referred to as a “wafer” and has nominal dimensions of $10.8 \times 2.5 \times 25.4 \text{ mm}$. The ends of all specimens were ground flat within 0.003 mm tolerance. All samples were visually inspected for significant flaws and general straightness of the surfaces. The physical dimensions of each specimen are listed in Table 1 with the assigned test types and conditions.

To create the poled PZST samples, an electrode silver paste (Dupont 7095) was applied to two opposing rectangular faces of the unpoled specimens. The specimens were then fired at 600°C for approximately 20 minutes. The electroded specimens were removed from the fire and “hot-poled” at 105°C under the electronic bias of 20 kV (Zeuch *et al.*, 1995; Yang *et al.*, 2003), corresponding to an electric field of approximately 2 kV/mm.

Typical instrumented specimens are shown in Figure 1a. On the left is a wafer sample with two pairs of orthogonal sets of axial and lateral strain gages mounted on opposite sides of the specimen (180° apart) at mid-height of the specimen. In addition, a smaller lateral gage is mounted on the thin edge. On the right is a rectangular parallelepiped with three pairs of orthogonal sets of axial and lateral strain gages mounted at specimen mid-height. The axial and lateral gages were oriented to be parallel and perpendicular to the axis of the specimen, respectively. The specimen assemblies were coated with an approximately 1-mm-thick impervious polyurethane membrane. The flexible membrane allowed the confining pressure to be applied uniformly to the surfaces of the specimen and at the same time, it prevented the confining fluid from infiltrating the specimen. To maintain uniform thickness of the membrane, the specimen was rotated in a lathe while the membrane cured. The specimen was aligned such that the centerline of the long axis of the assembly was oriented parallel with the axis of rotation of the lathe (Lee *et al.*, 2004).

For poled specimens (Figure 1b), additional strain gages were mounted on the electroded faces of the specimen, enabling measurements of lateral strain normal (ϵ_l – normal to poling) to, as well as parallel (ϵ_l – parallel to poling) with the poling direction. The discharge voltage and current that occurs during the phase transformation was measured directly from the sample faces using the wiring shown in Figure 1b. The confining pressure was measured using a pressure transducer mounted on the hydraulic line used to pressurize the hydraulic fluid in the vessel.

Table 1 List of mechanical tests conducted for PZST ceramic.

Specimen	Polarization	Test	T	$\sigma_1 - \sigma_3$	Length	Width	Height	Weight	Density
no.	type	type	(° C)	(MPa)	(cm)	(cm)	(cm)	(g)	(g/cm ³)
PZST 95 #1	Unpoled	HC	25	0	1.0795	1.0795	2.5451	22.822	7.69
PZST 95 #2	Unpoled	HC	25	0	1.0795	1.0808	2.5451	22.820	7.69
PZST 95 #4	Unpoled	HC	-55	0	1.0795	1.0795	2.5425	22.827	7.70
PZST 95 #5	Unpoled	HC	-55	0	1.0808	1.0782	2.5425	22.774	7.69
PZST 95 #6	Unpoled	HC	75	0	1.0795	1.0795	2.5438	22.815	7.70
PZST 95 #7	Unpoled	HC	75	0	1.0795	1.0795	2.5438	22.816	7.70
PZST 95 EX #12	Unpoled	HC	25	0	1.0795	1.0820	2.5425	22.837	7.69
PZST 95 EX #13	Unpoled	HC	25	0	1.0795	1.0795	2.5451	22.851	7.70
PZST 95 #A	Poled	HC	25	0	1.0833	1.0808	2.5387	23.080	7.76
PZST 95 #B	Poled	HC	25	0	1.0846	1.0808	2.5400	23.052	7.74
PZST 95 #C	Poled	HC	25	0	1.0795	1.0820	2.5400	23.072	7.78
PZST 95 #D	Poled	HC	-55	0	1.0770	1.0820	2.5400	23.094	7.80
PZST 95 #E	Poled	HC	-55	0	1.0770	1.0820	2.5400	22.978	7.76
PZST 95 #G	Poled	HC	75	0	1.0795	1.0820	2.5400	23.102	7.79
PZST 95 #H	Poled	HC	75	0	1.0795	1.0820	2.5400	23.093	7.78
PZST 95 EX #A	Poled	HC	25	0	1.0795	1.0795	2.5425	22.772	7.69
PZST 95 EX #B	Poled	HC	25	0	1.0795	1.0795	2.5425	22.875	7.72
PZST W1	Poled	HC	25	0	1.0770	0.2515	2.5425	5.235	7.60
PZST W2	Poled	HC	25	0	1.0795	0.2553	2.5451	5.328	7.60
PZST W4	Poled	HC	25	0	1.0795	0.2540	2.5438	5.336	7.65
PZST W3C	Poled	HC	-55	0	1.0795	0.2553	2.5451	5.335	7.61
PZST W5C	Poled	HC	-55	0	1.0795	0.2540	2.5451	5.336	7.65
PZST W6C	Poled	HC	-55	0	1.0795	0.2540	2.5451	5.331	7.64
PZST W7C	Poled	HC	-55	0	1.0820	0.2540	2.5451	5.342	7.64
PZST W10	Poled/1Kv bias	HC	25	0	1.0795	0.2540	2.5400	5.448	7.82

HC-Hydrostatic Compression

 σ_1 -major principal stress (axial stress); σ_3 -minor principal stress (confining pressure)

Figure 1 Typical poled PZST specimens. The wafer on the left is instrumented with two pairs of axial and lateral strain gages and a third lateral gage on the thin edge. On the right the rectangular parallelepiped is instrumented with three pairs of axial and lateral strain gages. The assembly is coated with a polyurethane membrane to prevent the confining fluid from infiltrating into the specimen (a); Configuration of strain gages with respect to poling direction and measurement of discharge voltage for poled specimen. Lateral strain measurements normal and parallel to polling are shown (b).

2.2 Experimental set-up and procedure

An externally cooled High-Pressure Low-Temperature (HPLT) triaxial pressure vessel (Zeuch et al., 1999d) was used to test the electromechanical responses of PZST ceramics under hydrostatic conditions. The same triaxial pressure vessel has been used to characterize other materials such as ALOX (Alumina Loaded Epoxy) and frozen soil (Lee et al., 2002). The pressure vessel is composed of HP 9-4-20 alloy steel and equipped with twelve coaxial feed-throughs. The vessel is capable of operating at a temperature range of -65 to 150 °C and confining pressures up to 500 MPa. Figure 2 shows the schematic of the load frame and instrumented PZST specimen with the HPLT triaxial pressure vessel. Owing to the extreme operating conditions in pressure and in

temperature and the likelihood of high piston-seal friction, the HPLT vessel is equipped with high-pressure feed-throughs allowing internal load and strain measurements to be made.

To achieve the lower testing temperatures, the pressure vessel was externally cooled by circulating liquid nitrogen through conduits mounted on the outside of the vessel. Elevated testing temperatures were obtained through the use of an internal heating coil that surrounded the specimen. Temperatures were measured inside the pressure vessel next to the sample by a single type K thermocouple. Internal data collected during testing consist of pressure, axial and lateral strains, and temperature. Discharge voltage and current including the aforementioned data were measured for the poled specimens. The data were transmitted from the internal transducers via electrical leads connected to coaxial feed-throughs and then to a data acquisition/control system located next to the testing system.

Figure 2 Externally cooled High-Pressure-Low-Temperature (HPLT) cell and an assembly of PZST specimen.

2.3 Hydrostatic loading path

Figure 3 shows the appropriate loading path for hydrostatic (HC) testing in terms of the maximum (σ_1) and the minimum (σ_3) principal stresses, respectively. Using a Mohr diagram (inset in graph in Figure 3) we can also show variations of mean stress (the center of the Mohr circle) and the shear stress (radius of the circle). In this report, the so called “rock mechanics sign convention” is utilized. That is, forces and displacements are reckoned positive when compressive (Jaeger and Cook, 1979). For the HC loading condition, the principal stresses were all equal, but simultaneously increasing ($\sigma_1 = \sigma_2 = \sigma_3 = P$). The line, denoted HC, in Figure 3 shows the stress path for the hydrostatic compression test. As shown in the Mohr diagram for HC, σ_1 , σ_3 and the mean stress σ_m are always equal. During HC testing, σ_m is increased while τ is suppressed.

Figure 3 Hydrostatic loading path designed for characterization of the electro-mechanical responses of PZST shown in the principal stress domain. The stress condition is also shown in the Mohr diagram.

3. Experimental characterization of unpoled PZST ceramic

3.1 Hydrostatic compression test

The mechanical behavior of unpoled PZST under hydrostatic loading was studied using a pressure (P)-volumetric strain (ϵ_v) plot. The test records for all tested specimens are shown in Appendix A. The hydrostatic pressure ($\sigma_1=\sigma_2=\sigma_3=P$) was applied at a constant rate (~ 0.69 MPa/s) up to ~ 500 MPa. At a specific hydrostatic pressure (P_u^H), the PZST ceramic undergoes a phase transformation from a FE rhombohedral perovskite structure to an AFE orthorhombic structure. The acronym for the phase transformation pressure consists of a subscript **u** or **p** representing the unpoled or poled ceramic and a superscript **H** for hydrostatic test type. The first segment of the P- ϵ_v plot, defined by a straight line with a bulk modulus of K_F as a slope, represents the mechanical behavior of PZST in the FE phase (Figure 4). This linear increase of ϵ_v as a function of P continues until the hydrostatic pressure reaches the critical phase transformation pressure P_u^H and the corresponding volumetric strain ϵ_{vu}^H . This phase transformation at critical pressure is marked by a sudden increase in volumetric strain (or reduction in volume), shown as a nearly horizontal line, by 0.4 to 0.6%. After completion of FE to AFE phase transformation, the P- ϵ_v plot shows a rather straight line with a bulk modulus K_A as a slope in the AFE phase. The point where phase transformation occurs (ϵ_{vu}^H, P_u^H) is determined quantitatively by finding the intersection of the initial slope (K_A region) and transformation slope (K_{F-A} region) on the P- ϵ_v plot and is illustrated in Figure 4.

Hydrostatic compression experiments, carried out on unpoled PZST ceramic, were performed across the FE-AFE boundary at three temperatures. The temperatures were -55 , 25 , and 75°C and all tests went above 400 MPa pressure (400 MPa is well above the phase transformation pressure). Figure 4 shows a typical record obtained at an ambient temperature of 25°C . The unpoled PZST underwent a distinct FE to AFE transformation at a hydrostatic pressure of approximately 255 MPa.

During pressurization, temperature inside the pressure vessel increased and during depressurization, the temperature decreased. Because the system is not adiabatic, heat is lost to the environment during pressurization and consequently the temperature inside the pressure vessel is colder at the end of testing than at the start. Table 2 shows the minimum and maximum temperatures and the corresponding range of temperature during the test for all -55 and 75°C tests. Temperature was not recorded for tests at 25°C but the temperature behavior described above is observed for tests conducted at -55 and 75°C and is illustrated on temperature versus pressure plots in the appendices.

A Eurotherm MTS 409.80 temperature controller was used for -55°C tests and a Watlow Series 965 temperature controller was used for 75°C tests. Each controller had difficulty maintaining a constant temperature during the test because of the large thermal mass of the pressure vessel. For example, when the highest pressure was reached for a -55°C test, the controller would have the most liquid nitrogen supplied to cool the sample in order to mitigate heating of the confining

fluid from the increase in pressure. When the pressure ramp decreased, the temperature controller would overshoot and not turn off the cooling supply soon enough. Combined with the delay involved with the large thermal mass of the pressure vessel, the vessel continued cooling well into the depressurization ramp. By the time the pressure was at zero, the ending temperature was always colder than the starting temperature. This is true for tests at -55 and 75 °C. This most likely occurred for the ambient temperature tests, but without a recorded temperature the magnitude is unknown. In addition to the temperature trends described above, the temperature/pressure plots in the appendices show variable temperature behavior during pressurization and depressurization. Some of this behavior correlates to the unload/reload loops performed periodically throughout the test. The remainder is due to limitations of the temperature controller. Temperature ranges shown in Table 2 are high for three of the four 75°C tests compared to the rest of the tests. The Watlow Series 965 temperature controller malfunctioned after the first 75°C test and subsequent tests had manual temperature control.

Figure 4 Quantitative description of phase transformation in unpoled PZST under hydrostatic loading. Initiation of phase transformation is represented by the point shown by the volumetric strain ϵ_{vu}^H and P_u^H . K_F , K_{F-A} , and K_A represent the bulk modulus of the ceramic in FE phase, during phase transformation, and AFE phase respectively.

Table 2 Summary of temperature history for -55 and 75°C tests on PZST

Specimen no.	Min temp	Unpoled Max temp	Range	Min temp	Poled Max temp	Range
PZST #4	-69	-49	20			
PZST #5	-62	-46	16			
PZST #6	57	82	25			
PZST #7	43	102	59			
PZST #D				-64	-45	19
PZST #E				-71	-48	23
PZST #G				64	95	31
PZST #H				43	91	48
PZST W3				-70	-35	35
PZST W5				-73	-48	25
PZST W6				-63	-40	23
PZST W7				-62	-37	25
Average cold	-66	-48	18	-67	-42	25
Average hot	50	92	42	54	93	40

Unload/reload loops were performed throughout the test for all unpoled material. Bulk modulus was calculated from the slope of the unload portion of the unload/reload loops. The bulk modulus of the material was grouped into three categories: 1) Before phase transformation (K_F), during phase transformation (K_{F-A}), and after phase transformation (K_A). Figure 4 illustrates these regions and has an example slope shown for bulk modulus determinations for each region. The average bulk modulus was calculated for each region for each test and is shown in Table 3 and illustrated in Figure 5. For each region, (K_F , K_{F-A} , and K_A), bulk modulus increases with decreasing temperature and more specifically, the increase in bulk modulus is approximately linear with temperature. Additionally from Table 3, the bulk modulus is lowest in the K_F phase, intermediate in the K_{F-A} phase and highest in the K_A phase.

Table 3 Summary of Bulk Modulus for Unpoled Hydrostatic tests on PZST

Specimen no.	Polarization	T (°C)	Average K_F (GPa)	Average K_{F-A} (GPa)	Average K_A (GPa)
PZST #4	Unpoled	-55	74.11	118.46	105.14
PZST #5	Unpoled	-55	92.57	111.30	120.46
PZST #1	Unpoled	25	77.12	88.73	95.76
PZST #2	Unpoled	25	71.00	79.07	93.60
PZST EX #12	Unpoled	25	75.88	84.52	95.74
PZST EX #13	Unpoled	25	77.97	85.79	100.35
PZST #6	Unpoled	75	68.82	74.91	85.48
PZST #7	Unpoled	75	62.21	81.04	103.21

Figure 5 Average bulk modulus of unpoled PZST in K_F , K_{F-A} , and K_A regions plotted against three test temperatures (-55, 25, and 75°C).

Figure 6 shows a typical pressure-volumetric strain record obtained for PZST material at a temperature of -55°C. At this temperature, the transition from FE to AFE phase in PZST is rather abrupt compared to the transition at ambient and higher temperatures. Upon depressurization, the volumetric strain did not recover following the downward slope of K_A (bulk modulus in AFE phase). At the low temperature condition, the phase transformation was irreversible from AFE to FE when the applied hydrostatic pressure was removed. At ambient and high temperatures (e.g. Figure 4), the FE to AFE transformation was reversible and the PZST ceramic recovered almost all of the volume reduction it exhibited earlier in the test. Each of the P - ϵ_v test plots of all eight unpoled ceramics are shown in Appendix A1.

Variation of pressure required for the onset of FE to AFE phase transformation depends on temperature. As shown in Figure 7, the average phase transformation pressure, P_U^H , is slightly higher (258 MPa) at 25°C than at -55°C (250 MPa). At 75°C the average P_U^H is the lowest of the three temperatures measured (200 MPa). Variation of P_U^H with respect to temperature is not stated due to the limited data set and trend of the average data at the three temperatures tested. More testing at different temperatures would validate the use of a best fit curve. Although data is limited to three temperatures, there appears to be a local maximum P_U^H between -55 and 75°C. This does not corroborate previous findings in PNZT ceramic (Lee et al., 2003, 2006) where generally the phase transformation pressure increases with temperature following a second-order polynomial function.

Figure 6 Pressure versus Volumetric Strain obtained during hydrostatic compression of unpoled PZST #4 at a temperature of -55°C.

There was an observed decrease in the bulk moduli with increasing temperature in PNZT ceramics (Lee *et al.*, 2003) and in general we have observed the same trend with PZST (Figure 9 and Table 3). A detailed quantitative description of phase transformation in the unpoled PZST ceramics under hydrostatic loading is summarized in Table 4.

Figure 7 Superimposed pressure versus volumetric strain (ϵ_v) plots for the hydrostatic compression tests on unpoled PZST specimens at temperatures ranging from -55 to 75°C .

Figure 8 Phase boundaries of unpoled PZST ceramic at three temperatures (-55, 25, and 75°C) versus pressure. (P_u^H – Phase transformation pressure under hydrostatic compression for unpoled PZST).

Figure 9 Superimposed pressure versus volumetric strain (ϵ_v) plots for the hydrostatic compression tests on unpoled PZST specimens in ferroelectric (FE) phase at temperatures ranging from -55 to 75°C . Initial bulk modulus values are represented by the slopes of the lines as quantified in the equations.

Table 4 Summary of hydrostatic compression (HC) tests on unpoled PZST.

Sample #	Unpoled P_u^H	Unpoled ϵ_{vU}^H	Temp. ($^\circ\text{C}$)
PZST #1	260	0.00369	25
PZST #2	259	0.00374	25
PZST #4	252	0.00318	-55
PZST #5	255	0.00251	-55
PZST #6	210	0.00314	75
PZST #7	211	0.00278	75
PZST EX #12	270	0.00364	25
PZST EX #13	271	0.00374	25

P_u^H – pressure for FE-to-AFE phase transformation under hydrostatic compression
 ϵ_{vU}^H – volumetric strain at P_u^H

4. Experimental characterization of poled PZST ceramic

4.1 Hydrostatic compression test

In poled PZST, the electric field used for polarization causes an adaptation of the ferroelectric domain structure within the material, for which the spontaneous polarization within the domain is aligned more closely to the direction of the electric field. Internal stress and grain boundary clamping within the ceramic prevent perfect alignment of the ferroelectric domains with the applied field. As a consequence, when the electric field is removed, a remnant polarization having a value less than that of the spontaneous polarization in the ferroelectric domain remains and binds charge to electrodes on the surface of the ceramic. If the hydrostatic pressure is increased past the critical pressure required for phase transformation to AFE state, the bound charge is released to generate current and voltage.

Figure 10 shows typical strain versus pressure plots under increasing hydrostatic pressure for the poled PZST #B specimen. All tests on poled PZST were conducted into low impedance circuits and consequently no significant electric fields were generated within the material. The axial strain (ϵ_a) was measured by either a pair or three strain gages. The response of each strain gage was similar, and is observable in the plot. Also shown are the values of the lateral strain measured parallel ($\epsilon_{l\text{-parallel to poling}}$) and normal ($\epsilon_{l\text{-normal to poling}}$) to the poling direction. A few samples used two lateral strain gages parallel to poling and one normal to poling. The configuration of strain measurements with respect to loading and poling directions are shown in Figure 1b.

Similar to the unpoled PZST ceramic, the poled ceramic indicates a transition from a FE rhombohedral perovskite structure to an AFE orthorhombic structure by a sudden increase in strain. The sudden increase in strain is shown as horizontal lines in Figure 10. The phase transformation pressures for all strains were equal for PZST tested at -55°C . At 25 and 75°C the phase transformation pressure for all strains is similar except for $\epsilon_{l\text{-parallel to poling}}$ which is slightly lower than the other strains.

The poled PZST ceramic shows a deviation from the typical response of the unpoled ceramic in that it demonstrates anisotropic strain behavior in the AFE phase and slightly anisotropic strain behavior in the FE phase for tests conducted at 25 and 75°C . Tests at -55°C displayed strain anisotropy only in the AFE phase. In the case of the poled PZST, $\epsilon_{l\text{-parallel to poling}}$ was greater than $\epsilon_{l\text{-normal to poling}}$ by approximately 32% (Figure 10). This distinctive and repeatable anisotropic strain behavior is caused by a preferred crystallographic orientation and locked-in, intra- and inter-granular strains created by poling (Zeuch *et al.*, 1999a). The degree of anisotropy of the PZST ceramic in lateral strains was approximately the same as the one obtained for different batches of PZST during previous experiments (Zeuch *et al.*, 1995 for HF424 and Lee, 2004 for PNZT).

Figure 11 shows the strain histories under increasing and decreasing hydrostatic pressures for the same specimen PZST #B shown in Figure 10. The FE to AFE transition is marked by the vertical lines at the depoling pressure, P_p^H . In this time-base plot, the anisotropic strain response of the poled PZST in AFE phase is represented as $\epsilon_{l\text{-parallel to poling}}$ showing about 32% higher than $\epsilon_{l\text{-normal to poling}}$. In the FE phase, differences among all axial strain and lateral strain normal to poling are insignificant indicative of isotropic strain behavior. However, lateral strain parallel to poling exhibits anisotropic strain behavior in both the FE and AFE phases for 25°C and higher temperature tests.

Figure 10 Anisotropic strain behavior in antiferroelectric phase of the poled PZST #B specimen under a hydrostatic loading condition (ϵ_a – axial strain; $\epsilon_{l\text{-parallel to poling}}$ – lateral strain parallel to poling direction, and $\epsilon_{l\text{-normal to poling}}$ – lateral strain perpendicular to poling direction).

In poled PZST ceramics, the charge release, measured across the poling direction at depoling pressure, can be used to confirm the FE to AFE phase transformation. As the hydrostatic pressure is reaching the critical pressure, the volumetric strain ($\epsilon_v = \epsilon_a + \epsilon_{l\text{-parallel to poling}} + \epsilon_{l\text{-normal to poling}}$) suddenly increases at the phase transformation pressure, P_p^H . At the same time the poled ceramic discharges the bound charge showing as another straight line in the discharge versus pressure plot. Figure 12 confirms that sudden increases in ϵ_v and discharge voltage were observed at the exact same P_p^H .

Figure 11 Strain histories of the poled PZST #B specimen under a hydrostatic loading condition. The initiation of phase transformation is represented by a sudden increase in strains (ϵ_a – axial strain; $\epsilon_{l\text{-parallel to poling}}$ – lateral strain parallel to poling direction, and $\epsilon_{l\text{-normal to poling}}$ – lateral strain perpendicular to poling direction). The spikes in Axial Strain 2 were caused by feed through problems in the test system.

Unload/reload loops were performed throughout the test for all poled material. Bulk modulus was calculated from the slope of the unload portion of the unload/reload loops. The bulk modulus of the material was grouped into three categories: 1) Before phase transformation (K_F), during phase transformation (K_{F-A}), and after phase transformation (K_A). The average bulk modulus was calculated for each region for each test and is shown in Table 5 and illustrated in Figure 13. Linear best fit lines are shown in Figure 13 to illustrate that as temperature increases, the material becomes less stiff. The best fit lines are drawn only when three temperature data sets exist. For each region, (K_F , K_{F-A} , and K_A), bulk modulus increases with decreasing temperature. From 25°C to -55°C the PZST material exhibits a large increase in stiffness whereas from 75°C to 25°C the increase in stiffness is minimal except in the K_F region where the 75°C tests are much less stiff than the 25°C tests. Additionally from Table 5, the bulk modulus is lowest in the K_F phase, intermediate in the K_{F-A} phase and highest in the K_A phase.

Figure 12 Volumetric strain (ϵ_v) versus pressure and discharge voltage versus pressure plots for the poled PZST #B specimen under a hydrostatic loading condition. The initiation of phase transformation is represented by a sudden increase in volumetric strain and discharge voltage.

Table 5 Summary of bulk modulus for poled-unbiased hydrostatic tests on PZST.

Specimen no.	Polarization	T (°C)	Average K_F (GPa)	Average K_{F-A} (GPa)	Average K_A (GPa)
PZST #D	Poled	-55	90.65	N/A	119.25
PZST #E	Poled	-55	90.90	N/A	125.57
PZST #A	Poled	25	81.21	94.21	107.85
PZST #B	Poled	25	79.67	93.54	108.03
PZST #C	Poled	25	79.36	86.13	106.71
PZST EX #A	Poled	25	78.56	86.49	101.78
PZST EX #B	Poled	25	78.80	88.00	102.97
PZST #G	Poled	75	64.52	93.97	102.26
PZST #H	Poled	75	67.47	87.22	98.33
PZST W3C	Poled	-55	78.43	N/A	121.60
PZST W5C	Poled	-55	84.94	94.04	105.23
PZST W6C	Poled	-55	80.93	N/A	109.60
PZST W7C	Poled	-55	87.40	N/A	104.66
PZST W1	Poled	25	73.82	78.29	90.43
PZST W2	Poled	25	80.66	98.57	108.50
PZST W4	Poled	25	80.76	87.54	90.93

N/A-no unload/reload loops were conducted in this region.

Figure 13 Average bulk modulus of poled-unbiased PZST in K_F , K_{F-A} , and K_A regions plotted against three test temperatures (-55, 25, and 75°C).

As shown in Figures 14, 15, and 16, the average depoling pressure, P_P^H , is higher (293 MPa) at 25°C than at -55°C (274 MPa). At 75°C the average P_P^H is the lowest of the three temperatures measured (221 MPa). Variation of P_P^H with respect to temperature is not stated due to the limited data set and trend of the average data at the three temperatures tested. Although data is limited to three temperatures, there appears to be a local maximum P_P^H between -55 and 75°C. This differs with previous findings in “mixed-oxide” ceramic (Lee et al., 2003, 2006) where generally P_P^H increases with temperature following a second-order polynomial function. More testing at different temperatures would validate the use of a best fit curve and establish a relationship between temperature and P_P^H .

Erratic strain behavior after phase transformation is present primarily in cold data as seen in Figures 14 and 15. This behavior is due either to strain gage delamination or feed through signal loss. Each test is presented in detail in Appendix B.

Figure 14 Superimposed volumetric strain (ϵ_v) versus pressure plots for the hydrostatic compression tests on poled-unbiased PZST specimens at temperatures of -55 , 25 , and 75°C .

Variations of bulk moduli K_F in poled PZST ceramic are shown in Figure 17. As in the unpoled PZST, there was an observed decrease in the bulk moduli with increasing temperature for poled-unbiased material.

It is also noted that K_A was significantly larger than K_F . The values of bulk moduli in poled PZST are about 5, 11, and 8% higher than in unpoled PZST in phases K_F - K_{F-A} , and K_A respectively. A detailed quantitative description of phase transformation in the poled PZST ceramic under hydrostatic loading is summarized in Table 6.

Figure 15 Superimposed volumetric strain (ϵ_v) versus pressure plots for the hydrostatic compression tests on poled-unbiased wafer PZST specimens at temperatures of -55 and 25°C .

Figure 16 Variation of phase transformation pressure, P_P^H , for poled PZST ceramic with temperature, T.

Figure 17 Superimposed pressure versus volumetric strain (ϵ_v) plots for the hydrostatic compression tests on poled PSZT specimens in ferroelectric (FE) phase at temperatures ranging from -55 to 75°C . Initial bulk modulus values are represented by the slopes of the lines as quantified in the equations.

Table 6 Summary of phase transformation in poled PZST under hydrostatic compression (HC).

Sample #	P _P ^H	Poled ϵ_{VP}^H	Temp. (°C)
PZST #A	286	0.00380	25
PZST #B	284	0.00398	25
PZST #C	286	0.00394	25
PZST #D	290	0.00311	-55
PZST #E	282	0.00331	-55
PZST #G	227	0.00363	75
PZST #H	233	0.00350	75
PZST EX #A	307	0.00434	25
PZST EX #B	308	0.00421	25
PZST W1	299	0.00397	25
PZST W2	303	0.00341	25
PZST W3C	290	0.00299	-55
PZST W4	276	0.00301	25
PZST W5C	246	0.00318	-55
PZST W6C	267	0.00347	-55
PZST W7C	275	0.00305	-55

P_P^H – pressure for FE-to-AFE phase transformation under hydrostatic compression

ϵ_{VP}^H – volumetric strain at P_P^H

The location of the phase boundaries for PZST in temperature-pressure space has been determined at three temperatures (-55, 25, and 75°C) from the hydrostatic compression experiments. Also, bulk modulus was analyzed at the aforementioned temperatures and compared in the K_F , K_{F-A} , and K_A phases for unpoled and poled samples.

4.2 Hydrostatic compression tests with electrical bias

One 25°C hydrostatic compression test (PZST W10) was completed on a wafer specimen with a 1kV electrical bias. Figure 18 compares the biased test with unbiased wafer tests conducted at the same temperature. The pressure verses volume curve of the 1kV bias test does not illustrate quantifiable deviation from the suite of unbiased tests. Additional testing with higher levels of voltage bias is recommended on PZST to further understand this effect on P_P^H , ϵ_{VP}^H , K_F , and other material properties.

Figure 18 Superimposed volumetric strain (ϵ_v) versus pressure plots for the hydrostatic compression tests on poled-unbiased and on one poled-biased (1kV bias) wafer PZST specimens at 25°C.

Previous work investigating the effect of a poled electrical bias condition was performed on composition PNZT 95/5-2Nb (Lee and Montgomery, 2006). Figure 19 shows pressure versus volume curves for five tests. One test is unbiased and the other tests have voltage biases of 1, 2, 3, and 4kV. P_P^H and ϵ_{VP}^H increase as voltage bias increases and conversely, initial K_F decreases as voltage bias increases. The increase of ϵ_{VP}^H with increasing voltage bias is due to the slight decrease in K_F along with higher P_P^H values. Figure 20 shows the rate that P_P^H increases as voltage bias increases. The rate is determined from a least squares best fit line and is 0.0168 MPa/V. The data in Figure 20 are well represented by the linear fit. Table 7 presents a detailed quantitative description of phase transformation from each of the five voltage bias tests on composition PNZT 95/5-2Nb.

Figure 19 Superimposed volumetric strain (ϵ_v) versus pressure plots for the hydrostatic compression tests on one poled-unbiased and four poled-biased (1, 2, 3, 4.5kV bias) wafer PNZT specimens at 25°C.

Figure 20 Variation of phase transformation pressure, P_P^H , for poled PNZT ceramic wafers with voltage bias. All tests were conducted at ambient temperature.

Table 7 Summary of phase transformation in poled-unbiased and poled-biased PNZT ceramic wafers under hydrostatic compression (HC) at ambient temperature.

Specimen no.	Bias (kV)	Poled		Initial
		P_P^H	ϵ_{VP}^H	K_F
PNZT-B00	0	279	0.00499	64570
PNZT-B12	1	302	0.00578	63339
PNZT-B11	2	317	0.00659	60951
PNZT-B13	3	334	0.00711	61295
PNZT-B16	4.5	356	0.00757	57383

P_P^H – pressure for FE-to-AFE phase transformation under hydrostatic compression

ϵ_{VP}^H – volumetric strain at P_P^H

5. Results and Conclusions

The specimens of unpoled and poled PZST ceramics, were tested under hydrostatic compression loading. The electro-mechanical behavior during phase transformation from a ferroelectric (FE) rhombohedral perovskite structure to an antiferroelectric (AFE) orthorhombic structure was investigated over three temperatures, with the lowest being -55°C and the highest 75°C . The results are summarized as follows:

- The FE to AFE phase transformation in PZST is marked by a sudden increase (decrease in volume) of 0.4 to 0.6% of volumetric strain.
- The phase boundary is different from previous findings for PNZT ceramic in the phase diagram (Fritz and Keck, 1978) in that 25°C requires the highest pressure for transformation and at colder and higher temperatures, transformation occurs at lower pressures for both unpoled and poled materials.
- There was an observed decrease in the bulk moduli with increasing temperature for unpoled and poled-unbiased material. The bulk moduli in the AFE phase (K_A) was significantly larger than in the FE phase (K_F). The values of bulk moduli in poled PZST are about 5, 11, and 8% higher than in unpoled PZST in phases K_F , K_{F-A} , and K_A respectively.
- The poled PZST ceramic undergoes anisotropic deformation in the AFE structure at -55°C . At 25 and 75°C , the ceramic undergoes anisotropic deformation in both the FE and AFE phases although the degree of anisotropy is greater in the AFE phase. The lateral strain parallel to the poling direction ($\epsilon_{l\text{-parallel to poling}}$) is typically 32% greater than the strain perpendicular to the poling direction ($\epsilon_{l\text{-normal to poling}}$) for the poled PZST ceramic.
- At the low temperature boundary of -55°C , the FE-to-AFE phase transformation is permanent and irreversible. However, at 25 and 75°C , the phase transformation is completely reversible from AFE to FE as the stress causing the phase transformation is removed.
- One poled-biased test at 1kV bias was completed and compared to poled-unbiased results. In pressure versus volume space, the biased test behaved the same as the unbiased tests. Additional testing is recommended at higher voltage biases to better understand the effect voltage bias has on various PZST parameters.
- Results of previous work on PNZT 95/5-2Nb material were presented. The effect of voltage bias was analyzed and a relationship between phase transformation pressure and voltage bias was established. The hydrostatic pressure required for FE to AFE transformation was increased by approximately 0.0168 MPa/V.

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APPENDIX A-1 Hydrostatic Compression (HC) Test Plots for Unpoled PZST

- **P-pressure**
- **ε_v - volumetric strain**
- **T-temperature**

APPENDIX A-2 Hydrostatic Compression (HC) Test Plots for Poled PZST

- **P-pressure**
- **ϵ_a -axial strain**
- **ϵ_l -parallel to poling-lateral strain parallel to poling direction**
- **ϵ_l -normal to poling-lateral strain perpendicular to poling direction**
- **ϵ_v - volumetric strain**
- **T-temperature**
- **S-time in seconds**
- **V-voltage**

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