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The Effects of Non-Hydrostatic Compression and Applied
Electric Field on the Electromechanical Behavior of Poled
PZT 95/5-2Nb Ceramic During the $F_{R1} \rightarrow A_O$
Polymorphic Phase Transformation

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Abstract

We conducted hydrostatic and constant-stress-difference (CSD) experiments at room temperature on two different sintered batches of poled, niobium-doped lead-zirconate-titanate ceramic (PZT 95/5-2Nb). The objective of this test plan was to quantify the effects of non-hydrostatic stress on the electromechanical behavior of the ceramic during the ferroelectric, rhombohedral $\rightarrow$ antiferroelectric, orthorhombic (FE $\rightarrow$ AFE) phase transformation. We also performed a series of hydrostatic and triaxial compression experiments in which a 1000 V potential was applied to poled specimens to evaluate any effect of a sustained bias on the transformation. As we predicted from earlier tests on unpoled PZT 95/5-2Nb, increasing the stress difference up to 200 MPa (corresponding to a maximum resolved shear stress of 100 MPa) decreases the mean stress and confining pressure at which the transformation occurs by 25-33%, for both biased and unbiased conditions. This same stress difference also retards the rate of transformation at constant pressurization rate, resulting in reductions of up to an order

of magnitude in the rate of charge release and peak voltage attained in our tests. This shear stress-voltage effect offers a plausible, though qualitative explanation for certain systematic failures that have occurred in neutron generator power supplies when seemingly minor design changes have been made. Transformation strains in poled ceramic are anisotropic (differing by up to 33%) in hydrostatic compression, and even more anisotropic under non-hydrostatic stress states. Application of a 1000 V bias appears to slightly increase (by $\leq 2\%$) the transformation pressure for poled ceramic, but evidence for this conclusion is weak. In a previous report we concluded that under non-hydrostatic stress, the FE-AFE transformation took place in unpoled ceramic when the maximum compressive stress equalled the hydrostatic pressure at which the transformation would otherwise occur. We have found that this stress criterion does not apply to the same transformation of poled ceramic. The reason for this is unknown. It may be that the correlation previously identified was merely coincidental. However, poled material is not the same as unpoled. The latter is isotropic, while the former clearly has a pronounced preferred crystallographic orientation and mechanical anisotropy. If the underlying thermodynamic basis for the correlation relies upon a random, polycrystalline structure, then the correlation would not apply to poled ceramic, which is clearly ordered and anisotropic. Our hypothesis could be further tested by performing comparable hydrostatic and CSD experiments on other materials which exhibit polymorphic transformations comparable to the one which we have studied to date.

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Executive Summary

PZT 95/5-2Nb ceramic is the active electrical element in shock-actuated power supplies used in neutron generators. In this report we present results of thirty-one hydrostatic and triaxial compression experiments on poled PZT 95/5-2Nb ceramic, in which we examined the effects of shear stress and applied electric field on electromechanical behavior during the ferroelectric-antiferroelectric (FE-AFE) phase transformation. The objective of this work is to provide data for refinement of the constitutive model for PZT 95/5-2Nb currently used in 3-D finite element simulations of neutron generator power supplies. Such simulations are increasingly important as cost-effective tools to evaluate the effects of proposed design changes and to analyze power supply failures.

Most importantly, our results clearly demonstrate that increasing shear stress systematically (1) retards the rate of charge release and (2) reduces the peak voltage attained during the depoling that accompanies the phase transformation. At the maximum resolved shear stress of 100 MPa these reductions are by up to an order of magnitude. At this time it is not clear exactly how these quasi-static results extrapolate to the dynamic conditions extant during neutron generator power supply operation. Nevertheless, discovery of this phenomenon provides a plausible qualitative mechanism for the origin of systematic failures that develop in shock-actuated power supplies when seemingly-minor design changes are introduced. Such changes might include substitution of one hardener for another in the alumina-loaded epoxy (ALOX) potting compound used in the power supplies, or changes in the volume fraction of alumina added to the epoxy. It is not difficult to imagine that as a shock-wave traverses the interface between two subtly mismatched materials, shear stresses could be generated that are sufficient to reduce electrical outputs to the point of failure. Our hypothesis can be evaluated by shock-wave experiments, numerical simulations, or preferably, both.

We have observed and quantified several other shear-stress-related phenomena which will be incorporated into the electromechanical constitutive model for PZT 95/5-2Nb. First, at a constant pressurization rate, increasing shear stress systematically slows, by up to an order of magnitude, the rate at which the FE-AFE transformation proceeds. Indeed, it is this retardation of transformation kinetics that is probably ultimately responsible for the observed electrical effects.

Second, increasing shear stress also lowers the mean stress (the hydrostatic component of the stress tensor) at which the transformation occurs. This reduction is between $\frac{1}{4}$ and $\frac{1}{3}$ of the pressure at which the transition occurs during hydrostatic compression. Thus, the mean stress is not a useful criterion for predicting the onset of the transformation under non-hydrostatic conditions. Our earlier test results for *unpoled* ceramic suggested that the maximum normal compressive stress was the relevant criterion for transformation, but the results contained herein now cast doubt on that conclusion.

Third, we have also observed significant strain anisotropy during the transformation of poled ceramic, under both hydrostatic and triaxial compression. Under the latter condition, all *three* principal strains are different during the phase transformation. Strains may differ by up to $\frac{1}{3}$. It would be useful to use numerical simulations to determine how sensitive power supply performance might be to this strain anisotropy.

Finally, we investigated the effect of an applied electrical field on the FE-AFE transformation under hydrostatic and triaxial compression. Dynamic experiments have suggested that the large, self-generated electric fields that can occur during depoling may suppress the transformation. Equipment limitations only permitted application of a 1000 V potential. Nevertheless, a small ($\leq 2\%$) but seemingly consistent and resolvable increase in the pressure for transformation was detected. This phenomenon could be further investigated by fabrication of a new end closure for our 1000 MPa pressure vessel, equipped with new high-pressure, high-voltage feedthroughs that permit application of a larger electrical potential.

Our observation that shear stresses suppress charge release rates and voltages provide not only a plausible explanation for certain power supply failures, but a possible avenue for improvement of power supply performance. Design modifications that minimize the development of stress deviators during operation are likely to maximize electrical outputs.

Experiments were conducted in a standard, liquid-medium, triaxial testing apparatus consisting of a 1000 MPa pressure vessel, 1.78 MN hydraulic actuator and reaction frame. The reaction frame permits transfer of deviatoric load from the actuator to a specimen contained in the pressure vessel *via* a movable loading piston that enters the vessel through a dynamic, high pressure seal. High pressure electrical feedthroughs permit strain gauge, capacitance and charge release/voltage measurements to be made directly on the specimens. Test specimens were right rectangular prisms, 1.080 cm-square by 2.540 cm long, jacketed in urethane to prevent intrusion of the confining liquid into the specimens. Samples were "hot-poled" in electric fields corresponding to 50 V per 0.003 cm of thickness (50 V/mil).

Hydrostatic compression experiments are straightforward and require no explanation. Constant-shear-stress experiments are conducted under microprocessor control, keeping the difference between axial and lateral stresses (and, hence, the maximum resolved shear stress) constant while increasing the mean stress to cross the FE-AFE phase boundary. The maximum stress difference used was 200 MPa, corresponding to a maximum resolved shear stress of 100 MPa. These relatively low shear stresses produced only elastic deformations: no evidence for even minor fracturing or pore collapse was observed in any of the experiments. Thus, the shear stresses that we apply are probably very low compared to those actually evolved during power supply operation.

Ceramic specimens from two WR-qualified hifires (sintering batches) were tested, 424 and 541-1. Although we observed the usual batch-to-batch variations characteristic of sintered PZT 95/5-2Nb, results from the two hifires are, nevertheless, generally consistent.

Chapter 1

Introduction

PbZrO_3 and PbTiO_3 form a complete solid-solution series (lead-zirconate-titanate, or PZT) of great technological importance. It is used in various Zr:Ti ratios and with numerous dopants to manufacture a wide range of electronic and electromechanical devices [e.g., Newnham, 1989; Haun *et al.*, 1990a]. One of these modifications, $\text{Pb}_{0.99}\text{Nb}_{0.02}(\text{Zr}_{0.95}\text{Ti}_{0.05})_{0.98}\text{O}_3$ (referred to hereafter as PZT 95/5-2Nb), is used in shock-actuated power supplies, and its properties are important for weapons applications. At room temperature, PZT 95/5-2Nb has a rhombohedral structure (F_{R1}) and is ferroelectric; that is, a crystal (as well as subdomains within a single crystal) exhibits a spontaneous polarization in any one of eight crystallographically-equivalent directions. Thus, single crystals or polycrystals can be polarized (“poled”) in an electric field. When the electric field is relaxed, some remnant polarization persists and a bound charge is stored. At a hydrostatic pressure of about 300 MPa, the poled material undergoes a displacive, first-order phase transformation to an orthorhombic, antiferroelectric (macroscopically electrically neutral) structure (A_O) [Fritz and Keck, 1978; Zeuch *et al.*, 1992a, b]. When this occurs, the bound charge is released. Under shock-wave conditions this takes place rapidly and high currents and voltages can be obtained.

As designs and testing become more expensive, it becomes increasingly cost-effective to use finite-element methods to model and optimize device designs prior to construction and testing of prototypes (e.g., Montgomery [1986]). In order to do this, constitutive models must be available for the various materials used in the component, including one for the electromechanical behavior of poled PZT 95/ 5-2Nb during the polymorphic transformation.

As part of an ongoing effort to develop constitutive models for the electromechanical behavior of PZT 95/5-2Nb during the ferroelectric-antiferroelectric (FE-AFE) polymorphic phase transformation, we have performed an extensive series of quasistatic, hydrostatic and triaxial compression experiments on unpoled PZT 95/5-2Nb specimens from several sintering batches, also referred to as “hifires.” Results of these investigations have been summarized by Zeuch

et al. [1992a,b; 1993; 1994], and will not be reviewed in detail here. Briefly, we showed that at room temperature ($\approx 20^\circ\text{C}$), application of increasing shear stresses which caused only elastic strains: (1) systematically lowered the mean stress and confining pressure at which the transformation occurred, (2) caused anisotropic strain behavior during the transformation, and (3) slowed the rate at which the transformation took place for a constant pressurization rate. We also found evidence for the shape-memory effect [Zeuch *et al.*, 1992a,b; 1993]. More recently, we have demonstrated that under nonhydrostatic compression, the transformation occurs when the maximum compressive stress equals the hydrostatic pressure under which the transformation would otherwise occur [Zeuch *et al.*, 1994].

In this report, we shift attention to the behavior of *poled* PZT 95/5-2Nb, and examine the effects of nonhydrostatic compression and electric fields on the polymorphic transformation and depoling behavior. Twenty-five experiments on specimens from a single hifire have been completed. With a single exception, all of the specimens were poled. Two experimental series were performed. In the first, approximately half of the poled specimens were transformed in either hydrostatic or triaxial compression, allowing the bound charge to drain to a capacitor in parallel with a high-impedance electrometer. The objectives of these experiments were to: (1) quantify any effect of poling on the position of the phase boundary as compared with unpoled material, and (2) investigate the effect of nonhydrostatic stress on transformation and/or depoling behavior.

In the second series, a 1000 V potential was applied to the test specimens during transformation under both hydrostatic and triaxial compression. The objective of this test series was to evaluate the influence of an electric field on the occurrence and kinetics of the transformation: unpublished results from shock wave experiments indicate that electric fields self-generated during depoling can serve to suppress or retard the transformation [S. Montgomery, unpublished results]. Field polarity coincided with that of specimen polarization. Comparison of the results of these tests with those from the series on unbiased specimens is clouded somewhat by necessary differences in electrical circuitry. Nevertheless, several conclusions can be reached.

First, our results confirm that poling markedly raises (by about 20%) the pressure for, and more sharply defines, the onset of the ferroelectric-antiferroelectric transformation at constant temperature (*e.g.*, Berlincourt *et al.* [1964]). Second, for both unbiased and biased, poled ceramic, application of increasing shear stress again systematically lowers the mean stress for onset of the transformation, and slows the rate of the transformation for a constant pressurization rate. This in turn results in a reduction in the peak voltages that are attained during transformation and depoling, and a broadening or "smearing" out of the discharge voltage curve. A maximum resolved shear stress of 100 MPa reduces discharge rates and peak voltages by up to an order of magnitude. Finally, our results suggest that application of an electric field increases the transformation pressure at constant temperature though the effect is small, $\leq 2\%$.

We conclude that maximum voltages and currents can be obtained by minimizing nonhydrostatic stresses during transformation, although it is not clear how practical this may be when

designing shock-actuated power supplies. Our observation that an applied electric field may affect the transition pressure merits further investigation. Self-generated electric fields during shock depoling can be very high, possibly influencing the pressure and rate at which the transformation proceeds. The electric field produced by our 1000 V potential ($9.26 \times 10^4 \text{ V m}^{-1}$) is very small by comparison, but was the maximum that we could safely apply. Our results indicate that a detectable effect is there, but it is not clear how it increases in proportion to an increase in electric field.

Chapter 2

Experimental Techniques and Materials

In all but five experiments, specimens were right rectangular prisms measuring $1.080\text{ cm} \times 1.080\text{ cm} \times 2.540\text{ cm}$, with the two opposing square faces ground flat and parallel within 0.0003 cm . Silver electrodes were evaporated onto the two opposing rectangular prism faces coincident with the direction of poling, to permit measurement of electrical discharge and to apply the electric field. The five remaining specimens were similar, but thinner, measuring $1.080\text{ cm} \times 0.508\text{ cm} \times 2.540\text{ cm}$. They were poled parallel to the shortest dimension, with electrodes evaporated on the faces normal to that dimension. The purpose to which these thin specimens were put will be discussed later.

Thick and thin specimens alike were "hot-poled" in electric fields corresponding to 50 V per 0.003 cm (0.001 in) of thickness. Specimens were heated in oil to $105\text{ }^{\circ}\text{C}$, and the field applied. The temperature was then lowered to $70\text{ }^{\circ}\text{C}$ over a period of 5 minutes, whereupon the field was removed. Cooling to room temperature then continued.

Strains were measured using strain gauges bonded to the rectangular prism faces. In the discussion that follows, axial strains are those parallel to the long sample dimension, and lateral (or transverse) strains are those measured on the prism faces in directions perpendicular to the axial direction. An axial and lateral gauge were mounted on each of the two electroded faces, providing some redundancy for those measurements; these gauges are subsequently referred to as "axial gauges 1 and 2" and "lateral gauges 1 and 2."

Owing to limitations on the number of high-pressure feedthroughs (see below), a single lateral gauge (lateral gauge 3) was mounted on one of the two remaining unelectroded rectangular faces, parallel to the poling direction. Volume strains are determined by summing of appropriately-averaged strain gauges on opposite prism faces (except, of course, for the single gauge parallel to the poling direction), unless a gauge was lost during testing.

Sintered aluminum oxide endcaps were glued to the ends of the samples. Use of insulating

endcaps eliminated the need to place mylar or mica insulation between the electroded specimen and the hardened steel endcaps used in our earlier experiments [Zeuch, 1992a,b]. The sample assemblies were coated with urethane to prevent intrusion of the confining fluid into the ceramic.

Because of the number of strains that had to be measured on poled specimens in addition to the discharge voltage, we lacked sufficient feedthroughs to also measure specimen capacitance during the experiments. We have shown that the dielectric anomaly that occurs is actually a less ambiguous indicator of onset of the transformation than the volume strain [Zeuch *et al.*, 1994]. However, the volume strain serves as an adequate indicator.

All experiments were done at room temperature in the same standard liquid-medium triaxial testing apparatus used by Zeuch *et al.* [1992a,b]. The apparatus consists of a 1000 MPa pressure vessel and 1.78 MN hydraulic actuator enclosed in a stiff reaction frame that allows transfer of force from the actuator to the test specimen *via* the moving piston. The pressure vessel end closure is fitted with twelve high-pressure electrical feedthroughs which make the strain gauge and voltage measurements on the specimens possible. In hydrostatic compression experiments, the piston was locked in place and only the confining liquid, ISOPARTM, was pressurized. In nonhydrostatic experiments, deviatoric stresses were applied axially using the actuator and piston following the loading path discussed below.

Load was measured using an external load cell with a maximum rating of 0.445 MN, and fluid pressure was measured with a pressure cell. Calibration against known standards indicates that the load cell is accurate to ± 480 N. The pressure cell is accurate to ± 0.008 MPa over the pressure range 0 to 448 MPa. We have measured friction of the moving piston as a function of confining pressure [Zeuch *et al.*, 1994], and shown that its effect on axial stress measurements is about 12 MPa in the range of the phase transformation (about 250 MPa) when referred to the sample's cross-sectional area. It must be remembered that during our constant-stress-difference experiments (see below), the loading piston is always moving *into* the vessel, so the measured loads and, hence, axial stresses (σ_1) will always be *greater* than those acting on the samples. The result is that the mean stresses that we calculate for our constant-stress-difference experiments are even *further* depressed below the hydrostatic experiments than we show later.

Hydrostatic compression tests are straightforward and require no further description. In order to evaluate the effect of shear stress on the rhombohedral-orthorhombic transformation, we performed constant-stress-difference tests, referred to hereafter as "CSD tests." The loading path for a typical CSD experiment is shown in Figure 2.1, with the relationship between the stress field and the sample illustrated schematically in the inset.

In CSD tests, the samples were first pressurized hydrostatically to 69 MPa. This initial pressurization was performed to minimize any possibility of microcracking. Then an additional axial load was superimposed, using the hydraulically-actuated piston, to increase the stress difference, $\sigma_1 - \sigma_3$, to 100, 150 or 200 MPa. (These stress differences are far below the uniaxial (*i.e.*, unconfined) compressive strength of approximately 600 MPa reported by Fritz [1979] for

Figure 2.1: Typical loading path for CSD experiments.

comparable material.) In our test geometry, the axial compressive stress corresponds to σ_1 , and $\sigma_2 = \sigma_3 =$ the fluid pressure. The axial stress, σ_1 , and fluid pressure, σ_3 , were then increased simultaneously under microprocessor control such that the stress difference, and hence the maximum resolved shear stress, $(\frac{\sigma_1 - \sigma_3}{2})$, remained constant through the transformation. In both hydrostatic compression and CSD experiments, the confining pressure, σ_3 , was first increased, and then decreased at the same constant rate, $0.55 \text{ MPa sec}^{-1}$. In our previous investigations, we have shown that the loading conditions discussed in this report leave the specimens completely intact, macroscopically and microscopically entirely free of any cracks, chips, pore collapse (this material has a porosity of $\approx 7\text{-}8\%$) or other evidence of damage [Zeuch *et al.*, 1992a,b]. We have seen no evidence in this study that contradicts our previous conclusion.

To illustrate the effects of such a loading path, individual strain gauge data are shown in Figure 2.2 for a typical CSD experiment on an unbiased, poled specimen. The sample is pressurized hydrostatically to 69 MPa ("HP" on Figure 2.2); during this phase, the five strain gauges on the sample behave identically. Upon reaching 69 MPa, the sample is loaded axially until a stress difference of 100 MPa is reached ("AL" on Figure 2.2). The lateral gauges record rarefaction, while the axial gauges record compression. (Following the usual rock mechanics convention, compressive stresses and strains are reckoned positive in this report.) Confining pressure and axial load are then increased together, keeping the stress difference constant while

Figure 2.2: Individual strain gauge data for a typical constant stress difference experiment. See text for detailed explanation.

increasing the mean stress. When the phase transformation occurs, strains in the three principal directions are all different, though the net transformation strain parallel to the poling direction approaches that for the axial direction. This result contrasts with that for CSD experiments on unpoled ceramic, in which axial and lateral strains were also different, but both lateral strains were identical (*cf.* Zeuch *et al.* [1992b; Figure 6(a)]). At approximately 420 MPa, the pressurization phase is terminated, and depressurization begins. Upon reaching 69 MPa, the axial stress difference is removed (“AU”) and the sample is then hydrostatically depressurized (“HD”).

In unbiased experiments, the charge released during the phase transformation was simply drained to a 33 μF capacitor (Figure 2.3A). Voltage on the capacitor was measured using a high-impedance electrometer with an analog output, wired in parallel with the capacitor. By allowing the specimen to charge the capacitor, and not allowing it to drain off until the test was complete, we could verify consistent charge release from test to test.

When running the biased experiments, safety considerations precluded the use of a capacitor in the circuit during application of the 1000 V potential, owing to the large amount of energy that would be stored in a 33 μF capacitor. Instead, circuitry was used as shown in Figure 2.3B.

Figure 2.3: Electrical circuitry for measurement of discharge voltage for unbiased (A) and biased (B) specimens.

During the phase transformation, a transient voltage drop occurs across the $100\text{k}\Omega$ resistor as current is accepted by the power supply, and the specimen also experiences a small change in the electric field. The value of the resistor was chosen to keep the voltage change small, in the range of 10 V. Thus, circuits for the biased and unbiased tests were different.

The 1000 V potential is relatively small compared to the potentials that are used for poling of the ceramic, or which might be generated during shock depoling. Prior to testing, one of us (S. Montgomery) estimated that the effects of a 1000 V potential might be near the limit of detectability, and it is clear from our tests that a higher voltage would be desirable. However, 1000 V was slightly below the maximum voltage that could be consistently sustained across the available high pressure feedthroughs. In the instances when high-voltage breakdowns occurred, feedthroughs were destroyed and time-consuming reconstruction was necessitated. The incidence of breakdowns decreased dramatically when water-bearing pyrophyllite feedthrough cones were replaced with VESPELTM. Overall safety of the experiments was guaranteed by the current-limiting feature of the high-voltage power supply.

The signals from the electrometer, strain gauges, and load and pressure cells, were sent to a Keithly 500 data acquisition system and written to the hard disk on an IBM-compatible personal computer [Hardy, 1993]. Preliminary data reduction was accomplished during acquisition with DATAVG [Hardy, 1993], and subsequent data analysis was performed using PSILOTTM, a commercially-available data processing and plotting package.

In the past [Zeuch *et al.*, 1992a, b], we have tested material from three different hifires: 435, 541-1 and 424. All three hifires were prepared in the Org. 7476 Ceramic Shop at Sandia

National Laboratories: hifire 424 was produced and war-reserve (WR) qualified as MC2756 current stack material and hifires 435 and 541-1 were produced and WR qualified as MC3422 voltage bar material [Keck, 1990]. Consistent with other investigations, [Dungan and Storz, 1985] we have found both inter- and intra-hifire variations, but have found hifire 424 material to exhibit very reproducible behavior comparable to material studied by others [Zeuch *et al.*, 1992a,b]. Consequently, most of our past data for unpoled response have been collected using specimens from this hifire; for that reason, we have continued almost exclusively with hifire 424 in this investigation. Additional details regarding hifire 424 are given by Zeuch *et al.* [1992a, b].

Nevertheless, six early hydrostatic and triaxial compression experiments were conducted on poled, unbiased specimens from hifire 541-1, prior to our understanding of its unusual and somewhat inconsistent behavior under unpoled conditions [Zeuch *et al.*, 1992a, b]. In the interest of completeness, we will discuss these tests toward the end of this report. However, we will not dwell on comparisons with the behavior of unpoled 541-1 specimens run under CSD conditions, owing to both the intra- and inter-hifire inconsistencies and peculiarities which we have remarked upon in the past [Zeuch *et al.*, 1992a, b]: it is not clear *which* results for unpoled 541-1 should be compared to the results discussed here.

Experiments on 541-1 ceramic were conducted in a manner virtually identical to that outlined above, save for a few details. First, hardened steel rather than alumina endcaps were used, insulated from the specimen and electrodes by a thin sheet of mylar. Second, lateral strains were measured only in the direction transverse to poling. Owing to the lateral transformation strain anisotropy that we have observed in poled material (see below), the true cross-sectional area of the sample, and hence, the volume strain and true axial stress on the sample are uncertain. Third, the bound charge was drained to a 33 μF capacitor, 62 $\text{k}\Omega$ resistor and the electrometer, all connected in parallel. Thus, discharge voltage measured at the electrometer would first rise as the capacitor charged, and then decay as charge drained across the resistor. Finally, two electrodes were painted onto the two rectangular faces parallel to the poling direction, for the purpose of performing capacitance measurements. Capacitance measurements were performed exactly as described by Zeuch *et al.* [1992a, b].

Chapter 3

Experimental Results and Observations

Tables 3.1–3.3 summarize the test conditions of the twenty-five experiments on specimens from hifire 424 discussed in this report. Data from the experiments are presented in their entirety in Appendices A, B and C for unbiased, biased and thin-specimen tests, respectively.

Test ID	Type	$\sigma_1 - \sigma_3$	Remarks
FE62	Hydrostatic	0 MPa	Discharge voltage leads reversed.
FE63	Hydrostatic	0 MPa	Unpoled. One redundant axial gauge failed.
FE64	Hydrostatic	0 MPa	
FE66	Hydrostatic	0 MPa	
FE76	CSD	100 MPa	Discharge voltage data lost.
FE77	CSD	100 MPa	Solder flux bridge short caused ≈ 1 V bias on discharge voltage channel; corrected in data reduction.
FE78	CSD	100 MPa	One redundant axial gauge failed.
FE79	CSD	150 MPa	
FE80	CSD	150 MPa	One redundant lateral gauge failed.
FE81	CSD	200 MPa	
FE82	CSD	200 MPa	One redundant lateral gauge failed during transformation; second gauge failed later at peak confining pressure.

Table 3.1: Experiments on Unbiased Specimens

Test ID	Type	$\sigma_1 - \sigma_3$	Remarks
FE65	Hydrostatic	0 MPa	Non-redundant lateral strain gauge lost just following completion of transformation.
FE67	Hydrostatic	0 MPa	
FE68	Hydrostatic	0 MPa	
FE69	CSD	100 MPa	
FE70	CSD	150 MPa	Discharge voltage data lost.
FE71	CSD	150 MPa	
FE72	CSD	100 MPa	
FE73	CSD	200 MPa	All strain gauges exhibit peculiar behavior before and during transformation. Volume strain-mean stress data inconsistent with other tests. Discharge voltage data also abnormal.
FE74	CSD	200 MPa	
FE75	CSD	200 MPa	Redundant axial strain gauge lost from outset of test; all others lost well after transformation completed.

Table 3.2: Experiments on Biased Specimens (1000 V Potential)

Test ID	Type	$\sigma_1 - \sigma_3$	Biased?	Remarks
FE83	Hydrostatic	0 MPa	No	
FE84	Hydrostatic	0 MPa	No	Gauges display abnormal, sluggish behavior just after transformation. Voltage discharge rate also slows prematurely, and then suddenly goes to expected completion.
FE85	Hydrostatic	0 MPa	Yes	
FE86	Hydrostatic	0 MPa	Yes	

Table 3.3: Experiments on Unbiased and Biased, Thin Specimens

In the remainder of this report, we will present the results of the foregoing experiments, and discuss the generalizations that follow. We will first look at the effects of poling and 1000V

potential on the transformation under hydrostatic pressure, with reference to our earlier results on unpoled ceramic. We will then examine the effects of nonhydrostatic stresses on the transformation, and associated depoling, of both unbiased and biased specimens. Our earlier prediction that nonhydrostatic stresses would retard the depoling kinetics are borne out by the results of this study. We will defer discussion of the results for hifire 541-1 until all of the results for hifire 424 have been presented. Finally, we will close with a summary of our findings, a few remarks on their implications, and suggestions for further work.

3.1 Hydrostatic Compression Experiments

Figure 3.1: Comparison of poled and unpoled specimens in hydrostatic compression. All specimens are unbiased. Arrows indicate sense of pressurization-depressurization path.

3.1.1 Unbiased Specimens: The Effects of Poling on Transformation Pressure and Strain Response

In Figure 3.1, we show results for three hydrostatic compression experiments on “thick,” poled, unbiased 424 ceramic. The onset of the phase transformation is indicated by the sharp

decrease in volume occurring at about 300 MPa. For comparison, data from four hydrostatic compression experiments on unpoled 424 specimens are also presented. Three of these were reported in our earlier investigations [Zeuch *et al.*, 1992a;b], while the results for experiment FE63 were obtained during the current test series. Poling raises the pressure for transformation by approximately 40 MPa. This increase is of the same order of magnitude as that reported by Berlincourt *et al.* [1964] (55 MPa) for Sn-doped lead-zirconate-titanate ceramic. The reason for the increase in transformation pressure with poling has been discussed by Berlincourt *et al.* [1964]: work done in the poling process increases the energy difference between the ferroelectric and antiferroelectric states, resulting in a similar increase in the mechanical energy required to force the transformation.

Figure 3.2: Individual strain gauge data for a poled specimen subjected to hydrostatic compression. Note that the strain in the direction of poling is anomalously large. Arrows indicate the sense of the pressurization-depressurization path.

Individual strain gauge data for experiment FE66 are presented in Figure 3.2. Unlike the isotropic response exhibited by unpoled material in hydrostatic compression [Zeuch *et al.*, 1992a, b], transformation strains in poled ceramic are distinctly anisotropic, with the maximum compressive strain parallel to the direction of poling. This is expected, as poling produces a preferred crystallographic orientation and intra- and intergranular strains prior to testing. Compressive strains parallel to the poling direction are typically greater by about 33%.

Figure 3.2 illustrates one of the peculiarities in strain gauge behavior that we often observe when testing poled specimens, under both hydrostatic and CSD conditions, whether biased or unbiased. At the end of the phase transformation, sudden, transient strain “overshoots” are often observed; the gauge measuring strain parallel to the poling direction in Figure 3.2 exhibits one such temporary overshoot. At the beginning of the transformation, sudden, transient strain “reversals” are also detected, though overshooting is far more common. Experiment FE83 (Figure 3.6), run in hydrostatic compression, shows one such sudden reversal.

There seem to be no systematics to the occurrence of these sudden overshoots or reversals, except that they are restricted to poled specimens; they were not observed in our earlier investigation of unpoled ceramic [Zeuch et al., 1992a,b]. Neither type appears to be restricted to any particular set(s) (*i.e.*, orientation(s)) of gauges. As noted above, they span all test types, but are altogether absent in some tests. Thus far, we have not been able to determine whether these “spikes” represent some temporary, spurious electrical effect of depoling on the strain gauges, or a real strain phenomenon. This could be investigated by using linear variable displacement transducers (LVDTs) to measure strains, but would require modification of existing test fixtures, and, possibly, use of a larger specimen. In any event, these spikes appear to be entirely transitory; once past, the gauges that experience them continue to function, exhibiting behavior consistent with unaffected gauges.

The depoling curve for FE66 is shown in Figure 3.3. In nominally “successful” experiments, the capacitor charges to about 2.5 V at the transformation. There is inevitably some loss of charge during the remainder of the experiment, probably across the specimen itself.

We digress briefly at this point to remark that there is a second type of strain gauge reversal that we frequently observe in lateral gauges just prior to onset of the transformation. Such a reversal is exhibited by one of the three lateral gauges shown in Figure 2.2. We have seen these reversals in both poled and unpoled specimens (*e.g.*, Zeuch et al. [1992b]; their Figures 6a and 10a), but in CSD experiments *only*. Like the rapid spikes that we have just mentioned, systematics of their occurrence are unclear; they are absent in some CSD experiments, or displayed by one (Figure 2.2), two (Figure A.16) or all three (Figure B.13) lateral gauges in others. Unlike the spikes, these reversals are gradual, spanning increases of 10-30 MPa in pressure prior to the transformation. The significance of these slow reversals, if any, is unknown. However, an interesting—if highly speculative—explanation exists. We reserve discussion of this possible explanation for this phenomenon for the final chapter of this report.

3.1.2 Biased Specimens: Added Effects of 1000 V Potential

Three hydrostatic compression experiments were carried out on thick poled specimens while applying the 1000V potential. A small difference in behavior was detectable when compared with unbiased specimens. Complete volume strain-pressure plots are given in Figure 3.4, and

Figure 3.3: Depoling curve for the same experiment shown in Figure 3.2. The transformation is indicated by the sudden increase in voltage. Arrows indicate the sense of the pressurization-depressurization cycle.

an enlargement of the onset of transformation is shown in Figure 3.5. The biased and unbiased specimens group distinctively, the latter transforming at a slightly higher pressure (roughly 6 MPa) than the latter. The precision of our pressure cell is sufficiently high that we believe that this small difference is, nevertheless, resolvable and real.

3.1.3 Hydrostatic Compression Experiments on Unbiased and Biased “Thin” Specimens

With our existing feedthroughs, increasing the applied voltage to quantify the effect was, and remains, unfeasible. However, another way to increase the field density is to apply the same potential to thinner specimens. We subsequently tested four poled specimens in hydrostatic compression that had an inter-electrode thickness of 0.508 cm. Two were tested without the applied voltage, and two with the 1000 V bias. Individual strain gauge and electrical discharge data for two of the four thin-specimen experiments are shown in Figures 3.6-3.9.

Figure 3.4: Comparison of biased and unbiased “thick” specimens in hydrostatic compression. The transformation pressures for the biased specimens are consistently slightly higher.

The limited number of tests, combined with problems with one experiment (FE84; see remarks in Table 2.1), make generalizations tenuous. However, it does appear that application of an electric field results in more pronounced strain anisotropy for thin specimens than thick. While there is weak evidence in one experiment that application of the electric field results in different strains in all three gauge directions in thick specimens (*e.g.*, experiment FE65, Appendix B), the difference in all three strains is pronounced in both of the thin, biased specimens (Figures 3.6 and 3.8). Compared with their thicker counterparts, discharge voltages are slightly lower for both biased and unbiased, thin specimens (Figures 3.7 and 3.9).

Pressure-volume strain data are presented in Figure 3.10, plotted for comparison at the same scale as the biased, thick specimens illustrated in Figure 3.4. The results are comparable for both thin and thick specimens, with the biased specimens transforming at a barely-detectable higher pressure. This is more clearly seen in Figure 3.11, in which the results for biased and unbiased, thin specimens have been overlain on the same detailed view of the transformation onset that was shown in Figure 3.5.

Within the resolution of our measurements, then, the thin specimens exhibit exactly the same

Figure 3.5: Detail of Figure 3.4, at the onset of transformation.

pressure-volume strain behavior as the thick specimens. This result is somewhat troubling. While it is possible that the 1000 V bias is simply too small to produce an effect distinguishable between thick and thin specimens, the possibility exists that the slight shift in transformation pressure *may* simply be a consequence of differences in the electrical states under which the biased and unbiased experiments were run, rather than differences in the electric field densities which were applied. This would explain why the pressure shifts were similar despite the difference in thicknesses.

Unfortunately there are other potential differences between the thick and thin specimens which further cloud our ability to interpret these results. The thin specimens were poled in the same electric field as the thick specimens, but owing to differences in thickness, they could not be poled at the same voltage without experiencing high-voltage breakdown. Owing to the possibility of field fringing, the specimens might not be perfectly identical, though the unbiased thin and thick specimens did transform at virtually the same pressure. This argues that differences between the thick and thin specimens are minimal.

We think that our results merit further investigation into the influence of electrical field on the transformation. However, future experiments must be done in a way which ensures that both specimens and electrical states are as similar as possible in the biased and unbiased tests. It

Figure 3.6: Pressure-strain plot for a hydrostatically compressed, unbiased thin specimen.

will also be important to apply fields much larger than that which we have used in this study. That must await design and acquisition of a new end closure for our 1000 MPa pressure vessel that will permit application of higher voltages without fear of arcing to the closure itself.

3.2 Constant-Stress-Difference Experiments

3.2.1 Unbiased Specimens: Effects of Triaxial Compression on Electromechanical Behavior During Transformation

Eight CSD experiments were performed on poled, unbiased specimens. Individual strain gauge data have already been presented for such an experiment, in Figure 2.2. All three principal strains are different during transformation. As stated earlier, this behavior is somewhat different than that observed in CSD experiments on unpoled material. In these latter tests, axial and lateral strains are different, but both lateral strains are identical. In tests on poled specimens, the net lateral strain parallel to the poling direction is comparable to the axial strain that accumulates during transformation. Again, we attribute this behavior to the preferred crystallographic that

Figure 3.7: Electrical discharge data for the experiment shown in Figure 3.6

develops during poling, and to release of any associated “locked-in” strains that also may have developed during the poling process.

A summary plot of volume strain *versus* mean stress data for these experiments is shown in Figure 3.12. Qualitatively, the results are identical to those for unpoled ceramic under nonhydrostatic stress [Zeuch *et al.*, 1992a,b]: with increasing shear stress, the mean stress for onset of transformation decreases. (As shown below, this conclusion is also nicely illustrated by plots of voltage discharge and discharge rate *versus* mean stress.)

Quantitatively, however, the same shear stress appears to have a somewhat reduced effect on the mean stress for transformation of poled ceramic, when compared to unpoled material. We found it necessary to apply a stress difference of 200 MPa to poled ceramic to achieve approximately the same effect produced by 150 MPa applied to unpoled material. We do not know the reason for this, but we speculate that it may be a consequence of the crystallographic preferred orientation that is imposed upon the specimens by poling and consequent domain realignment. It may be that the predominant domain orientation which results is particularly unfavorable for, or resistant to, transformation relative to the applied stress field. One way to test this hypothesis would be to compress specimens parallel to the poling direction, to see if the effect of the shear stress is greater than that observed in randomly oriented, unpoled ceramic.

Figure 3.8: Pressure-strain plot for a hydrostatically compressed, thin specimen with 1000 V potential applied.

We also observed that increasing shear stress has the same retarding effect on the rate of transformation that we observed during CSD testing of unpoled ceramic [Zeuch *et al.*, 1992a,b]. Recalling that pressure and mean stress are changed at the same constant rate in all experiments, (1) the increasing slope of the mean stress-volume strain curves with shear stress during transformation, and (2) the decreasing downward curvature of the curves at onset of transformation (Figure 3.12) both indicate that the rate of transformation *decreases* with increasing shear stress. Again, however, the effect is qualitatively somewhat less pronounced for the poled material.

We predicted [Zeuch *et al.*, 1992a] that the retarding effect of shear stress on the transformation kinetics of unpoled ceramic might have a similar retarding effect on the depoling rate of poled material. Our current study bears out this prediction. Representative plots of the voltage discharge during hydrostatic and triaxial compression of unbiased specimens are shown in Figure 3.13. Again recalling that the rate of increase in pressure and mean stress is constant for all experiments, (*i.e.*, directly proportional to time), it appears that the rate at which the capacitor charges decreases with increasing shear stress. This is qualitatively indicated by the increasing curvature of the discharge plots with increasing shear stress, where the voltage rises sharply, indicating onset of the transformation.

Figure 3.9: Electrical discharge data for the experiment shown in Figure 3.8

We attempted to quantify the effect by differentiating the voltage discharge data with respect to pressure or mean stress. Results for the four experiments shown in Figure 3.13 are given in Figure 3.14. The results are not entirely consistent because FE78, performed at a stress difference of 100 MPa, appears to have a slightly higher discharge rate than FE64, which was compressed hydrostatically. (Unfortunately, FE77, a replicate of FE78, did not discharge fully and thus was not suitable for differentiation; see Appendix B.) Nevertheless, the general trend indicated in Figure 3.14 is that of a reduction and “broadening” of the discharge rate with increasing shear stress; close examination of Figure 3.14 indicates that FE78 exhibits the same broadening of the discharge curve observable in the other two CSD experiments, FE79 and FE81. This broadening is *not* detectable in the pressure-derivative plot of FE64.

Clearly, additional data would be desirable. However, considering the intrinsic difficulties associated with direct differentiation of data, it appears reasonable to state that our results indicate that increasing shear stresses rapidly reduce the voltage discharge rate. Doubling the former may reduce the latter by about an order of magnitude.

Returning again to Figure 3.13, an interesting feature can be observed in the discharge curves for the CSD experiments at $P=\sigma_m=69$ MPa, the point where the stress difference is first applied. Unlike the curve for the hydrostatic compression test which shows only a small, smooth increase

Figure 3.10: Pressure-volume strain plots for hydrostatically-compressed, biased and unbiased thin specimens.

in voltage with pressurization, the CSD experiments exhibit a slight, but distinct drop in voltage upon loading. We think that this voltage drop can be attributed to alignment of additional dipoles parallel to the poling direction in response to the application of mechanical stress (*e.g.*, Fritz [1978]). Alignment of additional dipoles parallel to poling results in an increase in the bound charge. The sample actually draws charge (current) from the measuring circuit, resulting in the negative bias relative to initial zero potential.

J. D. Keck [personal communication] has pointed out the the magnitude of the voltage drop relative to total discharge voltage (about 4%) is comparable to the decrease in output voltage that occurs when PZT 95/5-2Nb “ages” after poling. It is believed that aging occurs because locked-in poling stresses caused by domain realignment eventually force some marginally oriented dipoles back out of alignment, resulting in a reduction of charge release. Our specimens are oriented such that the mechanical stress that we applied would tend to force such marginally oriented domains back into alignment with the poling direction. The change in discharge voltage that would occur if these domains were reoriented mechanically is consistent with what is observed upon loading [J. D. Keck, personal communication].

Insofar as we are aware, however, this small change in voltage cannot explain the order-of-

Figure 3.11: Same as Figure 3.5, with results from hydrostatically compressed, “thin”, biased and unbiased specimens overlain.

magnitude change in discharge rate that we observe with application of shear stress.

3.2.2 Biased Specimens: Added Effects of a 1000 V Potential on Electromechanical Behavior during Triaxial Compression

Ten CSD experiments were performed on specimens to which a 1000 V bias was applied during transformation. As stated above, biased specimens consistently transformed at a slightly higher pressure than unbiased specimens in hydrostatic compression. However, within the resolution of our equipment, individual strain gauge data for the biased, CSD experiments are indistinguishable from those for experiments on unbiased, poled ceramic (*e.g.*, Figure 2.2). This may be verified by comparing data for CSD experiments on unbiased specimens (Appendix A) with experiments performed at the same stress differences on biased specimens (Appendix B). A summary plot of the mean stress-volume strain data for all biased hydrostatic and triaxial compression experiments on thick specimens is given in Figure 3.15, for comparison with results on unbiased ceramic (Figure 3.12).

Figure 3.12: Summary plot of pressure or mean stress *versus* volume strain for hydrostatic and triaxially compressed, unbiased ceramic.

We remark that results for FE73 ($\sigma_1 - \sigma_3 = 200$ MPa) are not shown in Figure 3.15. This experiment exhibited unusual strain and electrical behavior throughout the test (Appendix B, Figures B.21 and B.22)), transforming at an anomalously high confining pressure and mean stress. It is the only experiment in this investigation to display behavior inconsistent with the systematics shown in Figures 3.12 and 3.15. The multiple “spikes” observed in the discharge voltage data (Figure B.22) suggest a possible explanation for this: Perhaps owing to an intermittent open circuit, this particular sample may not have been able to release its bound charge as rapidly as the others. This *might* have affected the transformation pressure for this particular test, forcing it to occur at an unusually high pressure [Burlage, 1965]. We have not, however, deliberately performed any “open circuit” experiments to confirm this hypothesis. While such tests would be easy to do, safety aspects remain uncertain.

As in virtually all of our CSD experiments, increasing shear stress systematically lowers the mean stress for transformation, and slows the rate of transformation at constant pressurization rate. However, as stated above, there is no clearly distinguishable difference between results of the CSD experiments on biased and unbiased specimens (*cf.* Figures 3.12 and 3.15). We have already shown that if the 1000 V potential has any effect on our hydrostatic compression experiments, it is small. CSD experiments are more complex than the straightforward hydrostatic

Figure 3.13: Representative electrical discharge curves for unbiased ceramic in hydrostatic and triaxial compression. Note the increasing radius of curvature and decrease in slope at onset of transformation as a function of increasing stress difference. This indicates a decrease in the rate of charge release.

tests, with greater cumulative errors introduced by the applied deviatoric load when calculating mean stress. This added error may completely obscure any already-small differences between CSD experiments on biased and unbiased samples.

Representative plots of the voltage discharge during hydrostatic and triaxial compression of the biased specimens are shown in Figure 3.16. These plots are different than those shown in Figure 3.13, owing to the difference in circuitry (*cf.* Figure 2.3). As stated previously, under the arrangement employed for the biased specimens, no capacitor is used. The charge release from the specimen is balanced by a voltage drop across the 100 k Ω resistor, and the change in voltage is proportional to the specimen discharge. The voltage rises, and then falls as discharge is completed.

Despite differences in the ways the charge release was monitored in the two types of test, close similarities are evident. Increasing stress differences result in lower, broader voltage peaks indicating not only lower overall voltages but a decrease in the rate of charge release as well. Though the monitoring technique is different, the interpreted result is identical with that for the

Figure 3.14: Results of differentiation of voltage discharge data presented in Figure 3.13.

CSD experiments on unbiased ceramic.

Figure 3.15: Summary plot of pressure or mean stress *versus* volume strain for hydrostatic and triaxially compressed, biased ceramic. Results for FE73 are omitted.

Figure 3.16: Representative electrical discharge curves for biased ceramic in hydrostatic and triaxial compression. Note the decrease in maximum voltage and broadening of the discharge peak as a function of increasing stress difference, indicating a decrease in the rate of charge release.

Chapter 4

Hydrostatic and CSD Experiments on Poled, Unbiased 541-1 Ceramic

Two hydrostatic compression and four CSD experiments were performed on poled specimens from hifire 541-1. Differences between tests on 424 and 541-1 ceramic have already been discussed in detail in Chapter 2. Test conditions for the 541-1 ceramic are summarized in Table 4.1.

Test ID	Type	$\sigma_1 - \sigma_3$	Remarks
FE53	CSD	100 MPa	
FE54	CSD	100 MPa	
FE55	Hydrostatic	0 MPa	
FE56	Hydrostatic	0 MPa	
FE57	CSD	100 MPa	
FE58	CSD	150 MPa	

Table 4.1: Hydrostatic compression and CSD experiments on poled ceramic from hifire 541-1

Representative plots for hydrostatic compression and CSD experiments on 541-1 ceramic are presented in Figures 4.1 and 4.2, respectively. Detailed test data are presented in Appendix D.

It is clear from Figures 4.1 and 4.2 and the data in Appendix D that with increasing shear stress, the confining pressure at which transformation occurs decreases. This result is at least qualitatively similar to results for 424 ceramic.

Owing to the absence of a strain gauge parallel to the poling direction, we do not present volume strain-mean stress plots like those that we have shown for experiments on 424 ceramic.

FE55, Hifire 541-1: Hydrostatic Compression, Unbiased

Figure 4.1: Representative strain gauge data for hydrostatic compression of 541-1 ceramic. As discussed in the text, only four strain gauges were used.

Data from the latter experiments indicate that lateral strain parallel to the poling direction is significantly greater (up to a factor of two) than lateral strain transverse to poling. Since for small strains

$$\epsilon_v = \epsilon_1 + \epsilon_2 + \epsilon_3, \quad (4.1)$$

the error in calculated volume strain could be large if we assume $\epsilon_2 = \epsilon_3$. Here, ϵ_1 is the axial strain, and ϵ_2 and ϵ_3 are the lateral strain transverse and parallel to poling, respectively.

Again based on our results for 424 ceramic, however, we might assume that though ϵ_2 and ϵ_3 may differ significantly, their absolute magnitudes are both small. Sample cross-sectional area changes computed assuming $\epsilon_2 = \epsilon_3$ would depart only one or two percent from the actual value, even if ϵ_2 and ϵ_3 differ by a factor of two. Thus, values for σ_1 and σ_m calculated assuming $\epsilon_2 = \epsilon_3$ are probably high by only one or two percent. We have calculated σ_1 and σ_m on this basis, and plot discharge voltage *versus* σ_m for 541-1 ceramic in Figure 4.3.

As for poled 424 ceramic, with increasing stress difference, there is a decrease in the mean stress at which the transformation occurs. Furthermore, there is a systematic decrease in peak

FE54, Hifire 541-1: $\sigma_1 - \sigma_3 = 100$ MPa

Figure 4.2: Representative strain gauge data for a CSD experiment on 541-1 ceramic. As discussed in the text, only four strain gauges were used.

voltage, and a broadening of the discharge peak; the latter indicates a decrease in the discharge rate with increasing stress difference.

Capacitance data are plotted against mean stress in Figure 4.4. Again, retardation of transformation kinetics is reflected in the decreasing slope of the curves prior to and during the final drop that marks the transformation. Like the discharge voltage, the capacitance drop is also shifted slightly towards lower mean stresses with increasing shear stress. However, unlike our results for *unpoled* 424 ceramic [Zeuch *et al.* 1994], there is little, if any, shift of the peak capacitance (as measured prior to transformation but after axial loading) to lower mean stresses with increasing shear stress. Indeed, unlike our capacitance measurements for unpoled 424 ceramic, the capacitance of poled 541-1 specimens changes hardly at all with increased pressurization. The reason for this is not known, but may reflect the peculiarities of hifire 541-1 that we have remarked upon previously [Zeuch *et al.*, 1992a, b]. Unfortunately, we have no capacitance data for poled 424 ceramic to which to compare these results. We discuss possible implications of this result later.

In summary, despite differences in experimental technique, poled 541-1 ceramic behaves qualitatively similarly to 424 ceramic in that (1) increasing shear stress lowers the confining pressure

Figure 4.3: Discharge voltage data for hydrostatic compression and CSD experiments on 541-1 ceramic.

and mean stress at which transformation occurs, and (2) slows the rate of transformation, both lowering and broadening the discharge voltage peaks.

Chapter 5

What is the Stress Criterion for Transformation of Poled PZT 95/5-2Nb in Triaxial Compression?

In a recent article [Zeuch *et al.*, 1994] we showed that during nonhydrostatic compression of 424 ceramic, the FE→AFE transformation apparently took place when the maximum compressive stress equaled the hydrostatic pressure at which the transformation otherwise occurred. We demonstrated this by examining volume strain and capacitance data, and making a small correction for piston friction, that otherwise results in a slight overestimate of applied axial stress. We have examined our data for poled 424 ceramic in a similar way, again looking for a criterion by which to predict when the FE→AFE transformation will occur. Though we have not collected capacitance data during the course of this investigation, it appears that either (1) our previous correlation between normal stress and transformation was fortuitous, or (2) the fundamental basis for the correlation—as yet unknown—relies upon an isotropic, randomly-structured polycrystal. Poled ceramic is definitely anisotropic and ordered.

In Figure 5.1 we plot σ_1 versus volume strain for several of the experiments on unbiased ceramic. (The sudden increase in σ_1 at 69 MPa is the point at which additional axial load was applied after initial hydrostatic compression.) Unlike an identical plot for experiments on unpoled ceramic [Zeuch *et al.*, 1994; Fig. 2] it is difficult to argue that under CSD conditions, the transformation occurs anywhere near the 280 to 290 MPa at which it takes place in hydrostatic compression. Results are similar for the experiments on biased material.

In our earlier study on unpoled material [Zeuch *et al.*, 1994], we found the capacitance data to be an unambiguous indicator for the onset of the transformation, unlike the volume strain data. In the absence of capacitance data for poled 424 ceramic, we have plotted discharge voltage versus σ_1 . Certainly, the sharp voltage “spikes” measured during experiments on biased ceramic show

Figure 5.1: Plot of σ_1 versus volume strain for several of the experiments on unbiased ceramic.

an excellent correlation with the transformation as indicated by the volume strain decrease (Figures 5.2–5.5); furthermore, the peaks can be picked unambiguously.

Figures 5.6 and 5.7 show plots of discharge voltage versus σ_1 for experiments on biased and unbiased ceramic. In neither instance are the onsets for transformation shifted into coincidence, which would indicate that the maximum compressive stress is a good criterion for onset of the transformation.

We have *both* discharge voltage and capacitance measurements for our few experiments on 541-1 ceramic, and we have plotted those data against σ_1 in Figures 5.8 and 5.9. Again, the curves are clearly *not* shifted into coincidence, as we would expect if σ_1 is an accurate criterion.

The reason for this difference in behavior of poled and unpoled 424 ceramic is unknown at this time. As stated earlier, it may be that the strong correlation that we observed between maximum compressive stress and onset of transformation of unpoled material is fortuitous. We have not yet had the opportunity to test that correlation using other materials which exhibit the same type of transformation. Alternatively, it must be remembered that poled material differs from unpoled in significant ways, beyond undergoing the FE–AFE transformation at a higher pressure or mean stress owing to added stored energy.

Figure 5.2: Dual plot of volume strain and discharge voltage *versus* time for biased 424 ceramic in hydrostatic compression. The drop from ten to zero volts at about 1900 s is simply the point at which the bias voltage was turned off.

The poling process aligns the spontaneous dipoles of the individual domains parallel to the electric field. This results in a preferred crystallographic orientation, and a mechanical anisotropy that is measurable during hydrostatic compression experiments. In Figures 5.10 through 5.12, we plot the strain gauge data for both poled (this study) and unpoled (this study, and Zeuch *et al.* [1992a, b]) specimens for each of the three corresponding gauge orientations: lateral parallel to the poling direction, lateral transverse to poling, and axial (also transverse to the poling direction). The mechanical anisotropy is most pronounced in the direction parallel to poling (Figure 5.10); it is clear that the poled specimens are visibly more compliant than unpoled in this direction. It is less obvious, but nevertheless true, that poled specimens are stiffer than unpoled in the two directions transverse to the poling directions (Figures 5.11 and 5.12). This orthotropic symmetry is precisely what one would expect from the poling process.

To quantify this comparison, we have performed linear least-squares fits to the pressure-strain data for each of the six gauge sets, for pressures of 200 MPa and below. 200 MPa was chosen somewhat arbitrarily, merely to ensure that we were well below the transformation for both poled and unpoled material. Strain was the dependent variable. Results are shown as dashed and dotted lines on the three plots, and values for the slopes of the lines are given in Table 5.1.

Figure 5.3: Dual plot of volume strain and discharge voltage *versus* time for a CSD experiment on biased 424 ceramic.

Correlation coefficients for all fits were 0.98 or better.

In the direction parallel to poling, poled ceramic is about 20% more compliant than unpoled; in the two directions transverse to poling, poled ceramic is about 7% stiffer. We remarked earlier that this expected anisotropy might explain why greater stress differences are required to reduce the mean stress for transformation of poled ceramic to the same degree that unpoled ceramic is affected. It would be interesting to compress comparably poled PZT 95/5-2Nb parallel to the poling direction, to see if the mean stress is lowered to a greater degree, compared with unpoled ceramic.

Clearly, poled ceramic has a definite mechanical anisotropy, and hence, a strong preferred (non-random) crystallographic orientation. If the thermodynamic basis—as yet not understood—underlying the correlation between maximum compressive stress and transformation in unpoled polycrystals relies upon a randomly-oriented structure, then the correlation would not be expected to hold for poled ceramic; some type of “structure factor” needs to be included. In order to further investigate the maximum compressive stress criterion that we have proposed [Zeuch *et al.*, 1994] it will be necessary to test other materials that exhibit the same type of displacive transformation, under hydrostatic and triaxial stress states. At this time, we have specimens of

Figure 5.4: Dual plot of volume strain and discharge voltage *versus* time for a CSD experiment on biased 424 ceramic. The drop from ten to zero volts at about 2400 s is simply the point at which the bias voltage was turned off.

tin-doped lead-zirconate-titanate ceramic available in our laboratory for immediate testing.

Figure 5.5: Dual plot of volume strain and discharge voltage *versus* time for a CSD experiment on biased 424 ceramic. The voltage increase from zero to ten volts at about 50 s is the point at which the bias voltage was turned on at the start of the experiment.

Specimen Type	Gauge Orientation	$\Delta\epsilon/\Delta P$ (% MPa) ⁻¹
Poled	Axial: Transverse to Poling	4.48×10^{-4}
Unpoled	Axial	4.81×10^{-4}
Poled	Lateral 1 & 2: Transverse to Poling	4.56×10^{-4}
Unpoled	Lateral 1 & 2	4.92×10^{-4}
Poled	Lateral 3: Parallel to Poling	4.79×10^{-4}
Unpoled	Lateral 3	3.85×10^{-4}

Table 5.1: Comparison of corresponding strain gauges from hydrostatic compression experiments on poled and unpoled ceramic from hifire 424.

Figure 5.6: Discharge voltage *versus* σ_1 for experiments on biased 424 ceramic.

Figure 5.7: Discharge voltage *versus* σ_1 for experiments on unbiased 424 ceramic.

Hifire 541-1: Discharge Voltage vs. σ_1

Figure 5.8: Discharge voltage *versus* σ_1 for experiments on unbiased 541-1 ceramic.

Figure 5.9: Discharge voltage *versus* σ_1 for experiments on unbiased 541-1 ceramic.

Figure 5.10: Comparison of non-redundant, lateral strain gauge 3 for poled and unpoled ceramic in hydrostatic compression. For the former specimens, this gauge parallels the poling direction.

Figure 5.11: Comparison of lateral strain gauges 1 & 2 for poled and unpoled ceramic in hydrostatic compression. For the former specimens, these gauges were transverse to poling.

Figure 5.12: Comparison of axial strain gauges 1 & 2 for poled and unpoled ceramic in hydrostatic compression. For the former specimens, these gauges were transverse to poling.

Chapter 6

Discussion and Conclusions

6.1 Principal Observations and Their Implications

We have completed a series of room-temperature, hydrostatic and triaxial compression experiments on poled PZT 95/5–2Nb ceramic, to evaluate the effects of non-hydrostatic stress on electromechanical behavior during the $F_{R1} \rightarrow A_O$ polymorphic transformation. We have also studied the influence of a 1000 V potential on the transformation. These results extend our previous investigation into the effects of non-hydrostatic stress on the same transformation for unpoled material [Zeuch *et al.*, 1992a,b; 1994]. The ultimate objective of this experimental program is to provide data for development of a constitutive model for ceramic undergoing the transformation; the constitutive model will, in turn, be used in 3D finite-element simulations of weapons components as a design aid.

As we predicted from tests on unpoled PZT 95/5-2Nb, increasing the stress difference to 200 MPa decreases the mean stress and confining pressure at which the transformation occurs by 25-33%, for both biased and unbiased conditions. That same stress difference also retards the rate of transformation at constant pressurization rate, resulting in reductions by up to an order of magnitude in the rate of charge release and peak voltage attained in our tests.

At this time it is not clear exactly how these quasi-static results extrapolate to the dynamic conditions extant during neutron generator power supply operation. Nevertheless, discovery of this phenomenon provides a plausible qualitative mechanism for the origin of systematic failures that develop in shock-actuated power supplies when seemingly-minor design changes are introduced. Such changes might include substitution of one hardener for another in the alumina-loaded epoxy (ALOX) potting compound used in the power supplies, or changes in the volume fraction of alumina added to the epoxy. It is not difficult to imagine that as a shock-wave traverses the interface between two subtly mismatched materials, shear stresses

could be generated that are sufficient to reduce electrical outputs to the point of failure. Our hypothesis can be evaluated by shock-wave experiments, numerical simulations, or preferably, both.

Interestingly, our results suggest that any reduction in shear stress components during shock activation might be expected to improve power supply performance in neutron generators. However, it is unclear how to practically accomplish that objective at this time.

Not unexpectedly, transformation strains in poled ceramic are anisotropic in hydrostatic compression (differing by up to about 33%). It is somewhat surprising, however, that the strains are even more anisotropic under non-hydrostatic stress states. A constitutive model needs to predict this behavior. Furthermore, it would be interesting to use numerical simulations to evaluate the sensitivity of power supply performance to strain anisotropy.

Our results suggest that application of a $9.26 \times 10^4 \text{ V m}^{-1}$ electric field detectably increases the transformation pressure for poled ceramic, though only by about 2%. However, this conclusion is clouded by the differing electrical states between our biased and unbiased experiments, and the absence of a detectable effect on the thinner specimens that we tested at the same applied voltage. It would be useful to give additional thought to the manner in which such tests might be conducted in the future in order to maximize the similarity of the two types of experiments. Further, it would be desirable to design and build a new vessel closure that would permit application of higher voltages. If, in fact, the 1000 V potential that we applied is having an effect, it is near the lower limit of our resolution.

In a previous report [Zeuch *et al.*, 1994], we concluded that under non-hydrostatic stress, the FE-AFE transformation took place in unpoled ceramic when the maximum compressive stress equalled the hydrostatic pressure at which the transformation would otherwise occur. We have found that this stress criterion does not apply to the same transformation of poled ceramic. The reason for this is unknown. It may be that the correlation that we previously identified was merely coincidental. However, poled material is not the same as unpoled. The latter is isotropic, while the latter clearly has a pronounced preferred crystallographic orientation and mechanical anisotropy. If the underlying thermodynamic basis for the correlation relies upon a random, polycrystalline structure, then the correlation would not apply to poled ceramic, which is clearly ordered and anisotropic. Our hypothesis could be further tested by performing comparable hydrostatic and CSD experiments on other materials which exhibit polymorphic transformations comparable to the one which we have studied to date.

6.2 Application to FE-AFE Phase Transformation Models

The FE-AFE phase transformation plays a fundamental role in the operation of explosively driven ferroelectric power supplies. A constitutive model describing the phase transformation

has been developed by Montgomery [1986]. It is used in the finite element code SUBWAY to model transient electromechanical responses of power supplies. The phase of the ceramic material is described in the model by using two order parameters to describe the magnitude of spontaneous electrical polarization, P_s , of the material, and the alignment of polarization, μ , of its microscopic structure. A generalized thermodynamic potential energy function dependent on stress, electric field, and the two order parameters provides a description of the material with equilibrium phases being given by values of the order parameters that minimize the potential.

The generalized thermodynamic potential allows the existence of paraelectric, ferroelectric, and antiferroelectric phases in the ceramic. While the potential function is very similar to others used to describe ferroelectric states in ceramics [Haun *et al.*, 1989b] through the dependence on the spontaneous polarization magnitude, the introduction of the polarization alignment parameter, μ , provides the flexibility needed to treat ferroelectric to antiferroelectric transformations in a straightforward manner. In particular, by requiring that μ be restricted to the range -1 to +1, with $\mu = +1$ corresponding to the ferroelectric state in which the microscopic structure has a uniform alignment of spontaneous polarization and $\mu = -1$ corresponding to the antiferroelectric state in which an antiparallel alignment of spontaneous polarization exists, the generalized thermodynamic potential can be constructed so that the only polar states that can exist in the material are purely ferroelectric or antiferroelectric, in accordance with physical observations for PZT 95/5-2Nb.

The thermodynamic potential developed by Montgomery [1986] produces a region of stress-electric field-temperature space in which both ferroelectric and antiferroelectric states of the material can exist. By assuming that the material remains in a given state until it is unstable, the model can produce the hysteresis observed in PZT 95/5-2Nb as the material transforms from ferroelectric to antiferroelectric and then back to ferroelectric.

Because detailed information on effects of stress and electric field on phase transition boundaries has hitherto been lacking, early development of the generalized thermodynamic potential function for PZT95/5-2Nb used simple dependencies on stress and electric field. In particular, it was assumed that stress state influenced the potential function through pressure. This allowed the measured forward transformation pressure, P_F , describing the transformation from ferroelectric to antiferroelectric state, and the back transformation pressure, P_B , describing the transformation back from the antiferroelectric to ferroelectric state to be used in characterizing the thermodynamic potential function. Information from this and our earlier study [Zeuch *et al.*, 1992a,b] has been used to provide guidance for simple modifications of the SUBWAY model for a generalized potential consistent with experimental observations. The development of a more realistic representation for the thermodynamic potential function of PZT 95/5-2Nb, using these results, is in preparation.

6.3 Speculation on the Origin of Transient Strain Reversals

We close with some speculation on the nature of the slow reversals that we observe in lateral strain gauges just prior to transformation, during CSD experiments on both poled and unpoled ceramic. The rapid reversals and overshoots (called "spikes", earlier) that we have reported occur only in poled material, in both lateral and axial gauges, and under both hydrostatic and CSD conditions. While they bear further investigation using different strain-measuring techniques (*e.g.*, using LVDTs), it seems likely that these are some type of electrical noise or interference with the strain gauges that occurs randomly upon discharge.

The slow reversals are somewhat more difficult to explain, because they occur in both poled and unpoled material, and under CSD conditions and in lateral gauges only. That they occur in unpoled specimens would seem to rule out electrical effects on the strain gauges. Beyond that, systematics are less clear, because all or none of the gauges may exhibit such behavior in any given experiment.

Certainly, microcracking could explain the rarefaction recorded by the reversing gauges. Highly localized, minor amounts of cracking could explain why all or none of the gauges might exhibit such behavior in any given test. However, in our CSD experiments the shear stress is kept constant while the mean stress increases. Unless the microcracking is time-dependent, we would expect maximum cracking to occur immediately upon loading where the confining pressure is lowest. Increasing σ_3 and σ_m would serve to progressively *suppress* microcracking. Instead, we see rarefaction increasing where confinement is greatest. Furthermore, our earlier optical and scanning electron microscope investigations argue against the occurrence of microcracking.

Similarly, eccentric loading might explain some aspects of these observations, but would not explain why all three lateral gauges suddenly exhibit rarefaction, as we have occasionally observed. This suggests very even loading. Furthermore, in rare, early experiments where eccentric loading has occurred, axial gauges also behaved peculiarly, especially at the outset of the tests; for example, one axial gauge might exhibit extreme compression, while the other records tension (*i.e.*, bending). We have seen no such unusual behavior in the axial gauges, thus we reject bad sample machining and uneven loading as explanations at this time.

We suggest that another explanation exists. Though it is complete speculation at this time, it would be an intriguing subject for future investigation.

During some polymorphic phase transformations, dynamic measurements have shown that the elastic shear modulus undergoes a transient "softening", or even complete disappearance [Novotny and Smith, 1965; Anderson and Demarest, 1971; Gunton and Saunders, 1974]. The lateral gauge reversals would be consistent with some premonitory shear weakening as the transformation pressure is approached. Under constant shear stress, some added lateral rarefaction and axial compression would be expected if suitably oriented crystals undergo

transient shear weakening prior to transformation. This qualitative model would explain why this phenomenon only occurs in CSD experiments, and how rarefaction can increase with increasing mean stress. It would also explain how the lateral tensile strain occurs without any microscopic evidence for microcracking: there would be none. It does not explain why the reversal does not occur in every CSD experiment, or why it is often not observed in all lateral gauges when it does. As with the microcracking hypothesis, we can only suggest the effect might be localized or too subtle for all but the most perfectly bonded gauges to detect.

At this time, this qualitative model is entirely speculative, though it explains a number of our observations. We could further test and quantify the model by repeating the CSD experiments while continuously measuring acoustic velocities across the phase boundary. This would require employing a larger specimen size than we have used in this investigation, in order to maximize wave travel times and optimize measurements. However, if larger specimens are obtainable, the Dept. 6117 Rock Mechanics laboratory already has the test equipment available to do such experiments, including a large-bore, 400 MPa pressure vessel equipped with coaxial feedthroughs, a 4.45 MN load frame, and an ultrasonic velocity measurement system.

Confirmation and quantification of this model would be of interest in several areas. First, it is important to our continuing program to better understand and model the behavior of PZT 95/5-2Nb in the shock-actuated power supplies used in neutron generators. Second, it is of general interest in the field of materials science and engineering, where polymorphic phase transformations are now being used to improve materials performance, as in "transformation toughened" ceramics. Finally, it may be of interest to earth scientists, where increased knowledge of polymorphic phase transformations among minerals is integral to refinement of our indirect determination of the composition, structure and physics of Earth's interior. An understanding of the transient effects of polymorphic transformations on elastic moduli and seismic wave velocities near phase boundaries in the earth is very important to our interpretation of the seismic signals that constitute much of our information about Earth's deep interior (*e.g.*, Anderson and Demarest [1971]). While much is known about simple systems and structures, (alkali halides and metals) information on oxides remains elusive.

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Chapter 7

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Appendix A

Unbiased Specimens

Figure A.1: Strain gauge data for FE62.

Figure A.2: Electrical discharge data for FE62.

FE63: Hydrostatic Compression, Unbiased & Unpoled

Figure A.3: Strain gauge data for FE63.

Figure A.4: Strain gauge data for FE64.

Figure A.5: Electrical discharge data for FE64.

Figure A.6: Strain gauge data for FE66.

Figure A.7: Electrical discharge data for FE66.

FE76: $\sigma_1 - \sigma_3 = 100$ MPa, Unbiased

Figure A.8: Strain gauge data for FE76.

FE76: $\sigma_1 - \sigma_3 = 100$ MPa

Figure A.9: Electrical discharge data for FE76.

FE76: $\sigma_1 - \sigma_3 = 100$ MPa, Unbiased

Figure A.10: Loading path for FE76.

FE76: $\sigma_1 - \sigma_3 = 100$ MPa, Unbiased

Figure A.11: Stress difference data for FE76.

FE77: $\sigma_1 - \sigma_3 = 100$ MPa, Unbiased

Figure A.12: Strain gauge data for FE77.

FE77: $\sigma_1 - \sigma_3 = 100$ MPa

Figure A.13: Electrical discharge data for FE77.

FE77: $\sigma_1 - \sigma_3 = 100$ MPa, Unbiased

Figure A.14: Loading path for FE77.

FE77: $\sigma_1 - \sigma_3 = 100$ MPa, Unbiased

Figure A.15: Stress difference data for FE77.

FE78: $\sigma_1 - \sigma_3 = 100$ MPa, Unbiased

Figure A.16: Strain gauge data for FE78.

FE78: $\sigma_1 - \sigma_3 = 100$ MPa

Figure A.17: Electrical discharge data for FE78.

FE78: $\sigma_1 - \sigma_3 = 100$ MPa, Unbiased

Figure A.18: Loading path for FE78.

FE78: $\sigma_1 - \sigma_3 = 100$ MPa, Unbiased

Figure A.19: Stress difference data for FE78.

FE79: $\sigma_1 - \sigma_3 = 150$ MPa, Unbiased

Figure A.20: Strain gauge data for FE79.

FE79: $\sigma_1 - \sigma_3 = 150$ MPa

Figure A.21: Electrical discharge data for FE79.

FE79: $\sigma_1 - \sigma_3 = 150$ MPa, Unbiased

Figure A.22: Loading path for FE79.

FE79: $\sigma_1 - \sigma_3 = 150$ MPa, Unbiased

Figure A.23: Stress difference data for FE79.

FE80: $\sigma_1 - \sigma_3 = 150$ MPa, Unbiased

Figure A.24: Strain gauge data for FE80.

FE80: $\sigma_1 - \sigma_3 = 150$ MPa

Figure A.25: Electrical discharge data for FE80

FE80: $\sigma_1 - \sigma_3 = 150$ MPa, Unbiased

Figure A.26: Loading path for FE80

FE80: $\sigma_1 - \sigma_3 = 150$ MPa, Unbiased

Figure A.27: Stress difference data for FE80.

FE81: $\sigma_1 - \sigma_3 = 200$ MPa, Unbiased

Figure A.28: Strain gauge data for FE81.

FE81: $\sigma_1 - \sigma_3 = 200$ MPa

Figure A.29: Electrical discharge data for FE81.

FE81: $\sigma_1 - \sigma_3 = 200$ MPa, Unbiased

Figure A.30: Loading path for FE81.

FE81: $\sigma_1 - \sigma_3 = 200$ MPa, Unbiased

Figure A.31: Stress difference data for FE81.

FE82: $\sigma_1 - \sigma_3 = 200$ MPa, Unbiased

Figure A.32: Strain gauge data for FE82.

FE82: $\sigma_1 - \sigma_3 = 200$ MPa

Figure A.33: Electrical discharge data for FE82.

FE82: $\sigma_1 - \sigma_3 = 200$ MPa, Unbiased

Figure A.34: Loading path for FE82.

FE82: $\sigma_1 - \sigma_3 = 200$ MPa, Unbiased

Figure A.35: Stress difference data for FE82.

Appendix B

Biased Specimens

Figure B.1: Strain gauge data for FE65.

Figure B.2: Strain gauge data for FE67.

Figure B.3: Electrical discharge data for FE67.

Figure B.4: Strain gauge data for FE68.

Figure B.5: Electrical discharge data for FE68.

FE69: $\sigma_1 - \sigma_3 = 100$ MPa, 1000 V Bias

Figure B.6: Strain gauge data for FE69.

FE69: $\sigma_1 - \sigma_3 = 100$ MPa, 1000 V Bias

Figure B.7: Electrical discharge data for FE69.

FE69: $\sigma_1 - \sigma_3 = 100$ MPa, 1000 V Bias

Figure B.8: Loading path for FE69.

FE69: $\sigma_1 - \sigma_3 = 100$ MPa, 1000 V Bias

Figure B.9: Stress difference data for FE69.

FE70: $\sigma_1 - \sigma_3 = 150$ MPa, 1000 V Bias

Figure B.10: Strain gauge data for FE70.

FE70: $\sigma_1 - \sigma_3 = 150$ MPa, 1000 V Bias

Figure B.11: Loading path for FE70.

FE70: $\sigma_1 - \sigma_3 = 150$ MPa, 1000 V Bias

Figure B.12: Stress difference data for FE70.

FE71: $\sigma_1 - \sigma_3 = 150$ MPa, 1000 V Bias

Figure B.13: Strain gauge data for FE71.

FE71: $\sigma_1 - \sigma_3 = 150$ MPa, 1000 V Bias

Figure B.14: Electrical discharge data for FE71.

FE71: $\sigma_1 - \sigma_3 = 150$ MPa, 1000 V Bias

Figure B.15: Loading path for FE71.

FE71: $\sigma_1 - \sigma_3 = 150$ MPa, 1000 V Bias

Figure B.16: Stress difference data for FE71.

FE72: $\sigma_1 - \sigma_3 = 100$ MPa, 1000 V Bias

Figure B.17: Strain gauge data for FE72.

FE72: $\sigma_1 - \sigma_3 = 100$ MPa, 1000 V Bias

Figure B.18: Electrical discharge data for FE72.

FE72: $\sigma_1 - \sigma_3 = 100$ MPa, 1000 V Bias

Figure B.19: Loading path for FE72.

FE72: $\sigma_1 - \sigma_3 = 100$ MPa, 1000 V Bias

Figure B.20: Stress difference data for FE72.

FE73: $\sigma_1 - \sigma_3 = 200$ MPa, 1000 V Bias

Figure B.21: Strain gauge data for FE73.

FE73: $\sigma_1 - \sigma_3 = 200$ MPa, 1000 V Bias

Figure B.22: Electrical discharge data for FE73

FE73: $\sigma_1 - \sigma_3 = 200$ MPa, 1000 V Bias

Figure B.23: Loading path for FE73

FE73: $\sigma_1 - \sigma_3 = 200$ MPa, 1000 V Bias

Figure B.24: Stress difference data for FE73.

FE74: $\sigma_1 - \sigma_3 = 200$ MPa, 1000 V Bias

Figure B.25: Strain gauge data for FE74.

FE74: $\sigma_1 - \sigma_3 = 200$ MPa, 1000 V Bias

Figure B.26: Electrical discharge data for FE74.

FE74: $\sigma_1 - \sigma_3 = 200$ MPa, 1000 V Bias

Figure B.27: Loading path for FE74.

FE74: $\sigma_1 - \sigma_3 = 200$ MPa, 1000 V Bias

Figure B.28: Stress difference data for FE74.

FE75: $\sigma_1 - \sigma_3 = 200$ MPa, 1000 V Bias

Figure B.29: Strain gauge data for FE75.

FE75: $\sigma_1 - \sigma_3 = 200$ MPa, 1000 V Bias

Figure B.30: Electrical discharge data for FE75.

FE75: $\sigma_1 - \sigma_3 = 200$ MPa, 1000 V Bias

Figure B.31: Loading path for FE75.

FE75: $\sigma_1 - \sigma_3 = 200$ MPa, 1000 V Bias

Figure B.32: Stress difference data for FE75.

Appendix C

“Thin” Specimens: Unbiased and Biased

Figure C.1: Strain gauge data for FE83.

Figure C.2: Electrical discharge data for FE83.

Figure C.3: Strain gauge data for FE84.

Figure C.4: Electrical discharge data for FE84.

Figure C.5: Strain gauge data for FE85.

Figure C.6: Electrical discharge data for FE85.

Figure C.7: Strain gauge data for FE86.

Figure C.8: Electrical discharge data for FE86.

Appendix D

Hifire 541-1: Hydrostatic Compression and CSD Experiments

FE53, Hifire 541-1: $\sigma_1 - \sigma_3 = 100$ MPa, Unbiased

Figure D.1: Strain gauge data for FE53.

FE53, Hifire 541-1: $\sigma_1 - \sigma_3 = 100$ MPa, Unbiased

Figure D.2: Electrical discharge data for FE53.

FE53, Hifire 541-1: $\sigma_1 - \sigma_3 = 100$ MPa, Unbiased

Figure D.3: Capacitance data for FE53.

FE53, Hifire 541-1: $\sigma_1 - \sigma_3 = 100$ MPa, Unbiased

Figure D.4: Stress difference data for FE53.

FE53, Hifire 541-1: $\sigma_1 - \sigma_3 = 100$ MPa, Unbiased

Figure D.5: Loading path for FE53.

FE54, Hifire 541-1: $\sigma_1 - \sigma_3 = 100$ MPa, Unbiased

Figure D.6: Strain gauge data for FE54.

FE54, Hifire 541-1: $\sigma_1 - \sigma_3 = 100$ MPa, Unbiased

Figure D.7: Electrical discharge data for FE54.

FE54, Hifire 541-1: $\sigma_1 - \sigma_3 = 100$ MPa, Unbiased

Figure D.8: Capacitance data for FE54.

FE54, Hifire 541-1: $\sigma_1 - \sigma_3 = 100$ MPa, Unbiased

Figure D.9: Stress difference data for FE54.

FE54, Hifire 541-1: $\sigma_1 - \sigma_3 = 100$ MPa, Unbiased

Figure D.10: Loading path for FE54.

FE55, Hifire 541-1: Hydrostatic Compression, Unbiased

Figure D.11: Strain gauge data for FE55.

FE55, Hifire 541-1: Hydrostatic Compression, Unbiased

Figure D.12: Electrical discharge data for FE55.

FE55, Hifire 541-1: Hydrostatic Compression, Unbiased

Figure D.13: Capacitance data for FE55.

FE56, Hifire 541-1: Hydrostatic Compression, Unbiased

Figure D.14: Strain gauge data for FE56.

FE56, Hifire 541-1: Hydrostatic Compression, Unbiased

Figure D.15: Electrical discharge data for FE56.

FE56, Hifire 541-1: Hydrostatic Compression, Unbiased

Figure D.16: Capacitance data for FE56.

FE57, Hifire 541-1: $\sigma_1 - \sigma_3 = 100$ MPa, Unbiased

Figure D.17: Strain gauge data for FE57.

FE57, Hifire 541-1: $\sigma_1 - \sigma_3 = 100$ MPa, Unbiased

Figure D.18: Electrical discharge data for FE57.

FE57, Hifire 541-1: $\sigma_1 - \sigma_3 = 100$ MPa, Unbiased

Figure D.19: Capacitance data for FE57.

FE57, Hifire 541-1: $\sigma_1 - \sigma_3 = 100$ MPa, Unbiased

Figure D.20: Stress difference data for FE57.

FE57, Hifire 541-1: $\sigma_1 - \sigma_3 = 100$ MPa, Unbiased

Figure D.21: Loading path for FE57.

FE58, Hifire 541-1: $\sigma_1 - \sigma_3 = 150$ MPa, Unbiased

Figure D.22: Strain gauge data for FE58.

FE58, Hifire 541-1: $\sigma_1 - \sigma_3 = 150$ MPa, Unbiased

Figure D.23: Electrical discharge data for FE58.

FE58, Hifire 541-1: $\sigma_1 - \sigma_3 = 150$ MPa, Unbiased

Figure D.24: Capacitance data for FE58.

FE58, Hifire 541-1: $\sigma_1 - \sigma_3 = 150$ MPa, Unbiased

Figure D.25: Stress difference data for FE58.

FE58, Hifire 541-1: $\sigma_1 - \sigma_3 = 150$ MPa, Unbiased

Figure D.26: Loading path for FE58.

Appendix E

Distribution

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