Electric Fatigue in Lead Zirconate Titanate Ceramics

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Electric fatigue is a major obstacle for some potential applications of ferroelectric materials based on reversals of spontaneous polarization, such as memory devices and high strain actuators. Our studies of fine-grained hot-pressed lead zirconate titanate with lanthanum dopant (PLZT 7/68/32) show that fast fatigue is actually caused by contaminated surfaces instead of intrinsic structure deterioration or the change of domain states. All of the specimens with conventionally cleaned surfaces showed significant fatigue after $10^6$ switching cycles, but specimens cleaned with a new cleaning procedure did not fatigue even after more than $10^6$ switching cycles. This type of fatigue is found to be due to generated microcracking at the ceramic–electrode interface.

I. Introduction

Many applications of ferroelectric materials, such as some piezoelectric, electro-optical, and electrostrictive devices, involve repeated reversals of polarization. One critical limitation on the performance of these devices is fatigue associated with repeated electrical cycling. Fatigue in ferroelectrics mainly refers to the degradation of ferroelectric properties upon repeated reversals of polarization, which appears in the hysteresis loop in the form of a decrease in remnant polarization ($P_r$) or saturated polarization ($P_s$) and is often accompanied by an increase of the coercive field ($E_c$).

In 1953, McQuarrie¹ first reported the time dependence of the $P–E$ hysteresis loop in a BaTiO$_3$ ceramic. He found that after several weeks of switching at 60 Hz, the square-shaped hysteresis loop was changed to a distinct propeller shape with a noticeable decrease in both the maximum polarization and the remnant polarization. Merz and Anderson² studied fatigue behavior in a BaTiO$_3$ single crystal. A gradual reduction of the polarization after a few million switching cycles was observed and the fatigue behavior was related to the wave patterns of the electric field (sine wave or pulse train wave). The ambient atmosphere was also reported to have an effect on the switching stability of BaTiO$_3$ single crystal.³ A loss of squareness of the hysteresis loop was observed when the crystal was switched under vacuum, N$_2$, H$_2$, or He gases. However, the deteriorated hysteresis loop could restore its original shape under ac cycling in O$_2$, or in dry air.

Fatigue experiments were also carried out on other ferroelectrics in the 1960s. Taylor¹ studied fatigue phenomena in 24 compositions of niobium-doped Pb(Zr,Sn,Ti)O$_3$ ceramics and discovered that the fatigue rate depended on the composition. Contrary to Ref. 2, he found little difference in fatigue behavior when the ac electric field pattern was changed from a sine wave to a pulse train wave. A more detailed study of fatigue in La- or Bi-doped PZT ceramics was carried out by Stewart and Cosentino.⁴ They showed that the polarization decreased rapidly, and the remnant polarization was reduced to half of its original value after $5 \times 10^6$ switching cycles. They concluded that the patterns of the electric field, the types of electrodes, and the ambient conditions had no significant effects on the fatigue behavior. Stewart and Cosentino also reported an interesting result: when a fatigued sample was heated above the paraelectric–ferroelectric phase transition temperature $T_c$, the properties could be restored. Contrary to Stewart and Cosentino, Fraser and Maldonado⁵ also studied the same La-doped PZT ceramics and reported significant effects of electrodes. They found that when indium was used as the electrode material instead of gold or silver, there was still 85% of the original remnant polarization left after $10^6$ switching cycles, but fatigue occurred much faster when using lead, aluminum, gallium, silver, and gold as electrode materials. Carl⁶ observed significant degradation in the La- or Mn-doped PbTiO$_3$ ceramics; after only a few thousand switching cycles the polarization dropped to 30% of its original value together with some increase of the coercive field, and some cracks were also observed under SEM on surfaces of the samples.

Although the fatigue phenomena in ferroelectrics have been studied for over 30 years, their origin is still not clear. Some possible causes of fatigue under high ac field are (1) the gradual reorientation of domains into a more stable, i.e., minimum energy, configuration;¹² (2) injection of charge carriers into the ferroelectrics which provide pinning for domain wall movement;³ (3) structural inhomogeneity which produces traps for domain walls, reducing domain wall mobility;¹³ (4) the appearance of microcracking caused by the large change of strain during switching.⁷¹¹

Despite the fact that the fatigue effect is the key factor which prevents some potential applications of ferroelectrics, very few conclusive results have been published. In addition, those published results by different investigators are often in contradiction, and there are no explanations for these discrepancies. Therefore, a systematic study of this subject is needed in order to understand the origin and mechanism of fatigue behavior. We report here an extensive study of the fatigue behavior of a La-doped lead zirconate titanate (PLZT) ceramic system. The reason for choosing a PLZT ceramic system is because of its relatively low coercive field, large polarization, and square-shaped hysteresis loop. Moreover, hot-pressed PLZT ceramics are transparent and are almost pore free, which can eliminate the structural complications in a regular ceramic, leading to some understanding of the fundamental aspects of fatigue. In this paper, the focus will be on the effect of surface contamination on the fatigue behavior. Inconsistencies reported in some previously experimental studies can be explained in terms of different surface conditions.

II. Experimental Procedure

Lanthanum-doped lead zirconate titanate ceramic specimens were fabricated from mixed oxides by hot pressing. The composition used in this study was Pb$_{70.93}$La$_{0.07}$(Zr$_{0.64}$Ti$_{0.36}$)$_{0.985}$O$_{3}$. Conventionally, this formula is simplified to the form 7/68/32 according to the mole ratio of La/Zr/Ti. The average grain size was about 5 μm. At room temperature 7/68/32 is in a rhombohedral phase. Samples were first cut into platelets with areas of

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³ Member, American Ceramic Society.
about 10 mm² and thicknesses in the range of 150–300 μm, and then annealed at 600°C for 2 h to release the mechanical stress generated during the cutting, grinding, and polishing processes.

Three different surfaces were prepared: (a) ground by 3-μm abrasive, (b) polished by 1-μm diamond paste, (c) etched in H₃PO₄ acid for 2 min at 140°C. In the conventional cleaning procedure, organic solvents (alcohol or acetone) were used to rinse the samples and then the samples were dried in air at room temperature. An improved cleaning method used in our experiments is described as follows: first the samples were cleaned by conventional procedure, then they were further cleaned ultrasonically in alcohol solvent, and finally the samples were heated in a furnace for 1 h at 500–600°C to burn off the organic solvent. Gold electrodes were sputtered onto the sample surfaces.

The properties studied here are the remnant polarization P_r, the maximum polarization P_m, the coercive field E_c, and the dielectric constant ε of the depoled state. A high-voltage sine wave ac field was used to switch the polarization, and the hysteresis loops were measured through a conventional Sawyer-Tower circuit and a Nicolet 214 digital oscilloscope. The temperature dependence of the dielectric constant was measured with a Hewlett-Packard 4274A LRC meter, and the temperature was measured using a Fluke 8502A digital multimeter. The heating rate was set at 3°C/min.

III. Results and Discussion

(1) Fatigue in PLZT Specimens Cleaned by Conventional Procedure

In order to compare the results from different specimens and to emphasize the changes of the measured properties, the relative polarization and the coercive field are used in this paper; they represent the percentages of the polarization and coercive field with respect to the initial polarization and the coercive field obtained at 10⁴ or 10⁴ switching cycles. Figure 1 shows the typical results obtained from specimens cleaned by conventional procedure. One can see that fatigue started at about 10⁴ switching cycles, and proceeded very rapidly between 10⁴ and 10⁵ cycles. The remnant polarization P_r dropped to 30% of the initial values after 10⁵ switching cycles. The changes of the maximum polarizations, which are not shown here, exhibit a similar behavior as the remnant polarization P_r. Figure 2 shows typical hysteresis loops before and after the fatigue test, observed from a sample with ground surfaces. The coercive fields E_c also increased with switching cycles. There is a direct correlation between the changes of E_c and P_r; i.e., while the polarization decreases, the coercive field E_c increases, which is consistent with the results obtained by other researchers.⁴,⁶,¹¹

We found that the ground sample fatigue earlier and faster than the samples with polished and etched surfaces. The same experiments were also carried out using a sine wave field at other frequencies. No apparent changes were observed for frequencies less than 600 Hz. Curves (a) and (e) in Fig. 3 show the weak field dielectric constant as a function of temperature for a sample with polished surfaces before and after the fatigue test, respectively. One can see a substantial decrease of the dielectric constant in the fatigued sample. Samples with the other two types of surfaces exhibit similar results which are not shown here.

(2) Fatigue in PLZT Specimens Cleaned by Improved Procedure

Figure 4 shows the changes in the polarization and the coercive field with switching cycles for samples cleaned by an improved procedure described in Section II. The experiments were carried out at a frequency of 100 Hz. Samples with all three types of surfaces did not show fatigue even after 10⁶ switching cycles. We found that the hysteresis loops recorded at 10⁴ and 2 × 10⁶ switching cycles are almost identical. These experimental results tell us that the fatigue shown in Fig. 1 is purely extrinsic, i.e., resulted from an improper cleaning method. The actual lifetimes of PLZT 7/68/32 ceramics with grain size of 5 μm are much longer than those shown in Fig. 1 and are not affected by the surface roughness.

(3) Fatigue Originating from Surface Contamination

(A) Deterioration of the Ferroelectric–Electrode Interface under High ac Field: In fatigue experiments the possible sources of contaminants are abrasive residue from the grinding process, residue of solvents (water, alcohol, or acetone), water in the air, residue of the bonding glue, and skin grease from finger touch. Without further cleaning these residues are left on the surfaces of specimens, being sandwiched between the sample surface and the electrode, producing a poor interface contact. The effects of solvents and skin grease were further

![Fig. 1](image-url) Changes of the relative remnant polarization P_r (a) and the relative coercive field E_c (b) with switching cycles for a conventionally cleaned PLZT 7/68/32 specimen. Test frequency is 10 Hz.

![Fig. 2](image-url) Typical hysteresis loops after 10⁴ (a) and 3 × 10⁶ (b) switching cycles for a conventionally cleaned PLZT 7/68/32 sample with ground surfaces. Test frequency is 10 Hz.
washed in water and acetone, then dried in air at room temperature; (c) sample 3 was washed in water and acetone, then heat-treated in a furnace at 500°C for 1 h.

Figure 5 shows the results from fatigue tests on these three samples using a 100-Hz sine wave ac field. The remnant polarization of sample 3 did not decrease at all after $10^8$ switching cycles; only $E_c$ increased slightly (we note that in all etched samples, $E_c$ shows a slight increase at the beginning and then becomes stable). $P_r$ of sample 2 fatigued to 85% of its initial value after $10^7$ switching cycles and $E_c$ increased about 18%. Sample 1 was the worst among the three samples; its $P_r$ reduced to 30% of the initial value and $E_c$ increased 50% after only $2 \times 10^8$ cycles. Heating PLZT ceramic samples to 500°C after washing had two effects: (1) burning off the organic residues on the surface, and (2) releasing bulk and surface stresses. Since these three samples were already heat-treated at 600°C for 2 h to release stresses before the surface preparation described above, heating sample 3 to 500°C for 1 h after washing should not have changed its properties except to burn off solvent residues on the sample surfaces. Since the three samples with the same etched surfaces differed only in surface treatments, the discrepancies in the fatigue results can be explained only in terms of the different degrees of surface contamination.

Experiments also indicate that fatigue is initiated at the ceramic–electrode interface. Possible explanations for what might have happened at the interface are the following: (1) electrochemical reaction, such as ionization of contaminants and field-induced chemical decomposition near the sample surface; (2) corona—high voltage can ionize water and organics, causing partial discharge which leads to a time related continuous degradation of the dielectric property; (3) a contact deterioration effect—residue of solvents and skin grease prohibit direct contact of the metal electrode with the sample surface, resulting in poor contact. Partial failure of the electrode was

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Figure 3. Temperature dependence of the dielectric constant in depoled state for a conventionally cleaned sample with polished surfaces: (a) fatigued sample; (b) fatigued sample after heat treatment at 500°C for 3 h; (c) fatigued sample after heat treatment at 600°C for 1 h; (d) a 15-μm-thick layer was ground off from each side of the sample; (e) results from a virgin nonfatigued sample.

Figure 4. Relative polarization (a) and the relative coercive field (b) versus switching cycles, respectively, for a specimen cleaned by an improved procedure. Test frequency is 100 Hz.

Figure 5. Effects of contaminations on the fatigue behavior. Sample 1 was contaminated by solvent and skin grease; sample 2 was contaminated by solvent; sample 3 was cleaned by an improved procedure.
Fig. 6. SEM photograph taken from the electroded surface of a fatigued sample. Part of the electrode was peeled off from the sample surface during the switching process.

directly observed under SEM on the electroded surface of fatigued samples as shown in Fig. 6.

(B) Nature of the Fatigue: Fatigue caused by surface contamination started at the sample surfaces where high field concentrations occurred. In order to see if the fatigue damage extended into the interior of the ceramic with a prolonged switching time, we measured the bulk dielectric constant as a function of temperature. The sample thickness was 200 μm and the measurements were done at 1-kHz frequency. The maximum temperature in the measurement was 190°C, which was above the Curie temperature (130°C for PLZT 7/68/32). The results are given in Fig. 3. One can see a drastic decrease of the dielectric constant in the fatigued sample (after $2 \times 10^6$ cycles), especially close to the Curie temperature region (curve (a) in Fig. 3).

Different heat treatments were applied to this fatigued sample to see if the fatigued physical properties could be recovered. Curve (b) in Fig. 3 is the temperature dependence of the dielectric constant measured after the fatigued sample went through a heat treatment at 300°C for 3 h. Only partial recovery was achieved. The sample then experienced further heat treatment at 600°C for 1 h and further improvement was observed as shown in curve (c) of Fig. 3. However, the dielectric constant still did not recover to its initial value, which means that part of the damage is permanent. In order to investigate the depth of the damage from the surface initiated fatigue, 15 μm at the sample surfaces was ground off and the sample was re-electroded using the sputtering technique. The measured results are shown in Fig. 3, curve (d). No further improvement was achieved. The high-field properties, i.e., the remnant polarization $P_r$ and the coercive field $E_c$, were also measured after each heating, re-electroding, and thinning (Table I). One can reach the same conclusion from the results in Table I as from the results of weak field dielectric measurements. The dielectric and polarization measurements were also performed in a sample with a thickness of 700 μm; fatigue was observed after $2 \times 10^6$ cycles. However, it was found that the dielectric constant and the polarization could almost be restored to their initial values after a 150-μm layer was ground off from the sample surfaces. The experimental results indicate that fatigue damage propagated fairly deeply into the interior of the sample after more than $10^6$ switching cycles (note the damage was only near the surface within $10^5$ cycles).

Previously, fatigue in ferroelectrics was explained as due to the stabilization of domain walls, which can be recovered by heating the fatigued sample into the paraelectric phase. In our experiments, total recovery did not occur even after the fatigued sample was heated to as high as 600°C, 470°C higher than the Curie temperature. Hence, the fatigue that we have observed cannot be due to domain wall pinning; instead, we believe that intergranular microcracking is responsible for the nonrecoverable fatigue initiated by surface contamination. Scanning electron microscopy was performed on a fatigued sample (Fig. 7(a)) and a nonfatigued sample (Fig. 7(b)) with ground surfaces (the samples were etched using H$_3$PO$_4$ acid to remove gold electrodes). On the micrographs in Fig. 7(b), we can see some grinding damage and etch-pits for the nonfatigued sample, while for the fatigued sample (Fig. 7(a)) the majority of the grains do not have grinding damage or etch-pits. This means that a whole layer over these grains was pulled off during etching, which indicates that the bonding between grains was weakened in the fatigued sample near the surface. In addition, some

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<th>Table I. Comparison of the Remnant Polarization and the Coercive Field for a PLZT 7/68/32 Sample under Different Treatments</th>
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Fig. 7. SEM micrograph taken from a fatigued sample (a) and a nonfatigued sample (b) after chemical etching. Etch-pits were not found on the surface of the fatigued sample because a loosened layer was etched off.
pressed PLZT 7/68/32 ceramics with a grain size of 5 μm. It was found that the observed fatigue occurred within 10² switching cycles and was caused by surface contamination. We suggest that the fatigue initiated by surface contamination in hot-pressed PLZT 7/68/32 ceramics is through microcracking at the boundaries of the switched and nonswitched regions near the ceramic-electrode interface, which progressively extends into the interior of the ceramic with prolonged switching.

The conventional cleaning method has proved to be inappropriate for specimens used under high ac field. An improved cleaning procedure described here can eliminate fatigue for at least 10⁶ switching cycles, which is a very encouraging result for some potential applications based on polarization reversals.

Contrary to some reported results, we found that fatigue damage is permanent, although it is only limited at the surface region at the beginning. Some physical properties of the fatigued sample can be partially recovered through thermal treatment; however, complete recovery is not possible.

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References