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# Effects of porosity on electric fatigue behaviour in PLZT and PZT ferroelectric ceramics

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Electric fatigue, namely the decay of the polarization and the consequent elastic strain with increased number of switching cycles under high a.c. field, severely limits the applications of ferroelectric and piezoelectric materials in high-strain electro-mechanical actuators and in thin films used in non-volatile memory devices. Electric fatigue tests have been conducted on lead zirconate titanate (PZT) and lanthanum-doped lead zirconate titanate (PLZT) ferroelectric ceramics. It was found that electric fatigue can be initiated by various factors, the porosity being one of them. Electric fatigue occurred in low-density(93%–97%) PLZT 7/65/35 ceramics after $10^4$ switching cycles, while the high-density (>99%)PLZT specimens of the same composition did not fatigue after $10^9$ switching cycles. It was also observed that for PZT ceramics, fatigue proceeded much more slowly in the samples with higher density (~98%) than those with lower densities (92%–96%). A tentative explanation for the origin of the fatigue mechanism associated with porosity is proposed.

## 1. Introduction

It is well known that under many circumstances when a ferroelectric crystal or ceramic is switched under high a.c. field, the switched charge (polarization) and the consequent elastic strain decay with increased number of cycles [1–4], which is the so-called electroactive or electric fatigue. This effect severely limits the applications of ferroelectric and piezoelectric materials in high-strain electro-mechanical actuators and in thin films used in non-volatile memory devices.

Our systematic study [5] has revealed that electric fatigue in ferroelectric ceramics is much more complicated than was originally expected. Fatigue could be initiated by various factors; surface conditions, ceramic microstructure, electroding methods, compositions, and temperature, can all make contributions to fatigue behaviour. In a previous paper [6], we reported that fatigue which occurred after only thousands of switching cycles in hot-pressed fine-grain lanthanum-doped lead zirconate titanate PLZT 7/68/32 was initiated by surface contamination. Fatigue of this type could be avoided by an improved cleaning procedure before electroding [6]. The present investigation is concerned with the effects of ceramic microstructure, i.e. densities and pores, on fatigue behaviour. The grain size, composition, temperature, and electrode effects will be discussed in following papers.

Study of the influence of porosity on dielectric failure strength (breakdown) in PLZT ceramic system by Furman [7] indicated that hot-pressed high-density (>99%) PLZT ceramics have a dielectric strength almost twice the value in conventionally sintered samples of the same composition (density 92%–96%). The existence of pores in sintered samples caused the reduction of the dielectric strength because of the enhanced field concentration and discharge in the voids. Another electric failure mode in ferroelectric ceramics is d.c. degradation [8, 9], which is also affected by porosity defects. Herbert [10] reported that the rate of d.c. degradation was greatly increased by voids and flaws in ferroelectric ceramics. It is rational to expect that the porosity or voids could also influence dynamic fatigue under high a.c. field because the field concentrations and space-charge accumulation in the pores also exist when ceramic samples are experiencing a.c. fields. However, no published work has been found on this subject. Because pores or voids are common in ceramic materials, it is necessary to know how these defects are related to fatigue behaviour. The study of the density (pore) effects was carried out on conventionally prepared PLZT, lead zirconate titanate (PZT), and hot-pressed PLZT ceramics; the results showed that the porosity could initiate and accelerate the fatigue process. The mechanism of fatigue of this type is discussed.

## 2. Experimental procedure

Lanthanum-doped lead zirconate titanate 7/65/35 (mole ratio of La/Zr/Ti) ceramic specimens were fabricated by both conventional-sintering and hot-pressing techniques. In the conventional-sintering procedure, the starting oxides powders of reagent grade were PbO, $La_2O_3$, $ZrO_2$, and $TiO_2$. The mixed oxides were milled in a rotary mill for 24 h. After milling, the slurry was dried in an oven. The dried powder was calcined at 780 °C for 6 h, and then ground and recalcined at 780 °C. Then the powders which were mixed with polyvinyl alcohol (PVA) binder and dried were pre-



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ssed into pellets using a 0.9 cm diameter die, and pressure up to 40 000 p.s.i. ($10^3$ p.s.i. = 6.89 N mm$^{-2}$). The thicknesses of the pellets ranged from 1–2 mm. After the binder was burned out, the pellets and a mixture of PbO and $ZrO_2$, which was used to control the lead atmosphere, were placed on platinum sheets in alumina crucibles which were then sealed with cement and sintered in an automatic temperature-controlled furnace with a heating rate of 200 °C h$^{-1}$. The sintering temperature was chosen as 1280, 1300 or 1320 °C. It was found that all three temperatures fall into the sintering-temperature range. However, the samples sintered at 1300 °C showed better dielectric properties. The average grain size was 2 μm. The hot-pressed PLZT samples with average grain size 5 mm were obtained from Honeywell Inc. Soft PZT samples were commercial PZT 5 made by both conventional-sintering and tape-casting techniques. Hard PZT samples were commercial PZT 8.

All samples had ground surfaces and their thicknesses ranged 150–300 μm. The improved cleaning procedure [5, 6] was applied to clean all specimens before electroding to avoid fatigue induced by surface contamination. Sputtered gold was used for the electrode.

The properties studied here were the remnant polarization, $P_r$, the maximum polarization, $P_m$, and the coercive field, $E_c$. Sinewave a.c. field was applied to switch the polarization. The hysteresis loops were measured through a conventional Sawyer–Tower circuit and recorded at intervals on a Nicolet 214 digital oscilloscope. The polarization and coercive field were calculated from the measured hysteresis loops.

## 3. Results

### 3.1. Fatigue in conventionally sintered 7/65/35 PLZT ceramics

The sintered PLZT 7/65/35 specimens have an average grain size of 2 μm, and their density is in the range of 93%–96% theoretical. The microstructure is shown in Fig. 1a, observed on the fractured surface by SEM. A large number of pores was found, and the sizes of the pores ranged from less than 1 μm to several tens of micrometres.

Fatigue experiments were carried out on several sintered samples which were cut from selected batches to obtain different densities. The normalized polarization and normalized coercive field which represent the percentages of the polarization and coercive field with respect to their initial values obtained at $10^2$ or $10^3$ switching cycles, are used in this paper in order to compare the results from different specimens and emphasize the changes of the measured properties. Fig. 2a and b show typical hysteresis loops measured before and after fatigue tests in a specimen with a density of 93%. The normalized remnant polarization and coercive field as functions of the switching cycles, for three samples at a frequency of 300 Hz are shown in Fig. 3. The remnant polarizations decrease with increasing switching cycles for all samples, while the rates of fatigue are different. After $10^8$ switching cycles, only 30% of the polarization of the original value in Sample 3 (density 93%) was left, but for Sample 1 (density 96%) 60% of the polarization was still switchable, and for Sample 2 (density near 95%) the fatigue rate lay between the other two samples. The maximum polarizations which are not shown here fatigued in a similar manner to the $P_r$. For a quantitative comparison, we define a parameter $C(P_n)$ which is the number of the switching cycles when the normalized polarization equals $P_n$ ($0 \le P_n \le 1$) to characterize the fatigue rate. For instance, in Fig. 3a the number of the switching cycles for $P_n = 70\%(0.7)$ is $4 \times 10^7$ for Sample 1, it is designated $C(0.7) = 4 \times 10^7$. The $C(P_n)$ data of the samples with three $P_n$ values and the sample densities are listed in Table I. The rates of fatigue for the samples of the same composition but different densities can differ by two orders of magnitude. Unlike the polarization, the coercive fields do not change significantly (Fig. 3b). $E_c$ either increases to some extent, or decreases slightly, or remains constant, depending on the individual sample. The fatigue rate does not significantly depend on the frequency in the range 1–600 Hz in our study.

Thermal treatments were applied to the fatigued samples at 300 °C for 2 h. Sample 3, which fatigued most severely, only had a slight change, as seen in Fig. 2c, but for the fatigued Sample 2, the polarization

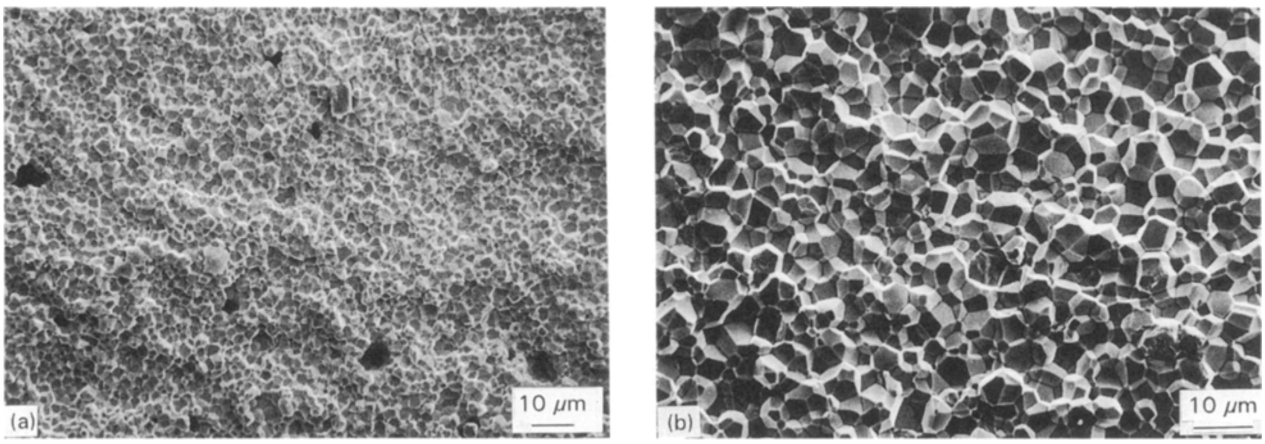



*Figure 1* Microstructures of (a) conventionally sintered and (b) hot-pressed PLZT 7/65/35 ceramics observed by SEM on the fractured surfaces.

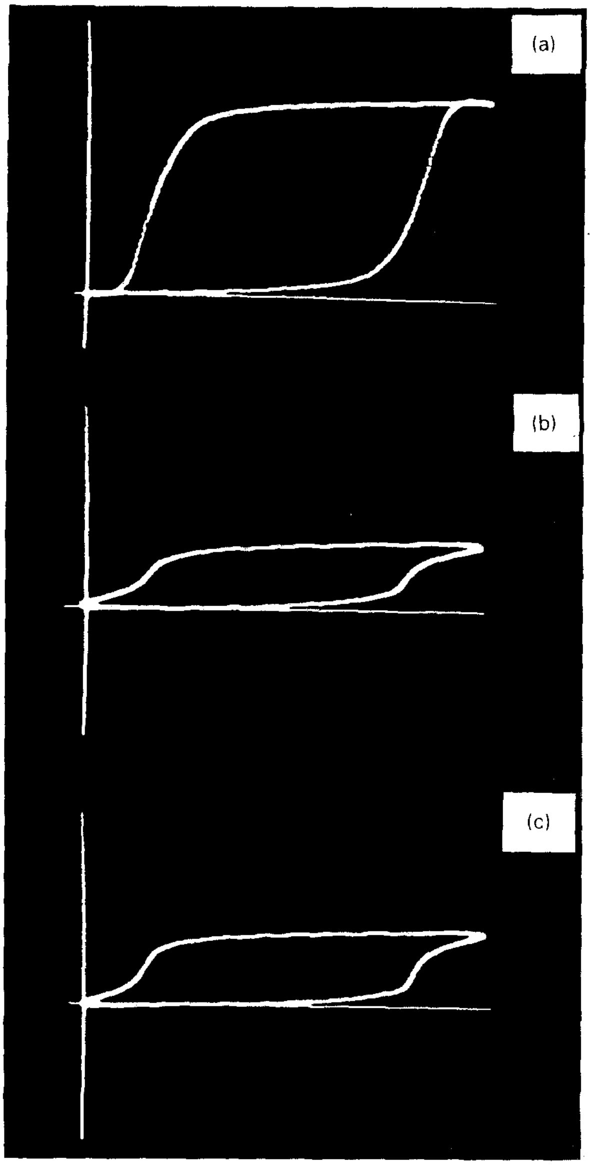



*Figure 2* Hysteresis loop curves for a sintered PLZT 7/65/35 sample, recorded at (a) $10^3$ cycles; (b) $10^8$ cycles; and (c) heated at 300 °C for 2 h after the fatigue test.

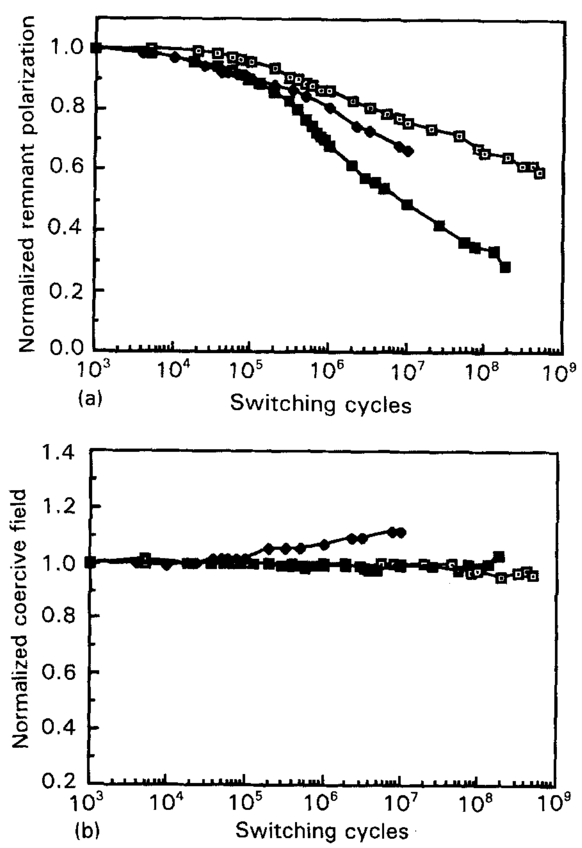



*Figure 3* (a) Normalized remnant polarizations and (b) normalized coercive field as functions of the switching cycles for the three sintered PLZT 7/65/35 samples. (□) Sample 1, (◆) Sample 2, (■) Sample 3.

and coercive field almost recovered to their original values after thermal treatment (Fig. 4). The changes of $P_r$ and $E_c$ for Sample 2 after fatigue test and heating at different frequencies are listed in Table II. The origin of the fatigue, the cause of the difference of fatigue rates, and the thermal treatment effects will be discussed in Section 4.

## 3.2. Fatigue in hot-pressed 7/65/35 PLZT ceramics

Hot-pressed 7/65/35 PLZT ceramics with average grain size 5 μm had high density (> 99%) and no pores were found by SEM. The microstructure is shown in Fig. 1b. Fatigue tests were conducted on several specimens; the results showed a good consistency for all samples. The hot-pressed 7/65/35 samples showed good resistance to fatigue, as can be seen from Fig. 5 which shows the normalized remnant polarization and coercive field as functions of the switching cycles and the hysteresis loops recorded before and after the fatigue test. After the samples were switched up to $10^9$ cycles under a.c. field at a frequency of 300 Hz, the polarizations and coercive fields did not change significantly. Similar results were also obtained for hot-pressed 7/68/32 PLZT samples, as discussed in our previous paper [6]. Comparing these

TABLE I Fatigue rates $C(P_n)$ (cycles) for PLZT and PZT ceramics

| | $C(0.8)$ | $C(0.7)$ | $C(0.6)$ | Density(%) |
|---|---|---|---|---|
| Sample 1 (7/65/35) | $3\times10^6$ | $4\times10^7$ | $3\times10^8$ | 96 |
| Sample 2 (7/65/35) | $1.5\times10^6$ | $7\times10^6$ | – | 95 |
| Sample 3 (7/65/35) | $3\times10^5$ | $8\times10^5$ | $1.4\times10^6$ | 93 |
| Commercial soft PZT | $1\times10^4$ | $1.5\times10^4$ | $2.4\times10^4$ | 92 |
| Tape-cast soft PZT | $5\times10^7$ | $5\times10^8$ | $> 10^9$ | 98 |
| Commercial hard PZT | $2\times10^7$ | $2\times10^8$ | – | 97 |

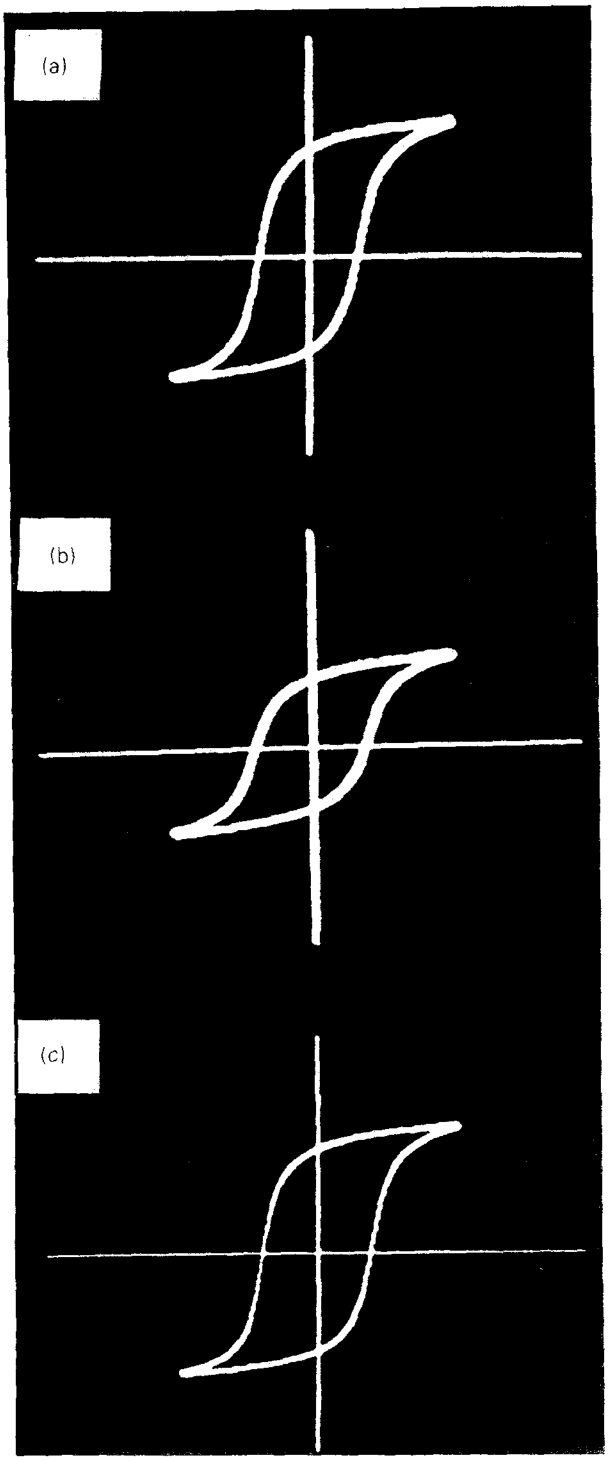
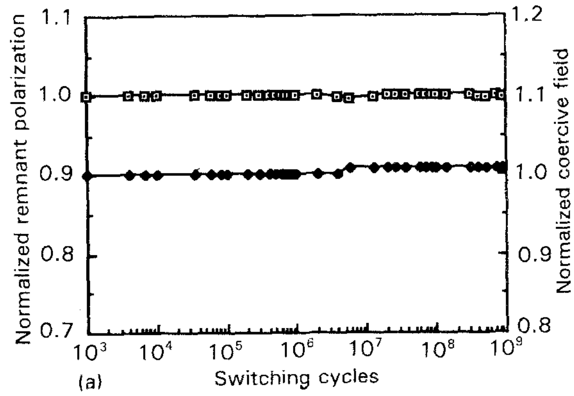



*Figure 4* Hysteresis loop curves for a sintered PLZT 7/65/35 sample, recorded at (a) $10^3$ cycles, (b) $10^7$ cycles, and (c) heated at 300 °C for 2 h after the fatigue test.



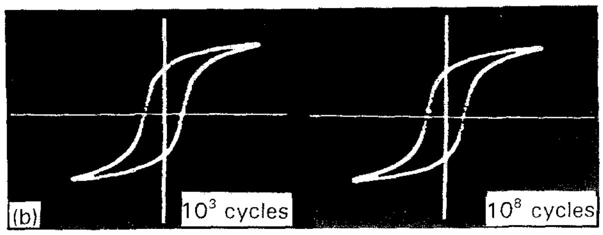




*Figure 5* (a) The (□) normalized polarization and (♦) coercive field as functions of the switching cycles, and (b) hysteresis loop curves for hot-pressed PLZT 7/65/35 ceramics.

results with the fatigue behaviour of the sintered samples, it is clear that the density (porosity) and ceramic-processing methods play an important role in determining the fatigue process. The improvement of fatigue behaviour in hot-pressed ceramics could be mainly due to the high density and the absence of defect pores, which will be discussed in detail in Section 4.

## 3.3. Fatigue in soft PZT ceramics

The remnant polarization and coercive field at a frequency of 1 Hz for commercial PZT 5 sintered samples with average grain size 3 μm are 36.5 $\mu C\,cm^2$ and 10 $kV\,cm^{-1}$, respectively, which fell into the reasonable ranges; the squareness of the hysteresis loops is excellent. The density is only about 92%. A large number of pores was found in the specimens as shown in Fig. 6a. Fatigue tests were conducted at frequencies of 1 and 100 Hz; similar fatigue behaviour was observed for the two frequencies. The results at 100 Hz

TABLE II The remnant polarization, $P_r$, and coercive field, $E_c$, for conventionally sintered PLZT 7/65/35 at the three frequencies

| | 1 Hz | | 10 Hz | | 100 Hz | |
|---|---|---|---|---|---|---|
| | $P_r$($\mu C\,cm^{-2}$) | $E_c$($kV\,cm^{-1}$) | $P_r$($\mu C\,cm^{-2}$) | $E_c$($kV\,cm^{-1}$) | $P_r$($\mu C\,cm^{-2}$) | $E_c$($kV\,cm^{-1}$) |
| Before fatigue test | 26.0 | 6.2 | 26.9 | 6.5 | 22.4 | 4.7 |
| After fatigue test | 15.6 | 5.9 | 15.6 | 6.7 | 15.2 | 5.5 |
| Heated at 300 °C for 2 h | 24.5 | 6.4 | 24.8 | 6.5 | 22.4 | 5.3 |

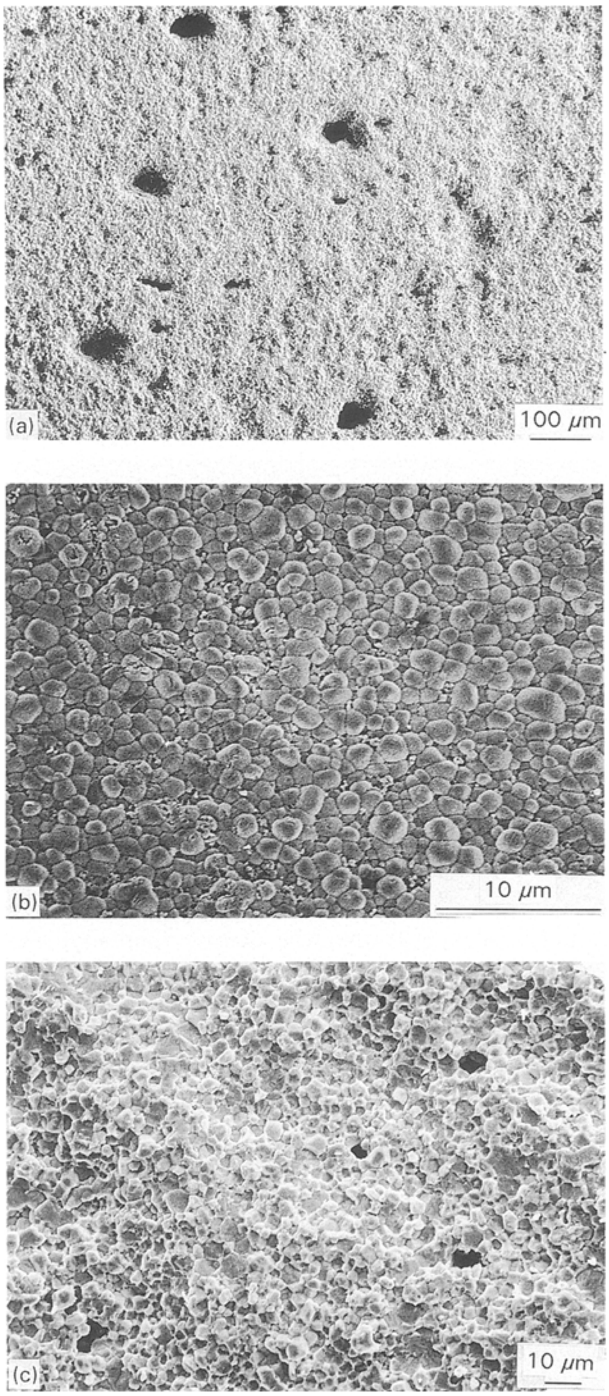



*Figure 6* Microstructures of PZT ceramics observed by SEM. (a) Commercial soft PZT 5, (b) tape-cast soft PZT, and (c) commercial hard PZT.

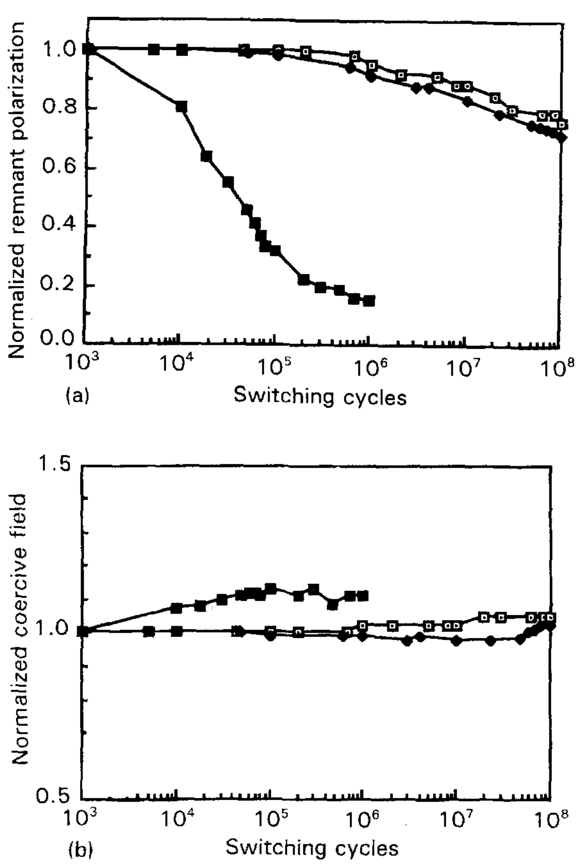



*Figure 7* (a) Normalized polarizations and (b) coercive fields as functions of the switching cycles for (■) commercial soft PZT 5, (□) tape-cast soft PZT 5, and (◆) commercial hard PZT 8 ceramics.

are shown in Fig. 7, curve (a); the polarization decreased very quickly and dropped below 20% of the original value within $10^6$ switching cycles, but the coercive field increased only slightly. Thermal treatment on the fatigued sample brought $P_r$ back to 15 $\mu C\,cm^{-2}$ from 5.3 $\mu C\,cm^{-2}$ (the initial value was 33.1 $\mu C\,cm^{-2}$). The changes in the shapes of the hysteresis loops are shown in Fig. 8.

Fatigue tests were also conducted on soft PZT specimens made by tape-casting which had much fewer pores than those made by conventional sintering. Fig. 6b shows the microstructure observed under the SEM. The average grain size is about 1 μm, and the density is near 98%. Fatigue results shown in Fig. 7 indicate that the tape-cast sample fatigued much more slowly than the sintered samples; the fatigue rates of the polarizations are four to five orders smaller (Table I). Of the original remnant polarization, 66% was still switchable after $10^9$ switching cycles, and the change of the coercive field was very small (Fig. 7). The hysteresis loops recorded during the fatigue process are shown in Fig. 9. After thermal treatment at 350 °C for 2 h the polarization and coercive field recovered almost completely.

## 3.4. Fatigue in hard PZT ceramics

Commercial PZT 8 samples which were conventionally sintered with a density near 97% have a coercive field twice the value of that in soft-PZT. The fatigue results are shown in Fig. 7. Like all other sintered PZT samples, hard PZT also fatigued under a.c. field switching. After $10^8$ switching cycles, 73% of the original $P_r$ was still switchable. The fatigue in hard PZT samples proceeded at a slower rate than that of the sintered soft PZT samples, close to the rate of the tape-cast soft PZT sample. $C(P_n)$ parameters of hard PZT 8 are listed in Table I. The $E_c$ of hard PZT in Fig. 7 was stable without obvious change during the fatigue process. The ceramic microstructure is shown in Fig. 6c; the number of pores is less than that of the commercial soft PZT samples, but more than that of tape-cast soft PZT samples, and the average grain size for hard PZT

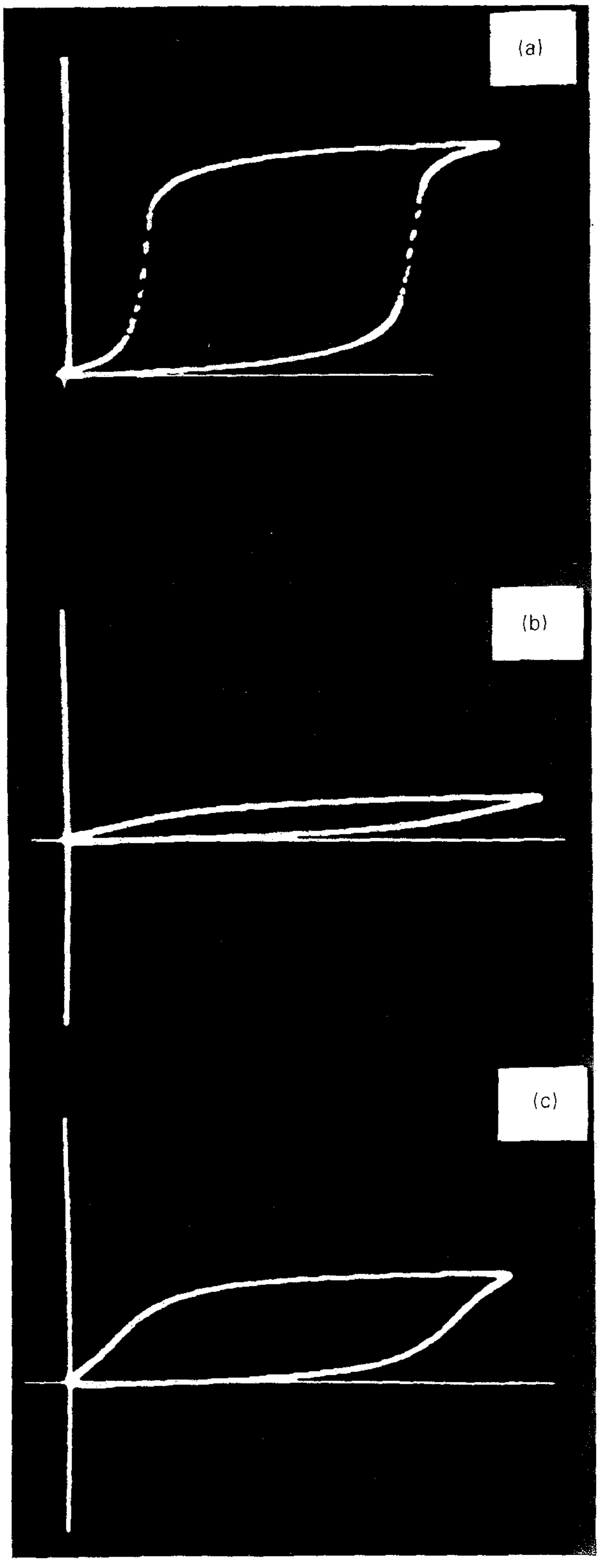



*Figure 8* Hysteresis loop curves for commercial soft PZT 5 ceramic, recorded at (a) $10^3$ cycles, (b) $10^6$ cycles, and (c) heated at 350 °C for 1 h after the fatigue test.

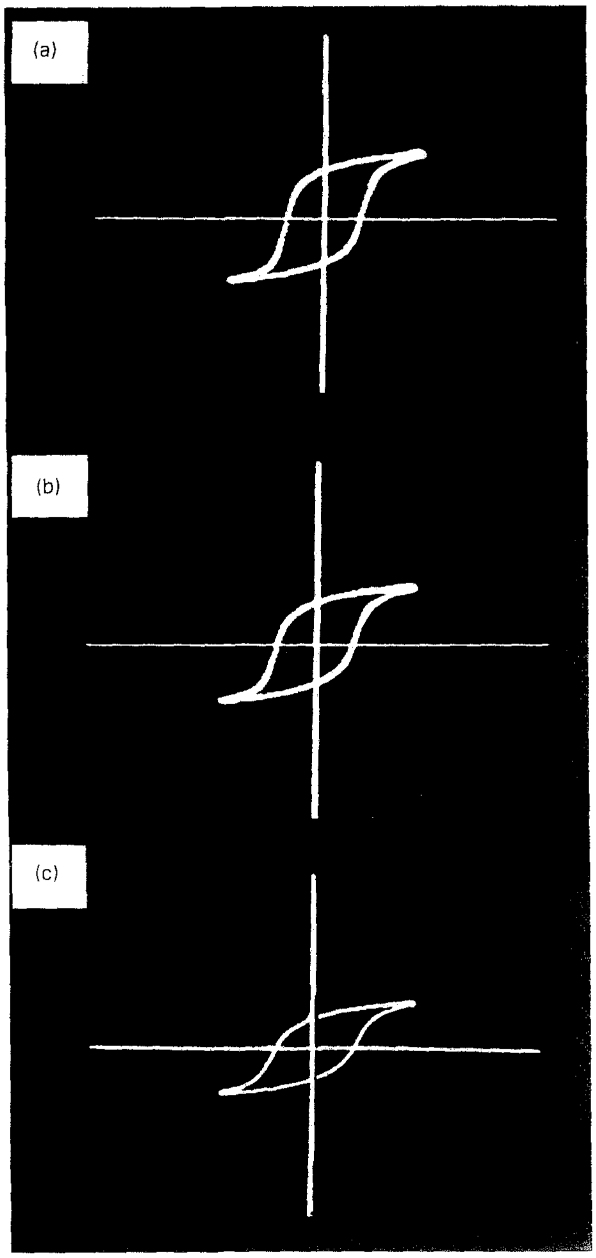



*Figure 9* Hysteresis loop curves recorded during the fatigue process for tape-cast soft PZT ceramic, recorded at (a) $10^3$ cycles, (b) $10^7$ cycles, and (c) $10^9$ cycles.

is 4 μm. The mechanism of fatigue in PZT ceramics will also be discussed in the following section.

## 4. Discussion

The fact that the hot-pressed 7/65/35 and 7/68/32 PLZT ceramics did not fatigue at least up to $10^9$ switching cycles indicates that fatigue occurred in conventionally sintered PLZT and PZT low-density ceramics is not concerned with the intrinsic behaviour. One of the possible mechanisms of the fatigue in specimens with pores and low densities is domain pinning caused by space charge [11–13]. The direct evidence is that the fatigued properties in some of the samples can be recovered by heating the samples to a temperature higher than the dielectric maximum temperature (to the paraelectric phase). When the fatigued samples were heated to their paraelectric phase, both pinned and switchable domains disappeared due to the elimination of the spontaneous polarization. With the temperature cooled down, the paraelectric phase transferred to ferroelectric phase and domains were formed again without pinning. Thus the samples were restored from their fatigued states. In Table II, after experiencing $10^7$ switching cycles, not more than 30% of the initial $P_r$ and $P_m$ (which is not shown in

Table II) could be switched; on heating at 300 °C for 2 h, $P_r$ and $P_m$ at 100 Hz completely recovered to the initial values, and for other frequencies, $P_r$ and $P_m$ recovered more than 95%. The most likely other possible mechanism of fatigue is microcracking [5, 6], but it is not possible to heal the cracks or microcracks at such low temperatures. Furthermore when acoustic emission tests were conducted on the recoverable samples during fatigue experiments, cracking signals were not detected.

Two questions must be addressed. Why does domain pinning happen in 7/65/35 PLZT and PZT ceramic samples with low density and pores, but not in high density 7/65/35 PLZT samples? Where does the space charge needed to pin domain come from? In the process of ceramic fabrication, when the temperature cools down, ferroelectric ceramics experience a phase transformation, from paraelectric to ferroelectric phase accompanied by the occurrence of the spontaneous polarization which forms domain structures to minimize electric energy, so that the macroscopic polarization is zero. On the surfaces the polarization is neutralized by the development of space charges, this is well proven by pyroelectric measurements. Pores inside the ceramics can produce a large area of internal free surface and the space charges must be accumulated on these internal surfaces to neutralize the spontaneous polarization. Therefore, the pores can be served as reservoirs of space charge. The grain boundaries are also polarization discontinuity regions and can trap charges. Under a high a.c. field the space charges can be pumped into the grains and grain boundaries, and react with domain walls and the defects in domains, and reorient domains into a more stable state, i.e. minimum energy configuration which can no longer be switched by the applied field, resulting in a decrease of polarization (fatigue). Campbell [14] studied the domain patterns of the fatigued $BaTiO_3$ single crystal; he found that the fresh crystals which were poled revealed a domain pattern which extended from one surface to another. In fatigued crystals, however, there was no correlation between the patterns of the two opposite surfaces; many of the domains do not go through the crystal but end somewhere in the bulk. This indicates the presence of domain pinning by space charges in the crystal. Using the pinning model, the more pores and thicker grain boundaries that exist, the more easily fatigue occurs. This explains well the different fatigue rates listed in Table I for samples with different densities. The soft PZT obtained by tape casting and the hard PZT fatigued much less severely than other samples because they have fewer pores than the others; the commercial soft PZT is most porous, and fatigued most severely. In addition to trapped space charges, large pores and voids can also cause fatigue by local breakdown mechanism due to electric field concentration.

For some of the most severely fatigued PLZT 7/65/35 and commercial soft PZT samples, the fatigued properties cannot be recovered, even to half of their initial values, by heating and annealing in the paraelectric phases (Figs 2 and 8). In these samples, fatigue was not solely caused by the stabilization of pinned domains. Observation by optical microscopy and the naked eye showed that the surfaces of these samples changed in colour from yellowish to dark blue or pale white and that parts of the surface layer were peeled off from the electrode edges in 7/65/35 samples or the whole electroded surfaces expanded (loosen) in PZT samples, as shown in Fig. 10 in which the area inside the circles is the electroded area, i.e. fatigued area, and the area outside the circles is non-fatigued regions (the electrodes were removed by polishing the surfaces after fatigue tests). In Fig. 10a, damage occurred along the electrode edge (some silver paint which was used to stick the silver contact wire is left in the centre region). The fatigued properties cannot be restored in these samples because of the permanent damage of the surfaces. The surface deterioration could be the result of electrochemical reactions which change the colour of the samples [15]. The discharge in the pores near the surfaces can cause both discoloration and mechanical damage. The increase of

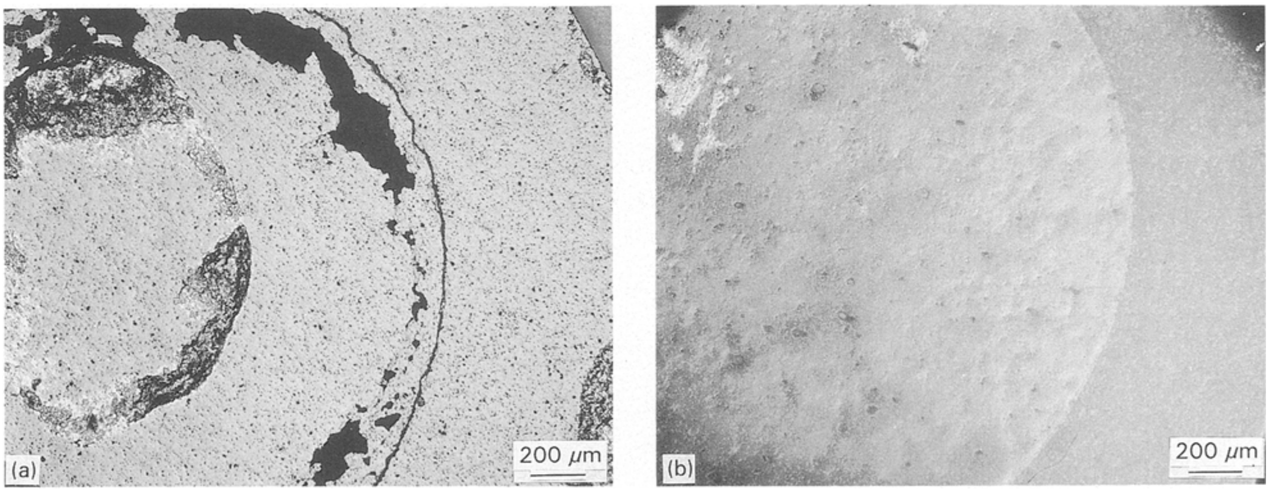



*Figure 10* Damaged surfaces of the fatigued samples observed by the optical microscope after removal of the electrodes by polishing the surface. (a) Sintered PLZT 7/65/35, and (b) commercial soft PZT 5.

the applied field can enhance these effects, which is in good agreement with the experimental results. The applied field for the soft PZT sample was twice the field applied to PLZT 7/65/35 samples, and more severe damage was observed on the surfaces of the commercial soft PZT than on those of sintered PLZT 7/65/35.

## 5. Conclusion

Electric fatigue occurring under high a.c. field in conventionally sintered PLZT and PZT ceramics is mainly caused by low densities (92%–98%) and the existence of pores. The rate of fatigue depends on the porosity of the specimens. Fatigue proceeds faster in specimens with high porosity than in those with low porosity. Within $10^9$ switching cycles, the fatigue rate could differ by two to four orders of magnitude. It is found that the hot-pressed PLZT 7/65/35 and 7/68/32 with high density ($>99\%$) and average grain size 5 μm did not fatigue after $10^9$ switching cycles. This is an encouraging finding for the application of PLZT and PZT ferroelectric and piezoelectric ceramics in actuators and memory devices. Two mechanisms for fatigue occurring in low-density PLZT and PZT ceramics are proposed: the gradual domain stabilization (pinning) by space charges and the surface deterioration caused by the large a.c. field.

## Acknowledgement

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