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# DOMAIN SWITCHING AND MICROCRACKING DURING POLING OF LEAD ZIRCONATE TITANATE CERAMICS

E. C. SUBBARAO,† V. SRIKANTH, W. CAO and L. E. CROSS
*Materials Research Laboratory, The Pennsylvania State University, University Park, PA 16802-4800 USA*

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The application of a DC electric field (poling) to a ferroelectric lead zirconate titanate (PZT) ceramic aligns domains in the field direction. The non 180°-domain switches involve mechanical deformations, which are detected as acoustic emission signals. Concurrent with AE signals, electrical current pulses arise from domain reorientations. When the poling field is large and domain switches are extensive, the resulting deformations, under the constraint of neighboring domains or grains, may exceed the elastic limit and cause microcracking. The onset and propagation of microcracking during poling of PZT is signalled by the appearance of continuous AE signals, unaccompanied by current pulses, in contrast to intermittent AE signals accompanied by corresponding current pulses during domain switching. The onset and extent of microcracking established by this method is confirmed by scanning electron micrographs and decrease in the value of piezoelectric coefficient ($d_{33}$) and mechanical quality factor ($Q_M$). The amplitude of AE signals due to domain switches are spread widely, while that of AE signals caused by microcracking occur in a narrow range around 50 db.

*Keywords: Acoustic emission, PZT, domain switching, microcracking*

## INTRODUCTION

The polar direction of ferroelectric crystals can be changed by an applied electric field. Due to the existence of many variants in the low temperature ferroelectric phase, a ceramic (polycrystalline) sample contains many randomly oriented regions of uniform polarization, called domains, upon transforming from the high temperature non-ferroelectric (paraelectric) phase, thus eliminating net polarization.[1] For many practical applications such as a piezoelectric device, the ceramic must be poled (i.e., subjected to a DC electric field) to align the polar axes as fully as possible in the field direction so that the ceramic acquires a net (non-zero) polarization. The fact that only partial alignment of domains is possible in a ceramic is reflected in the rounded D-E hysteresis loop compared to a square loop of a ferroelectric single crystal, and in a spontaneous polarization ($P_s$) value of about 8 μC/cm$^2$ for a ceramic versus 26 μC/cm$^2$ for a single crystal of $BaTiO_3$.[1]

Associated with the spontaneous polarization ($P_s$), there is a spontaneous strain ($e_s$), which is proportional to $P_s^2$. This strain is a consequence of the fact that the polar axis is elongated compared to other crystallographic axes. When the ferroelectric domain switches by 180°, there is no strain change and hence does not affect its neighbors. On the other hand, domain reorientations by 90° cause max-

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†Permanent address: Tata Research Development & Design Center, 1 Mangaldas Road, Pune 411001, India.

imum strain change, leading to intergranular stresses (Figure 1). Thus, domain switching during the poling process proceeds to minimize the total energy and accommodate the elastic deformation. For example, only 12% of the domains switch by 90° upon application of an electric field to ceramic $BaTiO_3$ and half of them revert back on removal of the field.[2,3] This constraint by surrounding grains does not affect domain switches by 180°, since no strain is involved in this case.

Extensive studies on $BaTiO_3$ single crystals have shown [4-7] that the domain switching is a nucleation and growth process. It starts with a wedge shaped domain of the new polarization state, proceed with a fast forward growth rate and slow sidewise growth rate, finally the wedge taking the shape of a stripe across the grain or crystal. Ultimately the two 180° domain walls move sidewise to widen the new polar region to complete the switching process.

Lead zirconate titanate (PZT) is a solid solution of ferroelectric lead titanate ($PbTiO_3$) and antiferroelectric lead zirconate ($PbZrO_3$). A composition at 48% $PbTiO_3$—52% $PbZrO_3$ exhibits a morphotropic phase boundary (MPB), separating a tetragonal $PbTiO_3$-rich and a rhombohedral $PbZrO_3$-rich ferroelectric phases. Many properties (dielectric constant, piezoelectric coefficients, etc.) peak at this

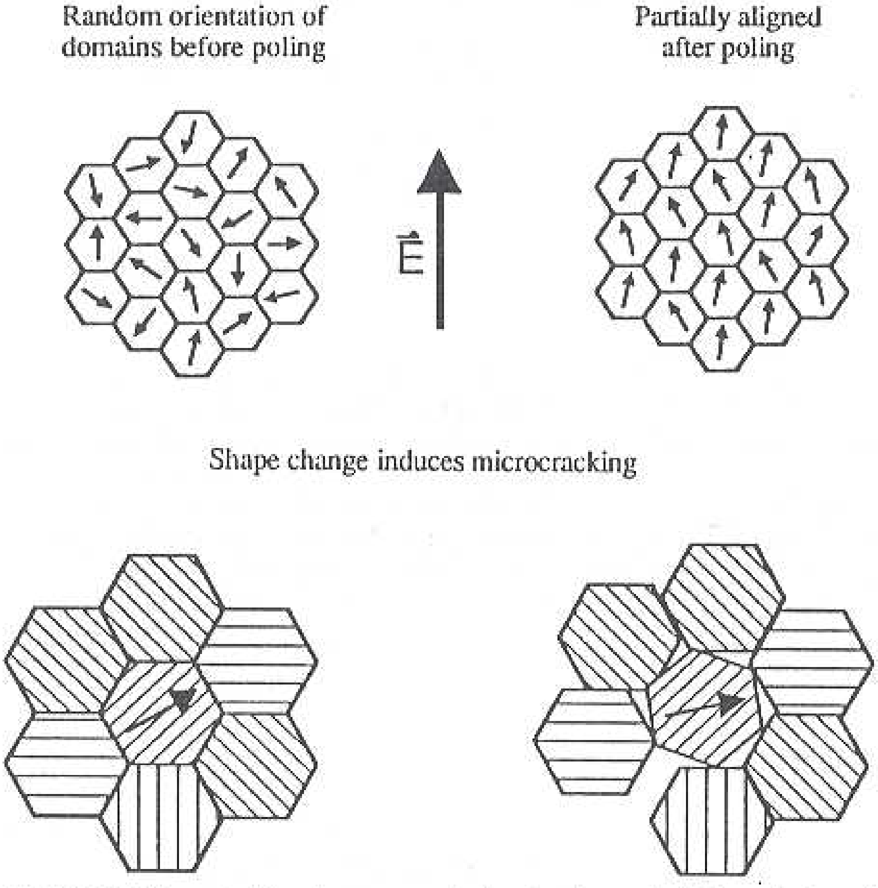

FIGURE 1 Schematic of domain structure of a ferroelectric ceramic before and after poling.

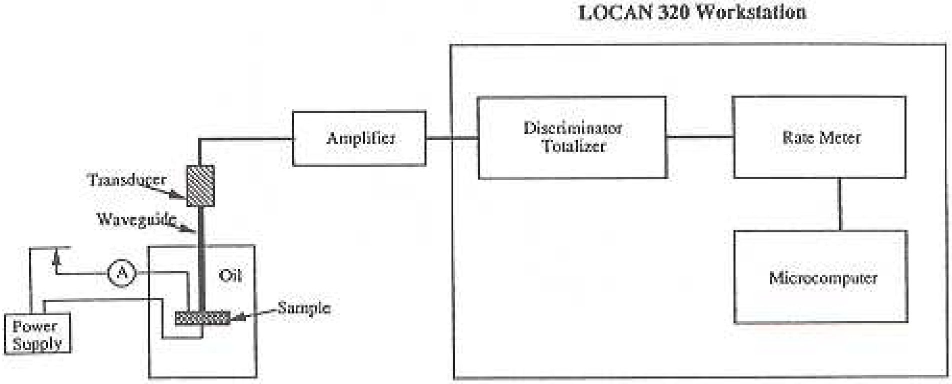

FIGURE 2 Schematic of experimental arrangement used for simultaneous detection of acoustic emission and current pulses during poling of a ferroelectric ceramic.

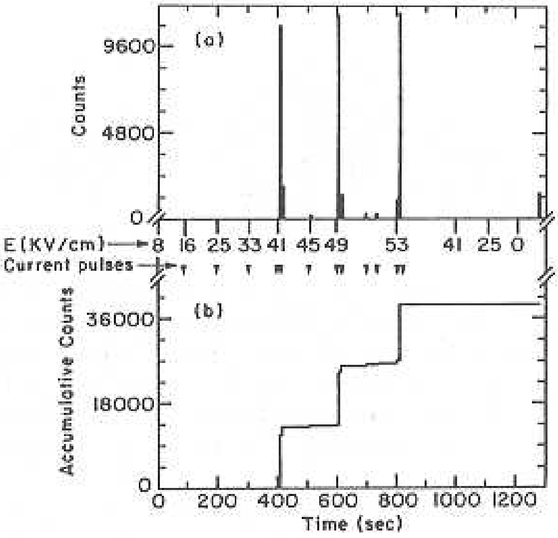

FIGURE 3 Acoustic emission count rate (a) and total AE counts (b) as a PZT ceramic (sample C) is poled to successively higher fields. The current pulses were observed at times indicated by triangles in this and succeeding figures (4 and 5).

TABLE I

Microcracking and electrical properties of poled PZT

| Sample | Extent of Poling and Microcracking | $d_{33}$ ($10^{-12}$ C/N) | $Q_M$ |
|---|---|---|---|
| C | Poled but no onset of microcracking | 333 | 89 |
| SS | Poled till microcracking barely starts | 350 | 65 |
| B | Poled till microcracking starts | 200 | 49 |
| E | Poled till extensive microcracking occurred | 119 | |

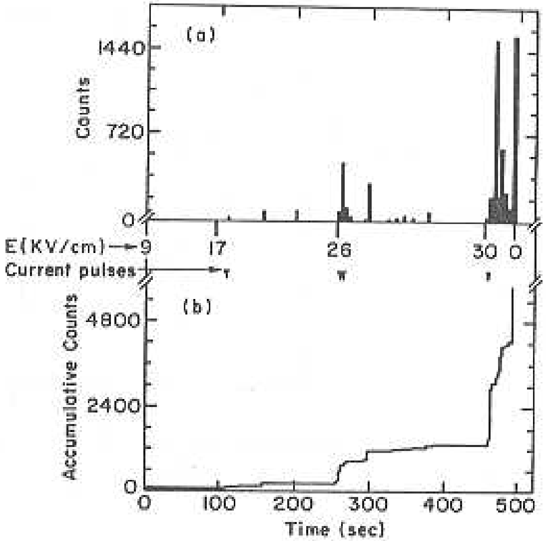

FIGURE 4 Similar data as in Figure 3 but for another sample B, poled till microcracking just starts.

composition, presumably due to the increase in the number of energetically degenerate states which makes the switching of domains easier under the influence of an electric field.[8] The higher Curie temperature (360°C vs 120°C), remanent polarization (47 vs 8 $\mu C/cm^2$) and piezoelectric coefficients make PZT far superior to $BaTiO_3$ for piezoelectric applications. In fact, PZT is the leading electromechanical transducer material for over a quarter century and therefore is chosen for the present study.

The effect of electric field on the extent of domain reorientations in PZT is somewhat different in the tetragonal and rhombohedral phase regions. In tetragonal PZT, it is estimated that $66\frac{2}{3}\%$ of all dipoles instead of the initial $16\frac{2}{3}\%$ become aligned within the sextant around the poling direction.[9] On the other hand, dipoles switch by 71°, 109° and 180° in the rhombohedral phase. For PZT modified by $Nb^{5+}$ ion addition, it is suggested that 74% of the dipoles are present in the octant around the policy direction.[8] The larger $P_s$ value and the higher degree of domain orientation in PZT make the remanent polarization of PZT substantially higher than that of $BaTiO_3$. The improvement in planar coupling coefficient ($k_p$) of PZT as a function of poling conditions (field, time and temperature) has been studied by Chiang *et al.*[10]

As already pointed out, the non-180° domain switches involve strain changes and hence demand the coordination of neighbor domains. The microdeformations arising from the domain wall movements, though small in magnitude, are detectable by sensitive acoustic emission methods.[11,12] The poling effects on acoustic velocity and attenuation in poled and unpoled PZT ceramics were studied as a function of temperature and frequency.[14] Application of a large electric field (or mechanical stress) can lead to microcracking, due to internal stresses.[15] Electrically induced microcracking in PZT has been shown to be dependent on grain size and tetragonality[10,14,16–19] and is detected by microscopy[20] and dielectric measurements. The external parameters influencing the extent of microcracking are the poling conditions (field, time and temperature).[19,21] Microcracking results in a deterio-

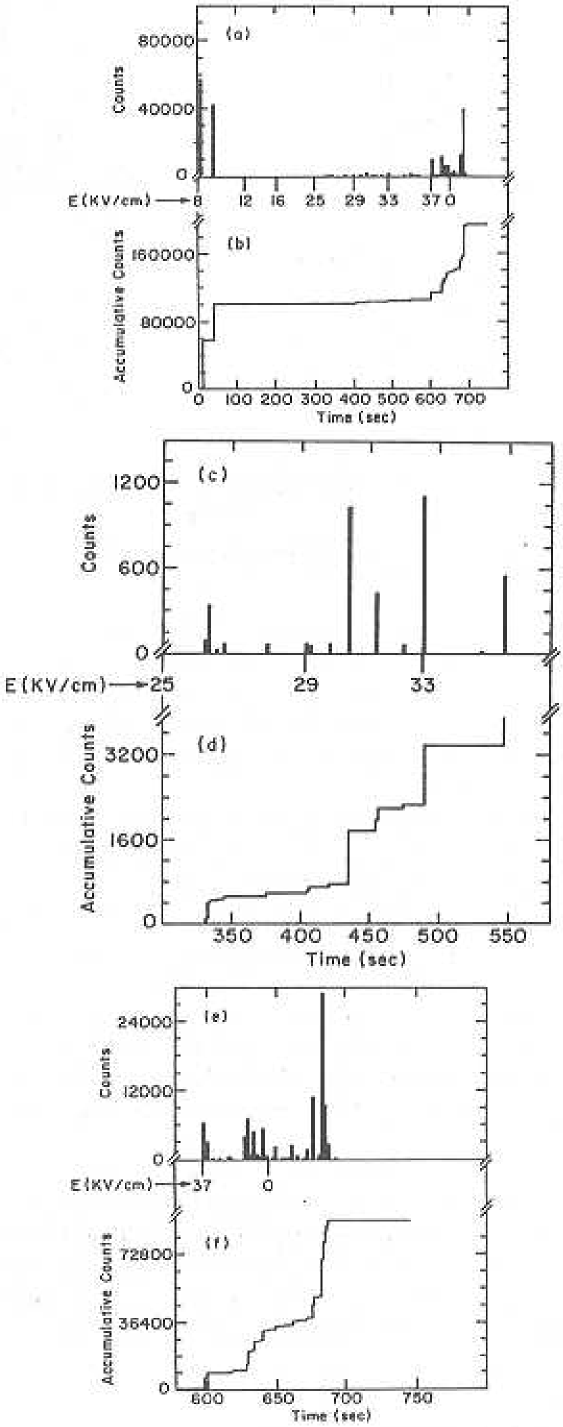

FIGURE 5 Same as in Figure 3 for sample *SS* but the electric field is maintained even after the onset of continuous AE counts, signifying beginning of microcracking. The regime just before [Figures (c) and (d)] and just after [Figures (e) and (f)] the onset of microcracking is shown in detail.

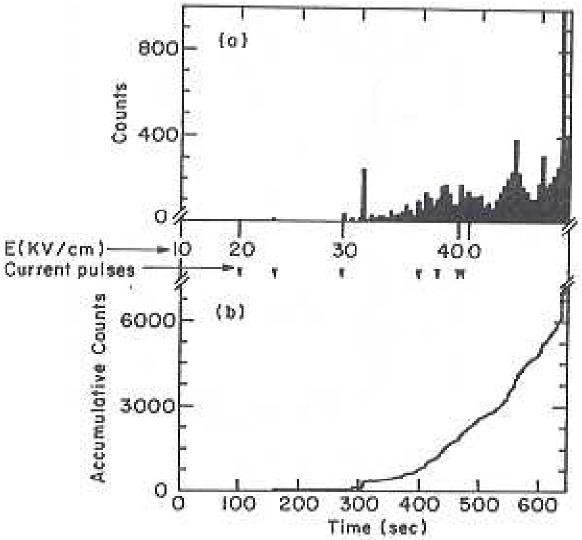

FIGURE 6 Same as in Figure 5 for sample *E* but the electric field is retained for extensive microcracking to occur, as indicated by continuous AE counts.

ration of electrical and mechanical properties of the ceramic[21-23] and hence should be minimized if not eliminated. Uchino *et al.* have studied AE signals in piezoelectric and electrostrictive actuators subjected to bipolar and unipolar electric fields and also after repeated cycles of thermal shocking.[24] They found that the unipolar field does not lead to acoustic emission, unless the samples have suffered mechanical damage as by thermal shocking.

The acoustic emission technique has recently been applied to the study of domain switching, as well as the occurrence and recombination of microcracks in ferroelectric $PbTiO_3$ ceramics as it is heated and cooled.[25]

From the above discussion it is clear that poling is a critical process for achieving optimum piezoelectric properties of a ferroelectric ceramic. The domain reorientations which give rise to enhanced piezoelectric behavior also give rise to mechanical stresses, which can lead to microcracking, if the induced stresses exceed the elastic limit of the material. Therefore poling should be carried out to obtain maximum domain reorientation, but without the onset of the microcracking process, provided there is a simple, reliable means to distinguish the two deformation processes.

The purpose of the present study is to delineate the microdeformations accompanying domain switching from those due to microcracking during poling of PZT ceramics, as a contribution toward a better understanding and optimization of the poling process. Simultaneous detection of acoustic emission and electrical current pulses were employed in the study and the results are substantiated by scanning electron micrographs and electrical property measurements.

## EXPERIMENTAL

Ceramic lead zirconate titanate (PZT) composition (52% $PbZrO_3$, 48% $PbTiO_3$) at the morphotropic phase boundary (MPB) was prepared by conventional method.

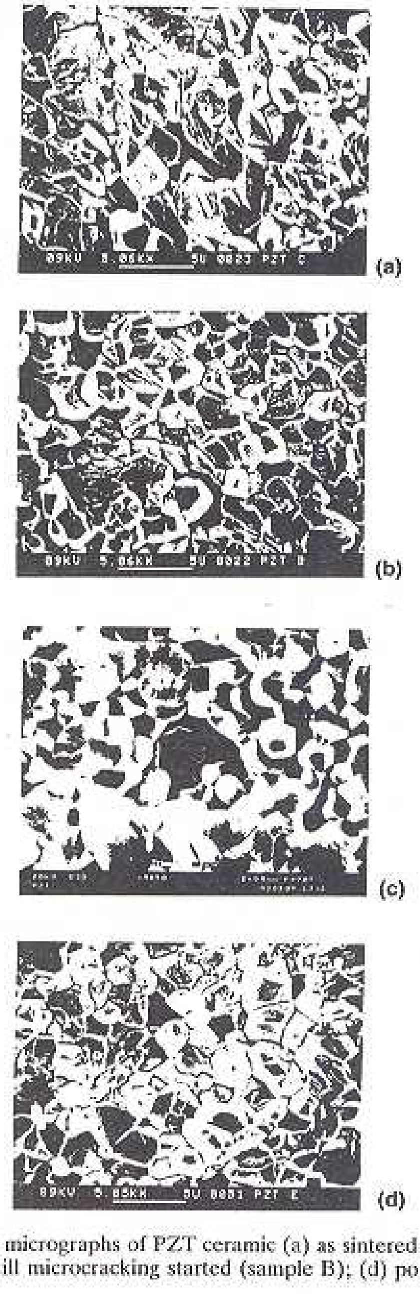

FIGURE 7 Scanning electron micrographs of PZT ceramic (a) as sintered; (b) poled, but not microcracked (sample C); (c) poled till microcracking started (sample B); (d) poled and extensively microcracked (sample E).

Stoichiometric proportions of reagent grade oxides (PbO from Hammond Lead Products, Potterstown, Pennsylvania, $ZrO_2$ from Harshaw Chemical Co., Cleveland, Ohio, and $TiO_2$ from J. T. Baker Chemical Co., Phillipsburg, New Jersey) were mixed in a polyethylene bottle for 12 hours using ethyl alcohol as wetting agent and $\frac{1}{2}$" diameter zirconia balls as grinding media. Excess lead oxide (0.5 wt%)

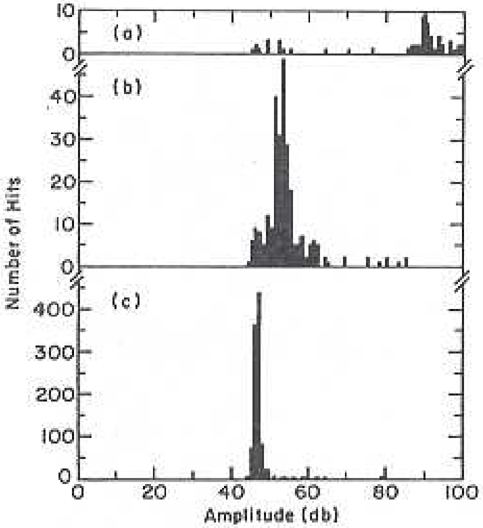

FIGURE 8 Number of AE hits vs amplitude for samples with (a) only domain reorientations (sample C), (b) both domain reorientations and initial microcracking (sample B) and (c) extensive microcracking (sample E). Note the scale change for (c) from (a) and (b).

was added to compensate for lead loss during calcination. The milled powder was dried at 80°C for 24 hours and calcined at 900°C for 24 hours. X-ray diffraction examination confirmed the formation of the perovskite phase. After mixing with 2% polyvinyl alcohol binder, the powder was pressed into pellets at 105 MPa. The binder was removed by heating at 350°C for three hours and 550°C for three hours. The pellets were sintered at 1250°C for five hours in closed crucibles in PbO atmosphere, at a rate of 5°C/min during heating and 3°C/min during cooling.

Sintered PZT ceramic discs were polished to obtain two parallel faces, which were then electroded with sputtered gold. The electroded disc is located in a suitable holder and immersed in a silicone oil bath at 50°C. High DC field is applied in a stepwise fashion from a power supply (Tred COR-A-TROL), while an alumina rod serving as a wave guide rests on the ceramic disc. A transducer is mounted at the other end of the wave guide. Acoustic emission signals are collected, filtered and analyzed by appropriate electronic circuitry and displayed as counts or count rate as a function of time (Locan 320 System from Physical Acoustics Corp.). The schematic of the experimental arrangement is shown in Figure 2. A microammeter is placed in the voltage input lead of the poling circuit, to detect current pulses arising from domain switching, superimposed on leakage current.

After various stages of poling, the samples were examined for piezoelectric coefficient, $d_{33}$, using a Berlincourt $d_{33}$ meter, for mechanical quality factor, $Q_M$, using IRE standard method, and for microstructure and microcracks from scanning electron micrographs.

## RESULTS AND DISCUSSION

A PZT ceramic sample (*C*) was poled in successive steps of increasing DC field at intervals of 100 sec, while acoustic emission signals and current pulses were recorded

(Figure 3). No AE signals were detected until a poling field of 41 kv/cm was applied (though a few current pulses were observed as soon as poling field ≥ 16 kv/cm was applied). The current pulses (2–12 mA) were superimposed on a steady leakage current of 0.5 to 3 mA. It can be seen that a substantial number of AE signals occur as soon as the poling field is increased, though a smaller number of AE counts were recorded at irregular time intervals during the application of a fixed poling field, in agreement with earlier reports.[12] Everytime AE counts occurred, there were accompanying current pulses. Evidently both the AE and current pulses arise from domain reorientations. After 800 sec, the field was reduced in steps to zero at 1200 sec. While no AE counts were detected till the applied field was dropped to zero, AE counts were indeed recorded nearly 60 sec after removal of the field and these AE events may reflect domain reversals. The piezoelectric coefficient, $d_{33}$, of this sample was $333 \pm 7 \times 10^{-12}$ *C/N*. The scanning electron micrograph of this sample [Figure 7(b)] is similar to that of a virgin sample [Figure 7(a)] and does not show clear microcracking, though grain boundaries become more obvious. The sample has a mechanical quality factory ($Q_M$) of 89 (Table I).

An example of a sample (*B*) which was subjected to a stepwise increase of the poling field till microcracking just starts, as evidenced by continuous AE counts instead of intermittent AE signals, is shown in Figure 4. The field was quickly reduced to zero soon after the appearance of continuous AE counts. While current pulses were observed corresponding to the intermittent AE signals, no current pulses were observed during the continuous occurrence of AE counts. The $d_{33}$ value of this sample is lower at $\sim 200 \times 10^{-12}$ *C/N* and the scanning electron micrograph does not show any significant microcracking [Figure 7(c)].

These results were confirmed with another PZT ceramic sample (*SS*) which shows a large number of AE counts as soon as a poling field of 8 kv/cm is applied (poling temperature 50°C), but no further AE counts till the field applied was 25 kv/cm at 300 sec (Figure 5). There were intermittent AE signals as the poling field was increased stepwise from 25 kv/cm to about 37 kv/cm at 600 sec [Figures 5(c) and (d)]. In this regime AE counts were invariably accompanied by current pulses up to 60 mA. As soon as continuous AE counts started appearing at about 620 sec, the poling field was turned off. The AE counts continued which may indicate domain reversals [Figures 5(e) and (f)]. Since the microcracking process was quickly interrupted, the $d_{33}$ was nearly unaffected (350).

The stepwise poling of another sample (*E*) was continued beyond the occurrence of intermittent AE signals accompanied by associated current pulses (of up to ~40 mA) to the regime where AE counts occur continuously but no current pulses are detected (Figure 6). We believe that the onset of continuous AE counts must signify the beginning of microcracking due to excessive mechanical stresses generated by extensive domain switching. The poling field was reduced to zero at 480 sec but AE counts persisted for sometime (at least up to 640 sec) suggesting further microcracking or propagation of cracks till adequate stress relief is attained. Due to the extensive microcracking, the $d_{33}$ value ($119 \times 10^{-12}$ *C/N*) and $Q_M$ were severely affected (Table I). The scanning electron micrograph of this sample [Figure 7(d)] shows extensive intergranular cracking.

The threshold amplitude for the AE experiments was set at 45 db. The distribution of the magnitude of the detected AE signals for three samples is given in

Figure 8. It can be seen that the number of hits increases and the amplitude spread decreases as the extent of microcracking changes from none to minor to extensive. When acoustic emission signals arise from domain reorientations, their amplitude reflects a wide range of accompanying microdeformations, depending upon the original domain orientations and the magnitude of the poling field [Figure 8(a)]. On the other hand, the initiation and propagation of microcracking is driven by stress concentrations in the ceramic and the corresponding AE signals occur in a narrow amplitude range [Figure 8(c)]. The case where domain reorientations and initial microcracking occur simultaneously represents an intermediate situation [Figure 8(b)]. This is in agreement with the observation of Pan and Cao,[13] who state that the AE signal amplitude is maximal at the polarization switching and minimal when the poling is established. Iwasaki and Izumi[11] also find that the peak of AE counts occurs at lower amplitude range and the spread of amplitude narrow as the poling field is increased.

## CONCLUSIONS

Application of a DC field to ferroelectric ceramics (poling) causes domain reorientations in the field direction. All but the 180° domain switches involve dimensional changes leading to mechanical stresses due to the constraint of the neighboring grains in a ceramic. When the stresses exceed the bonding strength between grains, the ceramic suffers microcracking, resulting in deterioration of electrical ($d_{33}$, $k_p$, $\epsilon$, etc.) and mechanical ($Q_M$, strength, etc.) properties. The present study established that concurrent AE counts and current pulses are observed when domain switches take place during poling. The onset and progress of microcracking is signalled by continuous AE counts but no accompanying current pulses. The delineation of domain switching from microcracking by this approach is corroborated by changes in electrical and mechanical properties and scanning electron micrographs and constitutes a simple, reliable, non-destructive in-situ means to control the poling process to achieve optimum piezoelectric properties in a ferroelectric ceramic.

### ACKNOWLEDGEMENT

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