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Influence of Electric Poling on Fracture Toughness of Ferroelectric-Ferroelastic PZT Ceramics

Zuokai Ke and Sunggi Baik

Dept. of Mater. Sci. and Eng., Pohang Univ. of Sci. and Tech. (POSTECH), Pohang 790-784, Kyungpook

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Nearly fully dense PZT samples both with tetragonal and with morphotropic phase boundary compositions were prepared by the conventional powder processing and sintering. A micro-indentation technique was used to evaluate the dependence of fracture toughness on remanent polarization, crack length and the direction of crack propagation. The result shows that the toughness increases with the remanent polarization along the poling direction and decreases in the transverse direction. The dependence of toughness on the remanent polarization is neither symmetric nor linear but rather shown to be saturated quickly with the increase in remanent polariztion. R-curve behaviors are observed in both poled and unpoled samples. Sequential SEM and XRD studies on annealed, poled, ground, fractured and etched samples show that domain switching is evident as a viable toughening mechanism but might depend upon the rate of crack propagation. Grain bridging is also observed as one of the active toughening mechanisms.

Key words : PZT, Fracture Toughness, Remanent Polarization, Domain Switching, Grain Bridging

I. Introduction

As the applications of ferroelectric ceramics have increased substantially in recent years, frequent mechnical failure of the materials has led to increasing concerns over the fracture mechanism of the ferroelectric ceramic components. Understanding the mechanical properties of ferroelectric ceramics is often difficult because their fracture process depends not only on the usual microstructure features such as grain size, porosity, flaw distribution, elastic anisotropy, crystallographic phases, but also on electric effects associated with domain structures and process under an applied stress. Particularly, domain switching is of the most important significance in understanding the unique feature of the fracture process of ferroelectric ceramics such as PZT.

Compared with the studies on deformation from the movement of twin boundaries, which may be traced back to early 50's,[1)] the experiments on the influence of twinning (domain switching) on the fracture behavior were much less conducted.[2)] One of the important earlier observations regarding the fracture behavior of ferroelectric materials was made in 1976 by Pohanka et al.,[3)] who found that the strength of polycrystalline barium titanate could be significantly different when measured in a paraelectric state above its Curie point and in ferroelectric state at room temperature. They proposed that the domain switching was responsible for the increased fracture toughness in ferroelectric state below its Curie point. The fracture of these ferroelectric materials as a function of composition and grain size has been examined later by them.[4)] McHenry and Koepke[5)] examined the effect of applied DC and AC fields of different frequencies on the slow crack growth of PZT ceramics and noted that the propensity of crack growth was enhanced by the applied field. The anisotropy of fracture behavior of the poled PZT samples was originally found by Okazaki[6)] in an indentation experiment and was analyzed further by Pisarenko et al.[7)] Further experiments on fracture mechanism by domain switching were made by Mehta and Virkar.[8)] They indicated that only the domains oriented parallel to the direction of crack propagation were available for switching their c-axis to the direction perpendicular to the crack surface and contributed to the increase in toughness. Domain switching has been attributed as one of viable toughening mechanisms for an R-curve behavior observed in PZT cearmics by Baik et al.[9)] The nonlinear deformation behavior of both hard and soft PZT has recently been reported by Cao and Evans.[10)] They indicated that the 90° domain switching responsible for the nonlinear deformation could occur at as low as 20~30 MPa in compression.

Although the domain switching has been accepted as a viable toughning mechnism in ferroelectric state, there still remains many uncertainties regarding its effectiveness under various microstructural and poling conditions in PZT since the domain switching is basically different from the dilatant transformational toughening mechanism. No volume change in the unit cell is associated with domain switching. In addition, the 90° domains can be switched either mechanically or electrically. The PZT components are used frequently after poling. Its effect on mechanical behavior is still poorly understood. Moreover, microcracking has been also suggested as another viable toughening process for ferroelectric-ferroelastic PZT materials by several authors,[4,8,9] However, its contribution to an overall toughness under various poling conditions is still to be explained. In this study, the electric poling is used to switch initially various amounts of ferroelectric domains. Then, the microindentation technique is employed to investigate the dependence of fracture toughness on remanent plarization, polarization direction and crack length. In the following paper,[11] an analytical model will be presented to account for the complex dependence of fracture toughness on the remanent polarization that could be varied by electric poling.

II. Experimental and Results

1. Sample preparation and characterization

Because the mechanical and ferroelectric properties are known to be closely related with the porosity of the samples,[12] fully dense PZT samples were prepared by adopting the cyclic oxygen sintering.[13] Two different PZT compositions were chosen: $Pb(Zr_{48}Ti_{52})_{0.976}Nb_{0.021}$(#4852), and $Pb(Zr_{52}Ti_{48})_{0.976}Nb_{0.024}O_3$(#5248). The purities of all starting powders, PbO, ZrO_2, TiO_2 and Nb_2O_5 exceeded 99.5%. 200-g batches were weighed, mixed and milled in ethyl alcohol for 24 hours with ZrO_2 balls as grinding media. Then the mixture was dried and calcined at 850°C for 4 h. The calcined powders were crushed and wet milled again. After sieving and drying, the powders were presssed isostatically at 200 MPa. Sintering was performed in an oxygen atmosphere following the temperature-time profile shown in Fig. 1. Sintered samples of the size 30×40×8 mm^3 were then cut into various test specimens. Some Sr-doped $Pb(Zr_{53}Ti_{47})O_3$ samples described previously[9] were also employed for the experiment.

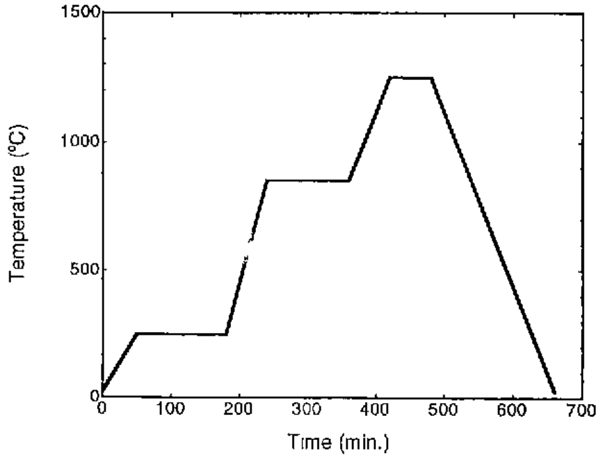


Fig. 1. Temperature-time profile used for sintering PZT samples.

Fig. 2 shows XRD results confirming that #4852 is tetragonal while #5248 is in MPB region. Fig. 3 shows the microstructure #4852, which confirmed that the sample was almost fully dense with negligible porosites.

2. Electric poling and remanent polarization

The sintered samples were cut into a size of 8×8×30 mm^3, ground, and polished gradually to 1 μm diamond paste on three surfaces. The polished samples were annealed at 600°C for 12 hr to eliminate the surface residual stress. Two opposite surfaces were pasted with silver electrodes and fired. The electroded samples were placed in a silicon oil bath at 115~120°C and poled for 10 minutes under electric fields of 0, 5, 10, 15, 20, and 25 KV/cm. The remanent polarization of the poled samples was estimated by obtaining P-E hysteresis curves measured by the standard Sawyer and Tower circuit technique[14] using thin samples cut in a size of 5×7×0.3 mm^3.

The relation between the remanent polarization and the poling field strength is shown in Fig. 4. Higher remanent polarization was observed in #5248, the MPB

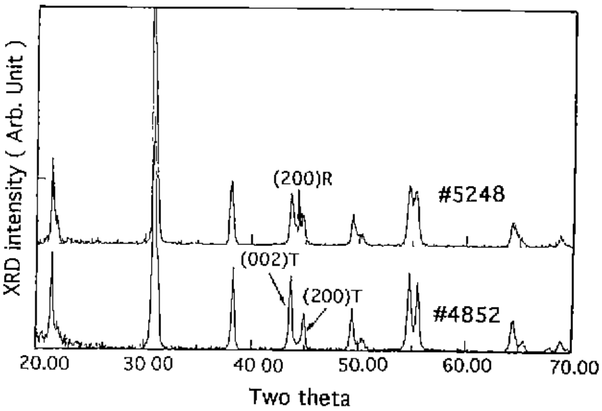


Fig. 2. XRD patterns of the samples showing tetragonal and MPB phases for #4852 and #5248, respectively.

Fig. 3. Microstructure of #4852 sintered in cyclic oxygen atmosphere.

composition. Although, the polarization did not saturate up to 30 KV/cm in the thin samples, the electric poling for the samples for mechanical testing was limited below 25 KV/cm because higher poling voltage could induce extensive microcrack formation and even breakdown in the thick specimens.

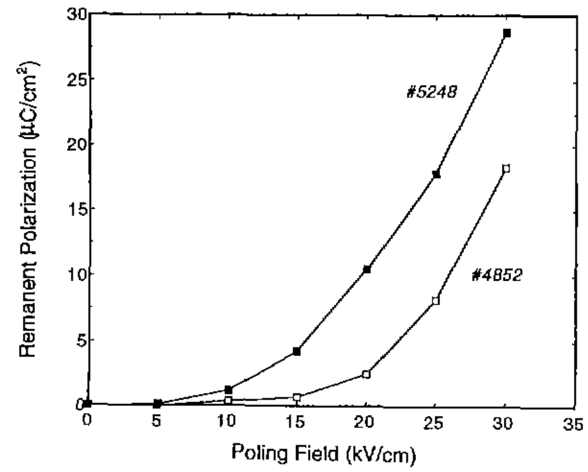


Fig. 4. Remanent polarization as a function of electric poling field strength.

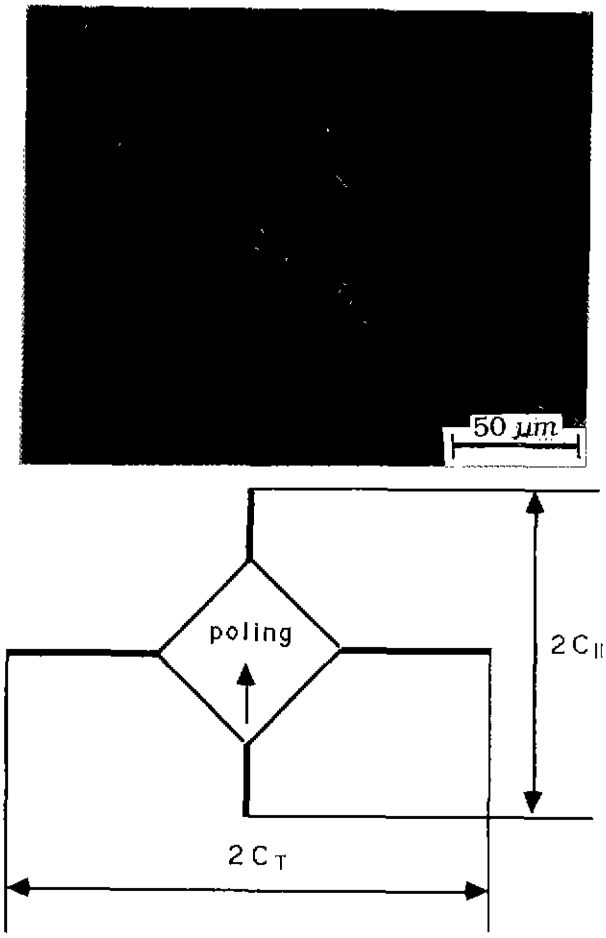


Fig. 5. An example of well developed indentation crack and the geometry used for toughness measurement.

3. Measurement of fracture toughness by indentation method

Direct crack length measurement in the standard Vicker's indentation test provides a simple quantitative estimation of fracture toughness as well as a qualitative R-curve estimation in a controlled crack propagation direction.[15,16] A series of indentation loads (0.3, 0.5, 1.0, 3.0, 5.0, 10.0, 15.625 N) were applied to make different crack lengths on each samples poled differently. A standard loading condition was employed and extra 10 seconds were given before unloading. Among five to ten indentation points for each load level, only the indentation points with the well developed crack pattern, as shown in Fig. 5, were used to calculate the toughness parallel and perpendicular to the poling direction. The crack length was measured immediately after unloading under an optical microscope with a fixed amplification (× 500). The fracture toughness, K_r was calculated using the equation[15]

$$K_r = 0.0726PC^{-3/2} \tag{1}$$

where P is the indentation load and C is the crack size defined in Fig. 5. Fig. 6 shows the plot of fracture toughness of unpoled samples as a function of crack size. The result shows that the unpoled PZT exhibits a rising crack growth resistance (R-curve) behavior and the toughness in MPB (#5248) is obviously lower than that in tetragonal phase (#4852), which is in agreement with the most of the previous observations.[4,9]

Fig. 7 shows the change in fracture toughnesses of poled #4852 as a function of the crack size for different poling field strengths, (a) in the parallel and (b) in the prependicular to the poling direction. Rising R-curves are found in both direactions of the poled samples even though the data scatter appreciably due to the nature of

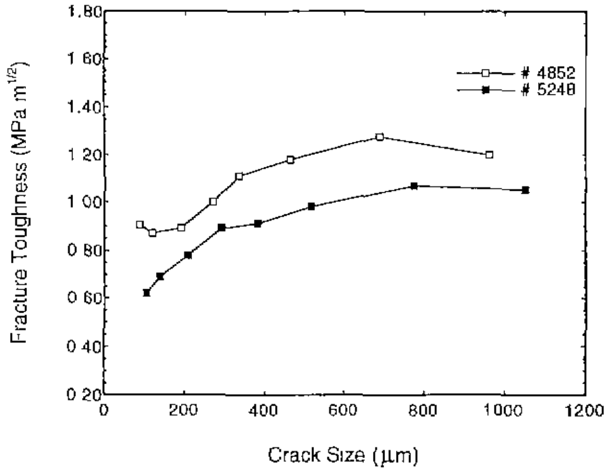


Fig. 6. Fracture toughness of unpoled samples as a function of crack size.

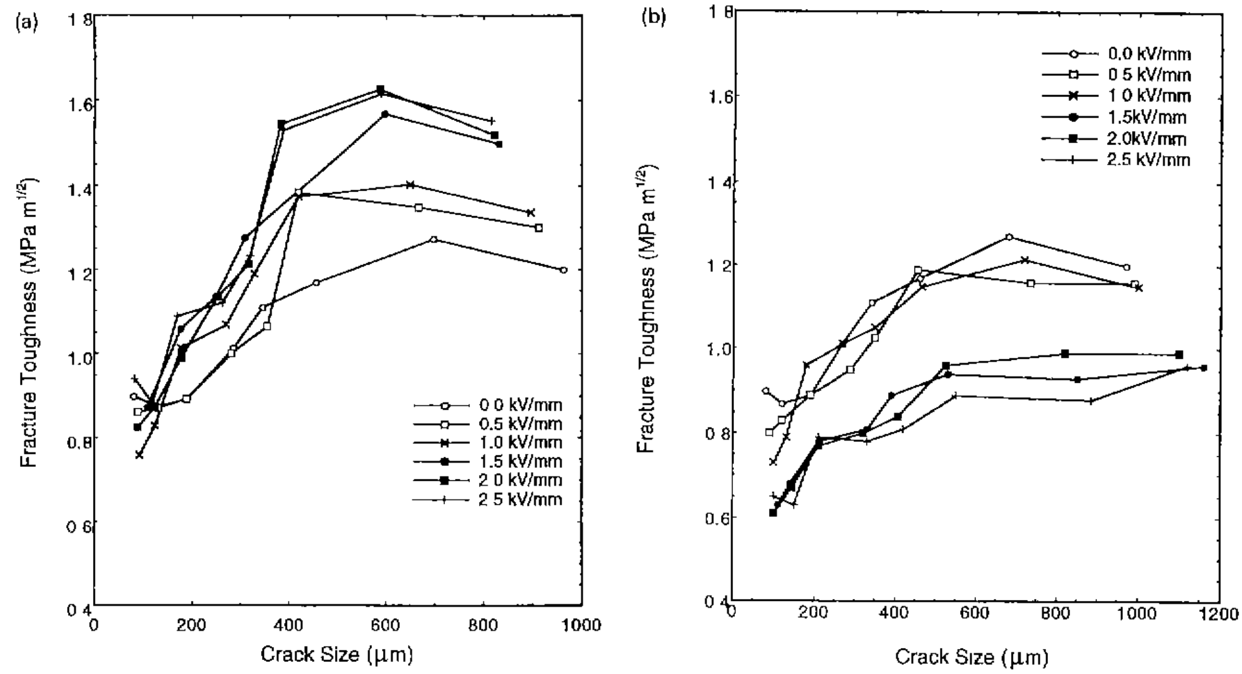


Fig. 7. Fracture toughness of #4852 as a function of crack size for various poling field strength applied, (a) parallel, and (b) perpendicular to the crack propagation direction.

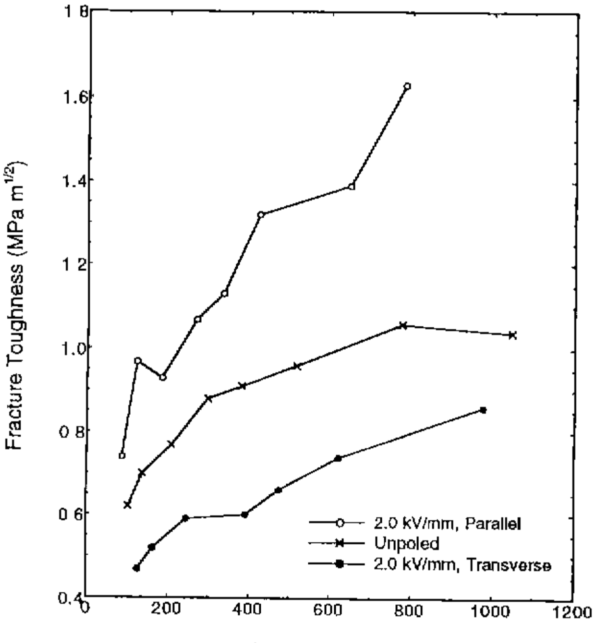


Fig. 8. Fracture toughness of #5248 poled at 2 KV/mm as a function of crack size.

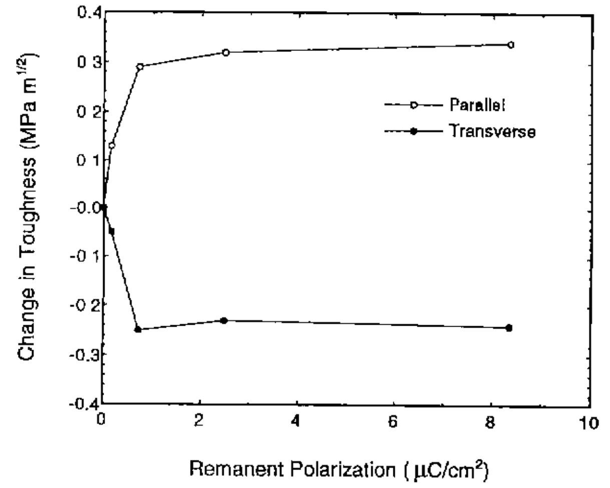


Fig. 9. SEM photograph of crack tip showing discontinuous crack extension after forming microcrack in front of crack tip.

indentation measurement. Along the poling direction, the R-curves become steeper and fast rising with higher maximum toughness values as the field strength increases. Whereas, in the transverse direction, the toughness decreases with increasing poling field strength and R-curves become shallower. The R-curve shown in the transverse direction at high field strength can be originated from other toughening mechanisms such as grain-bridging. Fig. 8 shows the R-curve behaviors of #5248 unpoled and poled at 2.0 KV/mm in parallel and perpendicular to the crack propagation direction.

After converting the poling voltage to remanent polarization using the relationship shown in Fig. 4, the maximum increase or decrease in fracture toughness (corresponding to an infinite crack size, Δa→∞), which was estimated under the maximum indentation load for well developed cracks, is obtained as a function of remanent polarization as shown in Fig. 9. Two major characteristics are found: one is that the toughness was

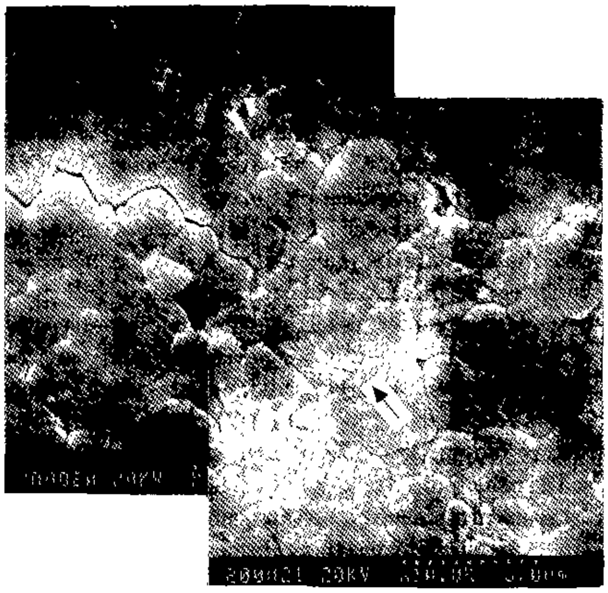
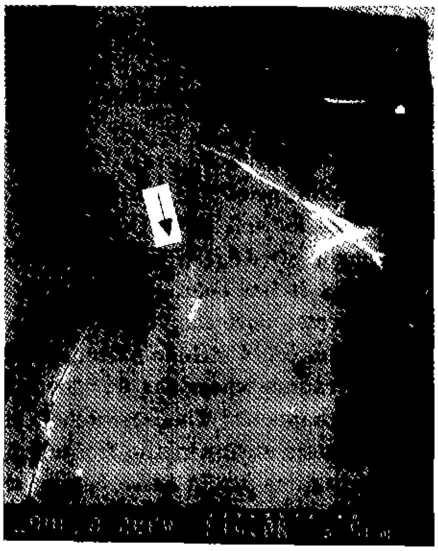
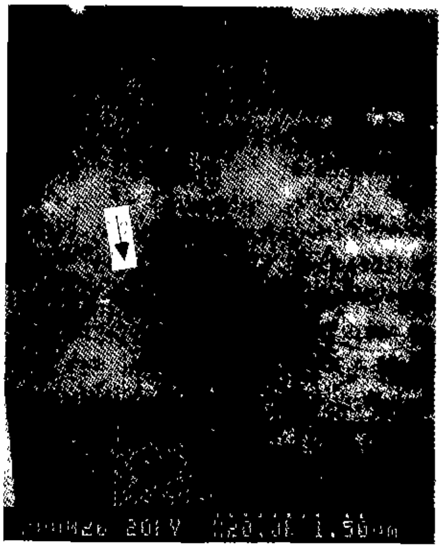


Fig. 10. SEM photograph of crack tip showing discontinuous crack extension after forming microcrack in front of crack tip.

Fig. 11. An evidence of grain bridging site in unpoled #4852 (bar=2 μm).



a) Parallel to polarization



b) Perpendicular to polarization

Fig. 12. Microstructural evidences of grain bridging sites in poled #4852. The direction of crack propagation is, a) parallel, and b) perpendicular to the poling field.

easily saturated with the remanent polarization; the other that the increase in toughness along the poling field was larger than the decrease in the transverse direction. The non-symmetry of the change in toughness in the two directions can be also found elsewhere.[5]

4. SEM observation of crack propagation

Fig. 10 demonstrates that the intergranular crack propagates discontinuously by forming a microcrack ahead of the main crack tip. The discontinuous nature of crack extension was also observed in the transgranular mode of fracture with a Sr-doped PZT of which the grain size was about 5~6 μm.

The evidence or grain bridging was observed unexpectedly in both unpoled and poled samples. Fig. 11 is the SEM photograph taken with an unpoled sample. Some grains along the crack path remained unbroken even after the crack tip extended several grains ahead (about 5~10 μm). Grain bridging was also observed in poled samples both for the cracks propagating parallel and perpendicular to the poling field as shown in Fig. 12. The evidence of grain bridging in Fig. 12(b) explains the

R-curve in the transverse direction at high field strength shown in Fig. 7(b).

III. Discussion

Unidirectional compression test[10] has already indicated that domain switching can occur under a stress as low as 20 MPa for soft PZT. During the indentation test, a high tensile stress field was developed in the vicinity of crack tip. It has been shown in our calculation that the mean stress above the yielding stress of 20 MPa for unpoled samples could include a frontal zone size of about 182 μm in radius where the 90° domain switching would inevitably happen.[11] These switched 90° domains produced an inelastic strain in the frontal zone. As the crack grew, the strains would leave behind the growing crack tip exerting an additional crack closing force on the cracked surface, and the R-curve behavior inevitably appeared.

The XRD pattern taken from the indentation fracture surface shows that I(002)/I(200) was greater than that from the pristine surface. This indicates that more domains aligned with their c-axis perpendicular to the fractured surface during crack extension. From this mechanism, the poling induced fracture anisotropy can be partly explained. In the poled samples, the domains available for switching increase with the remanent polarization along the poling direction and decrease in the transverse direction. During fracture, the increased domains can switch back with their c axis perpendicular to the fracture surface contributing to the increased toughness. As a result of the domain switching by poling and fracture, the toughness increases in the poling direction and decreases in the transverse direction as the remanent polariztaion increases.

The mechnism of domain switching at the advancing crack tip explains some part of the experiment, but fails to explain the easy saturation of the fracture toughness with remanent polarization in both directions. This peculiar result may be explained from the change in the yielding stress for domain switching by the polarization field around crack tip. As the remanent polarization increases, on one hand, the inelastic strain from the 90° domain switching increases or decreases with the polarization by adjusting the amount of 90° domains parallel to the crack surface in the two directions. On the other hand, the remanent polarization exerts an opposite effect on the yielding stress for the domain switching in the frontal zone. For example, along the poling direction there are more domains available for switching with the increase in remanent polarization, but any switch of the dipoles in this direction will undergo an increased resistance, i.e., the increased yielding stress, due to the increase in electric potentials exerted by the surrounding polarization field. Thus the frontal zone size of domain switching characterized by wake height will become smaller. The density of the switchable 90° domains and the size of the process zone would compensate each other above a certain remanent polarization. This seems to be the reason for the observed toughness saturation above a certain remanent polarization as shown in Fig. 9. In the transverse direction, the situation is just reversed. As the remanent polarization increases, the switchable domains are decreased, but the switch is made easier with the increase in remanent polarization because any switch of the dipoles inside these domains will decrease their electric potentials. Thus, the yielding stress is decreased by the remanent polarization and the frontal zone size becomes larger, making the total switchable domains tend to be in a stable amount. Therefore, the fracture toughness in the transverse direction will not decrease monotonically with the remanent polarization but rather saturate above a certain remanent polarization.

In this mechanism, the role of the polarization field must be considered. As it has been well recognized that the electric field is much more efficient in switching the domains than the mechanical stress,[14] the role of the polarization field surrounding the frontal zone of domain switching cannot be neglected in discussing the influence of electric poling on the fracture toughness of ferroelectric-ferroelastic materials such as PZT ceramics. Consideration of only the mechanical stress and strain around the crack tip would be inadequate to explain the observed nonlinear dependence between the change in fracture toughness and remanent polarization.

IV. Conclusions

1) The ferroelectric-ferroelastic PZT ceramic meterials exhibited a rising crack growth resistance (R-Curve) behavior both in the poled and unpoled, as well as in the tetragonal and MPB phases.

2) The increase and decrease in toughness in parallel and perpendicular to the poling field, respectively, were not linearly dependent on the remanent polalization. They varied abruptly and saturated quickly at relatively low remanent polarization. The behavior could not be explained properly by simple domain switching mechanism in the frontal zone of advancing crack. The effect of polarization field created by electric poling on yield stress for domain switching has to be taken into consideration to explain the nonlinear dependence.

3) Grain bridging is also found to be one of the active mode of toughening mechanisms both in poled and unpoled state.

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