Journal of the European Ceramic Society 21 (2001) 1391–1394
www.elsevier.com/locate/jeurceramsoc

Bipolar pulse poling and space charge field in lead zirconate titanate ceramics

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Received 4 September 2000; received in revised form 23 October 2000; accepted 30 October 2000

Abstract

We studied the effect of repeated bipolar pulses applied to soft and hard lead zirconate titanate (PZT) ceramics on ferroelectric properties. Almost symmetrical P-E hysteresis loops were observed in the case of soft PZT ceramics. On the other hand, the loops in the case of hard PZT ceramics were asymmetrical and shifted to the positive electric field. It was found that a space charge field was generated while applying pulse and the direction of the field was fixed independently of the pulse cycles. The possibility of bipolar pulse poling was investigated. Furthermore, we discuss the effect of pulses on planar coupling factor when the pulses were applied to poled soft and hard PZT ceramics.

Keywords: Bipolar pulse; Ferroelectric properties; Piezoelectric properties; PZT

1. Introduction

The degradation of lead zirconate titanate (PZT) thin films due to domain switching and rotation needs to be reduced for their application to ferroelectric random access memory (FRAM). Through the processes employed to develop the materials for FRAM, the evaluation and control of domain structures were recognized to be significant. Domain switching and rotation in PZT ceramics can be caused by either mechanical stress and electric field or both, because the ceramics possess ferroelastic and ferroelectric properties.[1] Since an electric field affects the dielectric and piezoelectric properties of PZT ceramics by switching and rotating domains, we had reported on the poling field dependence of ferroelectric properties in PZT ceramics.[2–6] Subsequent to this, we investigated the bipolar pulse cycle and pulse voltage dependences of ferroelectric properties in soft and hard PZT ceramics.

2. Experimental

The soft PZT ceramics were composed of $0.05Pb(Sn_{1/2}Sb_{1/2})O_3-y\,PbTiO_3-z\,PbZrO_3$ $(y+z=0.95)$, where $z=0.33$, 0.45, 0.48, 0.66 and 0.75, respectively. The hard PZT ceramics modified from the soft PZT ceramics with an addition of 0.4 wt.% MnO_2[7] were investigated in comparison with the soft ceramics. The powders were uniaxially pressed at a pressure of 150 MPa, and fired at 1240°C for 2 h. The sample disks post firing were 14 mm in diameter and 1 mm thick. Responses to repeated voltage pulses up to $V=\pm4.0$ kV applied to the ceramic disks were measured at 80°C by a high voltage test system (Radiant: RT6000HVS). The bipolar pulse with the periods (T) of 800 msec and 12 s as shown in Fig. 1 was applied up to 10 times. The P-E hysteresis and planar coupling factor (k_p), dielectric constant (ε_r) and frequency constant (fcp) were investigated each time the pulse was applied.

3. Results and discussion

3.1. P-E hysteresis

Fig. 2 ① shows P-E hysteresis loops of soft (dotted lines) and hard (solid lines) PZT ceramics at the composition of $z=0.48$, when the bipolar pulse (Fig. 1) with $T=800$ ms was applied to an as-fired sample (virgin ceramics) on the condition of the pulse field of $E=\pm3.0$ kV mm^{-1} and 80°C. The P-E loops start at $P=0$ μC cm^{-2} and finish at a minus remanent polarization of -Pr. Increasing the pulse cycles from ② to ⑩, the loops show

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0955-2219/01/$ - see front matter
PII: S0955-2219(01)00025-5

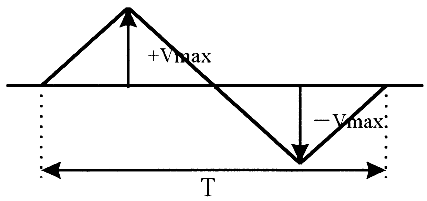

Fig. 1. Bipolar pulse to measured P-E hysteresis in PZT ceramics.

asymmetry, especially in the case of hard PZT ceramics. Furthermore, the loops were shifted to the positive electric field.

3.2. Space charge field

Since the asymmetrical P-E hysteresis means the fact that an internal electric field is generated in the ceramics, the ceramics have the possibility of poling by the bipolar pulses. Therefore, it was thought that space charge to stabilize the orientation polarization causes the ceramics the internal field. The direction of the space charge field was estimated by the shifted direction of P-E loops. Fig. 3 shows the schematic pictures to clarify the relationships between the pulse application, orientation polarization, space charge field and P-E hysteresis. From the asymmetry of P-E hysteresis loops of ① and ② in Fig. 2, the space charge field was generated while applying the first bipolar triangular pulse. Further applying bipolar pulse, the shifted direction was fixed as shown in Fig. 2 ②–⑩. These results indicated that after orienting the polarization by the first positive triangular pulse, 180°C domain switching mainly occurred in the ceramics by the repeated bipolar pulses.

3.3. Bipolar pulse poling

The possibility of bipolar pulse poling was studied. The comparison between bipolar pulse poling (open

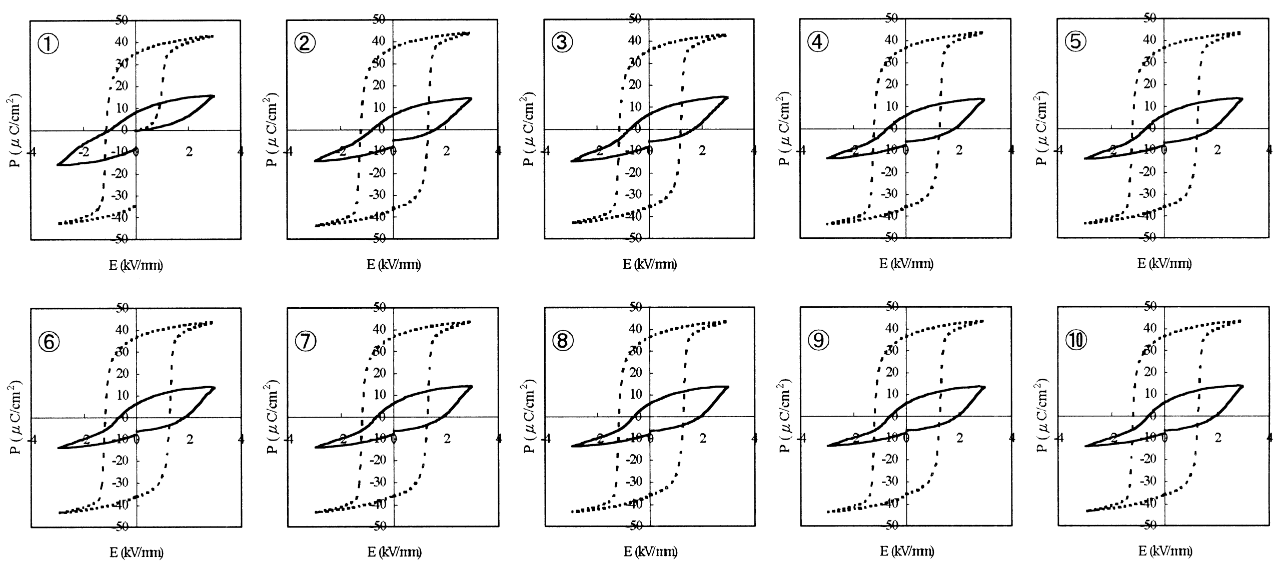

Fig. 2. P-E hysteresis loops measured by bipolar pulse up to 10 times (①→⑩) in soft (· · ·) and hard (––) PZT ceramics ($z = 0.48$).

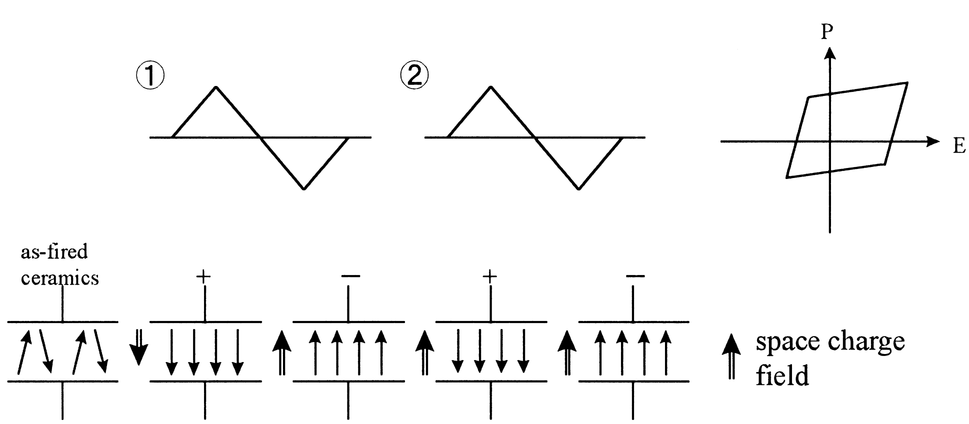

Fig. 3. Generation of space charge field by applying bipolar pulses.

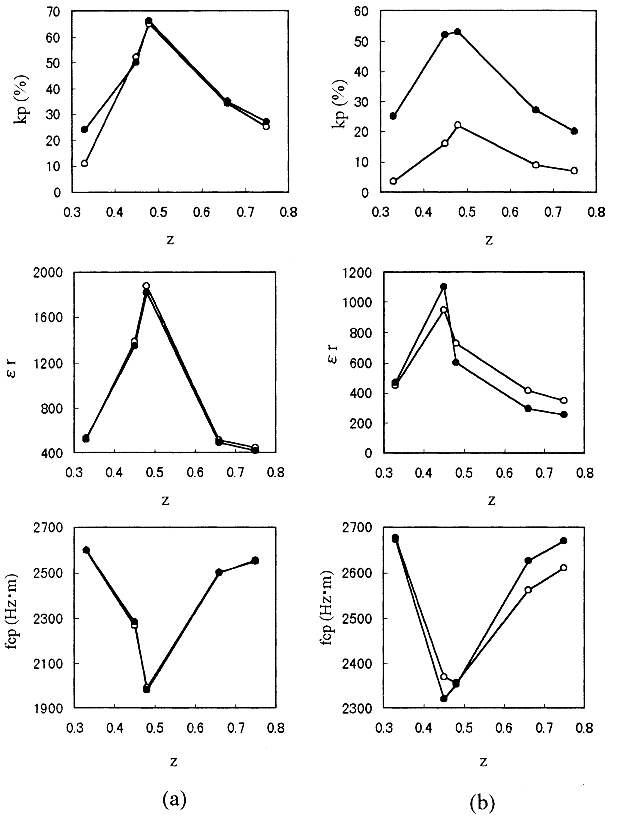

Fig. 4. Comparison of ferroelectric properties in (a) soft and (b) hard PZT ceramics between pulse poling (○) and DC poling (●).

circles) and ordinary DC poling (closed circles) is shown in the case of soft PZT ceramics [Fig. 4(a)] and hard PZT ceramics [Fig. 4(b)] at various compositions of z. The k_p, ε_r and fcp were measured after 10 times bipolar pulse ($E=\pm 3.0$ kV mm^{-1}, $T=800$ ms) applying, and after DC poling on the condition of 80°C, 3.0 kV mm^{-1} and 30 min. The k_p in soft PZT ceramics by bipolar pulse poling reached to the k_p obtained by ordinary DC poling except for the k_p in the tetragonal composition of $z=0.33$. The k_p in whole hard PZT composition, however, was less than a half of the k_p obtained by DC poling. We believe the difference in the poling effect is due to the difficulty of 90° domain rotation in tetragonal phase and 71 or 109° domain rotation in rhombohedral phase.

3.4. Bipolar pulse applied to poled ceramics

The bipolar pulse shown in Fig. 1 was applied to as-fired samples (virgin ceramics) and DC poled samples (poling conditions: 80°C, 3.0 kV mm^{-1}, 30 min) with a composition of $z=0.48$ up to 10 times. The pulse field and period were $E=\pm 3.0$ kV mm^{-1}, $T=800$ ms; $E=\pm 4.0$ kV mm^{-1}, $T=800$ ms; $E=\pm 3.0$ kV mm^{-1}, 12 s and $E=\pm$ 4.0 kV mm^{-1}, $T=12$ s, respectively. The pulse cycle dependence of kp was investigated, each time the pulse was applied, and it was shown in Fig. 5(a) on soft PZT

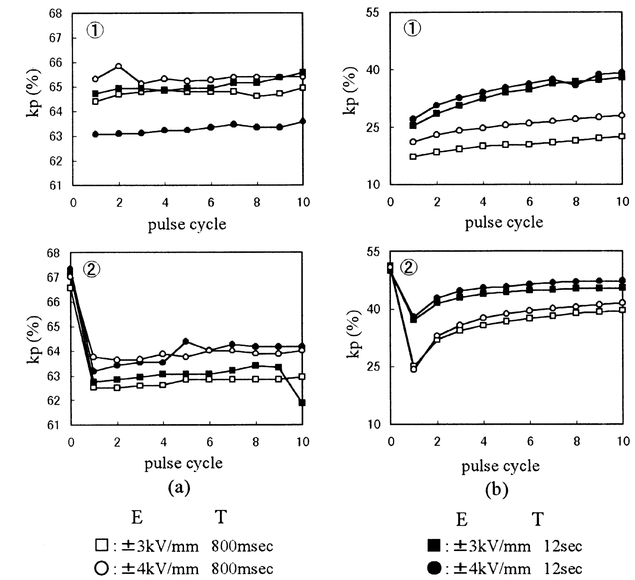

Fig. 5. Bipolar pulse cycle dependence of kp when the pulses were applied to ① as-fired and ② DC poled (a) soft and (b) hard PZT ceramics ($z=0.48$).

ceramics and in Fig. 5(b) on hard PZT ceramics. The effect of the pulse application on k_p in as-fired and poled soft PZT ceramics was almost the same independently of E and T. Moreover, the k_p decreased with the first pulse application in poled soft PZT ceramics and further application, the k_p was independently of the pulse cycles. We believe the decrease in k_p by the first pulse corresponded to 90° domain rotation accompanied with slightly depoling. Further increasing the pulse cycle, the k_p was independently of the cycles. It was thought that 180° domain switching mainly occurred at the cycles. The k_p at $E=\pm 4.0$ kV mm^{-1}, $T=800$ ms in as-fired hard PZT ceramics, however, was larger than the k_p at $E=\pm 3.0$ kV mm^{-1}, $T=800$ ms. Furthermore, increasing T from 800 ms to 12 s, the k_p was improved. In the case of poled hard PZT ceramics, the k_p took minimum at the first pulse application. This phenomenon was thought that the oriented 90° domains by DC poling were irritated by the bipolar pulse, as the result, the k_p became small to accompany with depoling. Further increasing the number of the pulse cycle, the k_p increased with the cycle due to poling again. Comparing the effect of the first pulse application on k_p between poled soft and poled hard PZT ceramics, it can be mentioned that 180° domains mainly affected the k_p in soft PZT ceramics, on the other hand, 90° domains as well as 180° domains affected the k_p in hard PZT ceramics.

4. Conclusions

The effect of repeated bipolar pulses on k_p was clarified in the case of as-fired (virgin) ceramics and poled soft and hard ceramics. The relationship between the pulse field and space charge field was estimated by the shifted direction of the asymmetric P-E hysteresis loop. It was found that a space charge field was generated while applying pulse and the direction of the field was fixed independently of the pulse cycles. The shifted direction was determined by the combination of the bipolar pulses. The possibility of bipolar pulse poling was investigated. The k_p in soft PZT ceramics by bipolar pulse poling reached to the k_p obtained by ordinary DC poling except for the k_p in the tetragonal composition. The k_p in whole hard PZT composition was less than a half of the k_p obtained by DC poling. Furthermore, 180° domain switching and 90° (71 or 109°) domain rotation were evaluated by applying repeated bipolar pulses to DC poled soft and hard PZT ceramics.

Acknowledgements

This work was partly supported by a Grant-in-Aid for Scientific Research (C) (Nos. 09650370 and 12650327) from the Japanese Ministry of Education, Science, Sports and Culture, and the Research Foundation between Academy and Industry of Fukuroi City in 1999.

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