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The Correlation Between Fatigue and Material Constants of PLZT Ceramics

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Abstract

Correlations between the ferroelectric fatigue and variations in mechanical properties have been investigated by simultaneous measurement of the fatigue and the piezoelectric resonance of bar 8/65/35 PLZT ceramics. It was found that the fatigue reflects itself only in dielectric and piezoelectric properties. Namely, the remanent polarization, the complex dielectric and piezoelectric constants and the electromechanical coupling factor all start to decrease at the same number of switching cycles. On the other hand, the complex elastic compliance remains almost unchanged during fatigue process. In addition, the electrical, mechanical and electromechanical quality factors, determined at the piezoelectric resonance frequency, remain constant with the increasing number of switching cycles. This suggests that no correlation exists between the ferroelectric fatigue process and the mechanical degradation in 8/65/35 PLZT ceramics. © 1999 Elsevier Science Limited. All rights reserved

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1 Introduction

Ferroelectric switching in thin films and bulk ferroelectric ceramics enables the application in various memory elements. Recently, it was shown that ferroelectric lead lanthanum zirconate titanate (PLZT) ceramics can also be used for high speed electrographic printing.[1] Material characteristics playing important role in this application are fatigue and piezoelectric properties. While the shape of the dielectric hysteresis loop and the value of the remanent polarization influence the quality of printing characteristics, the fatigue effect constrains the maximum number of rewriting cycles in PLZT material. In addition, the appearance of microcracks, i.e. the mechanical degradation of PLZT ceramics can also substantially reduce the overall quality of the imprinted image.

Ferroelectric fatigue effect and its consequences for commercial applications of ferroelectrics have been recently extensively studied.[2–7] Several important parameters controlling the fatigue have been identified. Among them the pinning of the domain walls by the accumulation of space charges[2,3,5–7] and the treatment of the material–electrode interface[4] are playing a key role. Also, it was found that the remanent polarization can be restored to some extent by thermal annealing above the ferroelectric–paraelectric phase transition temperature.[5] Electromechanical properties such as elastic, piezoelectric, and dielectric constants have been intensively studied by the piezoelectric resonance method in various ceramic materials,[8–11] however, the time dependence of the electromechanical properties under the external electric field stress has not yet been reported on these materials. Consequently, the answer on the question whether there exist some correlation between the ferroelectric fatigue and changes in electromechanical properties has not yet been clearly given.

In this work we present measurements of the fatigue and piezoelectric properties of bar 8/65/35 PLZT ceramics carried out simultaneously in order to assure equal conditions during cycling procedure for all measuring quantities. Such an experiment makes possible to identify existence of correlations between fatigue and variations in electromechanical properties in ferroelectric ceramics.

2 Experiments

Bulk 8/65/35 PLZT ceramics used in these studies was prepared as described elsewhere.[12] In fatigue experiments, the sample was cycled with an a.c. electric field at the frequency of 50 Hz and the

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amplitude of 15 $\mathrm{kV\,cm^{-1}}$. The hysteresis loops were measured via Sawyer–Tower technique and sampled by digital oscilloscope Nicolet Pro30. In order to determine the influence of the fatigue on the elastic and piezoelectric properties of PLZT ceramics the piezoelectric response was studied as a function of switching cycles. Namely, after each measurement of the hysteresis loop, the sample was poled by the d.c. electric field of 15 $\mathrm{kV\,cm^{-1}}$. Then, the admittance $|Y|$ and phase angle θ were measured in the frequency interval 1 kHz–1 MHz by using a HP 4192A Impedance Analyzer.

From the piezoelectric resonance data, the complex piezoelectric and dielectric constants as well as the elastic compliance can be determined. In the vicinity of the resonant frequency ($\omega^2/\omega_0^2 \approx 1$ the admittance of the piezoelectric bar resonator with a large piezoelectric losses can be expressed in terms of the complex dielectric constant $\varepsilon_{33}{*} = \varepsilon'_{33} - i\varepsilon''_{33}$, the complex piezoelectric constant $d_{31}{*} = d_{31}' - id_{31}''$, and the complex elastic compliance $s_{11}{*} = s'_{11} - is''_{11}$ as[11]

$$Y = i\omega\left[\varepsilon'_{33} - Re\left(\frac{d_{31}^{*2}}{s_{11}{*}}\right)\right]\frac{lw}{t} + \omega\left[\varepsilon''_{33} + Im\left(\frac{d_{31}^{*2}}{s_{11}{*}}\right)\right]\frac{lw}{t} + i\omega\frac{8wl}{t\pi^2}\left[Re\left(\frac{d_{31}^{*2}}{s_{11}{*}}\right) + iIM\left(\frac{d_{31}^{*2}}{s_{11}{*}}\right)\right]\left(\frac{\Omega - iM}{\Omega^2 - iM^2}\right) \quad (1)$$

where $M = s''_{11}/s'_{11}$, $\Omega = (\omega_0^2 - \omega^2)/\omega_0^2$ and resonant frequency is $\omega_0^2 = \pi^2/l^2\rho s'_{11}$. Here l, w, and t are length, width, and thickness of a piezoelectric bar resonator, respectively. The treatment of a piezoelectric bar resonator in the case of large piezoelectric losses can be simplified by using the equivalent circuit, which was introduced by Damjanović.[11] Equation (1) can be rewritten in the following form

$$Y = i\omega C_0 + \frac{1}{R_2} + \frac{1}{(i\omega C)^{-1} + i\omega L + R} + \frac{1}{(i\omega C_x)^{-1} + iwL_x + R_x} \quad (2)$$

Here parameters of the equivalent circuit C_0, R_2, C, L, and R are connected to complex material constants via $C_0 = [\varepsilon'_{33} - Re(d_{31}^{*2}/s_{11}{*})]\,lw/t$, $C = 8wlRe(d_{31}^{*2}/s_{11}{*})/t\pi^2$, $LC = 1/\omega_0^2$, $1/R_2 = \omega[\varepsilon''_{33} + Im(d_{31}^{*2}/s_{11}{*})]lw/t$, and $R = M/\omega C$. Parameters C_x, L_x and R_x, which describe piezoelectric losses, are connected to C, L, and R through $C_x = ixC$, $L_x = L/ix$, and $R_x = R/ix$, where $x = Im(d_{31}^{*2}/s_{11}{*})/Re(d_{31}^{*2}/s_{11}{*})$.

By defining $Y = G + iB$, expressions for conductance G and susceptance B can be derived from eqn (2) as

$$G = \frac{\omega^2RC^2 - x(\omega C - \omega^3LC^2)}{(1 - \omega^2LC)^2 + \omega^2R^2C^2} + \frac{1}{R_2} \quad (3)$$

$$\frac{B = \omega C - \omega^3LC^2 = x\omega^2RC^2 + \omega C_0}{(1 - \omega^2LC)^2 + \omega^2R^2C^2} \quad (4)$$

The set of complex material constants was calculated from the parameters of the equivalent circuit. These parameters were obtained by simultaneous fitting of the experimental data of G and B to eqns (3) and (4). Since the clamped capacitance C_0 was determined from the measurement at the frequency $\approx 2\omega_0$, the number of fitting parameters was reduced to five. The initial values of R_2, C, L, and R were approximated by separate fitting the conductance and the susceptance to equations of standard equivalent circuit. The initial value for x was then determined by fitting the susceptance to eqn (4).

3 Results and Discussion

The ferroelectric fatigue in 8/65/35 PLZT ceramics is shown in Fig. 1. The remanent polarization P_r decreases steeply above $\sim 2\times10^4$ switching cycles, above which also the coercive field E_c shows a weak change in the slope.

Figure 2 shows experimentally determined conductance G and susceptance B in a complex plane and the results of the simultaneous fitting to eqns (3) and (4) at four different numbers of switching cycles. Clearly, the radius of the circles starts to decrease rapidly after 10^4 switching cycles, indicating suppression of the piezoelectric resonance amplitude which occurs together with the decreasing of the remanent polarization.

The real and imaginary parts of the complex material constants determined from piezoelectric resonance data as a function of switching cycles are

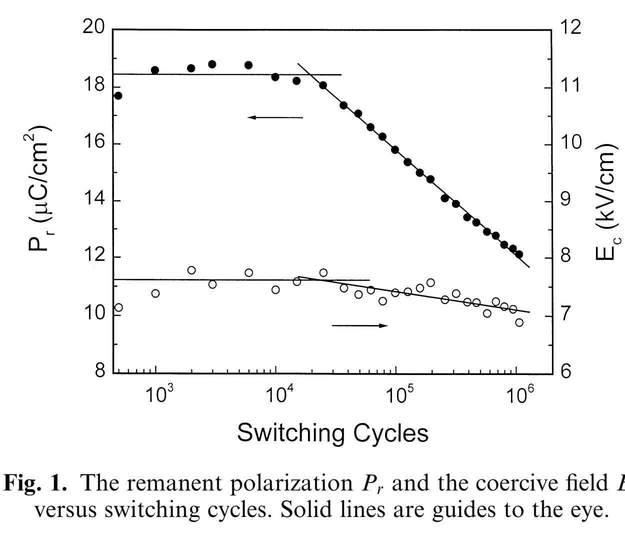

Fig. 1. The remanent polarization P_r and the coercive field E_c versus switching cycles. Solid lines are guides to the eye.

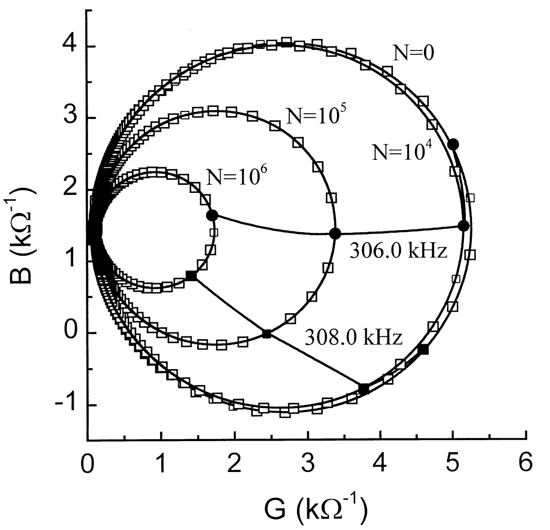

Fig. 2. Susceptance B versus conductance G obtained at four different numbers of switching cycles. Dots represent experimental points. Solid curves represent fits to eqns (3) and (4).

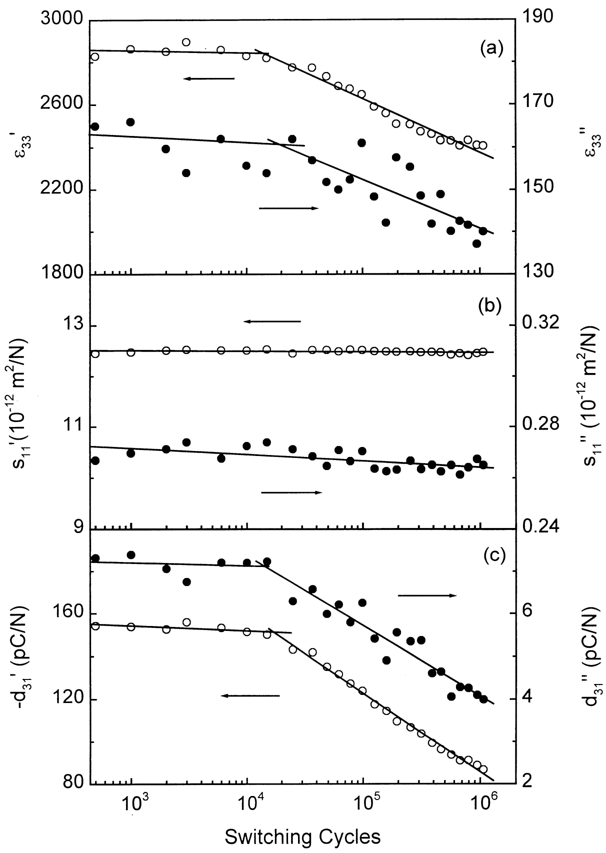

Fig. 3. Various material properties as a function of switching cycles: (a) the real ε'_{33} and imaginary parts ε''_{33} of the complex dielectric constant, (b) elastic compliances s'_{11} and s''_{11} and (c) piezoelectric constants $-d'_{31}$ and d''_{31}. Solid lines are guides to the eye.

shown in Fig. 3. After an initial plateau, both real ε'_{33} and imaginary ε''_{31} parts of the complex dielectric constant as well as real $-d'_{31}$ and imaginary d''_{31} part of the complex piezoelectric constant start to decrease steeply above $\sim 2\times 10^4$ switching cycles. Contrary to the behavior of the complex dielectric and piezoelectric constants, the elastic compliances s'_{11} and s''_{11} shown in Fig. 3(b), are nearly independent on switching cycles. Figure 3 shows that changes in slopes of dielectric and piezoelectric constants occur at the same number of switching cycles as in the case of the remanent polarization dependence. A similar behavior of piezoelectric constant d_{33} was recently observed in PZT thin films.[6] As can be seen in Fig. 3, the electrical $Q_e = \varepsilon'_{33}/\varepsilon''_{33}$ mechanical $Q_m = s'_{11}/s''_{11}\ldots$ and electromechanical $Q_{me} = d'_{31}/d''_{31}$ quality factors determined at piezoelectric resonance frequency are all independent on switching cycles. Namely, real part of the particular constant has the same dependence on the increasing number of switching cycles as its imaginary part.

Since the fatigue in PLZT ceramics reflects itself only in piezoelectric and dielectric properties, but not in elastomechanical properties, it can be concluded that, there is no correlation between the fatigue and the mechanical degradation of the sample, like for instance the appearance of microcracks. It is interesting to note that the thermal annealing of the fatigued sample at 590°C nearly completely restores the remanent polarization to its initial value. The same behavior was reported by Pan *et al.*[5] for PZT and PLZT ceramics pointing out that the pinning of domain walls due to entrapment of space charges at the electrode or domain interface is most likely responsible for the fatigue.

It should be mentioned that simultaneous measurements of piezoelectric properties and the fatigue in single measurement run on the same sample have an important advantage in comparison to the case where the same measurements are performed in separate runs on different samples. Namely after the fatigue is performed on one sample, this particular sample cannot be used anymore for another fatigue experiment even after being thermally annealed, simply because its properties never recover exactly to the same value. The second experiment performed on a newly prepared sample will bring additional scattering, when comparing these data to the data from the first run, due to the known problems with cleaning procedures and electrode deposition. But the most important problem which reduces the value of such separate measurements performed on one (annealed) or two different new samples is so called onshelf aging, i.e. variations in dielectric properties with time in zero-field conditions. This is particularly important in PLZT ceramics where decrease in the dielectric constant for more than 20% can be observed within a few hours after annealing. This phenomenon makes almost impossible to bring two different samples in exactly the same state since their histories will never be exactly the same after thermal annealing.

In conclusion, it was found that the fatigue in bulk 8/65/35 PLZT ceramics reflects itself only in dielectric and piezoelectric properties, but not in elastic compliances. On the basis that the electrical, electromechanical and mechanical quality factors are independent on switching cycles, it was concluded that there is no correlation between the ferroelectric fatigue and the mechanical degradation of the sample.

Acknowledgements

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