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Computer Simulation of P-E Hysteresis of Ferroelectrics

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The computer simulation of the polarization (*P*) and electric filed (*E*) hysteresis curves for ferroelectrics has been demonstrated by combining two Gaussian functions and one Error function to generalize and parameterize a *P-E* hysteresis curves. The Gaussian functions express the statistical distribution of the coercive fields in the process of domain switching. Moreover, the Error function is employed to describe the partial relaxation of switched domain reorientation. This model has successfully reproduced the *P-E* hysteresis curves for several ferroelectrics, which are $BaTiO_3$ ceramic, (001) $BaTiO_3$ single crystal, hard-$Pb(Zr,Ti)O_3$ (PZT) ceramic, and $Pb(Zr,Ti)O_3$-$Pb(Ni,Nb)O_3$ (PZT-PNN) ceramic.

Key Words: computer simulation, domain switching, *P-E* hysteresis curve, $BaTiO_3$, PZT

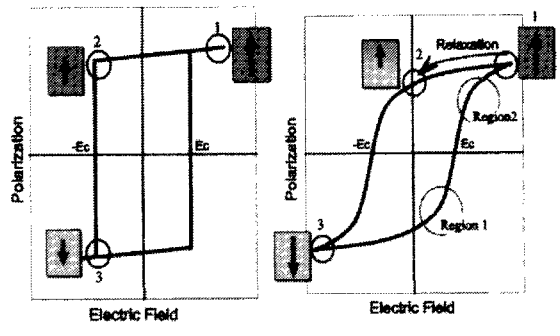
1.INTRODUCTION

Ferroelectric materials have been widely utilized in various electrical and optical devices using their ferroelectricity. As for the characterization of their properties, the relations between the polarization (*P*) and the electric field (*E*), that is, *P-E* hysteresis curves have been generally observed giving intuitive information about their ferroelectricity. The relationship between materials and electrical properties has not been fully understood yet owing to their complicate processes of the polarization reversals and the dependence on sample conditions. Although P-E hysteresis curves have been observed for the remanent polarizations (Pr) and coercive fields (Ec), detail interpretations of P-E hysteresis curves taken into account of the domain switching has not been carried out yet. Up to now, some kinds of models for simulating the electrical responses of ferroelectric capacitors have been proposed to explain the behavior of their polarization reversals. One of them is the parallel-element model [1] [2]. The parallel-element model expresses ferroelectrics as numbers of capacitor elements connected in parallel. Another approach is the model based on the Preisach theory [3] [4]. The model takes into account of ferroelectrics as only two different orientate polarization on the basis of magnetism. These models have assumed that ferroelectric materials have a distribution of Ec. However, they can apply to the particular conditions in which the *P-E* hysteresis curves have almost same curvature near zero voltage and beyond the Ec. Furthermore, they only simulate hysteresises in thin films. From these viewpoints, the universal model needs to be able to simulate for any kinds of ferroelectric materials, such as single crystals, ceramics, thin films, and different composition in order to generalize and parameterize a *P-E* hysteresis curves. As a first step, we propose the computer simulation model to reproduce accurately the *P-E* hysteresis curves of several types of ferroelectrics by employing two Gaussian functions and one Error function, taking into account of the distribution of Ec and the ferroelectric relaxation.

2.MODEL

Figure 1(a). shows an ideal single domain crystal with a parallelogram hysteresis curve. When E_c, the threshold electric field for domain polarization, is reached, the domain switching can be simultaneously occurred. On the other hand, a *P-E* hysteresis curve of ferroelectrics usually exhibits a smooth curve such that as shown in Fig. 1(b). For example, as the electric field increases from zero to the positive fields, polarization begins to reverse, in which *dP/dE* is small because electric fields are low to overcome the activation energy. With the increase of electric fields, a number of negative domains with the direction opposite to that of the field are switched over along the direction of the applied positive field in the vicinity of E_c so that the polarization increase rapidly around E_c until all the domains are aligned in the positive direction. This phenomenon can be interpreted such as that the threshold of electric fields for domain switching are statistically distributed according to Gaussian function. In addition, one more Gaussian function needs in order to raise accuracies. Because ferroelectric samples often shows that curvatures in their *P-E* hysteresis curves are asymmetric with respect to the coercive field E_c as follows. When an electric field increases from zero toward E_c, *dP/dE* stands up steeply (as shown in Region 1 of fig.1(b)). On the contrary, *dP/dE* increases more gradually and does not reach the saturation value easily as the field exceeds E_c and increases (as shown in Region 2 of fig.1(b)). Such a hysteresis cannot be reproduced by

using only one Gaussian function, tanh or arctan functions. Furthermore, *dP/dE* decrease sluggishly as the electric field decreases from the maximum field to zero. We will give a definition of this phenomenon as the partial "relaxation" of switched domain. The Error function is introduced in that electric field region to take into account of the relaxation of domain reorientation.



(a) (b)

Fig. 1. (a) Schematic diagram of a "parallelogram" *P-E* hysteresis curve of an ideal single domain crystal. From the state 1 to the state 2, there is no domain switching. From the state 2 to the state 3, the domain switching can be occurred in an instant. (b) Schematic diagram of an experimental *P-E* hysteresis curve. From the state 1 to the state 2, *dP/dE* decreases sluggishly. Polarization begins to reverse over the state 2.

The distribution function for the domain switching is explained in detail as follows: The assumption in this simulation model is that any switching of the polarization doesn't occur in the region of the relaxation (as shown fig. 1. (b)). It is that the oriented domains can be switch back only after the applied field turns over to opposite fields.

First, *f(E)* as a function of an applied electric field *E* is obtained by the sum of two Gaussian functions representing the probability of the threshold of electric fields for domain switching.

$$f(E) = \mathrm{h}_1 \exp\left[-\frac{1}{2}\left(\frac{E-E_{C1}}{\sigma_1}\right)^2\right] + \mathrm{h}_2 \exp\left[-\frac{1}{2}\left(\frac{E-E_{C2}}{\sigma_2}\right)^2\right] \quad (1)$$

where h_i, σ_i, and E_{Ci} are intensities, widths, and centers of Gaussian peaks, respectively. The suffix *i* is 1 and 2, which stand for the first and second Gaussian peaks. The narrow peak is allotted to the first Gaussian, and the broad peak is allotted for the second Gaussian expressing a broad distribution of the threshold of electric field for the domain switching. For the fitting of the rate of second Gaussian contribution, the ratio of the peak intensities $\mathrm{h}_1/\mathrm{h}_2$ is determined as a parameter. E_{C1} and E_{C2} at the maximum of the mean value of two Gaussian distributions are decided by the coercive electric field E_c from the saturated hysteresis curves obtained by measurements.

Next, the polarization decrease sluggishly because of domain motion, i.e., the partial "relaxation" of switched domain as the electric field decreases from the maximum field to zero. This phenomenon signifies new domain nucleation, domain splitting and domain wall displacement. However, in this study, it is separated from domain switching with the above assumption. The relaxation is represented by the error function as follows:

$$g(E) = h_3[1 - \mathrm{erf}(E)] \quad (2)$$

where h_3 is the height of the function implying the rate of the relaxation, and erf(*E*) is the Error function. In order to express the diminution of the polarization, erf(*E*) is subtracted from one. For the decision of the function *g(E)*, we need the parameter σ_3 which is the center of the error function. The value of *g(E)* represents the probability of relaxing domains as a function of the applied field *E*.

Last, the total polarization can be written as the sum of the paraelectric term and the ferroelectric term due to domain switching in the ferroelectric capacitors. The distribution functions eqs. (1) and (2) mentioned above give the polarization variation of the ferroelectric term,

$$\Delta P_{cal}(E) = f(E) \cdot \Delta E \quad (3)$$

(when an absolute value of *E* increases from zero to maximum applied field E_{max})

$$\Delta P_{cal}(E) = g(E) \cdot \Delta E \quad (4)$$

(when an absolute value of *E* decreases from maximum applied field E_{max} to zero)

$$P_{ferro}(E) = \frac{\mathrm{P_S}}{\mathrm{P_{Sful}}} P_{cal}(E) \quad (5)$$

where $P_{ferro}(E)$ is the ferroelectric term of polarization due to domain switching, $\mathrm{P_S}$ is spontaneous polarization as a material constant, $\mathrm{P_{Sful}}$ is the saturated polarization and $P_{cal}(E)$ is the ferroelectric term of polarization in the algorism.

The resultant equations as follows:

$$P_t(E) = P_{para}(E) + P_{ferro}(E) \quad (6)$$

$$P_{para}(E) = \varepsilon_r E \quad (7)$$

$$P_t(E) = -P_t(-E) \quad (8)$$

where $P_t(E)$ is the total polarization, $P_{para}(E)$ is the paraelectric term of polarization and ε_r is the relative permittivity which is extracted from the saturated hysteresis.

3. CALCULATION

In the calculation, it is assumed that the shape of the distribution function of the domain switching defined by eqs. (1) and (2) is independent of the oscillating

amplitude of E. Computer simulations are performed in three steps. In the first step, the distribution functions of domain switching with respect to the applied E shown in eqs. (1) and (2) are decided. For deciding the distribution functions, we have to fix a few parameters, such as E_{C1}, σ_1, E_{C2}, σ_2, h_2/h_1, E_{C3}, h_3, σ_3, ε_r and P_S. In the case of simulating an ordinary single hysteresis loop, a value of E_{C3} should be zero. A part of the relaxation of domain reorientation in the hysteresis curve is monotonously decreased for E = zero. In the second step, the saturated polarization (P_{Sfull}) of the ferroelectrics is obtained from the integration of eqs. (3) and (4) for sin waves with sufficient amplitude (E_∞) to saturate the polarization. P_{Sfull} means the spontaneous polarization of the ferroelectrics, which has the distribution decided in the first step. In the third step, for sin waves with arbitrary amplitudes of the applied field, the total polarization $P_t(E)$ is obtained from all summation eqs. (3)-(8). By changing the amplitude of the applied field, unsaturated hysteresis curves can be reproduced.

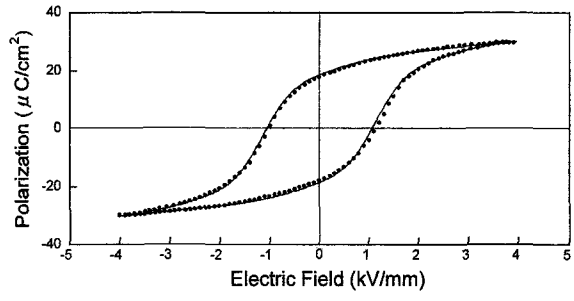
4. EXPERIMENTAL

Ferroelectric samples, hard-PZT ceramics and PZT-PNN ceramics, were prepared in order to compare simulation data of hysteresis curves with experimental data. The ceramics were prepared by an ordinary ceramic process. Hysteresis measurements were carried out using a conventional Sawyer-Tower circuit and a sinusoidal input with a frequency of 50Hz. The input signal was a symmetric sine wave with adjustable amplitudes. The data were acquired by a digital oscilloscope. The *P-E* hysteresis curves of $BaTiO_3$ ceramics and (001)$BaTiO_3$ single crystals are quoted from the well-known data [5].

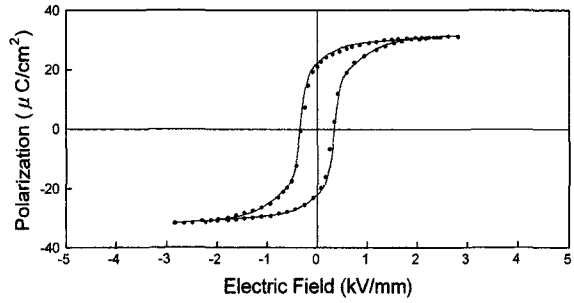
5. RESULTS AND DISCUSSION

Figure 2 (a) and 2 (b) show the hysteresis curves of hard-PZT and PZT-PNN ceramics. The simulated results give good agreement with the measurement data. The E_c of PZT-PNN ceramics is smaller than that of hard-PZT ceramics. Figure 3 shows the dP/dE versus E plots simulated with respect to hard-PZT and PZT-PNN ceramics. The shape of the distribution function of PZT-PNN is sharper than that of hard-PZT. These distribution functions of PZT-PNN were especially composed of such two peaks as follows: (1) the peak with high, sharp and narrow shape and (2) the peak with low and broad shape. The above results show that there are two kinds of domain switching. The ratio and position of the two peaks significantly depends on the materials.

Ceramics are composed of the randomly oriented grains. Therefore, the contributions of domain switching to the polarization are much complicated so that domain switching is affected by the presence of defects, grain boundaries, or stress. It is known that hard-PZT has a high Ec because domain wall movement is pined by defects. Therefore, the domains of hard-PZT are much influenced by defects so that hard-PZT has the high coercive fields. We are considering about the broad distribution



(a)



(b)

Fig. 2. Simulated P-E hysteresis of (a)hard-PZT ceramic and (b) PZT-PNN ceramic. The dots are measurements data, the solid line is simulation results, respectively.

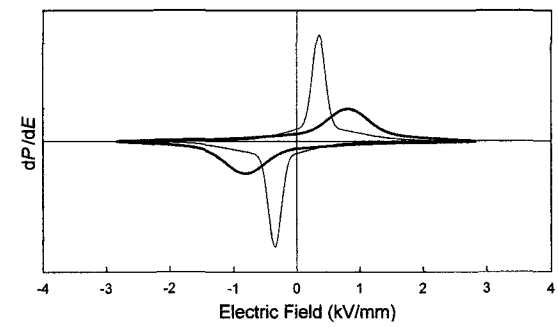
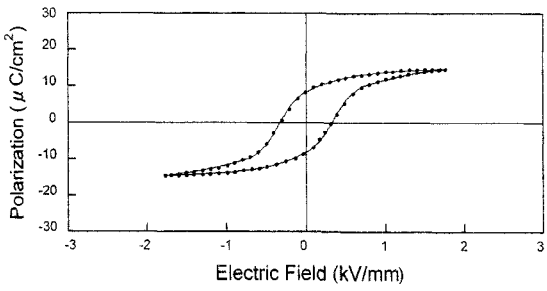


Fig. 3. The distribution functions (d*P*/d*E*) of hard-PZT and PZT-PNN ceramics. The bold line is of hard-PZT, the fine line is of PZT-PNN ceramics.

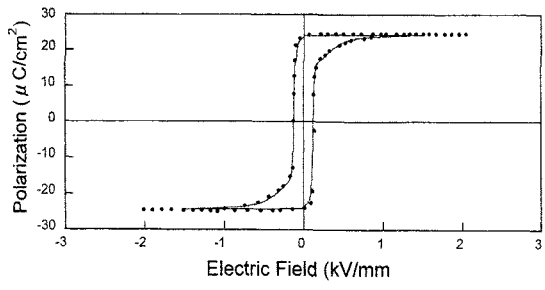
Figure 4 (a) and (b) shows P-E hysteresis curves of $BaTiO_3$ ceramics and single crystals, respectively. Simulation results for both of them are also very well in agreements with measurements. It is noteworthy that the curves of the $BaTiO_3$ single crystal have asymmetric curvatures between in the region toward saturating polarization and in the region around zero field to E_c such that as shown in Fig. 4(a). It can be verified that the use of two kinds of Gaussian functions are indispensable to fit such a kind of hysteresis curves with asymmetric

curvatures.

It is known well that there are two kinds of domains, such as 180° domains and non-180° domains and the behaviors of domain switching are closely related to crystallographic orientations in ferroelectrics. It is believed that the domains with different orientations contribute to the total polarization in a different way. Referred to the model to estimate the contribution of domain switching behaviors by the use of both the polarization versus electric field plots and the strain versus electric field plots, the 180° domain structure has no strain boundaries between domains and the non-180° domain structure has the mechanical strain boundaries between domains [6]. Therefore, the 180 ° domain can begin to switch around E_c, but the non-180° domain walls can be moved by both electric fields and stresses. Therefore, it can be inferred that the 180° domain switching has a narrow distribution and the non-180° domain switching has a broad distribution.



(a)



(b)

Fig. 4. Simulated P-E hysteresis loops of (a) $BaTiO_3$ ceramic and (b) single crystal. The dots are measurements data, the solid line is simulation results, respectively.

In this model, we have assumed that a statistical distribution of the threshold electric field of domain switching is expected to follow the Gaussian distribution function. In addition, the use of two Gaussian functions is very effective to perform the fitting of the P-E hysteresis curves with respect to any type of ferroelectrics including even $BaTiO_3$ single crystals. The two Gaussian functions correspond to a main peak with narrow width and to the broad distribution peak, respectively. In the case of $BaTiO_3$ single crystals and $BaTiO_3$ ceramics, the two functions seem to correspond to the 180° and non-180° domain switching.

Through this study, we know that two Gaussian functions and one Error function are required to simulate universally a P-E hysteresis curves and to parameterize them with the minimum number of variables. Moreover, the each functions used have shown to imply the behaviors of domain switching including the relaxation phenomenon. Consequently, these simulated and experimental results indicates the validity of our model by means of the computational algorithm governing the behaviors of domain switching and the minimum physical parameters.

6. CONCLUSION

In the present work, a new model for a computer simulation of the *P-E* hysteresis curve has been developed. This model is based on the statistical domain switching and evaluated accurately by the prediction of experimental curves. The distribution function of the domain switching with electric field is assumed as Gaussian functions. Two Gaussian functions are necessary to fit the P-E hysteresis curves of ferroelectrics. The relaxation of the domain reorientation is represented by the error function. This model has successfully explained the P-E hysteresis curves of ferroelectrics.

7. ACKNOWLEDGEMENT

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