Transactions of the Materials Research Society of Japan 29[4] 1223-1226 (2004)

Frequency Dependence of Piezoelectric *d*-constant of PZT Ceramics Determined from Direct and Converse Effects

T. Tsurumi, T. Sasaki, H. Kakemoto and S. Wada
Tokyo Institute of Technology, Japan
Fax: 81-3-5734-2514, e-mail: ttsurumi@ceram.titech.ac.jp

The domain contributions in the piezoelectric converse effect and the direct effect were compared for the soft- and the hard-PZTs by measuring piezoelectric d_{33} constant as a function of frequency. The d_{33} of the converse effect was determined from the electric-field induced strain. In the measurement of the direct effect, a sinusoidal stress was applied to the sample using a piezoelectric actuator and the polarization generated by the direct effect was detected as a displacement current. The degree of the domain contribution was estimated from the difference in the piezoelectric d_{33} constants determined from the resonance method and that from the converse or the direct effect. The domain contribution was larger in the soft-PZT than in the hard-PZT. The d_{33} determined from the two effects was consistent in the soft-PZT but the d_{33} of the hard-PZT determined from the direct effect was markedly larger than that from the converse effect or the resonance method. These results indicated that a fairly large degree of the domain contribution existed in the direct effect of the hard-PZT, and that the mechanism of the domain wall clamping did not effectively work in the direct effect.

Key words: Piezoelectricity, PZT, Domain contribution, Piezoelectric relaxation

1. INTRODUCTION

Perovskite ferroelectrics have 180 degree and non-180 degree domain structures. The domain switching with the domain wall motion markedly affects the dielectric and piezoelectric properties,[1-3] which is called as the "domain contribution". As the non-180 degree domain switching is ferroelastic, the velocity of domain wall motion should be restricted by the strains accompanied with the domain switching. Tsurumi *et al.*[4,5] have shown that the domain contribution of the non-180 degree domains to the electric-field (E-field) induced strain could be evaluated by measuring frequency dependence of piezoelectric *d*-constant. The domain contribution thus evaluated is that only for the piezoelectric converse effect. In the piezoelectric direct effect, there must be the domain contribution but the study on the frequency dependence of the direct effect has been limited.[6,7]

Piezoelectric properties are usually evaluated by the resonance method. Properties evaluated by this method are those under low fields and in the resonance state. Piezoelectric constants determined by the resonance method are sometimes different from those determined from the converse effect because of the domain contribution. In the measurement of the converse effect, the piezoelectric *d*-constant is determined from the slope of the strain with E-field. Strains can be measured under low to high fields in the resonance and in the off-resonance states using various apparatuses, such as a dilatometer, a laser interferometer and a laser Doppler vibrometer. In this sense, the measuring technique of the converse effect has been already established. On the other hand, a d_{33} meter is often used in the measurement of the direct effect. The d_{33} meter applies a periodic weak stress to the sample and detects an induced polarization. However, the stress intensity and its frequency cannot be changed in the measurement. Recently, the direct effect under high stresses is being important for the application of a piezoelectric power generation. However, the measuring technique has not been established.

In this study, we have developed a measuring system of the direct effect under relatively high stresses as well as the system to measure E-field induced strains due to the converse effect. Piezoelectric *d*-constants of the "soft" and the "hard" PZTs were measured as a function of frequency in order to evaluate the domain contribution in the direct and the converse effects of PZT ceramics.

2. EXPERIMENTAL PROCEDURE

2.1 Sample preparation

Chemical compositions of the soft- and the hard-PZTs are as follows:

Soft-PZT:$0.95[Pb(Zr_{0.53}Ti_{0.47})O_3]$
$-0.05[Pb(Sb_{0.5}Nb_{0.5})O_3]$
Hard-PZT:$0.95[Pb(Zr_{0.53}Ti_{0.47})O_3]$
$-0.05[Pb(Sb_{0.5}Nb_{0.5})O_3]-0.015[MnO_2]$.

PZT ceramics were prepared by a conventional solid state reaction process. The sintering temperature was 1260℃ for 2 h. Bar resonators with the size of 2.4 x 2.4 x 6.0 mm^3 were prepared from the sintered bodies. Electrodes were made by firing Ag paste on the 2.4 x 2.4 mm^2 surfaces. The bar resonators were used for the measurement by the resonance method. The sample sizes for the measurements of the converse effect and the direct effect was 3.0 x 3.0 or 1.0 x 1.0 mm^2 in area of the electroded surface and 1.0 or 3.0 mm in thickness. Poling treatment was done by applying E-field of 3.0 kV/mm at 80℃ for 10 min. for the soft-PZT and 120℃ for 10 min. for the hard-PZT.

Piezoelectric d_{33} constants determined by the resonance method were 397 pC/N for the soft-PZT and 193 pC/N for the hard-PZT.

2.2 Measurement of converse effect

The measuring system of E-field induced strain is shown in Fig. 1. A Michelson interferometer (Canon, DS-80) was used to measure piezoelectric displacement. Five to ten sinusoidal unipolar waves from a function generator (Agilent Tech, hp33120A) were amplified with a high voltage amplifier (Trek, 609D-6) and applied to the PZT ceramics of 3.0 x 3.0 x 3.0 mm^3 cube or 3.0 x 3.0 x 1.0 mm^3 rectangular plate. The signal from the interferometer and that from the function generator were stored into a personal computer through an AD-board (Interface, PCI-3174). The amplitudes of the displacement and the applied voltage were determined by fitting the observed waves to a sinusoidal wave using the least-squares method. Piezoelectric d_{33} constant was calculated from the amplitudes of the displacement and the applied voltage. Measurement was done in the frequency range from 0.1 Hz to 1.25 kHz at various applied voltages.

2.3 Measurements of direct effect

The measuring system of the direct effect is shown in Fig. 2. The structure and a photograph of the sample holder is shown in Fig. 3. Five to ten sinusoidal unipolar waves from a function generator (Agilent Tech., hp33120A) were amplified with an high voltage amplifier (TREK, PZD700) and applied to a piezoelectric actuator, which was used to apply a stress to PZT ceramics of 1.0 x 1.0 x 1.0 mm^3 cube. The stress was monitored with a stress sensor (Teak, TC-RS100N). The polarization generated by the direct effect on the surface of PZT was detected as a displacement current followed by integrating it with an operation amplifier. The signal from the stress sensor was amplified and stored into a personal computer through an AD board with the output signal from the integration circuit.

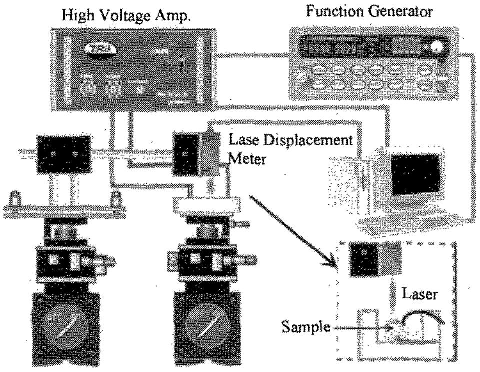

Fig. 1 Measuring system of E-field induced strain as a function of frequency.

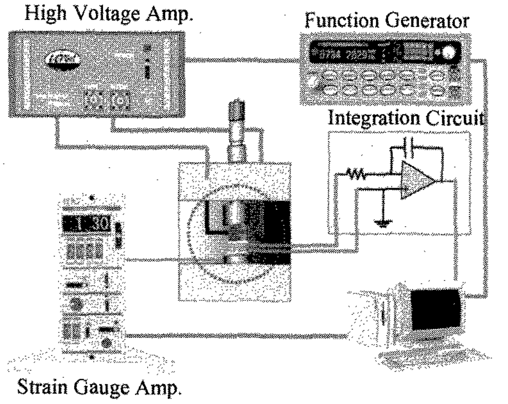

Fig. 2 Measuring system of the direct effect.

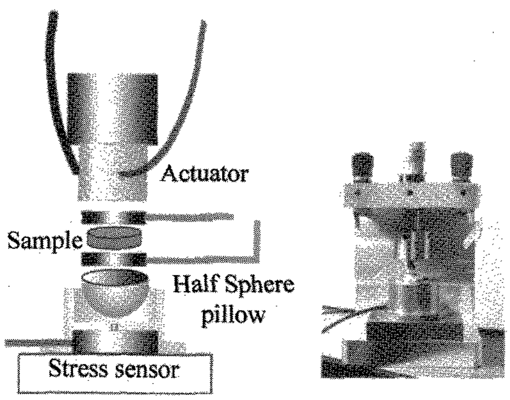

Fig.3 Structure and photograph of the sample holder.

In this measurement, it is very important to apply an uniform stress to the sample. We placed a hand-made half-sphere pillow under the sample to avoid a stress gradient in the sample surfaces. Another serous nuisance factor in the measurement was pyroelectric effect. To minimized the influence of this effect, the sample temperature should be controlled precisely during the measurement. The application of a continuous sinusoidal stress sometimes increased the sample temperature, giving rise to a serious drift of the polarization.

Piezoelectric d_{33} constant was determined from the electric displacement calculated from the polarization and the stress apply to the specimen. Amplitudes of these signals were determined by fitting observed wave forms to a sinusoidal wave using a least-squares method. Piezoelectric constant was evaluated in the frequency range from 0.1 to 850 Hz. at various applied stresses.

3. RESULTS AND DISCUSSION

3.1 Converse effect

At first, the piezoelectric d_{33} constants determined by the resonance method and the converse effect were compared in order to verify the accuracy of the system shown in Fig. 1. The E-field applied to the soft-PZT was 156 V/mm, which was the lowest limit in the measurement of the displacement. The frequency was selected around the highest limit of the interferometer. These conditions were selected to avoid the domain contribution. The piezoelectric d_{33} constant determined from the converse effect is shown in Table 1. The d_{33} from the converse effect agreed with that from the resonance method (397 pm/V) within the error of 1 %, indicating the accuracy of the measuring system.

Figure 4 shows the frequency dependence of piezoelectric d_{33} constant measured from the converse effect for the soft- and the hard-PZTs. The difference between the d_{33} from the resonance method and that from the converse effect is due to the domain contribution, which was indicated by arrows in Fig. 4. The domain contribution is obviously larger in the soft-PZT than in the hard-PZT because domain walls

Table 1 Piezoelectric d_{33} constant of the soft-PZT determined from the converse effect

Frequency (Hz)	d_{33} (pV/m)
800	404.2
900	402.5
1000	402.3
1100	400.6
1250	403.8

are clamped in the hard-PZT. Large piezoelectric relaxation is observed in the soft-PZT below 100 Hz. The d_{33} determined from the converse effect should approach the value determined by the resonance method as the frequency increases. The d_{33} measured at a low E-field approaches to the value of the resonance method with increasing frequency, but that measured at a high E-field has higher values up to 1 kHz. This may indicate that there is another piezoelectric relaxation at higher frequencies because the d_{33} measured at the resonance frequency should be consistent with the result of the resonance method. In the case of the hard-PZT, the piezoelectric d_{33} constants determined from the converse effect are almost consistent with the results of the resonance method, indicating that the domain contribution in the d_{33} is small.

3.2 Direct effect

Figure 5 shows the piezoelectric d_{33} constant determined from the direct effect as a function of frequency. The difference in the d_{33} from the resonance method (arrows in Fig. 5) is due to the domain contribution. The frequency dependence of the d_{33} in the soft-PZT is almost similar to that shown in Fig. 4. However, a large discrepancy is observed in the hard-PZT. The d_{33} from the direct effect is markedly higher than that determined by the resonance method, and furthermore, a piezoelectric relaxation is observed below 100 Hz. These results indicates that the degree of the domain contribution in the hard-PZT is larger in the direct effect than that in the converse effect.

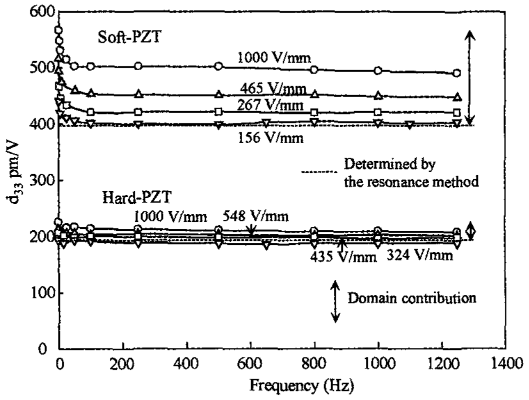

Fig. 4 Piezoelectric d_{33} constant determined from the converse effect as a function of frequency.

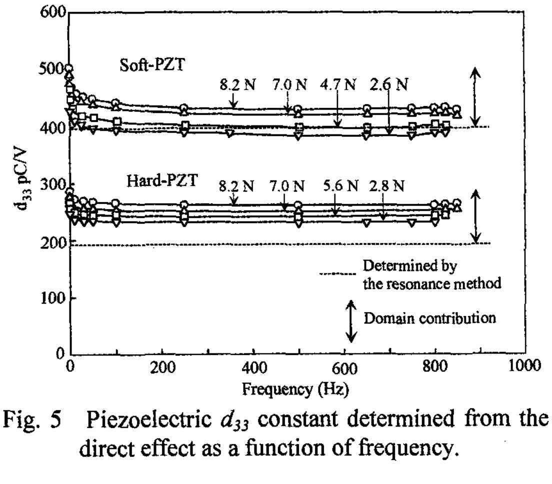

Fig. 5 Piezoelectric d_{33} constant determined from the direct effect as a function of frequency.

3.3 Domain contribution in the converse and the direct effects

In the soft-PZTs, donors are added to reduced the concentration of oxygen vacancies, which is considered to be the origin of the domain wall clamping. Therefore, domain walls move easily in the soft-PZT by external E-field, giving rise to a large domain contribution to various properties. On the other hand, acceptors are added to the hard-PZTs in order to increase the oxygen vacancy concentration. Figure 6 shows E-field induced strain *vs.* E-field curves of PZTs measured at 1 Hz. The soft-PZT shows a curve with hysteresis which increases with maximum E-field. This is a typical effect of the domain contribution. The domain switching of non-180 degree domains has a limit in velocity, which is the origin of the hysteresis in the strain *vs.* E-field curve. The curve of the hard-PZT does not shows the hysteresis because the domain contribution in hard-PZT is small.

From the comparison between Figs. 4 and 5, it was found that the domain contribution in the converse and the direct effects was different in the hard-PZT. The degree of domain contribution was larger in the direct effect. However, in order to compare the two effects under the same condition, the intensity of the stress and the E-field should be consistent because the domain contribution is a function of stress or E-field. This condition may be satisfied when the strains induced by

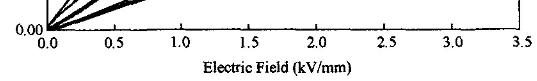

Fig. 6 E-field induced Longitudinal strain pf PZT.

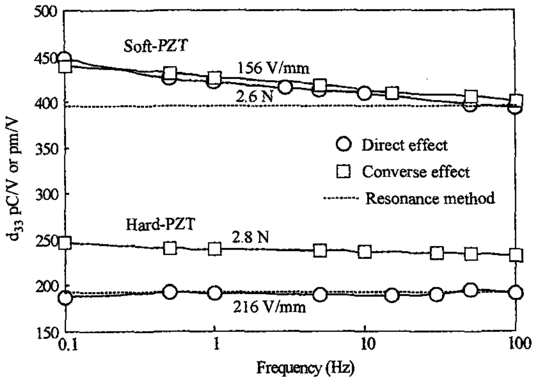

Fig. 7 Frequency dependence of piezoelectric d_{33} constant under approximately the same stress.

the stress and the E-field were consistent. The strain induced by the stress is given by $S_3 = s_{33}T_3$, where S is the strain, s is the elastic compliance and T is the stress. On the other hand, the strain induced by the E-field is given by $S_3 = d_{33}E_3$. When the both strains are equivalent, the following relation should be satisfied, $s_{33}T_3 = d_{33}E_3$. The strain due to the stress was calculated using elastic compliance determined by the resonance method (s_{33} = 22.5 pN/m^2 for the soft-PZT and s_{33} = 15.0 pN/m^2 for the hard-PZT). Figure 7 shows the frequency dependence of d_{33} determined from the converse and the direct effects up to 100 Hz under approximately the same strain. It should be noted that the d_{33} determined from the two effects is consistent in the soft-PZT but the d_{33} of the hard-PZT determined from the direct effect is markedly larger than that from the converse effect or the resonance method. From these results, it is confirmed that a fairly large degree of the domain contribution exists in the direct effect of the hard-PZT.

The domain walls in the hard-PZT are clamped by oxygen vacancies. The oxygen vacancies produced defect dipoles along the spontaneous polarization as shown in Fig. 8. These defect dipoles are stabilized by the space-charge field and restrict the domain switching by clamping the domain wall motion.[8] The switching of the defect dipoles requires the movement of oxygen vacancies. This mechanism of the domain wall clamping indicates that the walls are clamped electrically, therefore, the domain wall clamping is effective in the converse effect as shown in the result of the hard-PZT in Fig. 7. However, in the direct effect, the domain switching is caused by the stress. In the domain switching by stress, the direction of the spontaneous strain of the crystal lattice changes to minimized the elastic energy. Consequently, the domain wall motion cannot be clamped by the defect dipoles, giving rise to the large domain contribution in the direct effect of the hard-PZT.

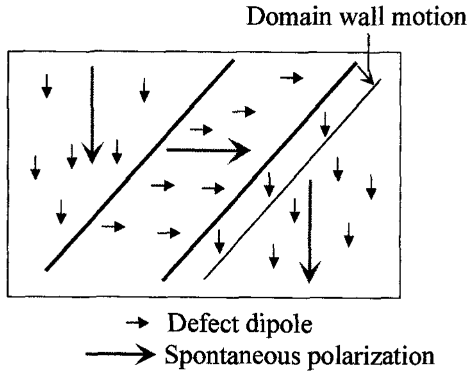

Fig. 8 Defect dipoles and domain wall motion.

4. CONCLUSION

Measuring systems for the piezoelectric converse effect and the direct effect were developed. In the system for the converse effect, the E-field induced strain was measured using a Michelson interferometer. In the measurement of the direct effect, a sinusoidal stress from 2.6 to 8.2 MPa was applied to the sample using a piezoelectric actuator and the polarization generated by the direct effect was detected as a displacement current. The domain contributions in the piezoelectric converse effect and the direct effect were compared for the soft- and the hard-PZTs by measuring piezoelectric d_{33} constant as a function of frequency.

The domain contribution was obviously larger in the soft-PZT than in the hard-PZT. Large piezoelectric relaxation was observed in the soft-PZT below 100 Hz. In the case of the hard-PZT, the piezoelectric d_{33} constant determined from the converse effect was almost consistent with the results of the resonance method, indicating that the domain contribution in the d_{33} was small. However, the d_{33} of the hard-PZT determined from the direct effect was larger than that determined by the resonance method, and furthermore, a piezoelectric relaxation was observed below 100 Hz. The piezoelectric d_{33} constants determined from the converse effect and the direct effect were compared under approximately the same strain. The d_{33} determined from the two effects was consistent in the soft-PZT but the d_{33} of the hard-PZT determined from the direct effect was markedly larger than that from the converse effect or the resonance method. These results indicated that a fairly large degree of the domain contribution existed in the direct effect of the hard-PZT. The mechanism of the domain wall clamping did not effectively work in the direct effect.

References

[1] N. Bar-Chaim, *et al.*, J. Appl.Phys., 45, 6 (1974).
[2] E. I. Bondarenko *et al.*, Ferroelectrics, 110, 53 (1990).
[3] Y. Masuda et al., Jpn. J. Appl. Phys., 33, 5549 (1994).
[4] T. Tsurumi *et al.*, Jpn. J. Appl. Phys., 39 5604 (2000).
[5] T. Tsurumi *et al.*, Ferroelectrics, vol. 224, 597-604 (1999).
[6] Y. Saito *et al.*, Jpn. J. Appl. Phys., 34, 5313 (1995).
[7] D. Dragan *et al.*, J. Appl. Phys., 82, 1787 (1997).
[8] G. Arlt and N. A. Pertsev, J. Appl. Phys.,7 0, 2283 (1991).

(Received October 11, 2003; Accepted March 10, 2004)