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# Contribution of the irreversible displacement of domain walls to the piezoelectric effect in barium titanate and lead zirconate titanate ceramics

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**Abstract.** The contribution from the irreversible displacement of non-180° domain walls to the direct longitudinal piezoelectric  $d_{33}$  coefficient of BaTiO<sub>3</sub> and Pb(Zr,Ti)O<sub>3</sub> ceramics was determined quantitatively by using the Rayleigh law. Effects of the crystal structure and microstructure of the ceramics as well as the external d.c. pressure on the domain wall contribution to  $d_{33}$  were examined. In barium titanate, this domain wall contribution is large (up to 35% of the total  $d_{33}$ , under the experimental conditions used) and dependent on the external d.c. pressure in coarse grained ceramics, and much smaller and independent of the external d.c. pressure in fine-grained samples. The presence of internal stresses in fine-grained ceramics could account for the observed behaviour. The analysis shows that the domain-wall contribution to the  $d_{33}$  in lead zirconate titanate ceramics is large in compositions close to the morphotropic phase boundary that contain a mixture of tetragonal and rhombohedral phases, and in rhombohedral compositions (up to 40% of the total  $d_{33}$ ). The domain-wall contribution to the piezoelectric response from the irreversible displacement of domain walls is significantly smaller in tetragonal Pb(Zr,Ti)O<sub>3</sub> samples where it decreases with increasing spontaneous strain.

## 1. Introduction

Two types of contributions to the piezoelectric effect in ferroelectric ceramics are usually distinguished: the intrinsic contribution, due to the piezoelectric effect of the lattice, and extrinsic contributions, that are mainly but not exclusively due to the motion of ferroelectric–ferroelastic (non-180°) domain walls [1–3]. The contribution from the irreversible displacement of domain walls leads to a nonlinear and hysteretic piezoelectric response, even at relatively low driving electric fields or pressures [4, 5]. The domain-wall motion and the piezoelectric response of the ceramics may be affected by many factors, including the crystal structure and microstructure of the ceramics, the presence of impurities, dopants, defects, and local variations in the composition of the ceramics [4, 6].

Presently, there is no satisfactory theory which describes the domain-wall contribution to the piezoelectric response of ferroelectric ceramics under weak-field conditions (well below the switching electric field or stress). The contribution of domain-wall displacement to material properties is better understood in other ferroic systems. In ferromagnetic materials, for example, the treatment of ferromagnetic domain walls moving in a medium in which the potential energy of domain walls varies irregularly with their position shows that magnetization and magnetic susceptibility can be described in the low-field region by the classical Rayleigh law [7–9]. Recently, it has been proposed that the Rayleigh law

can be extended to include the piezoelectric effect in ferroelectric ceramics [10, 11]. By analysing the piezoelectric response of ceramics in terms of the Rayleigh law it is possible to quantitatively describe the contribution of the irreversible motion of domain walls to the piezoelectric properties. In this paper, the Rayleigh analysis of the direct piezoelectric effect in BaTiO<sub>3</sub> (BT) and Pb(Zr,Ti)O<sub>3</sub> (PZT) ceramics is used to obtain information on the effects of the crystal structure and microstructure of the ceramics on contribution to the piezoelectric effect from the irreversible displacement of ferroelectric–ferroelastic domain walls.

## 2. Sample preparation

### 2.1. Barium titanate

The samples were prepared from a commercial undoped BaTiO<sub>3</sub> powder. The fine-grained samples were prepared by hot pressing for 15 min at 1250 °C under 45 MPa. The density of the samples was greater than 99% of the theoretical and the obtained grain size was 0.8 μm. The coarse grained samples were prepared by natural sintering at ~1350 °C with a heating rate of 1 °C min<sup>-1</sup>. The density was 97% of the theoretical and the average grain size was 26 μm. The relative dielectric permittivity at room temperature was 2300 for the coarse-grained and 5200 for the fine-grained ceramics. The ceramics were poled during cooling from 140 °C to 30 °C under a field of 20 kV cm<sup>-1</sup>.

### 2.2. Lead zirconate titanate

The general formula of the prepared PZT compositions was Pb<sub>(1-y/2)+0.012</sub>(Zr<sub>x</sub>,Ti<sub>1-x</sub>)Nb<sub>y</sub>O<sub>3</sub> with  $y = 0$  and 0.04 and  $x = 0.63, 0.53, 0.43,$  and 0.20. The powders were prepared by the mixed oxide route or from a *B*-site precursor (Zr<sub>x</sub>Ti<sub>1-x</sub>O<sub>2</sub>) when a better distribution of the *B*-site cations was needed (morphotropic compositions). The samples were naturally sintered in sealed crucibles containing a lead-rich powder to compensate for the lead loss. The final densities were 96–98% of the theoretical. The grain size was between 1 and 5 μm. In the further text, the PZT compositions are abbreviated by  $[x/(1-x)]$  so that, for example, (63/37) describes the composition with 63 at.% Zr and 37 at.% Ti. All PZT samples were poled at 120 °C with an electric field from 20 to 25 kV cm<sup>-1</sup>.

## 3. Rayleigh relationships and piezoelectric measurements

Recently, it has been shown experimentally that the dependence of the direct longitudinal piezoelectric  $d_{33}$  coefficient on a.c. pressure in several ferroelectric ceramics may be described at low a.c. pressures by the linear relationship [10, 11]

$$d_{33}(\sigma_0) = d_{init} + \alpha\sigma_0 \quad (1)$$

where  $\sigma_0$  is the amplitude of the a.c. pressure  $\sigma(t)$ . It was proposed [10, 11] that the linear pressure dependence (1) is due to the Rayleigh-type contribution [7–9] to  $d_{33}$  from moving domain walls. This interpretation implies that the term  $\alpha\sigma_0$  is due to the irreversible displacement of domain walls.  $d_{init}$  is due to the lattice piezoelectric effect and reversible displacement of domain walls. The Rayleigh coefficient  $\alpha$  (the slope of  $d_{33}$  against pressure amplitude) describes the increase in  $d_{33}$  per unit of the applied a.c. pressure that is due to the irreversible displacement of domain walls. At a given amplitude of the a.c. pressure,

expression  $\alpha\sigma_0/d_{33}(\sigma_0)$  gives the fraction of total piezoelectric response that is due to the irreversible displacement of domain walls.

The a.c. pressure dependence of the piezoelectric charge density is given by

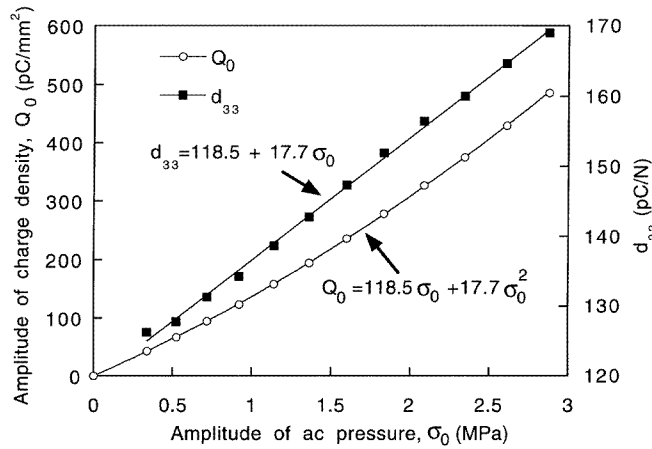
$$Q_0 = d_{init}\sigma_0 + \alpha\sigma_0^2 \quad (2)$$

where  $Q_0$  is the amplitude of the piezoelectric charge density  $Q(t)$ . An essential feature of the Rayleigh behaviour [7] is the following non-analytical expression for the piezoelectric ( $Q(t)$  against  $\sigma(t)$ ) hysteresis loop:

$$Q = (d_{init} + \alpha\sigma_0)\sigma \pm \frac{\alpha}{2}(\sigma_0^2 - \sigma^2) \quad (3)$$

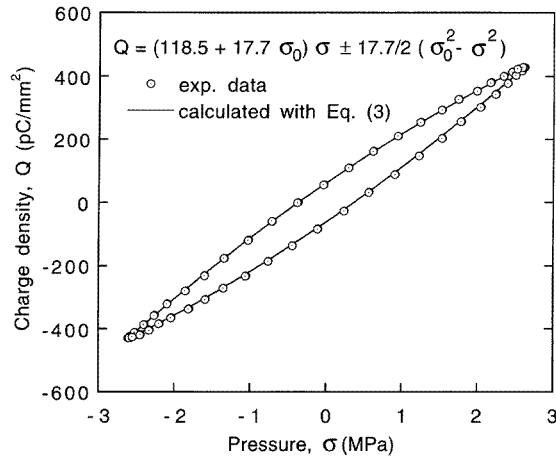
where ‘+’ corresponds to decreasing and ‘-’ to increasing a.c. pressure.

Figure 1 shows, as an example, the linear dependence of  $d_{33}$  and the quadratic dependence of  $Q_0$  against  $\sigma_0$  for a rhombohedral PZT composition. The Rayleigh parameters  $d_{init}$  and  $\alpha$  are calculated from figure 1 by fitting the  $d_{33}$  against  $\sigma_0$  data with equation (1). Once the Rayleigh parameters are known, the piezoelectric hysteresis curve can be calculated by using equation (3). As shown in figure 2, for  $\sigma_0 \approx 2.6$  MPa, the correlation between the calculated loop (full curve) and the experimental data (circles) is good. The fitting errors are small with the linear correlation factor  $R > 0.998$ . A detailed error analysis of the method is given elsewhere [10–12].



**Figure 1.** The longitudinal piezoelectric  $d_{33}$  coefficient and the amplitude of charge density  $Q_0$  as a function of the amplitude of a.c. pressure for the PZT (63/37) sample doped with 4% at Nb. The d.c. bias pressure is 15 MPa. The full lines represent fits with the Rayleigh relations (1) and (2) and the dots represent experimental data.

The examined samples were shaped in the form of disks (~1 mm thick, ~8 mm diameter) or square plates (~1–2 mm thick, ~7–8 mm wide). The direct piezoelectric  $d_{33}$  coefficient of the samples was determined by applying a sinusoidal a.c. pressure  $\sigma(t) = \sigma_0 \sin(\omega t)$ . The resulting charge density  $Q(t)$  was measured under short-circuit conditions. The piezoelectric coefficient was calculated as  $d_{33} = Q_0/\sigma_0$ . The frequency of the a.c. pressure was 1 Hz. The experimental set-up, measurement procedure and accuracy have been described in more detail elsewhere [5, 12]. A uniaxial d.c. compressive pressure in the range 1–15 MPa was applied on samples during the measurements. Each sample was left under a fixed d.c. pressure until the piezoelectric response was stable to ensure a constant polarization of the sample during the experiment.



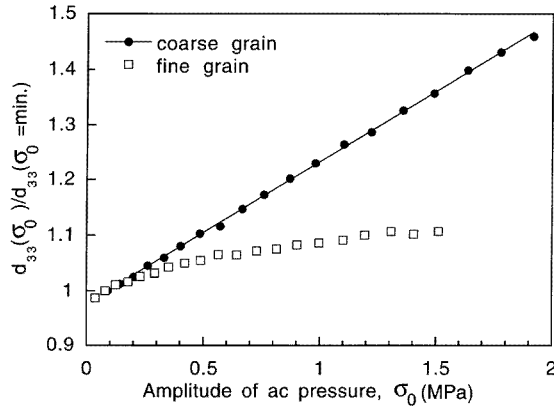
**Figure 2.** The charge density,  $Q(t)$ , against pressure,  $\sigma(t)$ , hysteresis loop for PZT (63/37) doped with 4 at.% Nb. The full curve is calculated with the Rayleigh relation (3) and the dots represent experimental data.

#### 4. Grain size effects in BaTiO<sub>3</sub>

The grain size effect on the dielectric properties of BaTiO<sub>3</sub> has been the subject of many studies in the past [13–16]. A high internal stress and large contribution from domain-wall vibrations have been proposed to explain the anomalously high dielectric permittivity in fine-grained ceramics. In this section, the Rayleigh analysis is used to estimate the contribution from the irreversible displacement of domain walls to the piezoelectric response in fine- and coarse-grained BT ceramics, and to obtain quantitative information on the dependence of this contribution on external d.c. pressure.

Figure 3 plots the relative  $d_{33}$  against  $\sigma_0$  for a coarse- and a fine-grained BT sample at  $\sim 1$  MPa external d.c. pressure. In the coarse-grained sample  $d_{33}$  increases linearly with  $\sigma_0$ , as expected from the Rayleigh law. The linear fit of the data gives  $d_{33}(\sigma_0) = 33.8 + 8.8\sigma_0$  pC N<sup>-1</sup>. The small  $d_{33}$  is due to a partial depoling of the sample by the external d.c. pressure [17]. The piezoelectric coefficient increases by 8.8 pC N<sup>-1</sup> (or more than 26% of the initial value) per 1 MPa due to the irreversible displacement of domain walls. The dependence of  $d_{33}$  on  $\sigma_0$  is much weaker and nonlinear in the fine-grained sample. The deviation from the Rayleigh behaviour in the fine-grained ceramic may be due to the fine domain-wall structure. In that case the coupling between moving domain walls and restoring forces due to stray fields cannot be neglected [8]. The weak increase of  $d_{33}$  against  $\sigma_0$  in the fine-grained ceramic indicates that the irreversible domain-wall displacement contributes much less to the piezoelectric response than in the coarse-grained ceramic. The different behaviour of fine- and coarse-grained ceramics is in agreement with the recent work of Arlt and Pertsev [15] who predicted that the force constant for vibrating domain walls is stiffer for thinner domains and that they are therefore more difficult to move.

The contribution of the irreversible displacement of domain walls to  $d_{33}$  in coarse-grained ceramics depends on the external d.c. pressure, as shown in figure 4. A deviation from the Rayleigh behaviour is observed for  $\sigma_0 < 0.3$  MPa at 2 MPa d.c. pressure, and for  $\sigma_0 < 0.6$  MPa at 3.6 MPa d.c. pressure. In the indicated low a.c. pressure region,

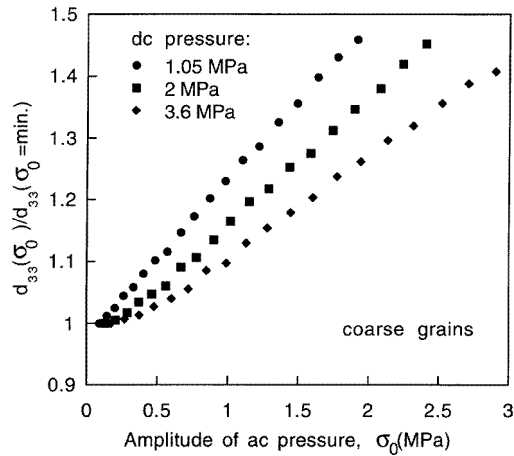


**Figure 3.** The relative direct  $d_{33}$  piezoelectric coefficient as a function of the amplitude of a.c. pressure for coarse- and fine-grained BaTiO<sub>3</sub> ceramics. The d.c. bias pressure is 1 MPa. The full line is the fit of the data with equation (1).

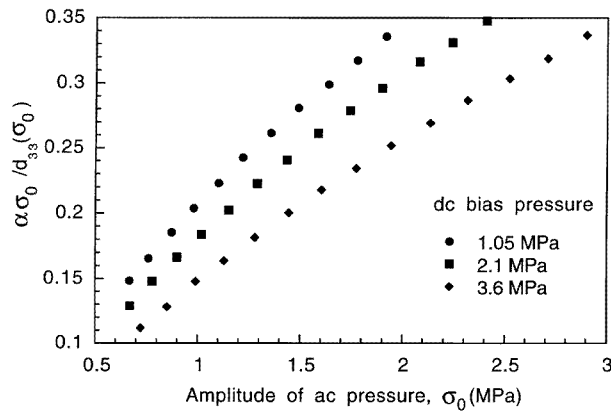
the slope of  $d_{33}$  against  $\sigma_0$  approaches zero as  $\sigma_0$  decreases, suggesting the existence of a threshold pressure [17–19]. Below the threshold pressure, the driving a.c. pressure is not sufficiently strong to move domain walls over potential barriers and, as a result, domain walls move only reversibly within potential wells. The increase in the d.c. pressure appears to increase the threshold pressure and reduces the contribution to  $d_{33}$  from the irreversible displacement of domain walls. Figure 5 plots  $\alpha\sigma_0/d_{33}(\sigma_0)$  against  $\sigma_0$  for the coarse-grained ceramic above the threshold pressure and at different d.c. pressures. For  $\sigma_0 = 2$  MPa, the fraction of the total piezoelectric coefficient that is due to the irreversible displacement of domain walls decreases from  $\sim 34\%$  at 1 MPa d.c. pressure to 25% at 3.6 MPa d.c. pressure. For fine-grained ceramics, the d.c. bias pressure has almost no effect on the pressure dependence of  $d_{33}$ , as shown in figure 6. Such behaviour is consistent with the presence of a strong internal stress in fine-grained ceramics, estimated to be  $\sim 70$  MPa by some earlier models [13, 16]. The origin of the internal stress in fine-grained BT ceramics is not well understood. It is possible, however, that the twinning in fine-grained materials is not as effective in reducing the internal stress produced by the phase transition as the twinning in coarse-grained ceramics. In analogy with the effect of the external d.c. pressure in coarse-grained ceramics, the internal stress in fine-grained ceramics appear to have a clamping effect on the irreversible displacement of domain walls. If the internal stress is much higher than the external d.c. pressure, the latter will have little effect on the piezoelectric response, as observed in figure 6.

## 5. Effects of crystal structure in PZT ceramics

Properties of PZT ceramics strongly depend on their composition. The highest piezoelectric coefficients are found near the morphotropic phase boundary (MPB) between tetragonal (Ti rich) and rhombohedral (Zr rich) phases. At room temperature, the composition of the boundary is approximately (53/47). In the region around the boundary, the free energies of rhombohedral and tetragonal phases are close to each other, the two phases coexist and there are effectively 14 possible directions of the spontaneous polarization vector. Both poling of the ceramics and mobility of domain walls are enhanced in compositions around the MPB,



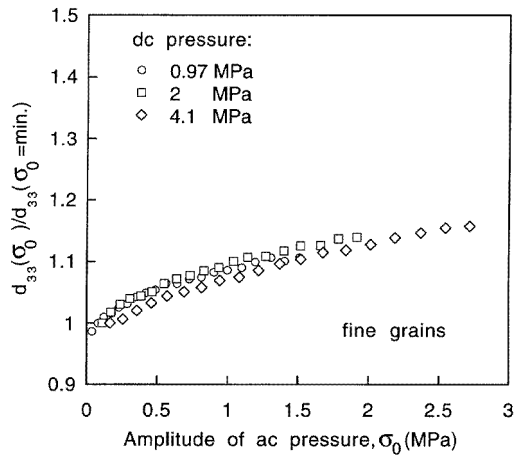
**Figure 4.** The relative direct  $d_{33}$  piezoelectric coefficient as a function of the amplitude of a.c. pressure for coarse-grained  $\text{BaTiO}_3$  ceramics. The d.c. bias pressure varies between  $\sim 1$  and  $\sim 3.6$  MPa. Compare with figure 6.



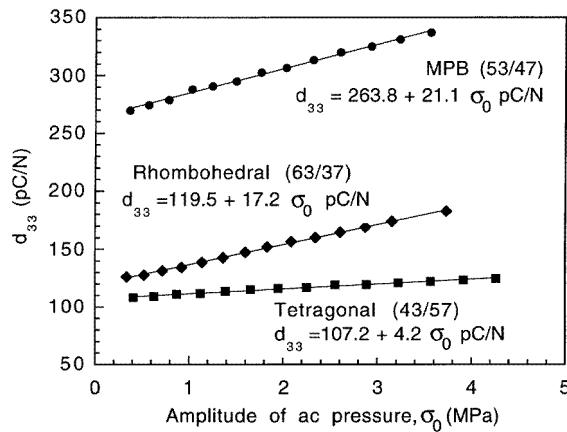
**Figure 5.** The calculated fraction of the total  $d_{33}$  that is due to the irreversible displacement of domain walls as a function of the amplitude of a.c. pressure, for the coarse-grained  $\text{BaTiO}_3$  ceramic, at different d.c. pressures. The data used for the calculation are shown in figure 4.

leading to a strong peak in the dielectric permittivity and piezoelectric coefficients [6]. In this section, we discuss effects of the crystal structure of PZT ceramics on the contribution to the direct piezoelectric effect from the irreversible displacement of domain walls.

Figure 7 shows  $d_{33}$  against  $\sigma_0$  dependence for three compositions of PZT doped with 4 at.% Nb: (i) rhombohedral PZT (63/37), (ii) PZT (53/47) near the MPB, and (iii) tetragonal PZT (43/57). X-ray diffraction patterns of the samples with composition (53/47) show a mixture of tetragonal and rhombohedral phases when samples are doped with Nb, whereas undoped samples are tetragonal. The Rayleigh relation (1) is valid for all three compositions in the pressure range shown. As expected, the Rayleigh parameter  $\alpha$  is largest in the composition close to the MPB ( $\alpha = 21.1 \text{ pC N}^{-1} \text{ MPa}^{-1}$ ). The rhombohedral composition exhibits a much higher  $\alpha$  coefficient than the tetragonal composition (rhombohedral,



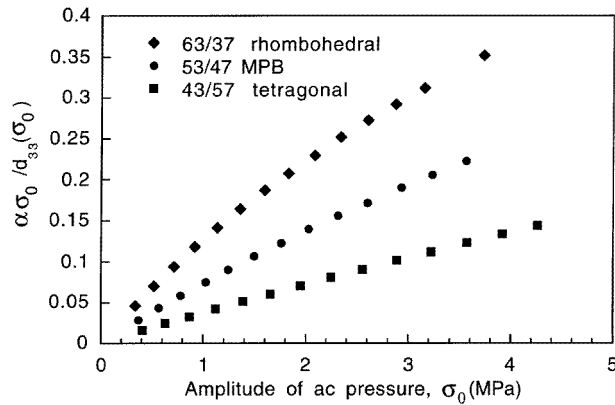
**Figure 6.** The relative direct  $d_{33}$  piezoelectric coefficient as a function of the amplitude of a.c. pressure for fine-grained BaTiO<sub>3</sub> ceramics. The d.c. bias pressure varies between ~1 and ~4 MPa. Compare with figure 4.



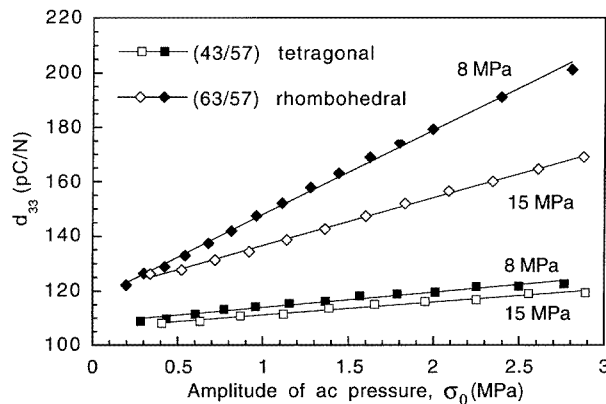
**Figure 7.** The direct  $d_{33}$  piezoelectric coefficient as a function of the amplitude of a.c. pressure for PZT (doped with 4 at.% Nb) ceramics with different crystal structure. The d.c. bias pressure is 15 MPa.

$\alpha = 17.2 \text{ pC N}^{-1} \text{ MPa}^{-1}$ ; tetragonal,  $\alpha = 4.2 \text{ pC N}^{-1} \text{ MPa}^{-1}$ ), even though they are equally distant from the MPB. The fraction of the piezoelectric response that is due to the irreversible displacement of domain walls is calculated and shown for the three compositions in figure 8. It is largest in the rhombohedral composition followed by the morphotropic and finally the tetragonal composition. For example, at 2 MPa a.c. pressure,  $\alpha\sigma_0/d_{33}(\sigma_0)$  is 22.4% for the rhombohedral, 13.8% for the morphotropic, and 7.3% for the tetragonal composition. Thus, even though for a given a.c. pressure the absolute contribution of the irreversible displacement of domain walls to  $d_{33}$  is largest in the MPB composition, this contribution relative to the total  $d_{33}$  is largest in the rhombohedral sample. One important practical implication of this result is that tetragonal or even MPB compositions are preferable to rhombohedral compositions for devices that require a high stability of the piezoelectric





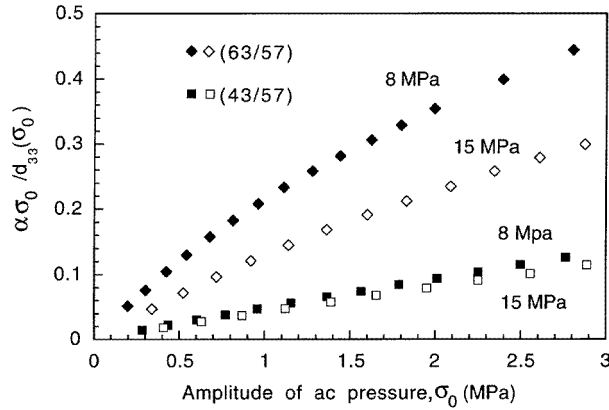
**Figure 8.** The calculated fraction of the total  $d_{33}$  that is due to the irreversible displacement of domain walls as a function of the amplitude of a.c. pressure, for the three PZT compositions shown in figure 7.



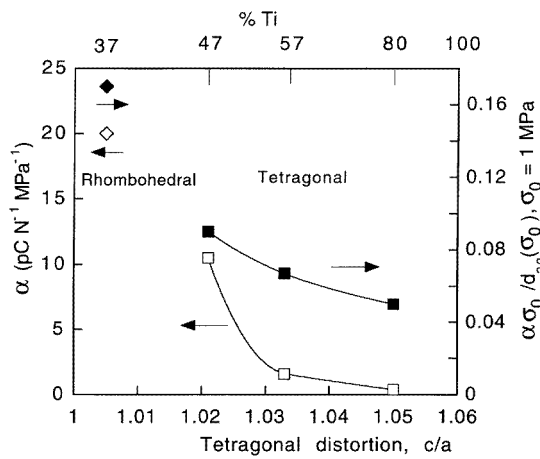
**Figure 9.** The direct  $d_{33}$  piezoelectric coefficient as a function of the amplitude of a.c. pressure for rhombohedral (63/57) and tetragonal (43/57) PZT ceramics doped with 4 at.% Nb, at 8 and 15 MPa d.c. pressure. The squares and diamonds represent the data points and the full lines are fits of the data with equation (1). Rhombohedral, 8 MPa:  $d_{33} = 116.9 + 31\sigma_0$ , 15 MPa:  $d_{33} = 119.1 + 17.5\sigma_0$ ; Tetragonal, 8 MPa:  $d_{33} = 108.3 + 5.6\sigma_0$ , 15 MPa:  $d_{33} = 106.5 + 4.7\sigma_0$ . Units of  $d_{33}$  are  $\text{pC N}^{-1}$ .

response. The same trend is observed in non-doped PZT samples. Present results suggest that the irreversible displacement of domain walls is less inhibited on the rhombohedral than on the tetragonal side of the MPB.

The effect of the external d.c. pressure on the piezoelectric response of tetragonal (43/57) and rhombohedral (63/57) PZT samples doped with 4 at.% Nb is shown in figure 9. In the rhombohedral sample,  $\alpha$  decreases by nearly 50% (from 31 to 17.5  $\text{pC N}^{-1} \text{MPa}^{-1}$ ) with a twofold increase in the external d.c. pressure (from 8 to 15 MPa). The external d.c. pressure has much less effect on the behaviour of the tetragonal ceramic, where  $\alpha$  decreases from 5.6  $\text{pC N}^{-1} \text{MPa}^{-1}$  at 8 MPa to 4.7  $\text{pC N}^{-1} \text{MPa}^{-1}$  at 15 MPa. Figure 10 plots the calculated fraction of  $d_{33}$  that is due to the irreversible displacement of domain walls as a function of  $\sigma_0$ , for the two samples shown in figure 9. These results may be interpreted



**Figure 10.** The calculated fraction of the total  $d_{33}$  that is due to the irreversible displacement of domain walls as a function of the amplitude of a.c. pressure, at 8 and 15 MPa d.c. pressure, for the two PZT compositions shown in figure 9.



**Figure 11.** The Rayleigh parameter  $\alpha$  (open squares) and the fraction of the total  $d_{33}$  which is due to the irreversible displacement of domain walls (full squares), as a function of  $c/a$  ratio for tetragonal undoped PZT. The values for the rhombohedral (63/37) undoped PZT sample (open and full diamonds) are shown only for a comparison. To plot the data for the rhombohedral composition, the equivalent  $c/a$  ratio (1.005) was chosen to give the equivalent tetragonal strain equal to the actual rhombohedral strain ( $\sim 0.5\%$ ) for this composition. The composition (53/47) is at the MPB but has tetragonal structure, as verified by x-ray diffraction.

by considering the fact that the spontaneous strain associated with the tetragonal distortion is much larger than the spontaneous strain associated with the rhombohedral distortion, and by assuming that the external d.c. pressure has a clamping effect on the irreversible displacement of ferroelectric–ferroelastic domain walls. The rhombohedral strain, given by  $[(90^\circ - \beta)/90^\circ]$ , where  $\beta$  is the angle of the rhombohedral unit cell [20], is less than 0.5% at the MPB and remains nearly constant with increasing Zr ratio [6]. The tetragonal strain, given by  $[(c - a)/a]$ , where  $c$  and  $a$  are the axes of the tetragonal unit cell, is greater than 2% at the MPB and increases with increasing Ti concentration up to more than 6% for

pure  $\text{PbTiO}_3$  [6]. The  $90^\circ$  domain walls in tetragonal PZT ceramics are likely to be already partly clamped by local internal stresses which originate in the high tetragonal distortion. On the other hand, the  $109^\circ$  and  $71^\circ$  rhombohedral domain walls are relatively free to move because internal stresses that are due to the structural distortion are significantly smaller in rhombohedral compositions. As a consequence, the external d.c. pressure has a weak effect on the domain-wall contribution to the piezoelectric response in tetragonal compositions and a strong effect in rhombohedral compositions.

If the local stresses that are due to the spontaneous strain have a clamping effect on the irreversible displacement of domain walls, the contribution to  $d_{33}$  from the irreversible displacement of domain walls should decrease with an increase in the Ti concentration. This is indeed observed. Figure 11 shows the Rayleigh parameter  $\alpha$  and  $\alpha\sigma_0/d_{33}(\sigma_0)$  at  $\sigma_0 = 1$  MPa for tetragonal (20/80), (43/57), and (57/43) undoped PZT as a function of  $c/a$  ratio. The lattice parameters were determined from the X-ray diffraction patterns of the samples. Both  $\alpha$  and the fraction of  $d_{33}$  that is due to the irreversible displacement of  $90^\circ$  domain walls decrease with the increase in tetragonal distortion.

## 6. Conclusions

The contribution to the longitudinal direct piezoelectric  $d_{33}$  coefficient from the irreversible displacement of domain walls has been analysed in barium titanate and lead zirconate titanate ceramics by using Rayleigh relations. This domain-wall contribution is strongly dependent on the microstructure and crystal structure of the examined ceramics. The study shows that the  $\text{PbTiO}_3$ -rich PZT and fine-grained BT ceramics behave similarly: (i) the contribution from the irreversible displacement of domain walls is small (with respect to coarse-grained BT and the MPB and  $\text{PbZrO}_3$ -rich PZT ceramics), and (ii) the piezoelectric coefficient shows a weak dependence on the external d.c. pressure. In both cases, the behaviour is consistent with the presence of internal stresses in the ceramics which have a clamping effect on the irreversible displacement of domain walls. The internal stress in the tetragonal PZT ceramics originates from the high spontaneous strain. The existence of the internal stress in fine-grained BT ceramics has been proposed before [13–16], but its origin is not clear. The domain-wall contribution to  $d_{33}$  is found to be significantly larger in coarse-grained BT ceramics, in PZT ceramics rich with  $\text{PbZrO}_3$  and in PZT compositions in the vicinity of the MPB that contain a mixture of rhombohedral and tetragonal phases. An interesting observation is that the fraction of  $d_{33}$  due to the irreversible displacement of domain walls is larger in the rhombohedral (63/37) composition than in the (53/47) composition near the MPB.

## Acknowledgment

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