Effect of electrical and mechanical poling history on domain orientation and piezoelectric properties of soft and hard PZT ceramics

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Effect of electrical and mechanical poling history on domain orientation and piezoelectric properties of soft and hard PZT ceramics

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Abstract

The superior piezoelectric properties of all polycrystalline ferroelectrics are based on the extent of non-180° domain wall motion under electrical and mechanical poling loads. To distinguish between 180° and non-180° domain wall motion in a soft-doped and a hard-doped lead zirconate titanate (PZT) ceramic, domain texture measurements were performed using x-ray and neutron diffraction after different loading procedures. Comparing the results to measurements of the remanent strain and piezoelectric coefficient allowed the differentiation between different microstructural contributions to the macroscopic parameters. Both types of ceramic showed similar behavior under electric field, but the hard-doped material was more susceptible to mechanical load. A considerable fraction of the piezoelectric coefficient originated from poling by the preferred orientation of 180° domains.

Keywords: ferroelectrics, doped PZT ceramics, x-ray diffraction, neutron diffraction, domain wall orientation

1. Introduction

The piezoelectric performance of ferroelectric devices is believed to depend strongly on the poling state of the material [1], which includes the preferred orientation of the ferroelectric and ferroelastic domains. Electric field and mechanical stress are known to affect the poling state through ferroelectric and ferroelastic domain reorientation, respectively. If present in the material, both 180° and non-180° domain walls are moved by electric field, whereas a compressive stress is a driving force for the motion of non-180° domain walls only.

Domain wall motion in single crystals has been well investigated for over 50 years. In principle, a perfect domain orientation can be achieved in a single crystal by applying a sufficient electric field at an adequate temperature; in such a case, all ferroelectric dipoles become oriented in the same direction [2]. In contrast, polycrystalline ceramics show a more complex switching behavior due to internal microstructural constraints, e.g. from the various grain orientations [3]. Hence they exhibit a maximum or saturated domain orientation state that is significantly weaker than that observed in single crystals. In general, the domain orientation state is created by orientation-dependent interactions of external loadings with a large number of material-dependent structural defects. Obviously those interactions can be different for mechanical and electrical loading, and additionally the achieved domain texture depends not only on the extent of external loading but also on the electromechanical loading history. As a result, the switching behavior of ferroelectric ceramics under multiaxial electromechanical loading is challenging to predict and this
problem has received much attention in recent years through modeling approaches [4–9] and experimental studies [10–18]. A reduction in the ferroelectric behavior is observed for a constant uniaxial stress applied parallel to the electric field direction [11, 17]. In the same manner a constant electric field acting in the direction of the applied stress reduces the ferroelectric reorientation [12]. If both electrical and mechanical loadings are combined then the phase between the two loading types becomes important. In-phase loading suppresses ferroelectric response, while out-of-phase loading enhances the ferroelectric response [13]. A constant uniaxial stress perpendicular to the field direction creates almost no changes in the ferroelectric response in the field direction but perpendicular to it [14]. This is different for radial mechanical loading perpendicular to the electric field where an enhanced poling behavior is observed [15]. The ferroelastic behavior of initially poled samples shows also a strong dependence on the angle between the initial poled direction and the applied stress [16, 18].

A powerful approach to measure non-180° domain texture distributions is provided by x-ray and neutron diffraction [19–21]. The domain orientation distribution function, \( f_{002}(\Psi) \), can be used to describe the domain orientation state in a ferroelectric material. For any given direction at an angle \( \Psi \) to the poling direction, the volume fraction of domains whose tetragonal \( c \)-axes are aligned with this particular direction is given by:

\[
 f_{002}(\Psi) = \frac{(I_{002}/I_{000})}{(I_{002}/I_{000}) + 2(I_{200}/I_{200})},
\]

where the value of \( f_{002} \) is given in the unit multiples of a random distribution (mrd). \( I_{002} \) and \( I_{200} \) are the integrated areas of the split peak belonging to the crystallographic [002] and [200] directions, respectively, where [200] includes both [020] and [200] which are indistinguishable. \( I_{002} \) and \( I_{200} \) are the integrated peak areas of an unpoled, randomly oriented sample. A fully oriented sample would exhibit a domain orientation distribution function that decreases from \( f_{002}(\Psi = 0°) = 3 \) mrd to \( f_{002}(\Psi = 90°) = 0 \) mrd and an unpoled material would show \( f_{002}(\Psi) = 1 \) mrd for all angles [21].

In the present work, nine different electromechanical poling procedures on a hard and a soft-doped lead zirconate titanate (PZT) ceramic were carried out, and the samples were investigated by texture measurements using x-ray and neutron diffraction. Such measurements provide a better understanding of ferroelectric as well as ferroelastic domain switching and a base for new modeling approaches.

2. Experimental procedures

The investigated samples of the two commercial-grade PZT ceramics PIC 151 (\( Pb_{0.99}(Zr_{0.45}Ti_{0.47})(Sn_{0.67}Ni_{0.33}O_{1.08})O_{3} \)) and PIC 181 (\( Pb_{0.99}(Zr_{0.47}Ti_{0.53})(Mn_{0.33}Sn_{0.33}Ni_{0.33}O_{1.05})O_{3} \)) (PI Ceramics, Lederhose, Germany) had a cylindrical shape with a diameter of 5.9 mm and a height of 6 mm. One circular surface was polished to a 1 \( \mu \)m finish for the x-ray diffraction (XRD) measurements.

The composition of both materials lies in the vicinity of the morphotropic phase boundary on the tetragonal side. In ferroelectric hysteresis measurements, PIC 151 shows the typical characteristics of a soft-doped PZT ceramic with a coercive field of 1.0 kV mm\(^{-1} \) [22], while PIC 181 behaves hard-doped with a coercive field of 1.8 kV mm\(^{-1} \) [23]. Considering ferroelastic domain switching in response to mechanical stress, the terms hard and soft are misleading: as expected, the hard-doped material has a significantly larger coercive stress of 168 MPa compared to 56 MPa for the soft-doped material. However, as the mechanical load exceeds a threshold level of 200 MPa, the hardening effect of the doping vanishes; hard and soft materials behave identically and show the same compliance [23].

Samples of each composition were prepared using nine different poling procedures (table 1). Before poling, all samples were annealed at 450 °C for 30 min to eliminate mechanical effects caused by drilling, grinding and lapping. One sample of each material was reserved as an unpoled reference. Gold-palladium electrodes approximately 50 nm thick were sputtered on the circular surfaces. The electric field as well as the mechanical compression was always applied parallel to the cylindrical axis, in the following referred to as poling axis (see figure 1).

Electrical poling was achieved by the so-called field-cooling method; the samples A, D and E were heated up to 150 °C in a silicon oil bath and loaded with an electric field of 2.0 and 3.0 kV mm\(^{-1} \) for PIC 151 and PIC 181, respectively. The oil was cooled while the electric field remained applied. The field was then turned off and the sample was taken out at 45 °C. Procedures B, C and F to I were carried out on initially unpoled samples. To mechanically compress the material, a uniaxial 10 kN screw-type load frame (Z010, Zwick, Ulm, Germany) was used at room temperature. The sample was either short circuited or exposed to an electric voltage (procedures F to I), while the compressive stress was applied. The force loading rate was 100 N s\(^{-1} \). One half of the procedures (B, D, F, H) involve loading to 385 MPa, a stress at which most of the ferroelastic domain switching is exhausted [23, 24]. It has been demonstrated that the percentage of domain backswitching in the stress range of 385 MPa is insignificant and comparable for the hard and the soft materials. The
other procedures (C, E, G, I) involve compression up to 56 and 168 MPa for PIC 151 and PIC 181, respectively, corresponding to the coercive stress of those materials where the percentage of backswitching reaches a maximum. For poling procedures B to E on unpoled (B, C) as well as on poled (D, E) samples, the stress was reduced as soon as the desired compressive stress was reached, leading to a triangular waveform for the stress application over time. It can be assumed for at least samples B and D that there is no influence of an increase in holding time due to ageing effects. The soft-doped material does not show any ageing behavior. After a compression of 385 MPa only an insignificant amount of backswitching can be observed. And, as mentioned before, the hard-doped material has the same characteristics as the soft-doped material above a compressive stress of 200 MPa.

Procedures F to I involve loading electrically and mechanically. For procedures F and G the compressive stress was applied first and for H and I the electric field was applied first (see figure 2). For this the electric voltage was ramped up at a rate of 100 V s⁻¹ until an electric field of 2.0 or 3.0 kV mm⁻¹ for the two different materials was reached and removed at the same rate. After the stress was applied in procedures F and G it was held constant for 60 s before the sample was loaded electrically. The electric field was kept constant for 10 s and removed completely before the compressive stress was released. In procedures H and I, the electric field was held for 10 s before the mechanical stress with triangular waveform was applied.

The piezoelectric coefficient $d_{33}$ was measured for each sample using a commercial Berlincourt meter with an accuracy of ±5 pC N⁻¹ (Sinocera, YE2730). The results are listed in table 1.

Neutron diffraction measurements were carried out on all samples to measure the domain orientation texture of the bulk material. These measurements were completed using the WOMBAT instrument on the OPAL reactor at the Australian Nuclear Science and Technology Organisation. The WOMBAT instrument was set to a take-off angle of 120° and a (113)-Ge-monochromator was used to select a

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### Table 1. Overview over the nine different electromechanical poling procedures (A to I) and the resulting piezoelectric coefficient $d_{33}$ for PIC 151 and 181 materials. When values are different for PIC 151 and 181 materials, the values for PIC 151 are listed first and the values for PIC 181 are listed second in brackets.

<table>
<thead>
<tr>
<th>Poling procedure for both materials</th>
<th>PIC 151</th>
<th>PIC 181</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$d_{33}$ (pC N⁻¹)</td>
<td>% of sample from procedure (A)</td>
</tr>
<tr>
<td>-------------------------------------</td>
<td>-----------</td>
<td>-----------------</td>
</tr>
<tr>
<td>A Poled (field-cooled at 2 [3] kV mm⁻¹ from 150 to 45 °C)</td>
<td>511</td>
<td>100.0</td>
</tr>
<tr>
<td>B Compressed to 385 MPa (100 N s⁻¹, triangle)</td>
<td>0</td>
<td>0.0</td>
</tr>
<tr>
<td>C Compressed to 56 [168] MPa (100 N s⁻¹, triangle)</td>
<td>0</td>
<td>0.0</td>
</tr>
<tr>
<td>D Poled (field-cooled from 150 to 45 °C) and compressed to 385 MPa afterwards</td>
<td>121</td>
<td>23.7</td>
</tr>
<tr>
<td>E Poled (field-cooled from 150 to 45 °C) and compressed to 56 [168] MPa afterwards</td>
<td>517</td>
<td>101.2</td>
</tr>
<tr>
<td>F Compressed to 385 MPa, held for 60 s, loaded to 2 [3] kV mm⁻¹ (100 V s⁻¹), held for 10 s, field removed, load removed</td>
<td>20</td>
<td>3.9</td>
</tr>
<tr>
<td>G Compressed to 56 [168] MPa, held for 60 s, loaded to 2 [3] kV mm⁻¹ (100 V s⁻¹), held for 10 s, field removed, load removed</td>
<td>370</td>
<td>72.4</td>
</tr>
<tr>
<td>H Loaded to 2 [3] kV mm⁻¹ held for 10 s, compressed to 385 MPa (triangle), field removed</td>
<td>511</td>
<td>100.0</td>
</tr>
<tr>
<td>I Loaded to 2 [3] kV mm⁻¹ held for 10 s, compressed to 56 [168] MPa (triangle), field removed</td>
<td>498</td>
<td>97.5</td>
</tr>
</tbody>
</table>

---

Figure 2. Loading sequences for the hard-doped material when the samples were loaded electrically and mechanically at the same time. For states F and G the compressive stress and for states H and I the electric field was applied first.
wavelength of $\lambda = 2.95 \text{ Å}$. A continuous bank of detectors spanned a $2\theta$ range of 160°. While the sample was immersed in the neutron beam, it was rotated with its cylindrical axis in the scattering plane to vary the angle $\Psi$ between the scattering vector and the poling direction from 0° to 180° in 10° steps. Figure 3 shows the split peak belonging to the crystallographic [002] and [200] directions of a fully poled sample (procedure A). A strong texture is visible indicated by the significant change in intensities with the angle $\Psi$. Parallel to the poling direction ($\Psi = 0°$ and $\Psi = 180°$), the intensity of the 002 peak is approximately equal to the intensity of the 200 peak while a smaller intensity of the 002 peak is observed perpendicular to the poling direction ($\Psi = 90°$).

To determine the domain texture distribution on the surface of the different PIC 181 samples, XRD measurements were performed with a lab diffractometer (X’Pert, Panalytical) where the incident beam consisted of Cu-K$_\alpha$ radiation with $\lambda = 1.542 \text{ Å}$. The X’Pert software controlled the sample stage position and the proportional point detector allowing $2\theta$ measurements for different sample orientations and scattering angles of interest. The angle $\Psi$ between the scattering vector and the poling direction was varied between 0° and 60° in 10° steps by tilting the sample axis perpendicular to the scattering plane. The measurement was taken on the polished circular surface.

3. Results

In figure 4(left) the domain orientation distribution function $f_{002}(\Psi)$ of the soft-doped material (PIC 151) is plotted for the fully poled state (A) as well as for all samples compressed up to 385 MPa (B, D, H). For clarity, $f_{002}(\Psi)$ is not plotted for sample F (exposed to a field while the stress was still applied) because it shows the same texture as samples B and D. Through the field-cooled poling, a maximum domain texture distribution of a polycrystalline PZT ceramic is reached. The texture created solely by mechanical compression (procedure B) and the texture of a fully electrically poled sample (procedure A) are of similar strengths but opposite sense: the fiber axis of the texture is the same in both cases and procedure A (B) results in an increased (decreased) intensity of the 002 poles in this direction and a decreased (increased) intensity perpendicular to this direction. In the following, the state A with $d_{33} = 511 \text{ pCN}^{-1}$ is used as a reference. Interestingly, the sample obtained from procedure H (where a compressive stress was applied during the poling process) possesses an equivalent $d_{33}$ value as procedure A although the texture is much less pronounced. The opposite effect can be observed for a solely compressed sample (procedure B) and a poled compressed sample (procedure D): they show no difference in texture although the latter has a nonzero $d_{33}$. The presented domain orientation distributions $f_{002}(\Psi)$ from neutron diffraction analysis (procedures A and D in figure 4(left)) were compared with previously published XRD measurements on PIC 151 samples [24] and these measurements are in good agreement. This agreement suggests that the same behavior can be observed in bulk material and close to the surface.

Figure 4(right) shows the domain orientation distribution calculated from the neutron diffraction measurements for those PIC 151 samples loaded up to the 56 MPa (C, E, G) and for the reference state A again. The domain orientation distribution $f_{002}(\Psi)$ for sample I is the same as for sample E and therefore it is not plotted. The texture of the solely compressed sample C is reduced by $\sim 2/3$ compared to sample B which is in good agreement with the reduction in remanent strain values from 3.0% to 1.4% obtained from [23]. The texture of sample E (a fully poled sample which is compressed up to the coercive stress after poling) looks equivalent to state H and I and all three states also exhibit similar $d_{33}$ values. Accordingly, the effect of a compressive stress of 56 MPa (figure 4(right)) or 385 MPa (figure 4(left)) during the application of the electric field on the domain texture is similar. Surprisingly, the texture created by the compaction in the sample that was exposed to a field during the application of a mechanical stress (procedure G) is more pronounced than without field (procedure C).

A partially different behavior can be observed for the hard-doped material PIC 181 (see figure 5). The field-cooled poled sample (procedure A) of the hard-doped material shows a saturated domain texture that is comparable with the fully poled soft-doped material texture (A in figure 4), although the piezoelectric coefficient for the hard material ($d_{33} = 268 \text{ pCN}^{-1}$) is significantly lower than that of the soft material ($d_{33} = 511 \text{ pCN}^{-1}$). In contrast, the texture that is achieved by a compression of 385 MPa (procedure B) is less pronounced compared to the same stress applied to PIC 151 (B in figure 4(left)), indicating that the stress cannot overcome the domain stabilization due to the hardening effects of the dopants. A solely compressive stress of 168 MPa leads to nearly no texture at all in an unpoled PIC 181 sample (procedure C). This is in good agreement with remanent strain measurements showing a small remanent strain and a large amount of backswitching for this poling procedure [23]. The impact of an electric field acting during the application of the coercive stress (procedure G) on the texture, as it can be seen in the soft material, is also present in the hard material. Furthermore in PIC 181 the texture created by a compressive...
stress of 385 MPa is also amplified by the application of an electric field during compression (procedure F). A similar effect is observed if a poled sample is compressed up to 385 MPa (procedure D) in comparison with an unpoled sample (procedure B). As in the soft material, states D and F (not plotted in figure 4(right) for clarity, but exhibit similar values to procedure D) exhibit the same texture although the $d_{33}$ value differs. In contrast to the soft-doped material, where procedure E leads to a reduced texture compared to procedure A, the hard-doped, poled sample which was compressed up to the coercive load (procedure E) shows a nearly saturated poled texture. Considering the facts that procedure E leads to a similar texture as procedure A and the texture created by procedure C shows little difference to the texture of an unpoled sample, the application of a stress equal to the coercive stress seems not sufficient to affect the domain orientation in the hard-doped material. The results for poling procedures H and I are not plotted because their texture looks like the partially compression texture of states B and C, respectively. While in PIC 151 the electric field was sufficient to pole the material even if mechanical compression is applied during the poling process, no poling can be achieved in PIC 181 at room temperature during application of mechanical compression.

In addition, a surprising result is found by the surface sensitive x-ray measurements (see figure 6). While the domain texture distribution in the soft material can be observed to the same degree using x-ray and neutron diffraction techniques, only sample A in PIC 181 shows a similar texture in bulk material and at the surface. For procedures B and D, no difference in texture can be observed with x-ray diffraction relative to the unpoled reference state.

4. Discussion

The change in the domain orientation texture of a sample represents the motion of non-180° domain walls. In the soft-doped material, procedures A (solely electrical poling)
and B (solely mechanical compression) result in similar texture strengths (albeit of opposite sense). Therefore, it is apparent that similar amounts of non-180° domain wall motion are accessible for the electrical and mechanical loading procedures, although different forms of domain wall interaction are present. This contradicts measurements of the remanent strain in PIC 151, which is also related to non-180° switching; procedure B results in a remanent strain of 0.3%, whereas procedure A results in a remanent strain of 0.16% (table 2). The hard-doped sample (PIC 181, figure 5), on the other hand, exhibited much stronger texture strengths in procedure A (solely electrical poling) than procedure B (solely mechanical compression), with A being of similar value to that observed in the soft-doped material (PIC 151, figure 4). After electrical loading (procedure A), the remanent strain in the hard-doped material is 0.19%; this strain is 20% larger than the remanent strain observed in a soft-doped material under the same type of loading. This difference in the remanent strain for the different materials is obviously no result of a different texture, but it can be explained considering the spontaneous strain of a unit cell without any external loading that is calculated from XRD measurements (table 2). The spontaneous strain of the unit cell is defined by the following equation:

$$\varepsilon_0 = \frac{c - a_0}{a_0} = \frac{2(c - a)}{c + 2a},$$

where $a$ and $c$ are the lattice parameters of the ferroelectric state and $a_0$ is the lattice parameter of the paraelectric state. This spontaneous strain is 1.02% for the soft-doped and 1.26% for the hard-doped material; the ratio of spontaneous strains (124%) is similar to the remanent strain ratio after electrical poling (120%). Something unexpected is observed for the difference in the remanent strain values of the two materials after the mechanical loading (procedure B); the hard-doped material shows a remanent strain that is 25% larger than the remanent strain of the soft-doped material (table 2). Without texture measurements, this result might imply that, similar to the electric case, both materials show the same texture. However, the mechanical compression results in different textures for both materials. This can be explained considering the origin of the remanent strain values; they depend at least on the domain orientation and spontaneous strain or the deformation of the unit cell. In earlier work, it has been shown that the unit cell can be strongly deformed by the external load [25, 26]. Thus the difference between the texture and the remanent strain measurements might be attributed to the different deformation of the unit cell.

Another interesting result is the same texture in samples B and D and in an unpoled reference for the surface sensitive XRD measurements. This means during the field-cooled poling the surface area is poled, but high internal mechanical and electric fields may be introduced recreating the random domain orientation when the mechanical stress is applied. However, the stress without any field is not sufficient to align surface domains perpendicular to the poling direction.

It was shown that procedure B (solely mechanical compression) leads to a maximum realizable (i.e. saturated) compression texture in the soft-doped material (figure 4(left)). Procedure G (electric field applied during compression using a stress equal to the coercive stress) results in a stronger texture than a sample solely compressed using the same stress (C). This is counter-intuitive because the electric field is applied parallel to the stress axis; thus, it could be thought that the electric field by itself might counteract the mechanical compression. However, the opposite effect is measured: application of an electric field parallel to the stress axis increases the resulting compression texture. This can be explained by an increase in the amount of ferroelastic domain walls and a higher domain wall mobility leading to a more oriented state that is possible by changing the internal defect or 180° domain wall structure. In PIC 181 the impact of the electric field on the compression texture for compressive stresses in the range of the coercive stress (compare G and C) is present as well.

A different behavior can be observed under the maximum applied compressive stresses of 385 MPa. In PIC 151 procedures F and B lead to the same texture while in PIC 181 a stronger compression texture can be found for procedure F. Thus in PIC 181 the mechanism discussed above seems also valid for a compressive stress of 385 MPa. This
indicates that the compression texture of state B is already a saturated texture in PIC 151, while for PIC 181 the saturated compression texture cannot be reached by a solely mechanical compression. Also in PIC 181 procedure D shows, similar to procedure F, a more distinctive compression texture than procedure B. This might be caused as well by the combination of electric and mechanical loading, although the electric field acts not during the stress application in this poling procedure but before.

The piezoelectric coefficient of a sample depends on many factors, primarily the dielectric and electromechanical behavior of the crystal structure itself. If comparing different poling states of the same material, this factor does not take effect. Instead, dominant factors are the domain wall mobility, the domain wall density and the degree of the poling which is defined as both the 180° and non-180° domain texture distributions [27, 28]. Considering the fact that the hard and the soft-doped materials show the same domain texture distribution in the fully poled state (A) but the hard-doped material has the significantly lower piezoelectric coefficient \(d_{33} = 268 \text{ pC N}^{-1}\) for PIC 181; \(d_{33} = 511 \text{ pC N}^{-1}\) for PIC 151), the dopant-created defects in the hard material likely influence the domain wall mobility, density, or the 180° domain wall motion. However, the amount of non-180° domain wall motion under an electric field is similar for both materials.

Some poling procedures result in similar textures but different \(d_{33}\) values within the same material, for example as observed in the soft PIC 151 material for poling procedures B, D and F. In contrast, an opposite effect is observed for other samples, i.e. similar \(d_{33}\) values but differing textures. For example, samples A, H and E of the soft PIC 151 material exhibit \(d_{33}\) values of 511, 517 and 511 pC N\(^{-1}\), respectively, even though they have markedly different textures (figure 4). These results demonstrate that a mechanical load can be applied during or after the electric poling process which produces a less pronounced texture but similar \(d_{33}\) value. They also reveal that the extent of non-180° domain wall motion is not directly related to the resulting \(d_{33}\) value. This behavior could be explained if a significant amount of the piezoelectric coefficient originates from 180° domain wall motion that occurs during electrical poling. On the other hand, the additional factors that strongly influence the piezoelectric coefficient might be different for the different poling procedures, e.g. the domain wall mobility, density and the amount of domains accessible for ferroelectric and ferroelastic switching.

A more complex external loading, such as a combined electric and mechanical loading, could also lead to a more complex domain structure with an increased amount of domains accessible for switching. This also could explain the large piezoelectric coefficient for procedures H and E which both include combined loading. Such an explanation is supported by the comparison of procedures B, D and F of the soft material. The textures of the solely compressed (B) and the combined electrical/mechanical loading procedure (D) of the soft PIC 151 material show no difference although the latter has a nonzero \(d_{33}\). This can be explained by different domain wall configuration leading to different domain wall mobilities and densities. However, procedure F (exposed to an additional electric field while the compressive stress was applied) also includes combined loading and there is no explanation for the large difference in \(d_{33}\) between samples D \((d_{33} = 121 \text{ pC N}^{-1})\) and F \((d_{33} = 20 \text{ pC N}^{-1})\) of the soft material.

On the other hand, after the compression all non-180° domains that are able to reorient are oriented perpendicular to the poling direction because samples B and D show the saturated compression domain texture. Those domains cannot account for the \(d_{33}\) value that reaches nevertheless 23.7% of the \(d_{33}\) of a fully poled sample. Hence at least 23.7% of the piezoelectric response of sample A could originate from a domain texture of the 180° domains during the poling process, which is not measured in the present experiment. Considering now the similar saturated texture of samples D and F, whether the electric field is applied before or during the mechanical loading makes no difference on the degree of non-180° switching. In contrast, the low \(d_{33}\) value of sample F indicates that there exists a difference for 180° switching. During the application of a solely electric field, 180° switching took place and is not cancelled by the later application of a stress, because the compressive stress is not coupled to 180° domain wall movement. But if the compressive stress is present the entire time during electric field application, 180° domain switching can be mostly suppressed. This supports a domain reorientation process where most of the 180° reorientation is accomplished through two successive non-180° reorientations. It is possible to estimate the amount of direct 180° reorientations from the \(d_{33}\) values of the samples D and F, 23.7 and 3.9%, respectively: in procedure D the piezoelectric coefficient of 23.7% results predominantly from 180° domain switching processes; 17% (3.9% out of 23.7%) of those 180° domain processes occur also in sample F where 180° domain switching via two successive non-180° domain switching processes is suppressed. The remaining 17% of 180° domains may switch via 180° domain wall motion. This portion of 17% is in good agreement with former publications [19]. The same calculation for the hard-doped material leads to 51.5% of the piezoelectric response originating from 180° domain wall movement \((d_{33} = 138 \text{ pC N}^{-1}\) for procedure D and material PIC 181) and only 4% of the 180° domain wall motion (1.9% out of 51.5%) being accomplished directly. Although the electric field in poling procedures H and I was not sufficient to pole the hard-doped material, 180° domain switching leads to a nonzero \(d_{33}\) value lying in between the piezoelectric coefficient of states D and F because the two successive non-180° switches are partially suppressed.

5. Conclusions

Domain orientation texture measurements based on neutron and x-ray diffraction were carried out on nine different electromechanical poling states and analyzed with regard to the piezoelectric coefficient and the remanent strain. The first salient result shows up in the comparison between the soft
and the hard-doped material as a discrepancy between the domain texture and the remanent strain. A similar discrepancy arises in the comparison of an electrically poled and a solely mechanically compressed soft-doped sample and is attributed to the difference in the deformation of a unit cell.

Besides, in the case of the hard-doped PZT ceramic, the domain textures differ in the bulk material and close to the surface. This indicates that the domain configuration stabilization effects caused by structural defects are not acting uniformly but are stronger close to the surface.

If two different samples show the same piezoelectric coefficient this does not imply that they exhibit the same domain texture—a significant part of the piezoelectric response seems to originate from \(180^\circ\) domain switching which is not detectable in the texture measurements. Likewise a matching texture profile does not allow the conclusion that the piezoelectric coefficient matches, because a mechanical stress can influence \(180^\circ\) switching if this is accomplished by two successive non-\(180^\circ\) switches. Here only 17% and 4% of the \(180^\circ\) switches in the soft and hard-doped material, respectively, take directly place.

Another important result is the observation that a combined electromechanical load increases the amount of switchable domains. Accordingly the electric field amplifies the compression domain texture distribution if the mechanical stress is not sufficient to create a saturated domain texture.

Acknowledgments

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