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Analysis of intrinsic lattice deformation in PZT-ceramics of different compositions

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Abstract

High resolution synchrotron X-ray diffraction was used to investigate extrinsic (domain switching) and intrinsic (lattice deformation) contributions to the total strain induced by external electric field in soft lead zirconate titanate (PZT) ceramics. Evidence was presented for both 180° and non-180° domain switching. The direction dependence of the lattice deformation was examined. It was found that in rhombohedral PZT, the highest lattice strain occurs in [100] direction, and for tetragonal PZT, the highest lattice strain occurs in [101] direction. Finally it was found, that the lattice strain gives a higher contribution to the total strain for rhombohedral PZT than for tetragonal PZT. © 2001 Elsevier Science Ltd. All rights reserved.

Keywords: Domain switching (−); Ferroelectric properties; PZT; X-ray methods

1. Introduction

Two types of contributions to dielectric and piezoelectric properties of ferroelectric ceramics, such as lead zirconate titanate, $Pb(Zr_xTi_{1-x})O_3$, (PZT), are usually distinguished.[1–5] One type is called an intrinsic contribution, and it is due to the distortion of the crystal lattice under an applied electric field or a mechanical stress. The second type is called an extrinsic contribution, and it results from the motion of domain walls or domain switching.[1] To provide understanding of material properties of PZT, several methods to separate the intrinsic and extrinsic contributions were proposed. These methods are indirect, and are based on measurements of the dielectric and piezoelectric properties of ferroelectric ceramics.[1,3–5]

In the experiments reported in this paper a different approach is adopted, which is based on measurements of high-resolution synchrotron X-ray powder diffraction. The shift in the positions of diffraction peaks under applied electric field gives the intrinsic lattice deformation, whereas from the change in peak intensities the domain switching can be calculated.[6] Thus, the intrinsic and extrinsic contributions can be measured directly using this method. In the present study, the high-resolution XRD was applied to study two compositions of PZT with rhombohedral and tetragonal modifications of the ferroelectric phase. The direction dependence of the lattice deformation was measured and subsequently compared with results of theoretical calculations by Du et al.[7]

2. Experimental

The studied samples were commercially available soft PZT ceramics ("CeramTec", Germany). Two compositions were investigated which correspond to tetragonal ($x = 0.51$) and rhombohedral ($x = 0.56$) modifications of the ferroelectric phase. The samples were discs with 12–15 mm diameter and 0.6–1 mm thickness. After polishing, they were annealed for 4 h at 500°C in order to remove mechanically induced texture effects. Afterwards gold electrodes were sputtered on the larger surfaces.

The electric field induced lattice deformation was measured in-situ by using high-resolution X-ray powder diffraction with radiation from a synchrotron source. The measurements were conducted at the B2 beam station in HASYLAB (Hamburg, Germany) using parallel beam geometry and a Si-(111) analyzer crystal. The wavelength of the synchrotron radiation was varied

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between 1.246 and 1.249 A. For both compositions, the scans were taken around (111), (200) and (202) pseudo-cubic peaks to investigate the direction dependence of intrinsic lattice deformation and to evaluate the contribution of domain switching. The electric field was varied from −4 kV/mm to +4 kV/mm stepwise with 0.3–0.5 kV/mm step size. At each step XRD was measured using Ω-2Θ scan mode. Before starting the actual measurement of lattice-strain-versus-electric-field loop, the samples were cycled 2–3 times using a bipolar field with 4 kV/mm amplitude. In addition to the XRD measurements, macroscopic strain was measured from the same samples using LVDT and a computer controlled setup.

3. Results and discussion

Fig. 1 shows diffraction peaks for the sample with rhombohedral structure, $x=0.56$. In the plots, the peaks correspond to three values of external electric field: at $E=0$ (poled remanent state), at coercive field E_c (where polarization switching occurs), and at the maximum field $E_{max}=4$ kV/mm, when the switching is completed. In Fig. 1(a) one can see that as the field changes from 0 to E_c and further to E_{max}, the position of the (200) peak shifts as follows: first, the peak moves to a higher diffraction angle 2Θ which corresponds to a contraction of the unit cell until the coercive field E_c has been reached. As the field increases beyond E_c, the peak position moves back to lower diffraction angles, which indicates an expansion of the unit cell. This effect can be attributed to 180° domain switching, where contraction and expansion of the unit cell occur due to the converse piezoelectric effect. The unit cell contracts when the spontaneous polarization is directed opposite to the electric field (at $E<E_c$), and expands when the polarization is directed along the field ($E>E_c$) after the switching occurred.

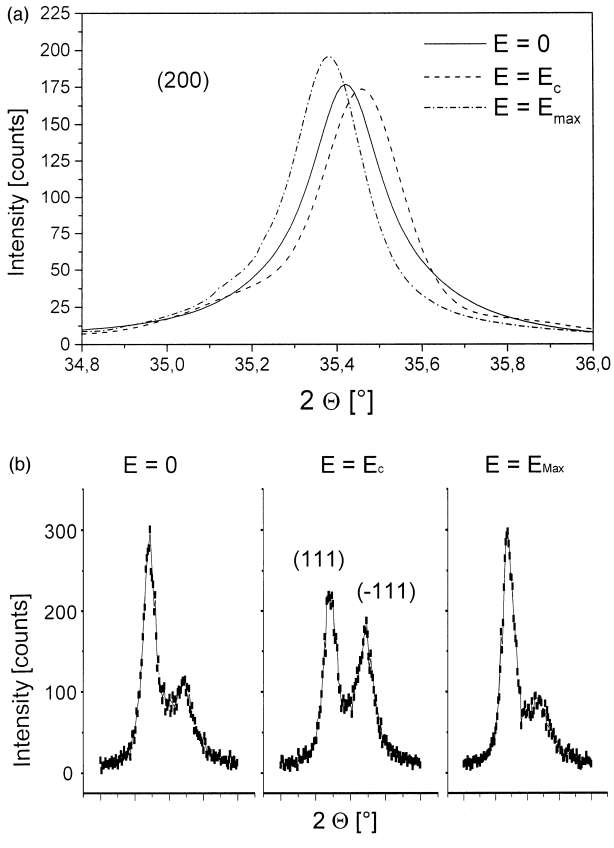

Fig. 1. Change in the XRD diffraction peaks induced by the applied electric field for PZT with composition $x=0.56$ with rhombohedral structure. (a) Shift in the position of (200) diffraction peak under applied field. (b) Change in the intensities of the (111)/(−111) diffraction peaks. The coercive field, E_c, is equal to 0.8 kV/mm and the maximum applied field E_{max} is equal to 4 kV/mm.

Fig. 1(b) demonstrates the change in the (111)/(−111) diffraction peaks with electric field, which can be explained in terms of a non-180° domain switching. At $E=0$, the sample has already been poled by preliminary cycling. Therefore the magnitude of the (111) peak, $I_{(111)}$, which is proportional to a number of domains with polarization direction along poling field, is higher than that of the (−111) peak, $I_{(-111)}$. From the ratio of the peak intensities $R=I_{(111)}/I_{(-111)}$, the volume fraction of domains, N, aligned along the poling field, can be estimated as follows: $N=R/(1+R)$. The volume fraction obtained from the data at $E=0$, Fig. 1(b) is approximately equal to 75%. As the applied electric field approaches the coercive field, E_c, the intensity ratio $I_{(111)}/I_{(-111)}$ becomes smaller. This reduction means that the number of domains with spontaneous polarization aligned along the field becomes smaller. At E_c only $N\approx55\%$ of the total amount of domains have their polarization direction either parallel or anti-parallel to the electric field. In the remaining 20% of domains, the spontaneous polarization changes its direction by 71° or 109° (since this material has a rhombohedral structure) and these domains now do not contribute to the (111) peak. As the field increases further from E_c to E_{max}, the intensity ratio changes again to the original value after poling. Taken together, the data shown in Fig. 1(b) can be interpreted as a polarization reversal which occurs as a two step process with non-180° domain switching: [111] → [−111] → [−1−1−1].

The direction dependence of the lattice deformation was studied and compared with theoretical calculations by Du et al.[7] Fig. 2 shows the field dependence of the lattice strain calculated from the shift in peak positions for the two studied compositions. In both cases the strain was plotted corresponding to the direction of the highest measured lattice deformation. Only one half of each cycle is shown for the sake of a clarity of the plot. Both curves have the typical shape of a butterfly loop for the electric-field-induced-strain in ferroelectrics. The left part of Fig. 2 corresponds to composition $x=0.51$

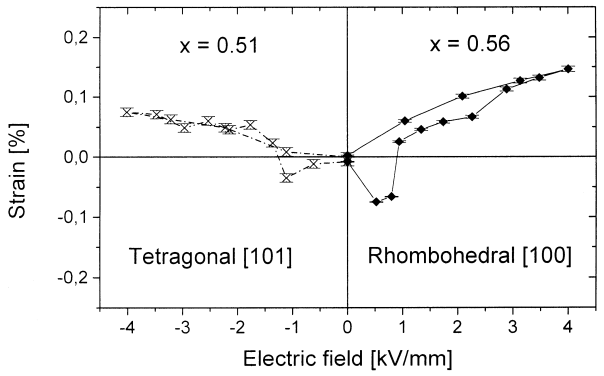

Fig. 2. Intrinsic lattice deformation measured along [101] direction in composition $x=0.51$ with tetragonal structure (left side), and along [100] in composition $x=0.56$ with rhombohedral structure (right side).

with tetragonal structure and the right part corresponds to composition $x=0.56$ with rhombohedral structure. From these curves, the so-called 'unipolar' strain can be evaluated, as the strain induced at the maximum electric field E_{max} with a reference to the remanent state (E = 0). For $x=0.51$, the 'unipolar' strain is equal to 0.075% in [101] direction, which was derived from the change in diffraction peak position of the tetragonal (202) reflection. For $x=0.56$ with rhombohedral structure the 'unipolar' intrinsic strain is 0.15% measured in the [100] direction, which was obtained from the rhombohedral (200) reflection. The intrinsic strain observed in other directions of the unit cell was smaller for both compositions.

Fig. 3 compares the lattice strain for composition $x=0.56$ in the [111] and [100] directions. It can be seen that the strain in the [111] direction, which is parallel to the spontaneous polarization, is markedly smaller than the strain in [100] direction, 0.02% versus 0.15%. This result agrees with theoretical calculations made by Du et al.,[7] which showed that the maximum value of the intrinsic component of the piezoelectric coefficient d_{33} should be in [100] direction in the case of the rhombohedral modification of the ferroelectric phase.

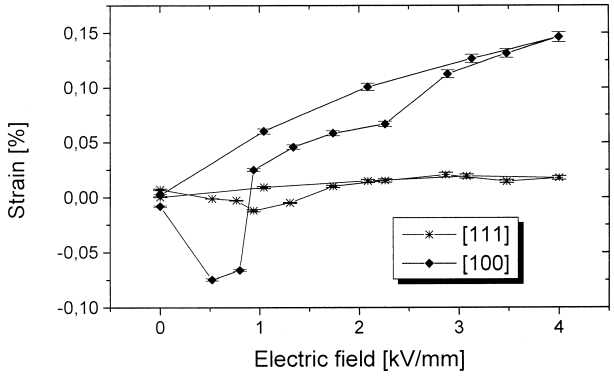

Fig. 3. Electric-field dependence of the intrinsic strain measured along [111] and [100] directions in PZT with composition $x=0.56$.

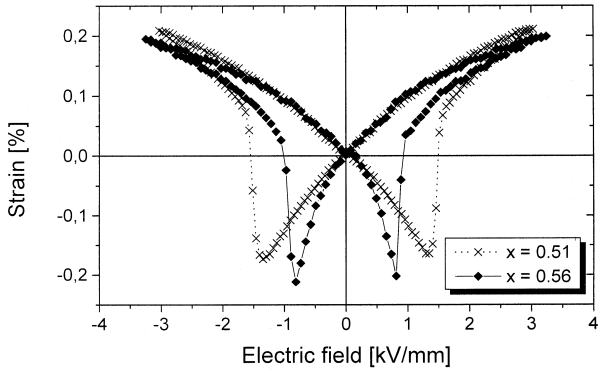

Fig. 4. Electric-field-induced macroscopic strain measured by using LVDT for both studied compositions.

Fig. 4 shows the electric-field dependence of macroscopic strain measured using LVDT, for the investigated PZT compositions. From this plot the 'unipolar' strain can be evaluated as 0.22% for $x=0.51$ and as 0.20% for $x=0.56$. From the comparison of these values with the data on lattice strain measured using XRD, Fig. 2, it can be concluded that in PZT with rhombohedral phase, $x=0.56$, the intrinsic contribution to the total strain is higher than that in PZT with tetragonal structure. For $x=0.56$, the lattice deformation accounts for up to 75% of the total strain, whereas for $x=0.51$, it is only 34%.

4. Summary

High resolution synchrotron XRD was used to investigate extrinsic (domain switching) and intrinsic (lattice deformation) contribution to the total electric-field-induced strain in soft PZT ceramics. Evidence was presented for both 180° and non-180° domain switching. The direction dependence of the lattice deformation was examined. It was found that in rhombohedral PZT, the highest lattice strain occurs in [100] direction, which was in a good agreement with theoretical calculations.[7] The comparison of the lattice strain measured using XRD with the values obtained by macroscopic strain measurements showed that for rhombohedral material the lattice strain gives about 75% contribution to the total strain. In tetragonal material, the lattice contribution is smaller, about 34% of the total strain, which means, that for PZT with tetragonal structure, the domain switching plays a more important role.

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