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Microscopic and Macroscopic Ferroelectric–Ferroelastic and Piezoelectric Behavior of PZT Ceramics

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Abstract

Synchrotron X-ray experiments on rhombohedral PZT ceramics with electric fields in between $-2{\cdot}4$ *and* $2{\cdot}4\,kVmm^{-1}$ *were performed in order to seperate between field-induced ferroelectric-ferroelastic and piezoelectric effects. The results are compared with results of macroscopic measurements. Additionally the influence of different dopands (La, Ag) and grain sizes on the intrinsic piezoelectric effect are investigated and coercive field strength are given.* *© 1999 Elsevier Science Limited. All rights reserved*

Keywords: X-ray methods, ferroelectric properties, piezoelectric properties, PZT, actuators.

1 Introduction

Ceramics based on PZT solid solutions ($PbZr_xTi_{1-x}O_3$) are distinguished because of their high piezoelectric strain constants compared to other electrostrictive materials. Therefore, PZT ceramics are preferred if applications require large piezoelectric strains (i.e. fuel injection devices). However, in difference to what the name 'piezoelectric' implies, there are further other effects (electrostriction 2nd order, field induced phase transition and coupled ferroelectric-ferroelastic domain switching) which may cause field induced strains. Especially in case of perovskites like PZT or $BaTiO_3$ additional field induced ferroelectric-ferroelastic switching of domains must be taken in to account. Because of the distinct nature of these two effects—the coupled ferroelectric-ferroelastic and pure intrinsic piezoelectric effect—it is reasonable to differentiate between both.

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In contrast to most other methods, X-ray diffraction allows to seperate between strains caused by the intrinsic piezoelectric effect and strains due to coupled ferroelectric-ferroelastic switching of domains. Both effects occur on a microscopic scale and are therefore predestinated for X-ray diffraction studies. The influence of the electric field on the lattice parameters affects the d-spacing and corresponds to the piezoelectric effect (Fig. 1), whereas domain switching corresponds to ferroelastic effects; it is a texture effect[1] and influences the intensities (Fig. 2).

2 Experimental

Because of the small magnitude of the field-forced macroscopic strain ($\leq 0{\cdot}2\%$) a diffractometer with high angular resolution is required. Therefore these experiment where carried out with synchrotron radiation with the high resolution powder diffractometer (B2) at HASYLAB Hamburg (Germany) in parallel beam geometry.[2] This geometry is especially well suited, because the sample position and thickness do not affect the measured diffraction angles. In-situ measurements (Ω–2θ stepscans) with electric fields in between $-2{\cdot}4$ and $2{\cdot}4\,kVmm^{-1}$ on rhombohedral $PbZr_{0{\cdot}6}Ti_{0{\cdot}4}O_3$ ceramics have been performed. The disc-shaped samples had a diameter of 10–15 mm and a thickness of 0·3–0·7 mm. They were prepared by grinding and polishing, in order to avoid a texture formation caused by cutting the bulk specimens into thin discs. The PZT ceramics themselves were produced by conventional mixed-oxides technique described by Hammer *et al.*[3] The Zr/Ti ratio was 60/40. Different grain sizes were obtained by variation of sintering temperature and time (1225°C/2 h and 1300°C/10 h) and 2·0 mol% La and 0·7 mol% Ag were used as dopands.

3 Results and Discussion

Figure 3 shows the effect of an applied electric field on the intensity ratio $I_{111}/I_{11\bar{1}}$ of an X-ray diffraction pattern for an undoped rhombohedral PZT ceramic. In case of unpoled samples the intensity ratio $I_{111}/I_{11\bar{1}}$ is approximately 1/3. When the electric field exceeds the coercive field the ratio increases because of the reorientation of domains from the $[11\bar{1}]$- into the [111]-direction. Further increase of the field will increase $I_{111}/I_{11\bar{1}}$ again, until saturation is achieved. If the field is switched off, the ratio may be constant or diminish again, indicating whether the domains are still aligned or not. In case of rhombohedral PZT 60/40 (undoped and doped with 2 mol% La or 0·7 mol% Ag, respectively) the ratio $I_{111}/I_{11\bar{1}}$ is almost constant.

An inversion of the polarity will show if a polarisation reversal will take place by a two step ($[111]\rightarrow[11\bar{1}]\rightarrow[\bar{1}\bar{1}\bar{1}]$) or a single step domain reorientation (only 180° switching $[111] \rightarrow [\bar{1}\bar{1}\bar{1}]$). In the former case the ratio $I_{111}/I_{11\bar{1}}$ would be sensitive for pole reversals, in the latter not. It is important to notice, that for all investigated rhombohedral samples the ratio $I_{111}/I_{11\bar{1}}$ is widely constant, even if the field is inverted, indicating that polarization reversal is predominantly a single step process.

In order to further investigate the pure intrinsic piezoelectric effect 2θ–Ω stepscans at various field strengths have been carried out. The subsequent analysis of the line position of the (200)-peak leads to typical butterfly loops, similar to the ones well known from macroscopic measurements. In Figs 4 and 5 this is shown for La- and Ag-doped PZT 60/40 ceramics with different grain sizes. In accordance to macroscopic measurements, the piezoelectric response is more sensitive for La- (soft) than for Ag-doped (hard) ceramics. For both dopands the grain size is important. Larger grains seems to increase the strain in case of Ag as dopand, whereas it decreases in case of La. Furthermore for Ag-doped samples reducing the grain size tends to round the butterfly loops and thereby broadens the coercive field strength into a coercive field range. The determined coercive field strength and the maximum piezoelectric strains (uni- and bipolar driven) is given in Table 1 and compared to the corresponding values macroscopically determined on identical samples.

Because of the nearly field independent ratio $I_{111}/I_{11\bar{1}}$ it is obvious that field induced macroscopic strain in rhombohedral PZT is predominantly attributed to a purely intrinsic piezoelectric effect. Contributions due to field induced ferroelectric–ferroelastic switching (non-180°) of domains are relatively small. This is in contrast to results found

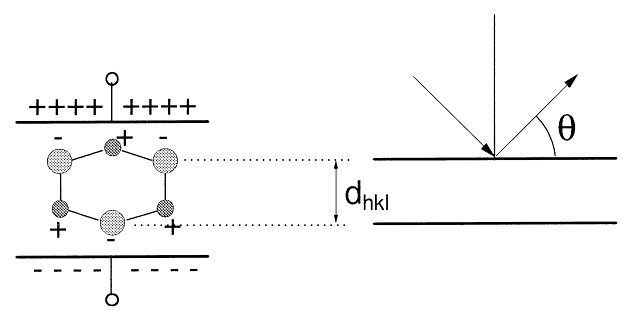

Fig. 1. Schematic diagram of the piezoelectric influence on the d-spacing.

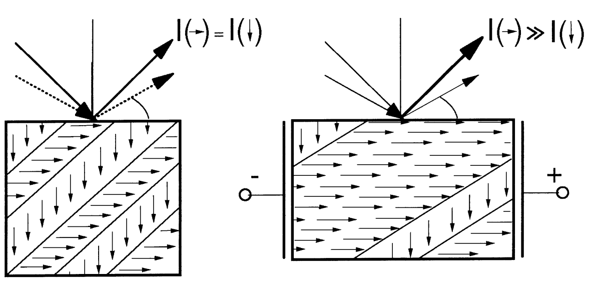

Fig. 2. Schematic diagram of coupled ferroelectric–ferroelastic domain switching and influence on the peak intensity.

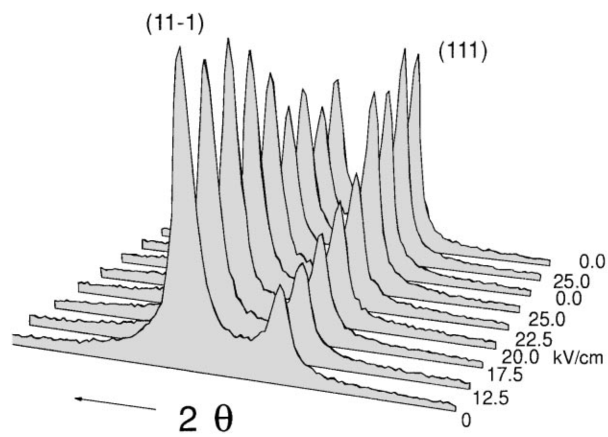

Fig. 3. Domain switching during and after poling for undoped PZT 60/40.

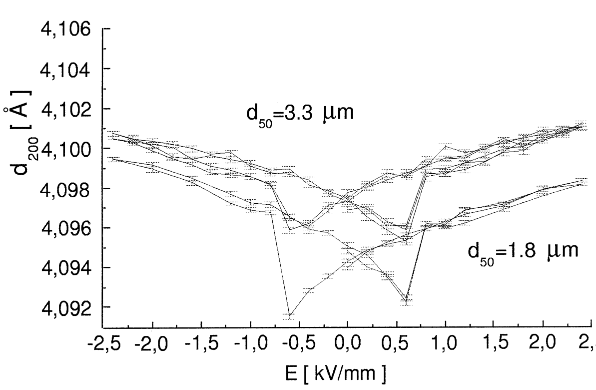

Fig. 4. Microscopic butterfly loops measured in PZT 60/40 doped with 2·0 mol% La for two different grain sizes.

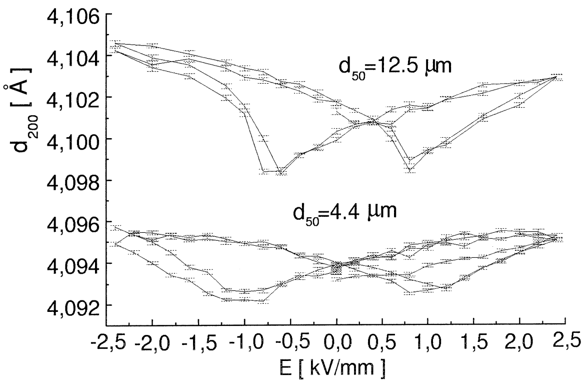

Fig. 5. Microscopic butterfly loops measured in PZT 60/40 doped with 0·7 mol% Ag for two different grain sizes.

Table 1. Microscopic strain in direction [100] compared to results of macroscopic measurements

Dopand (mol%)	d_{50} (µm)	E_c ($kVmm^{-1}$)	ΔL_{AC} (%)	$\Delta L_{AC}{}^m$ (%)	ΔL_{DC} (%)	$\Delta L_{DC}{}^m$ (%)
0·7 Ag	12·5	0·75	0·16	0·154	0·09	0·069
0·7 Ag	4·4	0·75–1·3	0·09	0·138	0·05	0·100
2·0 La	3·3	0·60	0·13	0·222	0·09	0·117
2·0 La	1·8	0·60	0·20	0·254	0·12	0·117

d_{50}: mean grain size, E_c: coercive field strengths, ΔL_{AC}: maximum strain bipolar drive, ΔL^m_{AC}: maximum strain bipolar drive (macroscopic measure), ΔL_{DC}: maximum strain unipolar drive, ΔL^m_{DC}: maximum strain unipolar drive (macroscopic measure). All ΔL values are related to maximum voltage ($2{\cdot}4\,kVmm^{-1}$).

for tetragonal and morphotropic PZT[4–6] and seems to be typical for single–phase rhombohedral PZT ceramics.

Surprisingly, the strain in direction parallel to the spontaneous polarisation, derived from the line position of the (111)-peak, is neglectibly small ($\leq$0·004%).

4 Summary

Synchrotron X-ray experiments have been been performed on single-phase rhombohedral PZT (60/40) in order to seperate between field induced coupled ferroelectric–ferroelastic and pure intrinsic piezoelectric strains. *In-situ* measurements of intensities and d-spacing at various field strengths revealed that the purely intrinsic piezoelectric effect is predominantly responsible for the field induced macroscopic strain.

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