J Mater Sci (2007) 42:8753–8756
DOI 10.1007/s10853-007-1962-6

LETTER

Permittivity and loss tangent of unpoled LaSr-doped PZT under compressive loading

Theo Fett · Hans Kungl · Michael J. Hoffmann

Received: 22 May 2007 / Accepted: 21 June 2007 / Published online: 16 July 2007

Piezoelectric ceramics are commonly applied under a compressive pre-stress in order to avoid failure under tensile stresses. This is the case for piezoelectric actuators, for instance. Under such stress states, the piezoelectric large signal behaviour is strongly affected [1–4]. More recent results on various ferroelectric materials and single crystals are reported by Viehland [5]. But also small signal parameters are influenced by compressive pre-stresses [6, 7]. In order to reveal the effect of material composition, measurements were performed for systematically changed Zr/Ti ratios, resulting in materials located on both sides of the morphotropic phase boundary (MPB). In this communication the effects of compressive load on the dielectric properties of LaSr doped soft PZT ceramics are investigated. Lanthanum is a typical donor dopant in PZT. The La^{3+} ion occupies the Pb^{2+} (A) site in the ABO_3 perovskite structure. The charge compensation occurs by formation of lead vacancies resulting in soft ferroelectric behaviour. Sr^{2+} also substitutes for the Pb^{2+}. The isovalent Sr doping reduces the Curie temperature T_c and enhances dielectric properties [8].

Measurements of the relative *dielectric permittivity* ε and *dielectric loss* $\tan\delta$ parallel and perpendicular to a compressive loading were performed for three PZT ceramics in the unpoled state and analysed as effects resulting from domain switching and lattice deformation.

T. Fett (✉) · H. Kungl · M. J. Hoffmann
Institut für Keramik im Maschinenbau, Universität Karlsruhe, Karlsruhe, Germany
e-mail: theo.fett@ikm.uni-karlsruhe.de

T. Fett
Forschungszentrum Karlsruhe, Institut für Materialforschung II, Postfach 3640, 76021 Karlsruhe, Germany

Three compositions of 1 mol% La-2 mol% Sr-doped morphotropic PZT with Zr/Ti ratios of 53/47, 54/46 and 55/45, respectively, were prepared by the mixed-oxide route. The powders were prepressed by uniaxial die pressing at low pressure and, after that, isostatically pressed at 400 MPa and sintered in closed alumina crucibles at 1225 °C in an oxygen atmosphere [9]. From the sintered specimens, bars with dimensions of $20 \times 4.5 \times 4.5$ mm^3 were fabricated by sawing and grinding. These samples were equipped with sputtering Au electrodes on two opposite 4.5×20 mm^2 surfaces.

X-ray diffraction patterns showed after sintering phase assemblage of both tetragonal and rhombohedral perovskite. Volume fractions of these phases were estimated from integral peak intensity ratios of {200} and {111} reflections. The tetragonal volume fraction of the PZT 53/47 is about 65% and of the PZT 54/46 about 37%. The PZT 55/45 is a predominantly rhombohedral phase material with a tetragonal volume fraction of about 16% [10].

For the dielectric measurements a sinusoidal voltage of 1 V amplitude and a frequency of $f = 1$ kHz was used [7]. The measurements were carried out with an LCR meter (HP-4263A).

Compressive loads were applied to the 4.5×20 mm^2 surfaces (Fig. 1a). For the dielectric measurements in compression direction, the specimens (1) with electrodes (2) were put on a steel block (3) and loaded by a second steel block (4). Their cross sections were identical with those of the test specimens. This yields a nearly homogeneous z-stress in the test piece with $\sigma_z = \sigma_z$ (PZT) $\cong$ σ_z (steel). Superimposed x- and y-stress components are very small and proportional to the difference in Poisson ratios, $\sigma_x, \sigma_y \propto \sigma_z\,(\nu_{PZT} - \nu_{Steel})$, $\nu_{Steel} \cong 0.3$, $\nu_{PZT} \cong 0.35 - 0.5$. This ensures maximum x- and y-stresses <10%

of the z-stress (the stresses σ_x, σ_y are additionally reduced by sliding effects in the contact surfaces). For a friction coefficient between specimen and loading block of about $\mu = 0.3$, these stresses are reduced on roughly 3–5% of σ_z resulting in a sufficiently uniaxial compressive stress state. The steel blocks were insulated from the testing machine by blocks made of Al_2O_3 (5). For the measurements perpendicular to the loading direction with the electrodes located on the side surfaces, the steel blocks were removed in order to avoid short-circuiting of the electrodes (Fig. 1b).

Figures 2a, 3a, and 4a show the permittivities in stress direction and perpendicular to stress as a function of load. The permittivity measured in stress direction, $\varepsilon_{\|}$, first increases with increasing compressive stress. A maximum value is reached at about $\sigma = -170$ MPa, followed by a decrease with higher stresses. A comparison of the maximum permittivities and the related compressive stresses is given in Table 1. At a stress of about –430 MPa, the bars were unloaded, if no fracture had occurred before. The permittivity perpendicular to the stress, $\varepsilon_{\perp}$, decreases continuously. The typical shape of the $\varepsilon = f(\sigma)$ dependency found for unpoled material shows the same typical shape as the curves given by Zhang et al. [6] for soft doped poled PZT with maximum value reached at somewhat lower stress than in our experiments. Especially their Fig. 3 agrees with our results plotted in Fig. 2.

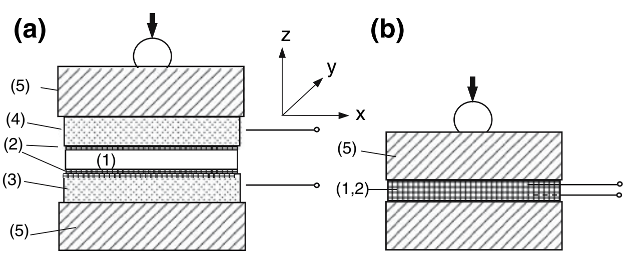

Fig. 1 Application of compressive load during electric measurements

The loss tangent $\tan\delta$ in both directions is shown in Figs. 2b, 3b, and 4b as a function of stress for the three different compositions. During measurement in stress direction ($\tan \delta \parallel \sigma$), the loss tangent decreases

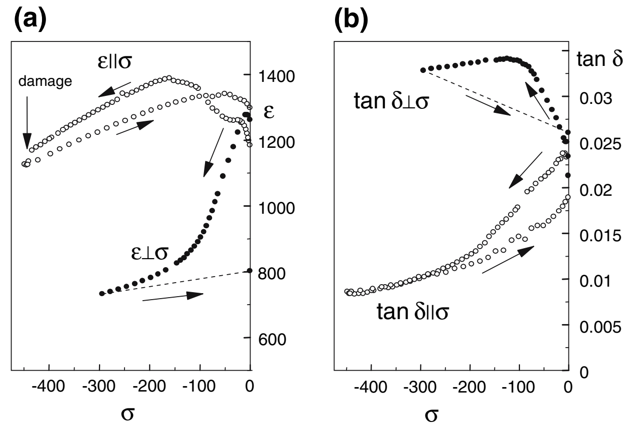

Fig. 3 Results for PZT with a Zr/Ti ratio of 54/46, (**a**) permittivity, (**b**) dielectric loss tangent

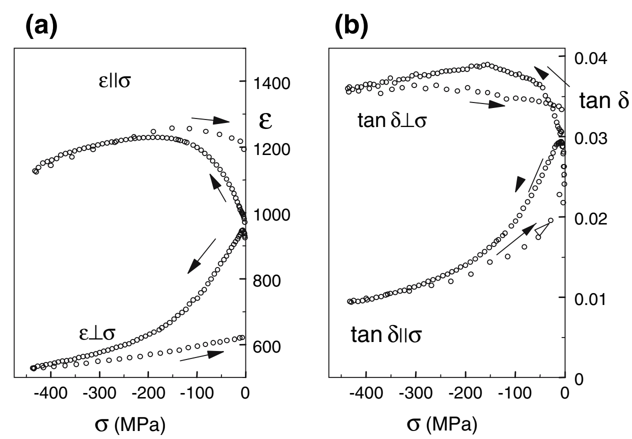

Fig. 4 Results for PZT with a Zr/Ti ratio of 55/45, (**a**) permittivity, (**b**) dielectric loss tangent

Fig. 2 Results for PZT with a Zr/Ti ratio of 53/47, (**a**) permittivity, (**b**) dielectric loss tangent

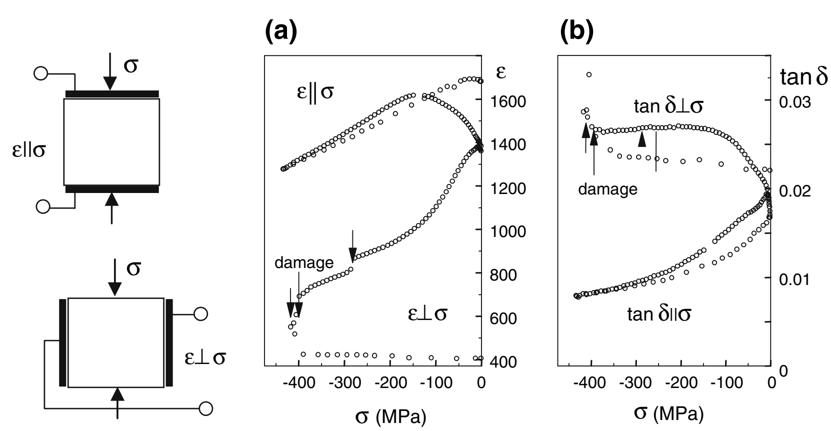

Table 1 Permittivity data (ε_i = without load, ε_{max} reached at $\sigma = \sigma_{max}$)

Zr/Ti ratio	Tetragonal phase content	ε_i	ε_{max}	σ_{max} (MPa)
53/47	60–75%	1400	1600	–150
54/46	35–50%	1190	1400	–160
55/45	10–25%	950	1220	–180

continuously and reaches values of <0.01 at high compressive stress. The shape of the general dependency corresponds to the permittivity perpendicular to the loading direction. The loss tangent perpendicular to loading direction shows a behavior similar to that of the permittivity parallel to loading. The arrows in Fig. 2 indicate small pop-ins in the load-time record, accompanied by cracking noise, which indicates the generation of damage. In Fig. 5 a comparison of the results for the different materials and directions is given. Figure 6 shows the influence of material composition on the maximum values of permittivity and loss tangent.

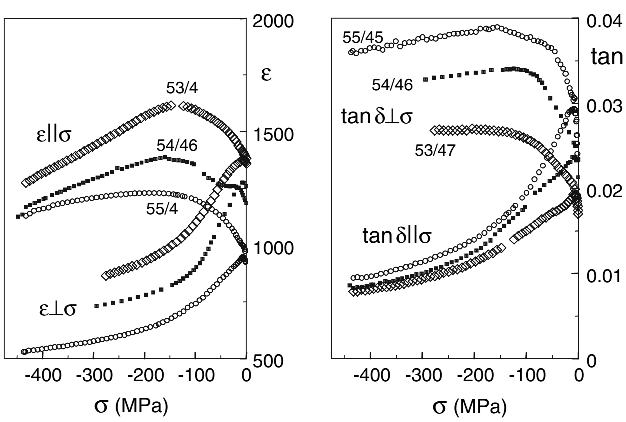

Fig. 5 Comparison of the electric measurements parallel and perpendicular to mechanical loading

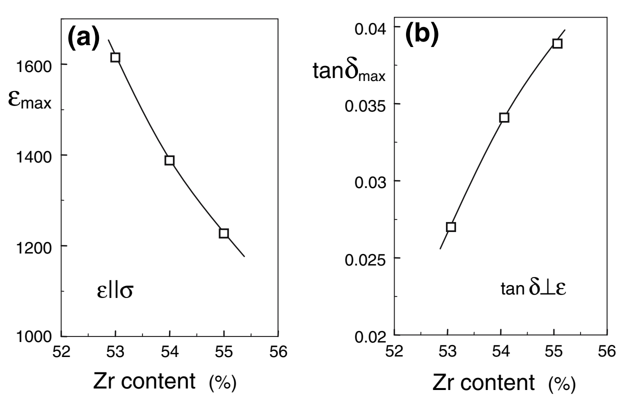

Fig. 6 Influence of the Zr content on the maximum values of the dielectric parameters

At very low load, the contact between specimen and compression dies occurs at a few single points only. With increasing pressure, this contact extends over the whole interface area and acoustic radiation can be transported from the specimen to the loading device. In this load range, the dielectric losses are expected to increase, as was found by the experiments for $|\sigma| < 10$ MPa (Figs. 2–4).

Permittivity and dielectric losses are influenced by the orientation of the domains and by the lattice deformation. Whereas the hydrostatic stress component affects the lattice spacing, the deviatoric stresses are responsible for domain switching. In order to separate these two effects, the following procedure was adopted.

For a completely isotropic state, 1/3 of domains and domain walls (see e.g. [11, 12]) of a tetragonal material are oriented in each direction. Under very high compressive stresses, the saturation in plastic strains is reached. All domains oriented in stress direction are switched into the plane perpendicular to the stress. Consequently, also the number of domain walls mobile in stress direction disappears and the number in the transverse directions becomes 1/2 each. We have to expect that the average permittivity $\bar{\varepsilon}$, given by

$$\bar{\varepsilon} = \frac{1}{3}\left(\varepsilon_{||} + 2\varepsilon_{\perp}\right) \tag{1}$$

must be independent of the domain orientation, whereas the deviation from the average

$$\Delta\varepsilon_{\perp} = \varepsilon_{\perp} - \bar{\varepsilon}\,, \quad \Delta\varepsilon_{||} = \varepsilon_{||} - \bar{\varepsilon} \tag{2}$$

must be a function of the domain orientation and should tend to a saturation value for high compressive stresses. An analogous procedure for the loss tangent results in

$$\overline{\tan\delta} = \frac{1}{3}\left(\tan\delta_{||} + 2\tan\delta_{\perp}\right) \tag{3}$$

$$\Delta(\tan\delta)_{\perp} = \tan\delta_{\perp} - \overline{\tan\delta}\,, \quad \Delta(\tan\delta)_{||} = \tan\delta_{||} - \overline{\tan\delta} \tag{4}$$

From Fig. 7, it is obvious that the saturation for $\Delta\varepsilon$ is reached at about –170 MPa for the compositions of 53/47 and 54/46 and at –200 MPa for 55/45. In all cases, it results $\Delta\varepsilon_{||} \cong 400$ and $\Delta\varepsilon_{\perp} \cong -200$. The average permittivity, which is decreasing with increasing compressive stress indicates that the permittivity contribution of the lattice must decrease. Saturation of loss tangent deviations is reached at about –250 MPa (Fig. 8).

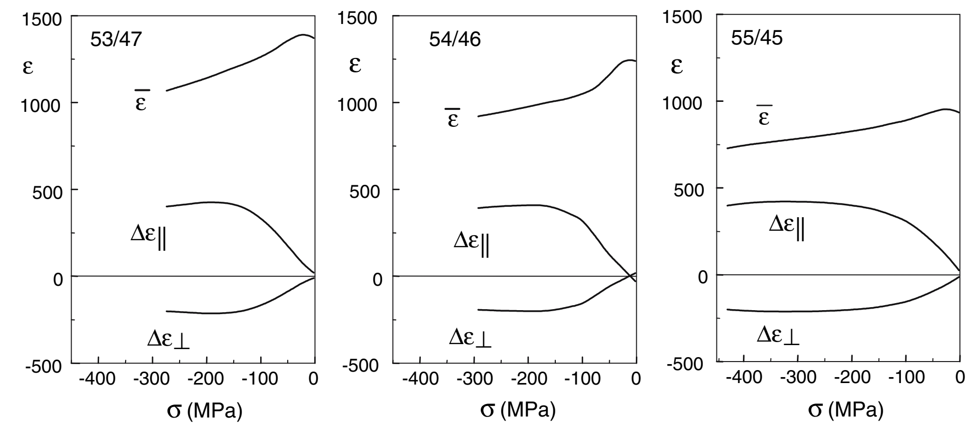

Fig. 7 Average permittivity $\bar{\varepsilon}$ and deviations in parallel and normal direction

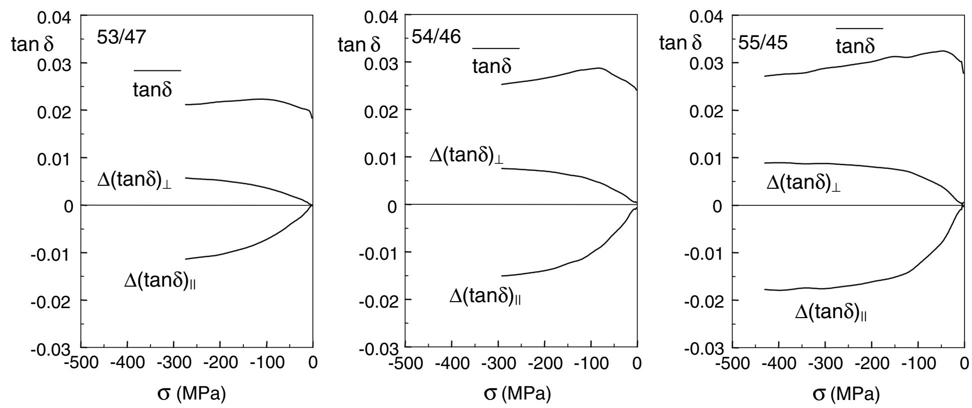

Fig. 8 Mean loss tangent and deviations from the mean-value curve

Conclusions

Maximum differences between permittivity in stress direction and perpendicular to the stresses from the average are reached at compressive stresses of about -170 MPa. Saturation of the non-symmetry in loss tangents is reached at about –200 MPa.

For all investigated compositions, the average permittivity decreases continuously with increasing compressive stress, i.e. for increasing $|\sigma|$. This decrease is not related to a change in the domain orientation. It reflects the fact that all unit cell dimensions are reduced by the negative hydrostatic stress component $\sigma_{\text{hyd}} = \sigma/3$ ($\sigma < 0$) that consequently reduces the mobility of the Ti^+/Zr^+ ions located near the cell centre. Also the average value of the loss tangent decreases slightly. The deviatoric components of ε, $\Delta\varepsilon_{\|}$ and $\Delta\varepsilon_{\perp}$, increase parallel and decrease perpendicular to the load direction. They reach saturation at about 170 MPa.

It can be concluded that with increasing Zr/Ti ratio, i.e. decreasing tetragonal phase content, the average and the maximum permittivity decrease. The average and maximum values of the loss tangent show the opposite trend.

Acknowledgement The authors would like to thank the Deutsche Forschungsgemeinschaft DFG for financing parts of this work within the SFB 595.

References

1. Lynch CS (1996) Acta Mater 44:4137
2. Chaplya PM, Carman GP (2001) J Appl Phys 90:5278
3. Zhou DY, Kamlah M, Munz D (2005) J Europ Ceram Soc 25:425
4. Kounga AB, Aulbach E, Granzow T, Rödel J (2007) Acta Mater 55:675
5. Viehland D (2006) J Am Ceram Soc 89:775
6. Zhang QM, Zhao J, Uchino K, Zheng J (1997) J Mater Res 12:226
7. Fett T, Munz D, Thun G (2002) J Mater Sci Lett 21:849
8. Jaffee B, Cook WR, Jaffee H (1971) Piezoelectric ceramics. R.A.N. Publishers, Marietta, OH
9. Hammer M, Hoffmann MJ, (1998) J Am Ceram Soc 81:3277
10. Kungl H, Fett T, Wagner S, Hoffmann MJ (2007) J Appl Phys 101:044101-1-9
11. Dederichs H, Arlt G (1986) Ferroelectrics 68:281
12. Arlt G, Dederichs H, Herbiet R (1987) Ferroelectrics 74:37