Temperature- and Stress-Dependent Electromechanical Response of Porous Pb(Zr,Ti)O$_3$

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The small-signal direct piezoelectric coefficient and dielectric permittivity are characterized as a function of temperature from 25 to 450 °C and uniaxial compressive stress up to 80 MPa in porous Pb(Zr,Ti)O$_3$ (PZT; 10, 20, 30, 40, and 50 vol% porosity). Results show retention of piezoelectric response throughout the temperature range with increasing porosity up to 30 vol%, above which a subsequent decrease is observed. Similarly, increasing porosity did not result in a significant change of the depolarization temperature, although a slight increase in the Curie point is observed with increasing porosity. Macroscopic experimental results are discussed together with microcomputed tomography, which shows the 3D pore structure. These results are important for sensing applications that operate at elevated temperatures and apply compressive stress to the electroactive element.

1. Introduction

Piezoelectric ceramics are of interest for numerous transduction applications, such as energy harvesting, ultrasound, and positioning systems, due to their electromechanical coupling, tunability through doping, and excellent temperature stability. In particular, porous piezoelectric ceramics are attractive for applications that require a high hydrostatic figure of merit (HFOM = $d_{31}$/$\varepsilon_{33}$), which depends on both the hydrostatic charge coefficient ($d_{31} = d_{31} + 2d_{13}$) and the voltage coefficient ($\varepsilon_{33} = d_{33}/\varepsilon_{33}$). Previous studies have demonstrated that the transverse piezoelectric coefficient ($d_{31}$) decreases relative to the longitudinal piezoelectric coefficient ($d_{33}$) with increasing porosity,[11] resulting in an enhancement of the generated electrical charge per unit hydrostatic force applied compared with dense materials. In addition, porosity is, typically filled with low dielectric air, generally results in a decrease in the relative permittivity, thereby improving $d_{31}$ and further increasing the HFOM. These factors can enhance the HFOM by a few orders of magnitude above corresponding dense materials.[2] Porous ceramics with an open 3–3 pore connectivity, in particular, exhibit special features and properties in comparison with dense ceramics. Porous ceramics are generally used for water purification, molten metal filtration, or ceramic scaffolds.[3–5] Three well-known methods can obtain ceramic foams with such high open porosity: replica[6] sacrificial templates, and direct foaming.[5] Details of different routes for the fabrication of porous piezoelectric materials can be found in the study by Galassi.[7]

For piezoelectric materials, such as lead-free Li-doped potassium sodium niobate or Pb(Zr,Ti)O$_3$ (PZT), the effects of pore morphology, pore size, amount of porosity, and degree of isotropy on the properties, e.g., enhanced $d_{31}$ and reduced relative permittivity compared with dense piezoelectric ceramics, were reported.[8–14] Despite the improvement in electromechanical response, porosity decreases the mechanical strength, effectively limiting pore content.[15] This is particularly critical, as many applications apply elevated electrical, thermal, and mechanical fields to the electroactive materials during operation. In addition to possible component failure due to reduced mechanical strength, external fields are known to change the large-signal[16–18] and small-signal[19–21] electromechanical response and can induce structural phase transitions, either stabilizing the high-temperature paraelectric phase or low-temperature ferroelectric phase depending on the stress state, i.e., uniaxial,[22] biaxial,[23] or hydrostatic.[24] For example, underwater sound projectors apply uniaxial compressive stresses up to 63 MPa,[25] whereas hydrophones mechanically load the piezoelectric ceramic in hydrostatic compression up to several MPa. Despite their technical importance, there are limited investigations on the temperature- or stress-dependent small-signal electromechanical properties. To that end, the longitudinal piezoelectric coefficient and relative dielectric permittivity are characterized as a function of temperature up to 450 °C and frequency for porous PZT up to a porosity of 50 vol%. Although experimental results reveal a decrease in piezoelectric response across this temperature region with higher pore content, the depolarization temperature and Curie point show insensitivity to
porosity. In addition, the piezoelectric coefficient was characterized at room temperature as a function of uniaxial compressive stress up to 80 MPa.

2. Experimental Section

Porous PZT ceramics were fabricated from commercial soft PZT powder (NCE51, Noliac Group, Kvistgaard, Denmark) with a mean particle size of \(d_{50} = 1.8 \mu m\) loaded with varying amounts (0–50 vol%) of 100 \(\mu m\) cellulose beads (VIVAPUR CS 100S, Rettemmaier & Söhne GmbH + Co. KG, Rosenberg, Germany). The microstructure of the utilized cellulose beads is shown in Figure 1. Blends of the PZT powder and the cellulose beads were homogenized for 30 min by dry mixing (AR 400, ERWEKA GmbH, Heusenstamm, Germany) and afterward uniaxially compacted to cylinders with a diameter of 10 mm by applying a uniaxial compressive stress of 60 MPa (PW 10 E, Paul-Otto Weber GmbH, Remshalden, Germany). Debinding and sintering were conducted at 850 °C for 1 h and at 1250 °C for 2 h, respectively, using heating rates of 1.5 K min\(^{-1}\). A preliminary thermogravimetric analysis of the cellulose was conducted to confirm the debinding temperature and found to be completely decomposed to CO/CO\(_2\)/H\(_2\)O in air within the temperature range of 800 °C. In addition, due to the high sintering temperature used for the PZT sample, it is expected that the cellulose pore former is decomposed completely without any residue. For the thermal treatment, the samples were placed on a ZrO\(_2\) powder bed (Thermo Fisher [Kandel] GmbH, Karlsruhe, Germany) and encapsulated with alumina crucibles. Sacrificial PbO and PbZrO\(_3\) (both, Sigma-Aldrich, St. Louis, USA) powders were added to prevent lead loss. During the following discussion, the various samples will be referred to the porosity content; PZT with 0, 10, 20, 30, 40, and 50 vol% porosity will be denoted as PZT0, PZT10, PZT20, PZT30, PZT40, and PZT50, respectively.

Prior to testing, cylindrical samples with a height of 6.0 (±0.01) mm and a diameter of 5.8 (±0.01) mm were ground and lathed with a surface grinder (JUNG JF 415 S) equipped with a diamond grinding wheel from the as-sintered discs. Subsequently, samples were annealed at 600 °C for 1 h with a heating and cooling rate of 5 and 1 K min\(^{-1}\), respectively. This step was performed to remove domain orientation due to the processing. The circular faces of the samples were sputtered with Au/Pt electrodes. Samples were electrically poled using corona poling, whereby six samples were placed under a multipin corona point setup, consisting of 21 needles spread over a circular area of 20 mm in diameter. The applied voltage/corona point heights were 11 kV/6 mm.

The piezoelectric and dielectric properties of the poled samples were characterized using a custom-built experimental arrangement previously described in detail.\(^{[19,26]}\) Measurements were performed in a screw-driven 30 kN load frame (5967, Instron) with an integrated thermal chamber (TK 26.600L2, Fresenberger). Force was applied to the sample through tungsten carbide loading dies, which were also the electrical contacts. The direct piezoelectric coefficient (\(d_{33}\)) was determined via a piezoelectric actuator (P-025.80, PI Ceramic GmbH, Germany) that varied the applied load on the sample and a Sawyer-Tower circuit.

During testing, the samples were partially unloaded using a sinusoidal waveform with an amplitude of ±0.5 MPa at various frequencies between 0.5 and 140 Hz. A custom LabVIEW program was developed to control the measurements and collect the data. The relative dielectric permittivity (\(\varepsilon_r\)) was also determined on the same sample with an LCR Meter (E4980AL, Keysight). A switching box was controlled by the custom control and analysis software to alternate between piezoelectric and dielectric measurements during the experiment. Temperature-dependent measurements were performed during heating with a heating rate of 2 K min\(^{-1}\), which was measured with a K-type thermocouple located in the lower loading die, approximately 6 mm from the sample. Stress-dependent measurements were performed at various constant bias compressive stress levels up to 80 MPa. Prior to measurement at each stress level, a wait time of 3 min was used to allow for sample creep. The error of the \(d_{33}\) measurements is approximately the size of the markers.

Large signal polarization and strain–electric field measurements were also performed on the same samples at room temperature. During testing, the samples were submerged in a silicone oil bath and applied with a bipolar, triangular waveform voltage at a frequency of 100 mHz using a high-voltage power supply (20/20 C, Trek Inc.), resulting in a maximum electric field of ±2 kV mm\(^{-1}\). Polarization was measured with a Sawyer-Tower circuit, whereas the strain was determined with a linear differential transformer (WA/2MM-T, HBH).

X-ray microtomography (μCT) investigations were performed on the same cylindrical samples used for electromechanical measurements. The scanning parameters were set to 80 kV and 100 μA using a tungsten X-ray tube in a SkyScan 1172 with an 11 MP detector at \(J = 0.024\) mm. To reduce the number of low-level energy photons, an Al/Cu filter was used, increasing the scanning time per image up to 9,500 ms. The samples were scanned for 180° with a rotation step of 0.4°. Restructions of the sonograms were done using the NReco Software (Client and Server, Version 1.7.2.4, Bruker, Koentgen, Belgium). A 3D visualization and pore network extraction were done using algorithms reported in our previous works.\(^{[14,27]}\) and Amira 2019.3 (Thermo Fisher Scientific, Berlin, Germany).

Figure 1. Microstructure image of the 100 μm cellulose spheres utilized as the sacrificial template for the fabrication of porous PZT.
3. Results and Discussion

Figure 2 shows the fractured surface of the sintered PZT samples with different volume fractions of pores. The pore size is related to the size of the initial pore former, with pore size being typically \( \approx 100 \mu m \). It should be mentioned here that no microcracking related to the pressing forces and/or poling process was observed. In addition, grain size and shape of the sintered PZT are not affected due to the addition of a large fraction of pore former.

By applying a defined universal threshold to the μCT images, pores and material can be separated and binarized. The analyzed μCT data shown in Figure 3 shows an increase in the mean cell size and amount of specific cell sizes with increasing porosity, which is in agreement with the experimental setup. It should be mentioned here that the cell size defines the diameter of the pores estimated by a volume-based algorithm using contracting filling spheres to determine the size. The variation in the material determined by strut thickness matches with the porosity. With increasing amount of pore formers, the amount of smaller strut thicknesses increases, whereas struts with larger thickness are reduced. This led to the change from a closed (30%) to an open-cell structure at 50% pore formers. The porous microstructure of 50% pore former is shown in Figure 3c, and the corresponding interconnecting open-pore network is shown in Figure 3d.

The large signal ferroelectric behavior was characterized at room temperature for PZT0, PZT10, PZT20, and PZT30 (Figure 4). Samples were in the annealed, unpoled state before the application of an electric field, providing information on the poling behavior as well as the remanent strain and polarization. Ferroelectric domains begin to reorient in the direction of the applied electric field during the initial application of an external electric field, resulting in the sharp increase in strain and polarization near approximately 1 kV mm\(^{-1}\). The inflection point in the polarization–electric field curve during this initial loading is referred to as the poling field \( (E_p) \), which was observed to increase with increasing porosity from 1.12 kV mm\(^{-1}\) for PZT0 to 1.18 kV mm\(^{-1}\) for PZT30. Similarly, the coercive field was also found to increase with porosity from a value of 1.02 kV mm\(^{-1}\) for
Recent investigations have also demonstrated that the irregular-shaped pores experience values over the entire temperature range with increasing porosity was observed, showing values of $\varepsilon$ and $d_{33}$ and is related to the reduction in the electric field in the ceramic due to the presence of lower dielectric pores (air). It should be noted that the electric field distribution is dependent on the pore shape and their orientation to the applied electric field direction. For example, Zeng et al. reported that the irregular-shaped pores experience higher concentrated electric field intensities and stress at the tips of the pores than the regular spherical-shaped pores. As such, the local electric field distribution can vary significantly depending not only on the volume fraction of the pores but also on the pore shape and their orientation. It has been previously shown that the composite nature of porous dielectric ceramics, which combine a high dielectric ferroelectric with low dielectric pores, results in an inhomogeneous electric field distribution, where lower electric fields are expected in the ceramic near pores. Similar strategies are also used in ceramic/polymer capacitors to increase the breakdown field through the redistribution of the electric field in the composite structure. Recent investigations have also demonstrated the ceramic/ceramic composite effect on the development of large unipolar strains in lead-free ferroelectrics.

Interestingly, the uniaxial strain response shows lower porosity sensitivity than polarization, which is demonstrated by the more significant decrease in remanent polarization (23%) compared with the remanent strain (≈0%). It is important to note that the geometrical area of the samples was used in determining the polarization. For dense samples, i.e., sintered density 95% of the theoretical density, this is sufficient. However, in the current study, the charge occurring during electric field loading is actually distributed across a significantly smaller area due to the presence of pores at the surface. Figure 4 shows the corrected polarization values that take the surface area reduction in account. It is apparent from the corrected polarization–electric field loops that the polarization does not decrease with increasing porosity, rather an increase in maximum and remanent polarization is observed. This correction, however, assumes that the electrode is only distributed on the outermost surface, which is not the case. During sputtering, electrode material can also be deposited in open pores at the surface, which in some cases could contribute to the observed polarization, thereby increasing the measured value. It is not possible to accurately determine the contribution from these areas. Interestingly, this simple analysis indicates that the changes in the local electric fields near pores of up to 30 vol% porosity do not have a significant influence on the remanent polarization and strain.

The effect of surface area reduction should not influence the strain–electric field response because strain is not sensitive to the electrode area, rather the sample height. This is seen through the nearly constant remanent strain up to 30 vol% porosity. In contrast, a reduction in large-signal piezoelectric coefficient $d_{33}$ with increasing porosity was observed, showing values of 680, 655, 640, and 610 pm V$^{-1}$ for 0, 10, 20, and 30 vol%, respectively. This approximately linear decrease with increasing porosity is significantly lower than predicted by the rule of mixtures, e.g., a nearly 10% decrease for 30 vol% porosity was found.

To determine the influence of porosity on the small-signal electromechanical behavior, temperature-dependent direct piezoelectric coefficient and relative permittivity were characterized from room temperature up to 450 °C as a function of frequency (Figure 5). PZT0 displays a temperature-dependent piezoelectric and dielectric response consistent with previous reports on PZT marked by a peak in $d_{33}$ followed by a subsequent sharp decrease at the depolarization temperature as well as dielectric peak at the Curie point. This peak in $d_{33}$ is due to the sharp increase in permittivity at the Curie point separating the ferroelectric and paraelectric phase and the subsequent loss of macroscopic polarization. Below the depolarization temperature, $d_{33}$ is observed to be frequency dependent, which is due to hysteretic extrinsic contributions such as domain wall motion. Interestingly, the $d_{33}$ values over the entire temperature range were not observed to decrease for porosities up to 30 vol%; a significant change in the frequency dispersion was also not found. In contrast, the maximum permittivity decreased with increasing porosity above 10 vol%, corresponding to a nearly linear decrease in the observed $\varepsilon^*$ at room temperature (1 kHz). It should be noted that the piezoelectric coefficient and relative permittivity were not corrected for surface area reduction.

![Figure 4. Room-temperature large field strain–electric field and polarization–electric field hysteretic ferroelectric response of PZT as a function of porosity. Measurements are performed at 100 mHz.](image-url)
The temperature-dependent $d_{33}$ for all materials is directly compared in Figure 6a for a measurement frequency of 90 Hz. It can be seen for a porosity content of up to 30 vol% that the temperature-dependence of the piezoelectric response is not significantly influenced. Variations in the observed $d_{33}$ can be due to variations in the poling; corona poling is sensitive to a number of factors, such as sample positioning, discharge rate, and so on, which can cause deviations in the completeness of poling and thereby the observed $d_{33}$ value. These variations were observed in this study to be on the order of approximately ±5%. The primary conclusions, however, are not affected by this variation, namely that the piezoelectric response is stable within the resolution of the measurements up to approximately 30 vol% porosity over the entire investigated temperature range. This also corresponds well to previous investigations, which have shown that the room-temperature $d_{33}$ value is stable at elevated porosity contents.[37] Bowen et al.[1], for example, have shown the porosity-dependent room-temperature $d_{33}$ and $d_{31}$ values for PZT, where after an initial drop from dense ceramics, the $d_{33}$ response was stable until approximately 40 vol% porosity. Above 30 vol% porosity content, a decrease in the room-temperature $d_{33}$ of approximately 16–24% is observed for PZT40 and PZT50, respectively. The room-temperature $d_{33}$ and $\varepsilon'$ are shown as a function of porosity in Figure 7. Interestingly, PZT50 displays a more temperature-insensitive piezoelectric response, where the observed $d_{33}$ only varied by approximately ±4% of the room temperature value up to 334 °C. The temperature-dependent piezoelectric voltage coefficient, $g_{33}$ ($=d_{33}/\varepsilon_0\varepsilon_0$), for various porosity contents is shown in Figure 6b. Efficient piezoelectric materials for vibration energy harvesting can be characterized by the large magnitude of the product of the $g_{33}$ and $d_{33}$, which is known as the transduction coefficient.[38] Our analysis shows an increase in $g_{33}$ with increasing porosity, which is related to a decrease in relative permittivity. However, to achieve an optimum transduction coefficient ($=d_{33} \times g_{33}$) for energy harvesting, a balance between sufficiently high $d_{33}$ and $g_{33}$ is required. For instance, the PZT30 sample exhibits a higher (11 427 × 10⁻¹⁵ m² N⁻¹) transduction coefficient than that of the PZT50 (9086 × 10⁻¹⁵ m² N⁻¹) despite the lower $g_{33}$ value. The transduction coefficients for samples with introduced porosity are higher than that of the PZT0

![Figure 5. Temperature-dependent piezoelectric coefficient and relative permittivity of a,g) PZT0, b,h) PZT10, c,i) PZT20, d,j) PZT30, e,k) PZT40, and f,l) PZT50 as a function of frequency.](image)

![Figure 6. a) Direct piezoelectric coefficient and b) piezoelectric voltage coefficient as a function of temperature for various porosity contents (0, 10, 20, 30, 40, and 50 vol%). Measurements are performed at 90 Hz.](image)
The stress-dependent piezoelectric coefficient is a function of porosity, i.e., PZT40 and PZT50. Previous experimental investigations have shown that increasing hydrostatic stress can shift the Curie point. In the current investigations, an apparent increase in Curie point indicates a stress relaxation. Assuming a purely triaxial residual stress state in the ceramic, internal residual stresses in ceramics can be caused by a number of factors, including anisotropic thermal expansion of neighboring grains. In a porous ceramic, the number of direct neighbors is reduced, which reduces the grain-to-grain thermal and elastic mismatch and subsequently the internal stress. However, the change in internal stress, in addition to the extent of incorporated pore fraction, is also possibly related to the homogeneity of the distribution of pores. Nevertheless, further comprehensive experimental works are required to validate the effect of porosity on the polar–nonpolar phase-transition temperatures.

Porous ferroelectrics are particularly attractive for sensing applications, such as hydrophones and ultrasonic transducers, due to their large HFOM originating from an increase in the hydrostatic strain coefficient and a decrease in relative permittivity. Typically, however, these applications expose the electroactive material to elevated stresses levels, such as 33-mode underwater sound projectors that are applied with a maximum of 63 MPa compressive stress. Compressive stress has been shown by numerous researchers to decrease the piezoelectric response through the irreversible motion of ferroelastic domain walls. The stress-dependent piezoelectric coefficient is, therefore, an important measure of the critical uniaxial stress that can be applied to the porous material without mechanical depolarization. As such, the stress-dependent $d_{33}$ was characterized at room temperature under uniaxial compressive stress up to 80 MPa (Figure 8). The data reveal samples as high as 30 vol% porosity can retain a $d_{33}$ of 150 pC N$^{-1}$ even after compressive stress of 80 MPa. The data shown in Figure 7 also highlights that the incorporation of 20 vol% porosity (PZT20) does not alter the mechanical depolarization significantly than that of without any incorporated porosity (PZT0). Therefore, the combination of enhanced $d_{33}$ without significant mechanical depolarization (Figure 8) and lower dielectric permittivity (Figure 7) can be achieved with 20 vol% porosity for the studied composition.

![Figure 7. Room-temperature piezoelectric coefficient and relative permittivity as well as the Curie point and depolarization temperature as a function of porosity.](Image)

![Figure 8. Stress-dependent $d_{33}$ at room temperature. Measurements were performed at 10 Hz. PZT40 and PZT50 were broken above 45 MPa. The color lines are guide to the eye.](Image)
4. Conclusions

Temperature- and stress-dependent electromechanical properties of porous PZT have been investigated in this work. The small-signal direct piezoelectric coefficient and dielectric permittivity were characterized as a function of temperature from 25–450 °C and uniaxial compressive stress up to 80 MPa in porous PZT (10, 20, 30, 40, and 50 vol%) porosity. Results show maintenance of piezoelectric response throughout the temperature range with increasing porosity up to 30 vol%, above which a significant decrease was observed. The macroscopic electromechanical response was explained in combination with the microstructure information obtained by microcomputed tomography. The results indicate that for the studied composition of PZT incorporation of 20 vol% porosity can be helpful in optimizing the HFOM for sensing applications.

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Conflict of Interest

The authors declare no conflict of interest.

Keywords

electromechanical properties, hydrostatic figure of merit, porous piezoelectric ceramics, transduction coefficients

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