Influence of porosity on nonlinear mechanical properties of unpoled porous $\text{Pb}(\text{Zr}_{0.95}\text{Ti}_{0.05})\text{O}_3$ ceramics under uniaxial compression

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A series of uniaxial compression experiments on unpoled porous lead zirconate titanate $\text{Pb}(\text{Zr}_{0.95}\text{Ti}_{0.05})\text{O}_3$ (PZT95/5) ceramics were performed to investigate the influence of porosity on the mechanical properties, domain switching and phase transformation via non-contact digital image correlation optical technique to measure the full-field strain. Four unpoled PZT95/5 ceramics were fabricated with a range of porosity levels via systematic additions of pore formers. The nonlinear compressive mechanical behaviors of unpoled PZT95/5 ceramics were measured and evaluated as a function of porosity. The nonlinear deformation mechanism of unpoled PZT95/5 ceramics was attributed to domain switching and ferroelectric (FE) to antiferroelectric (AFE) phase transformation processes, which was verified by analyzing the anomalous behavior between axial strain and radial strain. Normalized critical stresses for the onset of domain switching as well as the onset and exhaustion of phase transformation resulted in a very similar linear decrease with increasing porosity. We suggest that a critical macroscopic volumetric strain is needed for the onset of phase transformation that is nearly independent of porosity.

Keywords: porous PZT95/5 ceramics; mechanical properties; domain switching and phase transformation; uniaxial compression.

1. Introduction

$\text{Pb}(\text{Zr}_{0.95}\text{Ti}_{0.05})\text{O}_3$ (PZT95/5) ceramic is an important ferroelectric material, which can exhibit a transformation from the FE phase to the AFE phase under a shock-wave compression to generate megawatts of pulse electrical power (Lysne, 1977; Setchell, 2005). It has been demonstrated that porous PZT95/5 ceramics is superior to dense PZT95/5 for preventing high-voltage breakdowns at low temperature during explosive shock wave loading (Dungan and Storz, 1985). Since then, more attention has been paid to study the mechanical and electrical properties of porosity-controlled PZT95/5 ceramics. Tuttle et al. (2001) found that the hydrostatic FE-AFE transformation stress decreased with increasing porosity for PZT95/5 ceramics. Yang et al. (2003) investigated the effect of pore type and density on the depoling behavior of PZT95/5 ceramics subjected to hydrostatic pressure loading. Wang et al. (2013) studied the dielectric, ferroelectric and piezoelectric properties and fracture toughness of MgO nanoparticles-reinforced porous PZT95/5 ceramics. Setchell (2007) and Feng et al. (2010) investigated the effects of the microstructure and porosity on the response of PZT95/5 ceramics under shock wave compression.

Previous work is almost exclusively concerned the behavior of porous PZT95/5 ceramics under the hydrostatic pressure loading or shock wave compression loading. However, relatively few results have been reported concerning the mechanical response of porous PZT95/5 under static conditions of uniaxial compressive stress. In this paper, unpoled PZT95/5 ceramics as a function of systematic changes in porosity with controlled pore sizes and pore shapes were prepared by sintering compacts

consisting of PZT and pore formers. We present the results of a variety of quasi-static uniaxial compression experiments done on porous PZT95/5 ceramics and emphasize the importance of domain switching and phase transformation effects on the nonlinear stress-strain data. We then explore the porosity dependence of the critical stresses of domain switching, phase transformation and the parameters of basic mechanical properties.

2. Experimental Procedure

2.1 Materials and Sample Preparation

Porous PZT 95/5 ceramics were fabricated by mixing PZT powders with pore formers of polymethyl methacrylate (PMMA, $(C_5H_8O_2)_n$) (Zeng et al. 2007). The mixed powders were PZT+ α PMMA, where $\alpha=0, 1, 2$ and 3 wt.%, respectively. The size of spherical PMMA was about $30\text{ }\mu\text{m}$. The mixed powders were ball-milled for 6 h with zirconia balls as the grinding medium and alcohol as the solvent. After milling, the slurry was dried at $100\text{ }^\circ\text{C}$ for 24 hours, and the powders were mixed with 6 wt% PVA as an adhesive. The mixed powder was pressed at about 200 MPa with a 9 mm column with a height of 8 or 14 mm. The samples were heated to 850°C to remove the PMMA and sintered in a sealed alumina crucible at $1300\text{ }^\circ\text{C}$ for 2 h under a PbO-rich atmosphere to minimize the lead loss during sintering. The sintered porous PZT 95/5 ceramics without poling treatment were processed into columns with a diameter of 6 mm and a height of 12 mm.

The bulk density (ρ_b) is measured using the Archimedes method, and the porosity of the sample is calculated using the ratio of the bulk density to theoretical density ($\rho_t = 8.08\text{ g/cm}^3$). Figures 1(a)-1(d) illustrate the microstructures of porous unpoled PZT95/5 ceramics as a function of PMMA content observed with scanning electron microscopy (SEM) at $500\times$. Evenly distributed spherical

pores with approximately the same diameter are formed in the porous PZT95/5 ceramics after sintering by adding pore formers. The porosity of PZT95/5 was determined via the content of the pore formers. The pore shape and size are held as constant as far as possible to ensure a good correlation between the porosity and the mechanical response.

Fig.1 SEM micrographs of unpoled PZT 95/5 ferroelectric ceramics with different porosities: (a) 0 wt. % PMMA; (b) 1 wt. % PMMA; (c) 2 wt.% PMMA; and (4) 3 wt. % PMMA.

2.2 Testing Setup

Quasi-static compressive tests of unpoled porous PZT95/5 ceramics were performed on a servo-hydraulic MTS 810 universal test machine. For brittle PZT95/5 ceramics, accurate strain

measurements in compression are particularly difficult because the specimens are relatively small cylinders ($\phi 6 \text{ mm} \times 12 \text{ mm}$)—this requires special extensometers or bonded-on strain gauges that are cumbersome to handle and provide limited test data and require a highly skilled operator. Thus, the digital image correlation (DIC) technique is used to accurately measure the small compression strain on PZT95/5 ceramic specimens. A comprehensive review of the DIC technique was written by Sutton et al. (2009). The schematic graph of the experimental setup for uniaxial compression testing with DIC technique is shown in Figure 2. Polished tungsten-carbide (TC) inserts were used to avoid damage of the loading faces due to the high hardness of PZT95/5 ceramic. A commercial VIC-2D software (Correlated Solutions, Inc.) and 2D measurement system with a single camera was used to obtain the full-field strain of PZT95/5 ceramic specimens. A digital camera is used to capture gray-scale images of a random surface pattern. Image recording is done simultaneously with acquisition of the analog inputs from the test machine (e.g. force and displacement signal).

Fig.2 The schematic graph of the experimental setup for uniaxial compression testing

3. Results and Discussion

3.1 Nonlinear stress-strain characteristics

Typical compressive stress- strain curves of unpoled PZT95/5 samples with different porosities are shown in Figs. 3. These are strongly affected by porosity. For all of these tests, the data were taken as a function of increasing stress up to the fracture point. Thus, we did not obtain any data as a function of decreasing stress. As seen in Fig. 3, the stress-strain response of the porous PZT95/5 ceramics exhibits three distinct regimes.

Fig.3 Typical stress-strain curves of unpoled PZT95/5 ceramics with different porosities

At small loads, the compressive strain depends linearly on stress. With increasing loads, the relationship of stress versus strain is nonlinear, and a long approximate plateau region is formed. The third regime in the stress-strain response is truncation of the plateau region and a rapid linear rise in stress with further strain. This anomalous nonlinear behavior of porous PZT95/5 ceramics is very similar to the response of metal foams. It is well known that the macroscopic nonlinear deformation behavior of metal foams corresponds to the deformation, collapse, and densification of voids (Andrews et al., 1999). On the other hand, voids are well known to give noticeable plastic

deformability in high-strength metallic glasses (Wada et al., 2005). Therefore, we first suspect that nonlinear stress-strain curves of porous PZT95/5 ceramics is attributed to the evolution of voids. However, the SEM micrograph of the longitudinal section of the non-destructive post-compressed PZT95/5 sample with a porosity of 14.6% is shown in Fig. 4. This shows that no visible deformation and collapse of voids are detected inside the sample. This demonstrates that the nonlinear response of porous PZT95/5 ceramics is not directly related to collapse of the voids.

Fig.4 SEM micrograph of longitudinal section of non-destructive post-compressed PZT95/5 sample with 14.6% porosity

3.2 Domain switching and phase transformation characteristics

It is well known that nonlinear dependence of stress on strain for dense PZT ceramics is due to stress-induced domain switching process (Schäufele et al., 1996; Forrester and Kisi, 2004; Jones et al., 2007; Okayasu et al., 2011). Nevertheless, for porous PZT95/5 ceramics, the stress-strain curves as shown in Fig. 3 have additional complexities that cannot be attributed to domain switching alone. In our tests, the axial strain ε_a and radial strain ε_r of the sample surface can be measured simultaneously via DIC method. The volume strain can also be calculated from axial and radial strain

($\varepsilon_v = \varepsilon_a + 2\varepsilon_r$). Representative plots of radial strain versus axial strain and axial stress versus axial strain for porous unpoled PZT95/5 ceramics with 5.4% porosity are shown in Fig. 5. The short dash line with arrows is used to indicate that which dataset is using which axis.

Fig.5 The curves of radial strain, axial stress vs. axial strain and axial stress vs. volume strain

Initially, the radial strain decreases linearly with axial strain (designated by line AB in Fig. 5). The Poisson's ratio of unpoled PZT95/5 ceramic can be directly measured from the slope of line AB. Roughly concurrent with this, the axial stress exhibits a linear increase with increasing axial strain (designated by line A'B' in Fig. 5), and the elastic modulus E can be directly measured from the slope of line A'B'. This gives the expected linear elastic response of unpoled PZT95/5 ceramics in the ferroelectric phase. After exceeding point "B," the radial strain departs sharply from linearity—this is attributed to the onset of significant amounts of domain switching. The stress corresponding to B in Fig. 5 can be defined as the critical stress (σ_{ds}) required to initiate domain switching. However, the radial strain subsequently reverses from tensile (-) to compressive (+) strain at point "C." This means that the sample is cross-contracting. Such anomalous behavior is not consistent with any reasonable

domain switching mechanism because domain switching is an isovolumetric process and should result in anomalously exaggerated radial tensile strains—not their anomalous reversal.

The FE-AFE transformation of PZT95/5 ceramics during hydrostatic compression is accompanied by a 0.7-0.8% volume decrease (Zeuch et al., 2000). Thus, we concluded that the anomalous volumetric compression and temporary reversal of the radial strains should correspond to the FE-AFE transformation of the PZT95/5 ceramics. The volumetric decreases associated with FE-AFE transformation can overwhelm the tensile radial strain associated with ordinary elastic and domain switching processes. This results in an anomalous radial contraction during uniaxial compression. Therefore, the nonlinear characteristics of axial stress versus axial strain (indicated by "BCD" in Fig. 5) are attributed to the mechanisms of domain switching and phase transition.

Nevertheless, it remains unclear how to distinguish the domain switching and phase transitions. Unlike the distinctive phase transformation shown in previous studies that discussed the hydrostatic compression test results, the axial stress above the σ_{ds} changes very gradually as the axial strain is increased (Fig. 5). The onset of FE-AFE phase transformation should occur before the first reversal of radial strain. The stress level required for phase transformation should be below the stress corresponding to the first reversal of radial strain indicated as σ_c . Thus, we speculated that the critical stress for the onset of phase transformation should be between σ_{ds} and σ_c . The domain switching in response to the stress should produce an extra increase in axial strain and an extra decrease in radial strain versus the normal elastic compression. Still, it should not produce measurable change in the volume compression. Therefore, the onset of phase transformation can be separated from the domain switching by comparing axial stress-volume strain data (Fig. 5) using the upper abscissa. The overall

linear trend of the volume strain is maintained until the phase transformation initiates at σ_{pt} (Fig. 5). Finally, the second reversal of the radial strain versus axial strain is observed (indicated by "D" in Fig. 5); subsequently, the radial strain decreases linearly with the axial strain again (indicated by "DE" in Fig. 5). Meanwhile, the linear elastic mechanical response of unpoled PZT95/5 ceramics in a AFE phase can be designated by "DE'" in Fig. 5. The stress corresponding to point "D" can be defined as the critical stress (called as σ_{pe}) needed to exhaust the FE-AFE transformation.

3.3 Porosity dependence of mechanical properties, domain switching and phase transformation behaviors

For every PZT95/5 sample, the bulk density ρ_b was determined by the Archimedes method, and the sample porosity was calculated from the ratio of the bulk density to the theoretical density ($\rho_t = 8.08 \text{ g/cm}^3$). The mechanical characteristics of the four PZT95/5 ceramics with average porosities of 5%, 8.6%, 14.6%, and 18.6% are shown in Figs. 6(a)-(d), respectively. Figs. 6(a)-(d) show that the repeatability of the stress-strain data is acceptable for brittle PZT95/5 ceramics at approximately the same porosity condition.

Fig.6 Stress versus strain curves of unpoled PZT95/5 with different average porosities:(a) ~5%; (b) ~8.6%; (c) ~14.6%; and (d) ~18.6%

Fig. 7 shows the average Young's modulus of unpoled PZT95/5 ceramics in the FE phase determined from the slope of the initial linear elastic data as a function of porosity. Nearly fifty years ago, Spriggs (1961) proposed that the porosity dependence of the elastic modulus for brittle solids could be written as:

$$E / E_0 = \exp(-bp), \quad (1)$$

where E is Young's modulus at a given volume fraction porosity p . Term E_0 is the value of E for theoretically dense materials, and b is a material-dependent constant. When bp is much lower than 1, the (1) can be approximated as:

$$E / E_0 = 1 - bp. \quad (2)$$

The parameters E_0 and b are 81.3 GPa and 0.03 for unpoled PZT95/5 ceramics. They were determined by the linear fit of the Young's modulus versus porosity data via Eq. (2) using porosity values from 5% to 18.6%, respectively. Another elastic constant, Poisson's ratio, of unpoled PZT95/5 ceramic was determined via the initial linear slope of the radial strain versus axial strain curve (Fig. 7). This indicates that the average Poisson's ratio increases gradually with porosity.

Fig.7 Young's modulus and Poisson's ratio as a function of porosity for unpoled PZT95/5 ceramics

Fig.8 Fracture strength and fracture strain as a function of porosity for unpoled PZT95/5 ceramics.

The compressive fracture strength and fracture strain of unpoled PZT95/5 ceramics versus porosity are shown in Fig. 8. From 5% to 18.6% porosity, the fracture strength decreases dramatically and linearly by roughly 70%. There is only a small reduction in fracture strain—this

indicates that the dispersed voids do not improve the plasticity of the unpoled porous PZT95/5 ceramics under static compression.

Finally, we examined the porosity dependence of the σ_{ds} , σ_{pt} , and σ_{pe} stresses, which are defined in Fig. 5 as the critical stress for the initiation of domain switching, the critical stress for onset of phase transformation, and the critical stress for the exhaustion of FE-AFE transformation, respectively. First, the σ_{ds} , σ_{pt} and σ_{pe} are normalized as a function of porosity by σ_{ds0} , σ_{pt0} and σ_{pe0} where σ_{ds0} , σ_{pt0} and σ_{pe0} are the values of σ_{ds} , σ_{pt} and σ_{pe} for theoretically dense ($p=0$) materials. These values were determined to be 117 MPa, 137 MPa, and 342 MPa via the linear fit of the σ_{ds} , σ_{pt} , and σ_{pe} versus porosity curves, respectively. The normalized σ_{ds} , σ_{pt} , and σ_{pe} with increasing porosity indicate very similar declining trends as shown in Fig.9. Therefore, a simple and universal formulation similar to Eq. (2) was used to describe the relationship between the normalized σ_{ds} , σ_{pt} , and σ_{pe} and porosity as follows:

$$\frac{\sigma_{ds}}{\sigma_{ds0}} = \frac{\sigma_{pt}}{\sigma_{pt0}} = \frac{\sigma_{pe}}{\sigma_{pe0}} = 1 - cp, \quad (3)$$

Here, c is a material-dependent constant. Using the linear fit of normalized σ_{ds} , σ_{pt} , and σ_{pe} versus porosity curves, parameter c is determined to be 0.023 with coefficients of determination (R^2) of 0.995. Tuttle et al.(2001) showed that the hydrostatic FE-to-AFE transformation stress σ_p decreased with increasing porosity for poled PZT95/5 ceramics. The normalized σ_p by σ_{p0} ($\sigma_{p0} = 356$ MPa) as a function of porosity shows a similar trend as our previous data also shown in Fig. 9. They attributed the decrease in σ_p to a decrease in the bulk modulus. They further proposed a macroscopic volumetric strain (ε_{mv}) criterion for the FE-to-AFE transformation. Thus, similar to Tuttle et al., we measured the critical ε_{mv} corresponding to the σ_{pt} (critical stress for onset of phase transformation).

The critical ε_{mv} as a function of porosity is shown in Fig. 10. We show experimentally that the critical ε_{mv} under uniaxial compression is almost independent of porosity. This feature of critical ε_{mv} values independent of porosity is consistent with Tuttle et al.(2001) under hydrostatic compression. The average critical ε_{mv} for unpoled PZT95/5 ceramics is 0.114%, which is much smaller than the value (0.4%) obtained for poled PZT95/5 ceramics under hydrostatic compression. This difference is mostly due to the different definitions of FE-to-AFE transformation stress. The transformation stress is defined as the stress for which half the total charge has been released or at which half of the population of the FE crystallites transform into the AFE phase by Tuttle et al.(2001). This corresponds well with the stress between σ_{pt} and σ_{pe} as well as corresponding to the first reversal of radial strain indicated as σ_c . The ε_{mv} corresponding to σ_c is 0.4% (Fig. 5). This is in reasonable agreement with the value (0.4%) obtained by Tuttle et al.(2001).

Fig.9 The curve of normalized σ_{ds} , σ_{pt} and σ_{pe} versus porosity

Fig.10 The critical ε_{mv} as a function of porosity

4. Conclusions

The effects of porosity on the nonlinear mechanical behavior, domain switching and phase transformation of unpoled PZT 95/5 ceramics were investigated under uniaxial compression. The measured stress versus strain curves for porous unpoled PZT95/5 ceramics can be divided into three stages: the initial linear elastic region, the approximate plateau region, and the second linear elastic region. These correspond to elastic deformation of unpoled PZT95/5 ceramics in ferroelectric phase, domain switching and FE-to-AFE phase transformation processes, and the elastic deformation of unpoled PZT95/5 ceramics in the antiferroelectric phase, respectively.

The Young's modulus and fracture strength linearly decrease with increasing porosity, but Poisson's ratio and fracture strain are seldom dependent on porosity. Normalized critical stresses decrease linearly with increasing porosity. This can be described by a simple universal formulation. The macroscopic volumetric strain of triggering phase transformation is independent of porosity.

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References

- Andrews, E., Sanders, W., and Gibson, L.J., 1999. Compressive and Tensile Behavior of Aluminum foams, *Materials Science and Engineering A* 279,113-124.
- Dungan, R.H., Storz, L.J., 1985. Relation between chemical, mechanical, and electrical properties of Nb₂O₅-modified-95Mol% PbZrO₃-5Mol% PbTiO₃. *Journal of the American Ceramic Society* 68(10), 530-533.
- Forrester, J.S., Kisi, E.H., 2004. Ferroelastic switching in a soft lead zirconate titanate. *Journal of the American Ceramic Society* 24,595-602.
- Jones, J.L. Hoffman, M., Vogel, S.C., 2007. Ferroelastic domain switching in lead zirconate titanate measured by in situ neutron diffraction. *Mechanics of Materials* 39,283-290.
- Feng, N.B., Nie, H.C., Chen, X.F., Wang, G.S., Dong, X.L., He, H.L., 2010. Depoling of porous Pb_{0.99}(Zr_{0.95}Ti_{0.05})_{0.98}Nb_{0.02}O₃ ferroelectric ceramics under shock wave load. *Current Applied Physics* 10, 1387-1390.
- Lysne P.C., 1977. Dielectric properties of shock-wave-compressed PZT95/5. *Journal of Applied Physics* 48,1020-1023.
- Okayasu, M., Sato,K., Kusaba,Y., 2011. Domain switching characteristics of lead zirconate titanate piezoelectric

ceramics during mechanical compressive loading. *Journal of the European Ceramic Society* 31,129-140.

Schäufele, A.B., Härdtl, K.H., 1996. Ferroelectric properties of lead zirconate titanate Ceramics, *Journal of the American Ceramics Society* 79(10), 2637-2640.

Setchell, R.E., 2007. Shock wave compression of the ferroelectric ceramic $\text{Pb}_{0.99}(\text{Zr}_{0.95}\text{Ti}_{0.05})_{0.98}\text{Nb}_{0.02}\text{O}_3$: microstructural effects. *Journal of Applied Physics* 101,053525.

Setchell, R.E., 2005. Shock wave compression of the ferroelectric ceramic $\text{Pb}_{0.99}(\text{Zr}_{0.95}\text{Ti}_{0.05})_{0.98}\text{Nb}_{0.02}\text{O}_3$: Depoling currents. *Journal of Applied Physics* 97, 013507.

Spriggs, R.M., 1961. Expression for Effect of Porosity on Elastic Modulus of Polycrystalline Refractory Materials, Particularly Aluminum Oxide. *Journal of the American Ceramics Society* 44 (1961) 628-629.

Sutton, M.A. Ortu, J.J., Schreier, H.W. 2009. *Image Correlation for Shape, Motion, and Deformation Measurements*, Springer, New York, USA.

Tuttle, B.A., Yang, P., Gieske, J.H., Voigt, J. A., Scofield, T.W., Zeuch, D.H., and Olson, W.R., 2001. Pressure-Induced Phase Transformation of Controlled-Porosity $\text{Pb}(\text{Zr}_{0.95}\text{Ti}_{0.05})\text{O}_3$ Ceramics, *Journal of the American Ceramics Society* 84(6),1260-64.

Wada, T., Inoue, A., and Greer, A.L., 2005. Enhancement of Room-Temperature Plasticity in a Bulk Metallic Glass by Finely Dispersed Porosity. *Applied Physics Letter* 86, 251907.

Wang, J.X., Nie, H.C., Chen, C.F., Wang, G.S., Dong, X.L., Chen, X.F., Cao, F., He, H.L., 2013. Microstructure, electrical and mechanical properties of MgO nanoparticles-reinforced porous PZT95/5 ferroelectric ceramics. *Ceramics International* 39, 3915-3919.

Yang, P., Moore, R.H., Lockwood, S.J., Tuttle, B.A., Voigt, J. A., Scofield, T.W., 2003. Chem-Prep PZT95/5 for Neutron Generator Application: The Effect of Pore Former Type and Density on the Depoling Behavior of

Chemically Prepared PZT95/5 Ceramics, Sandia Report SAND2003-3866, Sandia National Laboratories, Albuquerque, NM.

Zeng, T., Dong, X.L., Chen, S.T., Yang, H., 2007. Processing and piezoelectric properties of porous PZT ceramics, Ceramics International 33, 395-399.

Zeuch, D.H., Montgomery, S.T., Holcomb, D.J., 2000. Uniaxial compression experiments on lead zirconate titanate 95/5-2Nb ceramic: Evidence for an orientation-dependent, "maximum compressive stress" criterion for onset of the ferroelectric to antiferroelectric polymorphic transformation. Journal of Material Research 15(3), 689-703.