

# Effects of pore shape and porosity on the properties of porous PZT 95/5 ceramics

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## Abstract

Porous lead zirconate titanate (PZT 95/5) ferroelectric ceramics were prepared by sintering compacts consisting of PZT and pore formers. The piezoelectric, dielectric and ferroelectric properties of porous PZT ceramics were investigated as a function of pore shape and porosity. Piezoelectric coefficient ( $d_{33}$ ), dielectric constant ( $\epsilon_{33}$ ) and remnant polarization ( $P_r$ ) decreased with an increase in porosity, and the porous PZT ceramics with spherical pores exhibited better properties than that with irregular pores. Furthermore, the electrical conductivities of PZT ceramics were investigated to explain the phenomena that porous PZT ceramics exhibited lower dielectric loss ( $\tan \delta$ ) than dense PZT ceramics in the temperature range from 250 to 500 °C.

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**Keywords:** PZT; Dielectric properties; Ferroelectric properties; Porosity

## 1. Introduction

PZT 95/5 ferroelectric ceramic which consist of about 95 mol% lead zirconate and 5 mol% lead titanate along with minor additions of niobia has been largely used in explosively driven power supplies for they can enforce a ferroelectric-to-antiferroelectric (FE–AFE) phase transformation driven by an explosive shock wave and release all the bound charge to generate megawatts of electrical power in a short period of time.<sup>1–5</sup> For high-voltage power supplies, as long as the shock wave has enough strength to induce phase transition, all the bound charge will release,<sup>6,7</sup> so a substantial high voltage will appear across the PZT 95/5 ceramic, which often lead to breakdowns in PZT 95/5 ferroelectric ceramics.

According to the viewpoint from Dungan and Storze,<sup>8</sup> many of the observed dielectric breakdowns are preceded by mechanical failure for they observed that fewer high-voltage breakdowns appeared for the materials with higher fracture toughness during functional explosive tests. The stresses occur under the

shock compression, which induce cracks in the PZT 95/5 ceramics to cause mechanical failure by rapid crack propagation.<sup>9</sup> Mechanical failure results in dielectric breakdowns by emitting charged particles, neutral molecules as well as ions and forming short circuit. However, compared with dense materials, porous materials have been testified more efficiently to buffer shock compression,<sup>10</sup> so porous PZT 95/5 ceramics can eliminate the probability of dielectric breakdowns under the shock compression. Porous PZT ceramics with different pore shape and porosities can be fabricated by burning pore formers with different shapes and contents<sup>11–13</sup> during the sintering process. Sandia National Lab<sup>7</sup> has demonstrated that porous ceramics helped prevent high-voltage breakdowns at low temperature during explosive shock wave transformation, and they<sup>14,15</sup> has also investigated the effects of porosity and pore shape on the hydrostatic FE–AFE transformation of porous PZT 95/5 ceramics. However, there are relative few results concerning the effects of porosity and pore shape on electrical properties of porous PZT 95/5 ceramics. The electrical properties of porous PZT 95/5 ceramics including ferroelectric, dielectric and electrical conductive properties are very important for applications. In our present work, we investigated the effect of porosity and pore shape on the properties of porous PZT 95/5 ceramics and found that porous PZT 95/5 ceramics can help to enhance electrical

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resistant and eliminate dielectric loss during the temperature from 250 to 500 °C, which have never been reported to our knowledge. These results showed resistance of ceramics in high temperature can be enhanced by inducing pore, which may be great helpful to the high-temperature application of ceramics such as bismuth layer-structured ferroelectric ceramics (BLSF).

## 2. Experimental

PZT 95/5 ceramics were prepared by solid-state reaction sintering and the designed compositions were  $\text{Pb}(\text{Zr}_{0.965}\text{Ti}_{0.035})\text{O}_3 + 1 \text{ wt.}\% \text{Nb}_2\text{O}_5$ . The starting raw materials used were  $\text{Pb}_3\text{O}_4$  of 97.33% purity,  $\text{TiO}_2$  of 99.44% purity,  $\text{ZrO}_2$  of 99.09% purity and  $\text{Nb}_2\text{O}_5$  of 99.86% purity. The porous PZT 95/5 ceramics were fabricated by mixing PZT powders with pore formers such as polymethyl methacrylate (PMMA ( $\text{C}_5\text{H}_8\text{O}_2$ ) $_n$ ) and dextrin ( $(\text{C}_6\text{H}_{10}\text{O}_5)_n \cdot x\text{H}_2\text{O}$ ). The mixed powders were PZT +  $\alpha$ PMMA and PZT +  $\beta$ dextrin, respectively, where  $\alpha = 0, 0.9, 1.5, 2.1, 2.7$ , and  $\beta = 0, 0.9, 1.8, 2.7, 3.6$ , and  $4.5 \text{ wt.}\%$ . The size of PMMA with irregular shape was between 100 and 120  $\mu\text{m}$ , while the size of PMMA with spherical shape and the size of dextrin with irregular shape were about 15  $\mu\text{m}$ . The mixed powders were ball milled for 6 h with zirconia balls as the grinding media and alcohol as the solvent. After milling, the slurry was dried at room temperature and then the powders were mixed with 5 wt.% PVA liquid addition. The mixed powder was pressed at about 200 mPa to  $\varnothing 16 \text{ mm}$  disks. The samples were heating up to 850 °C to assure the complete burn out of PMMA and dextrin. The compacts were sintered in a sealed alumina crucible at 1300 °C for 2 h under a PbO-rich atmosphere to minimize the lead loss during sintering. The sintered samples were ground to remove the surface layers, evaporated with silver electrodes in vacuum, and poled by applying a dc field of 3–4 kV/mm for 10 min in a silicone oil bath at 120 °C. Bulk density ( $\rho_b$ ) was determined by the Archimedes method, and the porosity of sample was calculated from the ratio of the bulk density to the theoretical density ( $\rho_t = 8.08 \text{ g/cm}^3$ ).

The sintered samples were analyzed by X-ray diffraction (D/max2550V, Rigaku, Japan) using Cu K $\alpha$  radiation with a step scan of 0.02° from 10° to 70°. The microstructures of pore formers and porous PZT ceramics were observed by scanning electron microscopy (SEM; Model JSM6700F, JEOL, Tokyo, Japan). The piezoelectric charge coefficient ( $d_{33}$ ) was measured by a direct method based on a Quasi-static  $d_{33}$ -meter (Model ZJ-3, Institute of Acoustics, Chinese Academy of Science). An LCR meter (Model HP 4284A) was used to measure the dielectric constant and dielectric loss at 1 kHz in the temperature range from room temperature to 500 °C. To investigate the effects of porosity and temperature on conductivity, the resistances were characterized during the temperature from 250 to 500 °C with a heating rate of 5 °C/min using a high-resistance meter (Model HP4329A) with applied voltages of 10, 25, 50, and 100 V. Each measurement was performed after stabilizing the temperature of the sample for about 30 min. The Young's modulus was determined from the values of resonance and anti-resonance frequencies measured by HP 4294A impedance bridge.

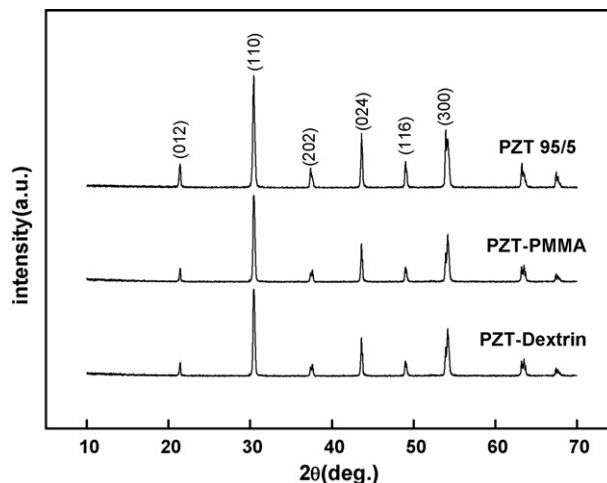


Fig. 1. XRD pattern of the sintered PZT 95/5 ceramics.

## 3. Results and discussion

### 3.1. Phase analysis and microstructures

Fig. 1 shows the XRD patterns of the PZT, PZT–dextrin and PZT–PMMA ceramics sintered at 1300 °C for 2 h. It is noted that single perovskite structure were exhibited for all the sintered ceramics. No other phase was detected. The porosity of porous PZT as a function of the content of pore formers is shown in Fig. 2. The porosity increased with an increase in the content of pore formers at a fixed sintering temperature, showing that porosity is determined by the content of pore formers. Fig. 3 shows the scanning electron microscopy (SEM) images of pore formers and porous PZT ceramics. It can be seen that for all the porous materials, macropores were formed in the ceramics after sintering, and the pore shape and sizes of porous PZT ceramics are determined by the shape and sizes of pore formers. The microstructure observations demonstrate that the porosity, pore shape, and pore sizes can be controlled by adding pore formers.

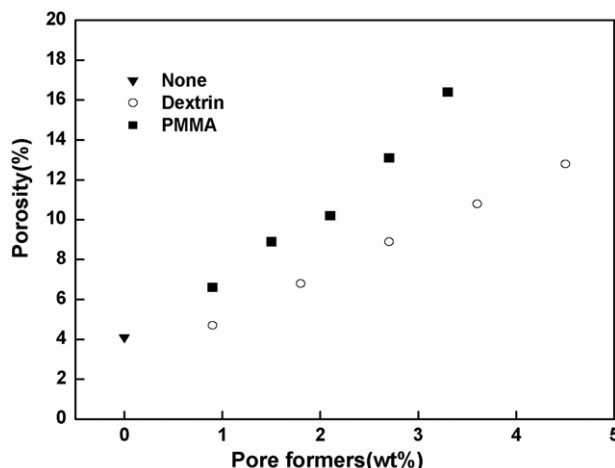


Fig. 2. Porosity of porous PZT as a function of the content of pore formers.

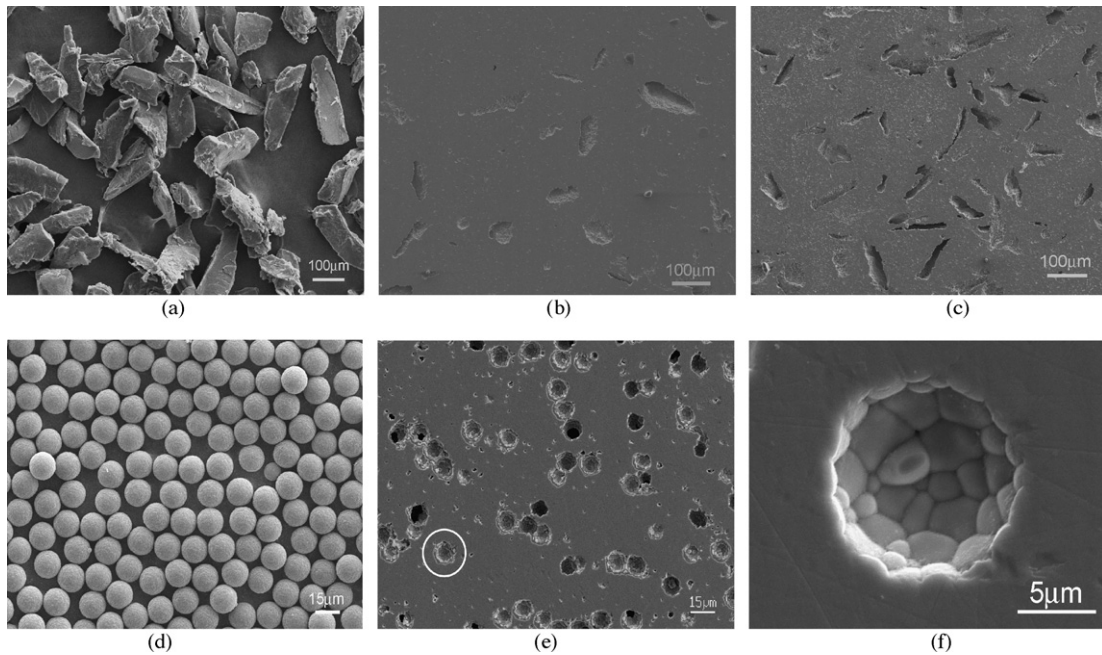


Fig. 3. SEM micrographs of porous PZT 95/5 ceramics: (a) PMMA with irregular shape; (b) PZT with irregular pores, porosity: 8.9%; (c) PZT with irregular pores, porosity: 16.4%; (d) PMMA with spherical shape; (e) PZT with spherical pores, porosity: 14.7%; (f) magnified microstructure of spherical pore.

### 3.2. Mechanical, piezoelectric and ferroelectric properties

Fig. 4 shows the Young's modulus of PZT 95/5 ceramics as a function of porosity. The Young's modulus decreased almost linearly with increasing porosity. Compared with porous PZT with irregular pores, the porous PZT ceramics with spherical pores have relative higher figures of Young's modulus. As for porous PZT ceramics with irregular pores, the stress will be amplified or concentrated at the tip of irregular pore,<sup>16</sup> which led to a low Young's modulus.

The amplified or concentrated stress near the pores leads to an increase in microscopic stress and strain,<sup>16</sup> which indicates an increased stress due to an increased volume fraction of pores in the porous PZT ceramics. An increased stress can

affect piezoelectric coefficient by inhibiting the movement of domain walls and decreasing grain size. According to the space-charge theory from Okazaki,<sup>17</sup> there are a certain amount of space-charge sites such as lattice vacancies or impurity atoms bounding inside grain boundaries and domain walls and forming the space-charge fields which inhibit the movement of domain walls. As the grain size increases, the surface area of the space-charge layers increase, thus the space-charge fields increase simultaneously. So the piezoelectric coefficient ( $d_{33}$ ) and remnant polarization decreased with increasing porosity and the porous PZT ceramics with spherical pores have relative higher piezoelectric coefficient and remnant polarization than that of porous PZT ceramics with irregular pores as seen from Fig. 5 and Fig. 6.

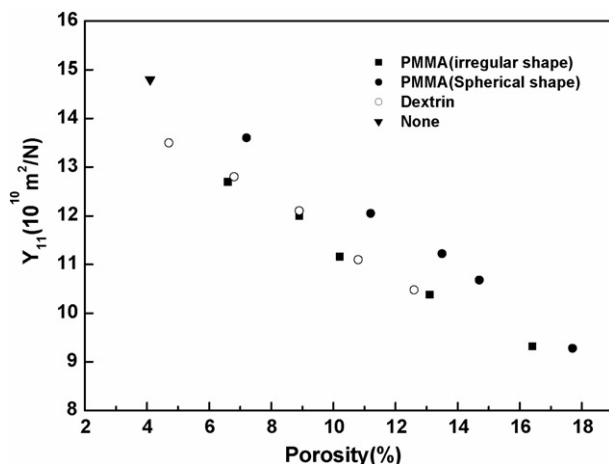


Fig. 4. Young's modulus of PZT 95/5 ceramics as a function of porosity.

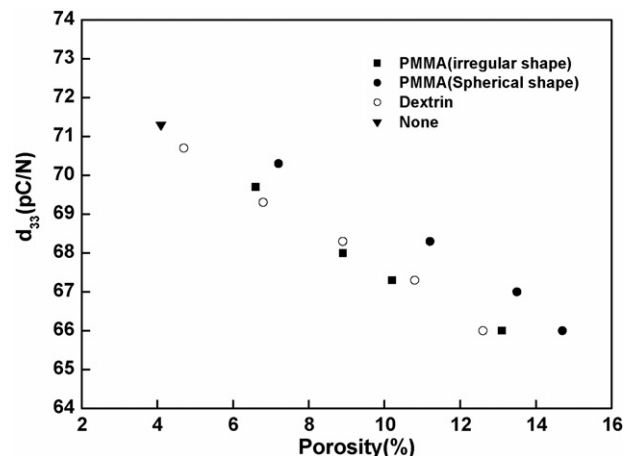


Fig. 5. Piezoelectric coefficient ( $d_{33}$ ) of PZT 95/5 ceramics as a function of porosity.

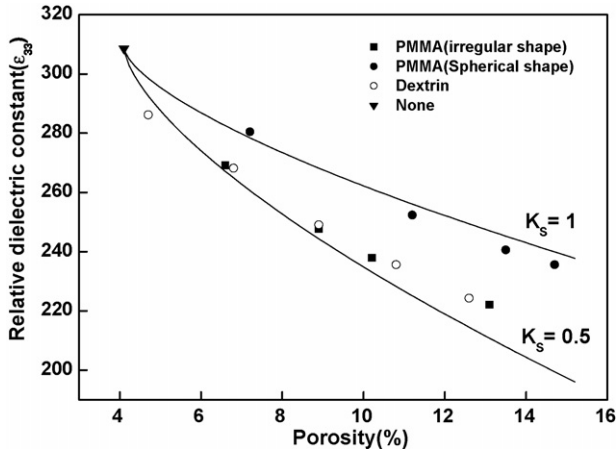


Fig. 6. Dielectric constant of PZT 95/5 ceramics as a function of porosity. The lines are the predicted values from Eq. (1) for two typical shapes of pores.

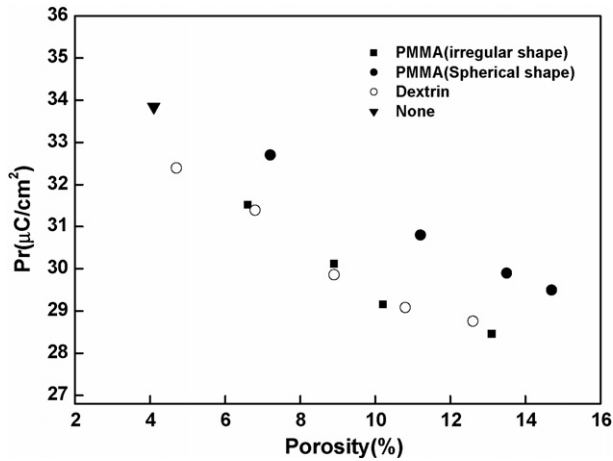


Fig. 7. Remnant polarization of PZT 95/5 ceramics as a function of porosity.

### 3.3. Dielectric properties and electrical conductivities

Fig. 7 shows that the dielectric constant of all the porous ceramics decreased with increasing porosity. Similar values are observed for the porous PZT ceramics with irregular pores (PMMA and dextrin) but the porous PZT ceramics with spherical pore exhibit a higher dielectric constant, which can be modeled

by the following equation:<sup>18</sup>

$$\varepsilon_{33}^* = \varepsilon_{33} \left[ 1 + \frac{1}{p^{1/3}(\varepsilon_{33}/\varepsilon_0 - 1)K_s^{2/3} + 1} \frac{p^{2/3}}{K_s^{2/3}} - \frac{p^{2/3}}{K_s^{2/3}} \right] \quad (1)$$

where  $p$  is porosity and  $K_s$  a parameter determined by the shape of a pore. For a spherical pore,  $K_s = 1$ ; for an oval pore,  $K_s = 0.5$ . As shown in Fig. 7, the measured dielectric constant of the porous PZT ceramics with irregular pore and spherical pores were located around the two predicted bounds for  $K_s = 0.5$  and 1.0, respectively. It was also observed that with increasing porosity the dielectric constant of porous PZT with spherical pores and irregular pores became gradually away from the predicted bounds. The possible reasons may be the incorporation of spherical pores into irregular pores and the coexistence of intrinsic and extrinsic pores. As we all know, the shape of intrinsic pore is almost spherical, so the  $K_s$  value of intrinsic pore is between 0.5 and 1.

Fig. 8(a) shows the dielectric constant of PZT ceramics as a function of temperature and porosity. From the maximum peak of the dielectric constant, Curie point  $T_c$  was obtained to be about 220 °C for both dense and the porous PZT ceramics. The maximum peak of dielectric constant decreases with increasing porosities. The dielectric loss increased slowly and then sharply with increasing temperature as seen from Fig. 8(b). It was also found that the porous PZT ceramics exhibited lower dielectric loss than dense PZT ceramics during the temperature from 250 to 500 °C, which can be explained by following equation:

$$\tan \delta = \frac{\sigma}{\omega C} \quad (2)$$

where  $\sigma$  is dc electrical conductivity,  $\omega$  the frequency,  $C$  is the capacitance. It is unclear why the porous PZT ceramics exhibited lower dielectric loss than dense PZT ceramics in the temperature range from 250 to 500 °C, but one possible reason may be related to the fact that the porous PZT ceramics have lower values of conductive than dense PZT ceramics, as shown in Fig. 9. We all know that carriers in PZT ceramics move faster with increasing temperature, which led to an increase in conductivity. As for porous PZT ceramics, pores will inhibit the movement of

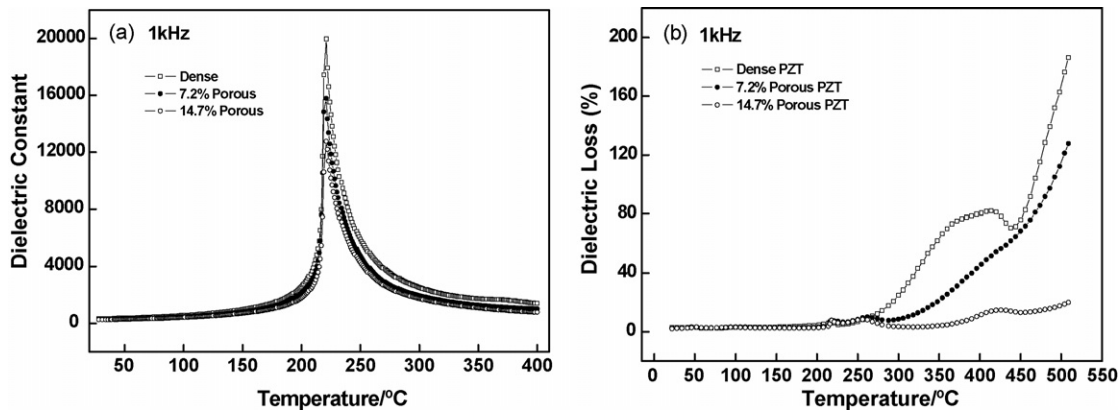


Fig. 8. Dielectric constant and dielectric loss of PZT 95/5 ceramics as a function of temperature and porosity: (a) dielectric constant and (b) dielectric loss.

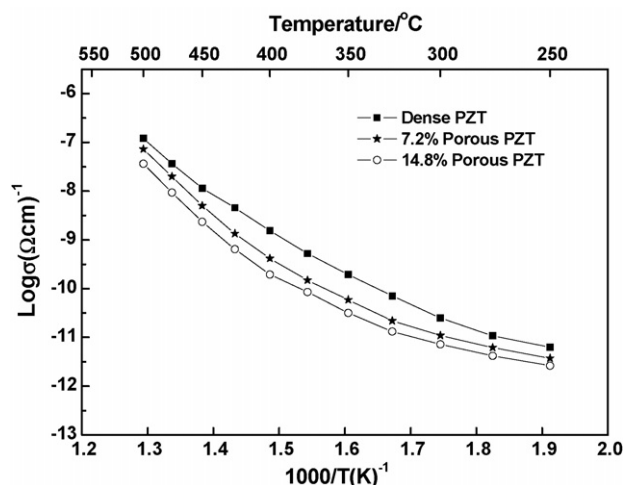


Fig. 9. The dc conductivity of PZT 95/5 ceramics as a function of temperature.

carriers, so porous PZT ceramics have lower conductivity when compared with dense PZT ceramics.

#### 4. Conclusions

Porous PZT 95/5 ceramics with different pore shape and porosity have been prepared by adding different kinds of pore formers such as dextrin and polymethyl methacrylate (PMMA) with different shape and sintered at 1300 °C over a range of porosity (5–15%). The effects of pore shape and porosity on the properties of porous PZT ceramics were investigated. The porosity increased with an increase in the content of pore formers, and the increased porosity led to a decrease in the Young's modulus, piezoelectric coefficient, dielectric constant, and remnant polarization. For the PMMA and dextrin-based PZT ceramics with irregular pores, no significant difference in properties was observed even though their pore size is different. Compared with porous PZT with irregular pore, porous PZT with spherical pores exhibited better properties including piezoelectric, dielectric and ferroelectric properties due to lower stress. The porous PZT ceramics exhibited high resistance and lower dielectric loss than dense PZT ceramics during the temperature from 250 to 500 °C, which may be great helpful to the high-temperature application of ceramics such as bismuth layer-structured ferroelectric ceramics (BLSF).

#### References

1. Neilson, F. W., Effects of strong shocks in ferroelectric materials. *Bull. Am. Phys. Soc.*, 1957, **2**, 302.
2. Dungan, R. H., Barnett, H. M. and Stark, A. H., Phase relations and electrical parameters in the ferroelectric–antiferroelectric region of the system  $\text{PbZrO}_3\text{–PbTiO}_3\text{–PbNbO}_6$ . *J. Am. Ceram. Soc.*, 1962, **45**, 382–388.
3. Berlincourt, D., Jaffe, H., Krueger, H. H. A. and Jaffe, B., Release of electric energy in  $\text{PbNb}(\text{Zr}, \text{Ti}, \text{Sn})\text{O}_3$  by temperature and by pressure enforced phase transitions. *Appl. Phys. Lett.*, 1963, **3**, 90–92.
4. Lysne, P. C., Dielectric properties of shock-wave-compressed PZT 95/5. *J. Appl. Phys.*, 1977, **48**, 1020–1023.
5. Lysne, P. C., Shock-induced polarization of a ferroelectric ceramic. *J. Appl. Phys.*, 1977, **48**, 1024–1031.
6. Lysne, P. C. and Percival, C. M., Electric energy generation by shock compression of ferroelectric ceramics: normal-mode response of PZT 95/5. *J. Appl. Phys.*, 1975, **46**, 1519–1525.
7. Setchell, R. E., Shock wave compression of the ferroelectric ceramic  $\text{Pb}_{0.99}(\text{Zr}_{0.95}\text{Ti}_{0.05})_{0.9}\text{Nb}_{0.02}\text{O}_3$ : hugoniot states and constitutive mechanical properties. *J. Appl. Phys.*, 2003, **94**, 1519–1525.
8. Dungan, R. H. and Storze, L. J., Relation between chemical, mechanical and electrical properties of  $\text{Nb}_2\text{O}_5$ -modified 95 mol%  $\text{PbZrO}_3$ –5 mol%  $\text{PbTiO}_3$ . *J. Am. Ceram. Soc.*, 1985, **68**, 530–533.
9. Wang, H. Y. and Singh, R. N., Crack propagation in piezoelectric ceramics: effects of applied electric fields. *J. Appl. Phys.*, 1997, **81**, 7471–7479.
10. Herrman, W., Constitutive equation for the dynamic compaction of ductile porous materials. *J. Appl. Phys.*, 1969, **40**, 2490–2499.
11. Lyckfeldt, O. and Ferreira, J. M. F., Processing of porous ceramics by 'starch consolidation'. *J. Eur. Ceram. Soc.*, 1998, **184**, 134–140.
12. Dunn, M. and Minoru, T., Electromechanical properties of porous piezoelectric ceramics. *J. Am. Ceram. Soc.*, 1993, **76**, 1697–1706.
13. Li, J. F., Kenta, T., Masaru, O., Wei, P. and Ryuzo, W., Fabrication and evaluation of porous piezoelectric cCeramics and porosity-graded piezoelectric actuators. *J. Am. Ceram. Soc.*, 2003, **86**, 1094–1098.
14. Tuttle, B. A., Yang, P., Gieske, J. H., Voigt, J. A., Scofield, T. W., Zeuch, D. H. and Olson, W. R., Pressure-induced phase transformation of controlled-porosity  $\text{Pb}(\text{Zr}_{0.95}\text{Ti}_{0.05})\text{O}_3$  ceramics. *J. Am. Ceram. Soc.*, 2001, **84**, 1260–1264.
15. Yang, P., Moore, R. H. and Lockwood, S. J., Chem-Prep PZT 95/5 for neutron generator applications: the effect of pore former type and density on the depoling behavior of chemically prepared PZT 95/5 ceramics. Sandia Report SAND2003-3866, Sandia National Laboratories, Albuquerque, NM, 2003.
16. Carroll, M. M. and Holt, A. C., Static and dynamic pore-collapse for ductile porous materials. *J. Appl. Phys.*, 1972, **43**, 1626–1635.
17. Okazaki, K. and Nagata, K., Effects of grain size and porosity on electrical and optical properties of PLZT ceramics. *J. Am. Ceram. Soc.*, 1973, **56**, 82–86.
18. Banno, H., Effects of shape and volume fraction of closed pores on dielectric, elastic, and electromechanical properties of dielectric and piezoelectric ceramics—a theoretical approach. *Am. Ceram. Soc. Bull.*, 1987, **66**, 1332–1337.