

Measurements of the thermal, dielectric, piezoelectric, pyroelectric and elastic
properties of porous PZT samples

Sidney B. Lang

Dept. of Chemical Engineering, Ben-Gurion University of the Negev, 84105 Beer
Sheva, Israel

Erling Ringgaard

Meggitt Sensing Systems, Hejreskovvej 18A, DK-3490 Kvistgård, Denmark

The introduction of porosity into ferroelectric ceramics has been of great interest in recent years. In particular, studies of porous lead-zirconate-titanate ceramic (PZT) have been made. In the research reported, samples of Ferroperm Pz27 with porosities of 20, 25 and 30% were studied. Very complete measurements were made of all of the physical properties relevant for ferroelectric applications including thermal conductivity and diffusivity, heat capacity, dielectric, pyroelectric, piezoelectric and elastic properties. Scanning electron micrographs indicated a change from 3-0 to 3-3 connectivity with increasing porosity. Although most of the physical properties are degraded by the presence of porosity, both piezoelectric and pyroelectric figures-of-merit are improved because of the markedly reduced relative permittivity. Porous ferroelectric ceramics are very promising materials for a number of applications.

1. Introduction

The effect of porosity on the physical properties of ferroelectric ceramics has been of significant interest in recent years. Because of its technological importance, porous lead-zirconate-titanate ceramic (PZT) has been studied extensively [1-12]. The porosity is created by the introduction of organic particles such as polymethyl methacrylate, methyl ethyl cellulose, camphene, starch, graphite and others. We studied samples of Ferroperm® Pz27 with porosities of 20, 25 and 30%. Pz27 is a soft piezoelectric ceramic made by Meggitt Sensing Systems, Denmark [13]. The thermal, dielectric, pyroelectric, piezoelectric and elastic physical properties are especially important for applications. The samples were examined with a scanning electron microscope. Pyroelectric and piezoelectric figures-of-merit were calculated for the various materials.

2. Materials

The PZT materials studied were Ferroperm® Pz27, a piezoelectric ceramic with a composition close to that of the morphotropic phase boundary (MPB) with a Zr/Ti ratio of about 52/48. They were prepared using conventional ceramic processing techniques but with the addition of organic particles which were burned out before sintering to yield samples with porosities of 20, 25 and 30%. Fired-on silver electrodes were applied and the samples were poled while immersed in a non-conducting poling fluid. In addition, a commercial sample of Pz27 was studied. It had a porosity of about 4% and is referred to in this paper as “dense” material. The properties were measured on samples that were 16 mm in diameter and 1 mm thick. Scanning electron micrographs of all of the materials are shown in Fig. 1. Newnham and co-workers introduced the concept of connectivity in 1978 for classifying two-phase composites [14]. They found that there were ten types of diphasic composites, each identified by a two-digit notation. The first digit represents the active phase and the second, the inactive phase. The connectivities of the porous materials shown in Fig. 1 appeared to be a mixture of 3-0 and 3-3 where the active phase was the PZT and the inactive phase was a mixture of poling fluid and air.

3. Property Measurements

3.1. Thermal Diffusivity and Conductivity

The thermal diffusivities of the samples were measured by a technique [15] that is a modification of ones originally developed by Lang [16] and Muensit and Lang [17]. The test sample is affixed by a very thin layer of silver paint to a pyroelectric thermal detector. The top surface of the test sample is exposed to a laser beam whose intensity is modulated at various frequencies. The energy of the beam is absorbed in a black absorption layer and the heat diffuses into the sample in the form of a fluctuating temperature wave superimposed on a steady-state gradient. The temperature fluctuations or thermal waves are attenuated as they travel through the sample and they are also retarded in phase. The phase of the thermal waves as they exit from the test sample is determined relative to the phase of the laser beam by means of the pyroelectric detector. Because only the phase is determined, both the detector pyroelectric coefficient and the laser beam intensity cancel out in the analysis and are not required. The pyroelectric detector was either a disk of dense Pz27 or a disk of porous material with the same porosity as the test sample. The sample structures were placed in an HFS91 Heating and Freezing Stage (Linkam Scientific Instruments, Ltd., UK) whose temperature was varied from 213 to 423 K. A Lisa HL25/M1 diode laser (Lisa Laser Products, Germany) with a power of 25 mW and a wavelength of 685 nm was used to heat the samples. A Stanford Research SR850 Lock-in Amplifier (Stanford Research Systems, USA) produced a sine wave output voltage to drive the laser modulator and also measured the real and imaginary components of the pyroelectric current from which the phase lag was calculated. Thermal conductivity, k , is a more fundamental property than thermal diffusivity, α . The two quantities are related by $\alpha = k / (\rho c)$ where ρ is density and c is the heat capacity per unit mass (SI units are used throughout). Heat capacity data in the range from 1.8 to 400 K were measured using thermal relaxation calorimetry [18] and from 400 to 423 K using differential scanning calorimetry (DSC) [15]. Density data were obtained from [19]. The thermal conductivities for the three porous samples and the dense sample are shown in Fig. 2. The temperature dependence of the thermal conductivities is weak but the conductivities decrease markedly with increasing porosity.

3.2. Pyroelectric coefficients

The pyroelectric coefficients were determined at specific temperatures by a combination of the Lang-Steckel [20] and the Byer-Roundy methods [21] using the following procedure. The samples were placed in the Heating and Freezing Stage and the stage temperature was cycled up and down over the range from 293 to 343 K six times at the rate of 1 K min⁻¹. The pyroelectric current was measured with a picoammeter (Keithley Model 487, USA). The pyroelectric coefficients were calculated at the temperatures 300, 310, 320 and 330 K using the following equation

$$I = pA \frac{dT}{dt} \quad (1)$$

where I = pyroelectric current, p = pyroelectric coefficient, A = electrode area of the sample and dT/dt = rate of temperature change. Then the temperature range was extended from -60 to 150°C by use of the Chynoweth method [22]. In this procedure, the samples were held at each of the four temperatures and were exposed to radiation from a 30 mW diode laser beam that was modulated sinusoidally at a frequency of 10 Hz. The pyroelectric current was measured with the lock-in amplifier. The dT/dt was calculated from the previously determined pyroelectric coefficients using Eqn. (1) and the four values were averaged. Then the current produced by the laser heating was measured as the temperature was varied over the entire temperature range. Using the average dT/dt , the pyroelectric coefficient was determined from -60 to 150°C as shown in Fig. 3. The pyroelectric coefficients increase with increasing temperature and decrease strongly with increasing porosity.

3.3. Permittivity and Loss Tangent

The ϵ_{33}^T relative permittivity and the $\tan\delta$ loss tangent were determined at room temperature on all of the samples using an impedance bridge. The frequency range was from 10 Hz to 10 kHz. The relative permittivity and the loss tangent are shown in Fig. 4. The permittivity varied only slightly over the frequency range with a small increase at very low frequencies. The permittivity values decreased markedly with increasing sample porosity. The loss tangents were between 0.01 and 0.02 for all frequencies. No trend could be ascertained for the variation of the loss tangent with porosity because of the scatter of the data.

3.4. Piezoelectric and Elastic Properties

The piezoelectric and elastic properties were determined according to the procedures of Alguero *et al.* [23] using a dielectric impedance bridge. Resonances were measured on a disk-shaped sample. The thickness resonances of a disk that was poled and excited along its thickness were used to determine the c_{33}^D elastic stiffness coefficient, the d_{33} piezoelectric charge coefficient and the k_t and k_{31} coupling coefficients. The radial resonances of the same disk were used to determine the c_{11}^D elastic stiffness coefficient, the d_{31} piezoelectric charge and g_{31} voltage coefficients and the k_p coupling coefficient. The g_{33} piezoelectric voltage coefficient was calculated from $d_{33} = g_{33} \epsilon_{33}^T$. The piezoelectric charge coefficients are shown in Fig. 5. The d_{31} coefficient decreases with increasing porosity whereas the d_{33} coefficient is relatively constant. The k_p and k_{31} coupling coefficients shown in Fig. 6 decrease with porosity but the k_t coefficient remains constant. Both the c_{11}^D and c_{33}^D elastic stiffness decrease with porosity, as illustrated in Fig. 7.

4. Discussion and analysis

As shown in the graphs, almost all of the properties decrease with increasing porosity. At first glance, this would appear to be disadvantageous for applications. However, the equations that describe the functioning of various devices contain combinations of physical properties called figures-of-merit. These may be enhanced in porous materials despite the fact that the individual physical properties are reduced. Table I shows the various figures-of-merit [24] for pyroelectric devices made from porous Pz27. The parameter ϵ_0 is the permittivity of free space (8.8542×10^{-12} F m⁻¹). The voltage figure-of-merit is important in pyroelectric infrared detectors in which a high-impedance amplifier is used. The current figure-of-merit is relevant for low-impedance amplifiers. The detectivity figure-of-merit is useful in applications with high-impedance amplifiers where the pyroelectric element is the principal noise source. The imaging figure-of-merit is relevant for pyroelectric imaging devices. The presence of porosity increases both the voltage and the imaging figures-of-merit significantly but has little effect on the current and detectivity figures-of-merit. The reason for the increases in the pyroelectric figures-

of-merit is the presence of the rapidly-decreasing relative permittivity value in the denominators

Among the major applications of piezoelectric materials are hydrophones. These are characterized by the hydrostatic or hydrophone figure-of-merit [25] and the acoustic impedance [26]. The equations for these parameters and the calculated results are presented in Table II. The hydrostatic figure-of-merit is used to characterize the sensitivity of the hydrophone. Because d_{31} and d_{33} have opposite signs, d_h is relatively small for the dense material. However, d_{31} rapidly decreases with porosity and d_{33} remains constant, thus causing d_h to increase with porosity. It is desirable for the acoustic impedance of a hydrophone to match as closely as possible to that of its environment, usually air or water. Thus the acoustic impedance of the hydrophone should be as small as possible. As shown in Table II, the acoustic impedance decreases strongly with increasing porosity because of the decrease in both density and elastic stiffness.

5. Conclusions

Measurements were made of a number of physical properties of a ferroelectric ceramic, Ferroperm® Pz27 with porosities of 20, 25 and 30%. Scanning electron micrographs showed that the materials had a mixture of 3-0 and 3-3 connectivities. The physical properties that were measured included thermal diffusivity and conductivity, heat capacity, pyroelectric coefficient, relative permittivity and loss factor, and several piezoelectric and elastic constants. Although the pyroelectric and piezoelectric coefficients diminished with increasing porosity, the pyroelectric voltage and imaging figures-of-merit and the hydrostatic figure-of-merit increased significantly with increasing porosity and the acoustic impedance diminished. The figures-of-merit are very important for applications, suggesting that the introduction of porosity in ferroelectric ceramics opens new technological possibilities.

6. Acknowledgements

The authors thank J.C. Lashley (Los Alamos Scientific Laboratory) and Y.W. Wong (Hong Kong Polytechnic University) for making the heat capacity measurements.

Figure Captions

1. SEM photos of poled Pz27 samples: (a) dense material with 4% porosity; (b) 20% porosity; (c) 25% porosity; (d) 30% porosity. Note presence of poling fluid in (d).
2. Thermal conductivities of poled porous Pz27 samples compared to that of dense Pz27. The dotted lines serve as a guide to the points and are not intended to be used for interpolation.
3. Pyroelectric coefficients of dense and porous Pz27.
4. Dielectric constants of dense and porous Pz27, as functions of frequency.
5. Piezoelectric charge coefficients of dense and porous Pz27.
6. Coupling coefficients of dense and porous Pz27.
7. Elastic stiffnesses of dense and porous Pz27.

TABLE I
PYROELECTRIC FIGURES-OF-MERIT

Figure-Of-Merit	Equation	Dense (4% Porosity)	20% Porosity	25% Porosity	30% Porosity
Voltage ($\text{m}^2 \text{C}^{-1}$)	$p / (c \rho \epsilon_0 \epsilon)$	0.0088	0.0131	0.0143	0.0157
Current ($10^{-12} \text{ m V}^{-1}$)	$p / c \rho$	133	134	133	121
Detectivity ($10^{-6} \text{ Pa}^{-1/2}$)	$p / [c \rho (\epsilon_0 \epsilon \tan \delta)^{1/2}]$	7.5	12.6	10.0	13.1
Imaging (10^3 s C^{-1})	$p / (c \rho \epsilon_0 \epsilon \alpha)$	20.4	27.9	33.6	41.2

TABLE II
PIEZOELECTRIC FIGURES-OF-MERIT

Parameter	Equation	Dense (4% Porosity)	20% Porosity	25% Porosity	30% Porosity
d_h ($10^{-12} \text{ C N}^{-1}$)	$d_h = d_{33} + 2 d_{31}$	105	178	208	240
g_h ($\text{mV m}^{-1} \text{ N}^{-1}$)	$g_h = g_{33} + 2 g_{31}$	6.9	17.3	22.3	31.0
$d_h g_h$ ($10^{-12} \text{ m}^2 \text{ N}^{-1}$)	$d_h g_h$	0.729	3.08	4.65	7.44
Acoustic impedance ($10^7 \text{ kg m}^{-2} \text{ s}^{-1}$)	$Z = (\rho c)^{1/2}$	2.53	2.12	1.85	1.55

References

1. Guo R, Wang C A and Yang A K: Effects of pore size and orientation on dielectric and piezoelectric properties of 1-3 type porous PZT ceramics. *Journal of the European Ceramic Society*. 2011;31: 605-609.
2. Guo R, Wang C A, Yang A K and Fu J T: Enhanced piezoelectric property of porous lead zirconate titanate ceramics with one dimensional ordered pore structure. *Journal of Applied Physics*. 2010;108: 124112.
3. He Z M, Ma J and Zhang R F: Investigation on the microstructure and ferroelectric properties of porous PZT ceramics. *Ceramics International*. 2004;30: 1353-1356.
4. Levassort F, Holc J, Ringgaard E, Bove T, Kosec M and Lethiecq M: Fabrication, modelling and use of porous ceramics for ultrasonic transducer applications. *Journal of Electroceramics*. 2007;19: 125-137.
5. Piazza D, Galassi C, Barzegar A and Damjanovic D: Dielectric and piezoelectric properties of PZT ceramics with anisotropic porosity. *Journal of Electroceramics*. 2010;24: 170-176.
6. Praveenkumar B, Kumar H H and Kharat D K: Characterization and microstructure of porous lead zirconate titanate ceramics. *Bulletin of Materials Science*. 2005;28: 453-455.
7. Praveenkumar B, Kumar H H and Kharat D K: Study on microstructure, piezoelectric and dielectric properties of 3-3 porous PZT composites. *Journal of Materials Science-Materials in Electronics*. 2006;17: 515-518.
8. Rybyanets A N, Porous Piezoelectric Ceramics - A historical overview, *Applications of Ferroelectrics (ISAF)*, 2010 IEEE International Symposium on the, 2010.
9. Stancu V, Lisca M, Boerasu I, Pintilie L and Kosec M: Effects of porosity on ferroelectric properties of Pb(Zr_{0.2}Ti_{0.8})O₃ films *Thin Solid Films*. 2007;515: 6557-6561.
10. Suyal G and Setter N: Enhanced performance of pyroelectric microsensors through the introduction of nanoporosity *Journal of the European Ceramic Society*. 2004;24: 247-251.
11. Whatmore R W, Zhang Q, Shaw C P, Dorey R A and Alcock J R: Pyroelectric ceramics and thin films for applications in uncooled infra-red sensor arrays. *Physica Scripta*. 2007;T129: 6-11.

12. Yang A K, Wang C A, Guo R and Huang Y: Microstructure and Electrical Properties of Porous PZT Ceramics Fabricated by Different Methods. *Journal of the American Ceramic Society*. 2010;93: 1984-1990.
13. Meggitt Sensing Systems, Denmark, <http://www.meggittsensingsystems.com/>.
14. Newnham R E, Skinner D P and Cross L E: Connectivity and piezoelectric-pyroelectric composites. *Mat Res Bull*. 1978;13: 525-536.
15. Lang S B, Ringgaard E, Muensit S, Wu X Q, Lashley J C and Wong Y W: Thermal diffusivity by Laser Intensity Modulation Method (LIMM-TD): A novel technique for the determination of thermal diffusivities and conductivities and its application to porous PZT and silica samples. *Ieee Transactions on Ultrasonics Ferroelectrics and Frequency Control*. 2007;54: 2608-2616.
16. Lang S B: Technique for the measurement of thermal diffusivity based on the Laser Intensity Modulation Method (LIMM). *Ferroelectrics*. 1989;93: 87-93.
17. Muensit S and Lang S B: Pyroelectric technique for measurement of thermal diffusivity of thin solid materials. *Ferroelectrics*. 2003;293: 341-350.
18. Lashley J C, Hundley M F, Migliori A, Sarrao J L, Pagliuso P G, Darling T W, Jaime M, Cooley J C, Hulst W L, Morales L, Thoma D J, Smith J L, Boerio-Goates J, Woodfield B F, Stewart G R, Fisher R A and Phillips N E: Critical examination of heat capacity measurements made on a Quantum Design physical property measurement system. *Cryogenics*. 2003;43: 369-378.
19. Ferroperm Piezoceramics, <http://www.ferroperm-piezo.com>.
20. Lang S B and Steckel F: Measurement of the pyroelectric coefficient, DC dielectric constant, and volume resistivity of a polar material. *Review of Scientific Instruments*. 1965;36: 929.
21. Byer R L and Roundy C B: Pyroelectric coefficient direct measurement technique and application to a nsec response time detector. *Ferroelectrics*. 1972;3: 333.
22. Chynoweth A G: Dynamic method for measuring the pyroelectric effect with special reference to barium titanate. *J Appl Phys*. 1956;27: 78-84.
23. Alguero M, Alemany C, Pardo L and Gonzalez A M: Method for obtaining the full set of linear electric, mechanical, and electromechanical coefficients and all related losses of a piezoelectric ceramic. *J Am Ceram Soc*. 2004;87: 209-215.

24. Whatmore R W: Pyroelectric devices and materials. Rep Prog Phys. 1986;49: 1335-1386.
25. Taylor G W, Gagnepain J J, Meeker T R, Nakamura T and Shuvalov L A: Piezoelectricity, London:Gordon and Breach Science Publishers; 1985.
26. Uchino K: Ferroelectric Devices, New York:Marcel Dekker; 2000.

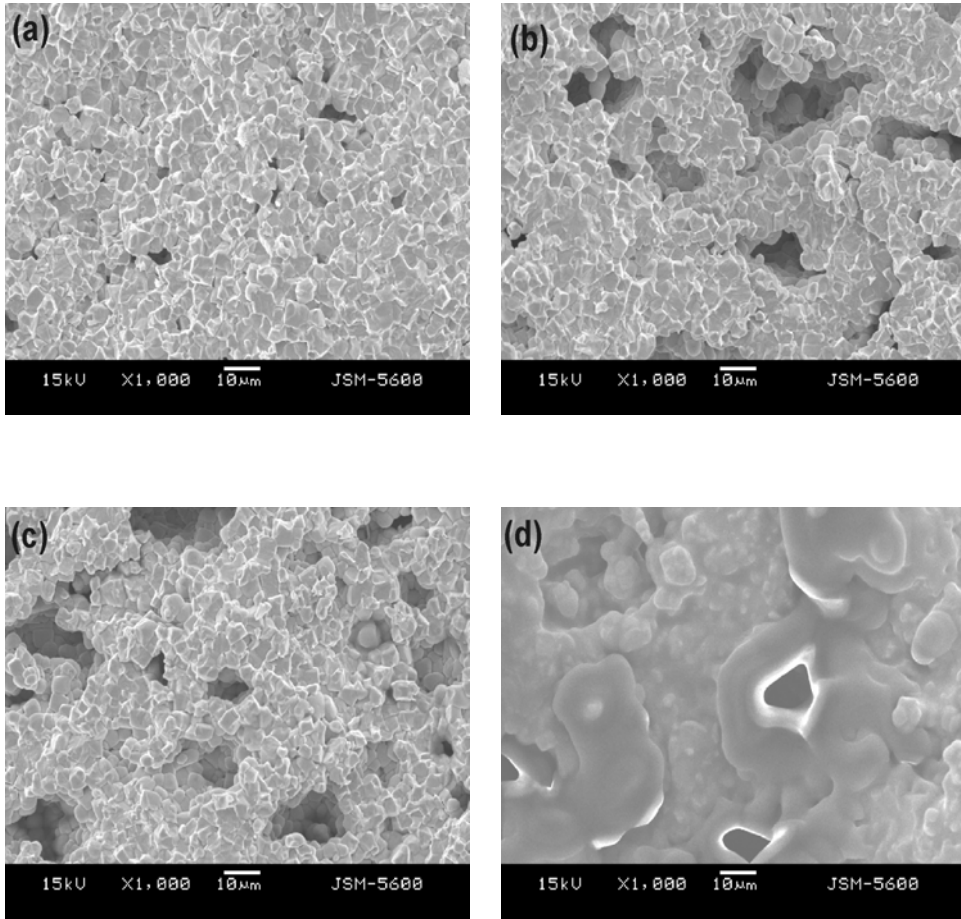


Figure 1. SEM photos of poled Pz27 samples: (a) dense material with 4% porosity; (b) 20% porosity; (c) 25% porosity; (d) 30% porosity. Note presence of poling fluid in (d).

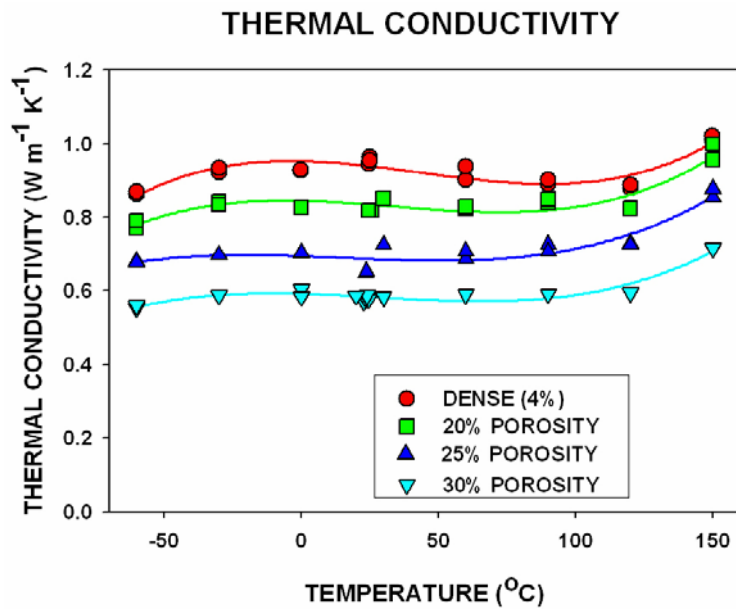


Figure 2. Thermal conductivities of poled porous Pz27 samples compared to that of dense Pz27. The dotted lines serve as a guide to the points and are not intended to be used for interpolation.

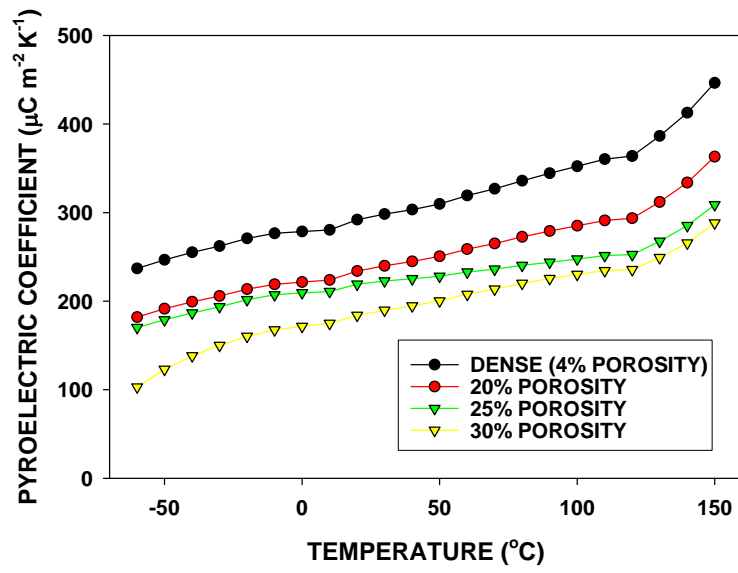
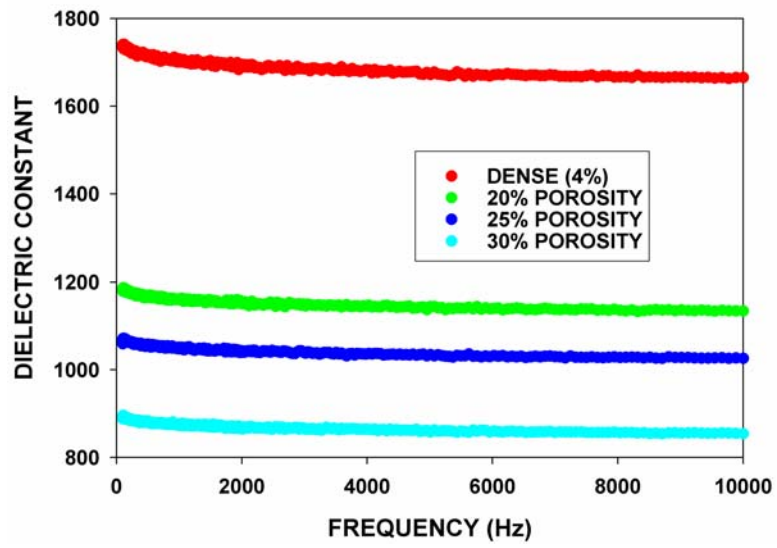
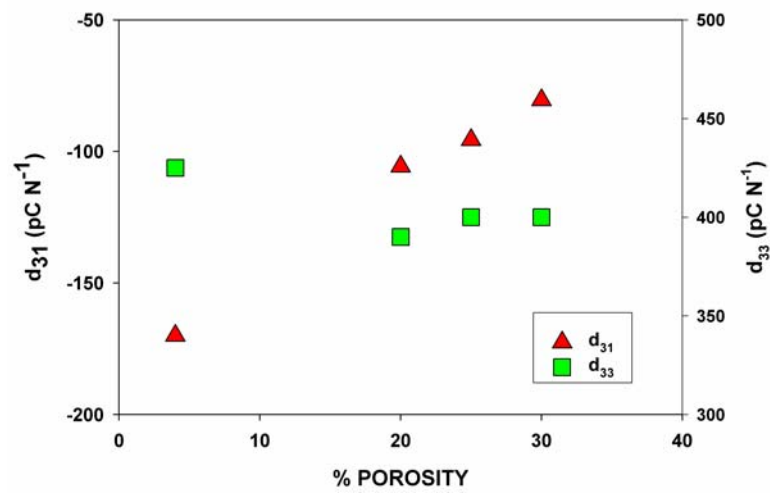


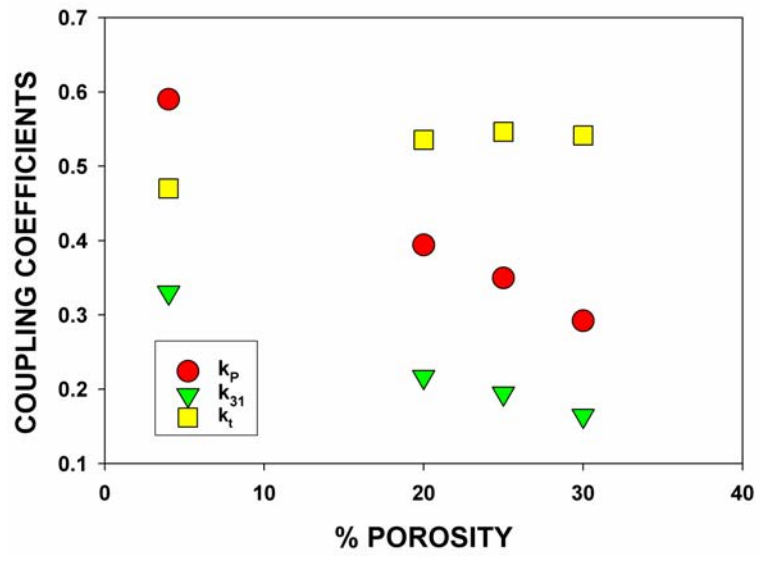
Figure 3. Pyroelectric coefficients of dense and porous Pz27.



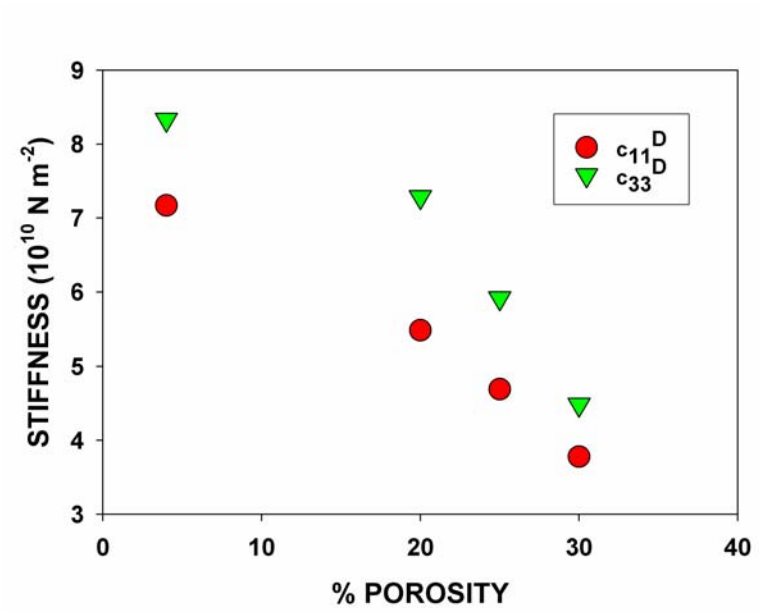
4. Dielectric constants of dense and porous Pz27, as functions of frequency.



5. Piezoelectric charge coefficients of dense and porous Pz27.



6. Coupling coefficients of dense and porous Pz27.



7. Elastic stiffnesses of dense and porous Pz27