

Robocast $\text{Pb}(\text{Zr}_{0.95}\text{Ti}_{0.05})\text{O}_3$ Ceramic Monoliths and Composites

B.A. Tuttle, J. E. Smay, J. Cesarano, III, J. A. Voigt, T.W. Scofield, and W.R. Olson
 Sandia National Laboratories, Albuquerque, NM 87185

J.A. Lewis,
 University of Illinois, Urbana, IL 61801

RECEIVED

AUG 17 2000

QSTI

Robocasting, a computer controlled slurry deposition technique, was used to fabricate ceramic monoliths and composites of chemically prepared $\text{Pb}(\text{Zr}_{0.95}\text{Ti}_{0.05})\text{O}_3$ (PZT 95/5) ceramics. Densities and electrical properties of the robocast samples were equivalent to those obtained for cold isostatically pressed (CIP) parts formed at 200 MPa. Robocast composites consisting of alternate layers of the following sintered densities: (93.9%- 96.1%-93.9%), were fabricated using different levels of organic pore former additions. Modification from a single to a multiple material deposition robocaster was essential to the fabrication of composites that could withstand repeated cycles of saturated polarization switching under 30 kV/cm fields. Further, these composites withstood 500 MPa hydrostatic pressure induced poled ferroelectric (FE) to antiferroelectric (AFE) phase transformation during which strain differences on the order of 0.8% occurred between composite elements.

I. Introduction

Direct fabrication techniques have recently attracted much interest for rapid, agile manufacturing and prototyping of ceramics. Examples include fused deposition of ceramics,¹ three dimensional printing,² and robocasting.³ Robocasting is a computer controlled slurry deposition technique developed by Cesarano and coworkers⁴ that deposits highly concentrated colloidal slurries with low organic content (less than 1% by weight) to construct complex 3-dimensional components in a layer-by-layer build sequence. The desired slurry rheology is pseudoplastic with a yield stress, facilitating extrusion through an orifice (200-800 μm diameter) and forming a continuous cylindrical bead. A low yield stress allows the as-deposited beads to flow together creating smooth interfaces, while simultaneously maintaining the overall shape of the part. Typically concentrated slurries are utilized, with a solids loading roughly 3 to 5 volume percent below the maximum solids loading of approximately 60%. Upon deposition, minimal drying converts the meshed beads to a dilatant mass with sufficient strength to support subsequent layers. Ceramic composites can be made with 3-dimensional phase assemblages by robocasting using a multimaterial delivery system⁵ where independent streams of material are diverted to a common deposition nozzle via a pneumatic valving system. This approach allows one to quantify the effects of different spatial distributions of compositional and structural heterogeneities within ceramics. We demonstrate in this report that high quality interfaces for two-dimensional, ceramic composites can be created that withstand high electric fields and large mechanical stress and strain levels.

DISCLAIMER

This report was prepared as an account of work sponsored by an agency of the United States Government. Neither the United States Government nor any agency thereof, nor any of their employees, make any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process, or service by trade name, trademark, manufacturer, or otherwise does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government or any agency thereof. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States Government or any agency thereof.

DISCLAIMER

**Portions of this document may be illegible
in electronic image products. Images are
produced from the best available original
document.**

A hydrostatic pressure of approximately 300 MPa⁶ is required to transform coarse grain size (approximately 15 μm) PZT 95/5 based ceramics from a poled ferroelectric state to the antiferroelectric state as shown by Fritz and Keck. Storz and Dungan⁷ demonstrated that external pore former additions, which resulted in closed porosity within the specimens, prevented high voltage breakdowns at low temperature during explosive shock wave transformation. A decrease in hydrostatic transformation pressure and an increase in the range of pressure over which the transformation occurred for PZT 95/5 based ceramics with increasing porosity⁸ has recently been reported. The change in transformation behavior was attributed to the enhanced magnitude and distribution of stress and strain in the vicinity of pores. Thus a composite consisting of elements of two different densities would exhibit a volumetric strain difference⁹ between elements of approximately 0.8% during pressure induced transformation when the low density element is AFE and the high density element is in the larger unit cell volume FE state.

II. Experimental Procedure

Chemically prepared PZT 95/5 powders were prepared using lead acetate and B-site cation alkoxide - glacial acetic acid solutions. Uniform, homogeneous powders were then precipitated from these solutions using oxalic acid.¹⁰ The specific composition used for this study was $\text{Pb}_{0.996}(\text{Zr}_{0.953}\text{Ti}_{0.047})\text{Nb}_{0.018}\text{O}_3$ which corresponded to 0.5 mol% PbO in excess of the stoichiometric value. These chemically prepared powders were then calcined at 900°C for 8 h to develop single phase perovskite material and to coarsen their particle size. Conventionally processed compacts were formed by uniaxially pressing roughly 70 grams of powder at 14 MPa (2 ksi) and then isostatically pressing the compact at 200 MPa (30 ksi).

Robocast PZT 95/5 samples were made both with 0.63 weight percent polyethylene (PE) spheres as a pore former and without any PE additions. First, a stock suspension of PZT containing no PE spheres was formulated with Darvan 821A dispersant in de-ionized water. Soft agglomerates were broken up by high shear agitation in a PE jar with ZrO_2 media. The stock suspension was divided and appropriate amounts of PE spheres were mixed into one sample. Both slurries were weakly coagulated with $\text{Pb}(\text{NO}_3)_2$ additions resulting in 45% solids loading. The suspensions were loaded into the robocaster syringes and connected to a common delivery nozzle. Material selection (i.e., with or without poreformer) was accomplished by opening or closing the appropriate valves. A 500 μm diameter nozzle was used for the deposition step to build 1.4 cm^3 cubes by following a serpentine fill pattern in each layer.

Both the robocast and conventionally pressed powder compacts were fired at 750°C for 4 h with a heating rate of 0.85°C/min. The robocast and iso-pressed specimens had green densities of 50% and 57%, respectively. This thermal treatment gently pyrolyzed the PE, creating 5 to 100 μm dimension pores, without causing significant damage to the rest of the ceramic. A double alumina crucible technique using chemically derived PZT 95/5 powders as atmosphere control was used to fire the ceramics. Typical weight losses compared to stoichiometric values were less than 0.5%. Firing

temperatures of 1345°C with 6 h hold times were used to densify the 10 g (robocast) and 70 g (iso-pressed) bodies. The Archimedes technique, with deionized water as the suspension fluid, was used to measure the densities of the specimens.

Dielectric hysteresis measurements were made with an RTV-6000 ferroelectric tester. All samples that were tested for hydrostatic depoling were encapsulated in urethane such that penetration of the pressure transmission fluid (Isobar H) into the pores of the ceramics was prohibited. Hydrostatic pressure was increased at a rate of 10.3 MPa (1500 psi) per second and an 8 μ F capacitor was used to collect the charge from the depoled ceramic with a capacitance of approximately 250 pF. These samples were sputter deposited with Cr//Au electrodes and were approximately 1 cm X 1cm X 0.1 cm in dimension.

III. Results and Discussion

Dielectric hysteresis characteristics of a robocast and iso-pressed PZT 95/5 ceramic are shown in Fig. 1. No organic pore former was added to these samples. Archimedes densities of 97.3% and 97.6% were measured for the cold isostatically pressed and robocast samples, respectively. The two samples have essentially the same remanent polarization (35.0 μ C/cm²) and coercive field (10.1 kV/cm) for a 30 kV/cm, 2 Hz applied field. Resistive loss at high fields (> 25 kV/cm) appears minimal for both samples as the dielectric hysteresis characteristics are well saturated and exhibit minimal spreading at high fields.

Hydrostatic pressure depoling curves are shown in Fig. 2 for robocast and iso-pressed PZT 95/5 ceramics. Both ceramics exhibit a sharp transformation from the FE to the AFE phase that is characteristic of large grain,^{11,12} high density,⁸ homogeneous materials. Transformation pressures of 337 and 327 MPa were measured for the robocast and iso-pressed samples, respectively, where the transformation pressure was defined as that pressure for which half of the total charge is released. The released polarizations of roughly 34.5 μ C/cm² were in reasonable agreement with the dielectric hysteresis data. Both materials show essentially no decrease in the charge characteristic as pressure is increased above 400 MPa and then reduced to atmospheric pressure. This indicates that catastrophic mechanical fracture or enhanced microcracking in the ceramic sufficient to produce increased leakage current has not occurred during the pressure induced phase transformation.

Before a composite PZT structure was robocast, cubic monoliths of 1 cm³ volume were robocasted using 0.63 wt.% and 0 wt.% additions of PE to the PZT powders. These monoliths were used to obtain density and electrical property values for the individual layers of our subsequently fabricated and fired composite. The robocast monoliths had densities of 96.1% and 93.9%, respectively; indicating a 1% decrease in density for a 0.3 weight percent PE addition. The 0% PE addition robocast ceramic was less dense and had lower polarization than the 97.6% dense ceramic shown in Fig.1 and Fig.2 due to a small amount of PE contamination from our original high impact energy slurry milling

process. The milling process was later replaced by an ultrasonication step so that PE contamination did not occur - leading to the higher densities and released polarizations for the samples depicted in Figs. 1 and 2. The 93.9% and 96.1% dense monoliths had measured hydrostatic transformation pressures of 296 MPa and 321 MPa, respectively. Thus a decrease in transformation pressure with increasing porosity of roughly 11.7 MPa per volume percent porosity was measured, in reasonable agreement with our more rigorous, previous work¹¹ of 12.0 MPa per volume percent porosity. For the 96.1% dense sample, 31 $\mu\text{C}/\text{cm}^2$ polarization was released, while 28 $\mu\text{C}/\text{cm}^2$ was released for the 93.9% dense sample.

A three-layer ceramic – ceramic composite of roughly 1 cm^2 cross-sectional area was fabricated by robocasting. The cross-sectional micrograph of the composite fired at 1345°C is shown in Fig. 3 depicting the 1.7 mm thick, 96.1% dense, intermediate region. The fired composite consisted of the following layers:

- (1) a 4 mm thick segment with 0.63 wt% PE,
- (2) a 1.7 mm thick segment with 0 wt% PE, and
- (3) a 4 mm thick segment with 0.63 wt% PE.

A schematic diagram of the 1 mm thick section sliced out of the cube shaped composite that was used for electrical and hydrostatic pressure testing is shown in the inset of Fig.4.

Initial attempts to fabricate high field composites with a single material deposition system resulted in failure at the interface between segments due to differential firing shrinkages or to high field breakdown below 1 kV/cm. This is largely attributed to poor bonding of the layers in the wet state that was exacerbated during firing and electrical testing. Multiple material deposition resulted in less time between depositions of dissimilar materials, limited moisture gradients between deposited layers, and produced a composite that exhibited a remanent polarization of 30 $\mu\text{C}/\text{cm}^2$. Initial electrical breakdown tests on three different composites indicated that breakdown occurred through the bulk of the more porous material not at the interface between composite segments.

The hydrostatic depoling characteristic of the composite is shown in Fig. 4. Calculated and measured transformation behaviors are quantitatively the same within experimental error. Transformation pressures and polarization releases for our calculation are obtained from hydrostatic pressure measurements of monoliths of the two different density materials. The double line corresponds to ideal, estimated, step-like transformation behavior that assumes that both elements transform at a single transformation pressure. In reality, both materials transform over a small range of pressures. Since the lower density ceramic occupies roughly 82 volume percent of the ceramic – ceramic composite, it is estimated that 23 $\mu\text{C}/\text{cm}^2$ of polarization will be released from the low density segments, before the high density phase transforms. Once the pressure reaches 321 MPa then another 5.4 $\mu\text{C}/\text{cm}^2$ from the high density segment is expected to be released. The overall value of calculated charge release of 28.5 $\mu\text{C}/\text{cm}^2$ is in good agreement with the 28 $\mu\text{C}/\text{cm}^2$ that is measured. Considering our assumptions, the measured hydrostatic transformation characteristic is very similar to that predicted.

IV. Summary

Robocast, chemically prepared PZT 95/5 ceramics were shown to have equivalent density, dielectric hysteresis properties and hydrostatic pressure induced FE to AFE transformation characteristics as PZT 95/5 ceramics formed by cold isostatic pressing at 200 MPa. Development of a multiple material nozzle system for the robocaster permitted fabrication of composites that withstood differential shrinkage during firing, 30 kV/cm electrical fields and hydrostatic pressures of 500 MPa. Pressure induced FE to AFE transformation characteristics of ceramic-ceramic composites were in quantitative agreement with the characteristics predicted from hydrostatic measurements on robocast monoliths with same amount of added pore former as the different segments of the composite. Our results indicate that robocasting has great promise for rapid manufacturing of complex, multiphase assemblage devices such as, piezoelectric ceramic- polymer composites, photonic band gap lattices and high frequency ultrasound elements.

Acknowledgments

Acknowledgments: The authors acknowledge enlightening discussions with Bruce King, Bob Anderson, Gordon Pike, Jeff Keck, David Zeuch, Steve Montgomery, George Samara, Paul Clem Ian Fritz, Rebecca Brannon, John Aidun and Steve Hwang. The authors also gratefully appreciate the technical support of Diana Sipola, Gary Zender, Bonnie McKenzie, Paul Hatch, Mark Grazier, Peter Manley, Abram Van Der Geest and Ted Montoya. Sandia is a multiprogram laboratory operated by Sandia Corporation, a Lockheed Martin Company, for the United States Department of Energy under contract DE-AC04-94AL85000.

References

1. T.F. McNulty, D.J. Shanefield, D.J. Danforth and A. Safari, "Dispersion of Lead Zirconate Titanate for Fused Deposition of Ceramics," *J. Amer. Ceram. Soc.*, 82, 1757-60 (1999)
2. U. A. Uhland, R. K. Holman, M. J. Cima, E. Sachs, Y. Enokido, " New Process and Materials Developments in 3-Dimensional Printing," *Mater. Res. Soc. Symp. Proc.*, 542, 153-58, (1999)
3. J. Cesarano III, R. Segalman, and P. Calvert, "Robocasting Provides Moldless Fabrication from Slurry Deposition," *Ceramic Industry*, Vol. 148, No. 4, pp 94-102, April (1998)
4. J. Cesarano III, P. Calvert, "Freeforming Objects with Low-Binder Slurry," U.S. Patent Number 6,027,326
5. J. Cesarano III, "Review of Robocasting Technology," *Mater. Res. Soc. Symp. Proc.*, 542, 133-39, (1999).
6. I. Fritz and J. Keck, "Pressure-Temperature Phase Diagrams for Several Modified Lead Zirconate Ceramics," *J. Phys. Chem. Solids*, 39, 1163-67, (1978).
7. R.H. Dungan and L.J. Storz, "Relation Between Chemical, Mechanical and Electrical Properties of Nb_2O_5 Modified 95 mol% $PbZrO_3$ -5 mol% $PbTiO_3$," *J. Amer. Ceram. Soc.*, 68, 530-33 Oct. 1985

8. B.A. Tuttle, P.Yang, J. H. Gieske, J.A. Voigt, T. Scofield, D.H. Zeuch, and W.R. Olson, "Pressure Induced Phase Transformation of Controlled Porosity $Pb(Zr_{0.95}Ti_{0.05})O_3$ Ceramics," *J. Amer. Ceram. Soc.*, (2000) submitted.
9. D. Zeuch, S. T. Montgomery and D. Holcomb, "Uniaxial Compression Experiments on Lead Zirconate Titanate 95/5-2Nb Ceramic: Evidence for an Orientation-Dependent Maximum Compressive Stress Criterion for Onset of Ferroelectric to Antiferroelectric Polymorphic Transformation" *J. Mater. Res.*, 15 689-703 (2000)
10. J. A. Voigt, D.L. Sipola, B.A. Tuttle, and M. Anderson, U.S. Patent No. 5,908,802, "Nonaqueous Solution Synthesis Process for Preparing Oxide Powders of Lead Zirconate Titanate and Related Materials," issued June 1, 1999.
11. B.A. Tuttle, J. A. Voigt, T.W. Scofield, T.L. Aselage, M.A. Rodriguez, P. Yang, D.H. Zeuch, W.R. Olson and D.L. Sipola, "Pressure Induced Phase Transformation of $Pb(Zr_{0.95}Ti_{0.05})O_3$ Ceramics: Grain Size Dependence," *J. Amer. Ceram. Soc.*, Accepted for Publication, (2000).
12. B. A. Tuttle, J. A. Voigt, T. W. Scofield, P. Yang, D. H. Zeuch and M. A. Rodriguez, " Dielectric Properties and Depoling Characteristics of $Pb(Zr_{0.95}Ti_{0.05})O_3$ Based Ceramics: Near-Critical Grain Size Behavior," *The 9th US and Japan Seminar on Dielectric and Piezoelectric Ceramics*, Nov.3-5, Okinawa, Japan, 354-8, (1999).

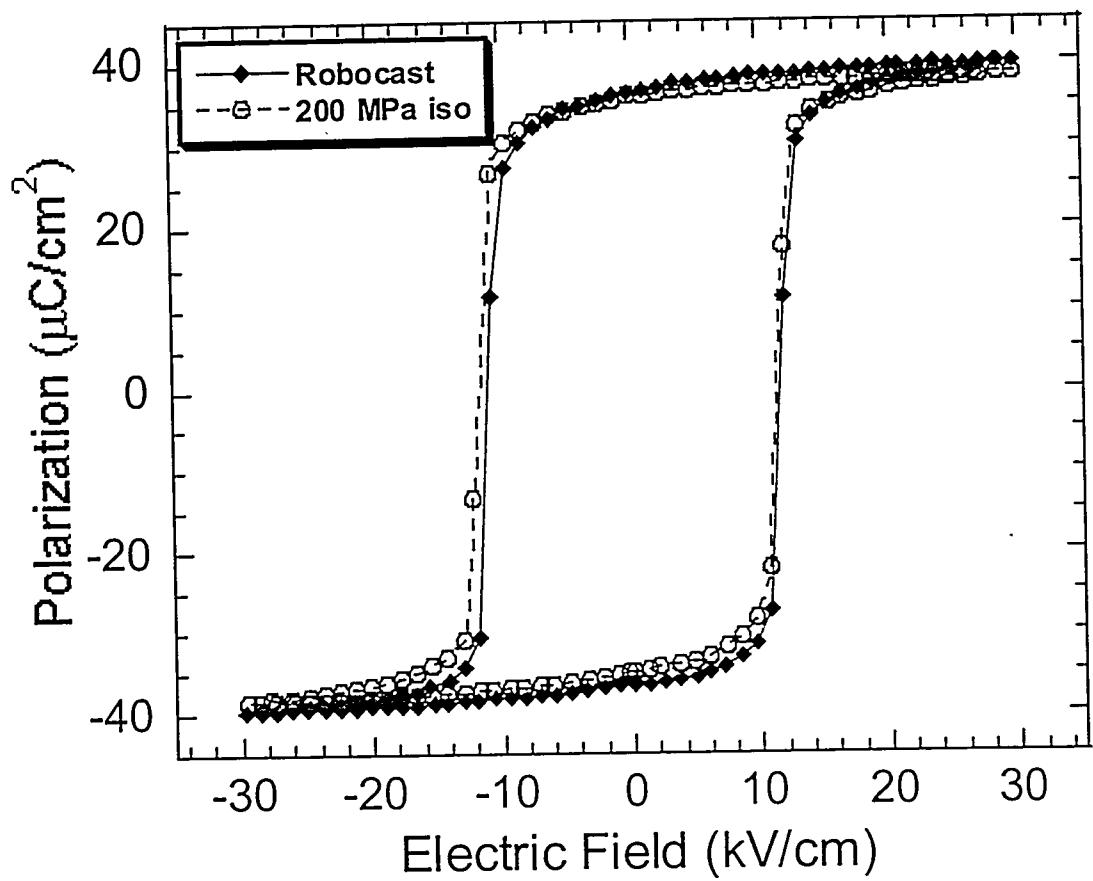


Fig. 1. Polarization versus electric field characteristics of chem-prep PZT 95/5 ceramics formed by robocasting and 200 MPa cold isostatic pressing.

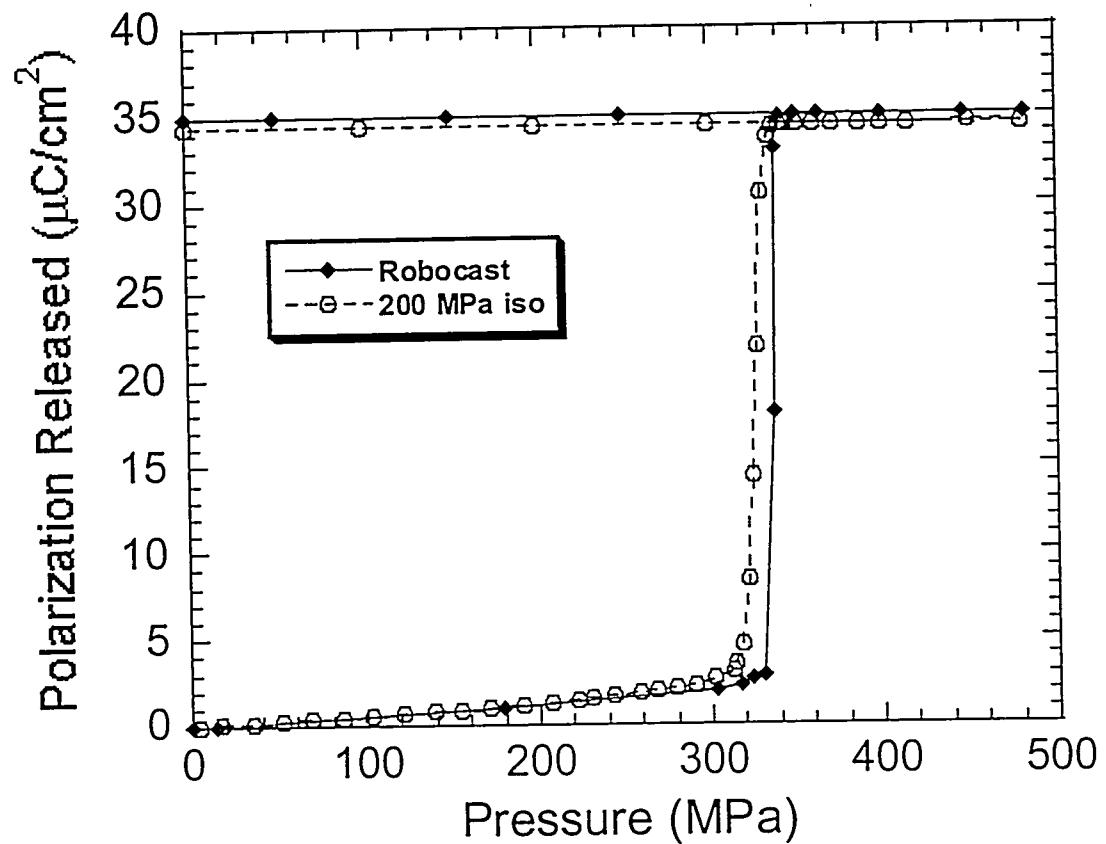


Fig. 2. Hydrostatic depoling characteristics of PZT 95/5 ceramics formed by robocasting and 200 MPa cold isostatic pressing.

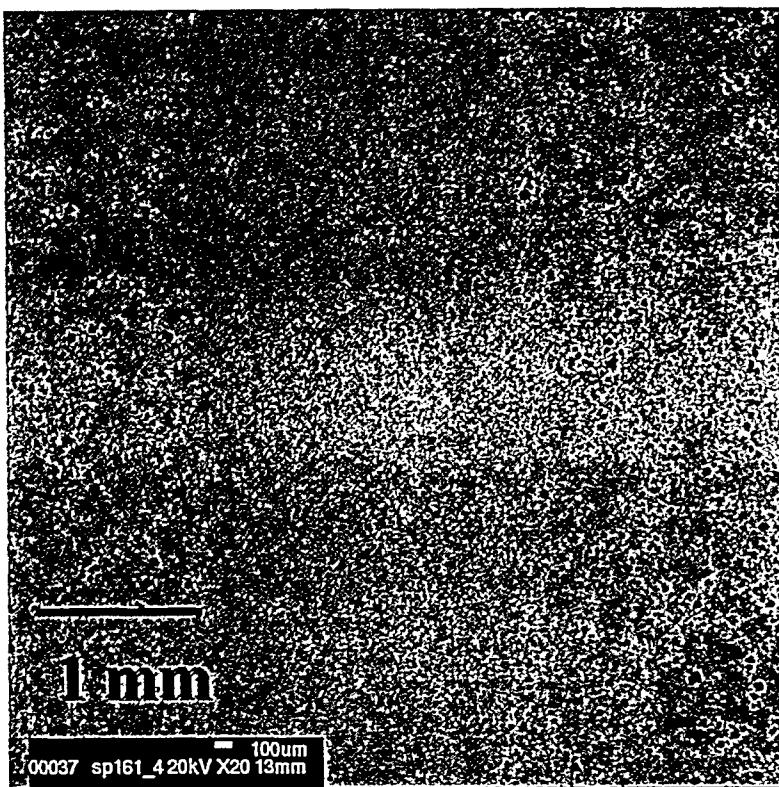


Fig. 3. Cross-sectional SEM image of robocast PZT 95/5 ceramic-ceramic composite consisting of a high density layer between two lower density PZT 95/5 layers.

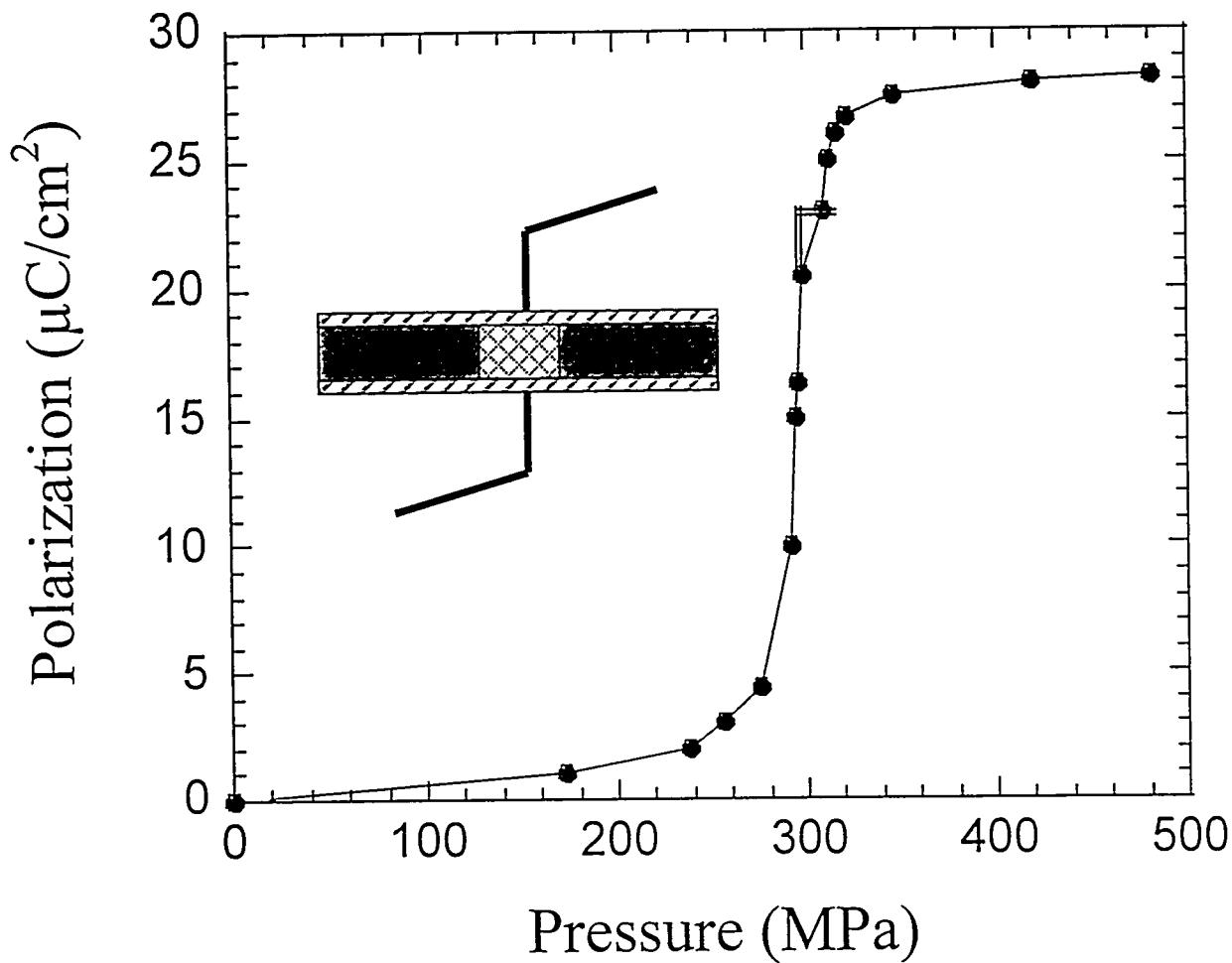


Fig.4.. Hydrostatic depoling characteristic of robocast PZT 95/5 ceramic – ceramic three-layer composite consisting of 96.1% dense layer between two 93.9% dense layers. Schematic diagram of composite electrical test configuration shown in inset.