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Robocast $Pb(Zr_{0.95}Ti_{0.05})O_3$ Ceramic Monoliths and Composites

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Robocasting, which is a computer-controlled slurry-deposition technique, was used to fabricate ceramic monoliths and composites of chemically prepared $Pb(Zr_{0.95}Ti_{0.05})O_3$ ceramics. The densities and electrical properties of the robocast samples were equivalent to those obtained for cold isostatically pressed parts formed under a pressure of 200 MPa. Three-layer robocast composites that consisted of alternating layers of different sintered densities—93.9%/96.1%/93.9%—were fabricated using different levels of organic pore-former additions. Modification from a single-material to a multiple-material deposition robocaster was essential for the fabrication of composites that could withstand repeated cycles of saturated polarization switching under fields of 30 kV/cm. Furthermore, these composites withstood a poled ferroelectric-to-antiferroelectric phase transformation that was induced by a hydrostatic pressure of 500 MPa, during which strain differences on the order of 0.8% occurred between the composite elements.

I. Introduction

DIRECT fabrication techniques recently have attracted much interest for the rapid, agile manufacturing and prototyping of ceramics. Examples include the fused deposition of ceramics,[1] three-dimensional printing,[2] and robocasting.[3] Robocasting is a computer-controlled slurry-deposition technique that was developed by Cesarano and Calvert;[4] this procedure uses the deposition of highly concentrated colloidal slurries with low organic content (<1 wt%) to construct complex, three-dimensional (3-D) components in a layer-by-layer build sequence. The desired rheology of the slurry is pseudoplastic when subjected to a yield stress, facilitating extrusion through an orifice (200–800 μm in 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. Typical concentrated slurries are used, with a solids loading of ~3–5 vol% below the maximum solids loading of ~60%. On 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-D phase assemblages via robocasting with a multimaterial delivery system,[5] 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. In this report, we demonstrate that high-quality interfaces for two-dimensional (2-D) ceramic composites can be created that can withstand high electric fields and large mechanical stress and strain levels.

Fritz and Keck[6] showed that a hydrostatic pressure of ~300 MPa is required to transform coarse-grained (~15 μm) ceramics that are based on $Pb(Zr_{0.95}Ti_{0.05})O_3$ (PZT 95/5) from a poled ferroelectric (FE) state to the antiferroelectric (AFE) state. Storz and Dungan[7] demonstrated that additions of an external pore former, which results in closed porosity within the specimens, prevent high-voltage breakdowns at low temperature during explosive shock wave transformation. Recently, decreases in the hydrostatic transformation pressure and increases in the range of pressure over which the transformation occurs for ceramics that are based on PZT 95/5, relative to increasing porosity,[8] have 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 that consists of elements with two different densities will exhibit a volumetric strain difference[9] of ~0.8% between elements 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 solutions of B-site cation alkoxide and glacial acetic acid. Then, oxalic acid was used to precipitate uniform homogeneous powders from these solutions.[10] The specific composition used for this study was $Pb_{0.996}(Zr_{0.953}Ti_{0.047})Nb_{0.018}O_3$, which corresponded to a PbO excess of 0.5 mol%, relative to the stoichiometric value. Then, these chemically prepared powders were calcined at a temperature of 900°C for 8 h to develop single-phase perovskite material and coarsen their particle size. Conventionally processed compacts were formed by uniaxially pressing ~70 g of powder at a pressure of 14 MPa (2 ksi) and then isostatically pressing the compact at a pressure of 200 MPa (30 ksi).

Robocast PZT 95/5 samples were made both with 0.63 wt% polyethylene (PE) spheres as a pore former and without any PE additions. The PE spheres had a density of 1 g/cm^3, and the theoretically dense PZT 95/5 had a density of 8 g/cm^3; therefore, the addition of 0.63 wt% of PE should result in ~5 vol% porosity in a well-sintered PZT 95/5 ceramic. This conclusion assumes no PE-derived pore shrinkage. A stock suspension of PZT that did not contain any PE spheres was formulated with a dispersant (Darvan

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821A, R. T. Vanderbilt, Norwalk, CT) in deionized water. Soft agglomerates were dispersed via high-shear agitation in a PE jar, using 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 $Pb(NO_3)_2$ additions, which resulted in a solids loading of 45%. The suspensions were loaded into the robocaster syringes and connected to a common delivery nozzle. Material selection (i.e., with or without pore former) was accomplished by opening or closing the appropriate valves. A nozzle with a diameter of 500 μm was used for the deposition step to build cubes with a volume of 1.4 cm^3 by following a serpentine fill pattern in each layer. The deformed cylindrical beads were ~425 μm thick and ~575 μm wide before firing.

Both the robocast and conventionally pressed powder compacts were fired at 750°C for 4 h, using a heating rate of 0.85°C/min. The robocast and isostatically pressed specimens had green densities of 50% and 57%, respectively. This thermal treatment gently pyrolyzed the PE, creating pores with dimensions of 5–100 μm without causing significant damage to the rest of the ceramic. A double-alumina-crucible technique that used chemically derived PZT 95/5 powders for atmosphere control was used to fire the ceramics. Typical weight losses, relative to the stoichiometric values, were <0.5%. Firing temperatures of 1345°C with hold times of 6 h were used to densify the 10 g (robocast) and 70 g (isostatically 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 a ferroelectric tester (Model RT6000-HVS, Radiant Technologies, Albuquerque, NM). All samples that were tested for hydrostatic depoling were encapsulated in urethane, such that penetration of the pressure-transmission fluid (Isopar H) into the pores of the ceramics was prohibited. The hydrostatic pressure was increased at a rate of 10.3 MPa/s (1500 psi/s), and an 8 μF capacitor was used to collect the charge from the depoled ceramic, which had a capacitance of ~250 pF. These samples were sputter-deposited with Cr/Au electrodes and had dimensions of ~1 cm × 1 cm × 0.1 cm.

III. Results and Discussion

Dielectric hysteresis characteristics of the robocast and isostatically pressed PZT 95/5 ceramics 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 had essentially the same remanent polarization (35.0 $\mu C/cm^2$) and coercive field (10.1 kV/cm) for applied-field conditions of 30 kV/cm and 2 Hz. Resistive loss at high fields (>25 kV/cm) seemed minimal for both samples, because the dielectric hysteresis characteristics were well saturated and exhibited minimal spreading under high fields.

Hydrostatic-pressure depoling curves are shown in Fig. 2 for the robocast and isostatically pressed PZT 95/5 ceramics. Both ceramics exhibit a sharp FE–AFE phase transformation 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 isostatically pressed samples, respectively; the transformation pressure is defined as the pressure at which half of the total charge is released. The released polarizations (~34.5 $\mu C/cm^2$) were in reasonable agreement with the dielectric hysteresis data. Both materials showed essentially no decrease in the charge characteristic as the pressure was increased to >400 MPa and then reduced to atmospheric pressure. This observation indicates that catastrophic mechanical fracture or enhanced microcracking in the ceramic that was sufficient to produce increased leakage current has not occurred during the pressure-induced phase transformation.

Before a composite PZT structure was robocast, cubic monoliths with a volume of 1 cm^3 were robocast using 0.63 wt% (5 vol%) and 0 wt% additions of PE to the PZT powders. These monoliths were used to obtain density and electrical-property data for the individual layers of our subsequently fabricated and fired composite. The robocast monoliths had densities of 96.1% and 93.9%, respectively. Shrinkage of the PE-derived pores during firing was the probable cause for the measured decrease in density being only 2.2%, rather than 5%, for the ceramic with added pore former. The robocast ceramic with 0% PE addition was less dense and had a lower polarization than the 97.6%-dense ceramic shown in Figs. 1 and 2, because of a small amount of PE contamination from our original, high-impact-energy, slurry-milling process. The milling process was replaced later by an ultrasonication step, so that PE contamination did not occur, which leads to the higher densities and released polarizations for the samples depicted in Figs. 1 and 2. The measured hydrostatic-transformation pressures of the 93.9%- and 96.1%-dense monoliths were 296 and 321 MPa, respectively. Thus, a decrease in the transformation pressure, relative to increasing porosity, of ~11.7 MPa per volume percent porosity was measured, which was in reasonable agreement with the value determined from our previous, more-rigorous work (12.0 MPa per volume percent porosity).[11] For the 96.1%-dense sample, the released polarization was 31 $\mu C/cm^2$, whereas a released polarization of 28 $\mu C/cm^2$ was observed for the 93.9%-dense sample.

A three-layer ceramic–ceramic composite with a cross-sectional area of ~1 cm^2 was fabricated by robocasting. A scanning electron microscopy (SEM) micrograph of the cross section of the composite that was fired at 1345°C is shown in Fig. 3; this figure depicts the 1.7-mm-thick, 96.1%-dense intermediate region. The fired composite consisted of the following layers: (i) a 4-mm-thick segment with 0.63 wt% PE, (ii) a 1.7-mm-thick segment with 0 wt% PE, and (iii) another 4-mm-thick segment with 0.63 wt% PE. (A schematic diagram of a 1-mm-thick section that has been excised from the cube-shaped composite used to test

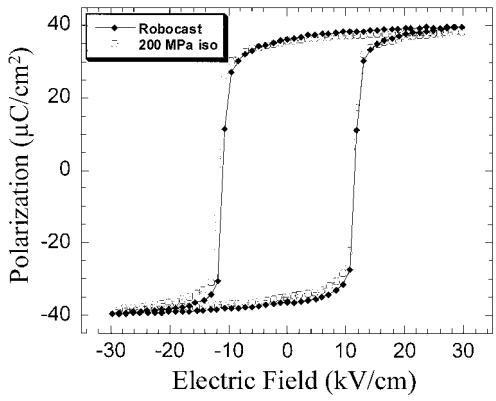

Fig. 1. Plot of polarization (*P*) versus electric field (*E*), showing the *P–E* characteristics of chemically prepared PZT 95/5 ceramics formed via robocasting and cold isostatic pressing at 200 MPa.

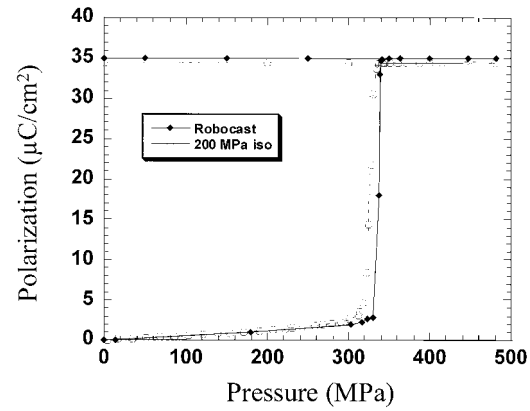

Fig. 2. Hydrostatic depoling characteristics of PZT 95/5 ceramics formed via robocasting and cold isostatic pressing at 200 MPa.

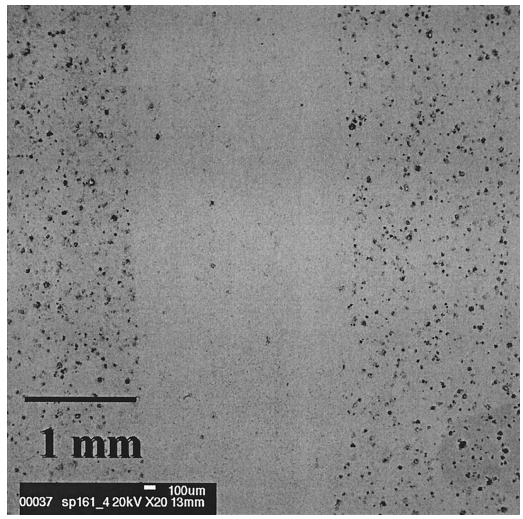

Fig. 3. Cross-sectional SEM image of a robocast PZT 95/5 ceramic–ceramic composite consisting of a high-density (96.1%-dense) layer between two lower-density (93.9%) PZT 95/5 layers.

the electrical properties and hydrostatic pressure 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, because of differential firing shrinkages or high-field breakdown at <1 kV/cm. This phenomenon is attributed primarily 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 $\mu C/cm^2$. 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 the composite segments.

The hydrostatic depoling characteristic of the composite is shown in Fig. 4. The calculated and measured transformation behaviors are quantitatively the same, within experimental error. Transformation pressures and polarization releases for our calculation are obtained from measurement of the hydrostatic pressure of monoliths of the two different-density materials. The double line in the figure corresponds to ideal, estimated, steplike transformation behavior that assumes that both elements transform at a single transformation pressure. In reality, both materials transform over a small range of pressures. The lower-density ceramic

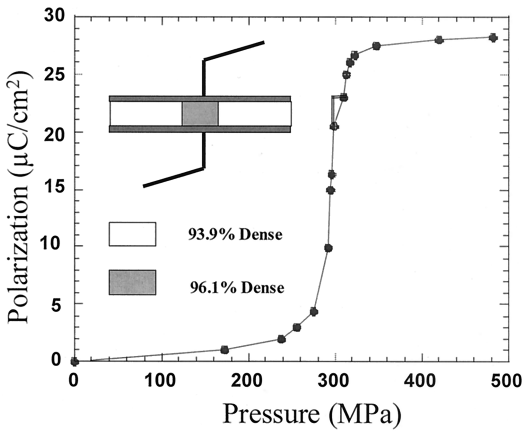

Fig. 4. Hydrostatic depoling characteristic of a robocast PZT 95/5 ceramic–ceramic three-layer composite consisting of a 96.1%-dense layer between two 93.9%-dense layers. A schematic diagram of the composite electrical test configuration is shown in the inset.

occupies ~82 vol% of the ceramic–ceramic composite; therefore, it is estimated that a polarization of 23 $\mu C/cm^2$ will be released from the low-density segments, before the high-density phase transforms. After the pressure attains a value of 321 MPa, then another polarization release of 5.4 $\mu C/cm^2$ is expected from the high-density segment. The overall calculated charge release of 28.5 $\mu C/cm^2$ is in good agreement with the measured value (28 $\mu C/cm^2$). Considering our assumptions, the measured hydrostatic transformation characteristic is very similar to that which has been predicted.

IV. Summary

Robocast, chemically prepared $Pb(Zr_{0.95}Ti_{0.05})O_3$ (PZT 95/5) ceramics were shown to have densities, dielectric-hysteresis properties, and hydrostatic-pressure-induced ferroelectric-to-antiferroelectric (FE–AFE) transformation characteristics that were equivalent to those of PZT 95/5 ceramics formed by cold isostatic pressing at a pressure of 200 MPa. Development of a multiple-material nozzle system for the robocaster permitted the fabrication of composites that can withstand differential shrinkage during firing, electrical fields of 30 kV/cm, and hydrostatic pressures of 500 MPa. The pressure-induced FE–AFE transformation characteristics of ceramic–ceramic composites were in quantitative agreement with the characteristics that have been predicted from hydrostatic measurements on robocast monoliths with the same amount of added pore former as the different segments of the composite. Our results indicate that robocasting has great promise for the rapid manufacture of complex, multiphase assemblage devices, such as piezoelectric ceramic–polymer composites, photonic-band-gap lattices, and high-frequency ultrasound elements.

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