Processing and Structure-Property Relationships for Fine Grained PZT Ceramics

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Abstract-Submicron grain sized PZT-5A ceramics have been produced with properties comparable to conventional coarse grained material. The degradation in dielectric and piezoelectric properties with decreasing grain size was compensated with a new dopant strategy. This made the materials piezoelectrically softer compensating for reductions in poling efficiency. The submicron grain sized material has been shown to be superior to coarse grained ceramic during fine scale dicing operations.

I. INTRODUCTION

Submicron grain sized piezoelectric ceramics may offer advantages due to improved strength in a number of applications including fine scale machining of biomedical ultrasound arrays [1] and low voltage multilayer actuators. However, below a grain size of 1 μm the dielectric and piezoelectric properties of PZT rapidly degrade (see Fig. 1) [2]. This degradation is an extrinsic effect; i.e., no significant decrease in properties are observed when the domain wall contributions are "frozen out" by cooling the ceramic to very low temperatures (see Fig. 2) [2].

TEM analysis and electric field induced polarization and strain measurements of fine grained PZT's [2,3] have revealed that much of the property degradation with grain size is due to a decrease in poling efficiency. Polarization and strain measurements showed an increase in the coercive field by a factor of two for an order of magnitude decrease in grain size. TEM studies revealed a significant decrease in the number of domain orientation variants with decreasing grain size. Transgranular domain coupling was also observed. Furthermore, domain size was found to follow the established 1/2 power relationship with grain size [2,4] except for samples with grain sizes less than 0.5 μm where the domain size was slightly smaller than predicted. Thus, domain density tended to increase slightly with decreasing grain size. The observed decrease in the domain orientation variants would result in fewer polarization alignment directions during poling. The resulting decrease in the remnant polarization [2] would then be responsible for the property degradation.

For PZT-5A type ceramics a possible solution to the property degradation problem may be to compensate the reduction in poling efficiency by making the material piezoelectrically softer. An increase in domain wall mobility might then increase the extrinsic contributions to piezoelectricity and make up for the loss in remnant polarization. For this article such a study was undertaken by adjusting the dopant levels and composition in a typical PZT-5A (DOD Type II) material. The resulting property improvements are presented and compared to commercially available coarse grained material. A comparison of the fine-scale machinability is also presented.

II. EXPERIMENTAL PROCEDURE

Fine grain sized PZT-5A ceramics were prepared using a combination of B-site precursor calcination and high energy milling. The process (which is described in more detail elsewhere [2,5]) can provide submicron grain sized ceramics without pressure assisted sintering. Thin disks were prepared from the PZT powders. Three sintering profiles were then

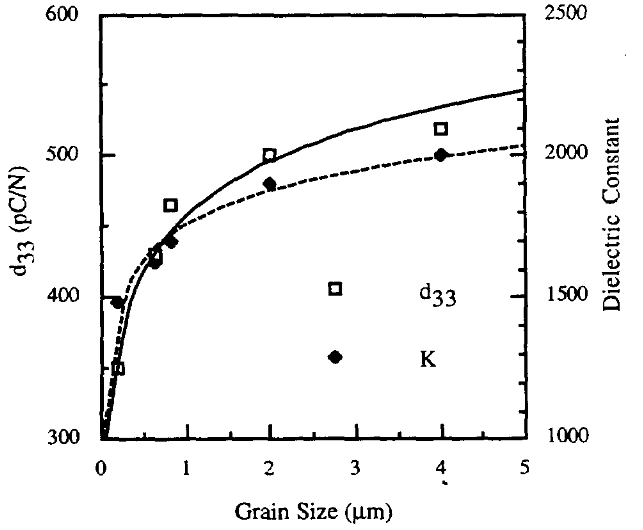

Fig. 1. Piezoelectric coefficient and dielectric constant as a function of grain size for a PZT-5A type ceramic [2].

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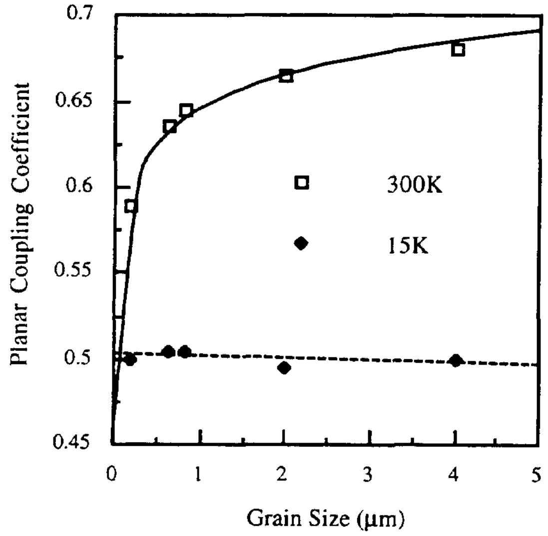

Fig. 2. Planar coupling coefficient versus PZT grain size at temperatures of 300 and 15 Kelvin [2].

used to provide dense ceramics with grain sizes ranging from 0.5 to 2 µm. The profiles were 1000 °C for 24 hours, 1100 °C for 24 hours, and 1250 °C for 2 hours. After sintering all samples were annealed at 900 °C for 6 hours in a flowing oxygen atmosphere. The final sample dimensions were 10 mm in diameter and < 1 mm thick, and the relative sintered densities of all samples were greater than 97%. Three compositions were investigated. One was a typical PZT-5A material [6], and the other two were prepared according to a proprietary dopant strategy aimed at compensating property degradations with grain size. The material designations for the remainder of the paper will be PZT-5A for the normal material and PZT5A-C1 and PZT5A-C2 for the two compensated materials.

After sintering and annealing geometric densities were measured, and the disk samples were electroded with sputtered gold. Dielectric constant and loss were measured 24 hours after poling with an LCR meter. Poling was performed in a heated silicone oil bath with an electric field of 35 kV/cm and at a temperature of 80 °C. The electric field was applied for 5 minutes. Piezoelectric coefficients (d_{33}) were measured using a Berlincourt d_{33} meter. Planar coupling coefficients and mechanical quality factors were determined from the radial mode piezoelectric resonance spectra of the samples. Resonance spectra were recorded with an impedance/gain-phase analyzer. Thickness mode coupling coefficients were measured in a similar manner. Curie temperatures for the ceramics were determined using an LCR meter with a heated sample holder controlled by a personal computer. Polarization and strain measurements were made using a Sawyer-Tower circuit. The strain sensor was a linear variable differential transformer (LVDT).

Grain size measurements were made using the line intercept method on SEM micrographs of fracture surfaces. Approximately 50 grains were measured for each sample. Grain size and electrical property measurements were also performed on commercially available PZT-5A materials for comparison to the compensated fine grained materials.

III. RESULTS AND DISCUSSION

The dielectric constant, dielectric loss, d_{33}, planar coupling coefficient, and curie temperature for the three compositions as a function of grain size are shown in Table I. Dielectric constant was the most affected by the new dopant strategy followed by d_{33}. Dielectric loss was minimally affected. Since d_{33} was less influenced by the new dopant strategies than the dielectric constant, planar coupling tended to be lower for the compensated materials than for the normal PZT-5A composition. Apart from the coupling coefficients, the new dopant strategy was successful in compensating the degradation in dielectric and piezoelectric properties with decreasing grain size.

Table II lists the polarization and coercive field data for PZT-5A (data from [2]) compared to an equivalently grain sized PZT5A-C2 ceramic. The saturation polarizations are about the same for both materials, but the coercive field is considerably lower for PZT5A-C2. These data support the reasoning behind the new dopant strategy. Making the material piezoelectrically softer, which resulted in a lower coercive field, did compensate the decrease in dielectric constant and d_{33}. The compensation may have been due to "easier" domain wall motion. However, the saturation polarization remained constant regardless of dopant levels. Thus, the reduction in domain orientation variants with grain size probably still remains. TEM analysis will be done in the future to verify this hypothesis.

TABLE I.
PROPERTIES OF NORMAL AND COMPENSATED FINE GRAINED PZT CERAMICS

Material & GS (µm)	K @ 1kHz	Loss	d_{33} (pC/N)	k_p	T_c (°C)
PZT-5A 0.8	1730	0.016	426	0.66	---
PZT-5A 1.7	1940	0.015	449	0.64	350
PZT5A-C1 0.4	1890	0.017	417	0.62	---
PZT5A-C1 0.7	1950	0.015	434	0.62	325
PZT5A-C2 0.5	2190	0.015	425	0.60	---
PZT5A-C2 0.7	2250	0.016	435	0.60	325

TABLE II.
SATURATION POLARIZATION AND COERCIVE FIELD FOR PZT-5A AND PZT5A-C2

Composition	Grain Size (μm)	Saturation Polarization (μC/cm^2)	Coercive Field (kV/cm)
PZT-5A	0.5	43.5	19
PZT5A-C2	0.5	42.0	14

Selected properties of the two compensated materials are compared to those of a commercial coarse grained PZT (Motorola 3195HD). For a relatively small decrease in coupling coefficient the compensated materials have and order of magnitude decrease in grain size. The microstructures of the PZT5A-C2 material and Motorola 3195HD are shown in Fig. 3. Resulting benefits of the submicron grain size for fine scale machining is demonstrated in Fig. 4. Shown are 25 μm saw cuts in the PZT5A-C2 material and the Motorola 3195HD. The fine grain material shows much smoother cut surfaces and edges with fewer grain pullouts. Experiments are currently underway to determine if use of fine grained material can decrease yield loss during dicing of transducer arrays for biomedical ultrasound applications.

IV. CONCLUSIONS

Submicron grain sized PZT-5A ceramics were produced by B-site precursor calcination and high energy milling. A new dopant strategy was used to compensate decreases in dielectric and piezoelectric properties with grain size. Adjusting the dopant levels made the ceramics piezoelectrically softer. This was indicated by a decrease in coercive field for compensated PZT-5A compared to normal 5A with the same grain size. However, the saturation polarization levels for compensated and normal PZT-5A were the same indicating that a reduction in domain orientation variants with grain size was not affected by dopant levels.

The properties of compensated fine grained materials were compared to a coarse grained commercial material. For an order of magnitude reduction in grain size the compensated materials had similar or superior properties than the coarse grained material. Only the electromechanical coupling coefficients were slightly reduced. Dicing tests were performed to demonstrate fine scale machinability for biomedical ultrasound applications. The fine grained material was found to have superior machining characteristics to the commercial coarse grained ceramic. Fine grained PZT had smoother diced surfaces and fewer grain pullouts than the coarser material. Thus, use of fine grained material in ultrasonic transducer array fabrication should decrease yield losses.

Future work will focus on TEM analysis to firmly establish the mechanisms of property compensation in the fine grained materials. Also, work is in progress to develop fine grained PZT-5H, -8, and -4 materials. The latter two offer potential for improved reliability, low voltage actuators.

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TABLE III.
PROPERTY COMPARISON FOR COMMERCIAL AND COMPENSATED PZT-5A CERAMICS

Property	Motorola 3195HD	PZT5A-C1	PZT5A-C2
K @ 1kHz	1800	1890	2190
Loss @ 1kHz	0.018	0.017	0.015
d_{33} (pC/N)	390	417	425
k_p	0.65	0.62	0.60
k_t	0.48	---	0.46
Q_m	90	---	40
T_c (°C)	350	325	325
Grain Size (μm)	3 to 5	0.4	0.5

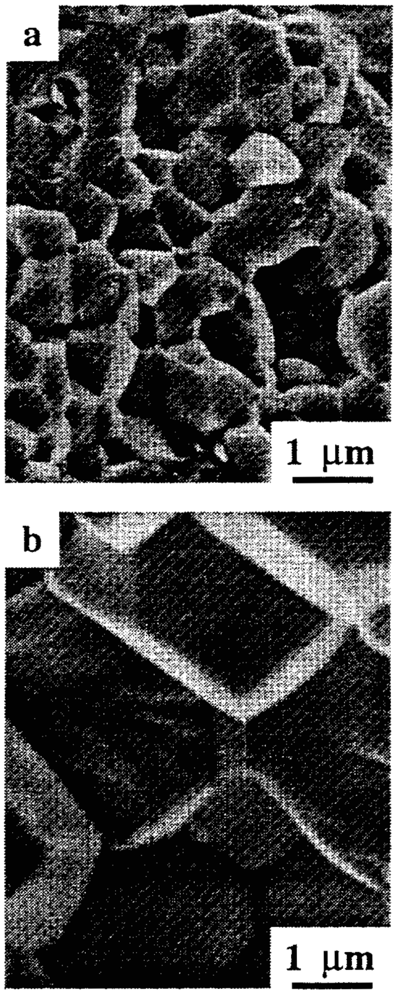

Fig. 3. SEM micrographs showing fracture cross sections for a) PZT5A-C2 and b) Motorola 3195HD.

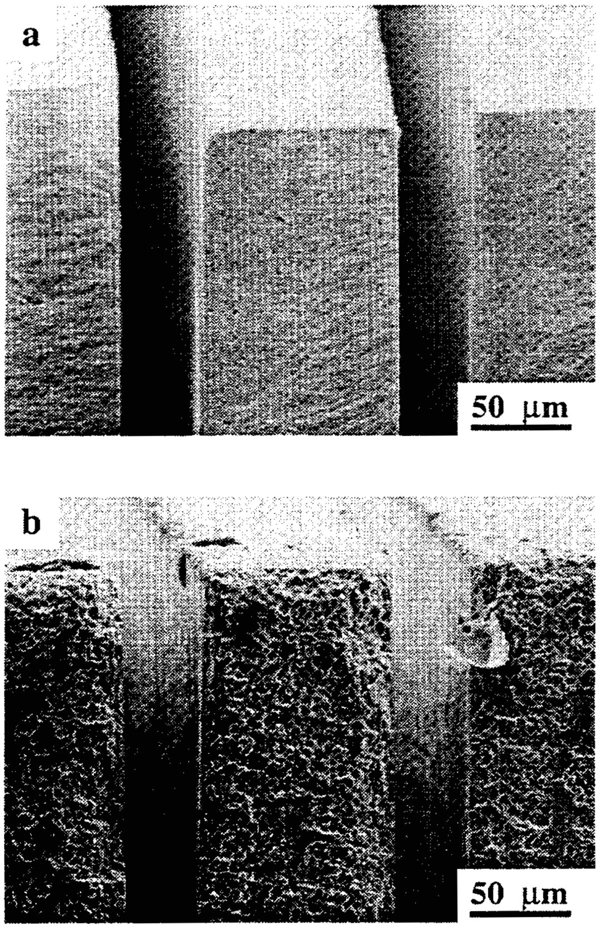

Fig. 4. Microstructures of diced PZT-5A ceramics: a) PZT5A-C2 and b) Motorola 3195HD.