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Chem-Prep PZT 95/5 for Neutron Generator Applications: Development of Laboratory-Scale Powder Processing Operations

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ABSTRACT

Chemical synthesis methods are being developed as a future source of PZT 95/5 powder for neutron generator voltage bar applications. Laboratory-scale powder processes were established to produce PZT billets from these powders. The interactions between calcining temperature, sintering temperature, and pore former content were studied to identify the conditions necessary to produce PZT billets of the desired density and grain size. Several binder systems and pressing aids were evaluated for producing uniform sintered billets with low open porosity. The development of these processes supported the powder synthesis efforts and enabled comparisons between different chem-prep routes.

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The authors thank Scarlett DeNinno, Steve Lockwood, Diana Moore, and Jim Voigt for providing the chem-prep powders used in these studies. Analyses of PZT powders and sintered ceramics were provided by Jeanne Barrera, Barry Ritchey, and Ralph Tissot. The authors are grateful to Kevin Ewsuk for identifying and providing binder systems and pressing aids, as well as attrition milled powders.

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INTRODUCTION

Considerable progress has been made in chemical preparation of PZT 95/5 powders for NG power supply applications.^{1,2} An integral part of the development effort was the processing of these powders into sintered ceramics suitable for fabrication of voltage bar elements. Due to the complexity of the powder synthesis and processing operations, it has been very difficult to predict, or even correlate, final component properties to the character, or processing, of the chemically prepared powder. Therefore, to evaluate the quality of chem-prep batches, it was necessary to process them into sintered ceramics and eventually into voltage bar components for electrical and functional testing. To support the development of the chem-prep methods, a robust powder processing approach was needed that would yield PZT 95/5 ceramic billets without introducing additional variables. Powder processing, in the present context, refers to those operations that convert the powder into sintered ceramic billets. Beginning with PZT powders that have been precipitated by chemical methods and calcined to form the PZT 95/5 solid solution, powder processing involves the admixing of organic additives (including binder and pore-former), compaction into billet form, bisque firing to remove the organic additives, and sintering at elevated temperature to densify the ceramics.

Early in this effort, the PZT Supply Team determined to pursue two separate powder synthesis routes to increase the probability of program success. Those two routes were the non-aqueous Sandia Process,¹ and the aqueous UK Process (see Appendix A). This document describes the powder processing development efforts with these powders and concludes with the down-selection to the SP process, which has subsequently been scaled to production levels.² The processes described in this report formed the basis for the scaled-up powder processes, to be described in a future report.

BACKGROUND

Prior to the initiation of the Chem-prep PZT program, the Ceramics and Glass Processing Department had ceased all production and development efforts with mixed oxide PZT, and the existing pilot-scale facility had been dismantled. The first efforts with chem-prep PZT started with several-hundred gram quantities of powder (eventually increasing to the 1 – 2 kg level). To these research-scale quantities, we added pore formers and binders via manual mixing or tumbling in poly mill jars. The first compaction efforts were with pellet sized samples followed by sintering at various temperatures. Throughout this early effort, it was clear that the powder processing was critical to obtaining useful PZT. Properly synthesized PZT powder could be rendered useless from poor binder selection, compaction defects, or loss of Pb content during sintering. Several designed and systematic experiments were carried out to investigate organic binders/pressing aids, the interaction of calcine and sintering temperature, and the sintering conditions which would yield high quality ceramic billets. Other processing steps (pore former or binder addition, bisque firing, etc.) were adapted from the prior mixed oxide PZT process³ or determined by engineering judgment.

BULK DENSITY MEASUREMENTS

The experiments described in this report were directed towards producing sintered billets of uniform density from as-calcined PZT 95/5 powders. Central to these efforts was the routine

measurement of fired sample density. For many ceramic products, density is a routinely measured and reported characteristic, but it is of special importance for PZT 95/5 voltage bars as their performance is strongly related to density.⁴ The technique used in this report is an aqueous immersion technique^{5,6} that employed three weight measurements: the dry weight, the weight while suspended in a liquid (deionized water), and the saturated, or infiltrated, weight. This technique is similar to ASTM C830-00,⁷ with one significant exception. The ASTM procedure calls for a vacuum-pressure vessel to aid in the infiltration of a fluid into the pores of the sample. Our procedure utilized a vacuum system to aid the infiltration, but did not overpressure the infiltrated samples (to 30 psi, minimum) as required by the ASTM procedure. The calculations for bulk density and open porosity agree with those in the ASTM procedure.

Several distinctions need to be made with the density procedure previously used during the manufacture of mixed oxide PZT at SNL.³ That technique is more accurately described as apparent density and is determined from measurements of the dry weight and suspended weight, alone. Apparent density is the ratio of the mass of the sample to its apparent volume,⁷ which is defined as the impervious portion of the sample. The bulk density, however, is the ratio of the sample mass to its bulk volume; which includes all solid material, open pores, and impervious portions. Since the volume of open pores is not included in the measurement, calculating the apparent density will yield a greater value than the bulk density. For most PZT samples, with little open porosity, the two techniques will give similar results. However, as the open porosity increases, the disparity between the two values increases. For example, a PZT sample with 0.5% open porosity yields an apparent density that is 0.04 g/cc greater than its bulk density. This is a significant variation as the useful density range is generally recognized to be between 7.2 and 7.5 g/cc. The bulk density method is also preferred as the saturated weight measurement permits the calculation of open porosity, which is useful for understanding hydrostatic depoling results.

During the course of this and follow-on work, several studies have been performed on the reproducibility and repeatability of our density measurement technique.^{8,9} From these studies, the technique's coefficient of variation was calculated as 0.00125. Measurement techniques with coefficients < 0.10 are considered to be adequate. In addition, any process change that causes an effect on the High Fire average bulk density was estimated to be detectable at the 0.01 g/cc level. For open porosity, the detectable level was 0.04%. This gives us reasonable confidence when comparing the average density and porosity values between High Fires.

CHEM-PREP PZT SINTERING STUDY

A four-factor interaction experiment was undertaken to research the sintering processes for both UK and SP powders. The four factors and their levels are listed in Table 1. The Pb mole fractions listed below correspond to stoichiometric, 3 wt. % excess, and 6 wt. % excess Pb contents, respectively.

Table 1 Chem-prep PZT Sintering Study Factors

Factor	Lower	Mid	Upper
Temperature, °C	1200	1275	1350
Soak Time, h	2	5	8
Avicel loading, wt. %	0	0.6	1.2
Mole fraction Pb in powder	0.9911	1.0015	1.0115

Both the UK and SP powders were fabricated using then “state-of-the-art” processes. The UK process powder (batches UK-6, -8, -9) was fabricated using “baseline” parameters as developed at AWE, Aldermaston. Specifically, the powders were precipitated using the original AWE-specified precursor and precipitant solution concentrations, spray dried, and washed. The SP powders were fabricated as part of the “2886” series, which were nominally 400 g synthesis experiments. Pore former* was mixed into the powders via ball milling for 2 h, followed by an addition of 5 wt.% DI water to impart moderate binding capacity during compaction. The powders were stored for 16 h, minimum, to equilibrate the moisture content throughout the powder. Fifteen grams of the powder were then pressed into pellets, 1.25 in. diameter x ~0.2 in thick, by compacting at 84 MPa (12 ksi). The pellets were bisque fired at 750°C for 4 h, using a 60°C/h heating rate. Following bisque fire, the pellets were sintered at elevated temperatures per the above table, in triple-enclosed alumina crucibles. Approximately 20 elements were stacked in three columns within the innermost crucible. Each pellet was dusted with zirconia powder^ to reduce bonding of pellets to adjacent samples. Zirconia powder was also used to seal the joints between the inverted crucible enclosures and the alumina base plate. Each innermost crucible contained ~650 g of mixed oxide lead zirconate powder to mitigate Pb loss during firing.

Table 2 shows the results of inductively coupled plasma atomic emission spectroscopy (ICP-AES) measurements of Pb content for the powders used in this study. The disparities between the targeted and measured values are likely due, to some extent, to uncertainties in the ICP-AES process (subsequent improvements have increased the reliability and precision significantly).

Table 2: Target and Actual Pb Contents as Measured by ICP-AES

Powder	Target	Actual
UK-6	.9911	0.9730
UK-9	1.0015	0.944
UK-8	1.0115	0.9526
2886-60	.9911	0.9567
2886-80	1.0015	1.0232
2886-74	1.0115	1.0356

Density Results for UK Process PZT

From the measured values of pellet bulk density and powder Pb content, the data were analyzed using STRATEGY[®] software. Fired pellet bulk density values ranged from 7.08 to 7.96 g/cc, depending on the levels of each factor. When the measured Pb contents (Table 2, above) were used to calculate the bulk density model, the contour plots predicted by the model indicated that bulk density decreases with increasing Pb content. From the ICP values, it appears that the UK powders are grossly deficient in Pb. This is unlikely given the high density levels achieved by many of the samples. Therefore, we concluded that the as-measured values contain substantial error in Pb content. If the model is recalculated based on the targeted Pb levels (assuming there was no Pb loss during synthesis or processing) then the contour plots show increasing density with increasing Pb content (Figure 1). Figure 2 shows the effect of increasing pore former on bulk density for the highest Pb (targeted) UK powder. In this figure, the peak pellet bulk density is not predicted to change significantly with increasing pore former. However, at zero pore former, density is dependent on both temperature and time, but at high pore former loadings,

* Avicel PH-105, FMC Corp., Philadelphia, PA

^Zirot 51664, Ferro Corp., Cleveland, OH

© Strategy, Experiment Strategies Foundation, Seattle, WA

density is mostly dependent on temperature. Increasing the pore former serves to increase the range of predicted density levels over the processing space, while having only a slight detrimental effect on the peak density, suggesting that at high temperatures, the intended effects of pore former are overcome.

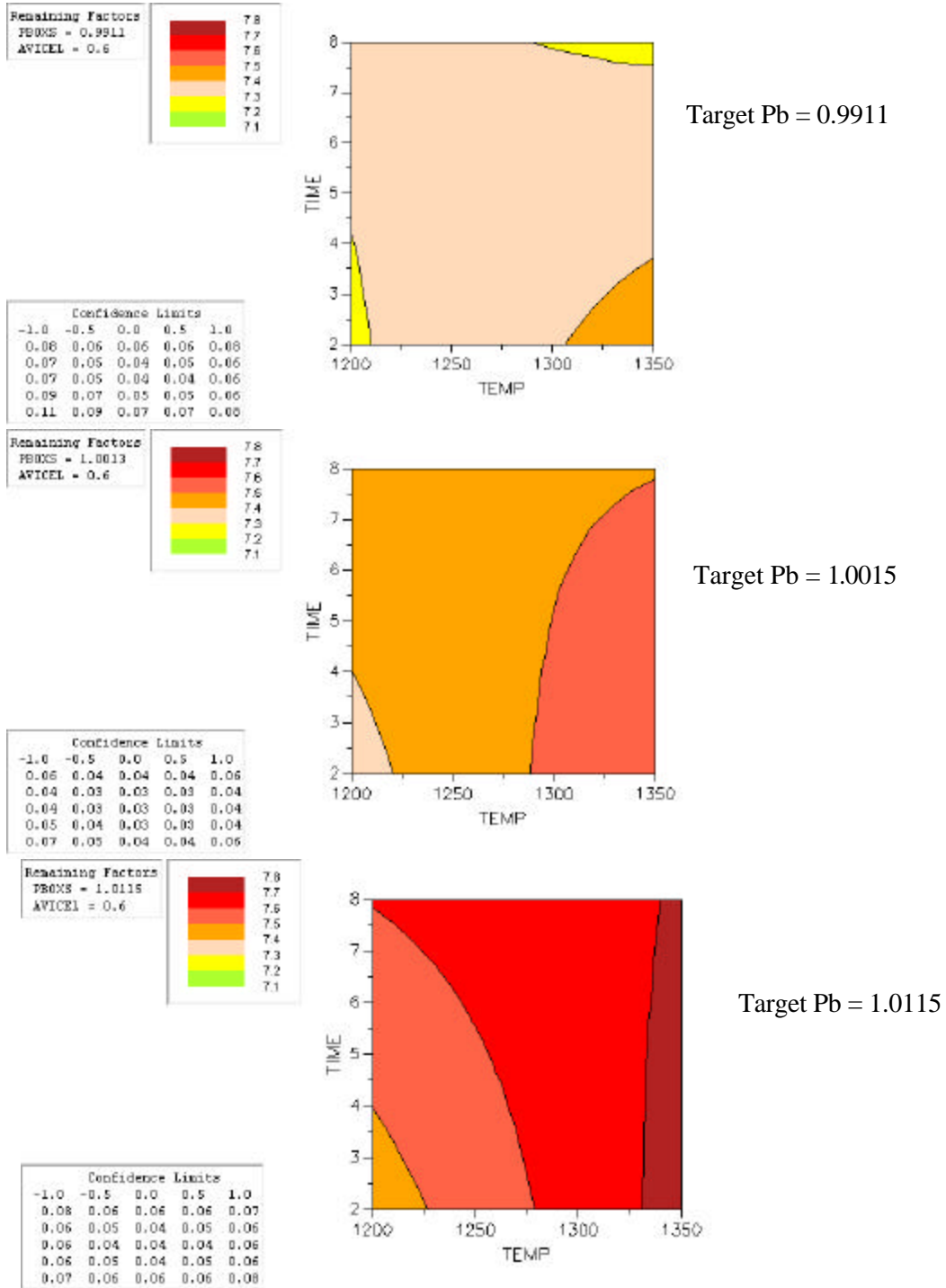


Figure 1: Bulk density contour plots for UK process PZT, as predicted from the target Pb contents and measured density values. The three targeted Pb levels are shown at a constant 0.6% avicel addition.

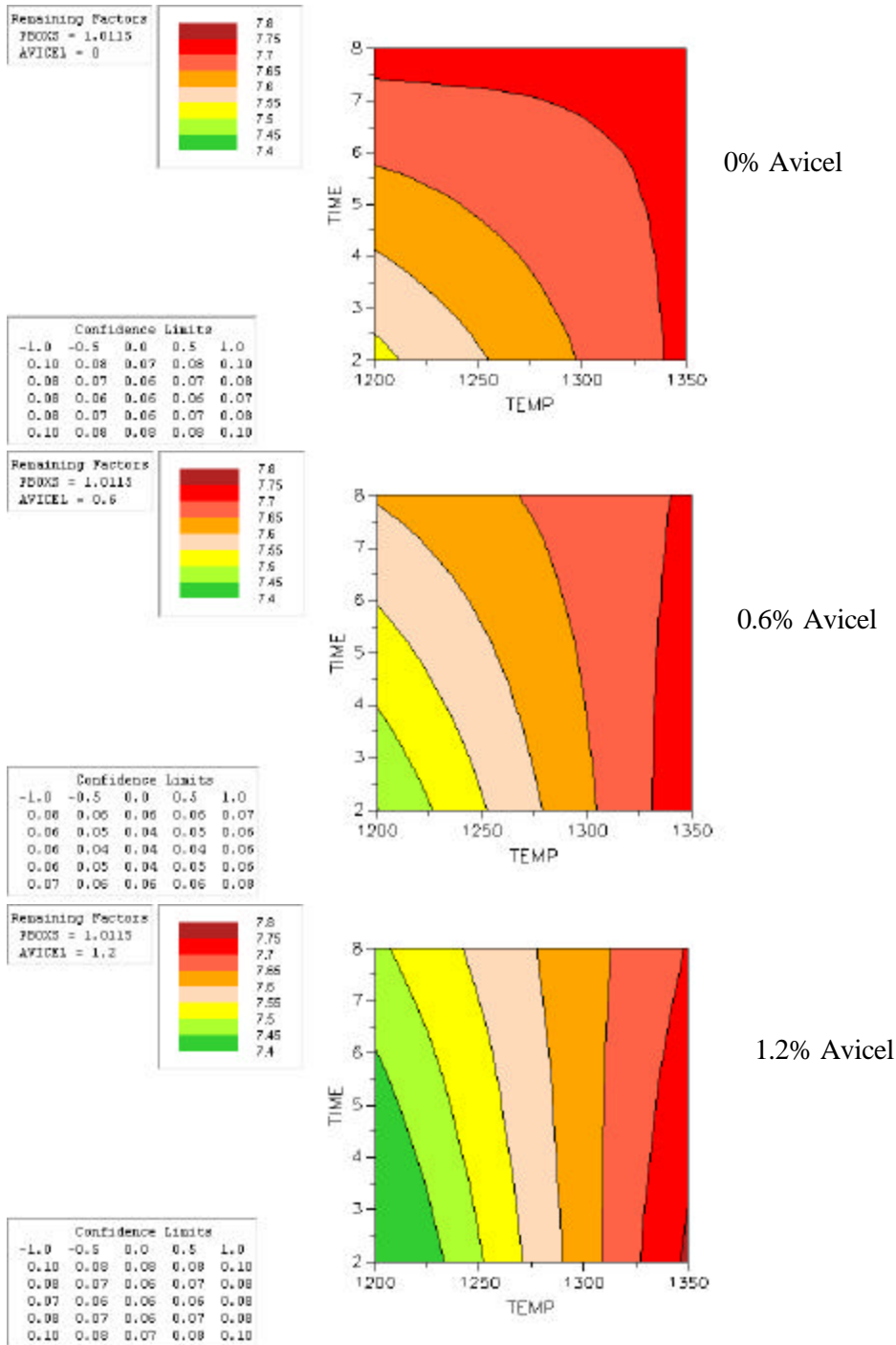


Figure 2: Bulk density contour plots for UK process PZT predicted from the highest targeted Pb content and measured density values. Three levels of pore former are shown.

Density Results for SP Process PZT

For the SP powders, the pellet density ranged from 6.03 to 7.9 g/cc. The bulk density model was calculated using the measured values for Pb content (see Table 2). This model indicated a slight decrease in density with increasing Pb content (Figure 3), therefore, some error is suspected in the ICP values for the SP powders as well. Figure 4 shows the effect of pore former level on density for the PZT powder with the highest measured Pb content. The shape of the contours

predicts that sintered density is dependent on both temperature and time (contrast this figure with Figure 2 for UK samples).

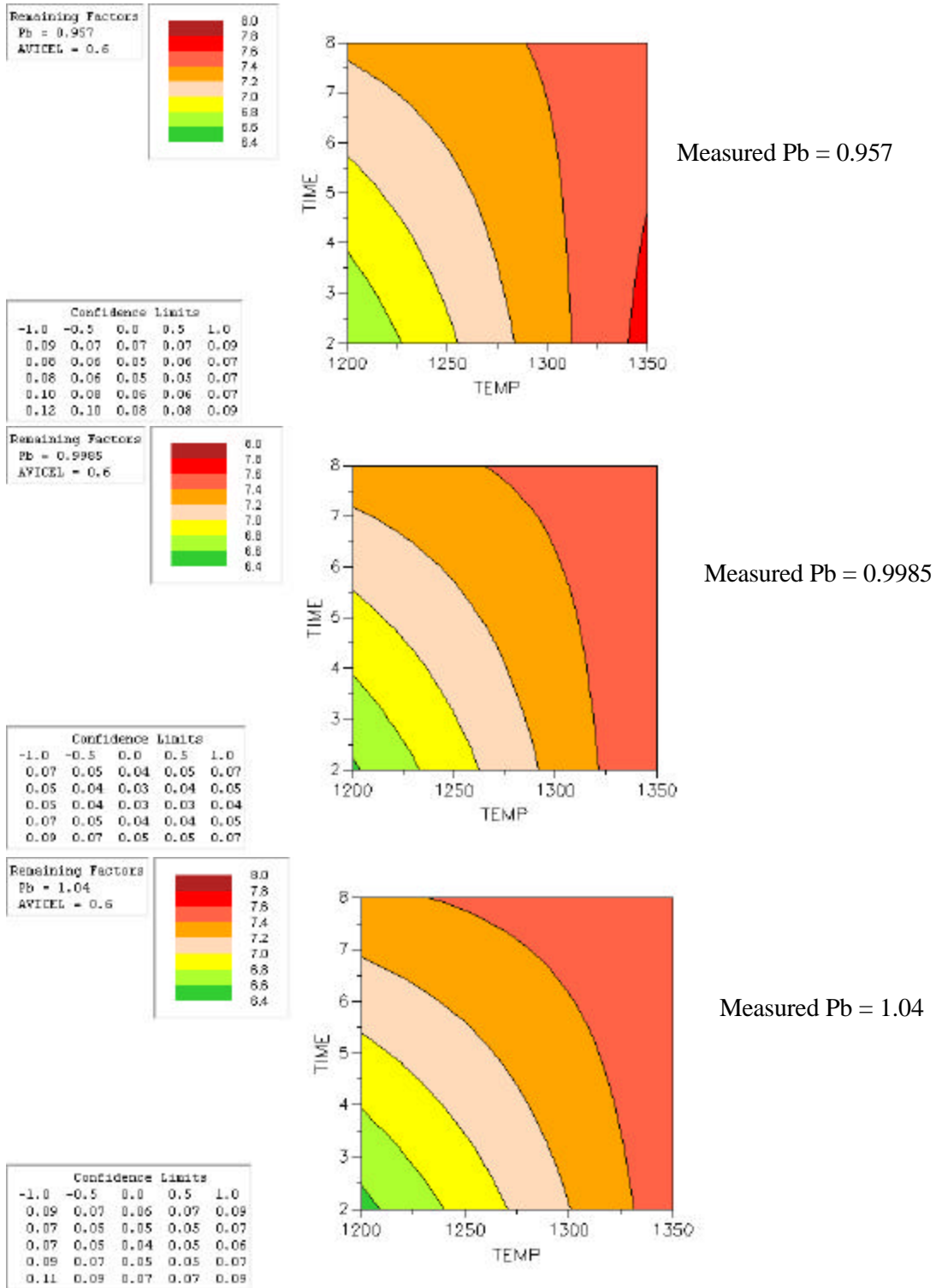


Figure 3: Bulk density contour plots for SP process PZT predicted from actual Pb values and measured density values. The three actual Pb levels are shown at a constant 0.6% avicel addition.

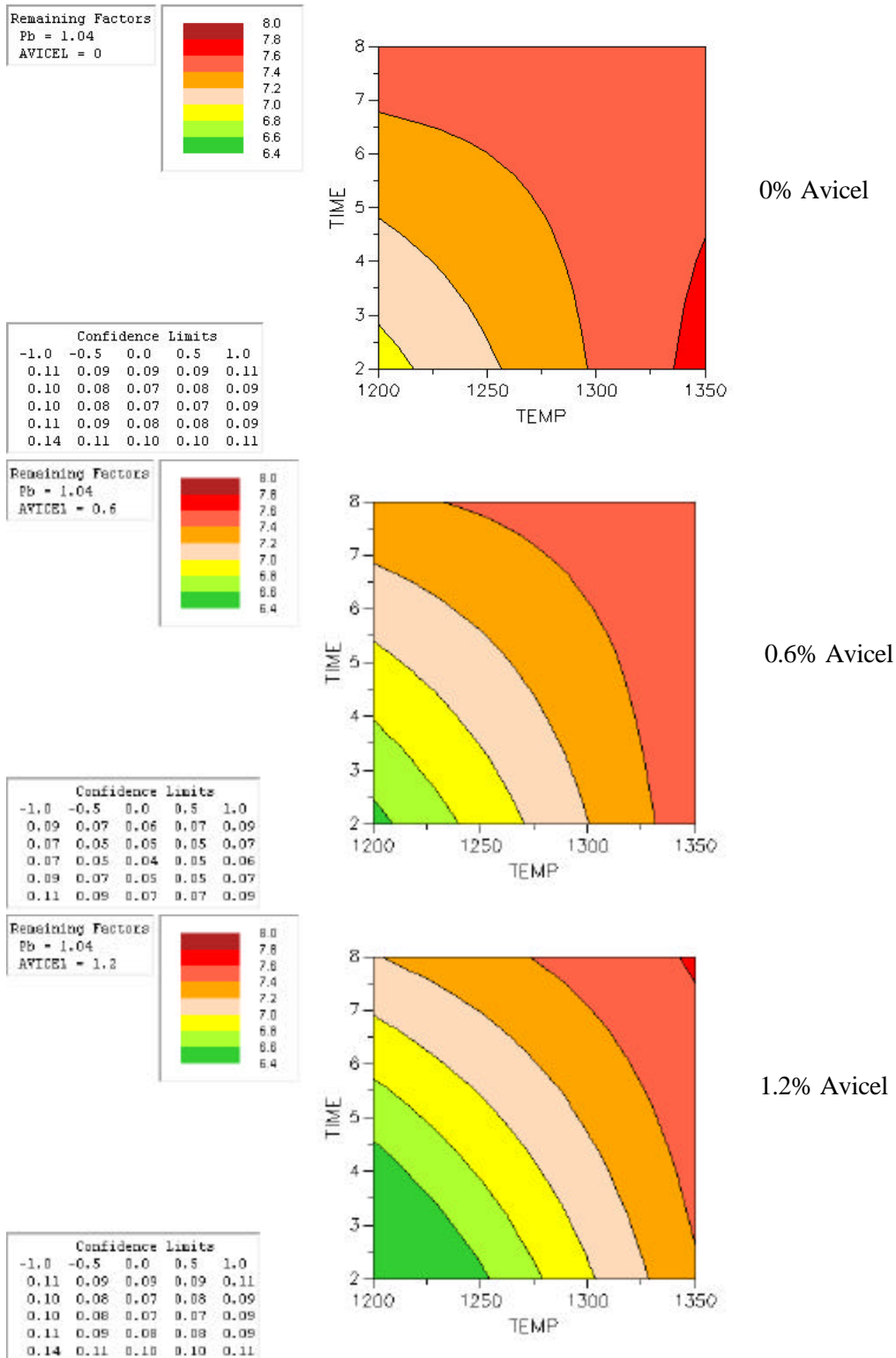


Figure 4: Bulk density contour plots for SP process PZT predicted from the highest actual Pb content and measured density values. Three levels of pore former are shown.

From these studies with UK and SP powders, bulk density is determined by a combination of pore former and sintering conditions, and that significant flexibility in final density could be

achieved. Physical defects in the pellets (cracks and delaminations most likely due to compaction flaws) limited the usefulness of these parts for ferroelectric property measurements. To support the powder synthesis development efforts, it was decided to fix the sintering conditions for subsequent experiments. For these purposes, the sintering conditions were set at 1350°C/6h, similar to the conditions used for mixed oxide 95/5. The long soak time, while not necessary to achieve high density, was selected to promote the development of a “mature” grain structure in the PZT. Subsequent powder synthesis and processing experiments were sintered with these conditions essentially unchanged.

SINTERING PROCESS (PZT BURIAL POWDER STUDY)

It is well known that a significant obstacle to sintering PZT is the volatility of PbO at elevated temperatures¹⁰ and the corresponding negative effects on sample density and electrical properties.^{11, 12, 13} It is common practice to fire PZT in enclosed crucibles containing a burial, or atmosphere, powder to increase the local vapor pressure of PbO and suppress its loss from the compacts. The effectiveness of this approach depends on a number of factors including the integrity of the enclosure, the particular composition of the powder, the temperature/time profile and heating rates, the composition of the product, etc. Many variations of burial powder composition have been reported.^{14, 15, 16, 17} PZT burial powder, of the same composition as the product, has been used routinely at SNL for production of mixed oxide 95/5 PZT.³ In addition, it was common practice to add some excess Pb to the batch, typically on the order of 0.5 - 1 wt. %.¹⁸ Success of the approach was usually determined by weight change of the product after firing, with weight losses <0.5% deemed acceptable. After some experimentation with higher Pb levels, this approach of adding 0.5 – 1 wt. % Pb excess to the batch¹ and using PZT burial powder was adopted for the present effort with chem-prep material.

A triple-enclosure system of high purity alumina crucibles (>98% alumina) has been developed for sintering of all materials described in this report. The innermost enclosure is a cylinder (diameter = 4 in, height = 1.5 in) with a corresponding alumina plate for a lid. The samples and burial powder are contained by this enclosure. The second and third enclosures are closed end tubes of successively larger diameters that are inverted to cover the smaller enclosure(s). All three enclosures are set on an alumina base plate and the inverted tubes are “sealed” to the base plate by packing a loose zirconia powder along the joints. During sintering, the zirconia partially densifies to form a rigid seal between the tubes and the base plate ensuring a closed atmosphere system. Prior to loading the samples into the innermost crucible, they are dusted with a small amount of zirconia powder to prevent bonding of the samples to each other.

It was preferred to use chem-prep PZT powders, of the same batch from which the compacts were formed, as burial powders but availability was not consistent. Therefore, powder batches of mixed oxide 95/5 were prepared by blending the constituent oxides and calcining at 1000°C for 30 min, followed by grinding and sieving through a 60-mesh screen. X-ray diffraction was used to verify that the burial powders were fully reacted and contained no free PbO or ZrO₂. To determine the quantity of burial powder needed to prevent excessive PbO loss, a series of firings were made with differing amounts of burial powder (see Table 3). For this study, 0.6 wt.% avicel pore former and 1.5 wt % PVA[&] binder were added to UK-15 powder. A series of 1.25 in. diameter pellets were pressed at 4.1 ksi, each weighing approximately 15 g. After bisque firing at 750°C for 4 h, 15 pellets were used in each of three sintering runs to 1275°C with a 5 h hold. The

[&] Gelvatol 20-30, Monsanto Corp., St. Louis, MO

pellets were placed inside the innermost crucible (3 stacks of 5 pellets each) with the mixed oxide 95/5 burial powder added to the remaining void space. For trial #1, the 572 g addition completely filled the void space around and on top of the PZT pellets. The other amounts for trials 2 and 3 filled roughly 50% and 25% of the void space, respectively.

Table 3 Burial Powder Trials

Trial	Burial Powder g	Total PZT/crucible volume g/in ³	Wt. Loss %	Density g/cc
1 (1275°C /5 h)	572	50	-0.13	6.15
2 (1275°C /5 h)	286	32	-0.37	6.11
3 (1275°C /5 h)	143	23	-0.28	6.38
4 (1350°C /6 h)	143	17	+0.23	6.75

As seen in the data above, the sintered densities were quite low; most likely due to a combination of no isostatic pressing before bisque firing, and the low sintering temperature used. Open porosities were measured at 15 – 20%. Despite the open, porous, structure of the pellets, the average weight losses were <0.5 % and did not appear to change significantly even at the lower levels of burial powder. A subsequent trial at 1350°C for 6 h (trial #4) resulted in slightly higher density, with open porosity typically <1%, and a slight weight gain. Based on these results, a total mass of PZT (pellets plus burial powder) per crucible volume ratio of ~20 g/in³ can be safely used as a guide for determining how much burial powder to use. For routine firings of PZT pellets or half slugs, we settled on 150 g of burial powder, regardless of the number of PZT compacts in the crucible. Weight losses were typically controlled to <0.3% for routine firings when using this procedure.

CALCINING TEMPERATURE STUDY

For mixed oxide PZT 95/5, it has been reported that the sintered bulk density is dependent on the calcining temperature and that the sintering temperature determines the grain size.¹⁹ In addition, the calcining and sintering soak times have a lesser effect on these characteristics. For the chem-prep material, a coarser calcined powder is desired to aid in the subsequent powder granulation step. Also, an earlier study showed that improved polarization and hydrostatic depoling properties were associated with a coarser grained microstructure.²⁰ To determine the effects of calcining and sintering temperatures on both UK and SP powder particle size, sintered density, and grain size, a two-factor experiment was performed per the conditions in Table 4 below.

Table 4 Oxalate Calcining and Sintering Trials

Run order	Calcine, °C	Sinter, °C	# Half slugs
1	950	1300	4
2	800	1250	2
	1100		2
3	800	1350	2
	1100		2
4	950	1300	4

Powder Processing:

Pyrolyzed oxalates (both SP7F-15 and UK-22) were partially calcined to 600°C/6 h to remove residual organics, cooled to RT, and split into sub-batches for the different calcining conditions. To reduce Pb loss during calcining, each powder was contained within a double crucible arrangement with a ZrO₂ powder seal between the inverted outer crucible and the alumina base plate. The powders were calcined at 800, 950, or 1100°C, all with 6 h holds. Afterwards, the powders were broken up by lightly grinding with a mortar and pestle. To each powder, 3% PVA/PEG[%] binder was added by spray bottle followed by twin shell blending for 15 min. After drying, the powder was sieved through a 30-mesh screen. Water (3 wt%) was then added by ball milling overnight with 15 – 20 zirconia media in a 1 liter poly bottle. No pore former was added. Approximately 70g of the powder were pressed into rectangular billets 1.4 x 1.4 in. and ~0.55 in. thick. This billet configuration is referred to as the “half-slug.” Half-slugs were dry pressed at 5 ksi, then isopressed at 30 ksi. The half-slugs were then bisque fired to 750°C with a 4 h hold. High firing was performed at 1250, 1300, or 1350°C, all with 5 h holds. Four half slugs were fired at a time with 150 g of mixed oxide 95/5 burial powder.

SP Powder Results:

After calcining at 800°C, the SP7F-15 powder poured easily from the crucible. The 950 and 1100°C calcines were slightly caked but were easily scooped from the crucibles. However, the 1100°C calcined powder was noticeably lighter in color. Phase analyses by x-ray showed that all calcined powders were cubic PZT with a possible trace of orthorhombic phase. At 800 and 950°C a small remnant of unreacted Pb and Zr was suspected. ICP-AES analyses show that the mole fraction of Pb after calcining decreased slightly with increasing calcine temperature (0.9804 mole % Pb at 800°C, 0.9788 at 950°C, and 0.9757 at 1100°C). The particle size distributions are shown in Figure 5. The mean particles sizes are very similar, but the distribution for the 1100°C suggests a bimodal population.

[%] Carbowax 20M, Union Carbide Corp. Danbury, CT

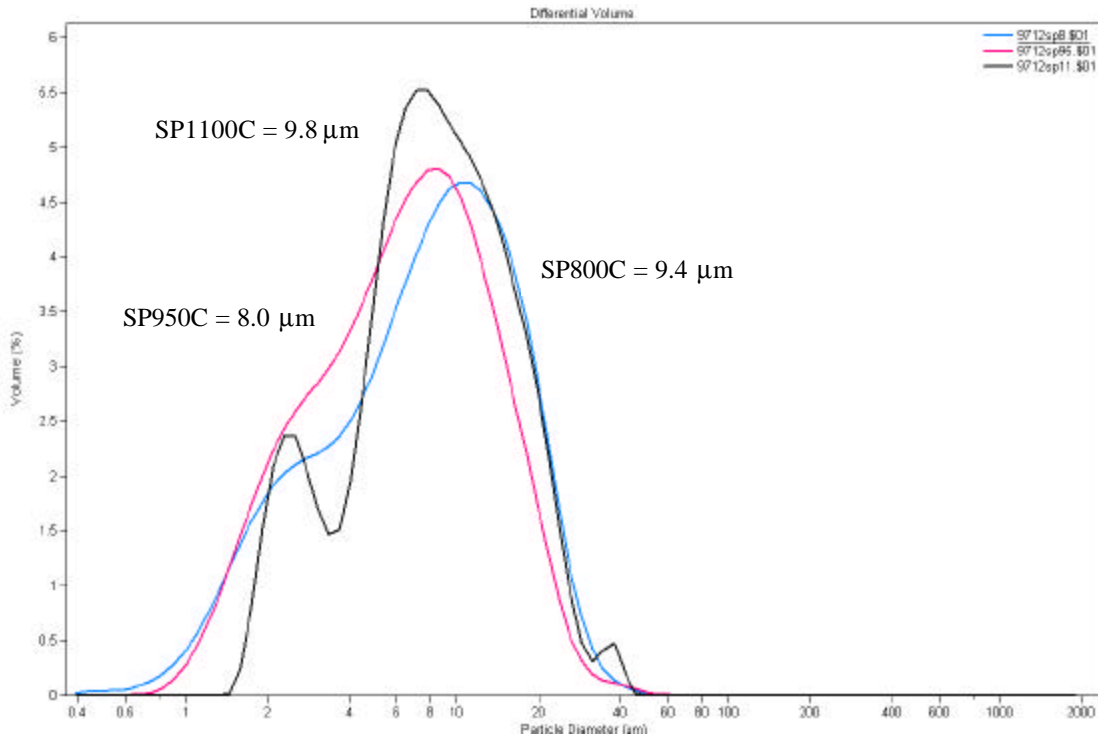


Figure 5: Particle size distribution for SP7F-15 powder calcined at various temperatures.

Particle morphology changes significantly with calcining temperature as seen in the following photomicrographs. At 800°C, the particles resemble thin flakes, <10µm long, containing hundreds of sub-micron particles. At 950°C, lacy, open structures have formed, and at 1100°C the lacy structures have coarsened, with little remnant of the earlier platy structure.

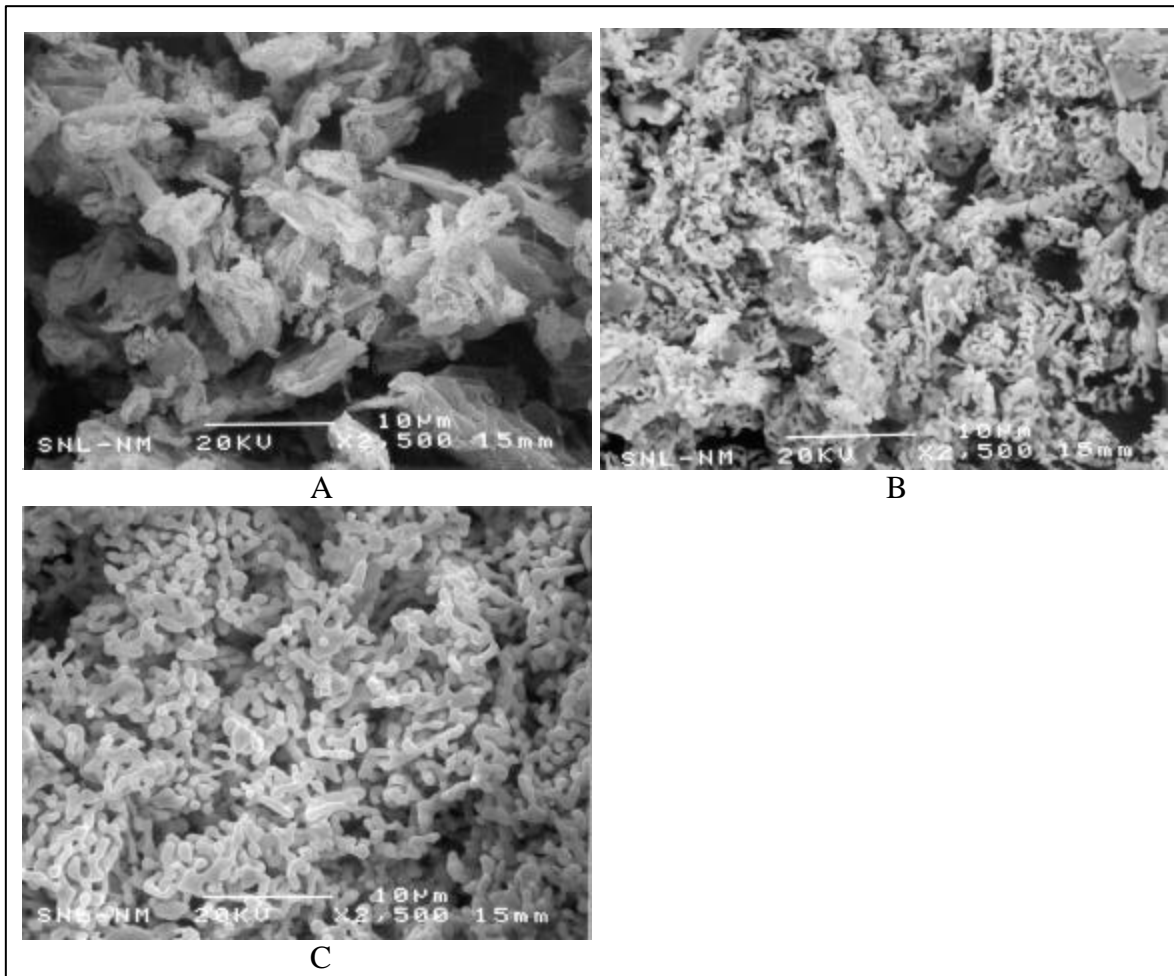


Figure 6: SP7F-15 powders calcined at A) 800°C, B) 950°C, and C) 1100°C.

As listed in Table 5, the densities of the dry and isopressed half-slugs increase with calcining temperature. This suggests that better powder flow, packing, and/or agglomerate breakdown occur with the better-formed particles. The density values were not corrected for moisture or organic content and the decrease in density after bisque firing is likely due to the loss of volatiles (little, or no, increase in physical dimensions were measured).

Table 5 Green and Bisque Density of SP7F-15 Samples

Calcine Temperature, °C	Dry Pressed Density, %	Isostatic Pressed Density, %	Bisque Fired Density, %
800	47	58	54
950	52	60	57
1100	57	64	60

Powders calcined at 800 or 1100°C had similar fired densities, ranging from 7.58 - 7.71 (depending on sintering at 1250 or 1350°C). But, the powder calcined at 950°C had the highest densities (7.70 - 7.88) when sintered only to 1300°C (no other sintering temperatures were used in this study). From these data, the bulk density was modeled and plotted below (Figure 7). As

shown in this figure, high sintered densities (~ 7.63 to 7.75 g/cc) are predicted throughout the experimental space, with sintering temperature playing a larger role than calcine temperature.

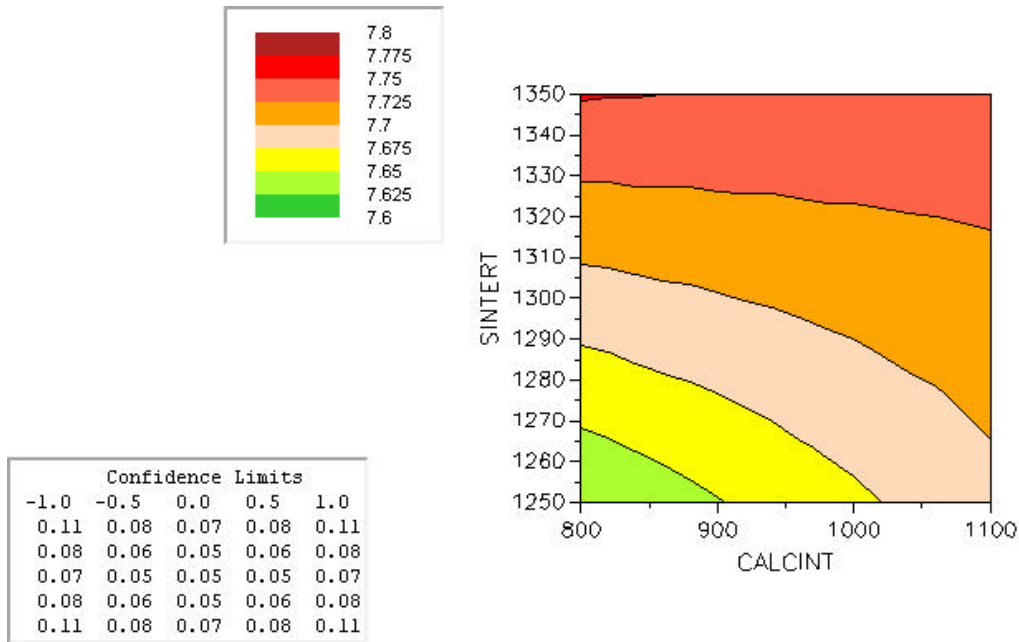


Figure 7: Bulk density contour plot for SP7F-15 PZT.

The average grain sizes were visually estimated from micrographs of polished and etched surfaces (Figure 8). The samples were etched with concentrated HCl, heated to 70°C , for 5 – 10 s before rinsing with DI water. Considering all experimental conditions, the grain sizes ranged from <1 μm to ~ 30 μm . Samples fired at 1250°C had average grain size ~ 5 μm , and samples fired at 1350°C were ~ 10 μm . Calcine temperature did not appear to have a significant effect on the sintered grain size.

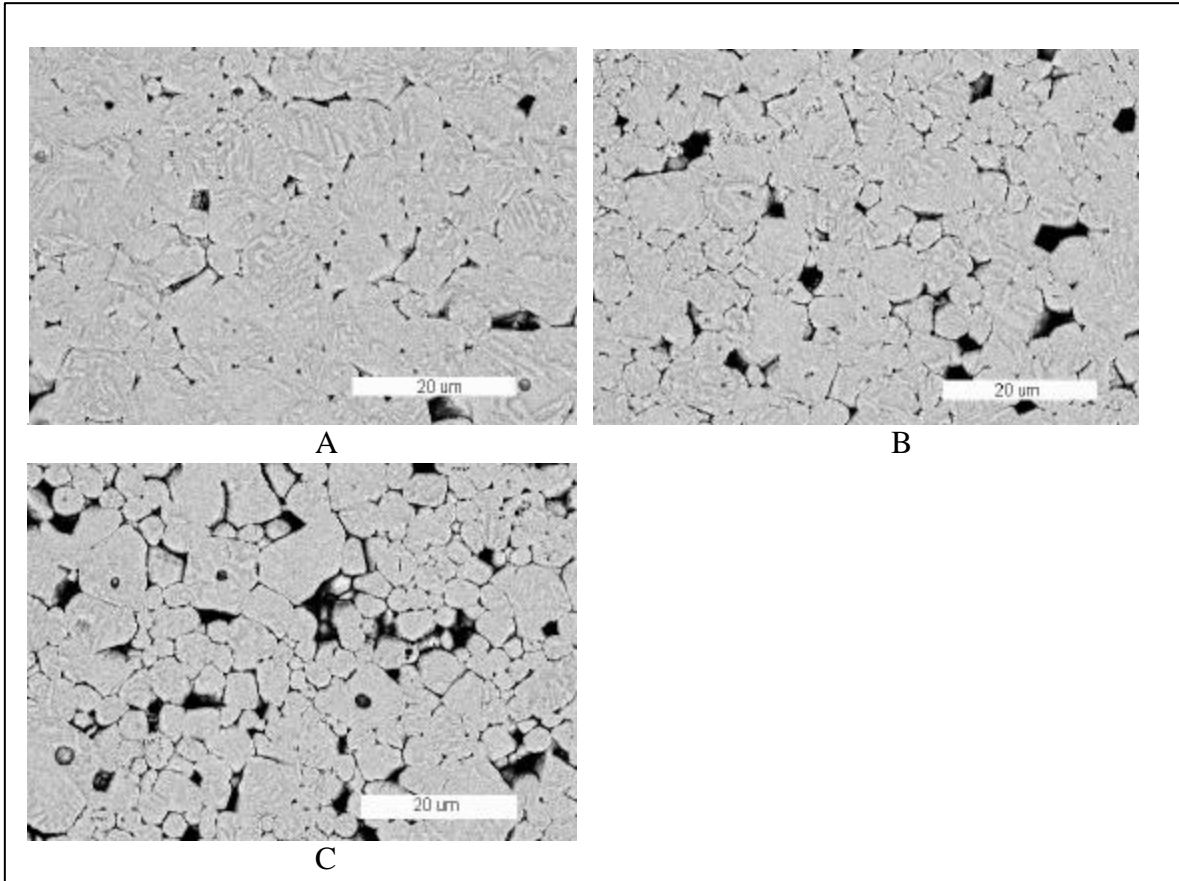


Figure 8: Back scattered electron micrographs of polished and etched SP derived PZT, A) 800°C/1350°C, B) 950°C/1300°C, and C) 1100°C/1250°C.

Based on these results, calcining temperature had little effect on particle size or crystalline phase, but a pronounced effect on particle shape. Due to concerns of calcining at high temperatures and the associated Pb loss, 950°C was selected as a compromise between particle development and Pb loss. Sintering temperature had a significant effect on bulk density, and a lesser effect on grain size. The sintering temperature remained at 1350°C/6 h based on this study.

UK-22 Powder Results:

Batch UK-22 oxalate was used in this study and the oxalate processing was somewhat different in that it was washed and oven dried (UK oxalate was usually oven dried, only, prior to calcining). Similar to the SP material, UK-22 poured easily from crucible after calcining at 800°C. At 950°C, the powder formed a rigid cake that required breaking to remove from the crucible. At 1100°C, the powder was partially sintered and came out in single chunk requiring grinding in a mortar and pestle. This material was also much lighter in color than the lower temperature calcines. Phase analyses by x-ray showed that all calcined powders were cubic PZT with a possible trace of orthorhombic phase. The particle size distributions indicate multi-modal size populations for each calcine temperature (Figure 9). Increasing temperature had a significant affect on average particle size, increasing it from 5 to 17 μm.

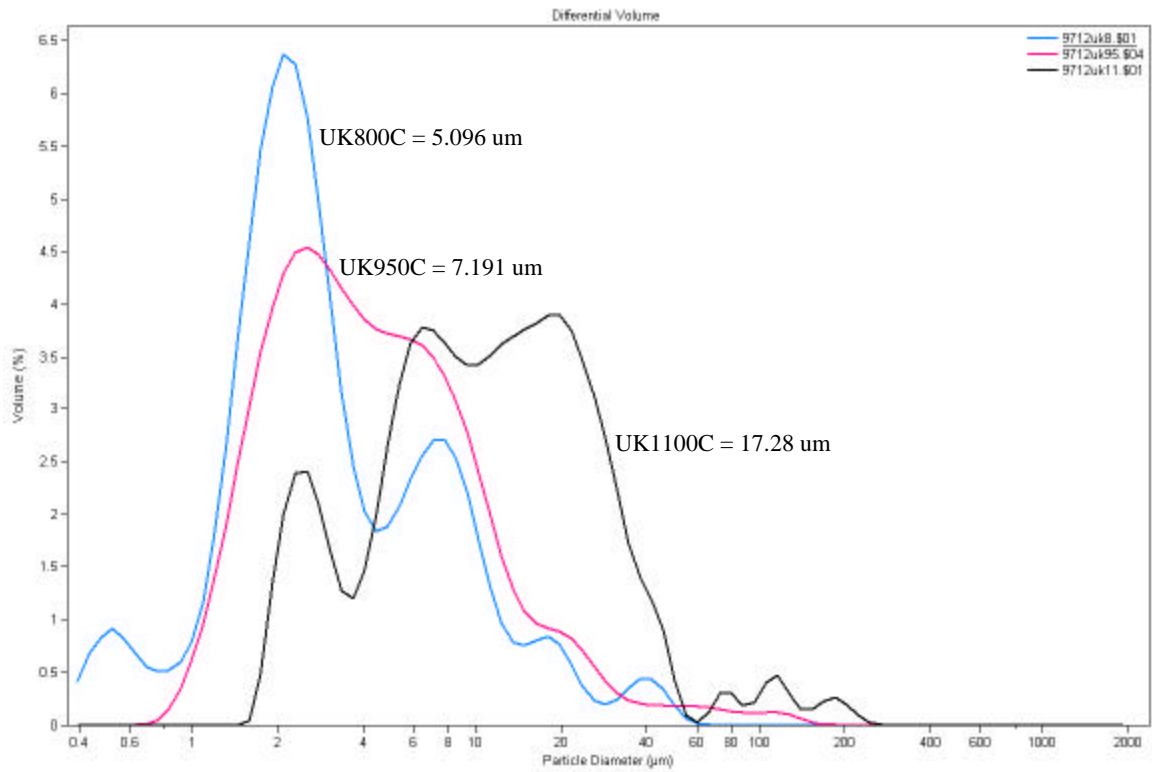


Figure 9: Particle size distribution for UK-22 powder calcined at various temperatures.

The progression in particle size and shape with increasing temperature is seen in the figures below. At 800°C, the powder is poorly formed and eventually coarsens to 10 – 20 µm particles at 1100°C.

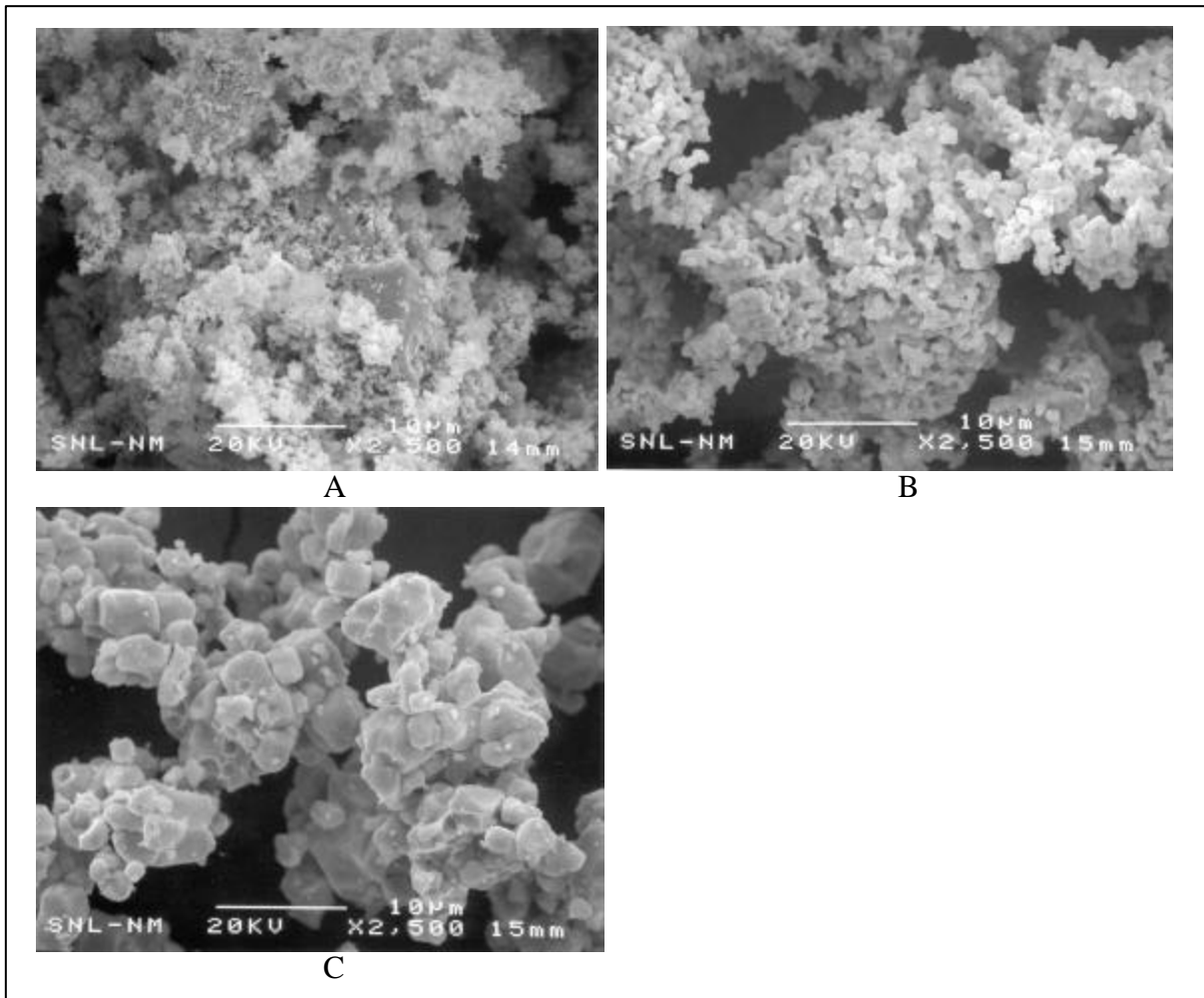


Figure 10: UK-22 powders calcined at A) 800°C, B) 950°C, and C) 1100°C.

The half-slug densities for the UK-22 powders are listed in Table 6. In every instance, these half-slugs were denser than the SP material in Table 5. As seen with the SP material, the densities of the dry and isopressed half-slugs increase with calcining temperature, probably due to the more complete development of the particles.

Table 6 Green and Bisque Density of UK-22 Samples

Calcine Temperature, °C	Dry Pressed Density, %	Isostatic Pressed Density, %	Bisque Fired Density, %
800	55.5	61	56.5
950	57.9	63.5	58.5
1100	57.1	64.8	63.9

The sintered bulk density for these samples ranged from 7.02 to 7.51 g/cc. As seen on the contour plot in Figure 11, increasing the calcining temperature increases the range of sintered densities. This UK material sintered to lower densities than SP7F-15 (Figure 7).

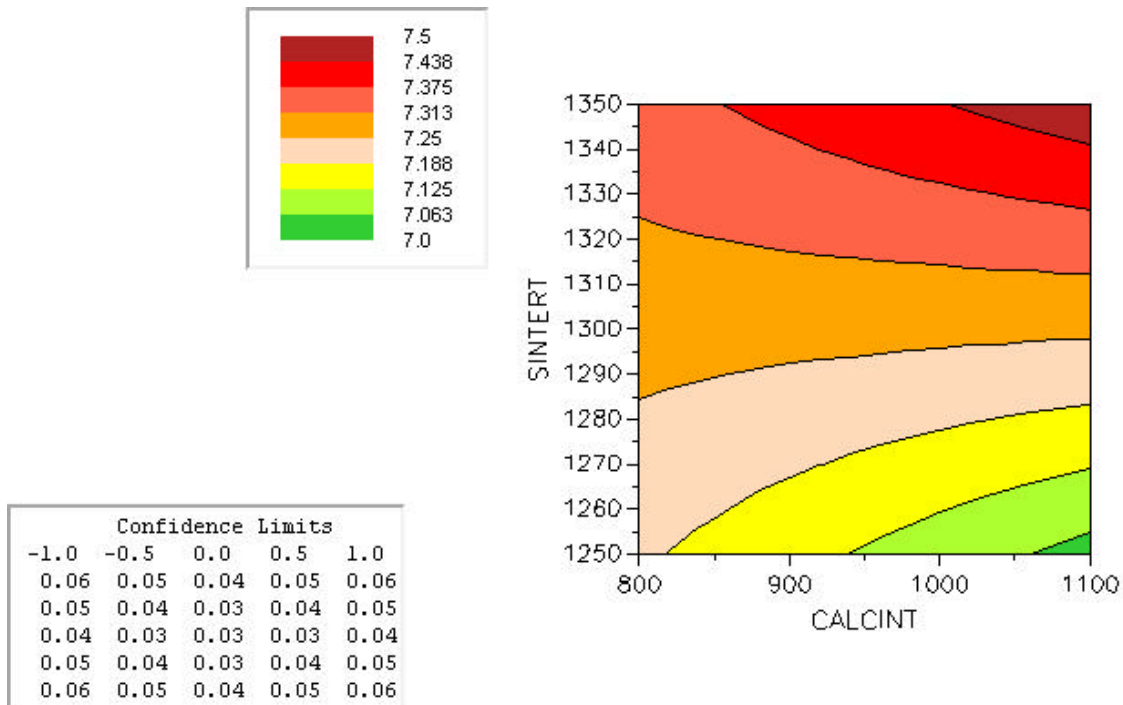


Figure 11: Bulk density contour plot for UK-22 PZT.

All half slugs contained surface craze cracking to some extent, with some samples cracked throughout. This cracking behavior had been observed with an earlier UK batch (UK-4) and is thought to be associated with washing and oven drying the oxalate instead of spray drying. This material also contained a significant amount of unreacted ZrO_2 located as nodules along grain boundaries and triple points in the PZT (Figure 12). Similar to the SP results, the average grain size was 8 to 12 μm and varied little between the calcining/sintering conditions.

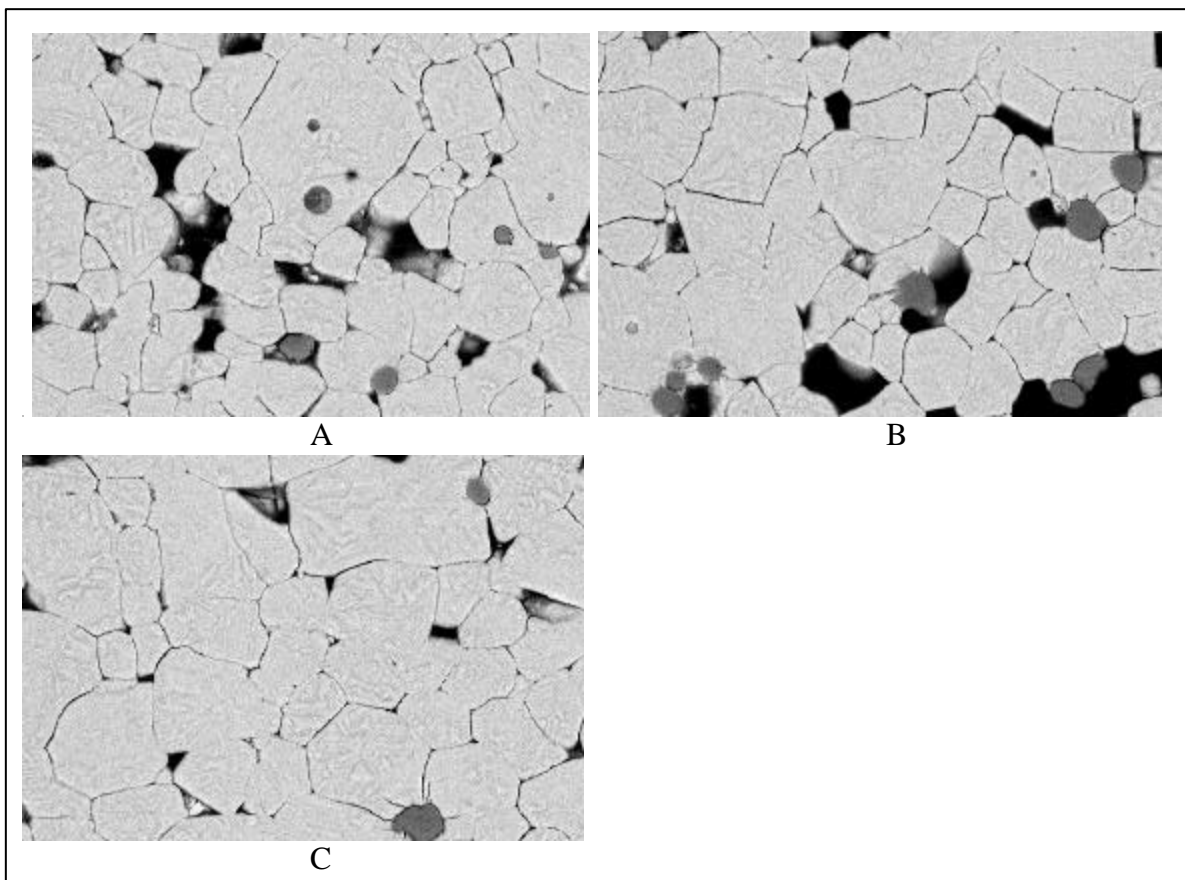


Figure 12: Back scattered electron micrographs of polished and etched UK-22 derived PZT, A) 800°C/1250°C, B) 950°C/1300°C, and C) 1100°C/1350°C.

UK-35 Powder Results:

Due to the craze cracking of UK-22 half slugs, the study was repeated with batch UK-35 oxalate, which was spray dried. Comparing Table 6 to Table 7 shows that the UK-35 material compacted to lower densities, but generally had higher isostatic and bisque densities (no particle size measurements or micrographs of the calcined UK-35 material were performed).

Table 7 Green and Bisque Density of UK-35 Samples

Calcine Temperature, °C	Dry Pressed Density, %	Isostatic Pressed Density, %	Bisque Fired Density, %
800	41.6	64.4	58.9
950	44.1	61.6	-
1100	51.1	67.9	65.9

Despite the slight improvement in bisque density, the UK-35 material sintered more poorly, yielding half-slugs with a density range of only 6.5 to 6.84 g/cc. Craze cracking was eliminated, but the low sintered density was unexpected. Measured weight losses during sintering were only ~0.5%, thus eliminating poor atmosphere control as a reason for the low density. This suggests that the materials were Pb deficient prior to sintering, perhaps via the calcining process. Given the unsatisfactory results of the UK-22 and UK-35 trials, calcining at these higher temperatures was abandoned for the UK process. The typical calcine temperature remained at 775°C.

BINDER STUDY

Polyvinyl alcohol (PVA) binder has long been the binder of choice for producing mixed-oxide PZT 95/5 billets at SNL and other suppliers to the weapons complex.²² However, ceramic systems with PVA binder can be adversely affected by changes in relative humidity.^{23, 24} Acrylic binder emulsions are less sensitive to moisture and have been shown to be superior to PVA in compact density, green strength, and binder removal.²⁵ Several binder systems were evaluated for effectiveness with UK and SP powders (development lot #9714). The binder systems included PVA (with polyethylene glycol (PEG) as a plasticizing agent), and an acrylic copolymer solution.[∞] To reduce inter-particle friction during compaction, a microcrystalline wax pressing aid[#] was added to the binder solutions.

The binder solutions were prepared as follows. A 6.7 wt. % PVA solution was first prepared by diluting a 20% stock solution with DI water. (The stock solution was previously prepared by heating the water to 80°C and dissolving the PVA into the water.³) A separate 6.7 wt. % solution of PEG was prepared by stirring/dissolving the PEG flakes in DI water. The two solutions were blended together via a stir plate and magnetic stirrer. To this blended solution, we added 1% of the EM-08 wax emulsion. This produced a binder stock solution of 8.2 wt % total organics (3.1% PVA, 3.1% PEG, and 2% EM-08 wax). This solution was sufficiently low in viscosity to permit addition via the liquid-solids feeder bar on the twin-shell blender.^α

The as-received HA4 acrylic binder solution was a 30 wt% concentration. This solution was diluted with DI water to make a 6.7 wt. % solution, to which we added 1% of the EM-08 wax emulsion, producing an 8.2 wt. % organic solution (6.1 % HA4 plus 2.1 % EM-08).

Several blending runs were prepared as listed in Table 8. The binder/wax solution additions are listed as weight percent of the PZT powder. Two of the blends used UK-34 powder and three blends used a separate blend of five SP powders (SP7A-15, SP7B-15, SP7E-15, SP5A-10 and SP5B-14), relative amounts unknown. The SP powders were blended via dry ball milling. No pore former was added to any powders in this study.

Table 8 Binder Addition Trials

Blending Run	Powder	Binder Addition
1	2 kg UK 34	1.5% PVA + 1.5% PEG + 1% EM-08
2	2 kg SP blend	1.5% PVA + 1.5% PEG + 1% EM-08
3	2 kg UK 34	3% HA4 + 1% EM-08
4	2 kg SP blend	3% HA4 + 1% EM-08
5	2 kg SP blend	3% HA4

The binders were added to the powders using a twin shell blender. Since each solution was diluted to pass through the liquid-solids feeder bar, the entire amount could not be added all at once without producing an aqueous slurry. Therefore, the binder was added in ~150 ml aliquots, with oven drying at 80°C for 2 h between each addition. Three or four binder addition/drying cycles were required for each powder. Following binder addition, three 70g half-slugs were

[∞] Glascol HA4, Allied Colloids, Suffolk, VA

[#] Hydrocer EM 08, Shamrock Technologies, Inc., Dayton, NJ

^α Blend Master, Patterson-Kelley, East Stroudsburg, PA

pressed from each binderized powder at 2 ksi and 5 ksi. Following die compaction, all billets were isostatically pressed at 30 ksi. Only two of the three billets from each powder/binder/pressure group were sintered at 1350°C with a 6 h hold. The UK and SP billets were fired in separate triple crucible enclosures during the same furnace run. The burial powder for the UK crucible was UK-17 (150 g) and SP9 powder (55 g) was used with the SP slugs. The billet densities are listed below, and are not corrected for organic content.

Table 9 Density Results for the Binder Study

Powder	Binder System*	Compaction Pressure, ksi	Die Pressed Density, g/cc	Isostatic Pressed Density, g/cc	Fired Density, g/cc	Open Porosity, %
UK34	PPE	2	3.91	5.28	7.48	2
UK34	PPE	5	4.32	5.34	7.48	2.1
UK34	HE	2	3.85	5.32	7.45	2.5
UK34	HE	5	4.25	5.36	7.38	3.1
SP Blend	PPE	2	3.00	4.64	7.59	1.0
SP Blend	PPE	5	3.35	4.68	7.58	1.8
SP Blend	HE	2	3.07	4.97	7.60	2.1
SP Blend	HE	5	3.68	4.96	7.58	1.3
SP Blend	H	2	2.99	4.66	7.76	0.0
SP Blend	H	5	3.46	4.69	7.74	0.03

*PPE = PVA/PEG/EM08, HE = HA4/EM08, H = HA4

From the data in Table 9, several trends are seen:

- For the SP billets, those without wax sintered to significantly higher fired densities and lower open porosities than those with wax.
- All billets with wax had open porosities that were unacceptably high (other studies indicate that open porosity >0.5% can cause misleading depoling and functional test results).^{21,+}
- The UK34 billets had significantly lower sintered densities than the SP billets, despite having higher die and isostatic densities.
- For all powders and binders, the density differences between 2 and 5 ksi were largely removed after isostatic pressing
- For the SP powders, the HA4/EM08 system produced a slightly higher isostatic pressed density than the PVA/PEG/EM08 system.
- For the SP billets with HA4 binder, the use of EM08 wax had little effect on the die pressed density but resulted in increased isostatic pressed density.
- For the UK34 billets, both binder systems yielded similar densities and open porosity.

Besides density, differences were observed in sintered billet appearance and defects. In general, the UK billets were more uniform in appearance, with very few cracks. The SP slugs had significant orange discoloration, determined by SEM/EDS to be Pb-rich platelets (Figure 13). Most of the SP billets also contained cracks. However, the SP slugs without EM08 wax were significantly improved, with uniform color and free of cracks. It's not clear why only the SP

⁺ Per T. W. Scofield, samples with 7.9% open porosity show a measured switching pressure of 54 ksi, but when jacketed with an impervious epoxy coating the switching pressure dropped to 41 ksi. Samples with open porosity as low as 0.5% sometimes gave differing switching pressure values for jacketed and unjacketed conditions. For this reason, we prefer ceramics with open porosity <0.5%.

billets containing wax (which was presumed to be completely removed during the bisque fire step) were discolored and/or cracked.

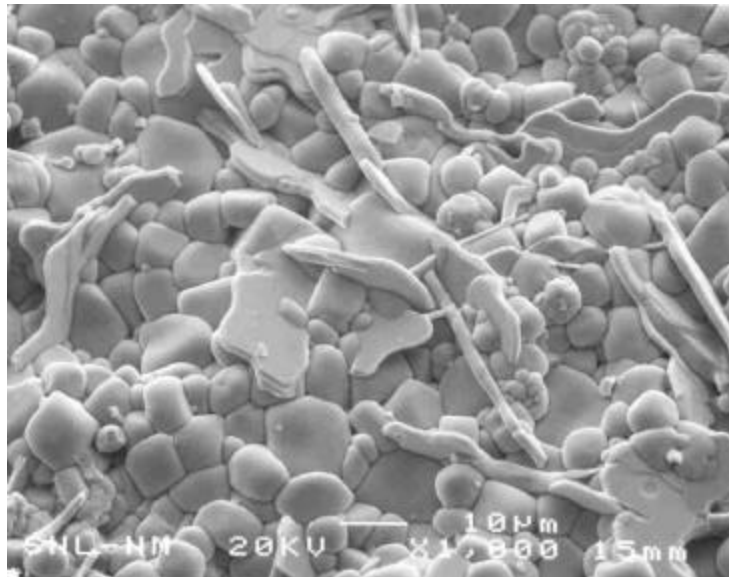


Figure 13: As-sintered surface of SP derived PZT processed with HA4 binder and EM-08 wax (lot #9714). Platelets contained a higher concentration of Pb than surrounding bulk material.

In addition to the above experiments, a smaller study was performed (lot #9809) with a paraffin wax emulsion binder.[∇] UK41 powder was binderized with Mobilcer C, and a blend of Mobilcer C plus EM-08 wax. A 3 wt.% addition of the paraffin emulsion was blended with 1850 g of UK41. For the second blending trial, 1% EM08 was pre-mixed with 3% of the paraffin emulsion by stirring for 16 h, then added to the UK41 powder. The powders were binderized, pressed, and sintered per the processes described above. Density results are tabulated below.

Table 10 Lot #9809 Density Results

Powder	Binder System*	Compaction Pressure, ksi	Die Pressed Density, g/cc	Isostatic Pressed Density, g/cc	Fired Density, g/cc	Open Porosity, %
UK41	3% M	2	3.55	5.42	6.854	7.0
UK41	3% M	5	3.87	5.47	7.153	4.0
UK41	3% M + 1% E	2	3.57	5.48	6.810	4.3
UK41	3% M + 1% E	5	3.92	5.50	6.951	7.1

*E = EM-08, M = Mobilcer C

Compared to the prior experiments, these billets had significantly lower sintered density and correspondingly higher open porosity. Since two different UK powder batches were used (UK34 and UK41), direct comparisons between the Mobilcer C binder and the previous binder systems were difficult. Other work with UK powders has shown significant variation in sintered density between UK powder lots, so the low values from lot 9809 may be due in part to the UK powder and not the particular binder used.

[∇] Mobilcer C, Mobil Oil Corp. Fairfax, VA

These binder studies were not exhaustive of the possible combinations of binder type or concentration, or the possible effects of binder on subsequent ferroelectric properties. But from this study, we concluded that HA4 binder, alone, was sufficient for promoting high quality green and sintered billets.

SINTERED DENSITY SUMMARY OF UK AND SP DERIVED PZT

As described earlier, two synthesis methods were being developed in parallel. Program resources could not support the parallel efforts indefinitely, and the SP process was eventually selected for continued development and scaling to production size. One of the principal concerns with the UK material was the apparent lack of control over the sintered density. As a general rule, the UK material sintered to a lower final density than SP material. Ferroelectric properties were also a strong consideration in the selection process, and those considerations are summarized in Appendix B. From Table 11 the densities of the UK materials are typically <7.4 g/cc, even when no pore former was added. Exceptions to this occurred when UK 24/25 or UK 34 powders were used. Even in those cases, when either 0% or 0.3% avicel was added, the density values were limited to <7.5 g/cc. Also note that the open porosity values for these lots were rarely <1% and ranged as high as 11.7%.

Table 11 Sintering Results of UK Derived PZT

Lot #	Powder ID	Binder*	Avicel	Bulk Density, g/cc	Open Porosity, %	Comments^
9712 800	UK22	3%PP	0	7.29	5.5	die pressed at 5ksi
9712 950	UK22	3%PP	0	7.24	5.1	die pressed at 5ksi
9712 1100	UK22	3%PP	0	7.27	5.3	die pressed at 5ksi
9712 repeat 800	UK35	3%PP	0	6.74	10	
9712 repeat 950	UK35	3%PP	0	6.73	9.9	
9712 repeat 1100	UK35	3%PP	0	6.61	11.7	
9714, PPW2	UK34	3%PPE	0	7.48	2.0	+ 1% EMO8 wax
9714, PPW5	UK34	3%PPE	0	7.48	2.1	+ 1% EMO8 wax, 5 ksi
9714, HW2	UK34	3% HE	0	7.45	2.5	+ 1% EMO8 wax
9714, HW5	UK34	3% HE	0	7.38	3.1	+ 1% EMO8 wax, 5 ksi
9733	UK37	3% H	0.6	7.22	5.2	bisque fired twice
9735	UK39	3% H	0.3	7.14	5.1	
9801	UK24/25	3% H	0.3	7.44	0.6	spray dried oxalate
9801A	UK24/25	3% H	0.3	7.43		spray dried oxalate, re-hydrated
9802	UK27/29	3% H	0.3	7.38	2.7	modified UK
9809 MC2	UK41	3%M	0	6.85	7.0	
9809MC5	UK41	3%ME	0	7.15	4.0	5 ksi
9809 MCW2	UK41	3%ME	0	7.16	6.8	+ 1%EM08 wax
9809 MCW5	UK41	3%ME	0	6.95	7.1	+1%EM08 wax, 5ksi
9817	UK57	3% H	0.15	7.22	5.1	7.15 including tops and bottoms
9824	UK596061	3% H	0	7.26	4.3	875 Calcine
9824,12	UK596061	3% H	0	7.34	3.9	875 Calcine, 12 ksi
9825	UK596061	3% H	0	7.23	4.5	825 Calcine
9825,12	UK596061	3% H	0	7.25	4.8	825 Calcine, 12 ksi
9826 875AM2	UK596061	3% H	0	7.21	4.4	875 Calcine, AM & FD
9826 875AM12	UK596061	3% H	0	7.24	4	875 Calcine, 12 ksi, AM & FD
9827 825AM2	UK596061	3% H	0	7.24	4.3	825 Calcine, AM & FD

9827 825AM12	UK596061	3% H	0	7.29	3.9	825 Calcine, 12 ksi, AM & FD
9830 825W2	UK596061	2% HE	0	7.21	6.2	825 Calcine, 1%EM08, 2 ksi
9830 825W12	UK596061	2% HE	0	7.25	5.3	825 Calcine, 1%EM08, 12 ksi
9831 875W2	UK596061	2% HE	0	7.29	4.1	875 Calcine, AM & FD, 1%EM08, 2ksi
9831 875W10	UK596061	2% HE	0	7.31	3.5	875 Calcine, AM & FD, 1%EM08, 10ksi
9739, PPW2	UK34	3% PP	0	7.47	2.7	+ 1% EMO8 wax, 2 ksi, 9714 powder
9939, PPW5	UK34	3% PP	0	7.47	2.3	+ 1% EMO8 wax, 5 ksi, 9714 powder
9939, HW2	UK34	3% H	0	7.48	2.1	+ 1% EMO8 wax, 2 ksi, 9714 powder
9939, HW5	UK34	3% H	0	7.47	2.5	+ 1% EMO8 wax, 5 ksi, 9714 powder
9942, W2	UK66	2% HE	0	7.32	3.4	UK34 repeat, AM & FD, +1% EM08, 2 ksi
9942, W5	UK66	2% HE	0	7.33	3.3	UK34 repeat, AM & FD, +1% EM08, 5 ksi

*PP = PVA/PEG, E = EM08, H = HA4, M = Mobilcer C

^AM&FD = attritor milled and freeze dried

Also included in the above Table are the results of several attempts to increase the sintered density. (Attempts to increase the density by altering the powder synthesis process steps were tried in parallel, but those experiments will not be addressed here.) Attritor milling, calcine temperature, die pressing pressure, half-slug aspect ratio, and additional trials with EM-08 wax were tried. While the details of these experiments will not be reported here, the results are summarized as follows.

Attritor milling of the calcined powder^{II} was attempted to decrease the discrete particle size and enhance the sintering rate. The milling was performed in an aqueous slurry and the water was removed by freeze-drying to prevent re-agglomeration of the powder that is common with oven drying. Attritor milling had little or possibly a slightly negative affect on density, with the highest values <7.3 g/cc without any pore former. Likewise, lowering the oxalate calcining temperature from 875 to 825°C produced a slight decrease in density, to 7.24 g/cc. Die pressing the half slugs at 2, 5, and 12 ksi (followed by isostatic pressing at 30 ksi) had only a marginal effect on density (<0.01 g/cc increase). Likewise, adding 1% EM-08 wax had little effect. It was observed in earlier trials that thinner samples sintered to higher density than the ~0.4 in. thick half slugs. However, when using a blend of UK59, UK69, and UK61 powder, and pressing the half slugs to one-half and one-quarter of the typical slug thickness, no consistent affect of compact aspect ratio on sintered density could be measured. In an attempt to repeat the success of UK34 material, UK66 was synthesized with identical procedures and was processed into half slugs with the most favorable powder processing parameters: attritor milling, 2% HA4 binder with 1% EM08 wax, and pressed at either 2 or 5 ksi, but no pore former added. These half slugs sintered to only 7.33 g/cc and had an open porosity of 3.3%

Typical sintered results for SP powders are listed in Table 12. The SP derived PZT materials sintered to high density (>7.4 g/cc) and low open porosity (typically <0.4%) even when 1.8 wt % avicel pore former was added. Based on these results and the observations contained in Appendix B, the SP process was selected for further development and process scale-up.

^{II} courtesy K. G. Ewsuk, Dept. 1843.

Table 12 Sintering Results of SP Derived PZT

Lot #	Powder ID	Binder*	Avicel	Bulk Density, g/cc	Open Porosity, %	Comments
9712SP 800	SP7F-15	3% PP	0	7.65	0.4	
9712SP 950	SP7F-15	3% PP	0	7.79	1.05	
9712SP 1100	SP7F-15	3% PP	0	7.68	0.5	
9714 PPW2	SP5&7 blend	3% PPE	0	7.59	1.0	+ 1% EMO8 wax
9714 PPW5	SP5&7 blend	3% PPE	0	7.58	1.8	+ 1% EMO8 wax, 5 ksi
9714 HW2	SP5&7 blend	3% HE	0	7.6	2.1	+ 1% EMO8 wax
9714 HW5	SP5&7 blend	3% HE	0	7.58	1.3	+ 1% EMO8 wax, 5 ksi
9714 H2	SP5&7 blend	3% H	0	7.76		
9714 H5	SP5&7 blend	3% H	0	7.74	0.03	5 ksi
9730	SP9ABDE	3% H	0.6	7.65	0.04	
9734 SP11C	SP11C	3% H	1.8	7.39	1.6	
9736 SP9	SP9abde	3% H	1.8	7.42	2.1	
9803 12B 1000Al	SP12B-15	3% H	1.8	7.37	0.3	1000 ppm Al
9813 12B 500Al	SP12B-15	3% H	1.8	7.31	0.2	500 ppm Al
9816 SP12E	SP12E-15	3% H	1.8	7.43	0.1	
9818 SP12G	SP12G-15	3% H	1.8	7.32	0.2	500 ppm Al
9819 12H	SP12H-16	3% H	1.8	7.43	0.2	
9828 14B	SP14B-16	3% H	1.8	7.44	0.1	High Ti
9938 SPC2	SPC-2	3% H	1.8	7.46	0.1	continuous batch
9941 SPC1	SPC-1	3% H	1.8	7.47	0.3	continuous batch
9944 14D	SP14D-16	3% H	1.8	7.47	0.2	RT oxalic acid
9907 SP14C	SP14C-16	3% H	1.8	7.42	0.2	double crucible
9954 SP16A	SP16A	3% H	1.8	7.49	0.03	Bldg. 897 prod. equipment

*PP = PVA/PEG, E = EMO8, H = HA4

SUMMARY

Chemical preparation methods are being developed as a future source of PZT 95/5 for neutron generator voltage bar applications. The quality and functionality of these chem-prep materials can only be determined from the character and testing results of the billets and voltage bars fabricated from these powders. As described above, laboratory-scale (typically <2kg) powder processes have been developed to produce PZT billets of controlled Pb stoichiometry, with desired densities and open porosities.

The calcining temperatures for UK and SP materials were established at 750°C and 950°C, respectively, as a compromise between particle development and preventing excessive Pb loss. To support the development of the chemical synthesis methods, the sintering temperature and time were held constant at 1350°C and 6 h. To control Pb loss during sintering, triple enclosures and a sufficient amount of burial powder were used to limit the weight loss to <0.3%. These conditions typically yielded ceramic microstructures with average grain sizes between 8 and 12 μm, and a range of 1 to 30 μm. The density of the billets depended on the level of pore former added and the sinterability of the PZT powders. After evaluating several binder systems and organic pressing aids, the acrylic binder was selected for routine use as it consistently produced uniform billets with low open porosity. Due to its more consistent sintering behavior and

electrical properties, the SP derived PZT 95/5 was selected for further development and process scale-up.

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APPENDIX A

The UK Process for the Synthesis of PZNT Powder

Steven J. Lockwood

The UK process for the synthesis of PNZT was developed by Dave Bennett (Atomic Weapons Establishment, Aldermaston, UK). Following the establishment of a collaborative agreement, the process description was shared with SNL for continued development. The first batch synthesized at SNL was initiated in March, 1996. The flow chart for the UK process is shown below. More specifically, the powder synthesis process can be described as follows: 1) Lead nitrate powder was dissolved in deionized water, 2) The titanium n-propoxide was added to the lead nitrate solution and dissolved with the slow addition of concentrated nitric acid, 3) To the Pb-Ti solution was added the zirconyl nitrate solution, 4) To the Pb-Zr-Ti solution was added niobium oxalate (prepared by the dissolution of niobium pentachloride in an aqueous oxalic acid solution), 5) The resulting metals solution was precipitated by mixing with an aqueous oxalic acid solution, 6) After two hours of mixing, the pH of the solution was raised to pH 9.0 by the addition of concentrated ammonium hydroxide, 7) The final slurry was washed extensively and filtered, 8) The washed precipitate was then spray dried, 9) Finally, the spray dried powder was calcined to form the PNZT powder.

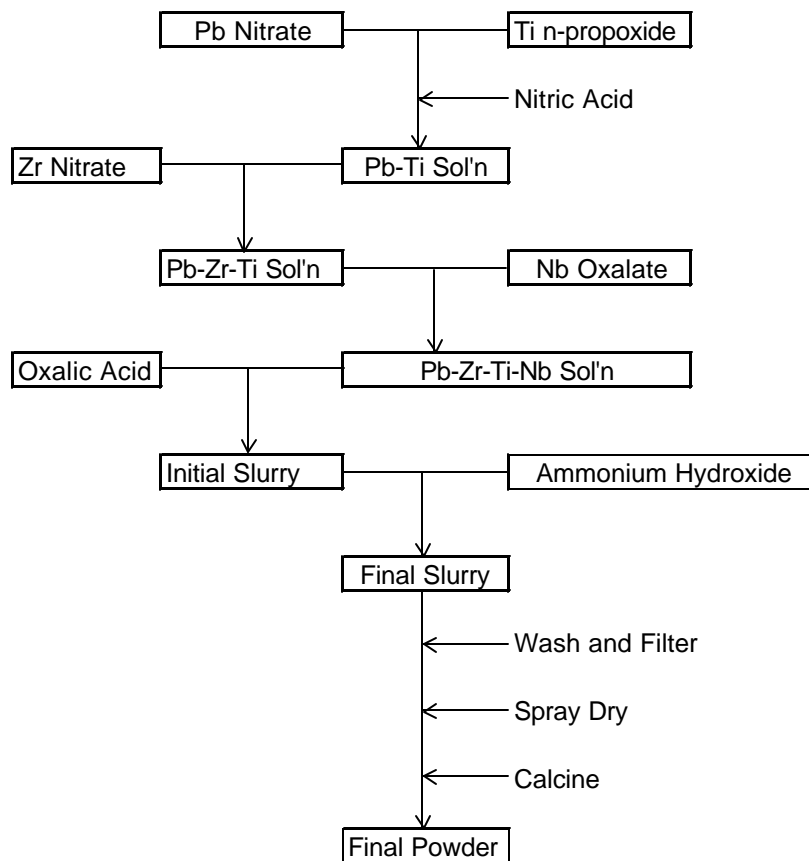


Figure 14: UK Process for synthesis of PNZT powder.

Throughout development a number of process modifications/improvements were investigated. These included adjusting the stoichiometry and precursor solution concentrations, changing the timing of mixing and ammonium hydroxide additions, modifying the washing and filtering processes, and altering the calcining profile. Analysis of the process and powder showed that the basic process, described above, led to sequential precipitation of the components, and resulted in segregation of the lead at the slurry filtering stage. It was decided to investigate a major modification to the process to generate a more homogenous material. Continuous processing was first attempted with batch 13. The preparation of the precursor solutions was unchanged, but instead of precipitating out the metals with oxalic acid and then raising the pH, the continuous process involved mixing the metals solution, the oxalic acid precipitant solution, and the ammonium hydroxide solution simultaneously so that the target pH of 9.0 was maintained throughout the entire precipitation stage. Batches 20, 26, 28, 30, were continuously processed, as were all batches from 33 on.

APPENDIX B

Selection of Sandia Process (SP) for Scale-Up to Production

James A. Voigt

As stated in the body of the report, two solution-based routes to PZT precursor powders were initiated at the onset of the PZT materials development effort: 1) the aqueous process (UK) - based on a process under development at AWE, Aldermaston, U.K. and 2) the non-aqueous process (SP) - developed and patented at Sandia as part of a LDRD project. By late in the calendar year 1998, the development team decided that one of the two processes needed to be selected for scale-up to the level required to meet future production needs.

The SP process was chosen for scale-up largely based on the encouraging explosive functional test results obtained for voltage bars prepared from SP-derived material. Functional test units were fabricated using voltage bars from seven different 1.5 kg SP powder batches that were prepared under nominally the same baseline batching conditions. For the 70 units explosively tested under MC3422 voltage bar test conditions, 69 units passed (10 units per lot were tested: 4 units/lot @ -54C, 3 units/lot @ room temperature, and 3 units/lot @ 74C); the unit that failed experienced a high voltage breakdown at the room temperature test condition.

A limited number of lots of UK voltage bar material were functionally tested using the same MC3422 test conditions. The UK material exhibited a large number of high voltage breakdowns. Because of these functional results and the difficulty in controlling the density and open porosity, further development work on the UK process was halted. At the time, the development team felt that the UK material could be made to work – it was just not as far along as the SP process. For completeness, Figure B1 shows representative ferroelectric hysteresis loops for the two PZT synthesis methods. It can be seen that the shape of the loops of the UK and SP materials are very similar.

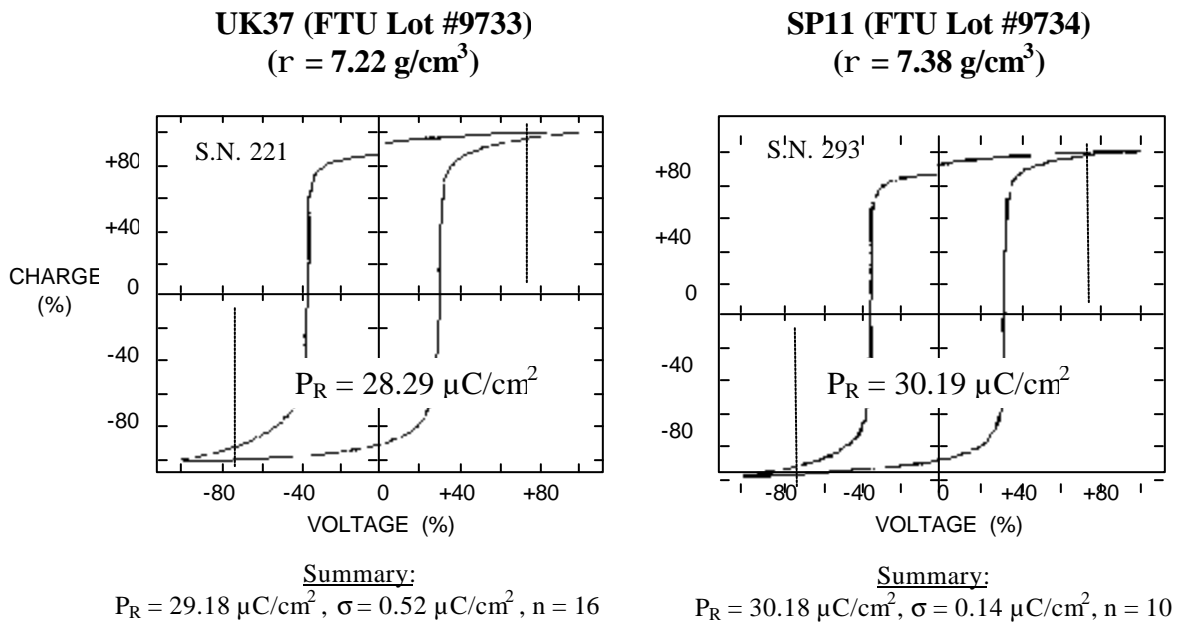


Figure 15: Comparison of ferroelectric hysteresis loops for UK and SP derived PZT 95/5 ceramics.

The hydrostatic depoling characteristics of the two materials were, however, somewhat different. This is shown in Figure B2 where representative depoling curves are given for UK and SP material (same material lots that were used to generate hysteresis data presented in Fig. B1). The UK material had a much sharper depoling transition than the SP material, which is probably related to its higher open porosity (5.2 % vs. 0.41 %).

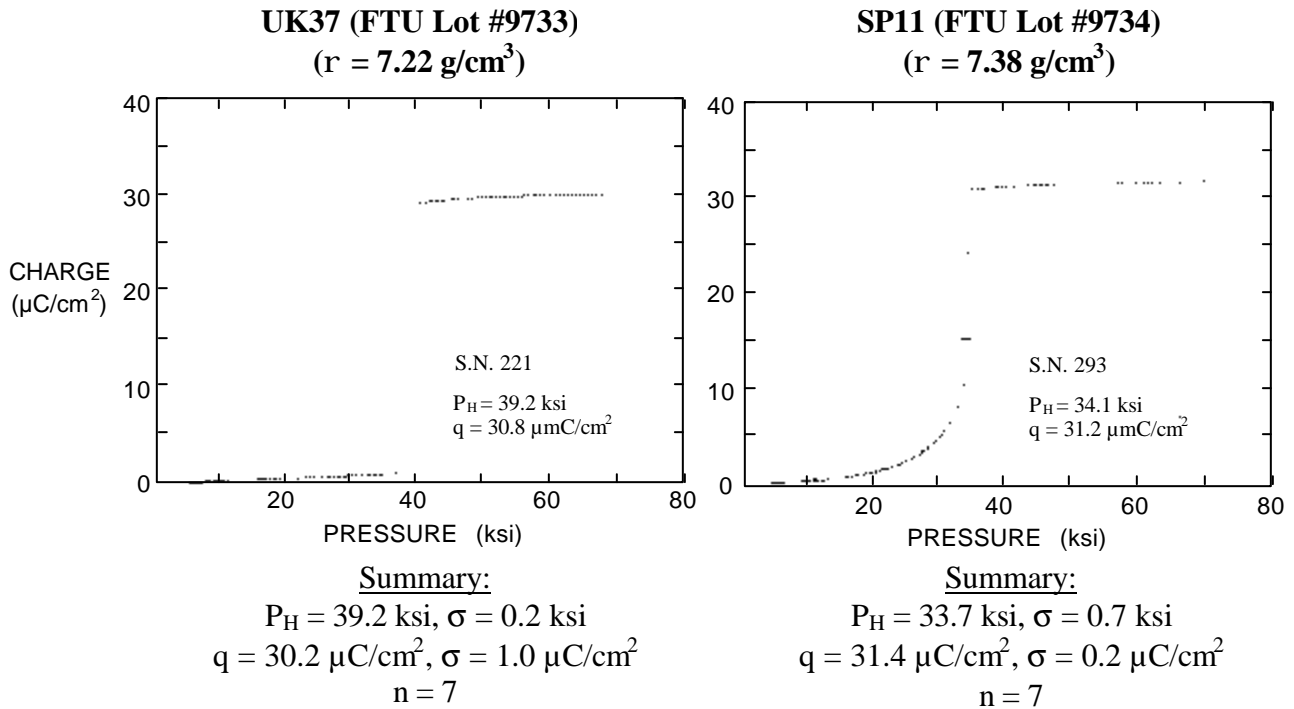


Figure 16: Comparison of hydrostatic depoling curves for UK and SP derived PZT 95/5 ceramics.

Distribution:

1	MS1421	G. A. Samara, 1120
1	1421	R. E. Setchell, 1122
1	MS0886	J.C. Barrera, 1822
1		
1	MS1349	K. G. Ewsuk, 1843
1	0889	S. J. Glass, 1843
1	1349	W. F. Hammetter, 1843
	1411	W. R. Olson, 1843
1	1411	B. A. Tuttle, 1843
1	0889	C. S. Watson, 1843
1	MS1411	D. L. Moore, 1846
1	1411	J. A. Voigt, 1846
1	MS0515	J. D. Keck, 2561
1	0521	S. T. Montgomery, 2561
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1	0959	C. B. DiAntonio, 14192
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