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EFFECT OF ZRO2 SOURCE VARIATIONS ON PBZRO3-PBTIO3 PIEZOELECTRIC--ETC(U)
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PbZrO$_3$-PbTiO$_3$ PIEZOELECTRIC PR

Technical Report No. 1
to the
Office of Naval Research

by

W. B. Harrison

Contract N00014-76-C-0623 NR

December 1977

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EFFECT OF ZrO_2 SOURCE VARIATIONS ON $PbZrO_3$-$PbTiO_3$ PIEZOELECTRIC PROPERTIES.

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ABSTRACT

ZrO_2, as derived from three zircon source minerals and many process variations, was physically and chemically analyzed. The impact of the ZrO_2 variations obtained was then evaluated in both dry and wet blended lead zirconate-lead titanate, high drive type piezoelectric compositions. Proper purification and blending of the ZrO_2 is shown to yield PZ-PT material with uniform low and high drive piezoelectric behavior. Single precipitated ZrO_2 and dry blending are shown to be highly variable processes.

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I. INTRODUCTION

Most of the Navy's active and passive transducers contain lead zirconate-lead titanate (PZ-PT) ceramic elements. These materials have been used extensively in transducers because they are capable of operating at both low and high frequencies, high stress amplitudes, high powers and large bandwidths at high efficiencies. Where these properties are required, PZ-PT ceramics are the most cost-effective approach known. However, there are still certain limitations in the uniformity of performance, related primarily to the variability of the source of ZrO_2 used. This program was initiated to study the source of variability in ZrO_2 and its impact on the piezoelectric performance of a typical high drive projector type PZ-PT composition. The impact of ZrO_2 derived from various zircon sources, in both a dry and wet blend PZ-PT batching approach, was evaluated.

II. EXPERIMENTAL PROCEDURE

Honeywell's approach to this study was based on a well-established capability in producing piezoelectric ceramic materials for various Navy programs over the past 20 years. Zircon ($ZrO \cdot SiO_2$) was obtained from a number of sources and processed into ZrO_2 by the standard commercial process used at the Harshaw Chemical Company* for piezoelectric grade ZrO_2. A second approach derived ZrO_2 from the standard Honeywell alkoxide process, which uses tetra-N-butyl zirconate (TNBZ) as a ZrO_2 source. The ZrO_2 produced by each of these processes was then fully chemically and physically characterized. The reactivity of each ZrO_2 in PZ-PT was evaluated and used to determine how these ZrO_2 variations impact the behavior and properties of PZ-PT. These processes are described in this section.

A. DERIVATION OF ZrO_2

There are essentially two minerals from which ZrO_2 may be derived. The most abundant and commonly used material is zircon, a zirconium silicate ($ZrO_2 \cdot SiO_2$). Commercial deposits of zircon are found in Florida and Georgia in this country and in extensive Australia, India and Africa deposits. A second mineral, baddelyite, is a naturally occurring ZrO_2 found in Brazil and Africa, and contains 10 to 20 percent impurities of SiO_2, TiO_2 and Fe_2O_3. Both materials are found in secondary deposits of heavy beach sands. After grinding, the lighter free silica is washed away from the zircon or baddelyite, and much of the TiO_2 and Fe_2O_3 in the form of a slightly magnetic ilmenite is magnetically eliminated.

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*Harshaw Chemical Company, Division of Kewanee Oil Company Cleveland, Ohio 44106.

For this program, about 2000 pounds of zircon sand were obtained from each of three sources: the Florida Starke mine (Harshaw's mormal source), the Folkston mine in Georgia, and an Australian source. Sand from the Georgia and Australian sources was procured and chemically analyzed by Harshaw as part of their subcontracted effort on this program. Two lots from each source were obtained because the first was accidentally contaminated during early stages of processing. Harshaw submitted a five-pound sample of each of these six lots to Honeywell. The particle size distribution was determined by a sieve analysis, and the bulk density and color of each was noted. Since the Australian zircon was obtained in an uncalcined state, a portion of the second lot sample was calcined at 900°C and reevaluated. Harshaw then converted each source of zircon to zirconium oxide by their standard purification process outlined below:

$$\overset{\text{(Zircon)}}{ZrO_2 \cdot SiO_2} + 4NaOH\ \text{(Typical)} \rightarrow Na_2SiO_3 + Na_2ZrO_3 + 2H_2O \qquad (1)$$

$$Na_2ZrO_3 + 2HCl \rightarrow ZrOCl_2 + 2NaCl + H_2O \qquad (2)$$

$$ZrOCl_2 + \overset{\text{(Typical)}}{2NH_4OH} + H_2O \rightarrow \overset{\text{First Precipitate*}}{ZrO_2 \cdot X\ H_2O} + 2\ NH_4Cl + H_2O \qquad (3)$$

$$ZrO_2 \cdot X\ H_2O + HCl + H_2O \rightarrow 2\ ZrO\ OHCl + H_2O \qquad (4)$$

$$ZrOOHCl + \overset{\text{(Typical)}}{NaOH} + H_2O \rightarrow \overset{\text{Second Precipitate**}}{ZrO_2 \cdot X\ H_2O} + NaCl + H_2O \qquad (5)$$

$$ZrO_2 \cdot X\ H_2O + Heat \xrightarrow{\text{Calcine**}} ZrO_2 + H_2O \qquad (6)$$

Zircon was reacted with a molten alkali, such as sodium hydroxide, to produce the products shown in equation (1). The water soluble sodium silicate was washed from the insoluble sodium zirconate, which was then reacted

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*Materials delivered to Honeywell from Harshaw.

with hydrochloric acid, according to equation (2), to form zirconium oxychloride. As shown in equation (3), this is next reacted with a hydroxide, such as ammonium hydroxide, to produce zirconium hydroxide or the first precipitate. This precipitate can be calcined to produce ZrO_2, as in equation (6), or redisolved in an acid, equation (4), and reacted with another hydroxide, equation (5), to produce a second precipitate.

About 500 pounds of each first precipitate, second precipitate and normal calcine were delivered by Harshaw to Honeywell for further processing. About 10 pounds of each first and second precipitated $ZrO_2 \cdot X\ H_2O$ materials were then calcined for eight hours in clean, dense MgO crucibles at 600, 900 or 1200°C. About four pounds of the calcined ZrO_2 were then micronized in a micropulverizer through an 1/8 inch opening screen. Table 1 gives a breakdown of the various ZrO_2 materials produced for this program.

A second method of generating five pound batches of ZrO_2 was investigated at Honeywell where tetra-N-butyl zirconate (TNBZ)* was hydrolyzed to $Zr(OH)_4$ and then calcined for 12 hours at 500°C to produce ZrO_2. In addition to a 100% ZrO_2 product made by this process, four other mixtures of zirconium and titanium oxide were produced by blending titanium-N-butyl titanate (TNBT)** with the TNBZ to study the impact of titanium impurities in ZrO_2. A five pound batch of each ZrO_2 was made, in which 0.02, 0.08, 0.18 and 0.36% TiO_2 was added.

The amount of water or other decomposition products associated with each material after the first or second precipitation, and all stages of calcination, were determined by measuring the weight loss on ignition after four hours at 900°C.

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*Obtained from Kay-Fries Chemical Inc., Montvale, NJ 07645, American distribution for Dynamit-Nobel.

**Obtained from E.I. DuPont Photo Products, Electronic Materials Division, Wilmington, DE 19898

Table 1. ZrO_2 materials produced.

Type Material	ZrO_2 Source	Calcination Temperature	Present State	Initial Quantity	
				Unmicronized	Micronized
Alkoxide ZrO_2	TNBZ	500°C	ZrO_2	5 lbs *	0
Alkoxide ZrO_2	TNBZ/T	500°C	ZrO_2 + 0.02% TiO_2	5 lbs *	0
Alkoxide ZrO_2	TNBZ/T	500°C	ZrO_2 + 0.08% TiO_2	5 lbs *	0
Alkoxide ZrO_2	TNBZ/T	500°C	ZrO_2 + 0.18% TiO_2	5 lbs *	0
Alkoxide ZrO_2	TNBZ/T	500°C	ZrO_2 + 0.36% TiO_2	5 lbs *	0
First Precipitate	Australia	0 **	$ZrO_2 + X\ H_2O$	758	
	Georgia	0 **	$ZrO_2 + X\ H_2O$	722	
	Florida	0 **	$ZrO_2 + X\ H_2O$	673	
	Australia	600	ZrO_2	0.5	4 *
	Georgia	600		1.0	4 *
	Florida	600		0.5	4 *
	Australia	900		1.0	4 *
	Georgia	900		1.0	4 *
	Florida	900		1.0	4 *
	Australia	1200		0.3 *	4 *
	Georgia	1200		1.0 *	4 *
	Florida	1200		1.0 *	4 *
Second Precipitate	Australia	0 **	$ZrO_2 + X\ H_2O$	477	
	Georgia	0 **	$ZrO_2 + X\ H_2O$	460	
	Florida	0 **	$ZrO_2 + X\ H_2O$	397	
	Australia	600	ZrO_2	3	4 *
	Georgia	600		3	4 *
	Florida	600		5	5 *
	Australia	900		3	4 *
	Georgia	900		4	4 *
	Florida	900		4	4 *
	Australia	1200		3 *	4 *
	Georgia	1200		3 *	4 *
	Florida	1200		3 *	4 *
	Australia	Unknown **			400 *
	Georgia	Unknown **			395 *
	Florida	Unknown **			334 *

* Material characterized and batched.

** Material supplied from Harshaw subcontract.

B. CHARACTERIZATION OF ZrO_2

Each of the ZrO_2 materials with asterisks in Table 1 was characterized to determine as much as possible about the physical and chemical differences that result from the ZrO_2 processing variables. The bulk density and pressed density (2900 psi) of each ZrO_2 were determined by the standard volumetric and weight approach. The ultimate crystallite size associated with each material was determined from high magnification photos (to 30, 000X) made with an electron transmission microscope. The particle or agglomerated size was also determined by the MSA centrifuge approach. The spectrographic approach was used to determine the chemical impurities associated with each type of ZrO_2.

C. WET BLENDED PZ-PT

Each of the ZrO_2 lots in Table 1, except the first shipment and unpulverized materials, was used to prepare a six kilogram, high drive PZ-PT batch according to the compositional formula:

$$Pb_{.94}Sr_{.06}(Zr_{.53}Ti_{.47})O_3 + 0.005 \text{ wt. } \% \ Fe_2O_3.$$

The only variation in materials used was the ZrO_2. The LOI of each ZrO_2 was used to compensate for the Zr content. Each batch was (1) wet ball milled for two hours with an equal amount of water, (2) pan dried, (3) granulated, (4) calcined at 900°C for five hours, (5) cooled and micropulverized, (6) wet blended with methocel and stearic acid, (7) spray dried, (8) pressed into 1 inch diameter by 0.2 inch thick disc at 6000 psi, (9) burned off in air at 830°C for five hours and cooled, and (10) checked for unfired density. Twelve discs were fired in closed magneisum oxide saggers with 10 grams of $PbZrO_3$ to 1290°C for two hours to a cone 13 at 6 o'clock. The density of the fired pieces was measured and each disc was ground to a thickness of 0.100 inch, electroded with silver paste, and fired at 750°C in a Trent wire mesh belt furnace.

After cooling, the unpoled capacitance and electrical dissipation were measured and each disc was polarized at 6kV for 60 seconds at 140°C. The low field capacitance, electrical dissipation, resonant frequency, anti-resonant frequency, and resonant resistance were then measured at 1, 5, 15, 30 and 90 days. The high field capacitance and electrical dissipation were determined at 1000 hertz after 100 days of aging and after 60 seconds running at 5, 10 and 15 volts/mil. A minimum of 24 hours was allowed between each successive higher driving field.

A small, fired fragment of each batch was optically polished and etched in 5:1:1 solution at 95°C for 30 seconds. This solution contained five parts of saturated NH_4Cl solution, one part H_2O and one part concentrated H_2SO_4. A typical area of each sample was photographed at magnification of 400X.

D. DRY BLENDED PZ-PT

Nine dry blended batches were prepared from the 600, 900 and 1200°C calcined double precipitated ZrO_2 produced from the three zircon sources. The same high drive composition used for the wet blended part of this program was used. Each raw material was dry blended for 10 minutes in a V-cone blender, starting with Fe_2O_3 and ZrO_2. Then, TiO_2, $SrCO_3$ and PbO were added and each blended another 10 minutes in the V-cone blender. The complete batch was emptied into a plastic bag and kneaded until a uniform color was obtained, and finally V-cone blended another 10 minutes. All batches were processed this way as uniformly as possible. The dry blended material was then calcined at 900°C for five hours, wet ball milled, spray dried and produced into test discs as discussed above. Thus, the only difference in these nine batches is the dry versus the wet blending approach used during the mixing of the oxides for this composition.

III. RESULTS AND DISCUSSION

This section discusses the characterization results obtained from the zircon sands and various ZrO_2 materials derived from these sands. The impact of these ZrO_2 variations on the physical and electrical behavior of a high drive piezoelectric composition is then analyzed.

A. ZIRCON RAW MATERIAL

The chemical and physical data obtained on the two samples each of Florida, Georgia and Australian zircon sand are reported in Table 2. Significant differences in the physical size of the zircon are apparent. The Australian zircon was coarsest, while the Georgia zircon had the finest grains. The Georgia zircon (2-2) also appeared to be slightly purer than the Florida (2-1) material; however, both domestic materials are substantially purer than the Australian zircon. Alumina and iron appear to be the most variable impurities. Heavy mineral (PbO and rare earth) impurities in the domestic zircon sands appear to be greater. The main mineral impurities in these materials appear to be ilmenite, rutile, kyanite, and possibly, monazite.

The dark Australian zircon sand used had not previously been calcined to burn off organic impurities; therefore, it contained an ignition loss of about 0.13 percent, opposed to 0.02 and 0.04 percent, respectively, for the previously calcined Florida and Georgia sands.

The sample of the Australian zircon calcined at 900°C for five hours had about the same particle size distribution as the uncalcined zircon. The bulk density of these materials varied from 2.69 to 2.89 gm/cc where the highest and lowest density were associated with the coarser and finer sand, respectively.

Table 2. Chemical and particle size analysis of zircon sand.

		Florida		Georgia			Australia	
		Lot 1-1	Lot 2-1	Lot 1-2	Lot 2-2	Lot 1-3	Lot 2-3	Calcine Lot 2-3
Percent Present	ZRO_2	66.60	65.98	65.43	66.58	65.16	64.29	
	SiO_2	32.29	32.26	31.77	31.96	31.91	31.54	
	TiO_2	0.143	0.119	0.314	0.118	0.338	0.202	
	Fe_2O_2	0.036	0.044	0.054	0.039	0.116	0.092	
	Al_2O_3	0.094	0.945	0.945	0.378	1.512	3.779	
	B_2O_3	0.006	0.003	0.006	0.003	0.006	0.003	
	CaO	0.070	0.070	0.070	0.070	0.028	0.028	
	CR_2O_3	ND	ND	ND	ND	ND	0.003	
	Ca_2O	ND	0.001	ND	0.001	ND	ND	
	La_2O_3	ND	0.059	0.094	0.094	ND	ND	
	PbO	0.086	0.054	0.086	0.054	0.022	0.022	
	MgO	0.083	0.133	0.133	0.133	0.083	0.083	
	MnO	0.003	0.001	0.010	0.001	0.006	0.001	
	Ag_2O	ND	ND	0.001	ND	ND	ND	
	V_2O_5	0.004	0.001	0.009	0.001	0.009	0.009	
	L.O.I.		0.016		0.044	0.116	0.142	
	Total	99.415	99.586	98.922	99.476	99.306	100.194	
Mesh Size	>60		ND	ND	ND	0.68	0.60	0.52
	-60+100		0.57	0.54	0.46	67.12	67.85	67.10
	-100+160		76.79	34.78	35.82	31.53	30.62	29.98
	-160+200		16.94	42.98	43.59	0.67	0.93	2.05
	-200+325		5.67	21.50	19.95	ND	ND	0.30
	< 325		0.03	0.20	0.18	ND	ND	0.05
Color			Grey	Grey	Grey	Brown	Brown	Reddish Tan
Sp. Gr.	gm/cc		2.77	2.69	2.68	2.84	2.83	2.89

NOTE: ND - Not Detected.

B. ZrO_2 MATERIALS

The first and second precipitates produced from each lot of zircon were received in a partially dried state ($ZrO_2 \cdot X H_2O$). Therefore, the loss in weight upon heating to 900°C was obtained for each of these and reported (Table 3), along with L. O. I. data for each of the 600, 900 and 1200°C calcined materials produced from the first and second precipitate material. The first precipitates were damp when received and contained between 30 and 50 percent water, while the drier second precipitated materials contained 10 to 22 percent water. The calcined material was apparently dry but contained between 0. 05 to 1. 0 percent of hydroscopic water. The amount of hydroscopic on residual water appears to relate to the final calcination temperature and storage conditions. For instance, the Honeywell ZrO_2 materials calcined at 500°C contained about 1. 0 percent water opposed to about 0. 4, 0. 2 and 0. 06 percent water for 600, 900 and 1200°C calcined Harshaw ZrO_2.

Table 3. Percent loss in weight of zirconium oxide materials.

		Florida		Georgia		Australia		Honeywell	
		Lot 1-1	Lot 2-1	Lot 1-2	Lot 2-2	Lot 1-3	Lot 2-3		500°C Calcined
First Precipitate	As Received	48. 4	31. 9	44. 6	44. 1	46. 9	43. 5		
	600°C Calcine		0. 34		0. 40		0. 44		
	900°C Calcine		0. 14		0. 18		0. 27		
	1200°C Calcine		0. 06		0. 04		0. 05		
Second Precipitate	As Received		10. 5		21. 8		15. 4		
	600°C Calcine		0. 22		0. 26		0. 39		
	900°C Calcine		0. 18		0. 16		0. 16		
	1200°C Calcine		0. 07		0. 05		0. 06		
	Harshaw Calcine		0. 55		0. 54		0. 60		
	Batch 2168								0. 86
	Batch 2169								0. 99
	Batch 2170								0. 89
	Batch 2171								0. 95
	Batch 2172								1. 00

The 29 lots of ZrO_2 prepared were chemically analyzed and the primary impurities found were Ca, Si, Ti, Fe and Al. The impurity variations between these lots are shown in Table 4 as a function of zircon source (Australia, Florida and Georgia), calcination temperature (600, 900 and 1200°C) and stage of processing from Harshaw's standard process (first precipitate, second precipitate or normal calcine). The impact of Honeywell's pulverization process for the hardest calcine material (1200°C) is also shown along with the purity of five lots of ZrO_2 prepared from tetra-N-butyl zirconate (TBNZ).

The Georgia and Florida zircon sands appear to produce ZrO_2 with essentially about the same concentration and types of impurities; namely, calcium, silicon and titanium. The Australian zircon had about the same level of iron, aluminum and calcium, but about twice the amount of silica and titanium. The first shipment of single precipitate (600°C - first shipment), contaminated during processing at Harshaw, contained high amounts of sodium, calcium and silicon. This material was scrapped and not used further in this program. The ZrO_2 derived from TNBZ was contaminated with an unusually high amount of silicon, iron and aluminum (caused by an unusually bad lot of TNBZ), but was evaluated further.

The second precipitation technique used by Harshaw to produce their normal electronic grade of ZrO_2 is effective in lowering the level of calcium, silicon and titanium.

Table 5 gives the results for ultimate crystallite size and agglomerate size of the ZrO_2 produced by these processes. The electron transmission data (ETM) showed that the ultimate crystallite diameter of the ZrO_2 produced was in the 100Å range at 600°C, 400Å at 900°C and 3000Å (0.3 μm) at 1200°C calcination temperatures. In general, the ultimate crystallite diameter

Table 4. Major impurities in calcining ZrO_2.

	Ca			Si			Ti			Fe			Al		
	Aus	Fl	Ga	Aus	Fl	Ga	Aus	Fl	Ga	Aus	Fl	Ga	Aus	Fl	Ga
First Precipitate															
600°C - First Ship.	0.040	0.010	0.025	0.030	>0.090	0.060	0.060	0.010	0.090	0.001	0.001	0.010	<0.001	0.006	<0.001
600°C - Pulverized	0.004	0.003	0.005	0.015	0.003	0.007	0.050	0.006	0.020	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001
900°C - Pulverized	0.004	0.007	0.008	0.025	0.015	0.015	0.075	0.030	0.035	0.001	0.004	0.010	0.001	<0.001	<0.001
1200°C - Pulverized	0.005	0.005	0.005	0.025	0.025	0.015	0.075	0.020	0.030	<0.001	<0.001	<0.001	0.002	<0.001	<0.001
1200°C	0.008	0.005	0.005	0.030	<0.015	0.015	0.070	0.020	0.015	0.006	<0.001	0.002	0.002	<0.001	<0.001
Second Precipitate															
600°C - Pulverized	<0.001	0.004	<0.001	0.006	0.010	<0.001	0.010	0.025	0.010	<0.001	0.004	0.005	<0.001	<0.001	<0.001
900°C - Pulverized	0.002	0.002	<0.001	0.004	<0.001	0.001	0.030	0.010	0.010	<0.001	0.002	<0.001	<0.001	<0.001	<0.001
1200°C - Pulverized	0.002	0.002	<0.001	0.002	<0.001	0.010	0.050	0.020	0.035	<0.001	<0.001	0.025	<0.001	<0.001	<0.001
1200°C	0.003	0.003	<0.001	0.010	0.005	0.003	0.060	0.020	0.020	0.001	<0.001	<0.001	0.001	<0.001	<0.001
Harshaw Calcine	0.003	0.003	0.002	0.010	0.002	0.001	0.020	0.006	0.004	0.005	0.004	0.004	<0.001	<0.001	<0.001
Honeywell															
2168			<0.001			0.020			0.050			0.025			0.007
2169			<0.001			0.030			0.060			0.020			0.006
2170			<0.001			0.060			0.200			0.025			0.009
2171			<0.001			0.030			0.080			0.030			0.010
2172			<0.001			0.020			0.090			0.070			0.008

Table 5. Particle size analysis of calcined ZrO_2 in 1976.

	Florida			Georgia			Australia			Honeywell		
	E. T. M. μ	Avg. Agg. Dia. μ	% <0.5μ	E. T. M. μ	Avg. Agg. Dia. μ	% <0.5μ	E. T. M. μ	Avg. Agg. Dia. μ	% <0.5μ	E. T. M. μ	Avg. Agg. Dia. μ	% <0.5μ
First Precipitate												
600°C First Shipment	-	8.4/8.7	0	0.008	10.1	0	0.008	8.7	0			
600°C Pulverized	0.012	9.5	0	0.036	9.4	1.0	0.012	7.6	0			
900°C Pulverized	0.040	10.1	0	0.020	9.7	0	0.020	7.9	0			
1200°C Pulverized	0.020	8.7	0	0.500	8.3	0	0.042	4.4	0			
1200°C Unpulverized	0.200	8.4	0	0.440	8.5	0	0.440	4.2	0			
Second Precipitate												
600°C Pulverized	0.010	1.4	16	0.018	1.1	21	0.016	2.1	18			
900°C Pulverized	0.036	1.4	15	0.036	1.3	18	0.042	2.2	18			
1200°C Pulverized	-	1.6	7	0.340	1.4	9	0.040	2.5	7			
1200°C Unpulverized	0.280	1.2	19	0.300	-	-	0.300	-	-			
Harshaw Calcine	0.044	1.3	16	0.024	1.4	15	0.036	1.4	15			
Honeywell												
2168										0.008	2.1	11
2169										0.008	2.0	9
2170										-	2.8	8
2171										0.008	2.2	10
2172										0.008	2.6	6

obtained was independent of the zircon source and precipitation process. High amounts of impurities associated with the contaminated first shipment and TNBZ derived ZrO_2 may have been responsible for the extremely fine 80Å crystallites observed for these materials.

The average agglomerate diameter obtained by the MSA centrifuge approach showed a significant difference between the ZrO_2 produced by the first and second stage precipitation processes. For instance, about 15 percent of the agglomerate particles from the second stage precipitated ZrO_2 materials and the normal Harshaw calcined material were less than 0. 5 μm, whereas most of the first stage ZrO_2 derived materials had agglomerated particles that were all larger than 0. 5 μm.

The impact of the small crystallites and agglomerated particles on the bulk and pressed density of ZrO_2 is shown in Table 6. This data reveals that the agglomerated particle size has a pronounced impact on the bulk density of the powders. For instance, the double precipitated ZrO_2 with consistantly smaller particles had a 0. 3 to 0. 6 gm/cc lower density than the single precipitated ZrO_2 materials. The pressed ZrO_2 powders, however, followed a relationship that was dependent upon the ultimate crystallite size. Note that both the 600° and 900°C calcined single and double precipitated ZrO_2 materials, which had a crystallite size of 0. 02 to 0. 04 μm, had pressed densities in the 1. 5 to 1. 6 gm/cc range although the average agglomerated particle size varied from about 9 to 2 μm for the first and second precipitates, respectively.

Calcining at 1200°C did not produce the same phenomenon. Apparently, the higher impurities associated with the first precipitate either promoted crystallite growth or partially sintered the crystallites together. This also appeared to be true for the Honeywell-prepared ZrO_2. It is apparent from the density results on the Harshaw calcined ZrO_2 that they calcine at about 900°C.

Table 6. Bulk and pressed density of ZrO_2 powders.

		Florida		Georgia		Australia		Honeywell	
		Bulk Density gm/cc	Pressed Density gm/cc	Bulk Density gm/cc	Pressed Density gm/cc	Bulk Density gm/cc	Pressed Density gm/cc	Bulk Density gm/cc	Pressed Density gm/cc
First Precipitate	600°C Pulverized	0.99	1.45	0.95	1.45	0.95	1.43		
	900°C Pulverized	1.15	1.60	1.08	1.60	1.10	1.57		
	1200°C Pulverized	1.91	3.01	1.78	3.11	1.68	3.27		
Second Precipitate	600°C Pulverized	0.64	1.33	0.47	1.39	0.57	1.32		
	900°C Pulverized	0.65	1.60	0.51	1.58	0.53	1.51		
	1200°C Pulverized	1.29	2.61	1.38	2.89	1.31	2.51		
	Harshaw Calcine	0.66	1.61	0.66	1.59	0.67	1.57		
	Batch 2168								1.88
	Batch 2169								1.85
	Batch 2170								1.79
	Batch 2171								1.81
	Batch 2172								1.78

C. PHYSICAL AND ELECTRICAL BEHAVIOR OF WET BLENDED PZ-PT

The impact of 26 ZrO_2 variations on a typical high drive piezoelectric lead zirconate-lead titanate compositions was determined by keeping all other compositional, processing and testing variations constant. These batches were prepared, processed and evaluated consecutively at the same times to minimize all other outside variations.

Table 7 gives unfired and fired density as well as the unpoled and poled dielectric constant results. The high unfired density (4.49 gm/cc) batches, containing the first precipitate type of ZrO_2, correlated well with the coarser nature of the agglomerated ZrO_2 material present in these batches. The more impure first precipitate and TNBZ ZrO_2 batches had moderately lower unfired densities of about 4.2 gm/cc, while the second precipitate ZrO_2

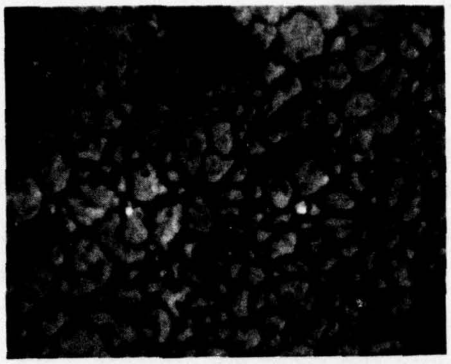
Table 7. Density and dielectric constant.

	Florida			Georgia			Australia			Honeywell		
	Density Green / Fired	Unpoled ε	Poled ε 5 Days	Density Green / Fired	Unpoled ε	Poled ε 5 Days	Density Green / Fired	Unpoled ε	Poled ε 5 Days	Density Green / Fired	Unpoled ε	Poled ε 5 Days
First Precipitate												
600°C Pulverized	4.448 6.876	848.	915.	4.461 6.558	785.	858.	4.308 7.004	790.	886.			
900°C Pulverized	4.426 5.662	860.	904.	4.454 6.860	827.	785.	4.354 6.881	813.	901.			
1200°C Pulverized	4.380 7.336	909.	931.	4.059 7.502	1003.	1043.	4.254 7.439	908.	947.			
Second Precipitate												
600°C Pulverized	4.014 7.520	998.	1023.	4.002 7.510	1019.	1099.	3.987 7.514	1012.	1080.			
900°C Pulverized	4.105 7.514	1006.	1047.	4.036 7.514	1010.	1045.	3.972 7.499	991.	1050.			
1200°C Pulverized	4.071 7.488	997.	1071.	4.080 7.516	995.	1007.	4.052 7.498	988.	976.			
Harshaw Calcine	4.081 7.500	990.	1003.	4.061 7.485	1005.	1090.	3.986 7.514	992.	1044.			
Honeywell:												
2168										4.256 7.409	933.	994.
2169										4.256 7.414	932.	956.
2170										4.247 7.415	925.	999.
2171										4.247 7.406	932.	919.
2172										4.215 7.436	923.	979.

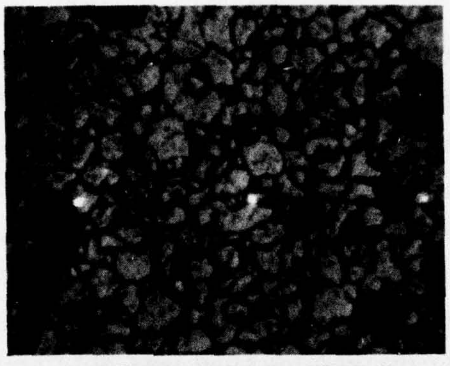
batched materials produced from smallest ZrO_2 agglomerates had the lowest unfired densities of 4.0 gm/cc. The fired densities also correlated well with the highest density material resulting from the lowest density pressed parts. Similarly, the unpoled and poled dielectric constants, in general, were highest for the highest fired density PZ-PT material. Higher calcination temperatures with the first precipitate ZrO_2 materials produced the highest densities and best piezoelectric properties in this group, but were still inferior to most of those in the double precipitate group.

The microstructure of the wet blended PZ-PT batches is shown in Figures 1, 2 and 3. Figure 1 shows the typical microstructure of those batches containing ZrO_2 produced from the single precipitated material. The average grain size was 5 to 6 μm except for the batch containing 600°C ZrO_2 from Georgia zircon which was 9 μm. The 4 to 6 μm grain size of the PZ-PT batches produced from ZrO_2 derived from double precipitated material and the standard Harshaw calcined material (AH, GH, FH) are shown in Figure 2. A more variable microstructure was obtained in the PZ-PT produced from ZrO_2 derived from the more impure TNBZ material, in Figure 3. Thus, most of the minor microstructual differences noted in these materials are probably related to their density and impurity variations.

Table 8 gives the low drive piezoelectric properties obtained from the PZ-PT batches obtained with various lots of ZrO_2. The radial coupling coefficient (kp), radial frequency constant (N_r) and mechanical quality (Q_m) are calculated from the resonant frequency data at the five day aging point. In general, the piezoelectric properties behaved in the fashion expected for the fired density present. The most significant variations in properties occurred with the PZ-PT batches produced from the first precipitate type of ZrO_2, whereas, all lots containing ZrO_2, which received the double precipitate process, produced essentially the same piezoelectric properties regardless of calcining temperature and zircon source. It was somewhat surprising that the 1200°C calcination temperatures did not deteriorate the properties of these batches.



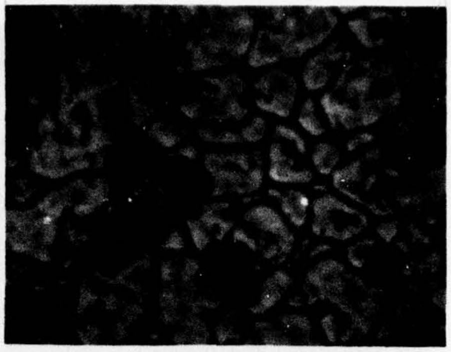
AVERAGE GRAIN SIZE 6μ
FSP-600



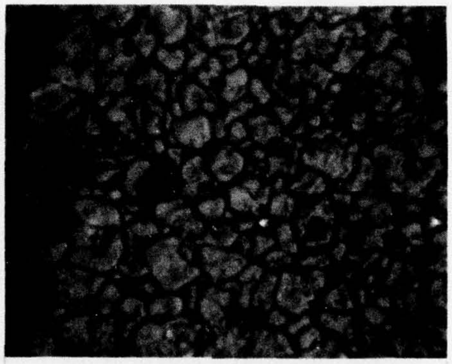
AVERAGE GRAIN SIZE 6μ
FSP-900

AVERAGE GRAIN SIZE 6μ
FSP-1200

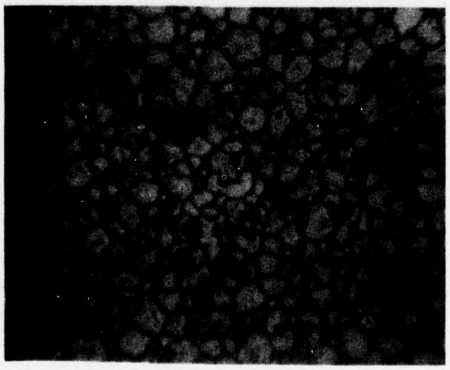
Figure 1. **Microstructure of PZ-PT compositions made from first precipitate ZrO_2. (Concluded)**



AVERAGE GRAIN SIZE 9μ
GSP-600

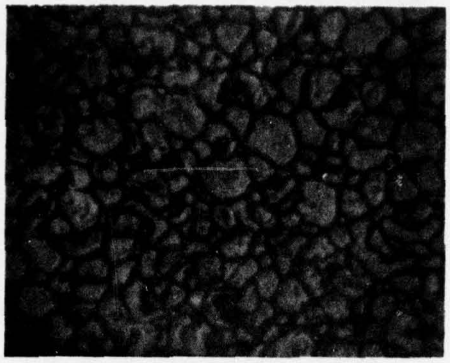


AVERAGE GRAIN SIZE 6μ
GSP-900

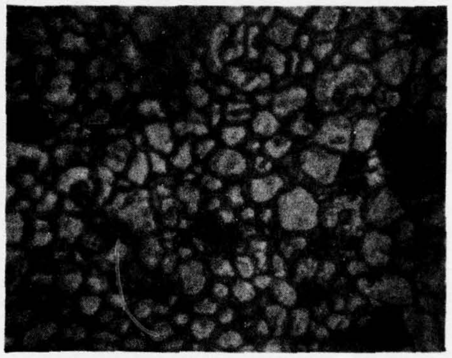


AVERAGE GRAIN SIZE 5μ
GSP-1200

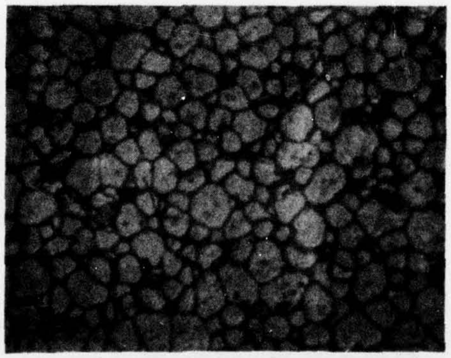
Figure 1. Microstructure of PZ-PT compositions made from first precipitate ZrO_2. (Continued)



AVERAGE GRAIN SIZE 6μ
ASP-600

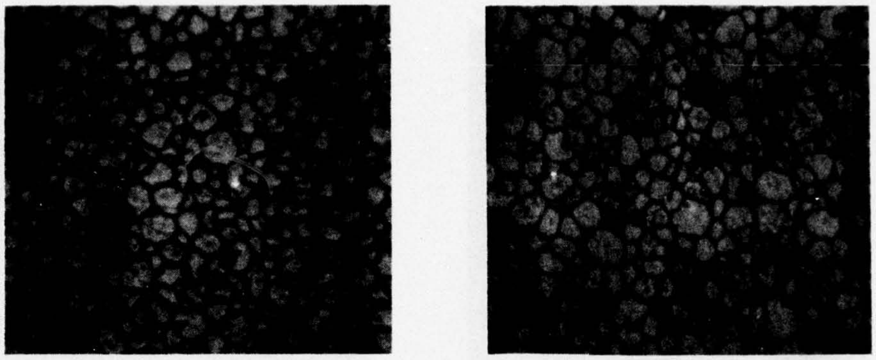


AVERAGE GRAIN SIZE 5μ
ASP-900



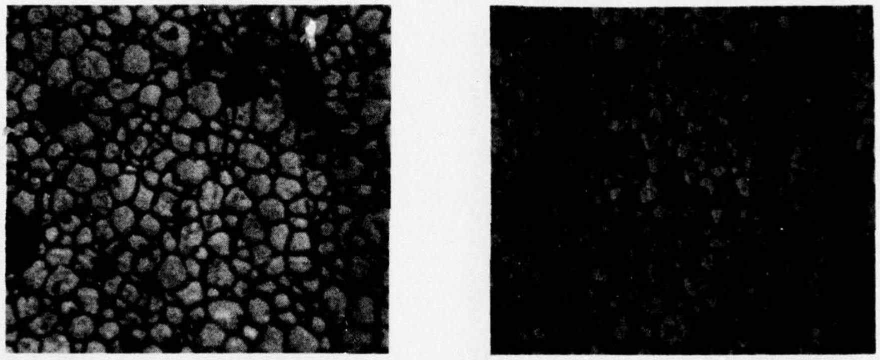
AVERAGE GRAIN SIZE 6μ
ASP-1200

Figure 1. Microstructure of PZ-PT compositions made from first precipitate ZrO_2.



AVERAGE GRAIN SIZE 5μ
ADP-600

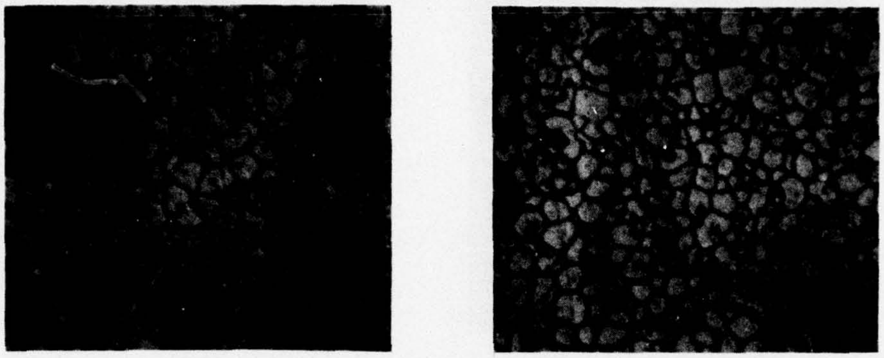
AVERAGE GRAIN SIZE 5μ
ADP-900



AVERAGE GRAIN SIZE 5μ
ADP-1200

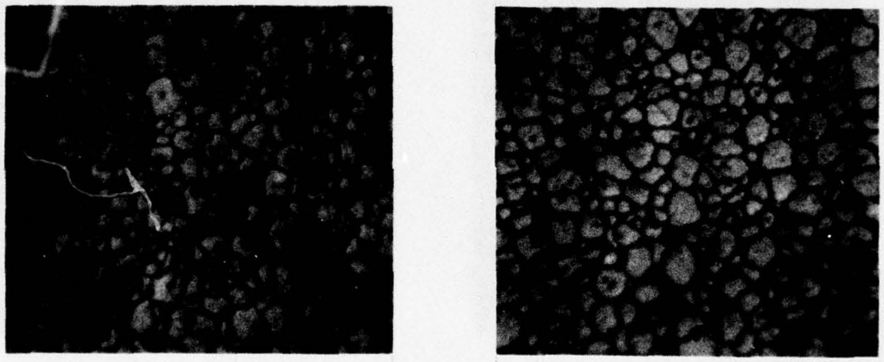
AVERAGE GRAIN SIZE 4μ
AH

Figure 2. Microstructure of PZ-PT compositions made from double precipitate and Harshaw ZrO_2.



AVERAGE GRAIN SIZE 6µ
GDP-600

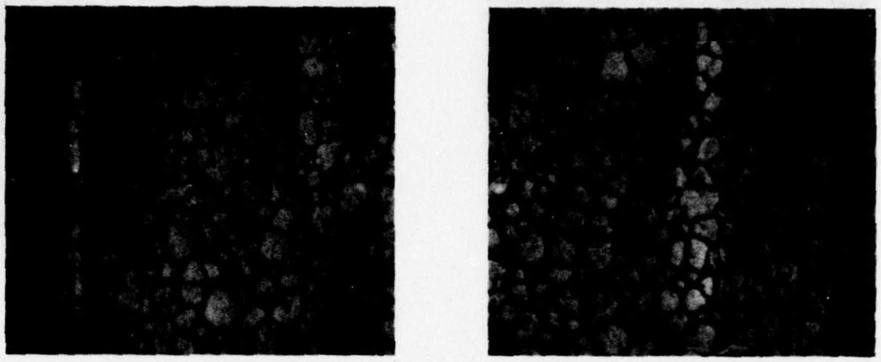
AVERAGE GRAIN SIZE 4µ
GDP-900



AVERAGE GRAIN SIZE 5µ
GDP-1200

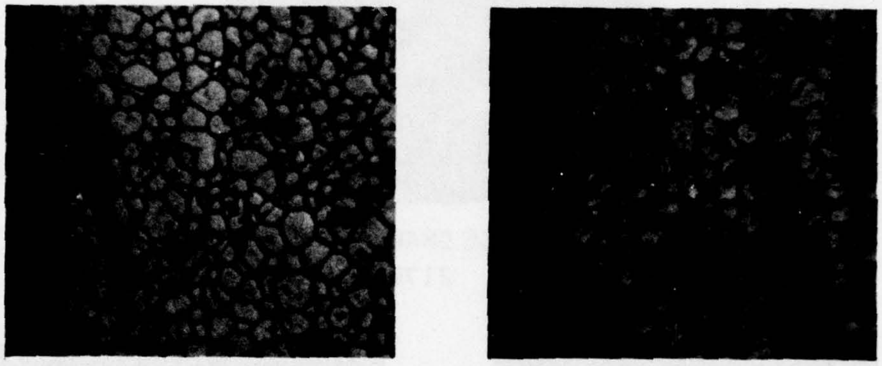
AVERAGE GRAIN SIZE 5µ
GH

Figure 2. Microstructure of PZ-PT compositions made from double precipitate and Harshaw ZrO_2. (Continued)



AVERAGE GRAIN SIZE 6μ
FDP-600

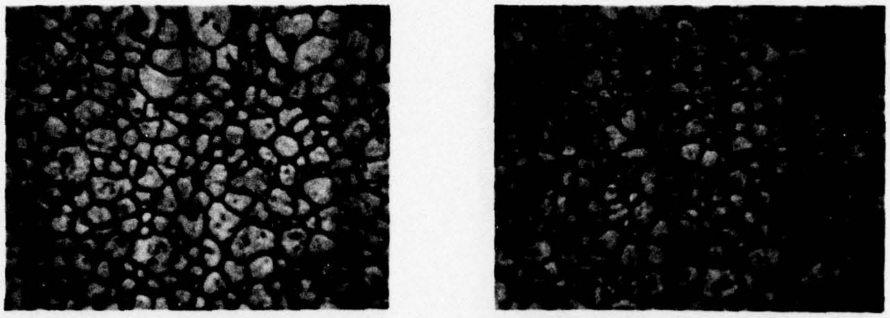
AVERAGE GRAIN SIZE 5μ
GDP-900



AVERAGE GRAIN SIZE 5μ
FDP-1200

AVERAGE GRAIN SIZE 5μ
FH

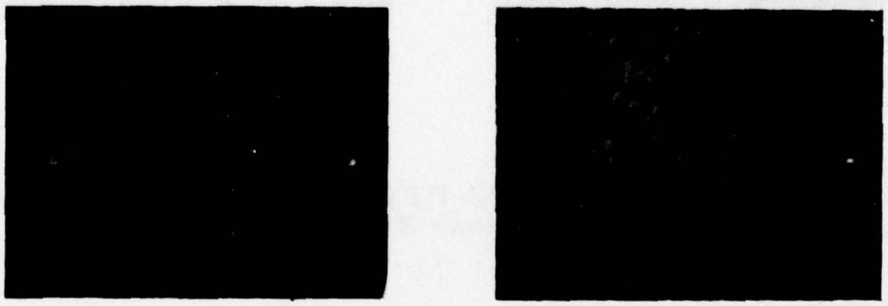
Figure 2. Microstructure of PZ-PT compositions made from double precipitate and Harshaw ZrO_2. (Concluded)



AVERAGE GRAIN SIZE 6μ
2168

AVERAGE GRAIN SIZE 5μ
2169

AVERAGE GRAIN SIZE 6μ
2170



AVERAGE GRAIN SIZE 4μ
2171

AVERAGE GRAIN SIZE 7μ
2172

Figure 3. Microstructure of PZ-PT made from Honeywell ZrO_2 derived from TBZ.

Table 8. Low drive piezoelectric properties at five days aging for wet blended batches.

	Florida			Georgia			Australia			Honeywell		
	K_p	N_r	Q_m	K_p	N_r	Q_m	K_p	N_r	Q_m	K_p	N_r	Q_m
First Precipitate												
600°C - Pulverized	0.436	83.33	723.0	0.383	80.61	534.0	0.374	86.10	614.0			
900°C - Pulverized	0.450	83.98	660.0	0.448	82.03	659.0	0.401	84.31	662.0			
1200°C - Pulverized	0.432	87.43	908.0	0.483	88.65	786.0	0.451	88.85	832.0			
Second Precipitate												
600°C - Pulverized	0.486	88.84	883.0	0.505	88.23	825.0	0.502	88.38	851.0			
900°C - Pulverized	0.491	88.70	872.0	0.490	88.55	883.0	0.492	88.58	858.0			
1200°C - Pulverized	0.505	88.11	802.0	0.508	88.35	846.0	0.503	88.21	849.0			
Harshaw Calcine	0.484	88.66	878.0	0.508	87.85	899.0	0.483	88.69	826.0			
Honeywell:												
2168										0.446	88.47	1039.0
2169										0.452	88.69	990.0
2170										0.447	88.70	933.0
2171										0.455	87.33	925.0
2172										0.429	89.18	983.0

The batches prepared from the TNBZ derived ZrO_2 produced fairly high mechanical quality factors, apparently because of the finer ZrO_2 in these batches.

Table 9 gives the high drive properties obtained for these compositions based on the percent increase in capacitance from low to high driving field (%ΔC/C) and the measured percent electrical dissipation at 5, 10 and 15 kV/0.001 inch of thickness.

The percent change in capacitance and the percent electrical dissipation of batches made from various ZrO_2 lots prepared from the second precipitate were reasonably consistent for each driving field. Changes of about 1.7, 4.0 and 10.5 percent for ΔC/C and 0.6, 1.4 and 3.1 percent for electrical dissipation were obtained for each driving field. Most of the batches produced from the ZrO_2 derived from tetra-N-butyl zirconate and several of those made from ZrO_2 produced from the single precipitate had similar high field properties. However, the physical and chemical variations associated with the ZrO_2 lots from the first precipitates appeared to cause larger ΔC/C and percent dissipations in the PZ-PT compositions where these materials were used.

The aging rate of the piezoelectric properties are given in Table 10 for the period between 10 and 100 days. Again, batches containing ZrO_2 made from the double precipitated materials had uniform aging behavior: -4.5 to -5.0 percent for dielectric constant, -2.0 to -2.5 percent for radial coupling coefficient, +0.9 to 1.3 percent for radial frequency constant and +20 to +30 percent for Qm. Batches containing ZrO_2 derived from TNBZ also fell within this range. As previously, batches containing ZrO_2 from the single precipitated material had a wider range in aging rates.

Table 9. High drive piezoelectric properties after 100 days aging for wet blended batches.

	Florida			Georgia			Australia		
	CAP %Δ/% Dis. 5V/Mil	CAP %Δ/% Dis. 10V/Mil	CAP %Δ/% Dis. 15V/Mil	CAP %Δ/% Dis. 5V/Mil	CAP %Δ/% Dis. 10V/Mil	CAP %Δ/% Dis. 15V/Mil	CAP %Δ/% Dis. 5V/Mil	CAP %Δ/% Dis. 10V/Mil	CAP %Δ/% Dis. 15V/Mil
First Precipitate									
600°C Pulverized	2.05 2.05 0.8	5.75 1.9	12.89 3.6	2.41 0.8	6.96 2.1	14.60 4.0	1. 6 0.6	5.60 1.7	11.55 3.2
900°C Pulverized	2.32 0.8	6.06 1.9	12.94 3.5	2.34 0.7	6.05 1.9	14.29 3.5	2.52 0.8	6.47 1.9	13.34 3.6
1200°C Pulverized	1.94 0.5	4.08 1.1	9.34 2.6	1.86 0.7	4.19 1.3	10.84 3.2	1.74 0.5	4.25 1.3	8.84 2.6
Second Precipitate									
600°C Pulverized	1.34 0.4	4.03 1.4	10.07 3.0	1.49 0.5	4.52 1.4	11.95 3.0	1.98 0.7	4.22 1.4	11.14 3.2
900°C Pulverized	1.52 0.6	3.69 1.3	10.47 3.0	1.93 0.7	4.73 1.6	11.93 3.4	1.73 0.6	4.33 1.5	10.59 3.2
1200°C Pulverized	1.96 0.7	4.04 1.3	10.57 3.0	1.77 0.6	3.75 1.3	10.16 3.0	1.66 0.6	3.67 1.4	10.32 3.1
Harshaw Calcine	1.69 0.6	3.99 1.3	9.75 2.9	1.91 0.7	4.32 1.4	11.12 3.3	1.72 0.7	3.97 1.4	10.66 3.2
Honeywell 2160	1.65 0.44	4.35 1.4	10.55 3.0						
2169	1.63 0.5	3.95 1.3	10.28 3.0						
2170	1.78 0.6	4.82 1.5	11.16 2.9						
2171	1.84 0.6	5.16 1.5	11.38 3.4						
2172	1.67 0.5	4.34 1.3	8.68 2.5						

Table 10. Aging rate of piezoelectric properties for wet blended batches.

	Florida				Georgia				Australia			
	K_3^T	K_p	N_r	Q_m	K_3^T	K_p	N_r	Q_m	K_3^T	K_p	N_r	Q_m
First Precipitate												
600°C - Pulverized	-3.38	-1.85	0.73	11.5	-3.29	-1.55	0.63	2.9	-2.85	-1.86	0.59	8.4
900°C - Pulverized	-3.71	-2.01	0.81	23.6	-4.33	-1.58	0.73	9.8	-5.89	-2.01	0.61	9.1
1200°C - Pulverized	-4.79	-2.58	1.16	31.5	-5.18	-2.09	1.24	25.7	-5.58	-2.23	1.05	37.4
Second Precipitate												
600°C - Pulverized	-4.43	-2.09	0.92	31.6	-5.07	-2.39	1.16	33.0	-4.98	-2.63	1.27	33.1
900°C - Pulverized	-4.56	-2.46	1.20	24.7	-5.14	-2.48	1.26	25.7	-5.13	-2.46	1.24	30.2
1200°C - Pulverized	-5.04	-2.39	1.15	25.9	-5.15	-2.97	1.18	17.7	-4.85	-2.62	1.12	26.3
Harshaw Calcine	-4.44	-2.08	0.96	20.3	-4.66	-2.57	0.70	17.7	-3.98	-2.34	1.14	23.5
Honeywell												
2168	-4.08	-2.27	1.00	19.3								
2169	-4.04	-2.33	0.92	19.3								
2170	-4.35	-2.25	0.94	24.3								
2171	-4.93	-2.20	1.01	19.0								
2172	-4.04	-2.59	0.89	17.4								

D. PHYSICAL AND ELECTRICAL BEHAVIOR OF DRY BLENDED PZ-PT

This section discusses the results obtained on nine PZ-PT batches produced by the dry blending approach from the nine second precipitate ZrO_2 materials. The pressed and fired density, as well as unpoled and poled dielectric constant of each batch, are given in Table 11. The green density of samples prepared from PZ-PT batches with the 600°C calcined ZrO_2 group was about the same for the dry blended batches as those from wet blended batches. However, the 900°C and 1200°C calcined ZrO_2 groups generally produced PZ-PT batches whose pressed density was greater for the dry than the wet blended materials.

The fired density of all dry blended PZ-PT variations was always lower than the wet blended PZ-PT batches. The dry blended batches containing ZrO_2 calcined at only 600°C were 7.0 to 7.3 gm/cc as opposed to 7.51 gm/cc for the wet blended batches. In five out of six instances, dry blended batches containing ZrO_2 calcined at 900 or 1200°C produced PZ-PT whose densities were 7.38 to 7.47 gm/cc as opposed to 7.49 to 7.51 gm/cc for the wet blended batches.

The lower density dry blended batches also produced lower dielectric constants. The fact that five out of six batches, which used 600 to 900°C calcined ZrO_2, contained lower dielectric constants after poling suggests that these batches were poorly blended during batching. Thus, wet milling after calcining the PZ-PT cannot be expected to correct a poor blending operation.

When dry blended batches were made from 1200°C calcined ZrO_2 the poled dielectric constant was also greater than in the upoled state. This may indicate that wet milling of the PZ-PT calcine containing dry blended 1200°C calcined ZrO_2 is less critical than where low calcined material is used. It is postulated that the thermal expansion accompanying the cubic to monoclinic

Table 11. Density and dielectric constant of fired dry blended PZ-PT batches.

		Florida				Georgia				Australia			
	Process	Density Green	Density Fired	ε Unpoled	ε Poled 5 Days	Density Green	Density Fired	ε Unpoled	ε Poled 5 Days	Density Green	Density Fired	ε Unpoled	ε Poled 5 Days
Second Precipitate													
600°C Pulverized	Dry Blend	3.992	6.958	855.	835.	3.987	7.313	957.	922.	4.025	7.124	901.	827.
900°C Pulverized	Dry Blend	4.238	7.420	948.	932.	4.077	7.474	988.	978.	4.151	7.377	931.	936.
1200°C Pulverized	Dry Blend	4.528	7.428	919.	946.	4.266	7.123	822.	879.	4.184	7.442	913.	935.

ZrO_2 inversion at about 1000°C in the 1200°C calcined material makes these larger crystallites more friable and reactive.

Table 12 gives the low drive piezoelectric properties for the dry blended PZ-PT batches. The high variability and low properties obtained can be blamed on the poor density and mixing of the ZrO_2 in these batches. The mechanical quality (Qm) of dry blended PZ-PT is the only property that approached the wet blended PZ-PT batches.

Table 13 shows the aging behavior of the various piezoelectric properties for those batches made from dry blended PZ-PT. Again, the variations can be attributed to the variations in density and mixing and their associated impact on the completeness of polarization.

Table 14 gives the high field data obtained for the dry blended batches. The relative low electrical dissipation and percent change in capacitance as a function of driving field are relatable to the low density and low polarization state in these materials.

Based on the results obtained, it is clear that each of the three sources of zircon can be used to produce satisfactory ZrO_2 for PZ-PT. The process used for deriving ZrO_2 from these sources is critical. It is not clear why the two different precipitation processes are required to produce uniform, high purity ZrO_2. A wide range of calcination temperatures can be used with double precipitated ZrO_2 without influencing the performance of the ZrO_2 in the high drive PZ-PT compositions evaluated. The calcination temperature used does appear to have a fairly strong dependence on how uniformly the ZrO_2 is blended with the other batch materials.

The completeness of the blending process is very critical. Dry blending is a relatively poor way of obtaining good mixing of the PZ-PT batch, which can not be completely compensated for by the normal subsequent calcination and wet grinding operations. More effort on the dry blending approach is necessary before it can be relied upon to produce uniform PZ-PT batches.

Table 12. Low drive piezoelectric properties at five days aging for dry blended PZ-PT batches.

	Florida			Georgia			Australia		
	Kp	Nr	Qm	Kp	Nr	Qm	Kp	Nr	Qm
Second Precipitate									
600° Pulverized	0.421	83.45	781.0	0.395	87.45	884.0	0.386	85.79	758.0
900°C Pulverized	0.328	89.29	738.0	0.365	89.66	863.0	0.285	89.95	883.0
1200°C Pulverized	0.279	91.71	914.0	0.334	88.66	955.0	0.244	92.18	845.0

Table 13. Percent aging rate of piezoelectric properties for dry blended PZ-PT batches.

	Florida				Georgia				Australia			
	K_3^T	K_p	N_r	Q_m	K_3^T	K_p	N_r	Q_m	K_3^T	K_p	N_r	Q_m
Second Precipitate												
600°C Pulverized	-4.11	-2.40	0.84	15.9	-4.61	-3.34	1.03	27.8	-4.04	2.62	1.16	28.2
900°C Pulverized	-5.34	-3.09	1.23	40.0	-5.19	-3.04	1.22	37.8	-4.55	4.55	1.13	35.9
1200°C Pulverized	-4.50	-3.24	0.92	30.6	-3.21	-4.82	0.73	19.2	-4.33	4.13	0.97	35.4

Table 14. High drive piezoelectric properties of dry blended PZ-PT batches.

	Florida			Georgia			Australia		
	CAP %Δ/% Dis. 5 V/Mil	CAP %Δ/% Dis. 10 V/Mil	CAP %Δ/% Dis. 15 V/Mil	CAP %Δ/% Dis. 5 V/Mil	CAP %Δ/% Dis. 10 V/Mil	CAP %Δ/% Dis. 15 V/Mil	CAP %Δ/% Dis. 5 V/Mil	CAP %Δ/% Dis. 10 V/Mil	CAP %Δ/% Dis. 15 V/Mil
Second Precipitate									
600°C Pulverized	1.64 0.47	4.61 1.38	9.22 2.98	1.66 0.50	4.25 1.45	9.16 3.03	1.63 0.47	4.43 1.45	9.70 3.2
900°C Pulverized	1.50 0.58	4.42 1.52	10.3 3.14	1.60 0.60	4.39 1.45	8.99 2.92	1.40 0.41	4.00 1.27	7.72 2.52
1200°C Pulverized	1.27 0.47	3.55 1.35	7.50 2.62	1.19 0.42	3.58 1.0	8.20 2.42	1.20 0.62	3.53 1.43	7.90 2.88

IV. SUMMARY AND CONCLUSIONS

The three sources of the mineral zircon ($ZrO_2 \cdot SiO_2$) obtained from concentrated Florida, Georgia and Australia sands varied significantly in their physical particle size and chemical impurities. However, in this current program we have shown that adequate chemical purification of each of these materials will yield ZrO_2 of essentially the same ultimate particle size and purity. Such fully processed materials also yield PZ-PT with uniform piezoelectric properties at both low and high drive conditions. Materials which are not fully processed, such as ZrO_2 derived from the calcination of first stage $Zr(OH)_4$ precipitate, proved to be very dependent upon the zircon source and calcination temperature. Such materials contained more silica, calcia and titania impurities, which appeared to act as a bonding media for bonding small (0.05 μm) crystallites into large (10 μm) agglomerates. Apparently, these large agglomerates prevented complete blending and densification of the compounded PZ-PT, which in turn caused extensive variability in its piezoelectric behavior.

It had been assumed that any dry blending variability obtained would be eliminated by the wet mixing/grinding approach performed after calcination of the PZ-PT. However, all nine of the dry blending compositions produced had fired densities of 6.96 to 7.47 gm/cc opposed to 7.49 to 7.52 gm/cc for the wet blended PZ-PT. The piezoelectric coupling coefficient was 13 to 51 percent lower than similar material produced by the wet blended process.

Thus, the dry blending approach is more difficult to control for producing uniform PZ-PT materials. Apparently, a more thorough mixing operation than the dry blending approach used in this effort is required. The slower aging behavior of the dry blending PZ-PT compositions appeared to be more dependent upon the lower coupling of these materials than on the blending approach.

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