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## EFFECT OF ZrO₂ SOURCE VARIATIONS ON PbZrO₃-PbTiO₃ PIEZOELECTRIC PROPERTIES

Final Report
and
Technical Report No. 2
to the
Office of Naval Research

by

W.B. Harrison

Contract N00014-76-C-0623 NR 032-566

August 1979

Honeywell Inc.
Ceramics Center
Defense Electronics Division
1885 Douglas Drive
Minneapolis, Minnesota 55422

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$ZrO_2$, 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 $ZrO_2$ was shown to yield PZ-PT material with uniform low and high drive piezoelectric behavior. Single precipitated $ZrO_2$ and dry blending were shown to be highly variable processes. Also, solution ceramic approaches produced a higher density PZ-PT.

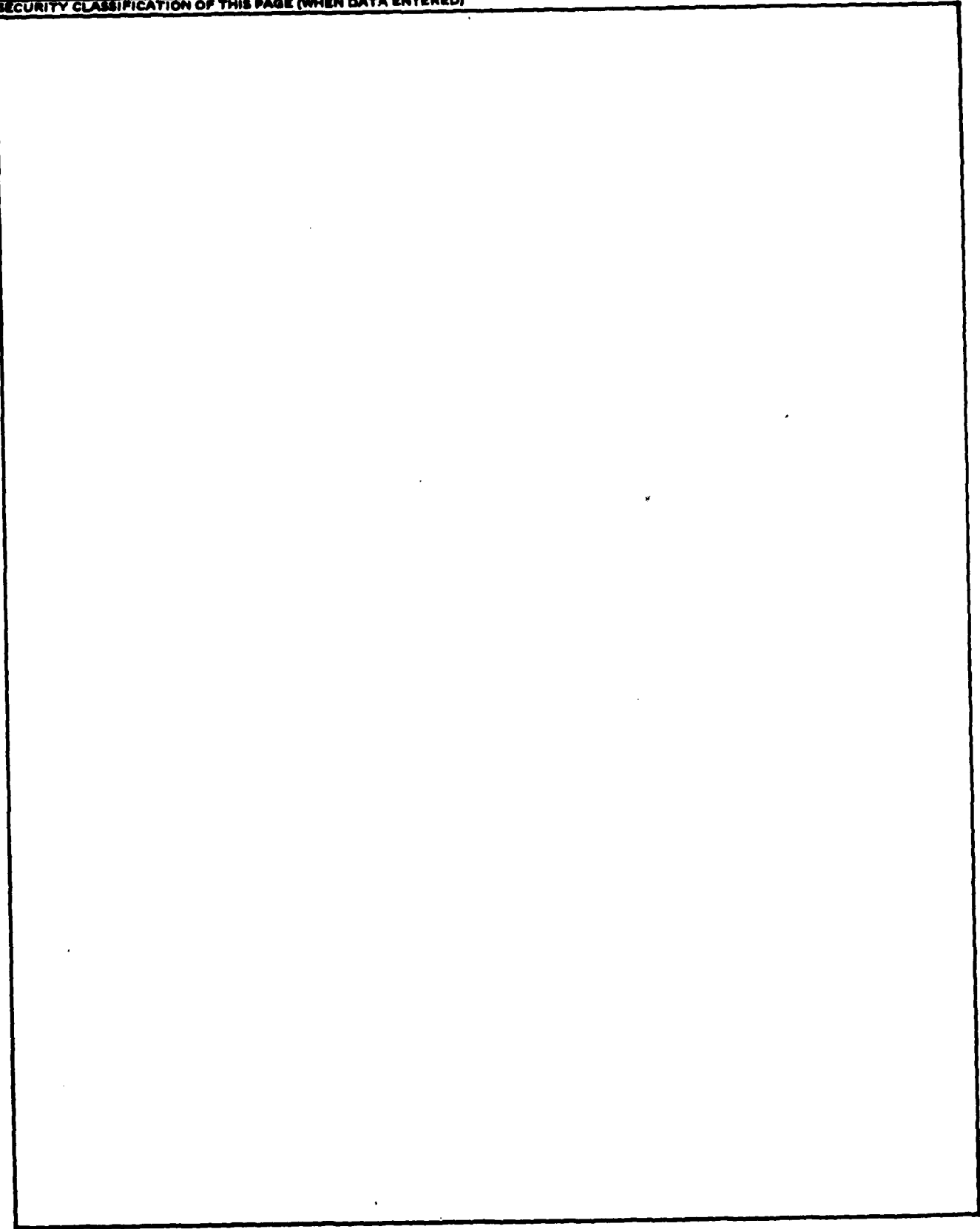HD-168 REV 11/74

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# Abstract

$ZrO_2$, 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 $ZrO_2$ was shown to yield PZ-PT material with uniform low and high drive piezoelectric behavior. Single precipitated $ZrO_2$ and dry blending were shown to be highly variable processes. Also, solution ceramic approaches produced a higher density PZ-PT.

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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 for producing piezoelectric ceramic materials used in various Navy and DoD programs over the past 20 years. Two approaches, described in the first technical report[1] on this program, were used to generate $ZrO_2$ for this study. Initially, zircon ($ZrO_2 \cdot SiO_2$) was obtained from three sources and processed into $ZrO_2$ by the standard commercial process used at the Harshaw Chemical Company* for piezoelectric grade $ZrO_2$. In the second approach, the standard Honeywell alk-oxide process, which uses tetra-N-butyl zirconate (TNBZ), was used to produce $ZrO_2$. The $ZrO_2$ produced by each of these processes was chemically and physically characterized, and then its impact on the behavior and properties of PZ-PT was evaluated as previously described[1]. This section updates the previous work and describes new approaches employed in the contract's final period.

The chemical reactions involved in the standard approach used by Harshaw to produce $ZrO_2$ from ziron, described in the first technical report,[1] contained several errors. The correct version of these reactions is shown in Equations 1 through 8.

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

$$Na_2ZrO_3 + 2HCl \rightarrow ZrOCl_2 + 2NaCl + H_2O \tag{2}$$

$$ZrOCl_2 + 0.6 \, H_2SO_4 \rightarrow ZrO \cdot 0.6 \, SO_4 \cdot x \, OH + 2 \, HCl \tag{3}$$

First Precipitation

$$ZrO \cdot 0.6 \, SO_4 \cdot x \, OH + 1.2 \, NH_4 \, OH + H_2O \rightarrow ZrO_2 \cdot x \, H_2O + 0.6 \, (NH_4)_2 \, SO_4 \tag{4}$$

$$ZrO_2 \cdot x \, H_2O + HCl + H_2O \rightarrow 2 \, ZrO \, OHCl + H_2O \tag{5}$$

$$ZrOOHCl + 0.6 \, H_2O \rightarrow ZrO \cdot 0.6 \, SO_4 \cdot x \, OH + HCl \tag{6}$$

Second Precipitation

$$ZrO \cdot 0.6 \, SO_4 \cdot x \, OH + 1.2 \, NH_4 \, OH + H_2O \rightarrow ZrO_2 \cdot x \, H_2O + 0.6 \, (NH_4)_2 \, SO_4 \tag{7}$$

Calcine

$$ZrO_2 \cdot x \, H_2O + HEAT \rightarrow ZrO_2 + H_2O \tag{8}$$
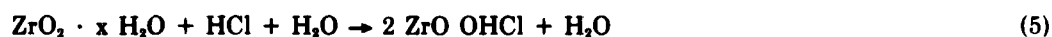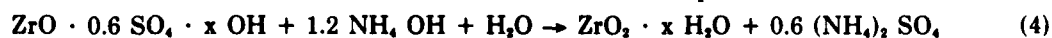
* Harshaw Chemical Company, Division of Gulf Oil Company, Cleveland, Ohio 44106

The exact details of the Harshaw process were not made available; however, since their process is based on the caustic fusion process, it is likely that it proceeds approximately as shown in Figure 1. This process has been described[2] as follows:

"Caustic soda has been found to be a suitable agent for the decomposition of zircon sand (zirconium silicate). By using an optimum ratio of 1.1 parts by weight of caustic soda to 1 part of unground zircon sand and a furnace temperature of 650°C, about 90% of the zircon reacts to form sodium zirconate, sodium silicate and a small amount of sodium silicozirconate. This reaction takes between 1 and 2 hours to reach completion and can be carried out in a container fabricated from mild-steel plate. The resulting product is a light-colored granular material from which the water-soluble sodium silicates can be easily removed by a hot-water leaching operation. In practice, this granular product from the caustic fusion is first agitated with hot water in a steel tank and then fed directly to a horizontal solid-bowl continuous centrifuge, where an excellent and convenient separation of solids from liquids can be made. The water-insoluble zirconates are then dissolved in hot hydrochloric acid. Zirconyl chloride is crystallized from this solution at 250°C to remove iron, titanium, aluminum, some silica and other soluble impurities. The crystalline zirconyl chloride is separated from its mother liquor on a perforated basket centrifuge which gives a very dry crystal. These crystals are put into a water solution, which is clarified in order to remove most of the residual silica. The resulting pure zirconyl chloride solution may be processed further to give high-purity zirconium (or zirconyl) compounds, such as the oxide, fluoride, nitrate, sulfate and hydroxide."

An alternate approach, known as carbon arc fusion process, is also shown in Figure 1. The zirconium carbonitride produced is chlorinated to produce zirconium tetra chloride which is then processed into $ZrO_2$. It has been stated[2] that this process produces less pure material than the caustic fusion process.

The physical characteristics of the $ZrO_2$ powders produced during the last portion of this contract were studied in more detail by comparing the surface area obtained versus the materials' agglomerated particle size. The surface area was measured with a Micromeritics Model 2200 Analyzer using nitrogen gas absorption.

The agglomerated particle size was measured by the MSA centrifuge sedimentation approach[3]. A typical curve is shown in Figure 2. The dispersion approach used consisted of mixing 0.7 gm of $ZrO_2$ powder with one drop of Triton X-100, Dravan-C, and ethyl

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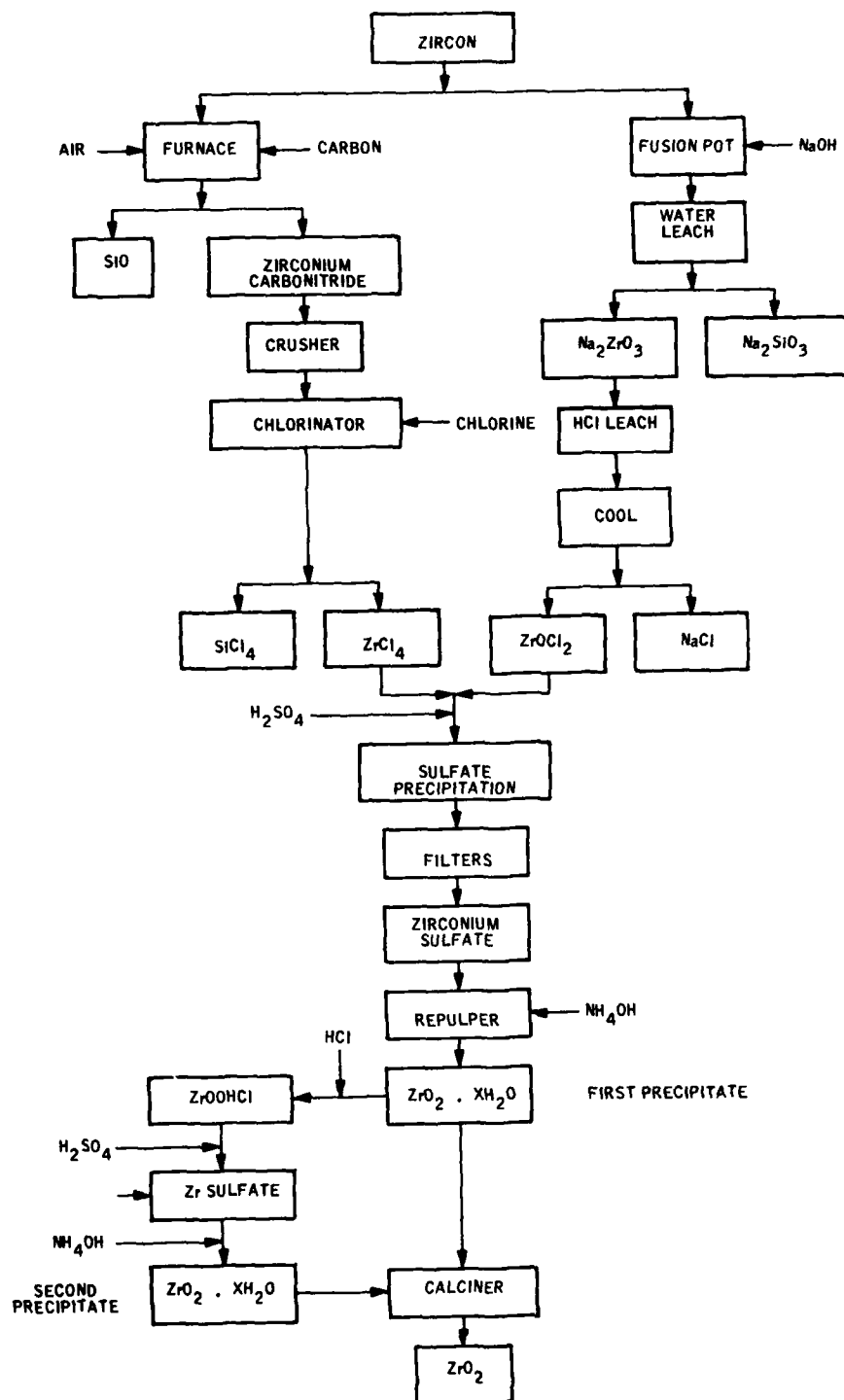
Figure 1. Flow diagram for ZrO₂ production.
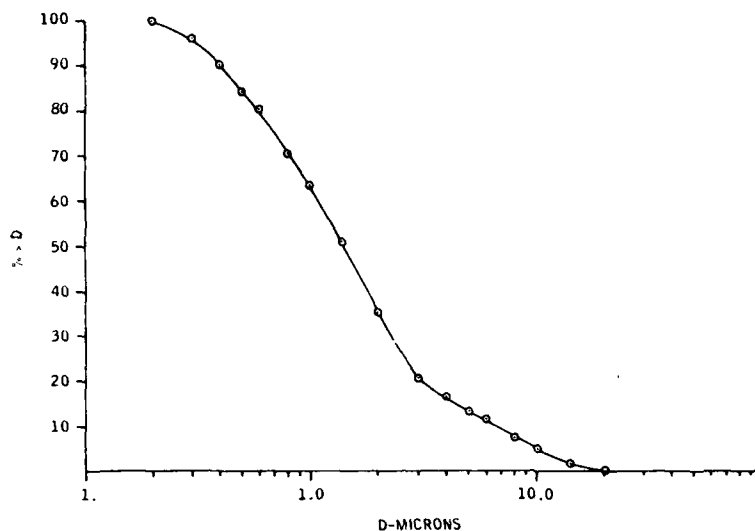
**Figure 2. Typical particle size distribution curve for $ZrO_2$ obtained by MSA approach.**

hexanol and then blending this mixture in a 30 percent acetone-70 percent $H_2O$ solution. This, in turn, was added to the sedimentation liquid (water) in the MSA equipment.

It was assumed that the average particle size obtained was that of strong agglomerated particles of $ZrO_2$, which probably approaches the particle diameter of the $ZrO_2 \cdot xH_2O$ particle from which the $ZrO_2$ was derived. This appears likely because basic zirconium sulfate particles are typically about 15 $\mu$m and the first stage precipitate particles were measured at 8-10 $\mu$m[1].

It was also desirable to determine if further improvements in the $ZrO_2$ produced for PZ-PT could be obtained with additional manipulations of the precipitation process.

## A. REPRECIPITATION OF $ZrO_2 \cdot XH_2O$

Since $ZrO_2 \cdot x H_2O$ was available from the six lots of Harshaw material produced from three zircon sources[1] each of these was reprecipitated by the following process.

Both of the first precipitate and second precipitate obtained as indicated in Equations 4 and 7 were dissolved in HCl according to Equation 5 to produce a solution of ZrOOHCl in water. This was accomplished by heating 2000 cc of 50 percent HCl/water solution and slowly adding 1000 gm of precipitate to the solution while mixing. The solution was

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boiled at 105°C for about 10 minutes to produce a straw-yellow clear solution. This solution was allowed to cool and stand several days during which time a slight amount of sediment settled to the bottom of the breaker. About 90 percent of the ZrOOHCl solution was carefully decantered from the beaker and the remaining 10 percent with sediment was discarded. It was assumed that most of the non-acid soluble impurities were removed by this process.

Next, ammonium hydroxide was added in 10 percent excess of the amount required to satisfy the amount of $ZrO_2$ present in the solution (400 to 600 cc). Precipitation of $ZrO_2 \cdot xH_2O$ occurred rapidly. The precipitate was allowed to settle for a day; about 25 percent of the liquid remaining was decanted and then 2000 cc of water were added and decanted. This rinsing process was repeated seven times to produce a pH of about 7 in the solution. The precipitated material was dried at 150°C for 24 hours and then calcined at 900°C for 3 hours.

The first set of three batches of $ZrO_2 \cdot xH_2O$ was prepared from the first stage precipitates of material derived from Florida, Georgia and Australia zircon sources, as described above.

The second set of three was processed as above except that after the ZrOOHCl solution was boiled, an additional 2000 ml of water was added to the solution and allowed to settle 2 days.

The third set of three was produced from the Harshaw double precipitate. Since the double precipitates contained more $ZrO_2$ (less loss on ignition), 4500 grams of 60 percent HCl 40 percent water were mixed with 750 grams of precipitate. The remainder of the process was the same as the second set except 2000 to 2200 ml of $NH_4 (OH)$ was required to bring the precipitate to a neutral state. In the fourth and fifth sets of single and double precipitates, respectively, the ratio of HCl to $ZrO_2$ in each batch of $ZrO_2$ was held constant. The weight of $ZrO_2$ present was based upon its 1200°C loss on ignition. The exact batch additions are given in Table 1. This table also shows the amount of $NH_4 (OH)$ required to bring each batch to a neutral condition.

An improvement was also found in the way the amonium hydroxide was added. The first 90 percent of the $NH_4OH$ was added quickly but steadily to the solution during continuous mixing. After about 95 was added, the $ZrO_2$ became a coarse mud and more

#### Table 1. Batch additions for reprecipitation of zirconium hydroxide.

| Source of Zircon Type $ZrO_2-X\ H_2O$ Precipitate | FS4 Florida Single | GS4 Georgia Single | AS4 Australia Single | FD5 Florida Double | GD5 Georgia Double | AD5 Australia Double |
|---|---|---|---|---|---|---|
| HCl in ml | 2480 | 1980 | 1980 | 3174 | 2768 | 3000 |
| $H_2O$ in ml | 3870 | 3168 | 3168 | 4974 | 4430 | 4800 |
| Based on LOI of | 31.9 | 44.4 | 44.4 | 10.8 | 22.2 | 15.7 |
| Gms $ZrO_2$ in 750 gm Precip | 511 | 417 | 417 | 669 | 584 | 632 |
| $NH_4$ (OH) | 1650 | 1200 | 1300 | 1850 | 1650 | 1850 |

$NH_4OH$ did not mix into the solution evenly. When the mixture became a coarse mud, $NH_4OH$ was slowly added and mixed thoroughly before addition of more $NH_4OH$. When this approach was used, the material went from a coarse to a creamy mixture and the PH was readily controlled.

Each reprecipitated lot of zirconium hydroxide was calcined at 900°C for 3 hours. The 15 batches of $ZrO_2$ processed were physically and chemically evaluated and were wet blended into the standard PZ-PT batch formulation given below and described previously.[1]

$$Pb_{0.94}\ Sr_{0.06}\ (Zr_{0.53}\ Ti_{0.47})\ O_3 + 0.05\ Wt\ \%\ Fe_2\ O_3$$
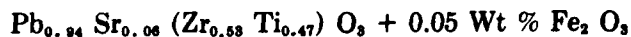
## B. COPRECIPITATION OF $ZrO_2$ INTO PX-PT

In the first part of this program one batch of pure $ZrO_2$ and four batches with 0.02 to 0.36 percent of $TiO_2$ were prepared by coprecipitation from tetra N-butyl zirconate and titanate (TNBZ and TNBT).[1] However, the TNBZ used had an unusually high amount of silicon, iron and alumina. This work was repeated with a new lot of TNBZ. Three batches were made containing 0.00, 0.10 and 0.40 percent $TiO_2$ and two batches containing all of the Zr/Ti of the batch. In this process 800 gms of TNBZ/TNBT and 1400 gm of isopropyl alcohol were mixed together and then premixed water/acetic acid solution (5000 gm/300 cc) was slowly added to precipitate zirconium hydroxide. This mix was dried at 100°C and crushed and calcined at 500°C for 12 hours.

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These materials were physically and chemically characterized and then processed by the wet blending method into the standard PZ-PT batch as was done previously[1]. A batching error was made in which the $TiO_2$ added through the TNBT was not compensated in the four batches with TNBT. Therefore, a second group of five batches of PZ-PT was produced and evaluated.

Three other approaches were evaluated to determine if more uniform PZ-PT batches could be produced in a state where all the ingredients were insolution prior to precipitation of the $ZrO_2$.

A stabilized ammonium zirconium carbonate (Bacote 20) and a zirconium acetate solution were obtained from Magnesium Elektron*. The loss on ignition (LOI) of these two solutions after heating to 1000°C for 1 hour was 79.93 and 77.92 percent, respectively. A second LOl indicated 79.95 and 77.76 percent, respectively.

Based on these results, two standard PZ-PT batches, Table 2, were prepared in a high intensity Waring blender. Each ingredient was added in the order given and mixed about 2 minutes before adding the next ingredient. After addition of the PbO and 10 minutes of mixing, the solution was poured into trays, dried at 190°C for 3 days, and calcined at 860°C for 5 hours. The Bacote 20 based material contained a black core that indicated incomplete oxidization of the carbon from the decomposed acetate. Therefore, both batches were crushed and recalcined at 800°C for 5 hours. This second treatment appeared to completely oxidize all the carbon in both materials.

In the next approach, material from either the Harshaw Florida first or second precipitate was dissolved in a boiling HCl/water solution as described earlier. A 250 gm batch of PZ-PT (standard composition) was prepared with 411 ml of ZrOOHCl solution (assayed previously to yield 50.84 gm of $ZrO_2$). An additional 100 cc of HCl and 200 cc of water were added to the ZrOOHCl solution and then 6.91 gm of strontium carbonate, 0.125 gm of $Fe_2O_3$ and 29.37 gm of $TiO_2$ were added and mixed thoroughly in the order given. All of these appeared to go into solution quite well. Before adding 163.32 gm of PbO, an additional 300 cc of HCl and 600 cc of water were added. Then the PbO was slowly added, and heated to 105°C to attempt to get all the lead oxide in solution. However, very little of the PbO appeared to be dissolved. Urea was dissolved in water and added in an at-

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* Magnesium Elektron Inc., Star Route A, Box 202-1, Flemington, N.J. 08822

Table 2. Batch formulations using chemical solutions of zirconium.

| | Amount Added | | |
|---|---|---|---|
| $H_2O$ (cc) | 590 | 550 | 1250 |
| Zirconium Acetate (cc) | 916.6 | | |
| Bacote 20 (cc) | | 1012.6 | |
| $SrCO_3$ (gm) | 27.68 | 27.68 | 6.91 |
| $Fe_2O_3$ (gm) | 0.50 | 0.50 | 0.125 |
| $TiO_2$ (gm) | 117.50 | 117.50 | 29.37 |
| PbO (gm) | 654.67 | 654.67 | 163.32 |
| HCl (cc) | | | 400 |
| Zr OOHCl Solution (cc) | | | 411 |
| Urea (gm) | | | 650 |
| $NH_4$ (OH) (gm) | | | 200 |

tempt to coprecipitate all of the ingredients. A total of 650 gm of urea and 450 cc of water were added with no apparent precipitation. Then 200 gm of ammonium hydroxide were added to achieve complete precipitation. The resulting mixture was dried at 120°C and calcined at 700°C for 5 hours.

While these three calcined batches appeared to be completely decomposed, they were extremely hard. No further work was done with this approach.

## C. CHEMICAL ANALYSIS OF LEAD ZIRCONATE TITANATE

X-ray fluorescence was used to determine the amount of PbO, SrO, $TiO_2$ and $ZrO_2$ present in fired disc of lead zirconate-lead titanate. A Diano XRD 410 unit was used to establish the standards and perform all subsequent analysis. A mask with an opening of 0.68 inch in diameter was placed over all samples. Standard curves were established from 10 samples where Pb was varied from 53.38 to 63.39 percent, Sr from 0.27 to 5.80, Ti from 4.71 to 7.40 and Zr from 14.10 to 20.56. All samples tested were fired, ground flat and had a diameter and thickness of 0.85 and 0.10 inches, respectively.

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The sensitivity of this approach was evaluated by measuring six different samples prepared from the same batch of PZ-PT. The results obtained, after converting to an oxide basis, are shown in Table 3. A standard deviation of 0.4, 0.2, 0.3 and 0.02 was obtained for PbO, $ZrO_2$, $TiO_2$ and SrO, respectively. This table also indicates that the approach tends to give slightly high (1.0 percent) results for PbO, while the other data are slightly lower than the theoretical compounded batch.

Table 3. Within batch chemical uniformity for six samples of wet blended PZ-PT using Florida precipitated $ZrO_2$.

| S/N | % PbO | % $ZrO_2$ | % $TiO_2$ | % SrO |
|---|---|---|---|---|
| 2 | 66.30 | 19.90 | 11.95 | 1.85 |
| 4 | 66.15 | 20.30 | 11.75 | 1.80 |
| 8 | 66.95 | 19.86 | 11.41 | 1.78 |
| 9 | 66.65 | 19.97 | 11.57 | 1.80 |
| 10 | 66.87 | 19.99 | 11.34 | 1.80 |
| 11 | 65.94 | 20.40 | 11.87 | 1.79 |
| $\bar{x}$ | 66.48 | 20.07 | 11.65 | 1.80 |
| $\sigma$ | 0.41 | 0.22 | 0.25 | 0.02 |
| THEORETICAL | 65.46 | 20.38 | 11.72 | 1.94 |

# III. Results and Discussion

In the first part of this study[1] it was shown that good high drive PZT could be fabricated from $ZrO_2$ whether produced from Florida, Georgia or Australia beneficiated zircon sand. These sands varied significantly in their physical particle size and chemical purity, but an alkali fusion, double precipitate process produced $ZrO_2$ with adequate chemical purity and essentially the same ultimate particle size. Such fully processed materials also produced PZ-PT with uniform piezoelectric properties at both low and high field driving conditions.

$ZrO_2$ derived from only the first precipitate material proved to be very dependent upon the zircon source and calcination temperature. These $ZrO_2$ materials contained more silica, calcia and titania impurities which appeared to act as media for bonding small (0.05 $\mu$m) crystallites into larger (10.0 $\mu$m) agglomerates. When such $ZrO_2$ was used to produce PZ-PT, these large agglomerates apparently caused incomplete blending and densification of the PZ-PT and extensive variability in the piezoelectric behavior of the material produced.

It was also shown that the dry blending approach for producing PZ-PT from fully processed $ZrO_2$ is more difficult to control than the wet blending mixing approach. It is incorrect to assume that poorly blended materials can be calcined and then wet ground to achieve satisfactory PZ-PT piezoelectric material. For instance, all nine of the dry blended compositions produced had fired densities of 6.96 to 7.47 gm/cc as opposed to 7.49 to 7.52 gm/cc for the same $ZrO_2$ wet blended PZ-PT compositions. Also, the piezoelectric coupling coefficient was 13 to 51 percent lower than similar wet blended material.

While the differences between the single and double precipitated $ZrO_2$ was attributed to the higher silica content and higher average particle size of the single precipitate $ZrO_2$, information on the surface area of the $ZrO_2$ was not available at that time. Therefore, the second portion of this effort was concerned with (1) a further analysis of the differences in the various $ZrO_2$ produced and (2) improvements in the $ZrO_2$ and PZ-PT by additional chemical processing.

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## A. SURFACE AREA OF $ZrO_2$

Figure 3 and Table 4 give the surface area of the $ZrO_2$ derived from various hydrates, sources of zircon sand and calcination temperatures. The TNBZ derived $ZrO_2$ produced at the Honeywell Ceramics Center and calcined at 500°C had surface areas of 47 to 56 square meters per gram, which was about the same as that produced by calcining
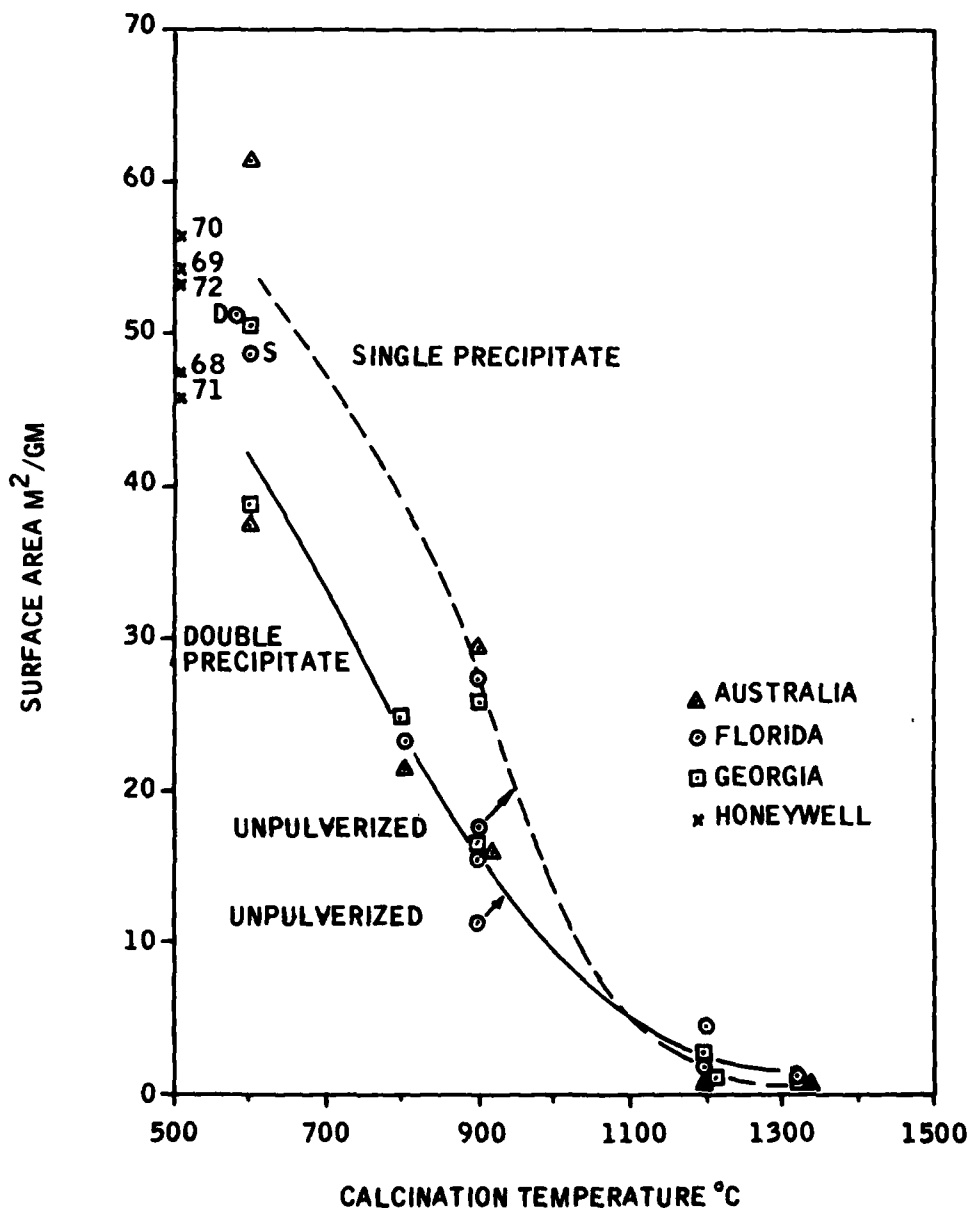


Figure 3. $ZrO_2$ surface area as a function on calcination temperature.

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Table 4. Surface area of $ZrO_2$ in square meters per gram.

| | Calcination Temperature °C | Micro-Pulverized | Florida Zircon | Georgia Zircon | Australia Zircon |
|---|---|---|---|---|---|
| First | 600 | Yes | 50.7 | 48.9 | 63.4 |
| Precipitate | 900 | No | 17.5 | | |
| | 900 | Yes | 27.3 | 25.7 | 29.4 |
| | 1200 | No | 1.66 | 1.19 | 0.57 |
| | 1200 | Yes | 1.79 | 1.47 | 0.98 |
| | 1320 | No | 0.74 | 0.79 | 0.86 |
| | 1320 | Yes | 1.03 | 0.84 | 0.83 |
| Second | 600 | Yes | 51.0 | 38.8 | 37.6 |
| Precipitate | 900 | No | 11.3 | | |
| | | Yes | 15.7 | 16.1 | 15.7 |
| | 1200 | No | 2.44 | 2.33 | 2.72 |
| | | Yes | 4.62 | 2.59 | |
| Harshaw Calcine | | Yes | 23.0 | 25.0 | 21.5 |
| Honeywell | | | | | |
| 2168 | 500 | Yes | 47.2 | | |
| 2169 | 500 | Yes | 54.0 | | |
| 2170 | 500 | Yes | 56.2 | | |
| 2171 | 500 | Yes | 45.7 | | |
| 2172 | 500 | Yes | 53.2 | | |

Harshaw's first stage zirconium hydrate at 600°C, but generally higher than the 600°C calcine second stage hydrate. It was shown previously[1] that the crystallites produced, after decomposition of the initial hydrate, are about 0.008 to 0.010 $\mu$m in size.

As the calcination temperature was increased, grain growth increased and surface area decreased, as shown in Figure 3. At the lower temperatures, $ZrO_2$ from the first stage precipitates generally had higher surface areas than the $ZrO_2$ from the second stage precipitates although crystalline sizes obtained were between 0.020 and 0.040 $\mu$m. This suggests that the purer double precipitates have more interfacial contact areas that are physically stronger than the single precipitates. The assumption is partially verified by the fact that the surface area of unmicronized $ZrO_2$ derived from Florida zircon was 17.5 and 11.3 $M^2$/gm for the single and double precipitates, respectively, as opposed to 27.3 and 15.7 $M^2$/gm for the micronized $ZrO_2$. Less new surface area was generated for the double precipitated $ZrO_2$. At 1200°C, the surface area of the first stage $ZrO_2$ produced was slightly less than the second stage $ZrO_2$ (0.57-1.66 versus 2.33-2.72 $M^2$/gm).

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The dry pressed density (after pressing at 2900 psi) of each type of $ZrO_2$ produced was also plotted in Figure 4 as a function of surface area of original $ZrO_2$ powder. The low surface area materials pressed to about 3.0-3.3 gm/cc, while the materials calcined below 1000°C produced pressed densities of 1.3-1.6 gm/cc. There appeared to be a slight dependency upon the purity difference between the first and second stage precipitates. A
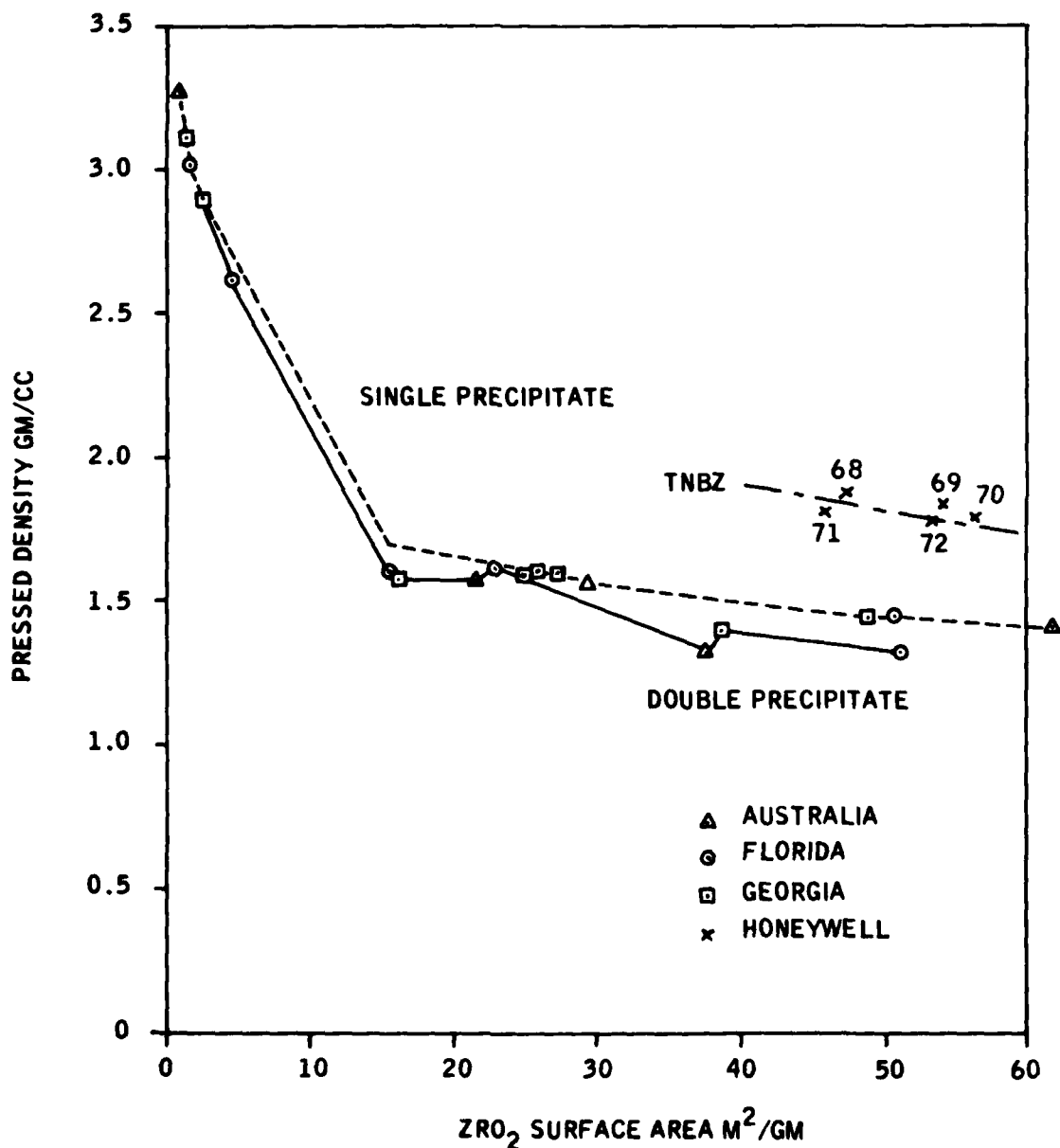


Figure 4. Influence of surface area on the dry pressed density of $ZrO_2$.

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more dramatic difference is noted for the very impure TNBZ derived $ZrO_2$ which pressed to 1.8-1.9 gm/cc.

After the various $ZrO_2$ materials were batched and processed into the standard PZ-PT formulation, the dry pressed and fired density of each batch was determined and plotted as a function of the surface area of the $ZrO_2$ used. These data are presented in Figure 5. Both the dry pressed and fired density data show that the double precipitated $ZrO_2$ produce superior material than the more impure $ZrO_2$ obtained from the single, first stage precipitate $ZrO_2$ or impure lot of Tetra N-butyl zirconate. It was somewhat surprising to see that the surface area and crystalline size of the $ZrO_2$ produced from double precipitated materials had only a very minor influence on both fired and unfired density. The wet blend process may be capable of some grinding of the larger crystallites, but it is more probable that the cleaner grain boundaries promote grain growth and densification more readily than in the more impure materials.

The trend of higher calcination temperatures to yield higher fired PZ-PT densities in the first stage, single precipitated $ZrO_2$ is also apparent. The fact that one 1200°C calcined $ZrO_2$ obtained from single precipitated Georgia zircon reached a fired density of 7.502 may relate to the fact that this zircon sand is finer and purer than the other two sources.

The impact of $ZrO_2$ surface area used to produce PZ-PT by the dry blending method is much more striking. The fired density of PZ-PT produced from double precipitated $ZrO_2$ by this blending method is compared in Figure 6 to that produced by the wet blending method. When the finer, fluffy, high surface area $ZrO_2$ was dry blended into a batch, the PZ-PT produced had fired densities of only 6.95-7.15 gm/cc, whereas the coarse, 2-4 $M^2$/ gm surface area type of $ZrO_2$ produced PZ-PT with a 7.42-7.44 gm/cc density.

## B. CHEMICAL UNIFORMITY OF FIRED PZ-PT

Use of the x-ray fluoresence technique described in Section II was a simple approach to obtain quantitative information on the chemical uniformity of the batches produced from various $ZrO_2$ powders and by the wet and dry blended processes. Table 5 gives the results obtained as a function of the $ZrO_2$ calcination temperature and zircon source. Theoretically, all compositions should have been 65.46 percent PbO, 20.38 percent $ZrO_2$, 11.72 percent $TiO_2$ and 1.94 percent SrO with the Zr/Ti ratio of 0.53/0.47.

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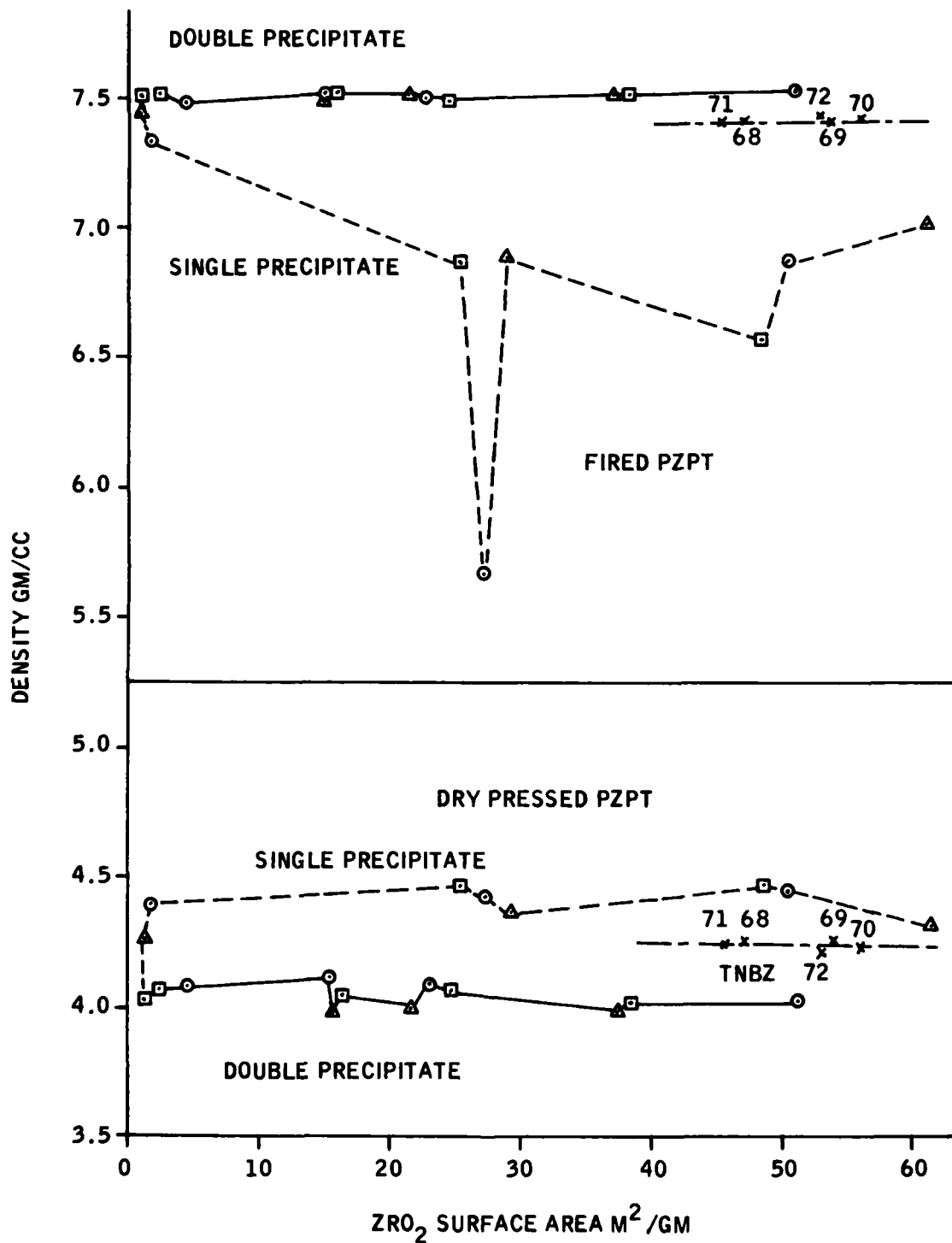
Figure 5. Influence of ZrO₂ surface area on the dry pressed and final PZ-PT densities.

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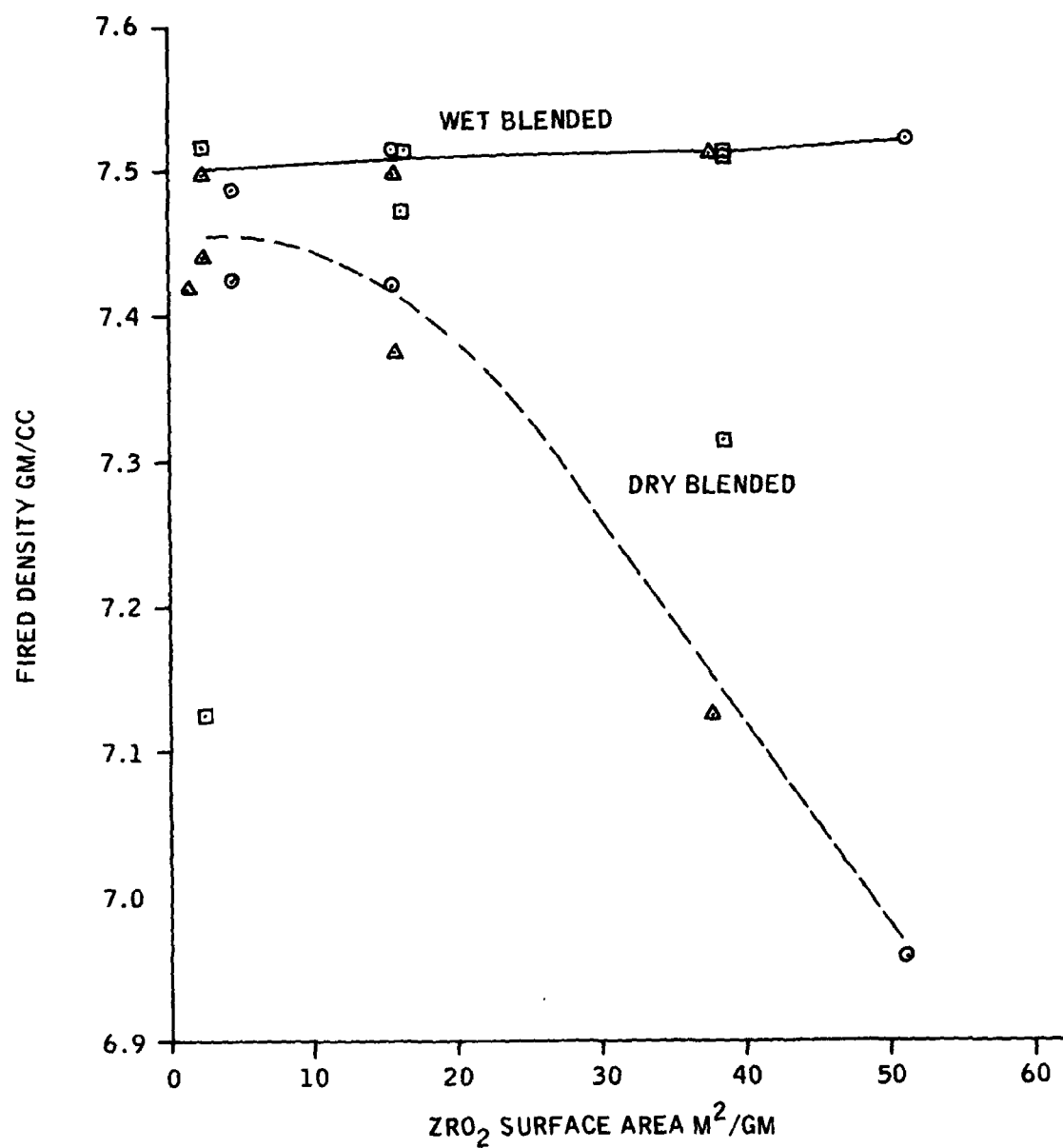
Figure 6. The impact of PZ-PT blending procedure on final density.

Table 5. X-ray diffraction results on final PZ-PT compositions.

| | Type Blending | Weight Percent PbO | | | Mols Zr/Ti | | | Weight Percent SrO | | |
|---|---|---|---|---|---|---|---|---|---|---|
| | | Florida | Georgia | Australia | Florida | Georgia | Australia | Florida | Georgia | Australia |
| First Precipitate | | | | | | | | | | |
| 600 | Wet | 67.51 | 67.26 | 67.05 | 0.542/0.458 | 0.562/0.438 | 0.551/0.449 | 1.83 | 1.83 | 1.85 |
| 900 | Wet | 67.37 | 67.33 | 66.55 | 0.540/0.460 | 0.545/0.455 | 0.541/0.459 | 1.82 | 1.82 | 1.84 |
| 1200 | Wet | 67.15 | 66.51 | 66.82 | 0.527/0.473 | 0.525/0.475 | 0.522/0.478 | 1.80 | 1.83 | 1.85 |
| Second Precipitate | | | | | | | | | | |
| 600 | Wet | 66.81 | 66.30 | 67.27 | 0.525/0.475 | 0.521/0.479 | 0.526/0.474 | 1.83 | 1.82 | 1.81 |
| | Dry | 67.44 | 66.98 | 66.97 | 0.554/0.446 | 0.536/0.464 | 0.545/0.455 | 1.88 | 1.92 | 1.86 |
| 900 | Wet | 66.76 | 65.91 | 67.02 | 0.525/0.475 | 0.524/0.476 | 0.525/0.475 | 1.86 | 1.87 | 1.83 |
| | Dry | 67.37 | 66.82 | 66.73 | 0.542/0.458 | 0.527/0.473 | 0.530/0.470 | 1.75 | 1.78 | 1.87 |
| 1200 | Wet | 66.18 | 67.23 | 66.97 | 0.520/0.480 | 0.534/0.466 | 0.542/0.458 | 1.83 | 1.82 | 1.82 |
| | Dry | 67.06 | 66.54 | 67.03 | 0.522/0.478 | 0.525/0.475 | 0.526/0.474 | 1.90 | 1.96 | 1.83 |
| Harshaw Calcine | Wet | 67.19 | 67.04 | 66.92 | 0.527/0.473 | 0.525/0.475 | 0.526/0.474 | 1.80 | 1.78 | 1.79 |
| Honeywell | | | | | | | | | | |
| 2168 | Wet | 66.43 | | | 0.535/0.465 | | | 1.83 | | |
| 2169 | Wet | 66.42 | | | 0.530/0.470 | | | 1.89 | | |
| 2170 | Wet | 66.91 | | | 0.547/0.453 | | | 1.82 | | |
| 2171 | Wet | 67.49 | | | 0.539/0.461 | | | 1.78 | | |
| 2172 | Wet | 66.05 | | | 0.530/0.470 | | | 1.85 | | |

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These data show the presence of a consistently higher amount of PbO than the theoretical composition and the presence of lower SrO and Zr/Ti ratio. These results might indicate the need for a better set of standards; however, the variability of the SrO and Zr/Ti ratio suggests that real deviations in the chemical composition do exist in these batches. This was confirmed by analyzing the impact of Zr/Ti ratio on frequency constant. As the Zr/Ti ratio increased above 53/47, the frequency constant dropped significantly, whereas values less than 526/474 caused the frequency constant to drop.

It was also interesting to note that at any given $ZrO_2$ calcination temperature wet blended compositions contained less variance in the SrO present than those of similar dry blended compositions. For instance, the wet blended single stage or double stage $ZrO_2$ materials produced 21 PZ-PT batches with 1.78 to 1.87 percent SrO, whereas the nine dry blended batches varied from 1.75 to 1.96 percent SrO.

Such Zr/Ti ratio data as given in Table 5 will be used to help understand the piezoelectric properties obtained for the various PZ-PT batch produced in this study.

## C. REPRECIPITATED $ZrO_2$ IN PZ-PT

This portion of the program examined the impact of additional reprecipitation processes for $ZrO_2$ and their influence on the fired properties of PZ-PT. Five lots of $ZrO_2$ from either first or second stage precipitate from each source of zircon (Florida, Georgia and Australia) were prepared. The process of redissolving the first or second stage zirconium hydroxide precipitate pulp with hot HCl and then reprecipitating with ammonium hydroxide was discussed in Section II.

It was assumed that the average particle size obtained was that of agglomerated particles of $ZrO_2$ or possibly the particle diameter of the zirconium hydroxide from which the $ZrO_2$ was derived. This appears likely because basic zirconium sulfate particles are typically about 15 $\mu$m and the first stage precipitate particles were measured at 8-10 $\mu$m[1]. The advantage of the double precipitation process appears to be to break up these agglomerates to yield 1 to 3 $\mu$m particles[1].

It was therefore desirable to determine if further improvements in the $ZrO_2$ produced for PZ-PT could be obtained with additional replications of the precipitation process.

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Tables 6 and 7 give the chemical and physical property data obtained for each of the three reprocessed lots produced from the first stage precipitate calcined at 900°C, along with the data obtained previously[1] for the direct calcination of this material. Similarly, the two reprocessed lots of second stage precipitate are compared to the standard Harshaw calcine and the direct calcination of the double precipitate.

Table 6 indicates that our reprocessing did not improve the chemical purity over that achieved by Harshaw in their process. In fact, the first two lots of reprocessed first precipitate appear to have been contaminated by silica. The silica may have come from the pyrex glass processing ware or chemicals used; however, if this was true, it should have also occurred in the reprocessed double precipitate. Since this did not occur, the high $SiO_2$ values reported are expected to be poor analytical data.

Table 7 gives the data obtained on $ZrO_2$ particle size, surface area and bulk density. All of the reprocessed $ZrO_2$ generally had smaller agglomerates but lower surface areas than those calcined materials from which they were derived. This was particularly true for the reprocessed Lot No. 4 and 5 materials believed to be our best approach.

After each reprocessed $ZrO_2$ material was wet blended and processed into our standard PZ-PT formulation, data was obtained on the chemical, physical and electrical properties of each batch. These data are reported in Tables 8 through 14 and are compared to similar wet and dry blended $ZrO_2$ formulated PZ-PT batches. Table 8 gives the chemical composition of the fired PZ-PT obtained by the x-ray fluorescence approach. The results are similar to those discussed above—consistently high PbO and low SrO. The ratio of zirconium to titanium is again expected to be most useful in understanding the piezoelectric data; therefore, these results are repeated in Tables 9 through 14.

Table 9 gives the dry pressed and fired density as well as the unpoled dielectric constant of each PZ-PT batch produced. The dry pressed density of each batch containing reprocessed $ZrO_2$ was consistently lower than its source $ZrO_2$ material. Similarly, the fired density was consistently higher. Densities of above 7.4 gm/cc and as high as 7.57 gm/cc were obtained from the first stage precipitated $ZrO_2$ as opposed to only 6.9 gm/cc for PZ-PT batches prepared from $ZrO_2$ from the original precipitate. Densities of 7.53-7.59 gm/cc were also obtained for PZ-PT produced from reprocessed double precipitated $ZrO_2$ as opposed to 7.5 gm/cc for the original $ZrO_2$. The unpoled dielectric constant was generally higher with the higher densities obtained, although the actual chemical

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Table 6. Chemical impurities in ZrO$_2$ powder.

| | Percent Si | | | Percent Ti | | | Percent Fe | | |
|---|---|---|---|---|---|---|---|---|---|
| | From Florida Zircon | From Georgia Zircon | From Australia Zircon | From Florida Zircon | From Georgia Zircon | From Australia Zircon | From Florida Zircon | From Georgia Zircon | From Australia Zircon |
| **First Precipitate** | | | | | | | | | |
| 900°C Harshaw Precipitate/Pulverized | 0.015 | 0.015 | 0.025 | 0.030 | 0.035 | 0.075 | 0.004 | 0.010 | 0.001 |
| 900°C Reprocessed Lot 1 | 0.10 | 0.20 | 0.270 | 0.035 | 0.033 | 0.098 | 0.037 | 0.005 | 0.003 |
| 900°C Reprocessed Lot 2 | 0.20 | 0.17 | 0.180 | 0.060 | 0.035 | 0.094 | 0.042 | 0.003 | 0.003 |
| 900°C Reprocessed Lot 4 | 0.031 | 0.012 | 0.066 | 0.037 | 0.011 | 0.036 | 0.020 | 0.003 | 0.003 |
| **Second Precipitate** | | | | | | | | | |
| Harshaw Calcine | 0.002 | 0.001 | 0.010 | 0.006 | 0.004 | 0.020 | 0.004 | 0.004 | 0.010 |
| 900°C Harshaw Precipitate/Pulverized | <0.001 | 0.001 | 0.004 | 0.010 | 0.010 | 0.030 | 0.002 | <0.001 | <0.001 |
| 900°C Reprocessed Lot 3 | 0.003 | 0.050 | 0.003 | 0.004 | 0.013 | 0.009 | 0.003 | 0.003 | 0.003 |
| 900°C Reprocessed Lot 5 | 0.003 | 0.016 | 0.003 | 0.010 | 0.030 | 0.014 | 0.003 | 0.020 | 0.003 |

Table 7. Physical properties of ZrO$_2$ powders.

| | Average Particle Diameter μm / Percent Less than 0.5 μm | | | Bulk Density gm/cc | | | Surface Area M$^2$/gm | | |
|---|---|---|---|---|---|---|---|---|---|
| | From Florida Zircon | From Georgia Zircon | From Australia Zircon | From Florida Zircon | From Georgia Zircon | From Australia Zircon | From Florida Zircon | From Georgia Zircon | From Australia Zircon |
| **First Precipitate** | | | | | | | | | |
| 900°C Harshaw Precipitate/Pulverized | 10.1/0 | 9.7/0 | 7.9/0 | 1.15 | 1.08 | 1.10 | 27.3 | 25.7 | 29.4 |
| 900°C Reprocessed Lot 1 | 7.4/8 | 10.1/5 | 10.0/5 | 0.850 | 0.879 | 0.820 | 15.6 | 16.6 | 21.6 |
| 900°C Reprocessed Lot 2 | 2.0/23 | 8.9/9 | 5.9/15 | 0.559 | 1.027 | 0.674 | 17.5 | 10.2 | 18.8 |
| 900°C Reprocessed Lot 4 | 3.0/16 | 5.8/11 | 6.7/10 | 0.749 | 0.819 | 0.776 | 10.1 | 12.5 | 11.0 |
| **Second Precipitate** | | | | | | | | | |
| Harshaw Calcine | 1.3/16 | 1.4/16 | 1.4/15 | 0.66 | 0.66 | 0.67 | 23.0 | 25.0 | 21.5 |
| 900°C Harshaw Precipitate/Pulverized | 1.4/15 | 1.3/18 | 2.2/18 | 0.65 | 0.51 | 0.53 | 15.7 | 16.1 | 15.7 |
| 900°C Reprocessed Lot 3 | 1.1/23 | 1.3/25 | 5.6/16 | 0.813 | 0.741 | 0.755 | 11.3 | 12.5 | 10.8 |
| 900°C Reprocessed Lot 5 | 2.8/17 | 2.4/17 | 6.0/12 | 0.518 | 0.539 | 0.658 | 9.5 | 9.5 | 9.1 |

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**Table 8. Chemical composition of fired PZ-PT.**

| | Blending Process | Percent PbO (Theorical 65.46 Percent) | | | Mols Zr/Ti | | | Percent SrO (Theorical 1.94 Percent) | | |
|---|---|---|---|---|---|---|---|---|---|---|
| | | From Florida Zircon | From Georgia Zircon | From Australia Zircon | From Florida Zircon | From Georgia Zircon | From Australia Zircon | From Florida Zircon | From Georgia Zircon | From Australia Zircon |
| **First Precipitate** | | | | | | | | | | |
| 900°C Harshaw Precipitate/Pulverized | Wet | 67.37 | 67.33 | 66.55 | 0.538/0.462 | 0.543/0.457 | 0.539/0.461 | 1.82 | 1.82 | 1.84 |
| 900°C Reprocessed Lot 1 | Wet | 67.33 | 67.19 | 67.11 | 0.522/0.478 | 0.524/0.476 | 0.513/0.487 | 1.88 | 1.87 | 1.78 |
| 900°C Reprocessed Lot 2 | Wet | 66.80 | 66.77 | 67.19 | 0.520/0.480 | 0.528/0.472 | 0.522/0.478 | 1.55 | 1.88 | 1.85 |
| 900°C Reprocessed Lot 4 | Wet | 66.30 | 67.47 | 67.36 | 0.520/0.480 | 0.525/0.487 | 0.525/0.487 | 1.85 | 1.77 | 1.82 |
| **Second Precipitate** | | | | | | | | | | |
| Harshaw Calcine | Wet | 67.19 | 67.04 | 66.92 | 0.527/0.473 | 0.525/0.475 | 0.526/0.474 | 1.80 | 1.78 | 1.79 |
| 900°C Harshaw Precipitate/Pulverized | Wet | 66.76 | 65.91 | 67.02 | 0.525/0.475 | 0.524/0.476 | 0.525/0.475 | 1.86 | 1.87 | 1.83 |
| 900°C Harshaw Precipitate/Pulverized | Dry | 67.37 | 66.82 | 66.74 | 0.542/0.458 | 0.528/0.472 | 0.530/0.470 | 1.75 | 1.78 | 1.87 |
| 900°C Reprocessed Lot 3 | Wet | 67.11 | 66.41 | 67.09 | 0.526/0.474 | 0.524/0.476 | 0.518/0.482 | 1.85 | 1.86 | 1.88 |
| 900°C Reprocessed Lot 5 | Wet | 67.10 | 67.52 | 67.30 | 0.522/0.478 | 0.527/0.473 | 0.522/0.478 | 1.76 | 1.77 | 1.83 |

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## Table 9. Density and unpoled dielectric constant of PZ-PT.

| | Blending Process | Green Density in gm/cc | | | Fired Density in gm/cc | | | Dielectric Constant Unpoled | | |
|---|---|---|---|---|---|---|---|---|---|---|
| | | From Florida Zircon | From Georgia Zircon | From Australia Zircon | From Florida Zircon | From Georgia Zircon | From Australia Zircon | From Florida Zircon | From Georgia Zircon | From Australia Zircon |
| **First Precipitate** | | | | | | | | | | |
| 900°C Harshaw Precipitate/ Pulverized | Wet | 4.426 | 4.454 | 4.354 | 5.662 | 6.860 | 6.881 | 860 | 827 | 813 |
| 900°C Reprocessed Lot 1 | Wet | 4.210 | 4.170 | 4.211 | 7.487 | 7.450 | 7.416 | 861 | 880 | 876 |
| 900°C Reprocessed Lot 2 | Wet | 4.204 | 4.194 | 4.113 | 7.554 | 7.478 | 7.501 | 922 | 862 | 876 |
| 900°C Reprocessed Lot 4 | Wet | 3.927 | 4.034 | 4.041 | 7.50 | 7.57 | 7.53 | 977 | 990 | 964 |
| **Second Precipitate** | | | | | | | | | | |
| Harshaw Calcine | Wet | 4.081 | 4.061 | 3.986 | 7.502 | 7.485 | 7.514 | 990 | 1005 | 992 |
| 900°C Harshaw Precipitate/ Pulverized | Wet | 4.105 | 4.036 | 3.972 | 7.514 | 7.514 | 7.499 | 1006 | 1010 | 991 |
| 900°C Harshaw Precipitate/ Pulverized | Dry | 4.238 | 4.077 | 4.151 | 7.420 | 7.474 | 7.377 | 948 | 988 | 931 |
| 900°C Reprocessed Lot 3 | Wet | 3.938 | 3.908 | 4.105 | 7.528 | 7.555 | 7.551 | 973 | 947 | 889 |
| 900°C Reprocessed Lot 5 | Wet | 3.861 | 3.839 | 3.900 | 7.59 | 7.590 | 7.56 | 997 | 1033 | 992 |

## Table 10. Poled dielectric constant of PZ-PT.

| | Blending Process | Mols Zr/Ti | | | Dielectric Constant Poled | | | Percent Aging Dielectric Constant | | |
|---|---|---|---|---|---|---|---|---|---|---|
| | | From Florida Zircon | From Georgia Zircon | From Australia Zircon | From Florida Zircon | From Georgia Zircon | From Australia Zircon | From Florida Zircon | From Georgia Zircon | From Australia Zircon |
| **First Precipitate** | | | | | | | | | | |
| 900°C Harshaw Precipitate/ Pulverized | Wet | 0.538/0.462 | 0.543/0.457 | 0.539/0.461 | 904 | 785 | 901 | -3.71 | -4.33 | -5.89 |
| 900°C Reprocessed Lot 1 | Wet | 0.522/0.478 | 0.524/0.476 | 0.513/0.487 | 910 | 936 | 862 | -4.78 | -5.00 | -4.55 |
| 900°C Reprocessed Lot 2 | Wet | 0.520/0.480 | 0.528/0.472 | 0.522/0.478 | 975 | 916 | 925 | -4.89 | -4.66 | -5.03 |
| 900°C Reprocessed Lot 4 | Wet | 0.520/0.480 | 0.525/0.487 | 0.525/0.487 | 1028 | 1006 | 967 | -5.45 | -5.05 | -5.03 |
| **Second Precipitate** | | | | | | | | | | |
| Harshaw Calcine | Wet | 0.527/0.473 | 0.525/0.475 | 0.526/0.474 | 1003 | 1090 | 1044 | -4.44 | -4.66 | -3.98 |
| 900°C Harshaw Precipitate/ Pulverized | Wet | 0.527/0.475 | 0.524/0.476 | 0.525/0.475 | 1047 | 1045 | 1050 | -4.56 | -5.14 | -5.13 |
| 900°C Harshaw Precipitate/ Pulverized | Dry | 0.542/0.458 | 0.528/0.472 | 0.530/0.470 | 932 | 978 | 936 | -5.34 | -5.19 | -4.55 |
| 900°C Reprocessed Lot 3 | Wet | 0.526/0.474 | 0.524/0.476 | 0.518/0.482 | 991 | 911 | 922 | -5.89 | -4.17 | -4.15 |
| 900°C Reprocessed Lot 5 | Wet | 0.522/0.478 | 0.527/0.473 | 0.522/0.478 | 984 | 1062 | 972 | -4.33 | -5.34 | 04.26 |

Table 11. Piezoelectric radial coupling coefficient of PZ-PT.

| | Blending Process | Mols Zr/Ti | | | Radial Coupling Factor | | | Percent Aging Radial Coupling Factor | | |
|---|---|---|---|---|---|---|---|---|---|---|
| | | From Florida Zircon | From Georgia Zircon | From Australia Zircon | From Florida Zircon | From Georgia Zircon | From Australia Zircon | From Florida Zircon | From Georgia Zircon | From Australia Zircon |
| **First Precipitate** | | | | | | | | | | |
| 900°C Harshaw Precipitate/ Pulverized | Wet | 0.538/0.462 | 0.543/0.457 | 0.539/0.461 | 0.450 | 0.448 | 0.401 | -201 | -1.58 | -2.01 |
| 900°C Reprocessed Lot 1 | Wet | 0.522/0.478 | 0.524/0.476 | 0.513/0.487 | 0.318 | 0.371 | 0.316 | -3.31 | -2.86 | -2.92 |
| 900°C Reprocessed Lot 2 | Wet | 0.520/0.480 | 0.528/0.472 | 0.522/0.478 | 0.415 | 0.341 | 0.398 | 03.02 | 03.15 | 03.37 |
| 900°C Reprocessed Lot 4 | Wet | 0.520/0.480 | 0.525/0.487 | 0.525/0.487 | 0.426 | 0.433 | 0.396 | -2.80 | -2.80 | -3.05 |
| **Second Precipitate** | | | | | | | | | | |
| Harshaw Calcine | Wet | 0.527/0.473 | 0.525/0.475 | 0.526/0.474 | 0.484 | 0.508 | 0.483 | -2.46 | -2.48 | -2.46 |
| 900°C Harshaw Precipitate/ Pulverized | Wet | 0.525/0.475 | 0.524/0.476 | 0.525/0.475 | 0.491 | 0.490 | 0.492 | -2.08 | -2.57 | -2.34 |
| 900°C Harshaw Precipitate/ Pulverized | Dry | 0.542/0.458 | 0.528/0.472 | 0.530/0.470 | 0.328 | 0.365 | 0.285 | -3.09 | -3.04 | -4.55 |
| 900°C Reprocessed Lot 3 | Wet | 0.526/0.474 | 0.524/0.476 | 0.518/0.482 | 0.322 | 0.407 | 0.346 | -3.10 | -2.44 | -3.01 |
| 900°C Reprocessed Lot 5 | Wet | 0.522/0.478 | 0.527/0.473 | 0.522/0.478 | 0.457 | 0.472 | 0.449 | -2.42 | -2.53 | -2.91 |

Table 12. Piezoelectric frequency constant of PZ-PT.

| | Blending Process | Mols Zr/Ti | | | Frequency Constant Hertz-Meters | | | Percent Aging Frequency Constant | | |
|---|---|---|---|---|---|---|---|---|---|---|
| | | From Florida Zircon | From Georgia Zircon | From Australia Zircon | From Florida Zircon | From Georgia Zircon | From Australia Zircon | From Florida Zircon | From Georgia Zircon | From Australia Zircon |
| **First Precipitate** | | | | | | | | | | |
| 900°C Harshaw Precipitate/ Pulverized | Wet | 0.538/0.462 | 0.543/0.457 | 0.539/0.461 | 2133 | 2083 | 2141 | +0.81 | +0.73 | +0.61 |
| 900°C Reprocessed Lot 1 | Wet | 0.522/0.478 | 0.524/0.476 | 0.513/0.487 | 2381 | 2353 | 2389 | +0.92 | +0.99 | +0.84 |
| 900°C Reprocessed Lot 2 | Wet | 0.520/0.480 | 0.528/0.472 | 0.522/0.478 | 2349 | 2385 | 2347 | +0.99 | +0.90 | +1.00 |
| 900°C Reprocessed Lot 4 | Wet | 0.520/0.480 | 0.525/0.487 | 0.525/0.487 | 2305 | 2323 | 2325 | +1.16 | +1.06 | +1.07 |
| **Second Precipitate** | | | | | | | | | | |
| Harshaw Calcine | Wet | 0.527/0.473 | 0.525/0.475 | 0.526/0.474 | 2252 | 2231 | 2253 | +0.96 | +0.70 | +1.14 |
| 900°C Harshaw Precipitate/ Pulverized | Wet | 0.525/0.475 | 0.524/0.476 | 0.525/0.475 | 2253 | 2249 | 2250 | +1.20 | +1.26 | +1.24 |
| 900°C Harshaw Precipitate/ Pulverized | Dry | 0.542/0.458 | 0.528/0.472 | 0.530/0.470 | 2268 | 2277 | 2285 | +1.23 | +1.22 | +1.13 |
| 900°C Reprocessed Lot 3 | Wet | 0.526/0.474 | 0.524/0.476 | 0.518/0.482 | 2363 | 2379 | 2421 | +1.11 | +0.82 | +0.75 |
| 900°C Reprocessed Lot 5 | Wet | 0.522/0.478 | 0.527/0.473 | 0.522/0.478 | 2323 | 2291 | 2340 | +0.99 | +1.22 | +0.88 |

## Table 13. Mechanical quality factor of PZ-PT.

| | Blending Process | Mols Zr/T: | | | Mechanical Quality Factor ($Q_m$) | | | Percent Aging $Q_m$ | | |
|---|---|---|---|---|---|---|---|---|---|---|
| | | From Florida Zircon | From Georgia Zircon | From Australia Zircon | From Florida Zircon | From Georgia Zircon | From Australia Zircon | From Florida Zircon | From Georgia Zircon | From Australia Zircon |
| **First Precipitate** | | | | | | | | | | |
| 900°C Harshaw Precipitate/Pulverized | Wet | 0.538/0.462 | 0.543/0.457 | 0.539/0.461 | 660 | 659 | 662 | +23.6 | +9.8 | +9.1 |
| 900°C Reprocessed Lot 1 | Wet | 0.522/0.478 | 0.524/0.476 | 0.513/0.480 | 1014 | 990 | 1034 | +31.1 | +29.2 | +31.9 |
| 900°C Reprocessed Lot 2 | Wet | 0.520/0.480 | 0.528/0.472 | 0.522/0.478 | 1081 | 1008 | 930 | +29.3 | +28.7 | +31.2 |
| 900°C Reprocessed Lot 4 | Wet | 0.520/0.480 | 0.525/0.487 | 0.525/0.487 | 722 | 875 | 910 | +32.5 | +29.6 | +29.7 |
| **Second Precipitate** | | | | | | | | | | |
| Harshaw Calcine | Wet | 0.527/0.473 | 0.525/0.475 | 0.526/0.474 | 878 | 899 | 826 | +20.3 | +17.7 | +23.5 |
| 900°C Harshaw Precipitate/Pulverized | Wet | 0.525/0.475 | 0.524/0.476 | 0.525/0.475 | 872 | 883 | 858 | +24.7 | +25.7 | +30.2 |
| 900°C Harshaw Precipitate/Pulverized | Dry | 0.542/0.458 | 0.528/0.472 | 0.530/0.470 | 738 | 863 | 883 | +40.0 | +37.8 | +35.9 |
| 900°C Reprocessed Lot 3 | Wet | 0.526/0.474 | 0.524/0.476 | 0.518/0.482 | 896 | 1512 | 1395 | +32.3 | +23.3 | +27.6 |
| 900°C Reprocessed Lot 5 | Wet | 0.522/0.478 | 0.527/0.473 | 0.522/0.478 | 1005 | 770 | 1095 | +27.5 | +32.1 | +21.9 |

## Table 14. High drive properties of PZ-PT.

| | Blending Process | Mols Zr/T: | | | Percent Increase in Cap./ Percent Dissipation at 10V/mil | | | Percent Increase in Cap./ Percent Dissipation at 15V/mil | | |
|---|---|---|---|---|---|---|---|---|---|---|
| | | From Florida Zircon | From Georgia Zircon | From Australia Zircon | From Florida Zircon | From Georgia Zircon | From Australia Zircon | From Florida Zircon | From Georgia Zircon | From Australia Zircon |
| **First Precipitate** | | | | | | | | | | |
| 900°C Harshaw Precipitate/Pulverized | Wet | 0.538/0.462 | 0.543/0.457 | 0.539/0.461 | 6.1/1.9 | 6.1/1.9 | 6.5/1.9 | 12.9/3.5 | 14.3/3.5 | 13.3/3.6 |
| 900°C Reprocessed Lot 1 | Wet | 0.522/0.478 | 0.524/0.476 | 0.513/0.487 | 2.7/1.0 | 3.2/1.2 | 2.4/1.0 | 5.4/2.0 | 6.3/2.2 | 5.0/1.8 |
| 900°C Reprocessed Lot 2 | Wet | 0.520/0.480 | 0.528/0.472 | 0.522/0.478 | 3.0/1.0 | 3.0/1.2 | 2.6/1.0 | 5.7/2.0 | 6.0/2.1 | 5.5/1.9 |
| 900°C Reprocessed Lot 4 | Wet | 0.520/0.480 | 0.525/0.487 | 0.525/0.487 | 5.2/1.9 | 4.0/1.4 | 4.6/1.4 | 10.4/3.7 | 8.1/2.8 | 7.6/2.5 |
| **Second Precipitate** | | | | | | | | | | |
| Harshaw Calcine | Wet | 0.527/0.473 | 0.525/0.475 | 0.526/0.474 | 4.0/1.3 | 4.3/1.4 | 2.7/1.4 | 9.8/2.9 | 11.8/3.3 | 10.7/3.2 |
| 900°C Harshaw Precipitate/Pulverized | Wet | 0.525/0.475 | 0.524/0.476 | 0.525/0.475 | 3.7/1.3 | 4.7/1.6 | 4.3/1.5 | 10.5/3.0 | 11.9/3.4 | 10.6/3.2 |
| 900°C Harshaw Precipitate/Pulverized | Dry | 0.542/0.458 | 0.528/0.472 | 0.530/0.470 | 4.4/1.5 | 4.4/1.5 | 4.0/1.3 | 10.3/3.1 | 9.0/2.9 | 7.7/2.5 |
| 900°C Reprocessed Lot 3 | Wet | 0.526/0.474 | 0.524/0.476 | 0.518/0.482 | 4.1/1.6 | 1.9/0.5 | 2.1/0.7 | 8.5/3.0 | 3.6/1.0 | 4.2/1.4 |
| 900°C Reprocessed Lot 5 | Wet | 0.522/0.478 | 0.527/0.473 | 0.522/0.478 | 3.4/1.1 | 5.0/1.9 | 3.3/1.0 | 7.0/2.4 | 10.6/3.2 | 5.9/2.0 |

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composition may have had some impact on some of the PZ-PT compositions obtained from $ZrO_2$ generated from reprocessed double precipitate.

The poled dielectric constant and aging rate of each PZ-PT batch compounded from the various types of $ZrO_2$ are given in Table 10. The increase in dielectric constant was more dramatic in those batches of PZ-PT compounded from reprecipitated $ZrO_2$ which originated from the first stage zirconium hydroxide. This was caused by the significant improvement in density with these materials. The aging rate was also significantly higher because these materials were more thoroughly polarized. Improvements obtained in PZ-PT from reprocessed $ZrO_2$ derived from double precipitated zirconium hydroxide were more variable and dependent upon not only the fired density obtained but the specific Zr/Ti ratio and composition obtained.

Data on the piezoelectric radial coupling coefficient is given in Table 11. In general, the coupling coefficient was lower than that obtained in the PZ-PT produced from the re-precipitated $ZrO_2$ materials. It is not clear why this occurred. Possibly, the more effective blending obtained with the reprocessed materials and higher densities shifts the point at which the Zr/Ti ratio must be optimized for maximum coupling coefficient. Aging rate again was highest for compositions with higher amounts of rhombohedral phase (higher Zr/Ti ratio) PZ-PT.

Similar conclusions can also be drawn from the data shown in Tables 12 through 14 for frequency constant, mechanical quality factor and the percent increase in capacitance and dissipation factor at high driving fields. For instance, Figure 7 shows the frequency constant as a function of Zr/Ti ratio. PZ-PT produced from $ZrO_2$, which gave fired densities of 7.45 to 7.59 gm/cc and a Zr/Ti ratio of 0.52/0.48 to 0.53/0.47, had a frequency constant of 2220 to 2380 hertz-meters. Lower amounts of $ZrO_2$ produced slightly higher frequency constants, while higher amounts of $ZrO_2$ produced significantly lower frequency constants. Lower densities also tended to yield PZ-PT with lower frequency constants. These results are consistent with those normally associated with PZ-PT compositions. The aging rate for each property was also consistent with the composition and extent of polarization obtained.

**D. COPRECIPITATION OF PZ-PT**

It was shown above that the $ZrO_2$ particle and agglomerate size and the uniform distri bution of $ZrO_2$ in the PZ-PT are important factors in controlling the properties of PZ-PT
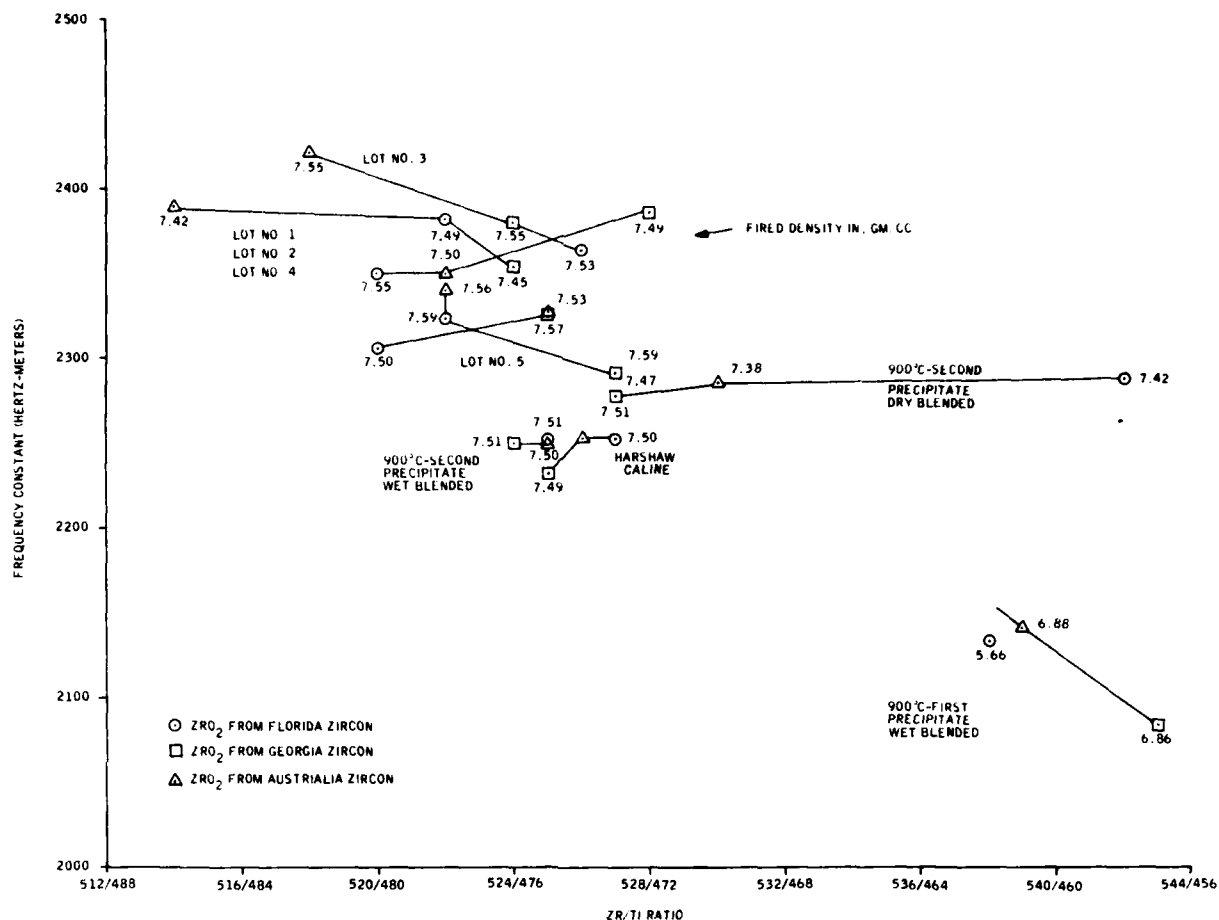
Figure 7. Zr/Ti ratio versus frequency constant for PZ-PT produced
from various $ZrO_2$.

piezoelectric ceramic. The generation of PZ-PT from chemical solutions should avoid
both of these problems by simultaneous precipitation of $ZrO_2$, $TiO_2$, SrO and iron oxide.
Such an approach would provide mixing on a molecular scale, and the particle size of the
solid solution compounds of these materials would probably not be important in the
early stages of processing. It should also produce more uniform fired behavior in the
PZ-PT produced. Since PbO has a high mobility during the calcination process, co-
precipitation of PbO in the batch may not be necessary.

Morgan[4] recently gave an excellent review of the basic approach of chemical proces-
sing of ceramics and points out, "It is often easier to change the starting powder than
embark upon prolonged studies of why a particular source material behaves as it does."

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He also points to a common ceramicist's myth that liquid chemical techniques for powders are expensive and not easily adaptable to the large scale ceramic processes. The irony of this situation is that the $TiO_2$ used in PZ-PT has been prepared by liquid chemical techniques in combination with barium and other pigments for years in the paint industry. Also, Zr is in chemical solution very early in the process for producing pure $ZrO_2$.

Several groups have studied the use of chemical solution processes in order to obtain more commercially acceptable or a superior optical quality PZ-PT material. Wright coordinated an extensive effort at the Canadian Department of Mines in the early 1960's[5] to produce PZ-PT via the process of mixing solutions of $Pb(NO_3)_2$, $Zr(NO_3)_4$ and $Ti(NO_3)_4$ and then precipitation with $(NH_4)_2CO_3$ and $NH_4OH$, ammonium gas or $H_2C_2O_4$ (oxcilic acid). However, they experienced difficulties in producing fine, friable calcined material suitable for further ceramic processing and were concerned over the acidic nature of the nitrates evolved during calcining.

Mulder[6] has shown that Ti, Zr, Pb, and other compounds can be dissolved with citric acid and then processed into PZ-PT. This was accomplished by dissolving purified hydroxide with ammonia and citric acid. Unfortunately, Ba and Sr form insoluble citrates and precipitate too rapidly to use in this process. However, he noted that barium formate and ammonium titanyl citrate remain in solution many hours. The aqueous solutions were spray dried into alcohol. In this process it was necessary to control (1) the acidity of initial aqueous citrate solution, (2) the final water content of alcohol after precipitation, (3) the type of alcohol used, and (4) the drying technique of powder.

Mazdiyasni[7] demonstrated a process for producing $ZrO_2$ and $BaTiO_3$ by the simultaneous hydrolytic decomposition of metal organic alkoxide compounds of $Zr(OC_5H_{11})_4$, $Ba(OC_3H_7)_2$ and $Ti(OC_5H_{11})_4$ in water. This general approach was then studied in more detail at Sandia[8] to produce PZ-PT from lead oxide, tetra N-butyl zirconate and tetra N-butyl titanate. By further doping with lanthanum acetate, a lanthanum doped PLZT was obtained which could be calcined and hot pressed into an optically transparent ferroelectric material. This process was first used on a production basis at Honeywell. Although the materials required are very expensive, it has been demonstrated that co-precipitation of PZ-PT can be used in production.

The three approaches of trying to make complete PZ-PT batches by chemical solution methods appeared to show promise; however, incomplete decomposition took place at

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lower temperature. At normal temperatures the calcined material reacted together so thoroughly that grinding of this material was not considered practical. While these techniques were not successful, the progress made appears to warrant consideration for a larger more concentrated program on the chemical solution preparation of PZ-PT.

The effort on chemical solution approaches was limited to those where $ZrO_2$ and $TiO_2$ were mixed as tetra N-butyl zirconate (TNBZ) or titanate (TNBT), calcined at 500°C and then wet blended into the PZ-PT composition and processed by conventional approaches. Table 15 compares the second and third groups of $ZrO_2$ materials prepared for this portion of the program. The purity of the TNBZ was typical of that used in production of PLZT ceramics as opposed to the impure TNBZ used previously.[1] Table 16 gives the chemical uniformity of the PZ-PT produced from the coprecipitated $ZrO_2/TiO_2$ produced. Batch Nos. 6643 and 6644 were formulated within the 53/47 $ZrO_2/TiO_2$ material produced where the $TiO_2$ was not compensated for in the batch. This was also true in Batches 6641 and 6642. Batch Nos. 6646-6649 were properly made. Therefore, the $ZrO_2 \cdot TiO_2$ in Nos. 6648 and 6649 were correctly formulated. X-ray fluorescence data for each of these is given in Table 16.

Note that the standard deviations obtained for each major oxide examined in these batches using TNBZ derived $ZrO_2$ and $TiO_2$ was significantly lower than those samples from a single batch of parts produced from $ZrO_2$ as in Table 3. The Zr/Ti ratio obtained was consistently lower (51/49 versus 53/47) than desired. Apparently, this was caused by improper compensation for impurities in the $ZrO_2$.

Table 15 gives the percent loss on ignition, bulk density, particle size and surface area of each $ZrO_2/TiO_2$ combination prepared. These are also compared to the previously[1] prepared TNBZ $ZrO_2$. The average agglomerate size was about three microns, whereas the surface varied between 26 to 56 $M^2/gm$. Bulk densities were about 1.0 gm/cc except 0.7 gm/cc for the 53/47 $ZrO_2/TiO_2$ material.

Table 17 gives the properties of the PZ-PT batches processed from all of the various chemically prepared $ZrO_2/TiO_2$ materials in this program. The high purity materials produced PZ-PT with a fired density consistently above 7.54 gm/cc compared to 7.41 to 7.44 gm/cc for PZ-PT with the impure TNBZ $ZrO_2$ materials. Where 53/47 coprecipitated $ZrO_2/TiO_2$ was used, densities of 7.60 gm/cc were achieved—the highest obtained in this program at the 1280°C firing temperatures. While the low Zr/Ti

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#### Table 15. Properties of TNBZ/TNBT derived $ZrO_2/TiO_2$ powders.

| $ZrO_2/TiO_2$ Cal. No. | Wt Percent $TiO_2$ Added to $ZrO_2$ | Percent Loss on Ignition | Bulk Density gm/cc | Average Particle Diameter μm | Percent Particles Less than 0.5 μm | Surface Area $M^2$/gm |
|---|---|---|---|---|---|---|
| 2168 | 0 | 0.86 | 0.98 | 2.1 | 11 | 47.2 |
| 3177 | 0 | 1.00 | 1.10 | 3.8 | 4 | 26.7 |
| 2169 | 0.02 | 0.99 | 0.94 | 2.0 | 9 | 54.0 |
| 2170 | 0.08 | 0.89 | 1.00 | 2.8 | 8 | 56.2 |
| 3178 | 0.10 | 1.06 | 1.04 | 4.8 | 3 | 31.0 |
| 2171 | 0.18 | 0.95 | 1.11 | 2.2 | 10 | 45.7 |
| 2172 | 0.36 | 1.00 | 1.03 | 2.6 | 6 | 53.2 |
| 3179 | 0.40 | 0.96 | 1.05 | 4.3 | 4 | 41.9 |
| 3180 | 36.50 | 9.92 | 0.76 | 3.0 | 1 | 40.0 |
| 3181 | 36.50 | 1.07 | 0.69 | 2.8 | 0 | 33.2 |
| FH* | 0 | 0.55 | 0.66 | 1.3 | 16 | 23.0 |

\* Harshaw Calcine Produced From Florida Zircon by Standard Process.

#### Table 16. Chemical uniformity of TNBZ/TNBT coprecipitated PZ-PT batches.

| Batch No. | Amt. $TiO_2$ | Percent PbO | Percent $ZrO_2$ | Percent $TiO_2$ | Percent SrO | Zr/Ti Ratio |
|---|---|---|---|---|---|---|
| 6625 | | 66.38 | 19.57 | 12.17 | 1.88 | 0.527/0.473 |
| 6640 | | 66.21 | 19.69 | 12.23 | 1.87 | 0.510/0.490 |
| 6650 | | 66.58 | 19.38 | 12.16 | 1.87 | 0.507/0.493 |
| 6641 | 0.1 | 66.24 | 19.64 | 12.24 | 1.88 | 0.510/0.490 |
| 6646 | 0.1 | 66.55 | 19.34 | 12.28 | 1.83 | 0.506/0.494 |
| 6642 | 0.4 | 66.43 | 19.51 | 12.22 | 1.84 | 0.507/0.493 |
| 6647 | 0.4 | 66.84 | 19.29 | 12.16 | 1.81 | 0.507/0.493 |
| 6648 | 53/47 | 66.70 | 19.38 | 12.12 | 1.80 | 0.508/0.492 |
| 6649 | 53/47 | 66.56 | 19.42 | 12.15 | 1.87 | 0.510/0.490 |
| X | | 66.48 | 19.48 | 12.19 | 1.85 | 0.510/0.490 |
| σ | | 0.17 | 0.13 | 0.05 | 0.03 | |
| 6643 | 53/47 | 63.19 | 16.85 | 18.15 | 1.81 | 0.375/0.625 |
| 6644 | 53/47 | 62.49 | 15.40 | 20.32 | 1.79 | 0.325/0.675 |

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## Table 17. Fired piezoelectric properties of PZ-PT prepared from coprecipitated $ZrO_2/TiO_2$.

| Zr:Ti Ratio | PZ-PT Batch No. | Weight Percent $TiO_2$ Added Via $ZrO_2$ | Pressed Density gm/cc | Fired Density gm/cc | | Unpoled Dielectric Constant | | Poled Dielectric Constant | | Radial Piezo Coupling Coeff | | Frequency Constant Cycle-Meters | | Mechanical Quality Factor | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | | | | 1280°C | 1320°C | 1280°C | 1320°C | 1280°C | 1320°C | 1280°C | 1320°C | 1280°C | 1320°C | 1280°C | 1320°C |
| 0.535 | 6600 | 0 | 4.26 | 7.409 | | 932 | | 1038 | | 0.455 | | 2228 | | 915 | |
| 0.510 | 6640 | 0 | 4.07 | 7.538 | | 941 | | 998 | | 0.236 | | 2344 | | 712 | |
| 0.507 | 6650 | 0 | 4.06 | 7.595 | 7.552 | 977 | 914 | 1039 | 1012 | 0.265 | 0.286 | 2353 | 2317 | 622 | 651 |
| 0.530 | 6601 | 0.02 | 4.26 | 7.414 | | 920 | | 994 | | 0.440 | | 2253 | | 817 | |
| 0.547 | 6602 | 0.08 | 4.23 | 7.415 | | 925 | | 1031 | | 0.451 | | 2237 | | 860 | |
| 0.510 | *6641 | 0.10 | 4.07 | 7.537 | | 997 | | 1060 | | 0.269 | | 2303 | | 796 | |
| 0.506 | 6646 | 0.10 | 4.18 | 7.595 | 7.556 | 958 | 924 | 1036 | 1034 | 0.258 | 0.298 | 2348 | | 735 | 689 |
| 0.539 | 6603 | 0.18 | 4.25 | 7.406 | | 932 | | 955 | | 0.464 | | 2212 | | 795 | |
| 0.530 | 6604 | 0.36 | 4.22 | 7.434 | | 923 | | 1001 | | 0.437 | | 2252 | | 930 | |
| 0.507 | *6642 | 0.40 | 4.09 | 7.563 | | 957 | | 1019 | | 0.230 | | 2346 | | 707 | |
| 0.507 | 6647 | 0.40 | 4.14 | 7.593 | 7.545 | 944 | 925 | 1048 | 1051 | 0.266 | 0.330 | 2336 | 2303 | 714 | 675 |
| 0.375 | *6643 | 36.5 | 4.15 | 7.535 | | 202 | | 207 | | 0.0 | | - | | - | |
| 0.508 | 6648 | 36.5 | 4.13 | 7.607 | 7.550 | 1018 | 956 | 1093 | 1083 | 0.248 | 0.355 | 2321 | 2276 | 658 | 650 |
| 0.325 | *6644 | 36.5 | 4.19 | 7.535 | | 260 | | 266 | | 0.0 | | - | | - | |
| 0.510 | 6649 | 36.5 | 4.11 | 7.611 | 7.558 | 1023 | 961 | 1101 | 1079 | 0.244 | 0.338 | 2326 | 2276 | 671 | 614 |
| 0.527 | 6625 | ** | 4.06 | 7.512 | 7.490 | 963 | 935 | 1082 | 1106 | 0.430 | 0.513 | 2272 | 2221 | 733 | 707 |

* Excessive $TiO_2$ added to batch (amount added via $ZrO_2$ not compensated)

** Harshaw Calcined $ZrO_2$ produced by Standard Process from Florida Zircon

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compositions produced inferior PZ-PT, the properties obtained are typical for the Zr/Ti ratios in these compositions. The impact of a higher firing temperature, 1320°C, is also shown to improve the piezoelectric behavior. Very excellent reproducibility was obtained in Batch Nos. 6648 and 6649, which used the coprecipitated 53/47 Zr/Ti ratio. Therefore, it can be concluded that chemical solution mixing approaches of the Zr and Ti will in themselves lead to a greatly improved PZ-PT.

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# IV. Summary and Conclusions

The chemical and physical properties of zirconium oxide have been shown to have a pronounced influence on the piezoelectric properties obtained in lead zirconate-lead titanate ceramics. Strongly bound agglomerated particles formed were about 10 to 15 $\mu$m in diameter and composed of 0.02 $\mu$m $ZrO_2$ crystallites. The standard alkali fusion process produced such material after the first stage precipitate of the zirconium hydroxide was calcined at about 900°C. The $ZrO_2$ produced at this stage also contained substantial amounts of silica and calcia impurities. Normal micropulverization techniques of the calcined $ZrO_2$ material and wet ball milling mixing procedures used with the PZ-PT batch did not disintegrate the $ZrO_2$ agglomerates sufficiently to produce a well distributed dispersion of $ZrO_2$ in the $TiO_2$, SrO and PbO. Thus, an effective method was not obtained for producing PZ-PT from this partially processed $ZrO_2$.

When the first stage zirconia hydroxide was redissolved in hot hydrochloric acid and reprecipitated with ammonium hydroxide, a second stage zirconium hydroxide material was obtained; this was much lower in silica and calcia and could be calcined and micronized to produce agglomerated particles 1 to 2 $\mu$m in diameter. This second stage material could be wet blended into a PZ-PT batch that produced good high drive piezoelectric material. A procedure was established to perform the second stage precipitation process, which produced $ZrO_2$ essentially comparable to that produced by Harshaw's standard process. The second stage zirconium hydroxide, produced by Harshaw, was also reprocessed with $HCl/NH_4OH$ reprecipitation process, but when the triple precipitated zirconium hydroxide was calcined and micronized, no further improvement in the $ZrO_2$ or PZ-PT was apparent.

The above results were essentially the same for $ZrO_2$ produced from three different sources of zircon. However, the fineness of the zircon sand appeared to have some impact on the $ZrO_2$ produced from the first stage zirconium hydroxide precipitate. The finer, purer Georgia zircon produced the best $ZrO_2$ and PZ-PT ceramics. More complete solution ceramic mixing and coprecipitation were initially investigated. While these approaches appeared attractive, they were not developed to the stage where good PZ-PT compositions were produced.

Coprecipitation of zirconium and titanium from their tetra N-butyl solutions was used to produce a $ZrO_2/TiO_2$ mixture and PZ-PT with superior densities at low temperatures. The purity of the $ZrO_2$ and the exact Zr/Ti ratio of the PZ-PT materials produced had a pronounced influence on the piezoelectric behavior of the ceramic obtained.

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# V. Acknowledgements

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